

MECHANISTIC STUDIES ON
SEMICONDUCTOR ELECTRODES

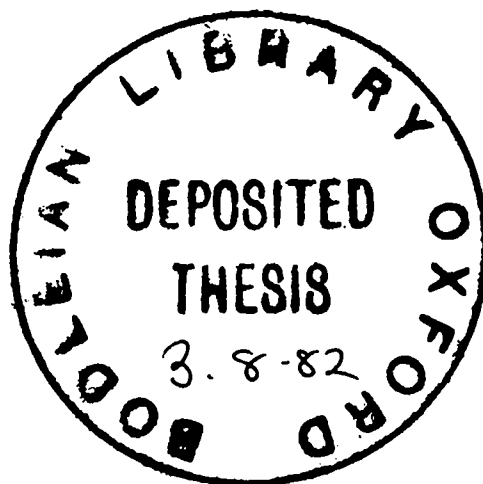
by

M.P. Dare-Edwards

Wolfson College

OXFORD

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CHAPTER ONE

INTRODUCTION

SECTION 1:1 INTRODUCTION

In the past ten years, with a growing concern for failing energy resources throughout the world, there has been an increasing attention to all methods of solar-energy conversion and storage. The most widely studied field has been that of solar heating through flat-plate collectors and other thermal devices. However, for the acquisition of higher grade energy, such as electricity, solid-state semiconductor devices, employing p-n junction, Schottky barrier and similar more complex junctions, have made the greatest advances. Recently, it has also been realized that electrochemical devices based on semiconductor electrodes can also be utilized for solar electricity generation and photochemical energy storage.

The purpose of this thesis was to study a range of semiconducting materials as electrodes in aqueous solution, with possible application to solar energy conversion and in particular for use in water photoelectrolysis cells to generate Hydrogen and Oxygen gases. Despite having this overall aim in mind, the electrochemical studies were in general aimed at gaining a more detailed understanding of the physical and chemical interactions at the semiconductor/electrolyte interface. These include:-

1. The charge and potential distribution at the semiconductor/electrolyte interface.
2. The transport of majority and minority carriers within the semiconductor surface (in the dark and under illumination).
3. The mechanisms and kinetics of redox processes occurring at the semiconductor electrode.
4. The nature of specific chemical interactions between the semiconductor and the solution-based species.

In the remaining Sections of Chapter 1, a brief resumé of the state of the art of semiconductor photoelectrochemistry will be given, concentrating on the various applications of semiconductor electrodes in solar-assisted devices. Chapter 2 concentrates on the theoretical aspects of semiconductor electrochemistry in general, not including some specific additions to the theory which arise from the results of later chapters. Chapter 3 then introduces the electrochemical apparatus and the detailed experimental procedures used in semiconductor photoelectrochemistry. The Results and Discussion Sections start with Chapter 4 where the electrochemistry of p-type GaP is studied in depth, in particular in use for the photoevolution of Hydrogen from aqueous solutions. Chapter 5 continues with work on p-GaP, but introduces the idea of surface modification of semiconductor electrodes for use in improving interfacial kinetics or electrode stability. Chapters 6 and 7 then complete the coverage of the electrochemistry of the major p-type III-IV semiconductors with studies on p-GaAs, p-InP and p-GaSb. Finally Chapter 8 deals with all the alternative strategies available for the use of semiconductor electrodes in solar photoelectrolyte cells. Included in this Chapter are some of the results obtained within the Oxford Semiconductor Electrochemistry Group during the past four years and with which the author has been directly associated.

SECTION 1:2 THE EARLY EVOLUTION OF SEMICONDUCTOR ELECTROCHEMISTRY

Although it is difficult to determine the authors of the first paper on a study of semiconductor electrochemistry, it is generally accepted that the foundation of the subject was laid in 1955 by W.H. Brattain and C.G.B. Garrett.¹ In their first paper in this field, they made a classical investigation of the effects of light on a Germanium electrode in contact with an aqueous electrolyte. The progress was continued with similar studies by Dewald on ZnO^{2,3} and by Williams⁴ on a number of compound semi-

conductors (CdS, CdSe, CuI, ZnO, ZnS, ZnTe and GaAs). Investigations with various other materials followed in the later 60's.⁵⁻¹¹ To keep pace with the novel findings of these studies, many of the fundamental theories of semiconductor electrodes in contact with solutions were formulated by Gerischer,¹²⁻¹⁴ Myamlin and Pleskov¹⁵ in several publications between 1965 and 1970.

Until the end of the 60's, studies of semiconductor electrochemistry were made for little more than academic interest; in particular to theoretically model the depletion layer formed at many semiconductor interfaces. However, a turning point came in 1971 when Fujishima and Honda^{16,17} reported on an electrochemical photocell based on an n-type TiO_2 electrode in contact with an aqueous electrolyte and a platinum counter electrode. On illumination from a Xenon lamp, spontaneous decomposition of water was observed to occur if a small ($\sim 0.2\text{V}$) positive bias was applied to the TiO_2 electrode. Oxygen evolution took place at the irradiated TiO_2 anode and hydrogen evolution at the Pt cathode.

The potential of this discovery in the use of semiconductor electrodes for the conversion and possible storage of solar energy as Hydrogen gas became immediately apparent. Indeed, since 1971, the number of papers published annually in the field of semiconductor electrochemistry has risen inexorably towards the present near-saturation level of about 250 papers a year.

The scope of the subject has, however, considerably widened to include studies on semiconductor/electrolyte cells that can generate electricity, catalyze thermodynamically downhill processes, and synthesize complex molecules all assisted by illumination with supra-bandgap irradiation. The next four sections will provide a brief description of the operation of these different types of semiconductor/electrolyte solar cells. In addition, a short resumé of the optimum results obtained with each type of cell will be provided.

SECTION 1:3 SEMICONDUCTOR PHOTOELECTROLYSIS CELLS

There are three different configurations available for photoelectrolysis cells that employ semiconductor materials as the light-captivating medium,¹⁸ (I) semiconducting anode + metal cathode (Fig.1.1), (II) semiconducting cathode + metal anode (Fig.1.2) and (III) two semiconducting electrodes (Fig.1.3). The diagrams illustrate the energetic relationship between the redox couples for the three configurations.

Fig.1.1 also illustrates the relationship between one hypothetical design for a solar photoelectrolysis cell (with configuration I) and the energy diagram of that cell. In this design, which is only one of many possible designs, it is envisaged that light will pass through a transparent metal cathode and non-absorbing aqueous solution onto the surface of the semiconductor material in contact with the electrolyte. The light absorbed in the surface region of the semiconductor creates electron-hole pairs that are separated under the influence of a surface electric field. This surface field arises at the interface due to the different work functions or electron affinities for the two materials forming the junction. The photogenerated holes are transported by the field towards the surface of the semiconductor where they may oxidize water to evolve oxygen. The electrons are transported into the bulk of the electrode and via an external short circuit to the metallic cathode where they may then effect the reduction of water to generate Hydrogen. The design shown with front illumination of the semiconductor through the solution is essential to ensure that the electron-hole pairs are created in the region of the electric field. If back illumination were used, there would be no driving force for the charge separation and the majority of electron-hole pairs would recombine generating low-grade heat.

A similar design to Fig.1.1a can be envisaged for the configuration (II) with a transparent metal anode on the front face of the cell.

Figure 1.1a
SEMICONDUCTOR
PHOTOELECTROLYSIS
SOLAR CELL

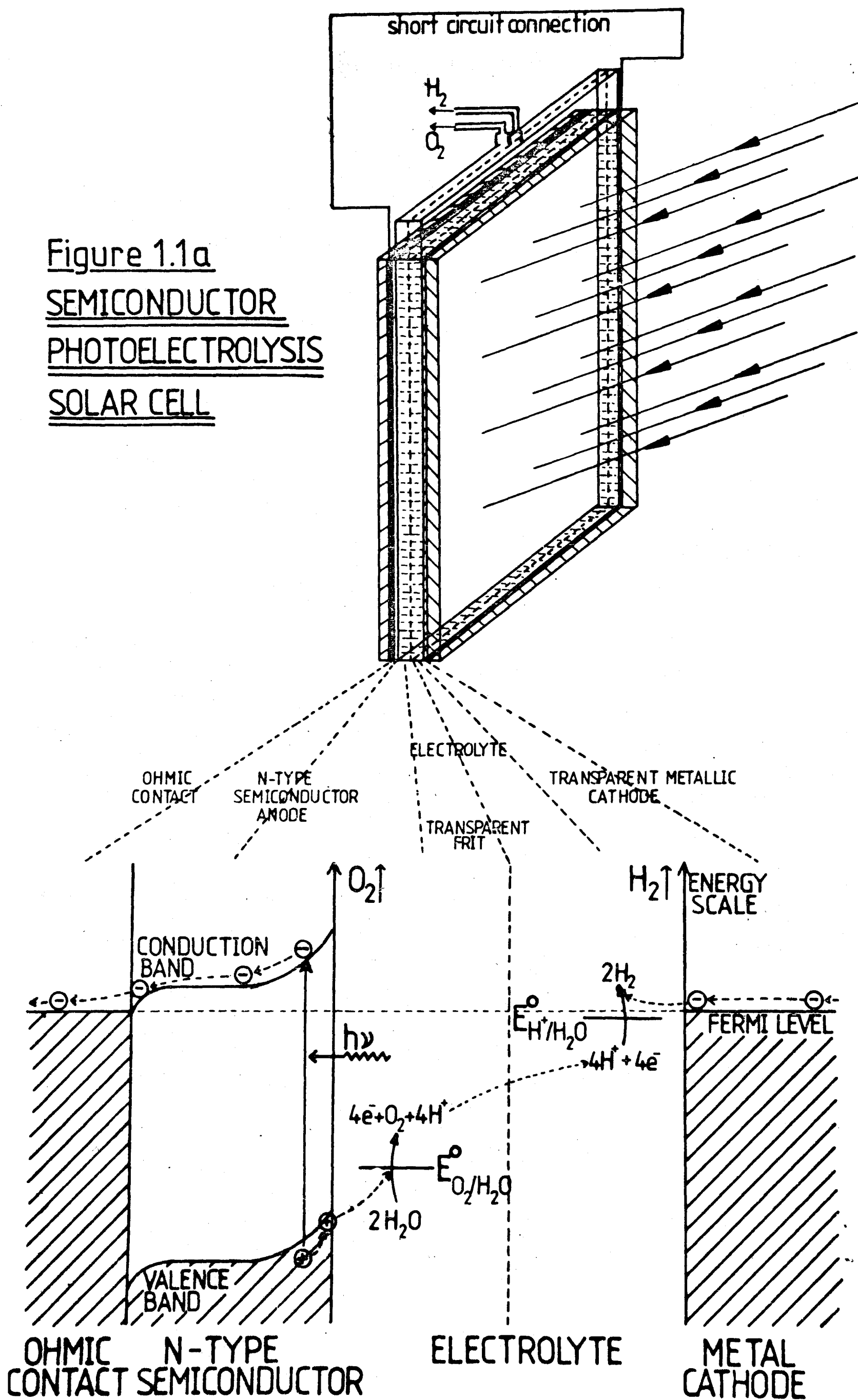


Fig. 1.1 Energy level diagram for configuration I
 photoelectrolysis cell

Fig.1.2 Energy level diagram for configuration II

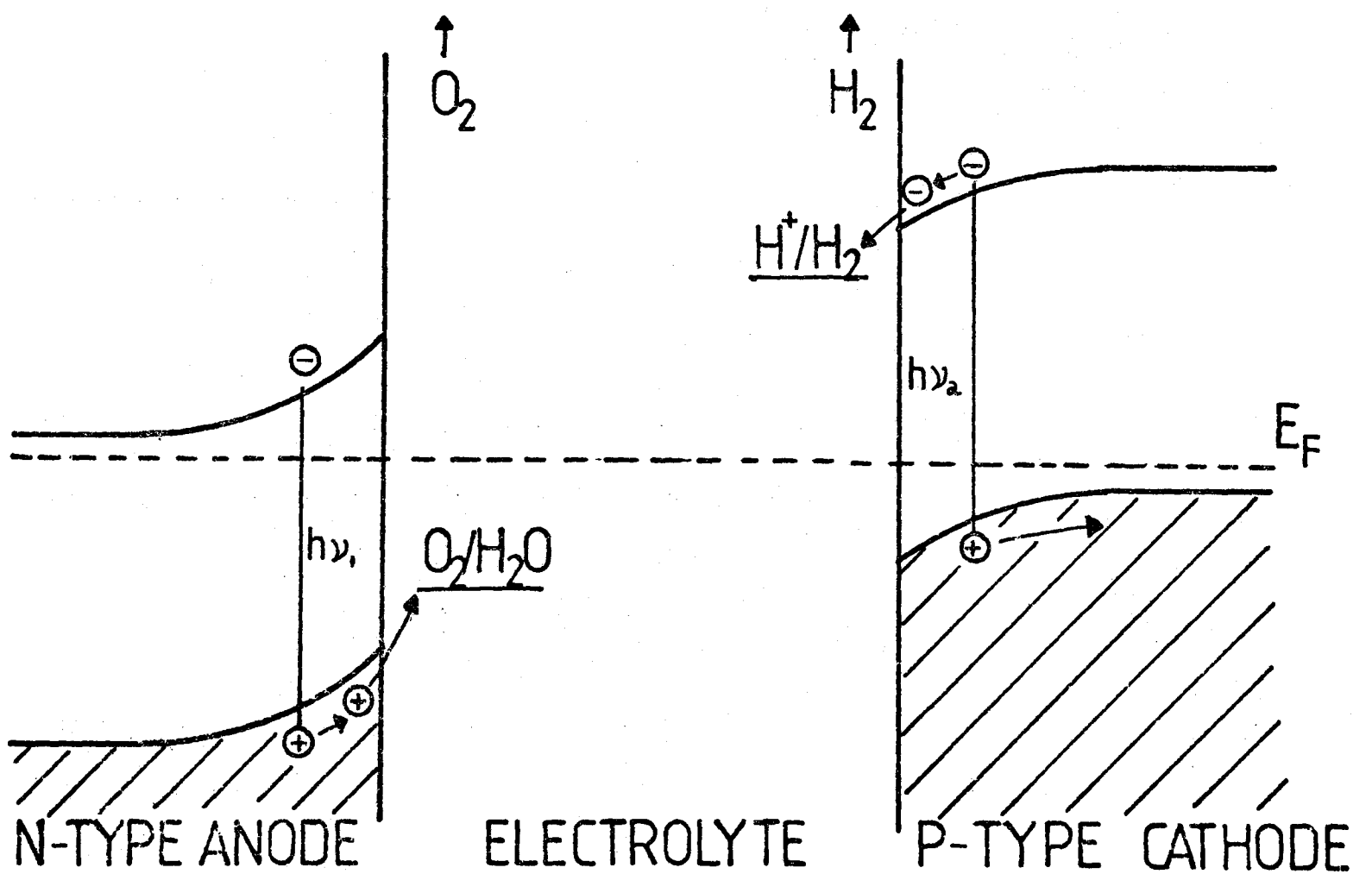
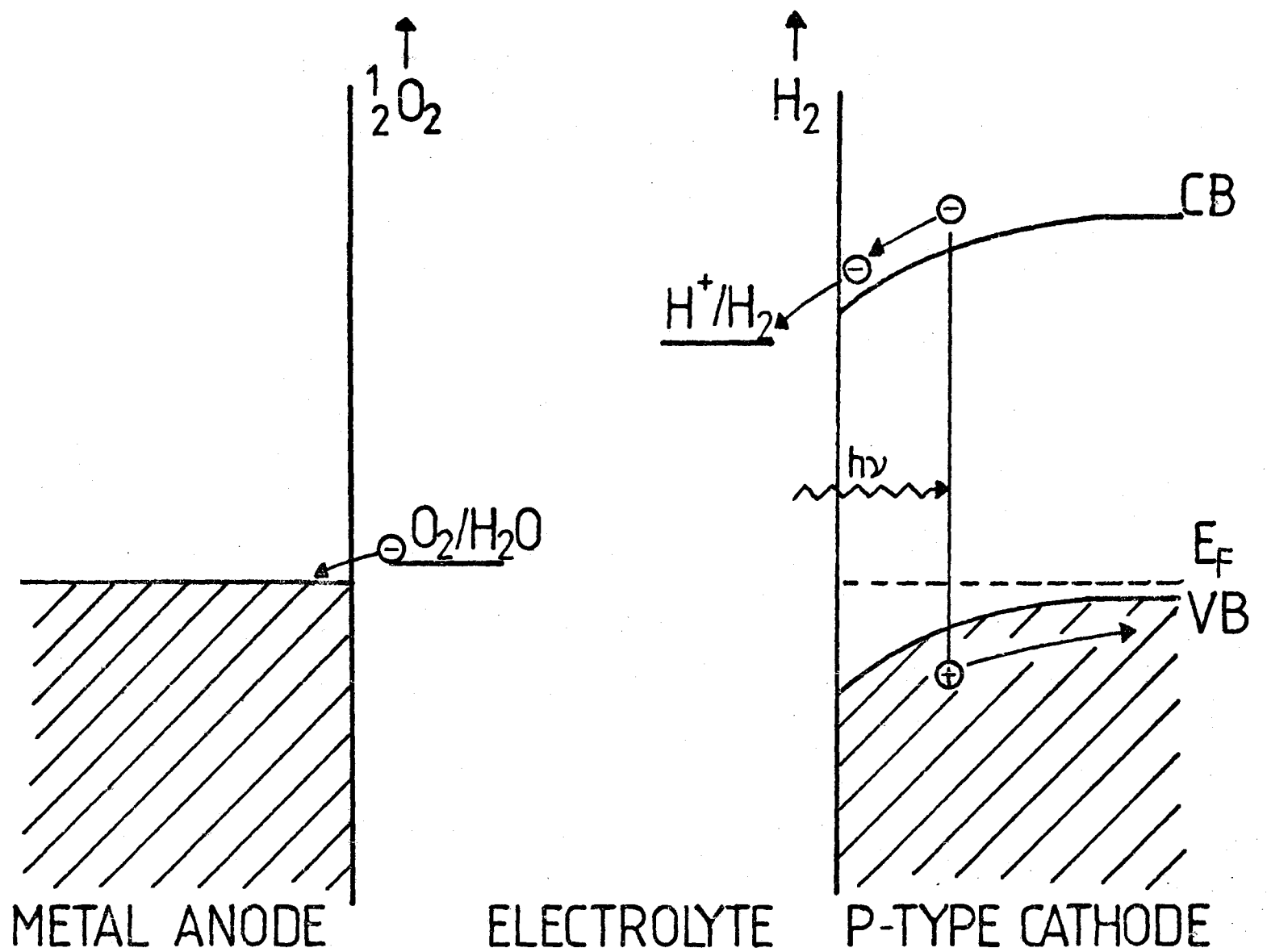


Fig.1.3 Energy level diagram for configuration III

However, there are many problems associated with the practical design of a photoelectrolysis cell operating with configuration III. Temporarily ignoring the detailed energetic constraints (to be dealt with in Section 8:4), there is still a problem of designing a device where the light has to be absorbed simultaneously by two semiconducting materials. The design of Fig.1.1a may still be used but the total thickness of the electrode closest to the light source would have to be engineered to match the extent of the electric field at the solution interface (the so-called space charge region - see Chapter 2). A number of alternative designs may also be applicable but in general they are of greater complexity than those necessary for configurations I and II. In general it seems that less attention has been paid in the literature to the design of cells operating in Configuration III.

The detailed materials-design constraints of semiconductor photoelectrolysis cells will be considered in Chapter 8, along with a brief description of the various novel approaches that have been attempted during the work for this thesis. The major part of the rest of this thesis contains results obtained on the photoevolution of Hydrogen from a number of p-type III-V materials for application to the photoelectrolysis of water in configuration II or III.

A very wide range of semiconducting materials has now been studied for use in photoelectrolysis cells. However, the optimal conversion efficiencies have been obtained with some of the originally investigated materials, notably $n\text{-TiO}_2$ (Configuration I $\sim 0.5\%$)¹⁹⁻²¹, $n\text{-SrTiO}_3$ (Configuration I $\sim 1\%$)²² and $n\text{-SrTiO}_3/p\text{-GaP}$ (Configuration III $\sim 1\%$)²³. A photoassisted device has also been recently developed using Ruthenium modified p-type InP in Configuration II, which with an external bias has claimed an overall efficiency of $\sim 3\%$ ²⁴. However, on the basis of the experiments discussed in Chapter 7 of this thesis, there is some cause for doubt concerning this latter result.

Table 1:1 summarizes the critical characteristics of semiconductor materials investigated for use in photoelectrolysis cells. The significance of these parameters is discussed in Chapter 2.

Table 1:1

<u>Material</u>	<u>Band-gap (eV)</u>	<u>Flat band potential vs. R.H.E.</u>	<u>Possible Configuration</u>	<u>Remarks</u>	<u>Refs.</u>
<u>(a) n-type materials</u>					
SrO	5.7	-	-	Cannot be made conducting	25
TiO ₂ (rutile)	3.0	0.05	I or III	Stable. Efficiencies ~0.5%	19-21 & Reviews 26a & b
ZrO ₂	5.0	-1.1	I	Stable	27
V ₂ O ₅	2.8	+1.2	III	Corrodes	25
Nb ₂ O ₅	3.4	0.0	I or III	Stable	27
Ta ₂ O ₅	4.0	-0.4	I	Stable	27
Cr ₂ O ₃	ca.3.0	-	-	Corrodes - poor response	25
MoO ₃	-	-	-	Corrosion protection agent	28
WO ₃	2.7	+0.5	III	Stable	29-34
MnO ₂	0.3	-	-	No response	25
Fe ₂ O ₃	2.2	+0.9	III	Stable in alkali/surface rearrangement problem	30,32 35-39
CoO	2.8	+0.8	III	Corrodes - poor response	25
ZnO	3.2	0.0	I or III	Corrodes	2-4, 12, 40-46
CdO	2.3	-	-	No response	25, 32
In ₂ O ₃	5.0	+0.35	III	Stable	47
SnO ₂	3.5	+0.5	III	Stable	48-50
PbO	2.8	+0.5	III	Corrodes	25, 51, 52
Bi ₂ O ₃	2.8	+0.7	III	Corrodes	25, 53
MgTiO ₃	3.5	-0.5	I	Stable	47
CaTiO ₃	3.6	-0.6	I	Stable	47
SrTiO ₃	3.2	-0.2	I	Stable. Efficiencies ~1%	22, 32, 54, 55, 56
BaTiO ₃	3.3	+0.1	III	Stable	57-59
BaTiO ₃ (Fe and F doped)	2.8	-	I	Photoresponse quenched	59

Table 1.1 continued

MnTiO ₃	2.9	-0.2	I	Unstable	60-62
FeTiO ₃	2.9	+0.1	I or III	Surface leached of Fe atoms	60,63
Fe ₂ TiO ₄	2.1	1.2	III	Unstable	63,64
Fe ₂ TiO ₅	2.2	1.5	III	Stable	63,64
CoTiO ₃	2.7	-	-	Unstable	60
NiTiO ₃	2.7	-	-	Unstable	60,65
Pb(La)TiO ₃	3.0	-	-	No conducti- vity	57
NaCeTi ₂ O ₆	1.8	-0.2	I	Unstable - Na ⁺ ions substitu- ted by H ⁺	60-62
Ce ₂ Ti ₂ O ₇	1.8	-0.2	I	Unstable	60
Pr _{2/3} TiO ₃	-	-	-	Unstable	60
NaPrTi ₂ O ₆	-	-	-	Unstable	60
SrTi _{0.75} Zr _{0.25} O ₃	3.3	-0.35	I	Stable - good O ₂ electrode	60-62
Sr _{0.5} Ba _{0.5} TiO ₃	3.3	-0.30	I	Stable	47
Ba _{0.8} Ca _{0.2} TiO ₃	3.2	-0.3	I	Stable	47
KNbO ₃	3.1	-0.15	I	Stable	47
Ba _{0.5} Sr _{0.5} Nb ₂ O ₆	3.38	-	I	Stable	66
Sr ₂ Nb ₂ O ₇	3.36	-	I	Stable	66
Hg ₂ Nb ₂ O ₇	1.8	1.1	III	Unstable	32
Sn ₂ Nb ₂ O ₇	2.2	-	III	Unstable	67
FeNbO ₄	2.1	1.0	III	Stable	68
KTaO ₃	3.5	-0.2	I	Stable	69,70
KTa _{0.77} Nb _{0.23} O ₃	3.3	-0.2	I	Stable	70
Hg ₂ Ta ₂ O ₇	1.8	+1.2	III	Unstable	32
LaCrO ₃	?	?	I	Stable?	71-73
YFeO ₃	2.6	0.5	III	Stable	74
CdFe ₂ O ₄	2.3	0.8	III	Poor response but stable	32
PbFe ₁₂ O ₁₉	2.3	1.0	III	Stable at high pH	32
CoFe _{1.86} Ti _{0.14} O ₄	1.6	-	III	Unstable	75
Pb ₂ Ti _{0.5} W _{0.5} O _{0.65}	2.4	0.4	III	Stable at high pH	32

Table 1:1 continued

Cd_2SnO_4	2.12	1.0	III	Unstable	76
CdIn_2O_4	2.23	1.2	III	Stable	76
Cd_2GeO_4	3.15	0.0	I or III	Stable	76
Other n-type materials investigated have included a number of solid solutions of the above as quaternary or more complex systems, see Rauh et al. (Ref. 77). Also many ions have been investigated as dopants in TiO_2 but all give lower efficiencies than pure TiO_2 . All non-oxide n-type materials photocorrode in blank aqueous solutions.					
<u>(b) p-type materials</u>					
NiO	3.5	+1.6	II or III	Poor response/ stable	78-85
Cu_2O	2.2	-	-	Corrodes	4, 86-88
CuO	1.7	1.0	-	Corrodes	25
$\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$	-	-	III	Unstable - poor response	75
$\text{Co}_{1.1}\text{Fe}_{1.9}\text{O}_4$	-	-	III	Unstable - poor response	75
NiCo_2O_4	-	-	III	Unstable - poor response	75
LuRhO_3	2.2	+0.9	-	Stable (prepa- ration requires high $p\text{O}_2$)	89, 90
CdTe	1.4	-	III	Corrodes	91, 92
ZnTe	2.3	-	-	Corrodes	91
GaP	2.24	+0.9	III	Stable (?)	91, 93-103
GaAs	1.43	+0.4	III	Corrodes	91, 104-110
GaSb	0.67	+0.2	(III)	Corrodes	111
InP	1.3	+0.8	III	Corrodes (?)	91, 112-119
SiC	3.0	+1.5	II or III	Stable	91, 120
Si	1.1	+0.3	III	Unstable (?)	91, 121-123
Ge	0.66	-	III	Unstable	1, 14

1:4 SEMICONDUCTOR/ELECTROLYTE PHOTOVOLTAIC CELLS

In the photoelectrolysis cell and the remaining semiconductor/electrolyte systems that follow, there is an overall chemical reaction obtained from the sum of the anode and cathode reactions which occur during the operation of the device (e.g. $\text{H}_2\text{O} \rightarrow \text{H}_2 + \frac{1}{2}\text{O}_2$). The output from these devices is thus in the form of chemical products; and for continuous operation, a constant supply of reagents must be provided to the cell. However, it is possible to devise a semiconductor/electrolyte cell where no net chemical reaction occurs from the sum of the anode and cathode reactions during its operation. Instead the same redox species are involved in oxidation and reduction reactions at the anode and cathode and electrical power is tapped off from the device. Such a cell is shown in Fig.1.4 using a p-type semiconductor + metal anode configuration. The electrolyte in this case contains a $\text{V}^{3+}/\text{V}^{2+}$ redox couple. At the semiconductor cathode, photogenerated electrons in the conduction band are sufficiently energetic to reduce $\text{V}^{3+} \rightarrow \text{V}^{2+}$; the photogenerated holes in the valence band have energy in excess of that required to reoxidize V^{2+} and so may perform useful electrical work in an external circuit. In performing this work, they pass through a potential drop before arriving at the metal anode where they may reoxidize the V^{2+} back to V^{3+} . The operating cell thus cycles V^{2+} and V^{3+} through the electrolyte and passes electric current through the external circuit.

For optimum output voltage determined by V_{oc} (open circuit voltage), the E^0 of the redox couple used should lie as near the conduction band edge as is compatible with rapid electron transfer kinetics from the semiconductor into solution. The operational output voltage (V_{out}) is then less than V_{oc} by the band bending and overpotential losses at the two electrodes.

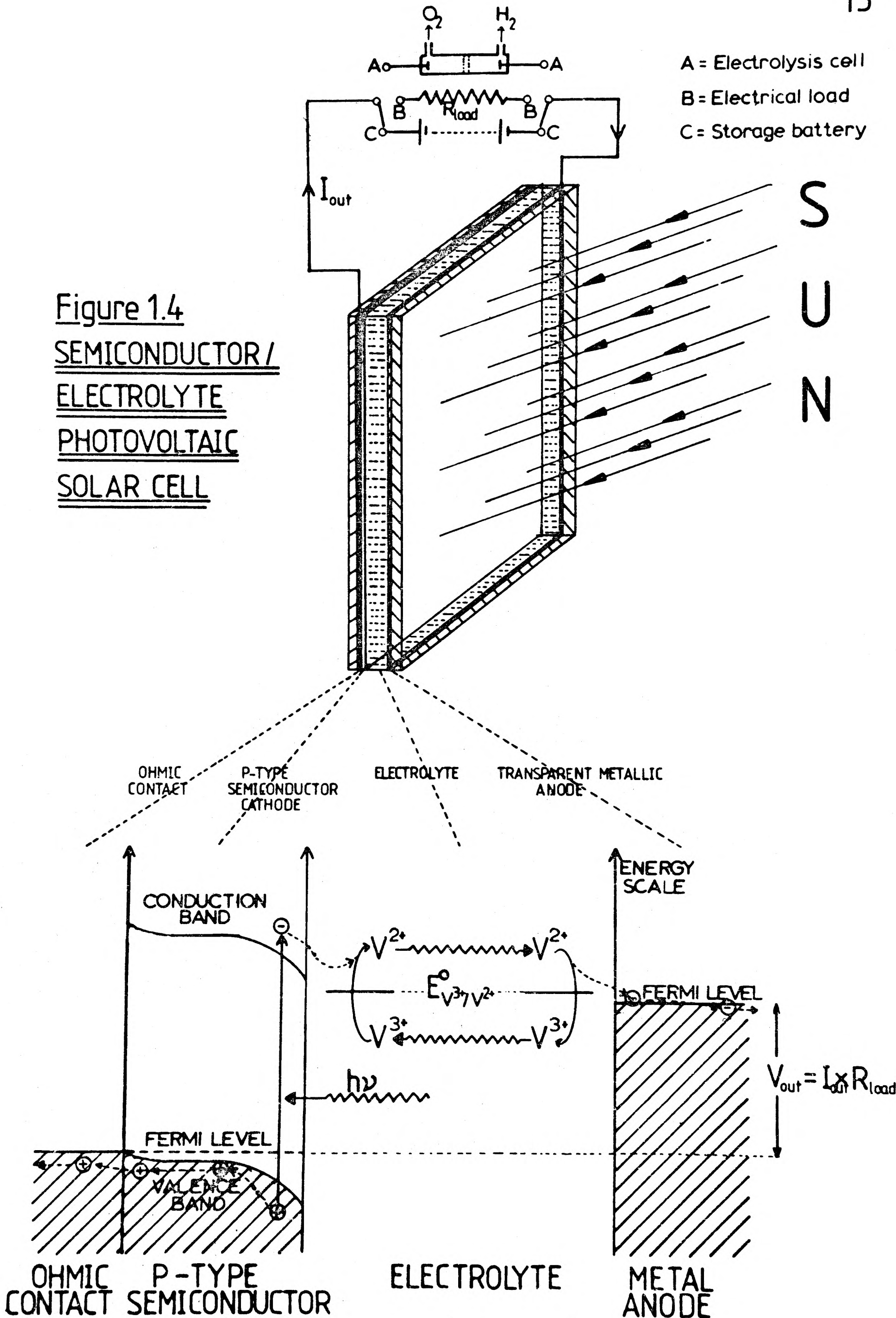


Fig. 1.4 Energy level diagram for 'wet-type' photovoltaic cell

A working cell adopting the V^{3+}/V^{2+} couple has been demonstrated using p-type Indium Phosphide; solar conversion efficiencies of up to 11% have been obtained with single crystal material.¹²⁴ However, the use of p-type electrodes in these devices is a recent innovation; the majority of the work on these so-called 'wet-type photovoltaics' has been performed on cells with the n-type semiconductor + metal cathode configuration. The first cell of this type was the $nCdS|Na_2S, Na_2S_2, NaOH|C$ cell,¹²⁵⁻¹²⁷ and quite high efficiencies - around 2-3% - have been obtained with single-crystal CdS ,¹²⁸ around 1-2% with polycrystalline-film electrodes.¹²⁹ In the absence of the added sulphide redox couple, n-CdS rapidly corrodes in aqueous solution; generating Cd^{2+} ions in solution and elemental sulphur at the electrode surface.¹³⁰ The original conception of the sulphide medium was as a stabilizing agent, since the oxidation of sulphide to polysulphide at the electrode surface is thermodynamically and kinetically favoured over the photo-corrosion reaction, providing the sulphide concentrations are maintained around 1 Molar.^{130,131}

Since the development of this CdS based cell, there have been a number of other successful operational devices used; these are indicated below along with their maximum efficiencies.

$nCdSe_{0.65}Te_{0.35} Na_2S, Na_2S_2, NaOH C(\text{graphite})$	Polycrystalline: 8%	¹³²
$nWSe_2 0.025M I_3^-, 1.0M I^- Pt$	Single crystal: 14%	¹³³
$n-GaAs 0.8M K_2Se, 0.1M K_2Se_2, 1M KOH Pt$	Single crystal: 12%	¹³⁴
(Ru modified)	Polycrystalline: 7.8%	¹³⁵

Table 1.2 illustrates a number of other systems that have been studied.

TABLE 1.2 Summary of experimental studies on electrochemical photovoltaic cells

Semiconductor electrode	Predominant redox couple	Maximum experimental efficiency, ^c (%)	References
<i>n</i> -CdS ^a	—	5	136,137
<i>n</i> -CdS	S ²⁻ /S _n ²⁻	1-2	125-131,136-140
<i>n</i> -CdS	Se ²⁻ /Se ₂ ²⁻	3(5000)	140,141
<i>n</i> -CdS	Te ²⁻ /Te ₂ ²⁻	1(4880)	140,141
<i>n</i> -CdS ^b	Fe(CN) ₆ ⁴⁻ /Fe(CN) ₆ ³⁻	6-7	142-144
<i>n</i> -CdSe	S ²⁻ /S _n ²⁻	7-8	125,128,138,140,145-147
<i>n</i> -CdSe	Se ²⁻ /Se ₂ ²⁻	2(6330)	140,141
<i>n</i> -CdSe	Te ²⁻ /Te ₂ ²⁻	1-2(6330)	140,141
<i>n</i> -CdTe ^a	S ²⁻ /S _n ²⁻	—	140,141
<i>n</i> -CdTe	Se ²⁻ /Se ₂ ²⁻	9(6330)	140,141
<i>n</i> -CdTe	Te ²⁻ /Te ₂ ²⁻	10(6330)	140,141,148
<i>n</i> -CdTe	—	5	149
<i>n</i> -GaAs ^a	S ²⁻ /S _n ²⁻	—	140,150,151
<i>n</i> -GaAs	Se ²⁻ /Se ₂ ²⁻	9-10	140,150
<i>n</i> -GaAs	Te ²⁻ /Te ₂ ²⁻	1-3(6330)	140,152
<i>n</i> -InP ^a	S ²⁻ /S _n ²⁻	—	140,152
<i>n</i> -InP ^a	Se ²⁻ /Se ₂ ²⁻	—	140,152
<i>n</i> -InP	Te ²⁻ /Te ₂ ²⁻	1(6330)	140,152
<i>n</i> -GaP	S ²⁻ /S _n ²⁻	—	140,150
<i>n</i> -GaP	Se ²⁻ /Se ₂ ²⁻	2(4550)	140,150
<i>n</i> -GaP	Te ²⁻ /Te ₂ ²⁻	1(4550)	140,150
<i>n</i> -Si	Fe(Cp) ₂ /Fe(Cp) ₂ ⁺	2(6330)	153
<i>p</i> -Si	—	—	154
<i>n</i> -ZnSe	S ²⁻ /S _n ²⁻	—	139
<i>n</i> -TiO ₂	O ₂ /H ₂ O	0.5-1	21,155
<i>p</i> -MoS ₂	Fe ³⁺ /Fe ²⁺	1	156,157
<i>n</i> -CdS/ <i>n</i> -GaAs	S ²⁻ /S _n ²⁻	3	158
<i>n</i> -CdSe/ <i>p</i> -CdTe	S ²⁻ /S _n ²⁻	—	159

^a Unstable system.
^b Stable in the absence of O₂.
^c Values not followed by a parentheses refer to sunlight conditions; values followed by a parentheses refer to monochromatic conditions (wavelength in parentheses, Å).

A major design problem facing all these systems is the extremely high absorptivity of the solution redox couples (S_2^{2-} , I_3^- and Se_2^{2-}) for visible light, and the necessity for concentrations approaching 1 molar. To achieve high efficiencies, the solution pathlengths need to be considerably less than 1mm, and preferably about 0.1mm. Considerable technical problems may then be encountered in the preparation of wide areas of such smooth electrode surfaces and prevention of direct contact of the anode and cathode faces. This problem seems little discussed in the literature. The cell employing the V^{3+}/V^{2+} couple goes some way towards a less strongly absorbing electrolyte, but the only aqueous couple used in these wet-type solar cells that has gone towards total transparency is the Eu^{3+}/Eu^{2+} couple. This was suggested by Memming for use in a device employing the p-GaP electrode^{160,161} but more recently has been revived by Heller et al. for use in conjunction with p-InP.¹⁶² Overall conversion efficiencies are quite high but from an economic standpoint, many acres of molar Europium solution does not present itself as a viable proposition.

As an alternative approach, Wrighton et al. have reported on a wet photovoltaic employing the near-transparent solution of Cl_2/Cl^- in acetonitrile, claiming single-crystal-based efficiencies of 5-6% with n-type MoS_2 .¹⁶³ In addition, an extremely interesting device has been reported where the mediating agent in solution between cathode and anode is the solvated electron in liquid ammonia. Efficiencies for this latter device were, however, very low (0.1%).¹⁶⁴

The principle disadvantage of all these wet photovoltaics and indeed of all semiconductor/electrolyte solar cells is their, as yet unproven, long-term stability. A number of devices have been operationally stable for periods of up to one year,¹⁶⁵ but a viable system must almost certainly operate without significant maintenance for periods in excess of 10 years. No solution-based system has yet approached this required durability, and

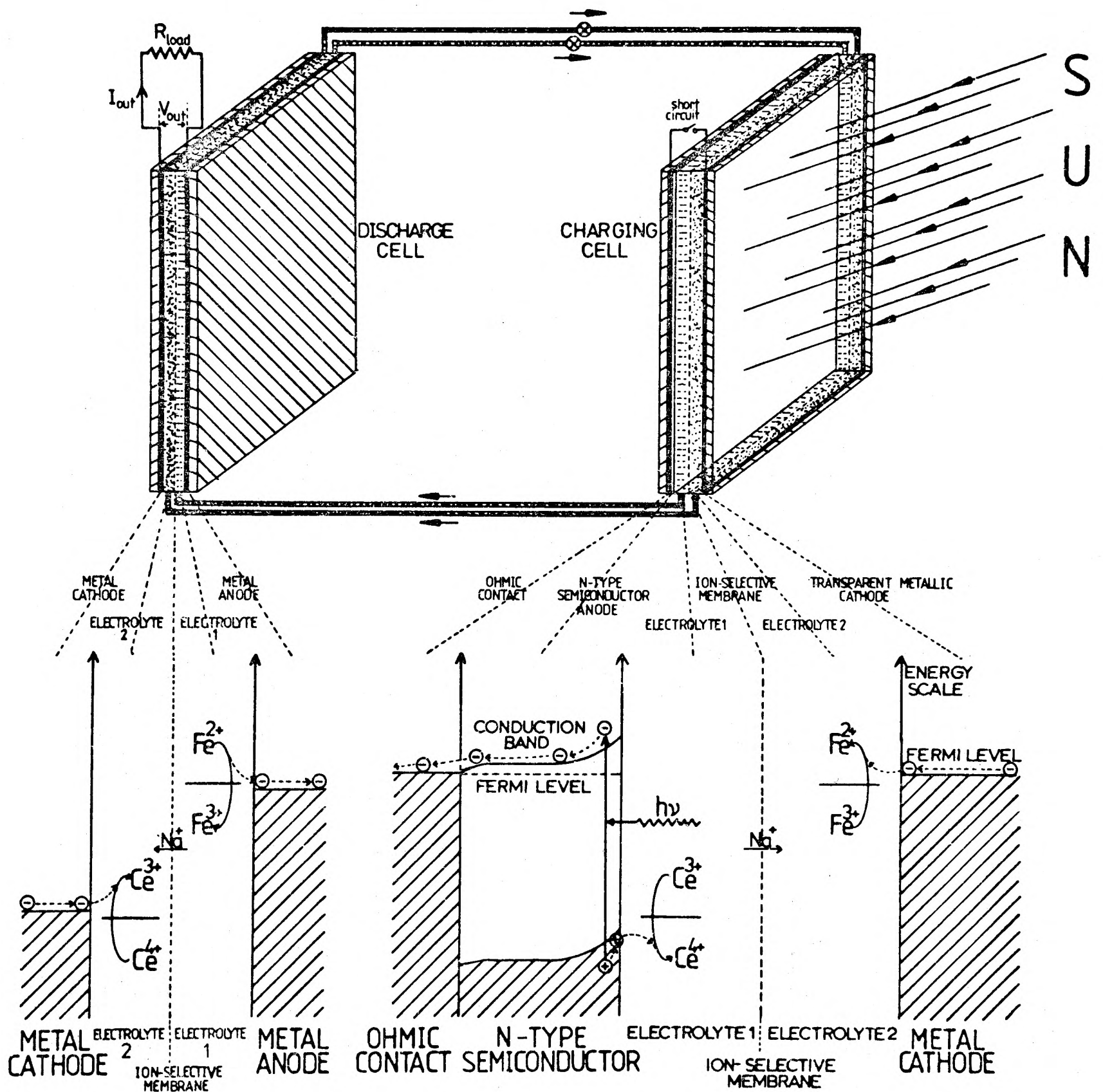
indeed the requirement is very stringent. A green leaf on a tree during its own solar energy conversion of one season will operate such that the fraction of side (degradation) reactions to the desired photosynthesis is less than 1 part in 10^9 . Nearly all the presently studied systems suffer from photocorrosion reactions, surface structural rearrangements, atom or ion diffusion.

Despite this pessimistic viewpoint, the great progress achieved with the study of wet-photovoltaics over the last few years is promising. At the present time, for further developments in this field, the study of surface preparation effects, surface modification, and corrosion protection are the main focusses of attention.

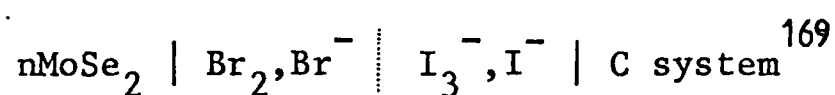
SECTION 1:5 THE SOLAR BATTERY

As well as creating a storable fuel or generating directly usable electricity, semiconductor/electrolyte solar cells may also be used for charging up a so-called solar battery.¹⁶⁶⁻¹⁶⁹ In these proposed devices (see Fig. 1.5), two different redox reactions are performed at the anode and cathode to create a more powerful oxidizing agent and reducing agent respectively. In the case shown in Fig. 1.5, Ce^{3+} is oxidized to Ce^{4+} at the illuminated semiconductor anode and Fe^{3+} is reduced to Fe^{2+} at the cathode. An ion-selective membrane is necessary to separate the two different solutions into an anode and cathode compartment, whilst still allowing electrical charge to pass from one side of the cell to the other. To avoid pH changes in the anolyte and catholyte during operation, the charge transfer will be best achieved using a Sodium-ion selective membrane. The charged anolyte and catholyte may then be pumped away and stored; the reverse processes are carried out in the dark on metal-electrodes such that electrical power may then be drawn during the discharge process.

Figure 1.5

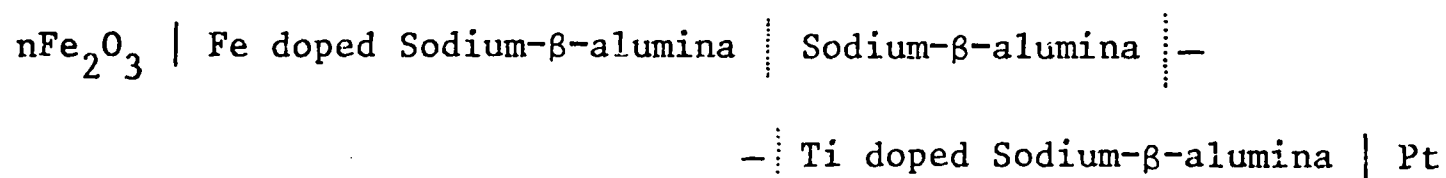
SEMICONDUCTOR/ELECTROLYTE SOLAR BATTERYFig. 1.5 Energy level diagram for solar battery

At first sight, the device looks particularly appealing due to the simplicity of the mechanism. However, if we envisage its usage in the domestic situation, a few figures may put the feasibility into perspective. An average demand for electricity for domestic purposes (lighting and low-level heating) might be approximated at 500W for 8 hours, which requires a storage capacity of about 4kW hours. This capacity is in turn equivalent to 14.4MJ which makes approximately 28.8MC of stored charge at an estimated 0.5V output voltage. Given single-electron redox couples, this requires a minimum of 300 moles of redox material each for both catholyte and anolyte. Unless the redox reagents are quite cheap, the capital cost of such a device could be enormous. Unfortunately, the only operational solar battery of this type, so far discussed at any length, has been the



where the capital cost of 300moles each of the redox reagents would be quite staggering. Nevertheless, if sufficiently cheap redox couples such as $\text{Fe}^{3+}/\text{Fe}^{2+}$ could be utilized, then costs might become more reasonable. Little attention seems to have been given to these devices in the literature but there remains considerable doubt concerning the viability of solar batteries.

A recent patent describes a novel solar battery that employs a solid-state ionic conductor as the electrolyte:-¹⁷⁰



operating with solid state redox couples $\text{Fe}^{3+}/\text{Fe}^{2+}$ and $\text{Ti}^{4+}/\text{Ti}^{3+}$ respectively. The output efficiency of this device was, however, exceedingly low (estimated at <0.1%) due to problems of mobility across the various interfaces in the system.¹⁷⁰ There seems little application for this device since high temperatures (>400°C) are required to reduce the internal resistance of the cell. A system based on a room-temperature proton-conducting medium might be of more interest.

SECTION 1:6 PHOTOCATALYTIC SYSTEMS

In all the systems presented so far, there is a net energy gain either in the form of chemical bonds, enhanced reagent oxidizing or reducing power, or electrical power generation. In a fourth device category, the semiconductor/electrolyte junction is used to photocatalyze a thermodynamically downhill process which otherwise would only occur very slowly, (see Fig. 1.6). Examples of such photocatalytic systems include the oxidation of cyanide ions to cyanate,^{171,172} sulphite to sulphate¹⁷³ and the Photo-Kolb  reaction - decarboxylation of carboxylic acids.^{174,175}

There has, however, been little study of these systems other than with n-TiO₂ electrodes used in particular for the Photo-Kolb  reaction. In practice, these photocatalytic devices may have practical applications with pollution control (e.g. of cyanide and SO₂ effluents).

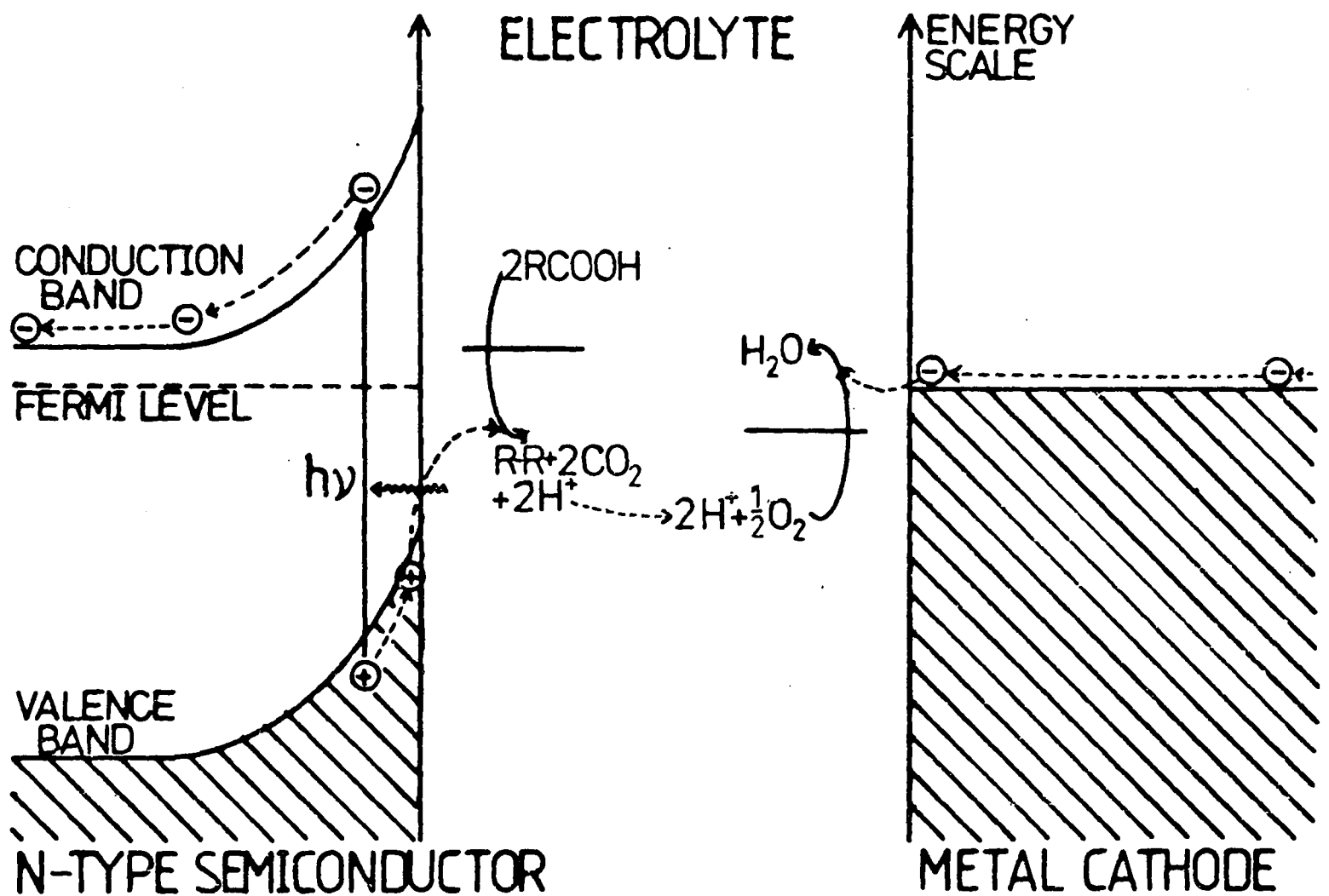
In all cases, the operation of these devices can be understood in terms of the multistep nature of the reactions concerned. For the photocatalytic reactions studied, the first electron transfer step leads to the formation of a high-energy intermediate (e.g. $\text{OH}^- \rightarrow \text{OH}^\bullet$ or $\text{RCO}_2^- \rightarrow \text{RCO}_2^\bullet$) requiring a considerable 'overvoltage' relative to the thermodynamic potential of the overall two-electron oxidation reactions concerned. The n-type semiconductor electrode is thus able to supply this necessary overvoltage by the excess energy of the valence-band holes created under illumination.

SECTION 1:7 PHOTOELECTROSYNTHESIS

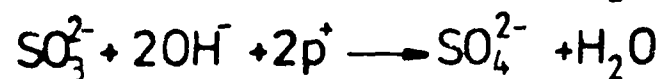
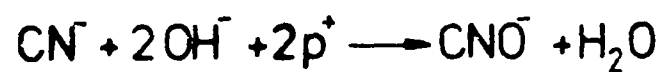
Apart from the energy-storing reaction of water photoelectrolysis, a number of other thermodynamically uphill reactions are possible using semiconductor electrodes and they lead to the creation of more complex, higher-energy molecules. Of particular interest are the reduction of CO₂ and Nitrogen. There have been claims of successful reduction of these reagents at p-type GaP and p-type GaAs:

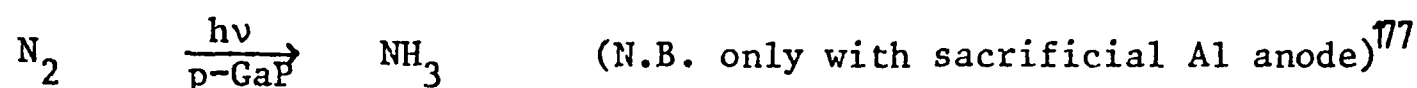
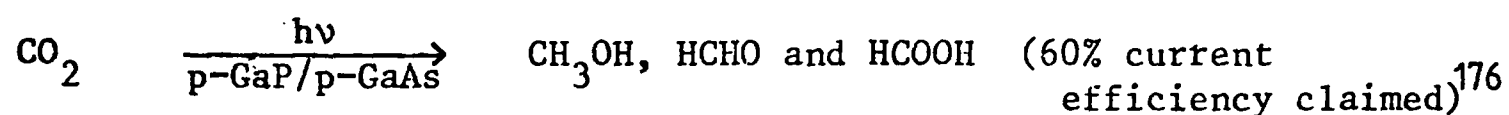
Figure 1.6

SEMICONDUCTOR/ELECTROLYTE CELL IN USE
AS A PHOTOCATALYTIC DEVICE



OTHER WASTE POLLUTANT PHOTOCATALYTIC OXIDATIONS INCLUDE:-

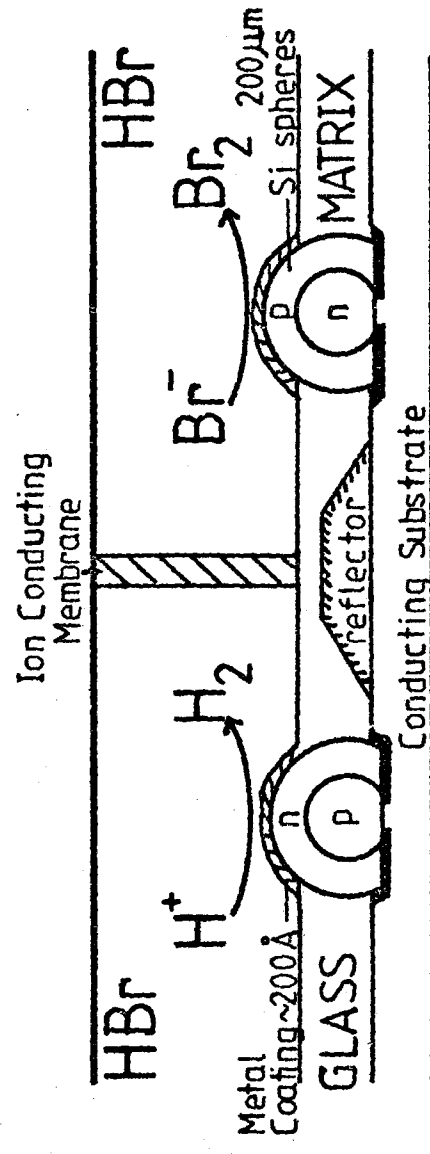




Some further studies of the former CO_2 reduction process are reported in Chapter 4 on p-GaP. The N_2 reduction as reported in the literature is, however, not a true photoelectrosynthesis, but rather a photocatalytic system since, in addition to the use of an illuminated p-GaP electrode, a sacrificial Aluminium anode was found necessary.¹⁷⁷ Since Aluminium is thermodynamically capable of reducing N_2 to NH_3 alone, the overall energetics of the process render the reaction thermodynamically downhill, although it does not occur without the assistance of the semiconductor electrode.

There has been a continued search in the field of photoelectrolysis for an alternative anodic oxidation reaction other than the oxidation of water to generate O_2 . Some suggestions have been made such as the oxidation of Cl^- to Cl_2 (e.g. 6% photoassisted electrolysis using p-InP)¹⁷⁸ and Br^- to Br_2 . Unfortunately, for continuous operation these systems require a constant supply of either HCl or HBr, so that the overall energetic balance of the reaction becomes less clear as one has to take into account the energy cost of creating the HCl and HBr. Nevertheless, the potentials of these systems for a fuel cell cycle that regenerates the HCl and HBr is attracting interest, and Texas Instruments has just reported a commercial solar HBr photoelectrolysis system.¹⁷⁹ The detailed operation of this device seems to indicate that it operates as a series combination of two Silicon p-n photovoltaic junctions connected to a 'traditional' HBr electrolysis cell that employs metallic electrodes. Thus strictly speaking, the system cannot be termed as a true semiconductor photoelectrolysis device, since the accepted meaning for such a device implies direct contact between solution and semiconductor. As Fig. 1.7 shows, no such direct contact is made with the Texas Instruments system.

Figure 1.7 Texas Instruments solar
HBr photoelectrolysis system



SECTION 1:8 MICROHETEROGENEOUS SYSTEMS

In 1975, Nozik first suggested the concept of a photochemical diode where the external use of a standard photoelectrolysis device is removed and the semiconductor and metal electrodes are connected directly back to back (see Fig. 1.8)¹⁸⁰. This idea may be taken a step further; Bard subsequently suggested the idea of a microheterogeneous system employing partially metal-coated semiconductor particles as a suspension in aqueous solution such that each particle, on illumination, could act as a miniature version of Nozik's photochemical diode.¹⁸¹ The idea was put into action for Pt coated TiO_2 particles for use in the photoelectrolysis of water^{182,183} (see Fig. 1.9). Unfortunately H_2 and O_2 are generated simultaneously from the same solution in this device so an additional gas separation technique would be necessary before H_2 storage. The efficiencies are, moreover quite low, since there is extensive scope for back-reaction (i.e. re-reduction of photogenerated O_2) and continuous gas flushing is necessary to achieve the highest conversion efficiencies ($\approx 0.1\%$).¹⁸³

However, these microheterogeneous systems have also been applied to a number of other reactions, notably CO_2 reduction¹⁸⁴ and the photocatalytic reactions mentioned in Section 1:5.¹⁸⁵ For the former case, illuminated suspensions of TiO_2 , SrTiO_3 , GaP, SiC and WO_3 were shown to reduce CO_2 to HCOOH , HCHO and CH_3OH with quite startling efficiencies (seemingly $>100\%$ current collection efficiencies)¹⁸⁴. No further detailed reports have come from the same workers, and one must doubt the validity of the values claimed in their initial paper.

More recently, Grätzel, after turning from purely solution-geneous systems for energy conversion to the microelectrogeneous system, has studied water photoelectrolysis using TiO_2 (anatase) particles partially coated with RuO_2 (for Oxygen catalysis) and Pt (for Hydrogen catalysis). In addition; microheterogeneous dye sensitization has been applied,¹⁸⁶ but

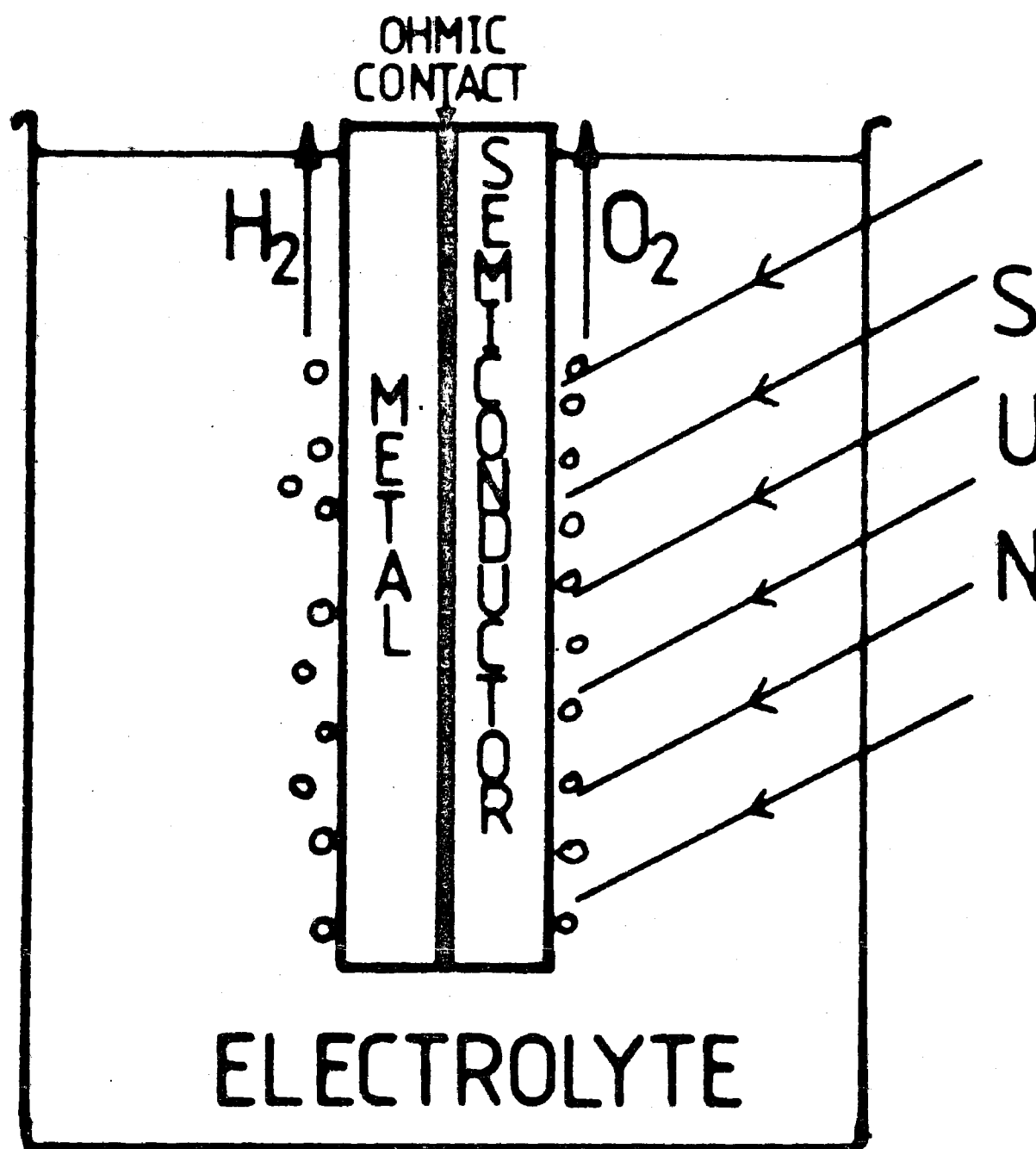
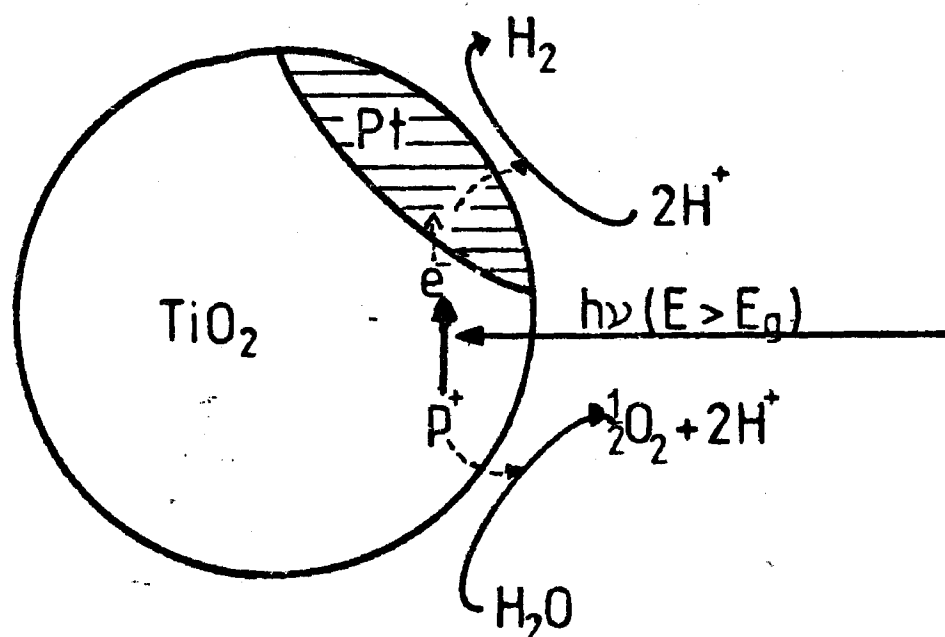


Figure 1.8 Schematic diagram of a photochemical diode in use for water photoelectrolysis.

Figure 1.9
PHOTOELECTROLYSIS
OF WATER ON PLATINIZED
SEMICONDUCTOR
POWDER PARTICLES
SUSPENDED IN
AQUEOUS SOLUTION



after careful analysis, the overall solar conversion efficiencies may be shown to be quite low ($<0.1\%$). Cr-doped TiO_2 (anatase) has also been used, and sensitization into the visible was achieved with moderate success.¹⁸⁷ (surprisingly in view of the very poor efficiencies of Cr-doped rutile in the macroscopic electrode system). Even CdS particles coated with RuO_2 have been reported to photoelectrolyze water in a stable system,¹⁸⁸ although attempts to reproduce this at the macroscopic-electrode scale has so far failed.^{189,190}

The full understanding of the operation of these microheterogeneous systems is still far from clear, and much controversy exists as to whether H_2 and O_2 can possibly be evolved from a single particle of only micron dimensions. Detailed kinetic and mechanistic studies are sorely lacking in this field, and so critical appraisal of the potential of these systems cannot as yet be made.

CHAPTER TWO

SEMICONDUCTOR ELECTROCHEMISTRY THEORY

SECTION 2:1 SEMICONDUCTOR ELECTROCHEMISTRY INTRODUCTION

Electrochemistry has grown up with a strong natural bias towards studies using metal electrodes. The majority of chemists are thus quite familiar with the essentials of the energetics of the metal/electrolyte interface, but unclear as to the changes that occur when the metal electrode is exchanged for that made from a semiconducting material. It is thus interesting to consider the major difference between metals and semiconductors when used as electrodes in contact with conducting electrolytes.

The essential details of the electronic structure and band theory of metals and semiconductors will be assumed to be understood. However, a few basic concepts are mentioned for the sake of clarity. A more complete discussion of the band structure and electronic properties of metals and semiconductors may be found in Refs. 191-193.

SECTION 2:2 PRIMARY DIFFERENCES BETWEEN METALS AND SEMICONDUCTORS RELEVANT TO ELECTROCHEMISTRY

Solid materials are generally classified as semiconductors or metals by the magnitudes and temperature dependences of their conductivities. Primarily the contrast in their conductivities are related to the different concentration of mobile charge carriers for the two materials, although other features such as mobility and effective mass of these carriers may also be important. Typical figures are given in Table 2.1 for materials that might be useful for electrochemical studies.

Table 2.1

<u>Material</u>	<u>Charge Carrier Concentrations</u> (cm^{-3})	<u>Conductivity</u> $\Omega^{-1}\text{m}^{-1}$
Metals	$\sim 10^{23}$	$10^6 - 10^8$
Doped Semiconductors	$10^{15} - 10^{19}$	$10^{-2} - 10^2$
1.0M Strong Electrolyte	$10^{20} - 10^{21}$	$10^3 - 10^4$

These differences have a striking effect on the distribution of charge and potential drop at interface between these materials, and this is discussed in detail in Section 2:4. A subsidiary point, however, is that these differences in conductivity may also affect the instrumentation required for the study of semiconductor electrochemistry. In particular, problems may arise from a significant I.R. potential drop through the bulk of the semiconductor if the conductivity is quite low. This potential drop may be compensated for, instrumentally, but generally studies are preferably performed on samples where front to back resistance is less than 10Ω so that I.R. drops are maintained to be less than 1mV.

A second fundamental difference between metals and semiconductors arises from their characteristic occupancy of the electron energy bands in the bulk material. For the former, the Fermi level actually lies within an energy band and thus there is electron density at the Fermi surface. For isolated semiconductors whether intrinsic or extrinsic (but not degenerately doped) the Fermi level always lies in the forbidden energy gap between the two electron energy bands (the so-called valence and conduction bands) and thus there is no electron density at the Fermi surface.

As a result, semiconductors may possess two distinct carrier types whereas metals possess a single species of charge carrier. For example, an intrinsic semiconductor (at temperature $>0K$) will possess equal numbers of mobile electrons in the conduction band^{and} of mobile holes in the valence band. The numbers of these charge carriers will depend on the temperature and will be governed by

$$n = \int_{E_c}^{E_{top}} N_c(E) F(E) dE \quad 2.1$$

$$\text{and } p = \int_{E_{bottom}}^{E_v} N_v(E) F(E) dE \quad 2.2$$

n = number of mobile electrons

E_{top} = Energy of top of Conduction Band

E_v = Energy of top of Valence Band

p = number of mobile holes

E_c = Energy of bottom of Conduction Band

E_{bottom} = Energy of bottom of Valence Band

$N_c(E)$ = density of states of conduction band

$N_v(E)$ = density of states of valence band

$F(E)$ is the Fermi-Dirac distribution function = $1/\{\exp[(E-E_F)/kT]+1\}$

For non-degenerate semiconductors this may be simplified to

$$n = N_c \exp\left(\frac{E_c - E_F}{kT}\right) \quad 2.3$$

$$p = N_v \exp\left(\frac{E_F - E_v}{kT}\right) \quad 2.4$$

where

N_c is the effective density of states in the conduction band

$$N_c = 2(2\pi m_c^* kT/h^2)^{3/2} \quad 2.5$$

N_v is the effective density of states in the valence band

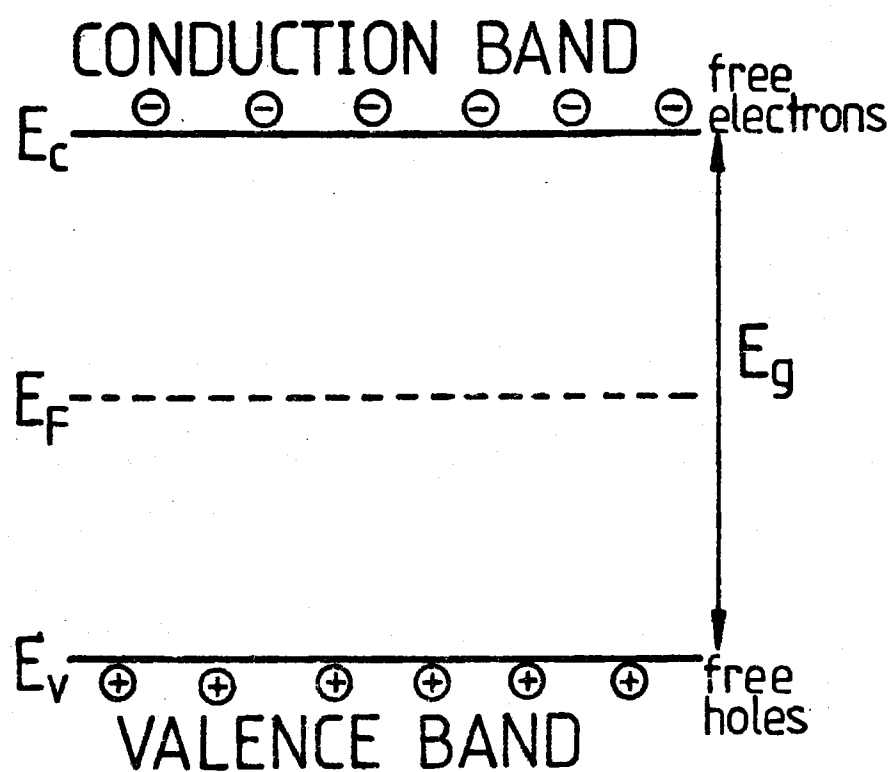
$$N_v = 2(2\pi m_v^* kT/h^2)^{3/2} \quad 2.6$$

E_F is the Fermi level, given by $E_F = \frac{1}{2}(E_c + E_v) + kT/2 \ln(m_c^*/m_v^*)$ 2.7

m_c^* = effective mass of electrons in conduction band

m_v^* = effective mass of holes in valence band

Fig. 2.1 illustrates the energy level diagram of an intrinsic semiconductor.



The semiconductor bandgap (E_g) is given by :-

$$E_g = E_c - E_v \quad 2.8$$

and

$$n_i = p_i = N_c N_v \exp(-E_g/kT) \quad 2.9$$

n_i = the intrinsic electron concentration.

However, for most electrochemical studies (and all those included in this thesis), extrinsically doped semiconductors are used in which the concentration of one set of charge carriers far exceeds the other, leading to two different classes of semiconductors: n-type (electron excess) and p-type (hole excess) materials. Under these circumstances the electron or hole densities may be given by :-

$$n \approx \frac{1}{\sqrt{2.2}} (N_D N_C)^{\frac{1}{2}} \exp (-E_d/2kT) \quad 2.10$$

$$\text{or } p \approx \frac{1}{\sqrt{2.2}} (N_A N_V)^{\frac{1}{2}} \exp (-E_a/2kT) \quad 2.11$$

where N_D = number of donor levels

$E_d = E_c - E_D$ where E_D is the energy of the donor levels

N_A = number of acceptor levels

$E_a = E_A - E_v$ where E_A is the energy of the acceptor levels

Equation (2.10) is true providing

$$N_D \gg \frac{1}{2} N_C \exp (-E_d/kT) \gg N_A \quad 2.12$$

and Equation (2.11) is true providing

$$N_A \gg \frac{1}{2} N_V \exp (-E_a/kT) \gg N_D \quad 2.13$$

i.e. the materials contain either donor or acceptor states, but not both to any significant concentration. Materials that possess approximately similar concentrations of donor and acceptor states are called compensated semiconductors, and these will not be discussed here since throughout the work the inequalities (2.12) and (2.13) will hold true for all materials used.

The Fermi level for doped semiconductors is now given by

$$E_F = E_c - kT \ln \frac{N_C}{N_D} \text{ for n-type materials} \quad 2.14$$

$$\text{or } E_F = E_v + kT \ln \frac{N_V}{N_A} \text{ for p-type materials} \quad 2.15$$

Fig. 2.2(a and b) shows the energy diagram of ideal n and p type semiconductors.

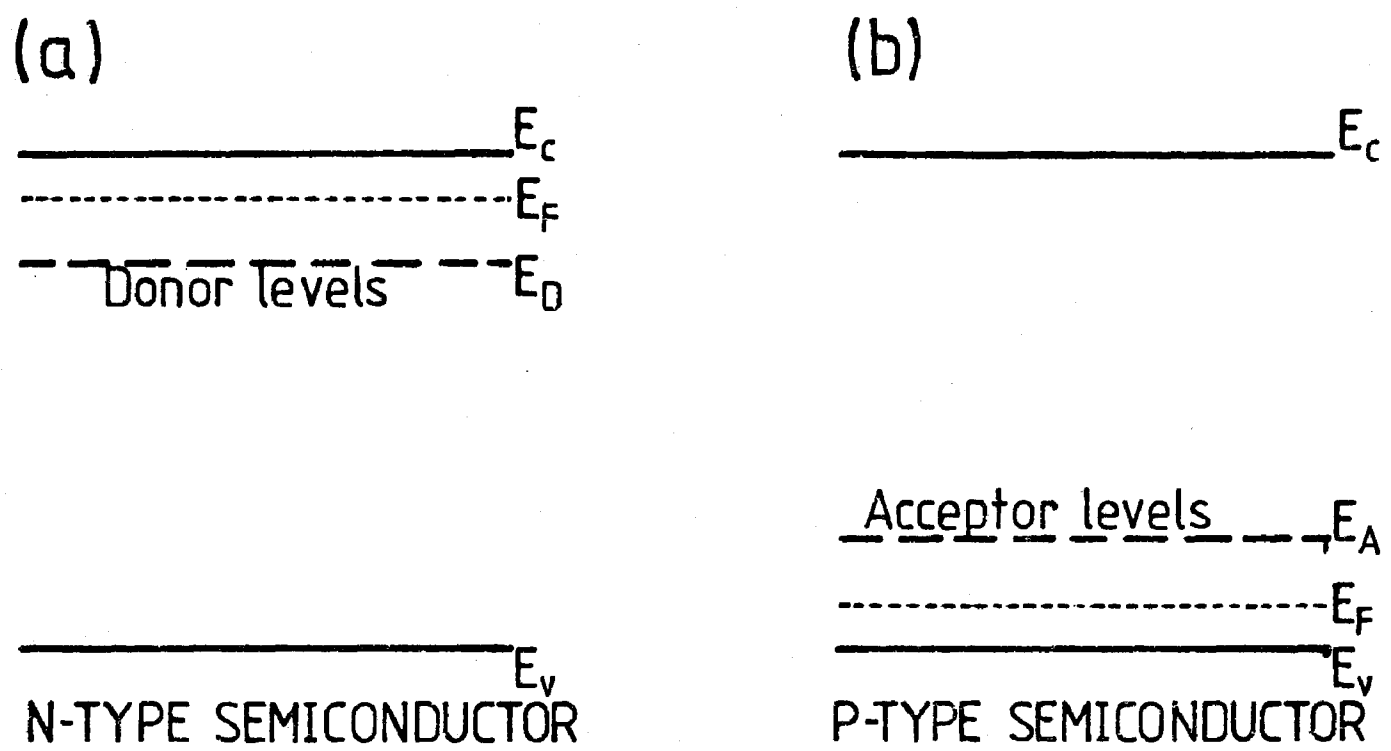


Figure 2.2 Energy level diagrams of ideal n- and p-type semiconductors

As will be seen, these different classes of semiconductors possess strikingly different characteristic electrochemical behaviour as a function of applied voltage. The current voltage behaviour of semiconductors in dark or illuminated conditions will be dealt with in Sections 2.10 and 2.11

SECTION 2:3 THE PHENOMENON OF SURFACE STATES

The above includes the essential features and characteristics of the bulk electronic behaviour of semiconductors, but one further complication may arise for real materials that necessarily are discontinuous. Apart from the system of energy levels forming the bulk properties of a semiconductor, there exists an additional system of energy levels at the surface. Corresponding to these surface levels are quantum states where electrons are localized at the surface and cannot enter the bulk without energy exchange with the surrounding medium. (Exceptions will be found to this latter point - see Section 4:7

These so-called 'surface states' may arise from adsorption (Shockley levels)¹⁹⁴ and from the inherent discontinuity of a crystal lattice (Tamm states)¹⁹⁵. A phenomenological theory exists for the description of their formal electrical characteristics¹⁵, but detailed descriptions of characteristic parameters such as their energy, relaxation time, electron and hole capture cross sections and the physiochemical properties of surface atoms have not yet been studied quantitatively.

The effect of 'surface states' on charge and potential distribution at semiconductor/electrolyte interfaces and the different capacity of the interface will be dealt with in Sections 2:8 and 2:9 respectively.

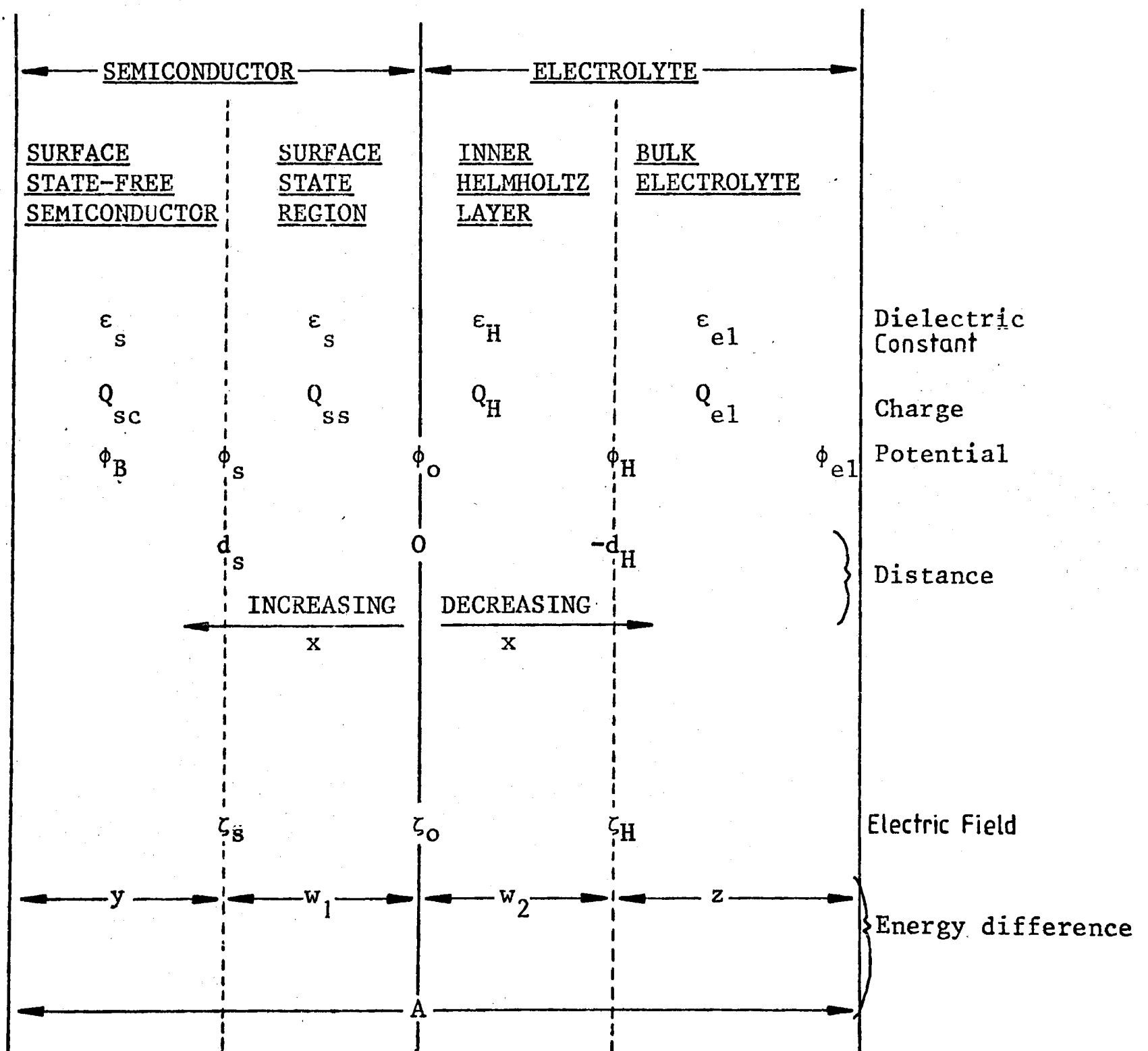
SECTION 2:4 THE THEORY FOR THE DISTRIBUTION OF CHARGE AND POTENTIAL
AT THE SEMICONDUCTOR/ELECTROLYTE INTERFACE

The semiconductor / electrolyte interface may be divided into four regions

- (i) The semiconductor
- (ii) Surface states within the surface of the semiconductor
- (iii) The inner Helmholtz layer of directly adsorbed ions
- (iv) The solution

The energetics of the interface are represented in Fig. 2.3.

Fig.2.3



ϵ_s = Dielectric constant of Semiconductor

ϵ_H = " " " Helmholtz layer

ϵ_{el} = " " " Solution

d_s = width of surface state layer

d_H = width of inner Helmholtz layer

Distance (x) is measured positive into the bulk of the semiconductor

x = 0 at the semiconductor/electrolyte interface

ϕ_B = electrical potential of bulk semiconductor

ϕ_s = potential at junction between surface-state-free (ssf) semiconductor with surface state layer

ϕ_o = Potential at Semiconductor/Electrolyte Interface

ϕ_H = " " outer edge of inner Helmholtz layer

ϕ_{el} = " " in bulk of solution

Q_{sc} = charge stored in Semiconductor

Q_{ss} = charge stored in surface state layer

Q_H = charge stored in Helmholtz layer

Q_{el} = charge stored in solution

y = Electron energy difference between bulk semiconductor and edge of surface-state layer

w_1 = Energy difference between semiconductor and surface sides of the surface state layer

w_2 = Energy difference between surface and edge of Helmholtz layer

z = Energy difference between bulk solution and edge of Helmholtz layer.

A = Total Electron Energy difference between bulk semiconductor and bulk solution.

(i) The semiconductor (surface state free material).

For ease of calculation, let us firstly redefine our zero point of distance as the interface between the surface-state layer and surface state-free semiconductor.

$$\text{i.e.} \quad X = (x - d_s) \quad 2.16$$

$$\begin{aligned} X &= 0 \text{ at interface of surface-state layer} \\ &\text{and surface-state free semiconductor} \end{aligned} \quad 2.17$$

Using Poisson's equation,

$$\frac{d^2 \phi(X)}{dX^2} = \frac{-e_0}{\epsilon_s \epsilon_0} [p - n + N_D - N_A] \quad 2.18$$

where ϕ is the potential at a point distance X from interface

p = concentration of holes in the valence band

n = concentration of electrons in the conduction band

N_D = concentration of ionized donor states

N_A = concentration of ionized acceptor states.

This may be solved according to the following boundary conditions:-

$$\frac{d\phi}{dX} = 0 \text{ as } \phi \rightarrow \phi_B \quad 2.19$$

$$\text{and} \quad \phi = \phi_s \text{ when } X = 0 \text{ (} x = d_s \text{)} \quad 2.20$$

The former condition implies that the bulk of the semiconductor is essentially field free. Thus solving equation 2.18, we find that the field at the surface of the semiconductor is given by:-

$$\begin{aligned} \zeta_s &= \pm \left(\frac{2kt}{\epsilon_s \epsilon_0} \right)^{\frac{1}{2}} \left[-(N_D - N_A) \cdot \left\{ \frac{e_0(\phi_B - \phi_s)}{kT} \right\} + p \left[\exp \left\{ \frac{e_0(\phi_B - \phi_s)}{kT} \right\} - 1 \right] \right. \\ &\quad \left. + n \left[\exp \left\{ \frac{e_0(\phi_B - \phi_s)}{kT} \right\} - 1 \right] \right]^{\frac{1}{2}} \end{aligned} \quad 2.21$$

$$= \pm \left(\frac{2kT}{\epsilon_s \epsilon_0} \right)^{\frac{1}{2}} [-(N_D - N_A)Y + p(e^{-Y} - 1) + n(e^Y - 1)]^{\frac{1}{2}} \quad 2.22$$

$$\text{where } Y = \frac{e_o(\phi_B - \phi_s)}{kT} \quad 2.23$$

$$\text{and } \zeta_s > 0 \text{ if } Y > 0 \quad 2.24$$

$$\zeta_s < 0 \text{ if } Y < 0 \quad 2.25$$

For an extrinsic semiconductor we have the relations $N_D \gg N_A$ and $n \gg p$, or $N_A \gg N_D$ and $p \gg n$. We shall also only consider the situation where the majority carrier concentration of the semiconductor is depleted near the surface such that, in this so-called depletion layer, for an n-type semiconductor we have $n \ll N_D$ and for a p-type material we have $p \ll N_A$. Given these constraints equation 2.22 reduces, for an n-type material, to

$$\zeta_s = - \left(\frac{2kTN_D}{\epsilon_o \epsilon_s} \right)^{\frac{1}{2}} (e^{-Y} + Y - 1)^{\frac{1}{2}} \quad 2.26$$

For a p-type material we have:-

$$\zeta_s = \left(\frac{2kTN_A}{\epsilon_o \epsilon_s} \right)^{\frac{1}{2}} (e^{-Y} + Y - 1)^{\frac{1}{2}} \quad 2.27$$

From this point we will consider only an n-type material, but the equations may be readily altered to suit a p-type material by replacing N_D with $(-N_A)$ throughout.

The charge per unit area in the depletion layer is given by

$$Q_{sc} = - \epsilon_s \epsilon_o \zeta_s \quad 2.28$$

(ii) Surface state layer within the surface of the semiconductor

If we imagine a thin layer of surface states in the semiconductor of depth d_s , there will be two contributions to the potential in this layer: that from the ionized donor states (from the dopant) and that from surface states. If we assume that all the surface donor states are fully ionized we have:-

$$\frac{d^2\phi}{dx^2} = \frac{-e_o}{\epsilon_s \epsilon_o} [N_D + N_s] \quad 2.29$$

N_s = the density of charged surface states.

When we obtain upon integration of 2.29

$$\frac{d\phi}{dx} = \frac{-e_o}{\epsilon_s \epsilon_o} [N_D + N_s]x + C_1 \quad 2.30$$

$$\text{and } \phi = \frac{-e_o [N_D + N_s]x^2}{2\epsilon_s \epsilon_o} + C_1 x + C_2 \quad 2.31$$

Now at $x = d_s$, the field must equal that at the surface of the s.s.f semiconductor i.e. $\zeta = \zeta_s$ and similarly the potential is defined as ϕ_s at this point. This gives:-

$$\frac{-e_o}{\epsilon_s \epsilon_o} [N_D + N_s]d_s + C_1 = -\zeta_s \quad 2.32$$

$$\text{Also when } x = 0 \quad C_1 = -\zeta_o^+ \quad 2.33$$

where ζ_o^+ is defined as the field on the semiconductor side of the semiconductor electrolyte interface at $x = 0$.

Now charge continuity across the semiconductor/electrolyte interface demands that:-

$$\zeta_o^+ \epsilon_s = \zeta_o^- \epsilon_H \quad 2.34$$

where ζ_o^- is the field on the solution side of the semiconductor electrolyte interface at $x = 0$.

$$\text{Hence } C_1 = \frac{-\epsilon_H \zeta_o^-}{\epsilon_s} \quad 2.35$$

$$\text{and } \zeta_s = \frac{\epsilon_H \zeta_o^-}{\epsilon_s} + \frac{e_o}{\epsilon_s \epsilon_o} [N_D + N_s]d_s \quad 2.36$$

$$\text{or } \epsilon_o \epsilon_s \zeta_s = \epsilon_o \epsilon_H \zeta_o^- + e_o [N_D + N_s]d_s \quad 2.37$$

Now from 2.31 and 2.35 we have:-

$$\phi = -\frac{e_o}{2\epsilon_s\epsilon_o} [N_D + N_S]x^2 - \frac{\epsilon_H\zeta_o^- x}{\epsilon_s} + C_2 \quad 2.38$$

$$= -\frac{e_o}{2\epsilon_s\epsilon_o} [N_D + N_S]x^2 + \frac{e_o}{\epsilon_o\epsilon_s} [N_D + N_S]d_s x - \zeta_s \cdot x + C_2 \quad 2.39$$

However, at $x = d_s$, $\phi = \phi_s$ and

$$\phi_s = \frac{e_o}{2\epsilon_o\epsilon_s} [N_D + N_S]d_s^2 - \zeta_s d_s + C_2 \quad 2.40$$

$$\text{and thus } C_2 = \phi_s - \frac{\epsilon_o}{2\epsilon_o\epsilon_s} (N_D + N_S)d_s^2 + \zeta_s d_s \quad 2.41$$

Combining 2.39 and 2.41 we obtain for $d_s \geq x \geq 0$

$$\phi = -\frac{e_o}{2\epsilon_s\epsilon_o} [N_D + N_S](d_s - x)^2 + \epsilon_s [d_s - x] + \phi_s \quad 2.42$$

At the actual semiconductor/electrolyte interface ($x = 0$)

$$\phi_o = \frac{-e_o [N_D + N_S]d_s^2}{2\epsilon_s\epsilon_o} + \zeta_s d_s + \phi_s \quad 2.43$$

$$\text{and } \zeta_o^+ = \zeta_s - \frac{e_o}{\epsilon_o\epsilon_s} [N_D + N_S] \quad 2.44$$

Now from 2.43

$$\omega_1 = \frac{e_o}{kT} (\phi_s - \phi_o) = \frac{e_o}{kT} \frac{e_o [N_D + N_S] d_s^2}{2\epsilon_s \epsilon_o} - \zeta_s d_s \quad 2.45$$

ω_1 = potential drop across the surface state layer.

Substituting in from 2.26

$$\omega_1 = \frac{e_o d_s}{\epsilon_o \epsilon_s kT} \left[\frac{e_o [N_D + N_S] d_s}{2} + (2kT N_D \epsilon_o \epsilon_s)^{\frac{1}{2}} (e^{-Y} + Y - 1)^{\frac{1}{2}} \right] \quad 2.46$$

(iii) The inner Helmholtz layer (ionsorbed layer)

An identical analysis to that made in the surface state region may now be performed in the inner Helmholtz layer, but with the density of absorbed ions being N_i .

$$\text{Thus } \frac{d^2 \phi}{dx^2} = \frac{-e_o N_i}{\epsilon_o \epsilon_H} \quad \text{for } 0 > x > -d_H \quad 2.47$$

Integrating we have

$$- \left(\frac{d\phi}{dx} \right) = \frac{e_o N_i x}{\epsilon_o \epsilon_H} + C'_1 \quad 2.48$$

$$\text{At } x = 0 \quad - \left(\frac{d\phi}{dx} \right)_o = \zeta_o^- = C'_1 \quad 2.49$$

$$\text{and at } x = -d_H \quad \left(\frac{-d\phi}{dx} \right)_{d_H} = \frac{-e_o N_i d_H}{\epsilon_s \epsilon_H} + C'_1 = \zeta_H \quad 2.50$$

$$\text{giving } \zeta_H + \frac{e_o N_i d_H}{\epsilon_o \epsilon_H} = \zeta_o^- \quad 2.51$$

Integrating 2.48 gives:-

$$\phi = -\frac{e N_i x^2}{2\epsilon_H \epsilon_o} - \zeta_o x + C_2 \quad 2.52$$

At $x = 0$, $\phi = \phi_o$

and thus $C_2 = \phi_o$ 2.53

giving

$$\phi = -\frac{e N_i x^2}{2\epsilon_H \epsilon_o} - \zeta_o x + \phi_o \quad 2.54$$

Substituting from 2.36 and 2.43 we obtain

$$\begin{aligned} \phi = & -\frac{e N_i x^2}{2\epsilon_H \epsilon_o} - \frac{\epsilon_s \zeta_s x}{\epsilon_H} + \frac{e_o [N_D + N_s] d_s x}{\epsilon_H \epsilon_o} \\ & - \frac{e_o [N_D + N_s] d_s^2}{2\epsilon_o \epsilon_s} + \zeta_s d_s + \phi_s \end{aligned} \quad 2.55$$

Hence at $x = -d_H$

$$\begin{aligned} \phi_H = & -\frac{e N_i d_H^2}{2\epsilon_H \epsilon_o} + \frac{\epsilon_s \zeta_s d_H}{\epsilon_H} - \frac{e_o [N_D + N_s] d_s d_H}{\epsilon_H \epsilon_o} \\ & - \frac{e_o [N_D + N_s] d_s^2}{2\epsilon_o \epsilon_s} + \zeta_s d_s + \phi_s \end{aligned} \quad 2.56$$

and $\zeta_H = \frac{\epsilon_s \zeta_s}{\epsilon_H} - \frac{e_o [N_D + N_s] d_s}{\epsilon_H \epsilon_o} - \frac{e_o N_i d_H}{\epsilon_H \epsilon_o}$ 2.57

From 2.56 and 2.43 we may find the potential drop across the inner Helmholtz layer (w_2)

$$\omega_2 = \frac{e_o}{kT} (\phi_o - \phi_H) = \left[\frac{e_o N_i d_H^2}{2\epsilon_H \epsilon_o} + \frac{e_o (N_D + N_S) d_s d_H}{\epsilon_H \epsilon_o} - \frac{\epsilon_s \zeta_s d_H}{\epsilon_H} \right] \frac{e_o}{kT} \quad 2.58$$

$$\omega_2 = \frac{e_o d_H}{\epsilon_o \epsilon_H kT} \left[\frac{e_o N_i d_H}{2} + e_o (N_D + N_S) d_s + (2kT N_D \epsilon_o \epsilon_s)^{\frac{1}{2}} \times (e^{-Y} + Y - 1)^{\frac{1}{2}} \right] \quad 2.59$$

(iv) The solution

We have for a (1:1) electrolyte

$$\frac{d^2 \phi}{dx^2} = - \frac{e_o}{\epsilon_o \epsilon_e} [C_+ - C_-] \quad 2.60$$

C_+ = concentration of cations, C_- = concentration of anions

$$= - \frac{e_o C_o}{\epsilon_o \epsilon_e} \left\{ \exp \left[-e_o \frac{(\phi - \phi_{el})}{kT} \right] - \exp \left[e_o \frac{(\phi - \phi_{el})}{kT} \right] \right\} \quad 2.61$$

C_o = concentration of 1:1 electrolyte

$$= \frac{2\epsilon_o C_o}{\epsilon_o \epsilon_e} \sinh [e_o (\phi - \phi_{el}) / kT] \quad 2.62$$

Integrating 2.62 gives

$$\frac{1}{2} \left(\frac{d\phi}{dx} \right)^2 = \frac{2C_o kT}{\epsilon_o \epsilon_e} \cosh [e_o (\phi - \phi_{el}) / kT] - \frac{2C_o kT}{\epsilon_o \epsilon_e} \quad 2.63$$

If $\frac{d\phi}{dx} \rightarrow 0$ as $\phi \rightarrow \phi_{e1}$ and

2.64

the bulk solution is essentially field free, we have:-

$$\frac{d\phi}{dx} = \pm \left[\frac{8C_o kT}{\epsilon_o \epsilon_e} \right]^{\frac{1}{2}} \sinh [e_o(\phi - \phi_{e1})/2kT] \quad 2.65$$

Integrating 2.65 gives

$$\frac{2kT}{e_o} \log \tanh [e_o(\phi - \phi_{e1})/4kT] = \pm \left[\frac{8C_o kT}{\epsilon_o \epsilon_e} \right]^{\frac{1}{2}} x + C_2'' \quad 2.66$$

Now when $x = -d_H$, $\phi = \phi_H$ and so:-

$$\log \tanh [e_o(\phi_H - \phi_{e1})/4kT] = \frac{C_o e_o}{2kT} + \left[\frac{8C_o kT}{\epsilon_o \epsilon_e} \right]^{\frac{1}{2}} d_H \quad 2.67$$

and $\tanh [e_o(\phi - \phi_{e1})/4kT] = \{ \tanh [e_o(\phi_H - \phi_{e1})/kT] \}$

$$\exp \left[+ \left(\frac{2C_o e_o^2}{\epsilon_o \epsilon_e kT} \right)^{\frac{1}{2}} (x + d_H) \right] \quad 2.68$$

for $-d_H > x > -\infty$

Now if we assume $\phi - \phi_{e1} \ll \frac{4kT}{e_o}$, then

2.69

$$\frac{e_o(\phi - \phi_{e1})}{4kT} \approx \left[\frac{e_o(\phi_H - \phi_{e1})}{kT} \right] \exp \left[+ \left(\frac{2C_o e_o^2}{\epsilon_o \epsilon_e kT} \right)^{\frac{1}{2}} (x + d_H) \right] \quad 2.70$$

The field in the solution at $x = -d_H$ is given by E_2

$$E_2 = - \left(\frac{d\phi}{dx} \right)_{-d_H} = - \left[\frac{8C_o kT}{\epsilon_e \epsilon_o} \right]^{\frac{1}{2}} \sinh [e_o(\phi_H - \phi_{e1})/2kT] \quad 2.71$$

and for charge continuity across this interface

$$\epsilon_e \zeta_2 = \epsilon_H \zeta_H \quad 2.72$$

The charge per unit area in the Gouy Chapman layer (Q_2) is thus given by

$$Q_2 = - (8C_o kT \epsilon_o \epsilon_e)^{\frac{1}{2}} \sinh [e_o (\phi_H - \phi_{el}) / 2kT] \quad 2.73$$

For a complete solution of the potential distribution of the semiconductor/electrolyte interface, we must compile the relevant information.

A. The charges per unit area stored in each of the four layers

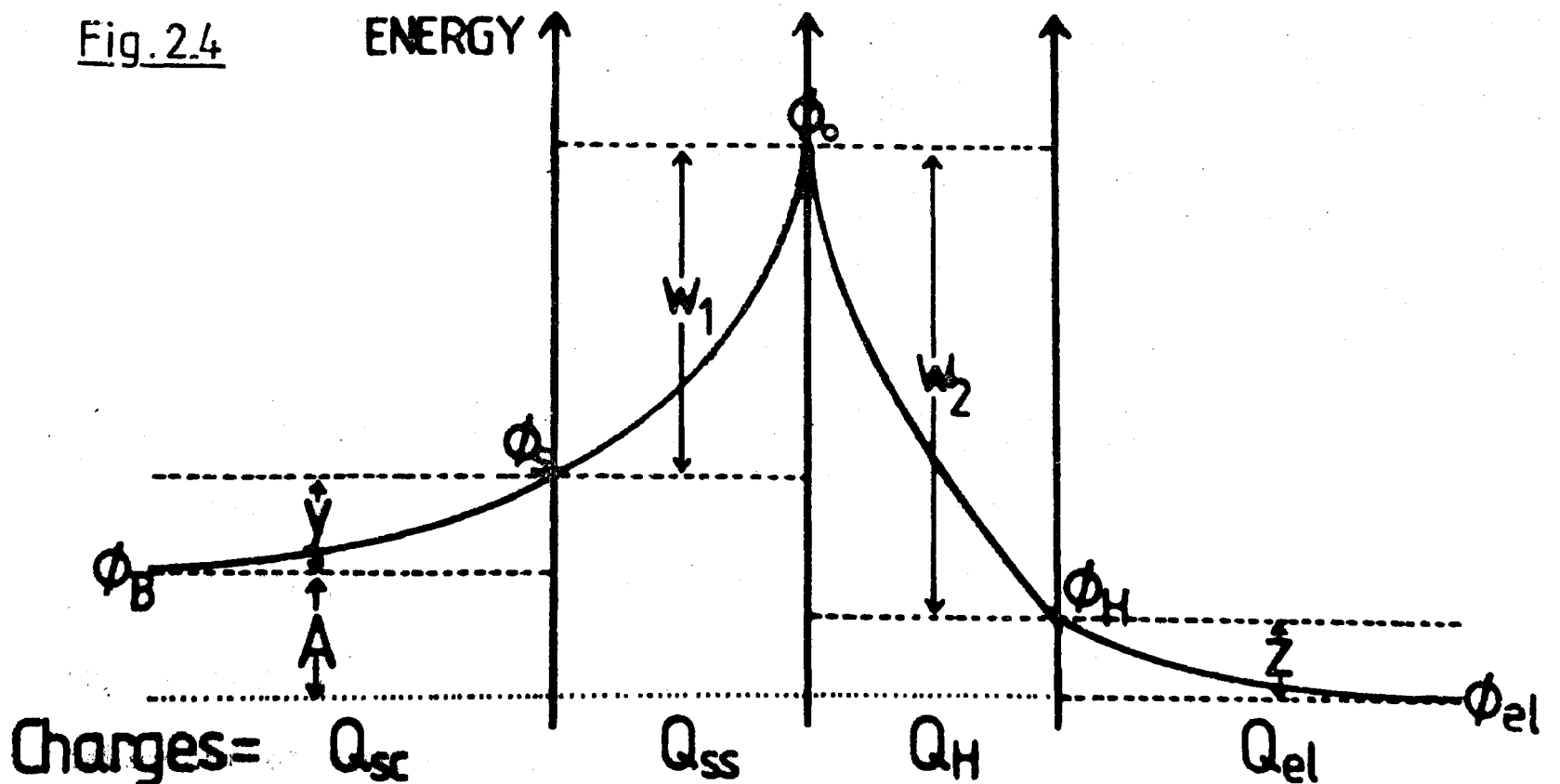
$$Q_{sc} = (2kTN_D \epsilon_o \epsilon_s)^{\frac{1}{2}} (e^{-Y} + Y - 1)^{\frac{1}{2}} \quad 2.74$$

$$Q_{ss} = e_o N_D + N_s d_s \quad 2.75$$

$$Q_H = e_o N_i d_H \quad 2.76$$

$$Q_2 = - (8C_o kT \epsilon_o \epsilon_e)^{\frac{1}{2}} \sinh [e_o (\phi_H - \phi_{el}) / 2kT] \quad 2.77$$

B. The energy difference across each of the four layers. See Fig.2.4



$$Y = e_o(\phi_B - \phi_s)/kT$$

$$w_1 = e_o(\phi_s - \phi_o)/kT \text{ and also as given in 2.46}$$

$$w_2 = e_o(\phi_o - \phi_H)/kT \text{ and also as given in 2.59}$$

$$z = e_o(\phi_H - \phi_{el})/kt$$

We may define the total energy difference between bulk semiconductor and bulk solution as

$$A \equiv e_o(\phi_B - \phi_{el})/kT \quad 2.78$$

To solve the potential distribution across the whole semiconductor/electrolyte interphase region, the following requirements must be satisfied.

(1) For overall energy balance

$$A = Y + w_1 + w_2 + Z \quad 2.79$$

and (2) for overall electroneutrality

$$Q_{sc} + Q_{ss} + Q_H + Q_2 = 0 \quad 2.80$$

To obtain a solution, the following parameters must be known if ϕ_B is taken as zero: $(\phi_B - \phi_{el}) = \text{Applied Voltage } (V_{appl})$, N_D , N_s , N_i , d_H , d_s , ϵ_s , ϵ_H , ϵ_o and C_o . This leaves three unknowns ϕ_s , ϕ_o and ϕ_H . There are explicit relationships between ϕ_s and ϕ_o (2.43) and ϕ_H and ϕ_s (2.56) and thus we may solve for the remaining unknowns by using the conditions 2.80 and 2.79 as tests for validity. In practice, this has been achieved by means of an iterative computer program.¹⁹⁶ The above known parameters are fed into the computer along with a rational guess for the value of ϕ_s . The computer then calculates Y , w_1 , w_2 , z , Q_{sc} , Q_{ss} , Q_H and Q_2 and adjusts the running variable ϕ_s until the equation 2.80 is best satisfied. The values of ϕ_o and ϕ_H may then be calculated corresponding to the best fit value for ϕ_s . In the next section we shall discuss the consequences of the above analysis for the potential-dependent behaviour of semiconductor electrodes in contact with conducting electrolytes

SECTION 2:5 THE CALCULATED POTENTIAL DISTRIBUTION AT THE IDEAL SEMICONDUCTOR/ELECTROLYTE INTERFACE.

If we take an ideal semiconductor as being one that possesses no surface states and to which there is no specific ion adsorption from the electrolyte, we may calculate the percentage potential drop across the semiconductor depletion layer as a function of carrier concentration, when the electrode is placed in contact with a strong ($\sim 1M$) electrolyte solution. Some results taken for the case of a p-type semiconductor (dielectric constant = 10) and a solution concentration of $\approx 0.83M$ in 1:1 electrolyte, are shown in Fig.2.5. It may be seen that, providing the semiconductor doping density is kept below $10^{25} m^{-3}$ ($10^{19} cm^{-3}$) then the majority (>95%) of the interfacial potential is dropped across the semiconductor.

For a metal, the carrier concentration is typically about $10^{23} cm^{-3}$; consequently if one still uses the same model, the majority of the potential is dropped across the Helmholtz layer. In both cases, providing the electrolyte concentration is maintained at about 1.0 Molar, little potential will be dropped across the Gouy layer in the solution. Indeed in order to meet this latter requirement, the majority of electrochemical investigations are carried out in solutions of high ionic strength.

Whilst maintaining the semiconductor as ideal (i.e. possessing no surface states), we may allow charged species to adsorb onto the semiconductor and thus contribute excess charge to the Helmholtz layer. Fig.2.6 shows how the interfacial potential drop varies as a function of the concentration of adsorbed charge. It can be seen that once the concentration of adsorbed species exceeds $5 \times 10^{26} cm^{-3}$ (or for a typical surface $10^{12} cm^{-3}$) then there will be significant potential drop across the Helmholtz layer. However, as Fig.2.7 shows, variation in the total potential drop across the semiconductor/electrolyte interface does not

Fig.2.5 Plot of Interfacial Potentials $\phi_0(=\phi_s)$ and ϕ_H as a function of semiconductor doping density for a constant semiconductor/electrolyte potential drop of $-1.0V$.
 $N_D = \text{Variable}$, $\epsilon_s = 10$, $N_s = 0$, $N_i = 2 \times 10^{27}$, $C_o = 1 \times 10^{27}$, $d_H = 2 \times 10^{-10}$
 $\epsilon_{el} = 80$, $\epsilon_H = 6$, $d_s = 0$ (All units S.I.standard)

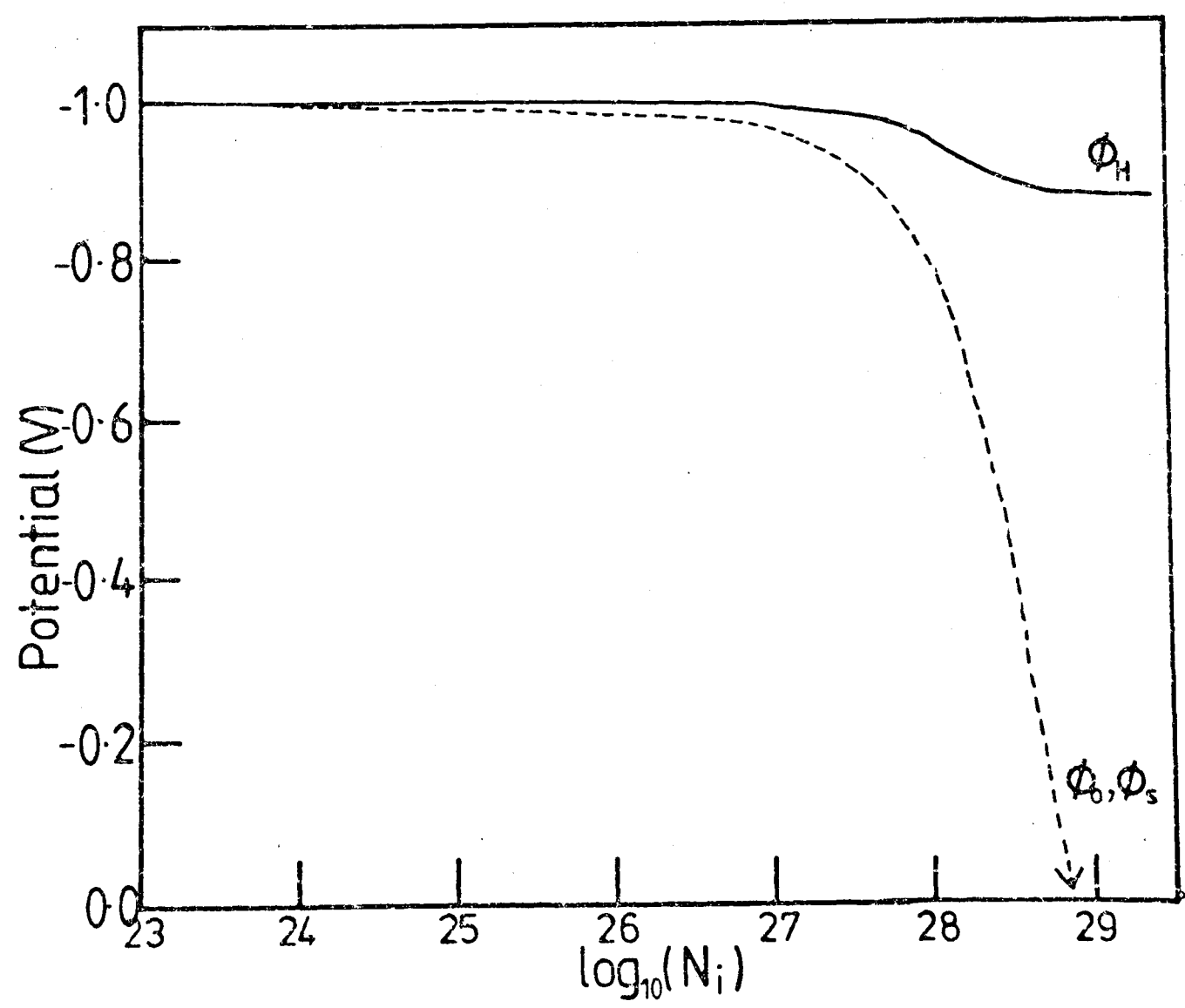
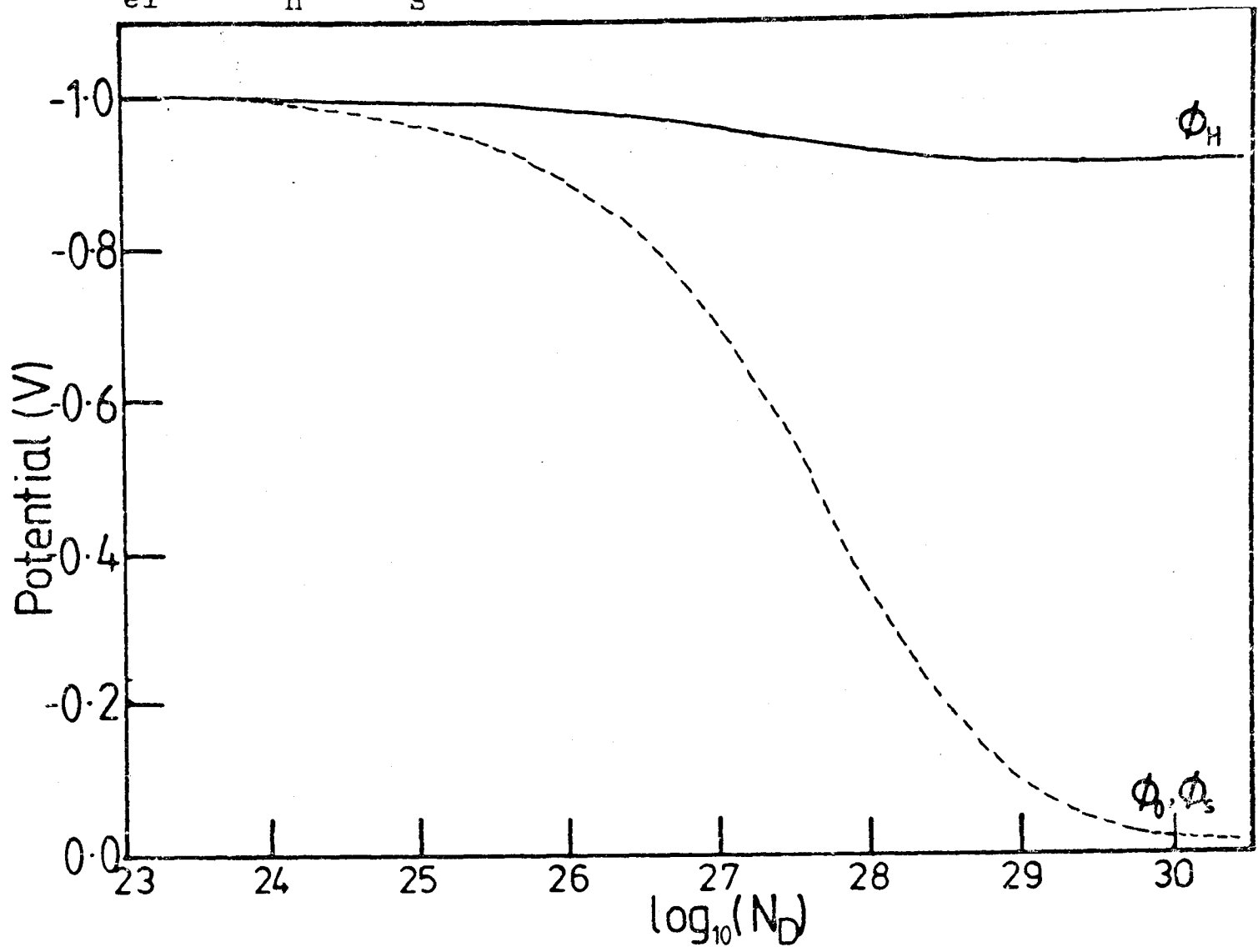


Fig.2.6 Plot of Interfacial Potentials as a function of the concentration of adsorbed charge in the Helmholtz layer
 $N_D = 2 \times 10^{24}$, $d_H = 2 \times 10^{-10}$. All other parameters as in Fig2.5

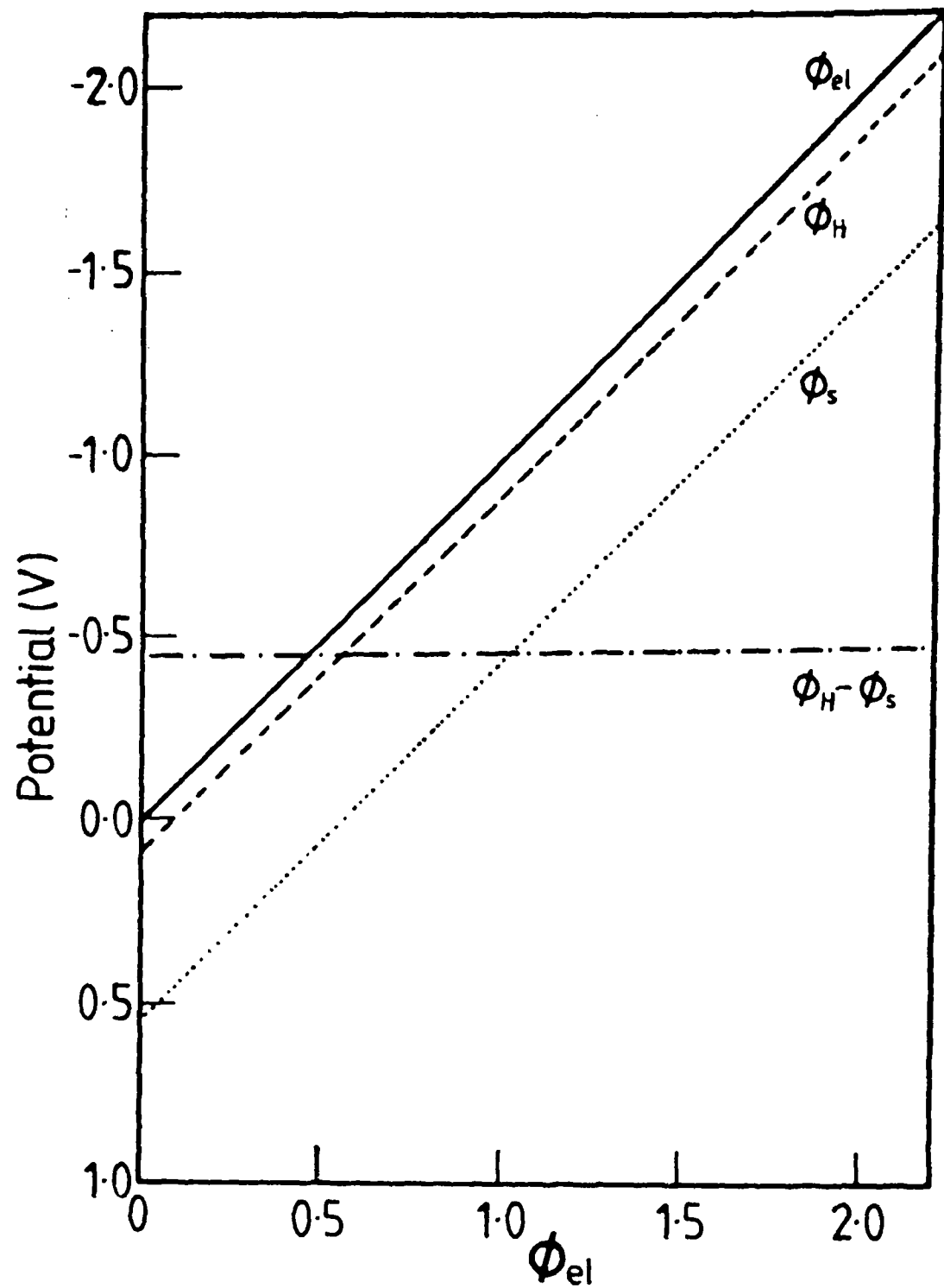


Fig.2.7 Variation in Interfacial Potentials as a function of of total semiconductor/electrolyte potential drop for a typical semiconductor , $N_D = 2 \times 10^{24}$

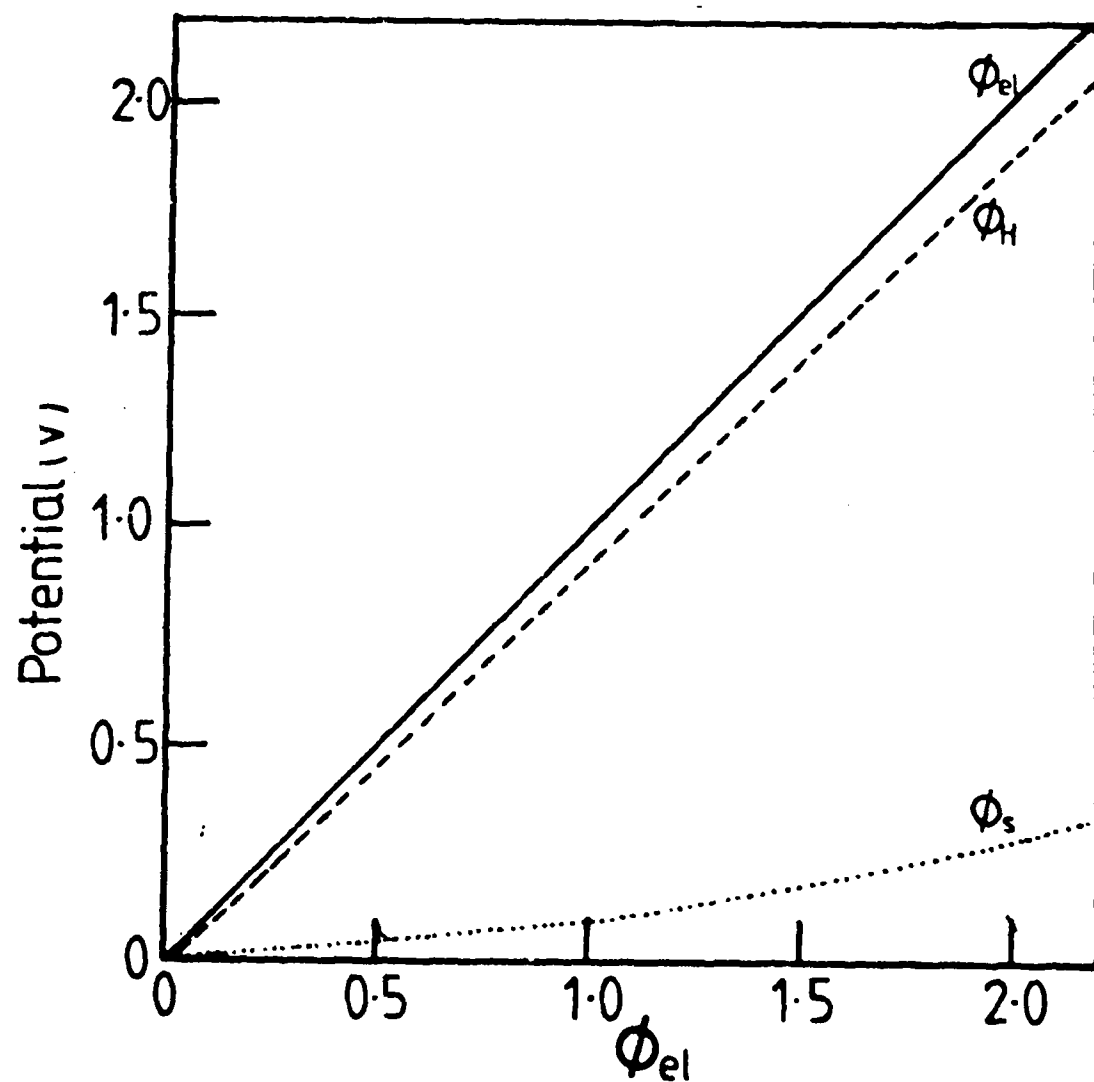


Fig.2.8 Variation in Interfacial Potentials as a function of total electrode/electrolyte potential drop for a typical metal , $N_D = 1 \times 10^{29}$

cause any significant change in potential drop across the Helmholtz layer. In other words variations in applied potential are virtually all taken up by corresponding changes in the potential drop across the depletion layer. In consequence, throughout any change in applied potential, the energies of electrons and holes at the surface of a semiconductor are invariant, only the energies in the bulk are altered. In the case of a metal, however, as Fig.2.8 shows, variations and applied potential almost all appear across the Helmholtz layer. Thus the energy of the electrons at the surface of a metal are altered by changes in applied potential.

Finally for comparison Fig.2.9 depicts the variation in potential across a typical ideal semiconductor/electrolyte interface and a typical metal/electrolyte interface.

SECTION 2:6 THE CONCEPT OF BAND BENDING IN THE SEMICONDUCTOR.

Since the energy of an electron level in an electric field changes by the value $e\phi(x)$, where $\phi(x)$ is the electric potential at point x within the electrode surface, the energy bands will also be bent at the semiconductor where there is an electric field $\zeta = e_0 d\phi/dx$ see Fig.2.9. Given a systematic convention for energy diagrams with energy increasing in an upward direction, this means that with cathodic bias the bands are bent downward towards the surface; and at anodic bias, upwards. This is illustrated in Fig.2.10 for an intrinsic semiconductor ($n = p$).

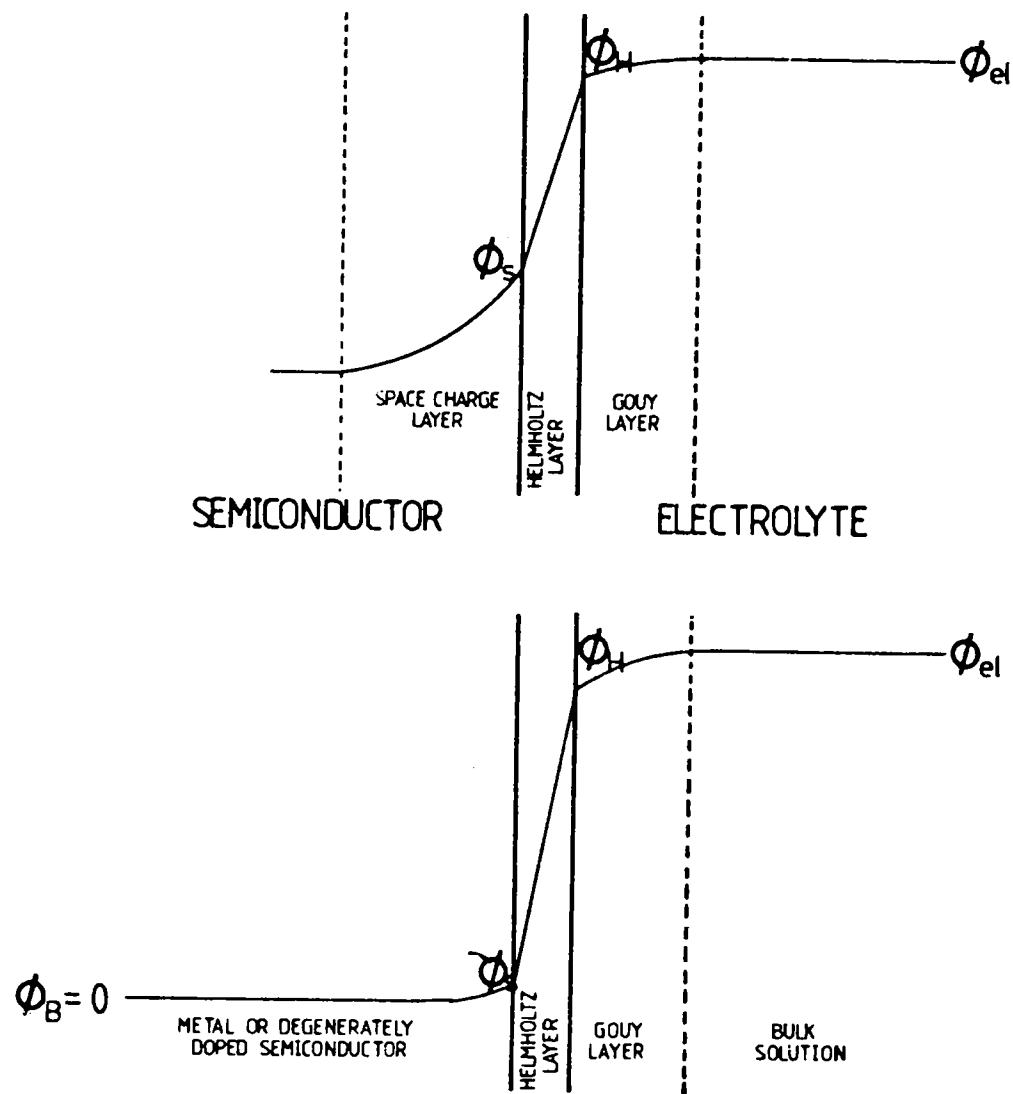


Fig.2.9 Comparison of potential distribution across typical ideal semiconductor/electrolyte and metal/electrolyte interfaces

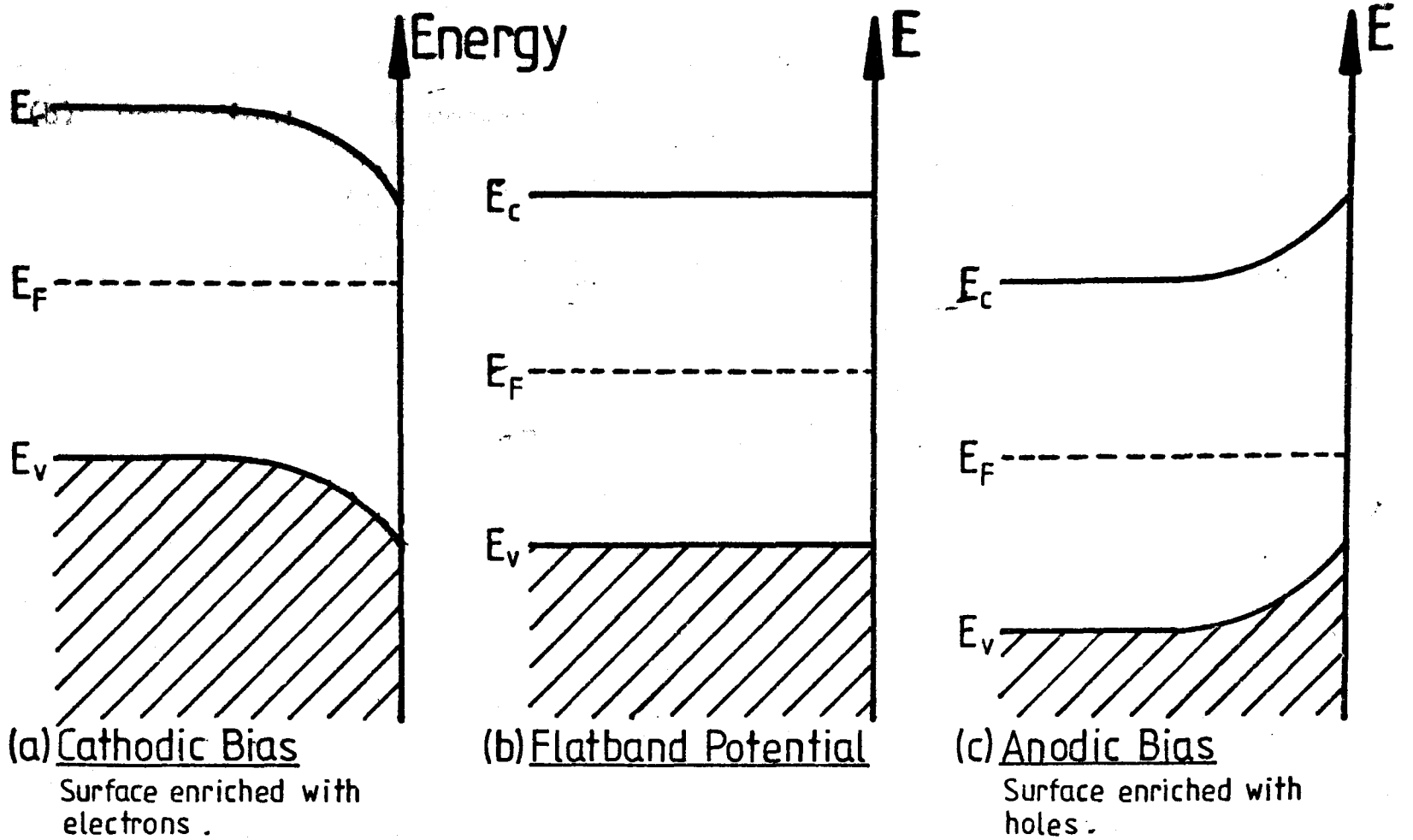
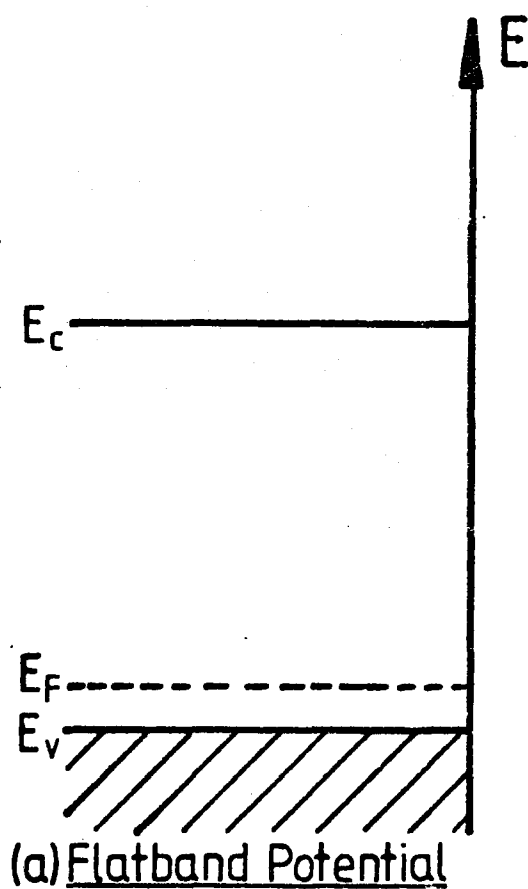


Fig.2.10 Energy level diagrams for an intrinsic semiconductor under (a) cathodic bias, (b) no bias, (c) anodic bias.

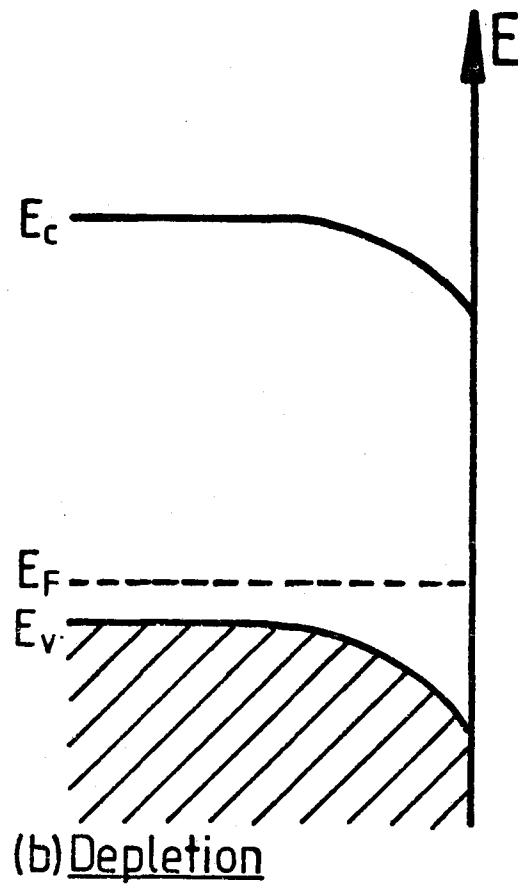
For an extrinsic semiconductor five cases may be distinguished, as are represented in Figs.2.11(a-e) for a p-type material.

(a) Flat-band potential: This is the potential at which the semiconductor electrode is uncharged; it is equivalent to the potential of zero (free) charge for a metal electrode.

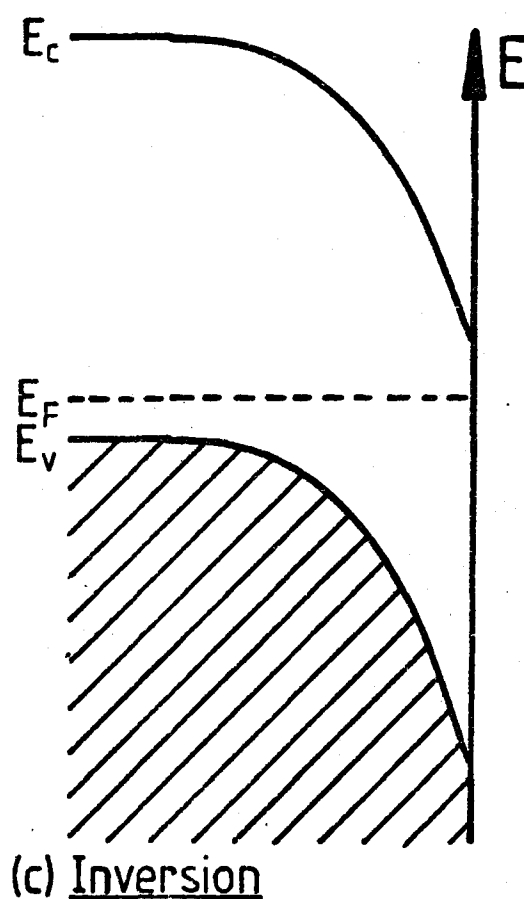
Figure 2.11 a



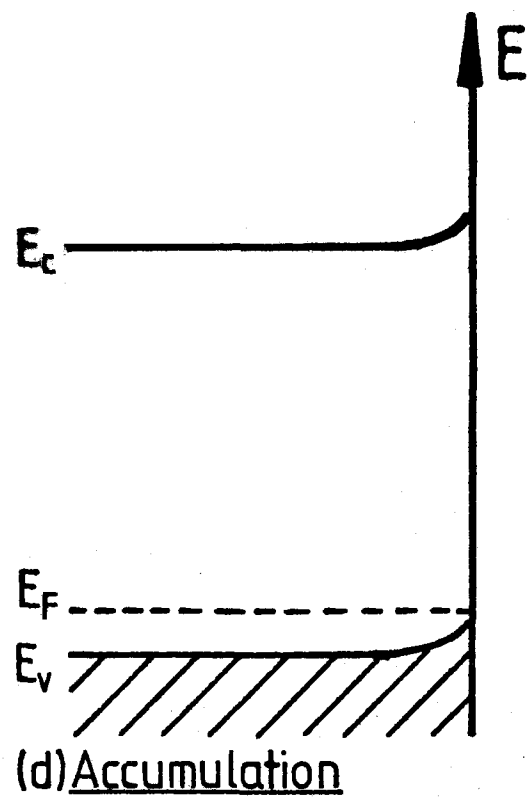
(b) Depletion: This occurs for any potential where the semiconductor space charge is composed of ionized impurity atoms and the surface is thus depleted of majority carriers (this is the situation dealt with in the Theory of Section 2.4)



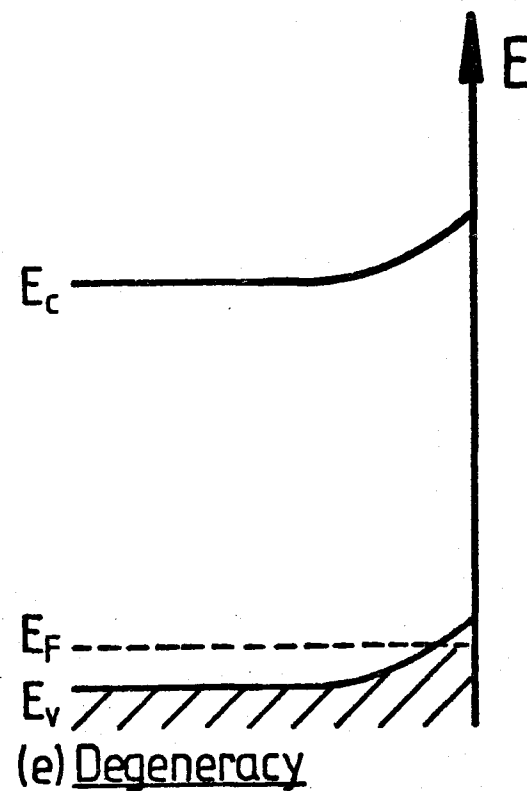
(c) Inversion: This occurs when the surface region is enriched with minority carriers so that their contribution to the space charge exceeds the contribution from the (bulk) majority carriers.



(d) Accumulation: This occurs for potentials where the surface region is enriched with majority carriers.



(e) Degeneracy: This occurs when the Fermi-level intersects the majority carrier band edge such as to produce an electrode with electron density at the Fermi-level. At this point the free carrier concentration at the semiconductor surface becomes $\approx N_c$ or N_v where $N_c = N_c^0 (E - E_c)^{1/2}$ or $N_v = N_v^0 (E_v - E)^{1/2}$ and N_c^0 and N_v^0 are the density of states at the bottom of the conduction band and top of the valence band respectively. N_c^0 and N_v^0 are typically $\approx 10^{21} - 10^{22} \text{ cm}^{-3}$, so the electrode approaches the behaviour of a metal and consequently the space-charge layer contracts towards that expected for the metal/electrolyte interface.



SECTION 2:7 THE DIFFERENTIAL CAPACITY OF THE SEMICONDUCTOR/ ELECTROLYTE INTERFACE.

At a semiconductor/electrolyte interface, the conduction changes from electronic to ionic. If any available interfacial electron transfer process (electrochemical reaction) is slow in the potential range of interest, the interface will present a barrier to the passage of direct electric current. Electric charges may then be accumulated at both sides of the barrier, and the electrode interface behaves as a capacitor.

As the potential is altered, this accumulation will be limited by leakage caused by the electrochemical reactions occurring at the interface. However, as long as this leakage current is negligible or small compared with the rate of exchange of charge carriers between the space charge and the bulk, the static charge distribution at both sides of the phase boundary can be described in terms of a capacitor model with separate treatments of the equilibrium charge distribution in the two phases.

The Galvani potential difference¹⁹⁷ $[(\Delta\phi)_{el}^{sc}]$ is made up, for a surface-state free material, of three terms:

$$(\Delta\phi)_{el}^{sc} = (\phi_B - \phi_O) + (\phi_O - \phi_H) + (\phi_H - \phi_{el}) \quad 2.81$$

As with the metal/electrolyte interface it is not measurable itself. However, it can be determined, except for an additive constant, if the electrode potential V_s is measured with respect to some standard. Therefore, changes in Galvani potential can be reliably determined.

$$V_s = (\Delta\phi)_{el}^{sc} + \text{constant} \quad 2.82$$

$$\text{and } \Delta V_s = \Delta(\Delta\phi)_{el}^{sc} \quad 2.83$$

where the constant contains the sum of all the Galvani potentials of all the other phase boundaries in the electric circuit and V_s is equivalent to the e.m.f. of the Galvanic cell.

Corresponding to the separated potential distribution, the electrode capacity may be divided into three differential capacitances in series

C_G , C_H and C_{sc} .

C_G = capacitance of Gouy layer

C_H = capacitance of Helmholtz layer

C_{sc} = capacitance of space charge region of semiconductor

If we define

$$\frac{1}{C_{TOTAL}} = \frac{d(\Delta\phi)_{el}^{sc}}{dq} \quad 2.84$$

where q = charge in the space charge layer, then

$$\frac{1}{C_{TOTAL}} = \frac{d(\phi_B - \phi_o)}{dq} + \frac{d(\phi_o - \phi_H)}{dq} + \frac{d(\phi_H - \phi_{el})}{dq} \quad 2.85$$

$$= \frac{1}{C_{sc}} + \frac{1}{C_H} \left[\frac{dq_H}{dq} \right] + \frac{1}{C_G} \left[\frac{dq_{el}}{dq} \right] \quad 2.86$$

q_H = charge in the Helmholtz layer

q_{el} = charge in the electrolyte

If we use semiconductors possessing $<10^{19}$ charge carriers cm^{-3} and solutions of approx. 1.0M, then $(\phi_o - \phi_H)$ and $(\phi_H - \phi_{el})$ vary only insignificantly with changes in the potential across the semiconductor space-charge layer (and hence the charge q) as determined in Section 2:5. The total differential capacity will thus be essentially determined by the changes in the space charge capacitance.

$$\frac{1}{C_{TOTAL}} \sim \frac{1}{C_{sc}} = \frac{d(\phi_B - \phi_o)}{dq} \quad 2.87$$

and from 2.84, this gives

$$C_{sc} \approx \frac{dq}{d(\Delta\phi)_{el}^{sc}} = \frac{dq}{dV_s} \quad 2.88$$

If we consider only an extrinsic semiconductor, it is found that after a number of simplifications¹⁵ that the capacity potential relationship has a form identical with the Schottky-Mott capacity.^{198,199}

$$C_{sc} = \left[\frac{\epsilon\epsilon_o e N_D}{2} \right]^{\frac{1}{2}} (\phi_B - \phi_o - \frac{kT}{e_o})^{\frac{1}{2}} \quad 2.89$$

We may also redefine $\phi_B - \phi_o$ as equal to $V_s - V_{fb}$, where V_s is the potential of the semiconductor bulk measured with respect to some solution standard and V_{fb} is the flat band potential of the semiconductor. Rearrangement of equation 2.89 gives:-

$$\frac{1}{C_{sc}^2} = \left[\frac{2}{\epsilon\epsilon_o e N_D} \right] (V_s - V_{fb} - \frac{kT}{e_o}) \quad 2.90$$

Thus, plots of C_{sc}^{-2} vs V_s (Mott-Schottky plots) will produce straight lines that intersect the potential axis at $(V_{fb} - kT/e_o)$, thus enabling estimation of the semiconductor flatband potential. From the straight-line slope, it is also possible to determine the dopant concentration of the semiconductor:

$$N_D = \frac{2}{\epsilon\epsilon_o e} \left[\frac{dV_s}{d(1/C^2)} \right] \quad 2.91$$

(If the material is p-type, N_D is replaced by $-N_A$).

SECTION 2:8 THE EFFECT OF SURFACE STATES AND ADSORBED CHARGE ON THE POTENTIAL DISTRIBUTION.

The surface states may be characterized primarily by their energy E_{ss} and their concentration N_s . The occupancy of the energy levels at equilibrium will be determined by the Fermi function

$$F(E_{ss}) = 1 + \exp \left[\frac{(E_{ss} - E_F)}{kT} \right]^{-1} \quad 2.92$$

so that the total number of electrons at the surface level is

$$n_s = N_s \cdot F(E_{ss}) \quad 2.93$$

The surface electric field also affects the occupation of the levels by electrons. The electron energy in the electron field varies so that E_{ss} should be represented as

$$E_{ss} = E_{ss}^0 + e_o(\phi_B - \phi_s) \quad 2.94$$

For donor surface levels (positively charged when free of electrons and neutral when occupied by electrons), one can write the total surface-region charge per unit area as

$$Q_{ss} = e_o(N_s - n_s + N_D) \quad 2.95$$

$$Q_{ss} = e_o N_D + e_o N_s \left[1 + \exp - \frac{(E_{ss}^0 - E_F) + e_o(\phi_B - \phi_s)}{kT} \right]^{-1} \quad 2.96$$

Now this additional charge may be included into the detailed analysis of potential and charge distribution of Section 2:5. If we initially consider the situation where the occupancy of the surface states is independent of voltage, we can plot out the variation in potentials at the three interfaces as a function of surface-state density (see Fig.2.11). In a manner similar to the way that the density of adsorbed states affect the potential distribution there is a significant potential drop across the surface-state region once the

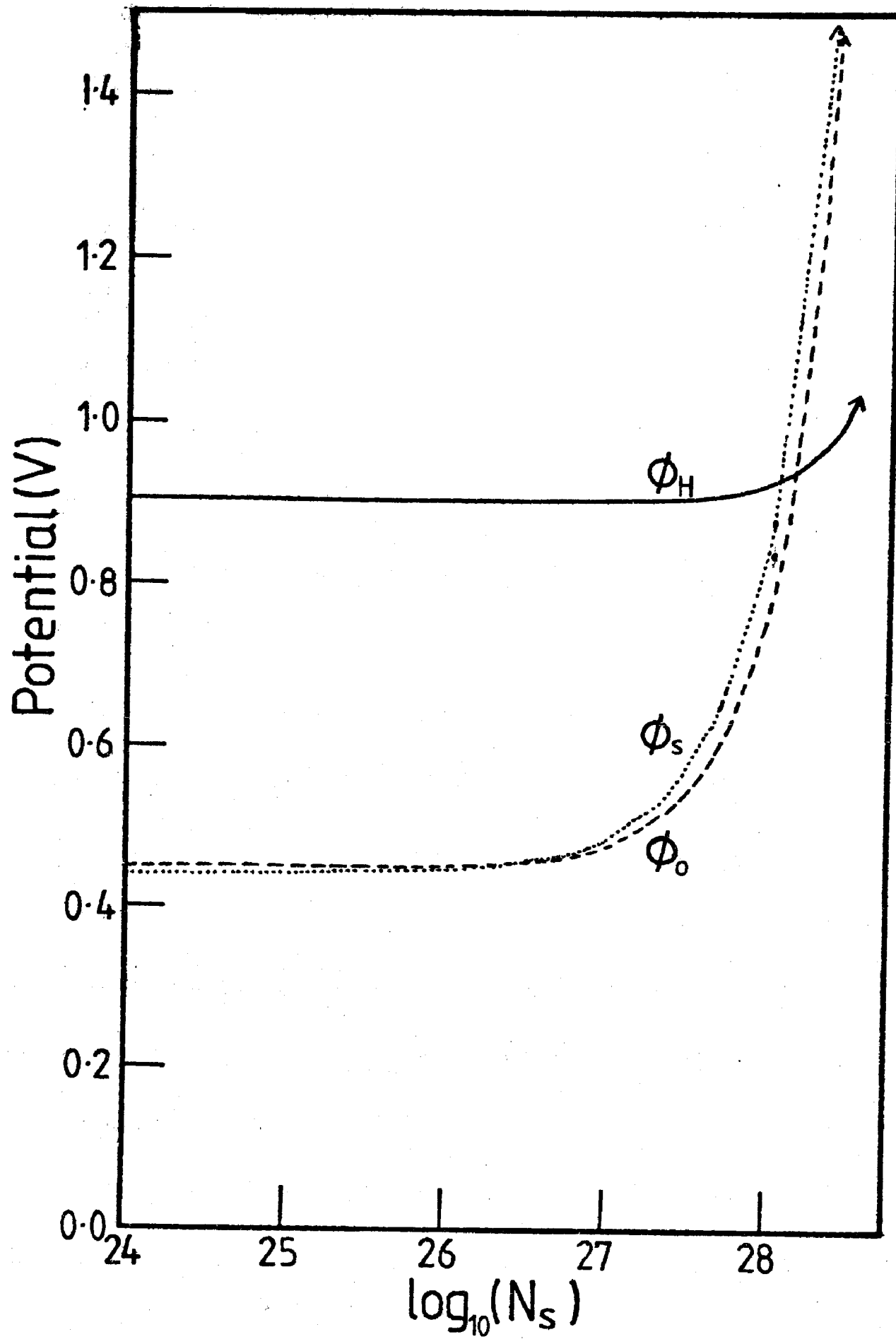


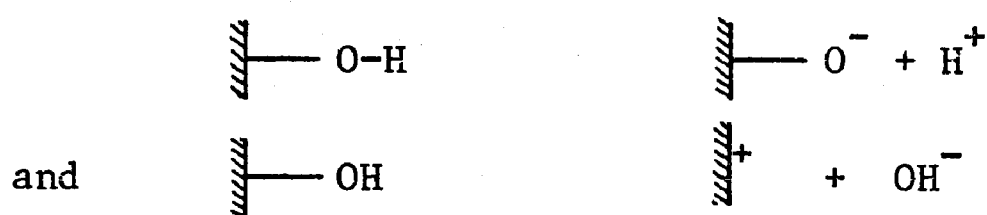
Fig. 2.11 Plot of interfacial potential as a function of surface state density (N_s). $d_s = 2 \times 10^{-10}$
 $N_i = 2 \times 10^{27}$. Other parameters as in Fig. 2.5

surface-state density exceeds 10^{27} m^{-3} for a surface state layer thickness of 0.1 nm (i.e. $10^{12} - 10^{13} \text{ cm}^{-2}$). Such a value corresponds to about 1% of the density of surface atoms. Indeed if $Q_{ss} \approx kT\epsilon_s/4\pi e_o d_s$, then $(\phi_B - \phi_s) \approx (\phi_s - \phi_o)$. Similarly if $Q_H \approx kT\epsilon_H/4\pi e_o d_H$ then $(\phi_o - \phi_H) \approx (\phi_B - \phi_o)$.

Now some surface states may possess energies outside the band-gap region; their occupancy will not vary significantly as a function of electrode potential. Similarly, the redox potential of a surface-adsorbed species may lie outside the band-gap region. Such a situation may be encountered when the only adsorbed species are H^+ or OH^- ions in aqueous solution. For many oxide electrodes, the $E^0(\text{H}^+/\text{H}_2)$ energy level lies above the conduction-band edge as illustrated in Fig.2.12. However, the $E^0(\text{O}_2/\text{H}_2\text{O})$ energy level generally lies above the valence band edge in oxide materials. Therefore under equilibrium conditions, the occupancy of the redox states at the surface of the electrode should be governed by the position of the Fermi level (i.e. by the potential) of the semiconductor material. On oxide materials, a likely surface bound redox couple which is also an intermediate step towards the evolution of Hydrogen, is the $\text{OH}^-/\text{OH}_{\text{ads}}^{\cdot}$ couple.²⁰⁰ On TiO_2 , this level has been suggested to be above the valence band edge²⁰¹⁻²⁰⁴ and is responsible for O_2 evolution on illumination and therefore the positions of equilibrium and hence the surface adsorbed charge should be governed by the potential in the semiconductor. However, evidence against this equilibrium comes from Mott-Schottky plots on TiO_2 which are linear over ranges of $>3.0 \text{ Volts}$ ^{205,206} (greater than the band-gap energy) suggesting that there is no change in the charge of the surface adsorbed species in this voltage range. This in turn suggests that the equilibrium occupancy of the surface states is not attained (at least in the absence of illumination) i.e. there is a large kinetic barrier to the transfer of electrons from the bulk of the semiconductor to the surface. The equilibrium charge on the surface is

therefore governed by the ionic exchange with the solution rather than by the electron exchange with the bulk of the semiconductor.

In fact, the flat band potential or ϕ_o (both of which are determined by the magnitude of the surface charge) of a wide range of semiconductors depends on the pH of the solution, independent of electrode potential, indicating that the rate of exchange of adsorbed species with the solution is independent of the electron exchange with the bulk electrode. In particular for many materials including non-oxide semiconductors the suggested equilibria responsible for this variation of V_{fb} with pH are



Many materials also obey a 59mV per pH unit variation in flat band potential. An attempt at rationalizing this observation has been made by Lohmann.²⁰⁷

On the other hand, if the surface states have energies with the band-gap and do 'communicate' (have rapid electron exchange) with the bulk semiconductor, the surface charge is a steep function of potential from equation 2.96 above. For monoenergetic states (i.e. all possessing energies E_{ss}^0), the surface charge Q_{ss} as well as the potential drop in the surface state layer changes rapidly, as we vary the potential drop at the semiconductor surface ($\phi_B - \phi_s$), from approximately zero to a limiting value. In fact the occupancy will all change in the vicinity of the value of ($\phi_B - \phi_o$) where $E_F = E_{ss}^0 - e(\phi_B - \phi_o)$, the width corresponding to several kT/e units. (See Fig.2.13).

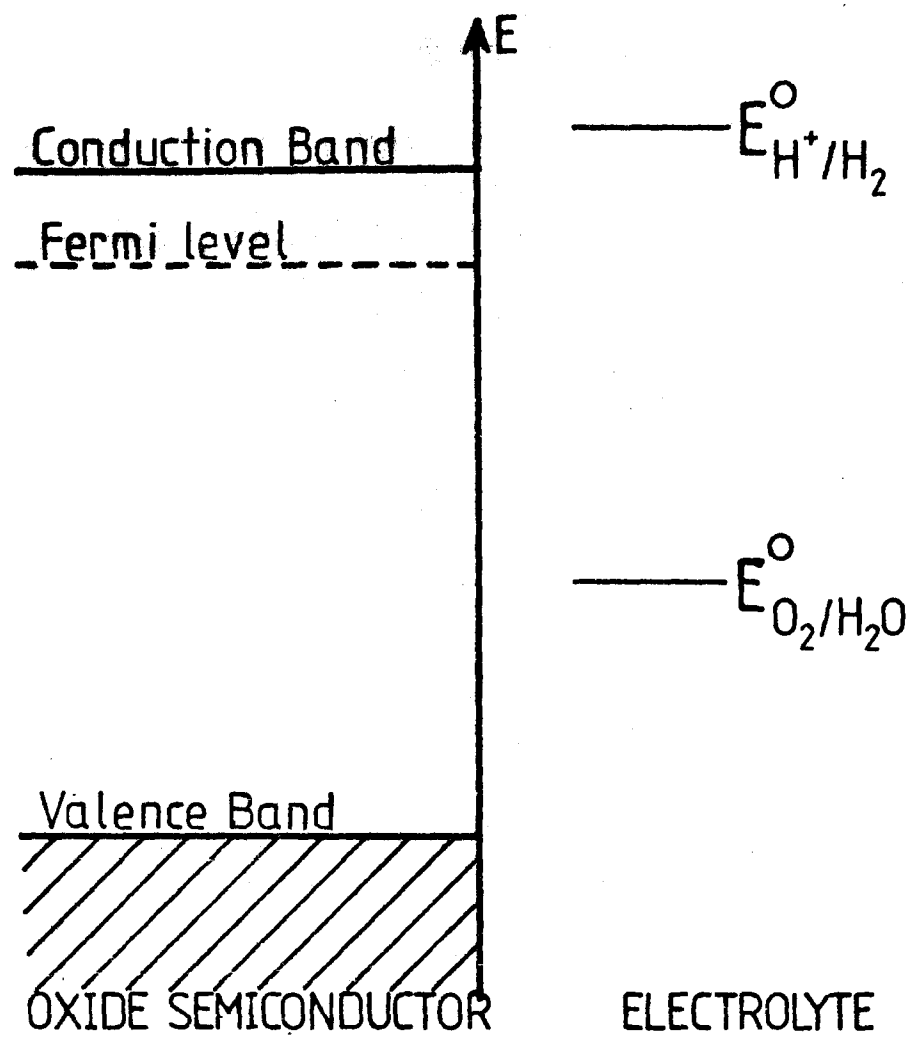


Fig. 2.12 Energy level diagram for typical oxide semiconductor in aqueous solution.

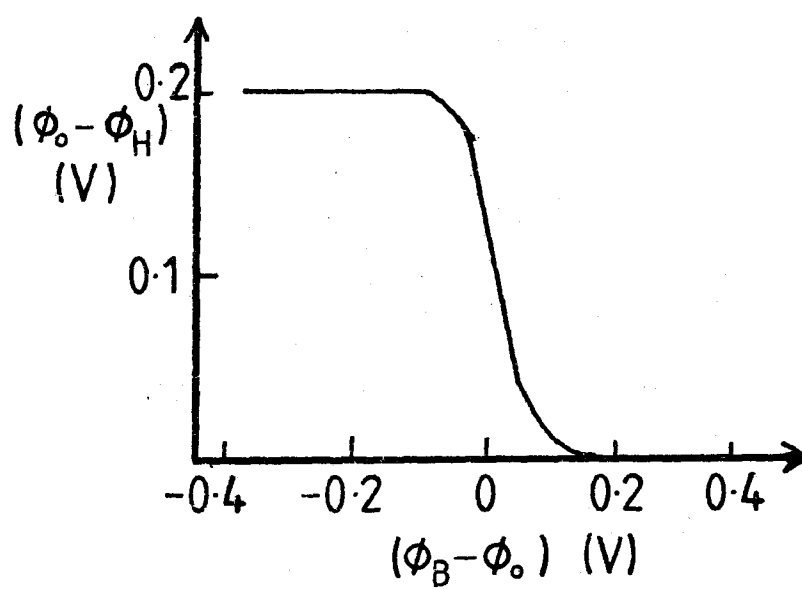


Fig. 2.13 Variation of Helmholtz p.d. in presence of monoenergetic surface states as total interfacial p.d. is varied.

For a surface at which there is a set of levels characterized by different energies, the potential drop in the surface layer varies smoothly in a wide potential range. With sufficient surface-state density, the semiconductor surface begins to lose its specific features: it becomes metal-like. This means that as one varies the semiconductor electrode potential the energy of electrons at the surface will alter as for a metal electrode (see Section 2:5). The particular consequence of this is to produce effects such as Fermi-level pinning^{208,209} or Band-edge unpinning²¹⁰ where the positions of the semiconductor band edges, relative to solution redox levels, may become variable. Also changes in semiconductor potential may not produce variation in the band-bending in the space-charge layer, but rather alter the potential drop in the surface-state layer.

Some cases have been observed where these "communicating" surface states may be traceable in origin to surface adsorbed species with redox potentials within the band-gap region.^{103,104,211} This is in contrast to the situation discussed above for non-communicating redox couples on TiO_2 and many other materials. In the case when the redox equilibrium of these adsorbed state is a function of potential, changes in semiconductor potential will alter the potential drop across the Helmholtz layer analagous to that occurring at a metal/electrolyte interface.

In reality, there may be no definite distinguishing physical feature of inherent surface-states (those which are a permanent feature of the semiconductor material) and surface-bound redox couple (which are a function of the electrolyte composition). The only important dividing line which can be drawn is between those surface states (inherent or otherwise) which possess rapid electron exchange with the semiconductor and those which essentially do not communicate with the semiconductor bulk. From this definition we may arrive at the terms 'fast' and 'slow' surface states.¹⁵ However, in each experimental investigation in addition to this classification attempts should be made to determine whether the surface states are inherent to the semiconductor or are a property of chemical interaction between the semiconductor surface and the electrolyte.

SECTION 2:9 - THE EFFECT OF SURFACE STATES ON THE DIFFERENTIAL CAPACITY OF THE INTERFACE.

Since the charge on the surface states is a function of potential, there will be a corresponding differential capacity (C_{ss}) due to the presence of surface states. The dependence of C_{ss} on the potential drop in a semiconductor is represented by a curve with a single maximum.

At large positive or negative values of $(\phi_B - \phi_s)$ such that $\left| \frac{E_F - E_{ss}^0}{kT} \right| \ll e_o(\phi_B - \phi_s)kT$, the capacity per unit area of the surface states falls off exponentially with potential.

$$C_{ss} = \frac{e_o^2}{kT} N_s d_s \exp \left(- \left| \frac{e_o(\phi_B - \phi_s)}{kT} \right| \right) \quad 2.97$$

At $\frac{e_o(\phi_B - \phi_s)}{kT} = \frac{E_F - E_{ss}^0}{kT}$, the capacity of the surface states

is maximal and equal to:-

$$C_{ss}^{\max} = \frac{e_o^2 N_s d_s}{kT} \quad 2.98$$

For high concentrations of surface levels (e.g. 10^{14} cm^{-2}), this capacity is around $100 \mu\text{F cm}^{-2}$, comparable with the capacity of the Helmholtz layer.

The total charge per unit area on the semiconductor plate of the double layer is equal to the sum of $Q_{sc} + Q_{ss}$, and thus the capacity of this plate is also equal to the sum of $C_{sc} + C_{ss}$. For this reason, in the equivalent electric circuit of the interface, the capacity of the space charge layer and that of the surface state layer are connected in parallel.

For real surface states, however, there will be some time constant corresponding to the rate of charge transfer between the semiconductor bulk

and the surface states. For adsorbed surface species, this may be equivalent to the rate of electron transfer to the surface-bound redox species similar to the heterogeneous rate constant for metal/redox couple electron transfer reactions. Thus, for a given surface state or adsorbed species, one might expect to find a fixed time constant. This may be modelled in the equivalent circuit by placing a resistor (R_{SS}) in series with the surface-state capacitance such that the product $R_{SS} \cdot C_{SS}$ reflects the time constant for the particular surface state. As will be seen later (Chapters 4 and 5), this model bears up well with experimental evidence on certain materials, the constancy of the $R_{SS} \cdot C_{SS}$ product being found to be accurate to within $\pm 3\%$. So far no detailed theoretical model has been constructed to explain this observation although work is in progress.

SECTION 2.10

REDOX PROCESSES UNDER DARK AND ILLUMINATED CONDITIONS AT SEMICONDUCTOR/
ELECTROLYTE INTERFACES.Dark

Like metal electrodes, semiconductor electrodes can perform redox reactions by electron transfer between the electrode and a redox system in solution. There is, however, an important difference due to the existence of a band gap in the energy distribution of electronic states in a semiconductor. Electron transfer can only occur within two energy ranges corresponding either to the conduction band or to the valence band.

In the classical model, the currents in the conduction band and valence band are expressed separately

$$j_c = j_c^+ - j_c^- = k_c^+ \cdot C_R \int_{E_c}^0 K(E) D_+(E) \cdot W_R(E) dE \\ - k_c^- \cdot C_{ox} \int_{E_c}^0 K(E) D_-(E) \cdot W_{ox}(E) dE \quad 2.99$$

$$\text{and } j_v = j_v^+ - j_v^- = k_v^+ \cdot C_R \int_{-\infty}^{E_v} K(E) D_+(E) W_R(E) dE \\ - k_v^- \cdot C_{ox} \int_{-\infty}^{E_v} K(E) D_-(E) W_{ox}(E) dE \quad 2.100$$

where j^- is the current density for electron transfer from the electrode to oxidized species in solution

j^+ is the current density for electron transfer from the reduced species in solution to the electrode

v and c are subscripts representing electron transfers taking place via the valence and conduction bands respectively

C_{ox} and C_R are the concentrations of oxidized and reduced species in solution

$D_+(E)$ and $D_-(E)$ are the densities of occupied and unoccupied states in the semiconductor at energy E

$W_{ox}(E)$ and $W_R(E)$ denote distribution functions for finding, respectively,

an oxidized or a reduced component in a solvation state at energy E .

These distribution functions represent the time-averaged distribution over all possible thermal fluctuations in energy caused by interaction with the solvent or with directly bonded ligands. The probability function has a maximum at the most probable solvation state and has a Gaussian energy distribution about this most probable state.

$K(E)$ is a factor that gives the transfer probability for electrons, including the quantum mechanical transfer probability summed over all distances.

Fig.2.14 shows the above functions and their products. The results of such an integration are indicated for two redox system, one with E_{redox}^0 close to the conduction-band edge (E_c) and another with E_{redox}^0 close to the valence-band edge (E_v).

As a general conclusion the following is obtained. Redox systems that have a standard potential in the neighbourhood of the semiconductor conduction-band edge may exchange electrons with the conduction band. Redox systems with standard potentials in the neighbourhood of the valence band-edge may exchange electrons with the valence band.

Since the majority of the electron transfer takes place in a narrow edge above and below the band-edge energies E_c and E_v , the situation may be well described by the approximations

$$j_c = k_c^+ \cdot K(E_c) \cdot C_R \cdot W_R(E_c) \cdot N_c - k_c^- \cdot K(E_c) \cdot C_{ox} \cdot W_{ox}(E_c) \cdot n_s \quad 2.101$$

$$j_v = k_v^+ \cdot K(E_v) \cdot C_R \cdot W_R(E_v) \cdot p_s - k_v^- \cdot K(E_v) \cdot C_{ox} \cdot W_{ox}(E_v) \cdot N_v \quad 2.102$$

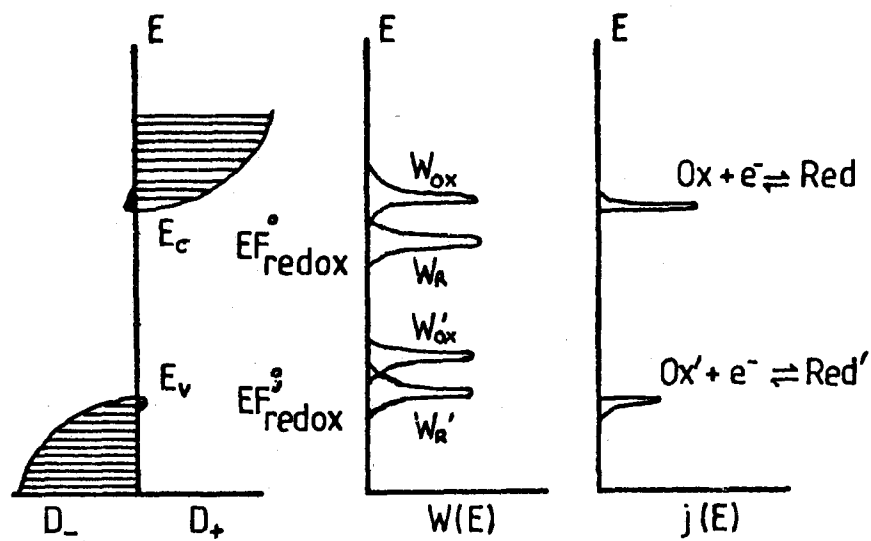


Fig.2.14 Distribution functions of energy states for electrons D_- , and holes D_+ , as well as for the reduced and oxidized components of two different redox systems, W_R and W_{ox} , vs. energy. The right part shows the resulting rate of electron transfer for the two redox couples according to Eqs.2.99 and 2.100.

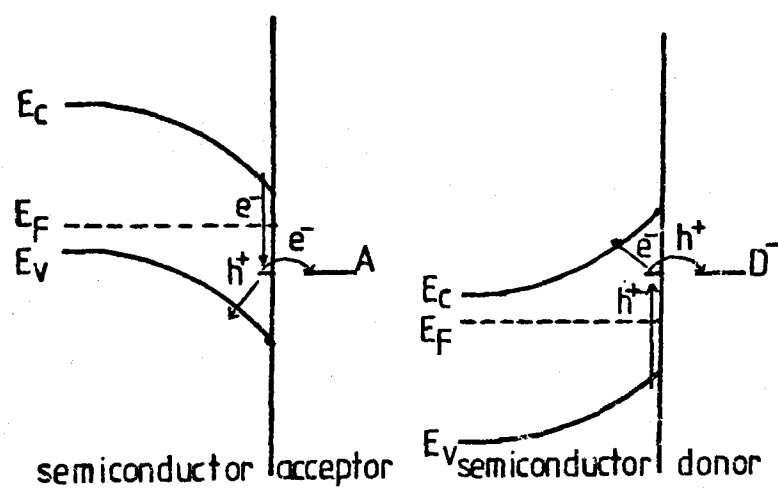


Fig.2.15 Electron transfer via surface states at cathodic (left side) or anodic (right side) polarization.

where $K(E_c)$, $K(E_v)$, $W(E_c)$ and $W(E_v)$ are the values of these functions at the band edges. The densities of occupied and unoccupied electron states in the semiconductor are represented by the concentrations of electrons and holes in the surface and by the effective densities of states at the band edges.

The values of $K(E)$ and $W(E)$ are independent of applied voltage as long as the charge in the Helmholtz layer does not vary considerably in the presence of surface states or redox-active adsorbed species. Equations 2.101 and 2.102 indicate, therefore that the variation of current due to applied potentials can be attributed mainly to a variation of the concentrations of electrons and holes in the surface.

If we take the situation with equilibrium between semiconductor and solution such that j_c and j_v both equal zero and if n_s^0 and p_s^0 are the concentrations of electrons and holes in the surface for the respective redox reaction, then we may write

$$j_c = j_c^0 \left[\frac{C_{R.s}}{C_{R.o}} - \frac{C_{ox.s}}{C_{ox.o}} \cdot \frac{n_s}{n_s^0} \right] \quad 2.103$$

$$\text{and } j_v = j_v^0 \left[\frac{C_{R.s}}{C_{R.o}} \cdot \frac{p_s}{p_s^0} - \frac{C_{ox.s}}{C_{ox.o}} \right] \quad 2.104$$

with the exchange currents at equilibrium j_c^0 and j_v^0 given by

$$j_c^0 = k_c^+ \cdot K(E_c) \cdot C_{R.o} \cdot W_R(E_c) \cdot N_c \quad 2.105$$

$$= k_c^- \cdot K(E_c) \cdot C_{ox.o} \cdot W_{ox}(E_c) \cdot n_s^0 \quad 2.106$$

$$j_v^0 = k_v^+ \cdot K(E_v) \cdot C_{R.o} \cdot W_r(E_v) \cdot p_s^0 \quad 2.107$$

$$= k_v^- \cdot K(E_v) \cdot C_{ox.o} \cdot W_{ox}(E_v) \cdot N_v \quad 2.108$$

where $C_{R,s}$ and $C_{ox,s}$ are the concentrations of the redox components within interaction range of the electrode surface.

If the variation of electrode potential at varying polarizing voltage occurs fully over the space-charge layer, $\phi_H - \phi_O$ remaining constant, the surface concentrations of carriers follow the applied voltage exponentially.

$$\frac{n_s}{n_s^o} = \exp \left[\frac{e[(\phi_o - \phi_\infty)_s - (\phi_o - \phi_\infty)_o]}{kT} \right] = \exp \left[\frac{-e_o \eta}{kT} \right] \quad 2.109$$

$$\text{and } \frac{p_s}{p_s^o} = \exp \left[\frac{-e_o[(\phi_o - \phi_\infty)_s - (\phi_o - \phi_\infty)_o]}{kT} \right] = \exp \left[\frac{e_o \eta}{kT} \right] \quad 2.110$$

where $\eta = V - V_o$ is the overvoltage applied to the electrode over the equilibrium conditions where $E_F \equiv E_{redox}^o$.

Combining equations 2.103, 2.104, 2.109 and 2.110 results in a simple current-voltage curve that in the absence of concentration polarization reads

$$j_c = j_c^o [1 - \exp -(e_o \eta/kT)] \quad 2.111$$

$$\text{and } j_v = j_v^o [1 - \exp (e_o \eta/kT)] \quad 2.112$$

The characteristic feature of this current-voltage relationship is that, in the conduction band, only the cathodic process is influenced by the applied voltage whereas in the valence band only the anodic process depends on voltage.

Complications in the rate processes can arise by shifts in the Helmholtz layer potential drop with externally applied voltage. For some semiconductors, intra band-gap surface states may act as additional donor and acceptor energy levels in the forbidden band gap and this contributes to the electron transfer processes. Examples of such processes are illustrated in Fig. 2.15.

SECTION 2.11

Effect of Illumination

General Considerations

If light of energy greater than the band-gap is incident on a semiconductor, electron-hole pairs will be generated in the surface region and thus the thermal distribution of charge carriers will no longer be maintained. (This non-equilibrium situation has been dealt with at length by Gerischer²¹² in terms of separate 'quasi-Fermi levels' for electrons and holes. This approach will not be dealt with further here.) If the surface region is field free, as at the flat-band potential, the electron and hole may recombine within a period of about 10^{-8} - 10^{-5} seconds (c.f. metals $\sim 10^{-13}$ s). However, under the influence of an electric field in the space-charge layer, the charge carriers may be swept in opposite directions, thus allowing a fraction of minority carriers to reach the surface of the electrode before recombination takes place. Transfer of minority carriers into solution may then be possible, providing vacant redox energy levels exist in solution to which the minority carriers may be transferred adiabatically. Essentially this latter requirement will be satisfied providing there exists in solution a redox couple with standard potential

- (1) lying above the valence-band edge for hole injection into solution

or

- (2) lying below the conduction-band edge for electron transfer into solution.

The problem of the kinetics of electrode processes at illuminated semiconductors has been tackled by a number of authors. Gärtner²¹³ and later Wilson²¹⁴ obtained analytical expressions for very limited conditions. Laser and Bard²¹⁵ have employed digital simulations, but since the minority-carrier concentrations vary over many orders of magnitude in a small region of the space-charge layer, results were obtained only for times very soon after

the onset of illumination. Reiss²¹⁶ made an attempt to include both minority and majority carriers, but avoided the field coupling terms and arrived at some analytically intractable semi-linear equations. The results were rather unwieldy and of little interest to the experimental electrochemist.

Reichman²¹⁷ has attempted an improved model allowing for recombination in the space-charge and neutral regions, but his approach is not particularly satisfying since little physical significance may be applied to any of his derived mathematical terms.

A brief description will be presented of a recent theoretical model due to Albery and Hamnett²¹⁸ that is based on the approach of Gärtner and Wilson. Fewer simplifications are made, and like the Reichman model, specific allowance is made for the recombination of electrons and holes in the depletion layer. The model is of particular value to the practical electrochemist since the derived analytical expression can be separated into terms each corresponding to a simple physical process.

The Model

A p-type semiconductor will be taken as the example. The semiconductor may be separated into two regions:- the depletion layer and the field-free region.

In the depletion region, the potential is given by

$$\theta = \theta_0 (1 - x/\sqrt{2}\theta_0 L_D)^2 \quad 2.113$$

$$\theta = VF/RT \quad \theta_0 > 4 \quad 2.114$$

L_D is the Debye length for the semiconductor.

$$L_D = \left[\frac{\epsilon \epsilon_0 kT}{e^2 N_D} \right]^{\frac{1}{2}} \quad 2.115$$

Light of irradiance $I_0 \text{ mol cm}^{-2} \text{ s}^{-1}$ is normally incident on the surface of the electrode, and absorption is assumed to follow the exponential

Beer-Lambert law with a characteristic absorption coefficient $\alpha \text{ cm}^{-1}$.

To avoid inverse units, a new critical length may be defined

$$L_{\epsilon} = 1/\alpha \quad 2.116$$

The first approximation, made to avoid the cross coupling terms with majority carriers, is the assumption that the build-up of minority carriers at the surface does not affect the distribution of potential. This allows consideration to be restricted to only the motion of the minority carriers.

The second region, $x > \sqrt{2}\theta_0 L_D$, is essentially field-free. The minority carriers in this region diffuse under a concentration gradient only. Wilson used the principle of superposition of charges to evaluate the flux. The Albery and Hamnett model²¹⁸ uses the alternative procedure of matching the concentration and flux of minority carriers at the boundary of the depletion layer.

The equation of motion of the minority carriers

In a steady state, the equation of motion describing the transport and kinetics of the minority carriers (electrons for a p-type semiconductor) is

$$D \frac{\delta}{\delta x} \left[\frac{\delta c}{\delta x} - c \frac{\delta \theta}{\delta x} \right] + \frac{I_0}{L_{\epsilon}} \exp \left[\frac{-x}{L_{\epsilon}} \right] - k c = 0 \quad 2.117$$

where it is assumed that the carriers have sufficiently low mobility for this equation to be applicable and c is the concentration of electrons with diffusion coefficient D . The field in the depletion layer is described by the dimensionless variable θ . The first two terms reflect transport by diffusion and migration. The next term describes the photogeneration of the carriers by light with a Beer-Lambert profile characterized by L_{ϵ} . It is assumed that electrons recombine by first-order kinetics with a rate constant k , this being likely to be true for the field-free region.

In the depletion layer, traps may be filled or emptied by the field, so the order of kinetics may change.

Equation 2.117 must be solved with two boundary conditions:

$$\text{as } x \rightarrow \infty \quad c \rightarrow 0 \quad 2.118$$

$$\text{at } x = 0 \quad NI_0 = D \left[\left(\frac{\delta c}{\delta x} \right)_0 - c_0 \left(\frac{\delta \theta}{\delta x} \right)_0 \right] = k'_\Sigma c_0 \quad 2.119$$

The boundary condition as $x \rightarrow \infty$ holds if the thermal population of minority carriers is negligible compared to that population generated by the light. The boundary condition at $x = 0$ related the flux described by either NI_0 or the transport terms to the kinetics on the surface of the semiconductor described by an overall heterogeneous rate constant k'_Σ . The collection efficiency, N , compare the flux of minority carriers lost at the surface by, for instance, recombination and Faradaic processes to the flux of incoming photons. If surface recombination (k'_R) and a Faradaic reaction (k'_F) are the two main processes, we define a Faradaic collection efficiency, N_F , as

$$N_F = (k'_F / k'_\Sigma) N \quad 2.120$$

$$\text{where } k'_\Sigma = k'_F + k'_R \quad 2.121$$

To solve equation 2.117, we must first solve the equation with boundary condition (2.118) for the field-free region with $\theta = 0$ and $x > W$, where W is the width of the depletion layer

$$W = (2\theta_0)^{1/2} L_D \quad 2.122$$

A relation is thus obtained between the concentration c_w and the flux c'_w at $x = W$. Similarly equation (2.117) may be solved for θ , for the depletion layer with boundary condition (2.119) and using equation (2.113) to obtain a second relation for the concentration and the flux at $x=W$. Elimination of c_w and c'_w then leads to an expression for N .

The Field Free Region

Using Laplace transforms and equation 2.117 with boundary condition 2.118 gives

$$Dc'_w = -\frac{Dc_w}{L_R} + \frac{L_k}{L_k + L_\epsilon} \beta I_o \quad 2.123$$

$$\text{and } c = c_w \exp\left[\frac{-x'}{L_k}\right] + \frac{\beta I_o L_\epsilon k^{-1}}{L_k^2 - L_\epsilon^2} \left[\exp\left(\frac{-x'}{L_k}\right) - \exp\left(\frac{-x'}{L_\epsilon}\right) \right] \quad 2.124$$

$$\text{where } x' = x - W$$

$$\beta = \exp(-W/L_\epsilon) = \exp[-(2\theta_o)^{1/2} L_D/L_\epsilon] \quad 2.125$$

$$\text{and } L_k = (D/k)^{1/2} \quad 2.126$$

The parameter β describes the fraction of the light that is absorbed in the field-free region and the length L_k is the diffusion length or reaction layer thickness. These results are identical to those obtained for the similar concentration profile for photogeneration in a homogeneous photogalvanic cell. Equation 2.123 shows that the flux at the edge of the depletion layer can be either negative or positive. The first negative term describes the diffusion of electrons out of the space charge layer and their subsequent loss by recombination in a reaction layer of thickness L_k . The second positive term describes the injection of electrons into the depletion layer from photogeneration in the field-free region; the light absorbed is βI_o and the fraction recovered is $L_k/(L_k + L_\epsilon)$. For good recovery L_k must be larger than L_ϵ .

The Depletion Layer

$$\text{Let } c = ue^\theta \quad 2.127$$

Substitution in Equation (2.117) together with equation (2.113) gives

$$\frac{\theta \delta^2 u}{\delta \theta^2} + (\theta + \frac{1}{2}) \frac{\delta u}{\delta \theta} - \frac{1}{2} \gamma u = -\frac{1}{2} g e^{-\theta} \quad 2.128$$

$$\text{where } \gamma = L_D^2 / L_k^2 \quad 2.129$$

$$\text{and } g = \frac{\beta I_o L_D^2}{DL_\epsilon} \exp \left[\frac{L_D (2\theta)^{\frac{1}{2}}}{L_\epsilon} \right] \quad 2.130$$

Equation 2.128 is an inhomogeneous Kummer²¹⁹ equation and may be solved completely. However, a much simpler approach may be taken using certain approximations yielding results where the mathematics reveals greater physical significance.

Two approximate methods may be chosen for the conditions $L_D < L_k$ and $L_D > L_k$. The former case only will be considered here since the materials used throughout this thesis were cut from single crystals having dopant and defect concentrations sufficiently small to render this former approximation true. The other case and the more complete solution may be found elsewhere.²¹⁸

Approximate Solution for $L_D < L_k$

With the following approximations and assumptions

$$\begin{aligned} \theta_o &> 6 \\ L_D^2 &\ll L_\epsilon^2 \\ L_D^2 &< L_k^2 / \ln(1 + \pi^{\frac{1}{2}} \theta_o^{\frac{1}{2}}) \end{aligned}$$

the equation for the photocurrent efficiency may be shown to be:-

$$N = \frac{1 - \exp \left[-\frac{(2\theta_o)^{\frac{1}{2}} L_D}{L_\epsilon} \right] + \frac{L_k}{L_k + L_\epsilon} \exp \left[-\frac{(2\theta_o)^{\frac{1}{2}} L_D}{L_\epsilon} \right]}{1 + \frac{k}{k_\Sigma} \left[\frac{L_D}{(2\theta_o)^{\frac{1}{2}}} + \frac{L_k}{\exp(\theta_o)} \right]} \quad 2.131$$

Each of the terms in equation 2.131 has a simple physical significance. The first two terms in the numerator describe the fraction of light that is absorbed in the depletion layer; the third term describes the fraction absorbed in the field-free region multiplied by the fraction of those generated that reach the depletion layer boundary. Thus the numerator describes the supply of minority carriers to the surface of the electrode and may be called the "generating term". The denominator describes their subsequent fates:- The first term, reaction at the surface; the second term, recombination in the depletion layer; and the third term, recombination in the field-free region - each of the terms normalized to reaction at the surface. This group of terms may be called the "kinetic term". Each of the recombination terms contains a characteristic length that describes the volume in which recombination takes place. In the depletion layer this length is $L_D/(2\theta_0)^{1/2}$. This is because the concentration of minority carriers is largest at the surface of the electrode so that for first-order kinetics, most recombination takes place close to the surface. At a distance of $L_D/(2\theta_0)^{1/2}$, $c/c_0 \approx e^{-1}$ and thereafter the concentration continues to fall off as θ drops. For the recombination in the field-free region, the characteristic length is L_k . The exponential term describes the difference in concentration between the surface and the boundary of the depletion layer. Therefore the collection efficiency, N , consists of the generating term, which describes the supply of minority carriers to the electrode surface, divided by the kinetic term, which compares the proportion of the carriers that react at the surface with those that recombine either in the depletion layer or in the field-free region.

CHAPTER THREE

EXPERIMENTAL AND TECHNIQUES

SECTION 3:1 INTRODUCTION

Since the majority of the literature regarding electrochemical techniques pertains to the study of metal electrodes, it is useful to consider the similarities and differences of semiconductor electrochemical techniques. In general, it is possible to say that all the techniques applied to studies of metal electrodes may also be applied to semiconductors, but there are a number of additional requirements peculiar to the semiconductor case.

In common with the former, a basic requirement is a system capable of accurately controlling the potential of the subject electrode with respect to some known standard. Such a device is labelled a potentiostat, and 3 electrodes are found necessary to satisfy the potential control: a Working Electrode (WE), a Reference Electrode (RE), and a Counter or Auxiliary Electrode (CE). The reasons for this requirement are outlined in Section 3:3. Since, in general, current will pass from one electrode to another in such a system, precise current measurement is also needed; and in most modern apparatus this is achieved in the same potentiostat instrument. Finally various ancillary electronic apparatus may be included either inside or externally connected to the 'potentiostat'. These may provide specific waveforms for driving the potential control or may give visual or digital display of the signal input to or output from the electrochemical cell. Indeed, it has been found that the application of sinusoidal voltage modulation to the working electrode is of particular importance for semiconductor electrochemistry.^{14,15} This has provided much

information concerning the impedance of the semiconductor/electrolyte interface which is itself interpretable in terms of physical processes taking place at or across the interface. The theory relating to this experimental technique is outlined in Section 2:7

In common with studies of metallic electrodes, the electrolyte solution must be maintained under precise temperature control and atmospheric conditions. This requires the electrochemical cell to possess a thermostatted water jacket along with gas purification and bubbling facilities. A further complication to cell design for semiconductor photoelectrochemistry is generally the requirement for controlled conditions of illumination. The cell must therefore cater for well defined optical passage of the full spectrum of light onto the frontface of the electrode from some external source.

Specific to semiconductor electrochemistry is the problem of attaining ideal electrical contact to the semiconductor material: a so-called Ohmic Contact. By ideal one means that over the whole voltage range required, current flow across the metal contact/semiconductor interface must be a linear function of the potential differences between the two materials. This problem is discussed at greater length in Appendix 1.

The following block diagrams illustrate the schematic arrangement of the apparatus for the various basic types of experiment that were used during the course of the experimentation described in this thesis. The diagrams show the breakdown of the equipment into various subsections: Electronic, Optical and Mechanical. Each subsection is then dealt with at greater length in the remaining sections of this chapter. There follows a discussion of the chemicals and electrode materials used in the investigations. The application of computer fitting programs to the analysis of the results in terms of an impedance model

of the semiconductor/electrolyte interface is dealt with in Appendix 2.

SECTION 3:2 TYPES OF EXPERIMENT

3:2:1 Potentiostatic Current Measurement in Dark and Illuminated Conditions (Apparatus as in Fig. 3.1.)

This simplest of all possible experiments allows for the measurement of steady-state current flowing through the electrode as a function of electrode potential and illumination intensity. The experiment provides the greatest resemblance to an operational solar cell. However, whereas the latter would employ only two electrodes, three electrodes are still used in this system, the working electrode potential is thus kept constant. The advantage of this method is to separate out contributions to overall solar-cell-efficiency due to the processes occurring at both anode and cathode. Since the work concerned the study of the mechanisms at the semiconductor alone, this experiment ideally revealed the contributions to cell efficiency from the semiconductor/electrolyte interfacial processes.

In conjunction with the monochromator, so-called 'action spectra' of photocurrent as a function of illumination wavelength were readily prepared; but some alternative way had to be found to measure the lamp output intensity also as a function of the wavelength. In such a way an absolute quantum efficiency could be obtained at each wavelength. This of course was only possible if photocurrents were found to be constant over long periods.

Finally, used in conjunction with a Y-t recorder, slow photocurrent transients could be traced and long-term photocurrent stability studied to determine electrode durability over long periods.

In this experimental set-up, the triangle-wave generator is disconnected and the electrode potential set by the input voltage from

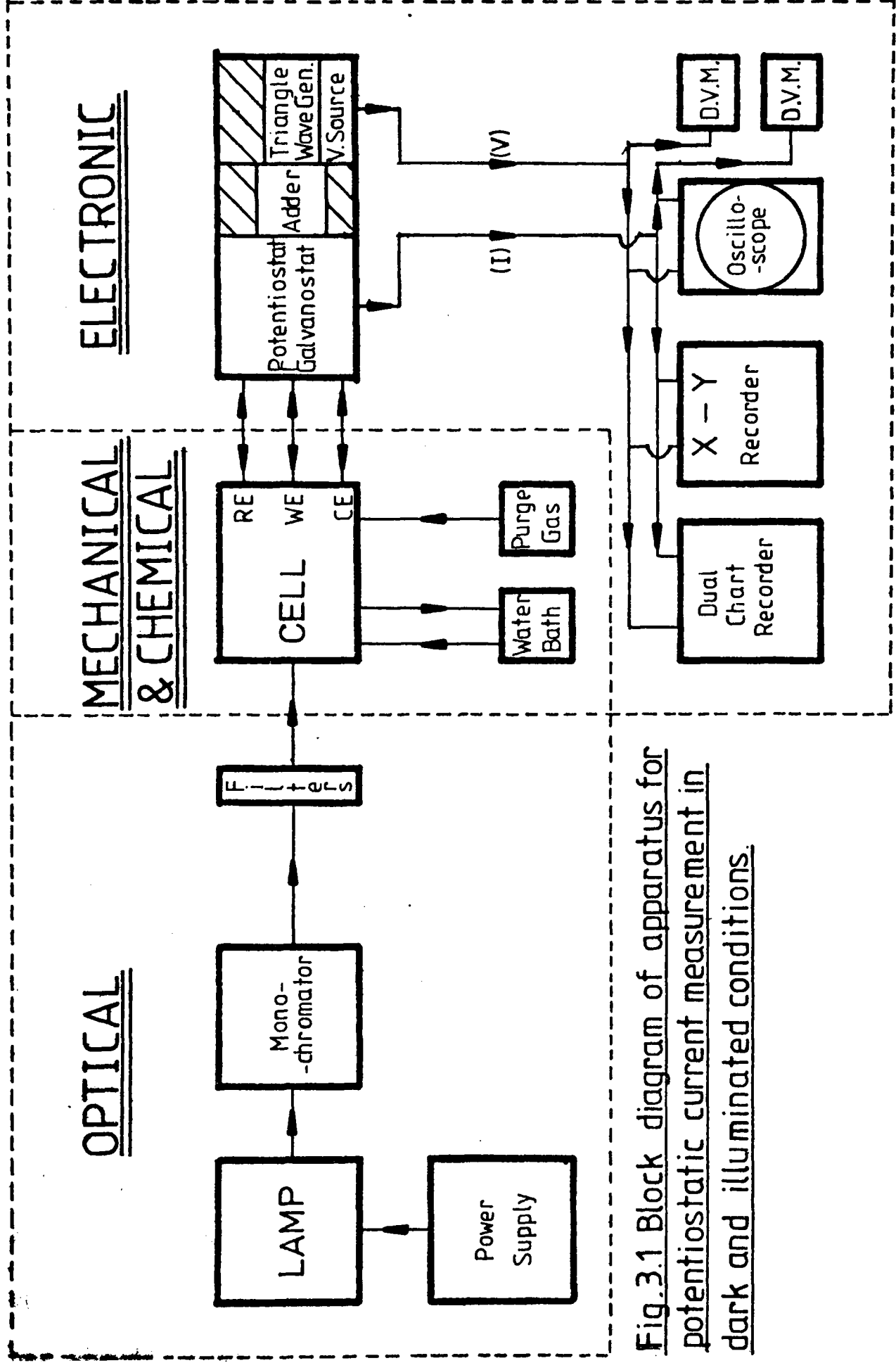


Fig. 3.1 Block diagram of apparatus for potentiostatic current measurement in dark and illuminated conditions.

a d.c. voltage-source module. Light filters may be used to cut out certain sections of the illuminating spectrum. The output of a Xenon lamp is particularly rich in U-V light; and to better mimic a solar spectrum, a U-V filter may be used (see Section 3:4)

3:2:2 Linear Voltage Sweep and Cyclic Voltammetry (Apparatus as in Fig. 3.1)

This technique has long been used in the study of redox processes at metal electrodes and may be readily applied to semiconductor electrochemistry with or without added solution redox species. In particular, the technique can rapidly provide information regarding electrode stability, since ideal electrodes would create reproducible cyclic voltammograms; deviation from reproducibility generally reflects irreversible surface corrosion, although each case needs to be considered more carefully once such discrepancies are discovered.

Another particular advantage of this technique is to study electrochemical processes under non-equilibrium conditions, i.e. surface redox concentrations not at the steady state values obtained in potentiostatic measurements. In addition, varying sweep rate provides another variable parameter that may be used to great effect in determination of reversibility of electrode reactions. The subject is described in great detail in a number of seminal articles.²²⁰⁻²²³

The linear and cyclic voltage sweeps may be obtained from the triangle-wave generator described in Section 3:3. Display at low sweep rates ($1\text{mV} - 1\text{V s}^{-1}$) is simplest with an X-Y recorder, but at higher speeds, a digital storage scope facility may be required. However, throughout this work sweep rates were maintained within the bounds for display on an X-Y recorder.

3:2:3 Photocurrent Voltage Measurement Using Square-Wave Illumination (Apparatus as in Fig. 3.2)

In this experiment, square-wave-modulated light is applied to the semiconductor electrode. By means of phase-sensitive detection, the in-phase current corresponding to the photo-induced current may be accurately measured even in the presence of large background currents flowing under dark conditions. This latter point is the most common reason for the application of this technique since, in many cases, large currents flow through the electrode even in the dark; these currents may be highly voltage or time dependent. Measurement of small photocurrent against such a background is impossible without phase-sensitive detection.

An added advantage of the sensitivity of this lock-in technique is that very low light intensities may be used, which allows for photocurrent measurements where the passage of the photocurrent itself does not significantly alter the interfacial concentration of redox species within the time scale of the experiment. In particular, photocurrents may be reduced to the point where it may take a number of seconds, or even minutes, to build up a monolayer of some redox species. An example of this is seen in Section 4:2

As with d.c. measurements, the locked-in photocurrent may be measured as a function of electrode potential (in static or linearly varied conditions) and 'illuminating' intensity or wavelength. In particular, action spectra may be built up with greater accuracy as measurements can be made at low net photocurrent; time-dependent phenomena caused by photo-induced variations in an electrode surface can thus be minimized.

The central feature of the apparatus is the lock-in amplifier; on being simultaneously fed with the current signal and some reference signal from the light modulator (chopper), it can produce

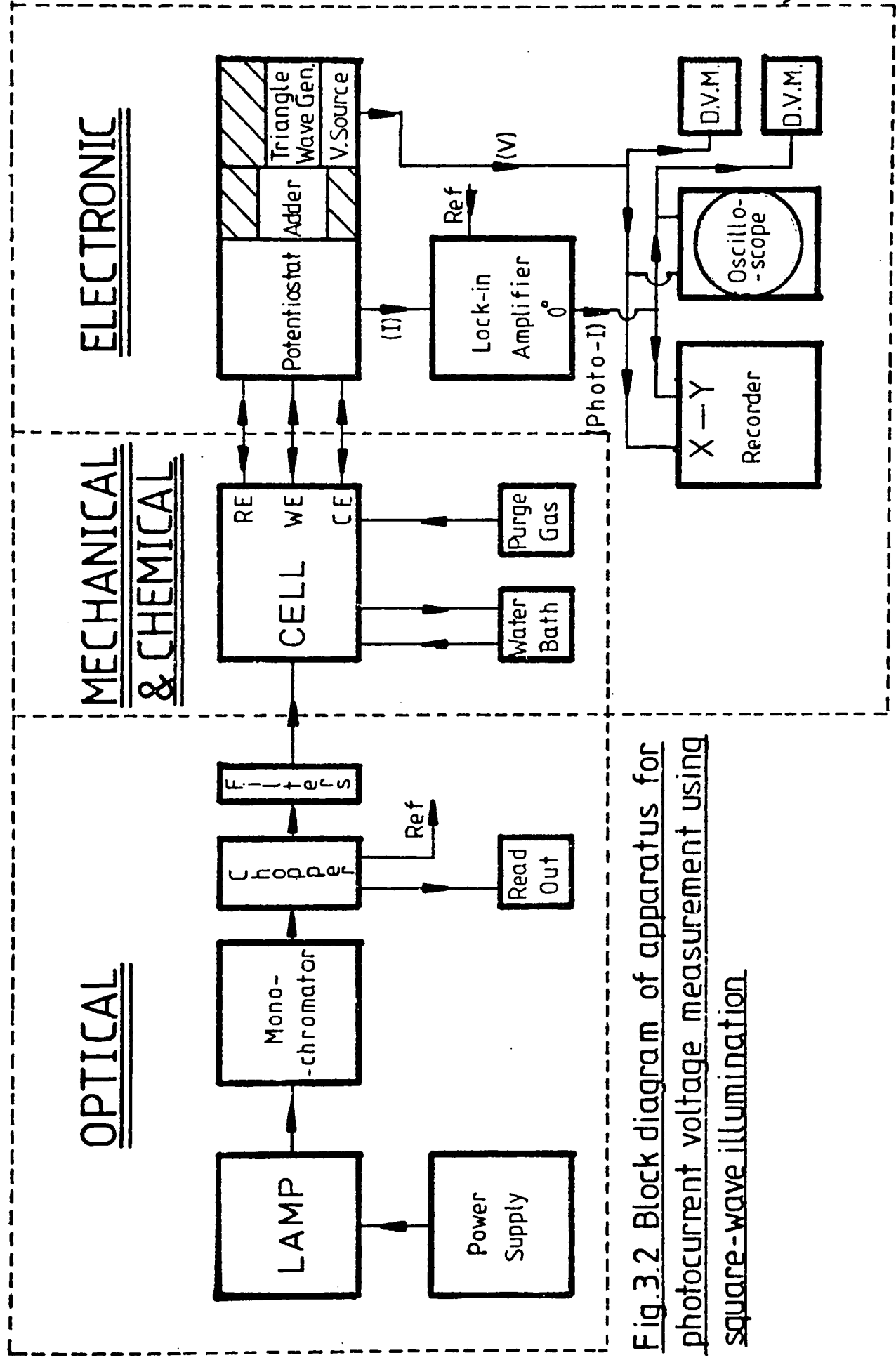


Fig.3.2 Block diagram of apparatus for photocurrent voltage measurement using square-wave illumination

a signal directly proportional to the in-phase portion to the current even in the presence of significant non-synchronous variation in that cell current. This is described in more detail in Section 3:3:3d

Section 3:2:4 Measurement of Cell Admittance (Apparatus as in Fig. 3.3)

For the purposes outlined in Chapter 2, Section 2:7 measurement of the admittance or impedance of the electrochemical cell can provide very valuable information regarding the distribution of potential and the presence of interband energy states at the semiconductor-electrolyte interface. To achieve this, we have to apply some small sinewave modulation to the potential controlling the electrode voltage via the potentiostat. Since this latter device generally provides a voltage output proportional to the current flowing, we may preferably measure differential cell admittance (cell current/applied voltage) by measuring in-phase and 90° out-of-phase current signals with the assistance of a lock-in amplifier.

For detailed analysis purposes (described in Section A:2) these results must be taken as a function of frequency and under steady-state mean potential control. However, as with d.c. cyclic voltammetry it is, in some cases, of interest to linearly or cyclically vary the mean electrode potential to observe non-equilibrium processes occurring at the electrode/electrolyte interface. This can be achieved by superimposing on the small sinewave modulation a linearly varying triangular-voltage sweep that possesses a frequency considerably smaller than the sinusoidal modulation. This technique is loosely termed "a.c. cyclic voltammetry" but in this thesis it differs from the more traditional application in metal electrochemistry²²⁴ in that fairly fast sweep rates are deliberately chosen (typically $10\text{-}50\text{mV s}^{-1}$) in order to pick up non-equilibrium concentrations of

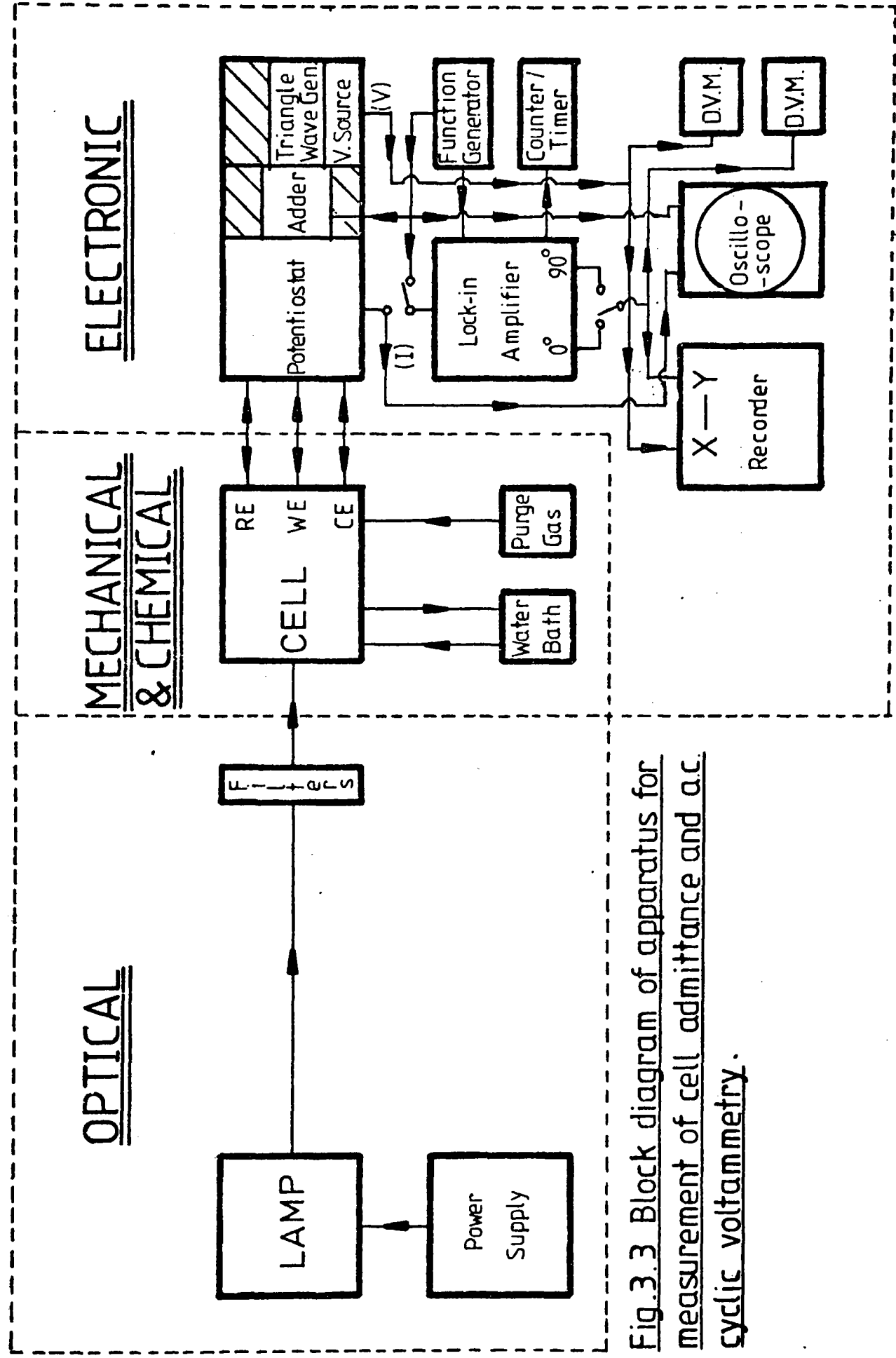


Fig.3.3 Block diagram of apparatus for measurement of cell admittance and a.c. cyclic voltammetry.

electroactive species. These species are created at potentials other than that at which one may observe an a.c. peak. In metal electrochemistry, the term a.c. cyclic voltammetry generally applies to very slow cyclic sweeps, typically $<1 \text{ mV s}^{-1}$, where measurements are then made under essentially equilibrium conditions at each potential.²²⁴ To date no satisfactory theory exists for the detailed interpretation of this new breed of fast a.c. cyclic voltammetry; but its sensitivity can still be of great qualitative value. The interpretation of some of the time-dependent phenomena seen on semiconductor electrodes is particularly illustrated in Chapter 4, Section 4:8

3:2:5 Rotating Ring Disc Electrode (RRDE) Studies (Apparatus - see Fig. 3.4)

This novel experiment makes use of a technique that takes advantage of a controlled supply of electroactive species to the edge of the diffusion layer adjacent to a ring electrode; this controlled supply is provided by a planar circular electrode rotating in a liquid solution. Its detailed application has been discussed at length by Filinovskii²²⁵ and Alberly.^{226,227}

In our experiments, we used a semiconductor electrode as the disc electrode and a concentric metallic ring. Both electrodes may have separate potential control, and the central electrode may or may not be illuminated. The idea of this technique was to use the outer metal electrode as a probe for the electrochemical reactions taking place at the central semiconductor electrode. This is possible since solution flow proceeds from the centre such that electroactive species created at the central disc are swept past the metallic ring.

Since detailed mathematical analysis has been made of the liquid flow to and from the RRDE, it should be possible to obtain valuable information concerning the mechanisms and rates of electrochemical

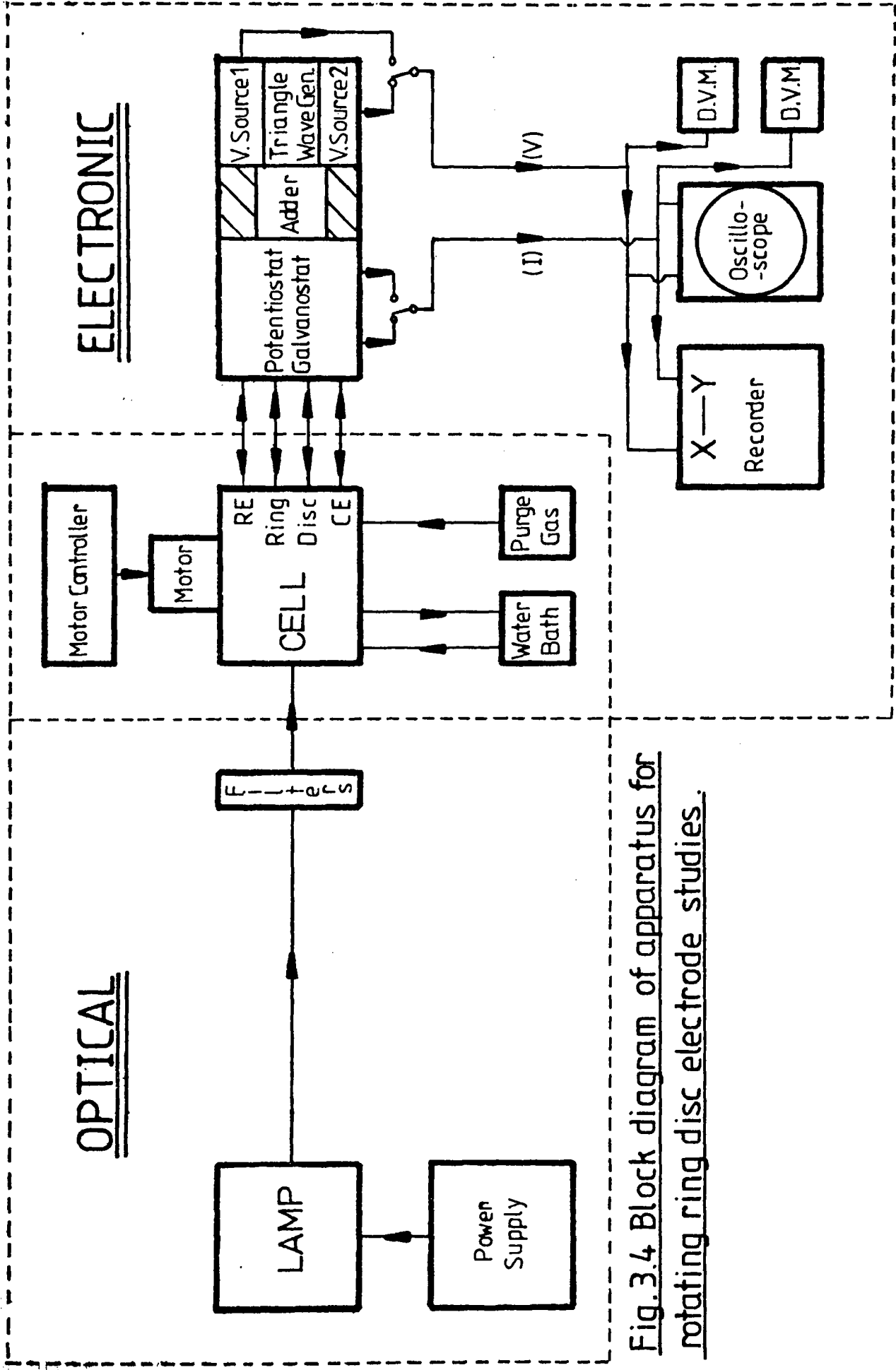


Fig.3.4 Block diagram of apparatus for rotating ring disc electrode studies.

reactions at the disc electrode. In practice, much difficulty is found in construction of the semiconductor RRDE. However, some preliminary studies were made of the technique as applied to rotation speed dependence of electrode currents and the electrochemical analysis of electrode dissolution products picked up at the metallic ring electrode.²²⁸

SECTION 3:3 DESCRIPTION OF ELECTRONIC CIRCUITRY AND APPARATUS

3:3:1 Control Circuitry

As described in the introduction, accurate potential control and current measuring apparatus is essential for any detailed electrochemical investigation. Throughout this experimentation, the apparatus used to satisfy this requirement was a "home-built" system tailor-made to suit the particular voltage and current requirements of small-scale semiconductor electrochemistry in aqueous solution, i.e. voltage requirements $\approx \pm 2$ V, current capacity ≈ 10 mA (corresponding to approximately $40\text{--}50\text{ mA cm}^{-2}$ for typical electrode areas of $20\text{--}30\text{ mm}^2$).

The general design was made according to standard literature circuits. Modular construction was chosen for greatest experimental versatility, ease of fault-finding, and maintenance. Each module was chosen to perform a single particular function or mathematical function and thus incorporated operational amplifiers as the main active components. The separate modules were all mounted in one metal shielded box and powered from a single, stabilized $+15\text{V}/0/-15\text{V}$ power supply (R.S. components).

The detailed circuit descriptions have been described elsewhere. However, Fig. 3.5 illustrates the schematic layout of the various modules, and the following sections provide brief descriptions of each individual module.

Fig.3.5 Schematic circuit diagram of potential control and current measuring circuitry

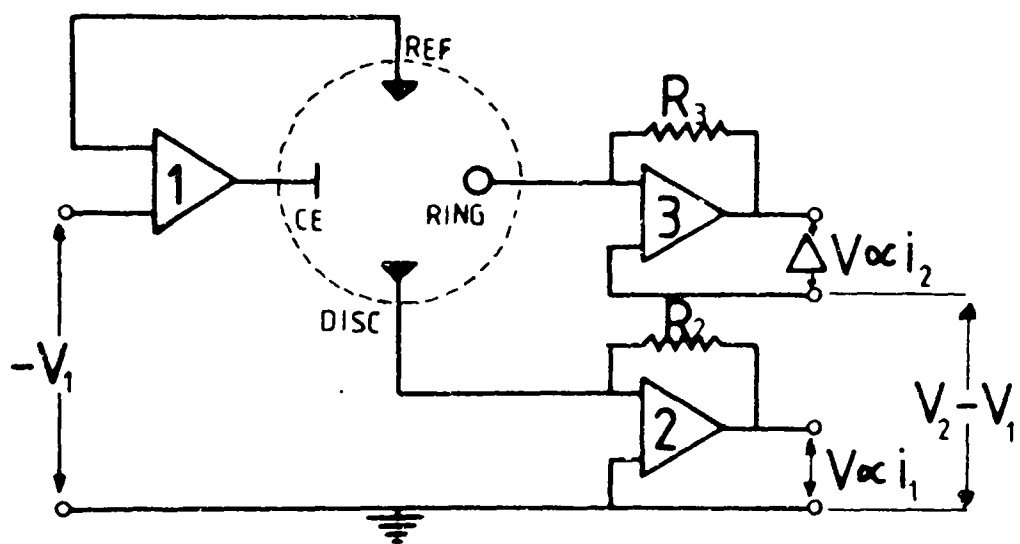
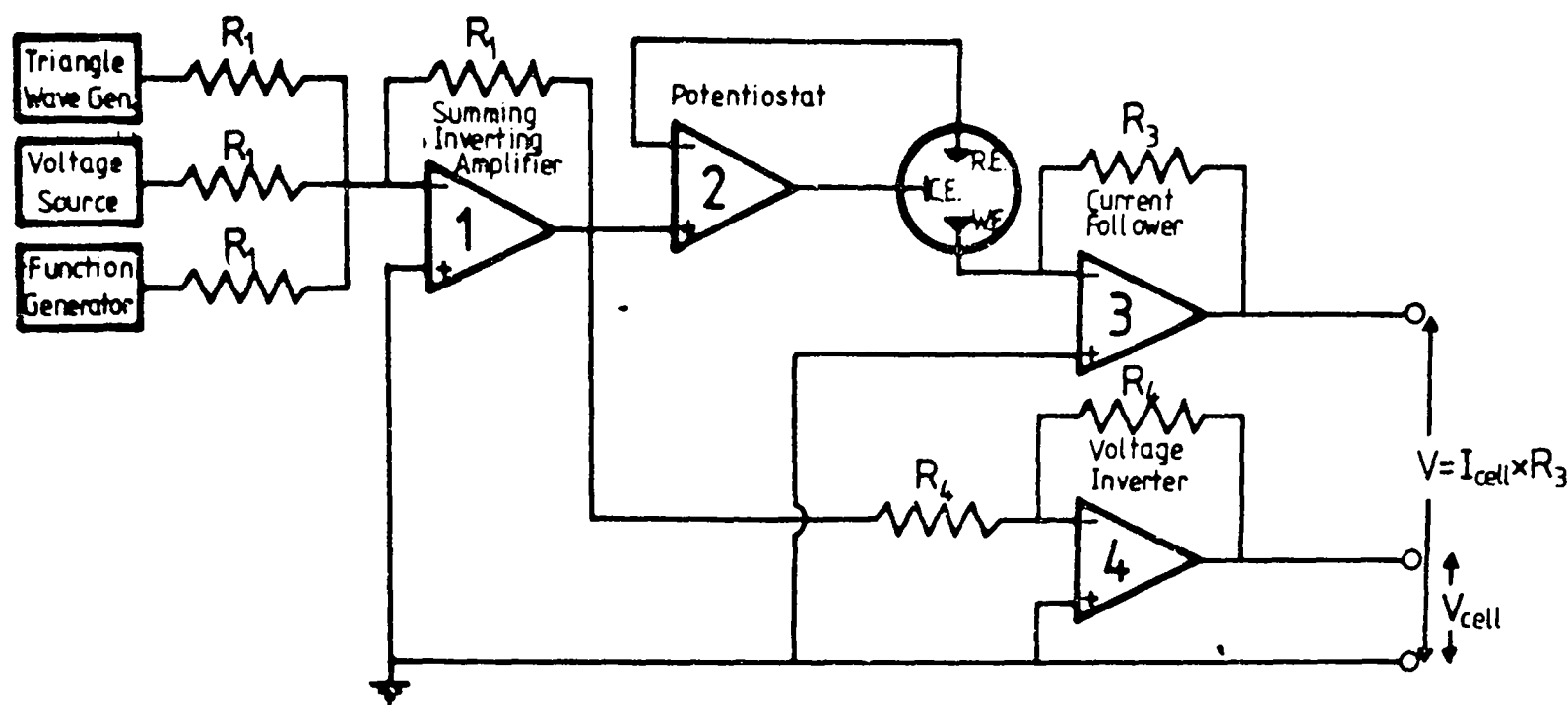


Fig.3.6 (a) POTENTIOSTAT FOR INDEPENDENT CONTROL OF THE POTENTIAL FOR RING AND DISC ELECTRODES

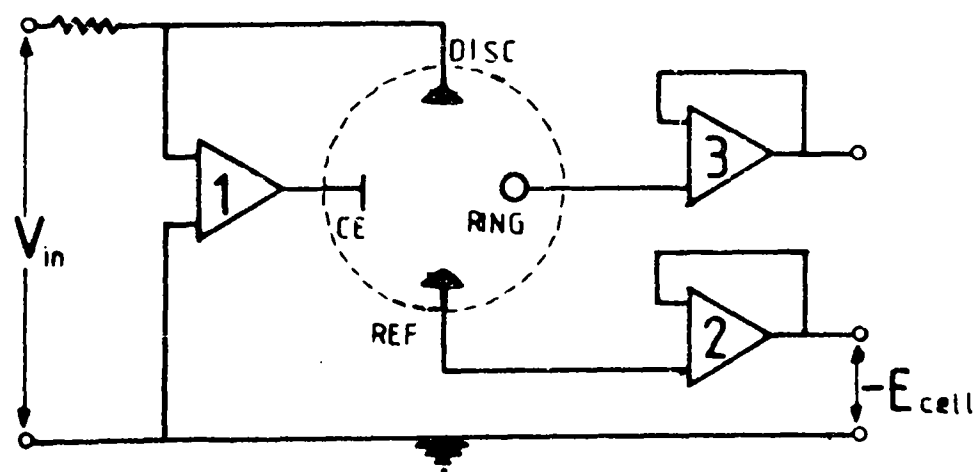


Fig.3.6 (b) DISC ELECTRODE GALVANOSTAT

(a) Potentiostat/Galvanostat. This was a multi-purpose module serving (1) to form the potential of up to two working electrodes relative to a reference electrode (potentiostatic mode) or (2) to maintain a pre-defined current passing through a single working electrode (galvanostatic mode). The simplified circuit diagrams are illustrated in Figs. 3.6a and 3.6b.

The potentiostat is essentially a negative-feedback control circuit that maintains the potential of a working electrode at a pre-set level relative to a fixed potential reference electrode. It achieves this by passing an appropriate current between the working electrode and a third-electrode called the counter (or auxiliary) electrode. In addition to accomplishing accurate potential control, this circuit also provides for voltage outputs proportional to the current flowing through the working electrode with a current-to-voltage converter (current follower). In most operations, except the RRDE experimentation, only one working electrode was used. In those cases, the potential control signal was applied to Op. Amp (1), and the working electrode was maintained throughout at virtual ground with the current follower Op-Amp (2). The detailed operation of this and the four-electrode system has been described previously.²³⁰

(b) Summing-Inverting Amplifier (SIA) (Adder) (See Fig. 3.7). This device served to combine the inputs from the triangle-wave generator, voltage source, and oscillator for input into the potentiostat module.

(c) Voltage Inverter (See Fig. 3.8). The control voltage is applied via the potentiostat to the reference electrode, and the working electrode (WE) potential is held constant at virtual ground. Therefore, in order to read out the potential of the WE vs Reference, the potential control voltage must be inverted before supplying

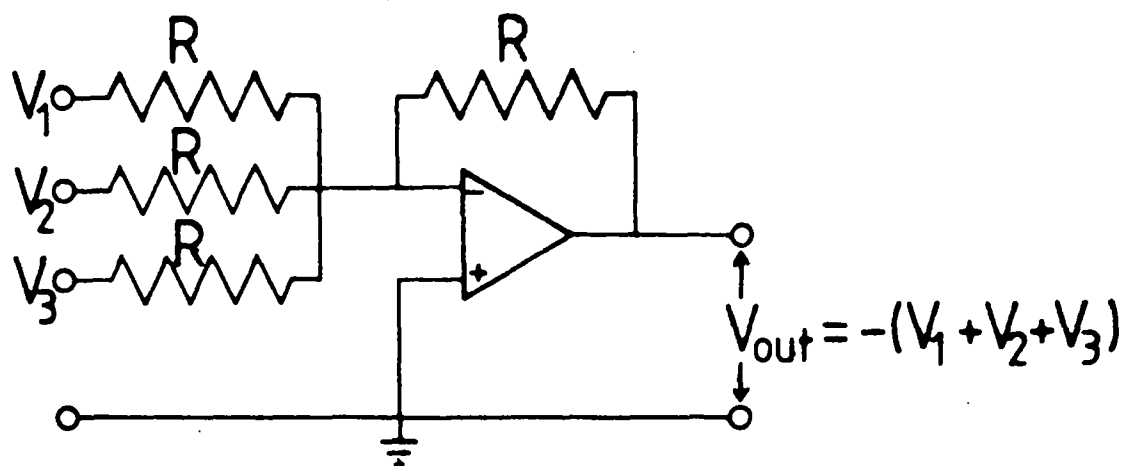


Fig.3.7
SUMMING
INVERTING
AMPLIFIER

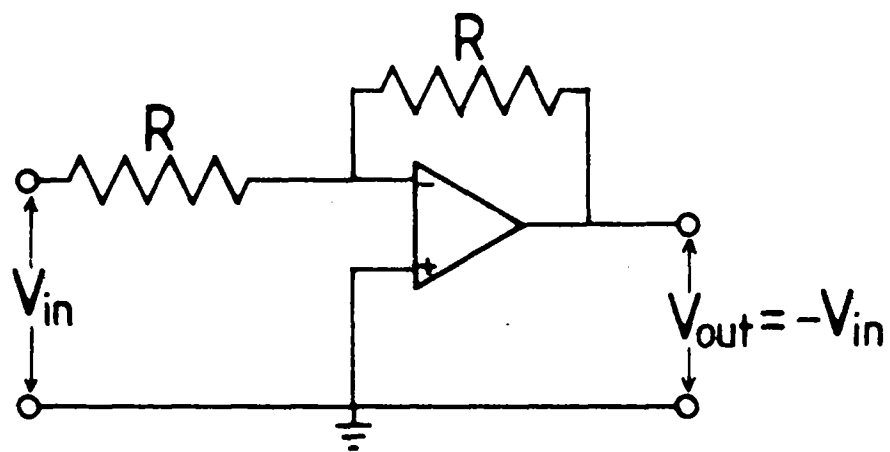


Fig.3.8
VOLTAGE
INVERTER

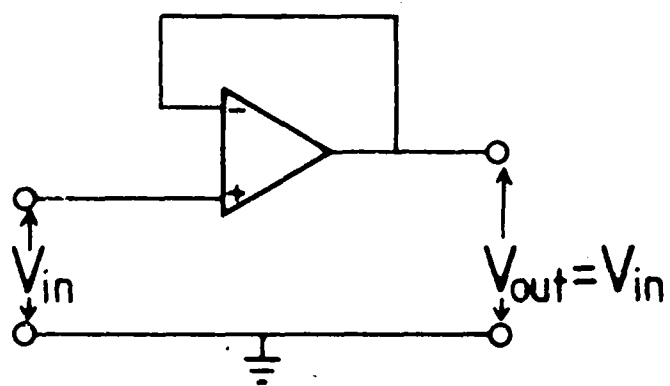


Fig.3.9
VOLTAGE
FOLLOWER

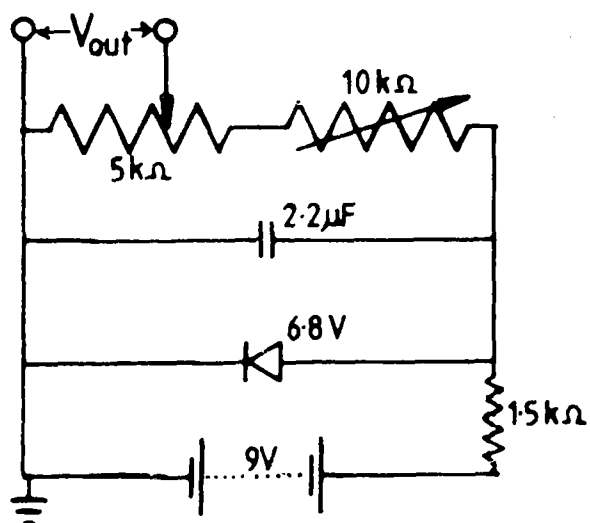


Fig.3.10
VOLTAGE
SOURCE

to the X axis of the XY recorder and Electrode Potential display D.V.M. The voltage-inverter module achieves this function simply; it also provides for a high input impedance and low output impedance such that there is negligible current draw from the voltage source or triangle-wave generator modules (see next section also).

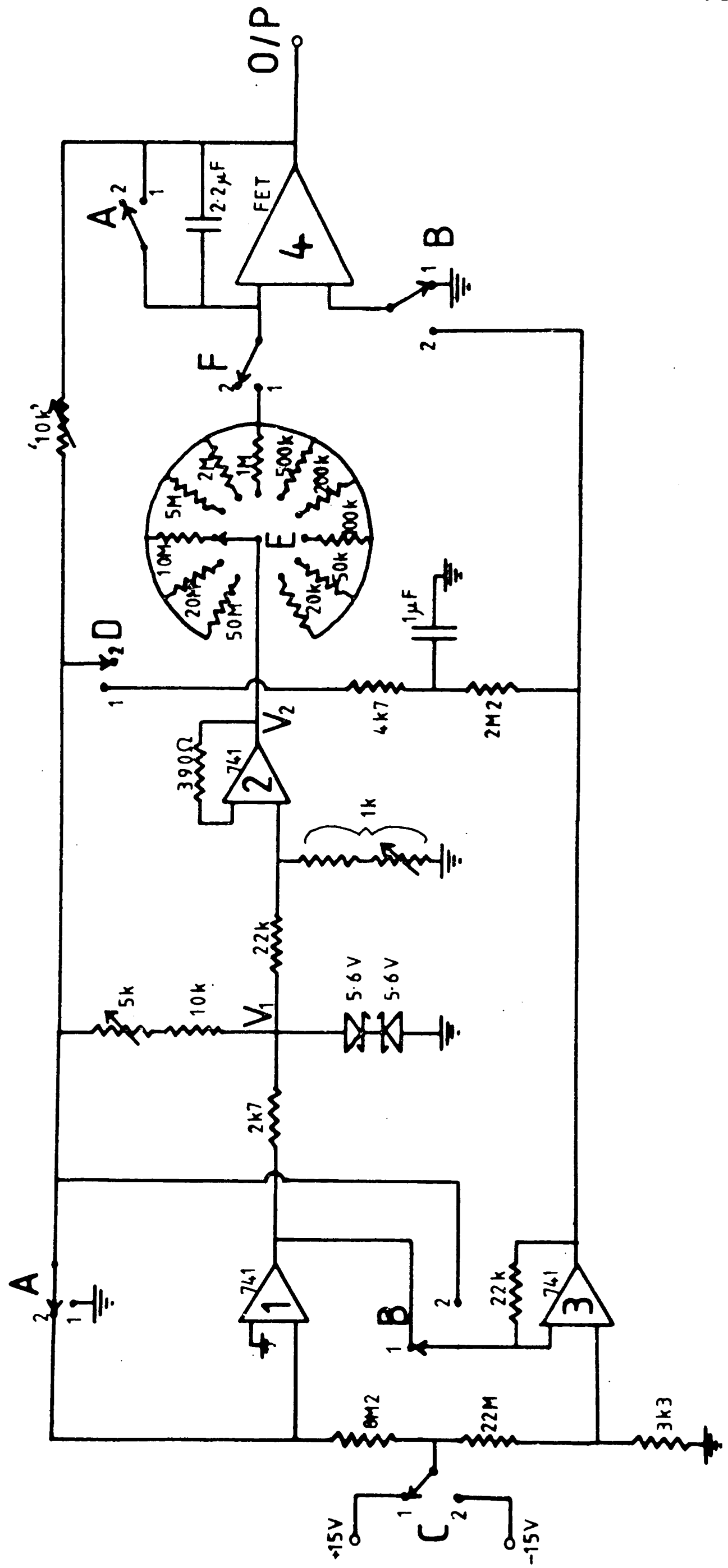
(d) Voltage Follower (See Fig. 3.9). Voltage followers were used in cases where the low input impedance of the display apparatus (X,Y recorder or D.V.M.'s) caused significant current drain on potentiostat or voltage source op-amps. They are used as impedance-matching units providing low output impedance whilst maintaining very high input impedance (up to $10^{11} \Omega$) to give low current drain on sensitive components.

(e) Voltage Sources (See Fig. 3.10). These battery-driven modules provided 'zero' ripple, constant voltage sources for potentiostat input voltage control, and a "backing-off" facility, when signals with high d.c. and low non-synchronous a.c. components were encountered.

(f) Triangle-Wave Generator (T.W.G.) (See Fig. 3.11). This device is built around the central active component of an integrating operational amplifier circuit. It provided the voltage ramp for linear sweep voltammetry and possessed additional facilities for variable limits, pausing, reversing, and cyclic operation. Its circuit is described in detail elsewhere.

(g) Function Generator. This signal generator provided the sinusoidal voltage input for the cell admittance analysis and a.c. cyclic voltammetry. The device used was a Wavetek function generator (Model 30). It provided high quality sinewave signals between 0.2Hz and 200,000 Hz, generating small output signal (0-10mV ms) for direct application to the S.I.A. and a larger, synchronous square or sinusoidal signal that could be used as the reference signal to the lock-in amplifier.

Fig. 3.11

TRIANGULAR WAVE GENERATOR

3:3:2 Display and Measuring Circuitry

(a) X.Y. recorder (Bryans 29000A4). This device served as the major, hard graphical record of the experimentation. The major use was for representing the direct outputs from cyclic voltammetry, photocurrent vs voltage and a.c. voltammetry.

(b) Oscilloscope (Gould OS250B). Throughout all experimentation, a close watch was kept on the quality of the input and output signals to and from the cell and potentiostat. In the preliminary stages of all novel experimentation, noise minimization was essential for producing accurate and reproducible results. Noise detection is simplest with the fast visual output of the oscilloscope. Output data signal-to-noise ratio was optimized with the assistance of this instrument according to standard literature procedures.

In experiments involving chopped illumination, the rapid photocurrent transients so produced could also be observed; these provided further qualitative evidence concerning electrode photoresponse.

(c) Chart (y,t) Recorder (Servoscribe 220). This device was used for the monitoring of cell current and voltage during long-term tests on the performance and stability of the photoelectrode under continuous illumination.

(d) Lock-In Amplifier (Brookdeal 9502 Dualphase or 9503 SC Single phase). Synchronous detection with this device was essential for photocurrent measurement involving chopped illumination and for the admittance analysis of cell current with sinewave-modulated electrode potential. In the former application, single-phase operation only was necessary to produce an output proportional to the in-phase photocurrent. However, for the latter, dual-phase operation facilitated the simultaneous monitoring of 0° in-phase and 90° out-of-phase admittance at various frequencies for the complete impedance analysis of the electrochemical cell.

(e) Digital Voltmeters (D.V.M's) (Fluke 8030A and Exel XL35). These modules facilitated accurate digital readout of electrode potential, cell currents, photocurrent, 0° and 90° admittance signals.

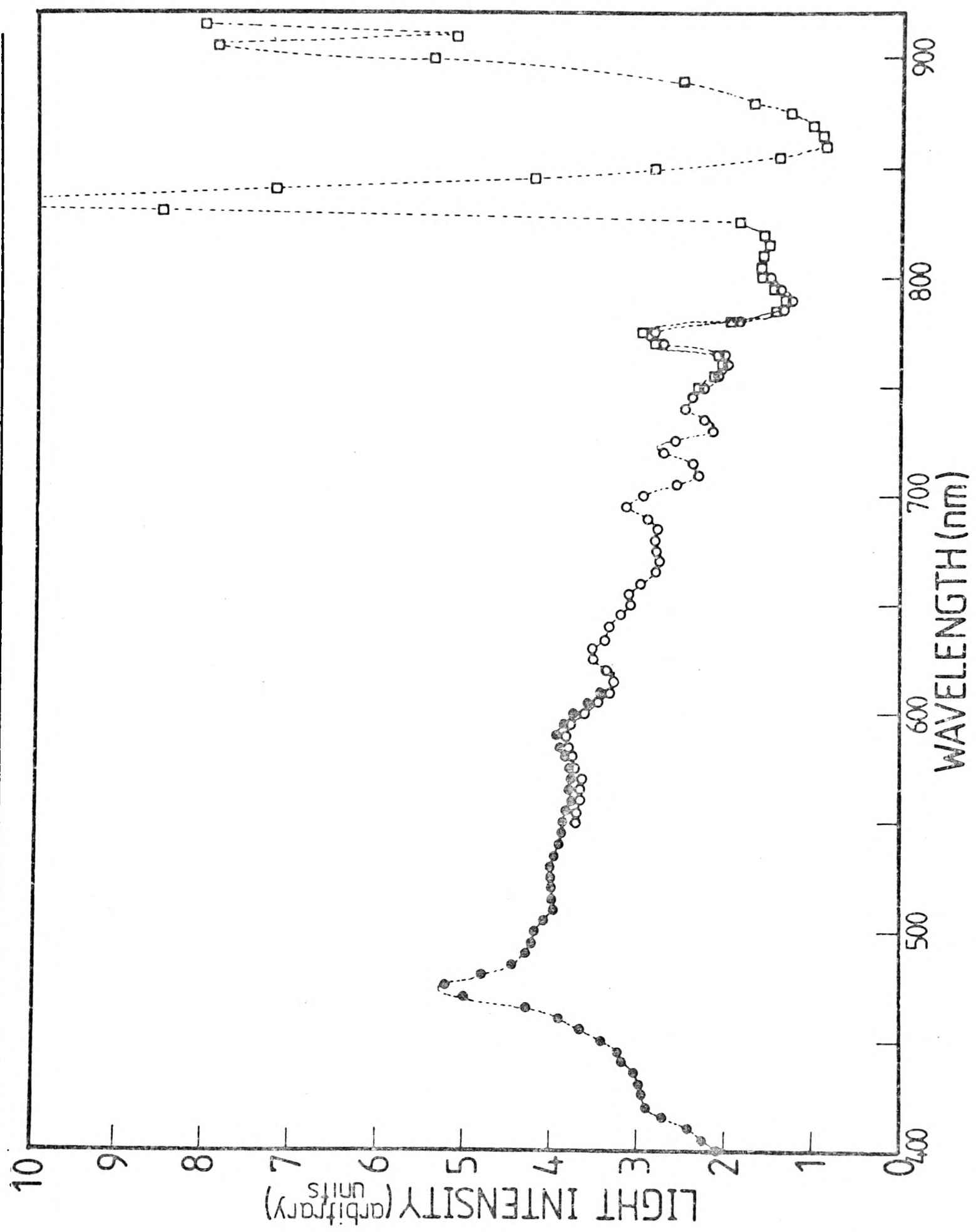
(f) Counter Timer (Racal 9905). This device could provide a continuous display of the frequency or period of oscillation when provided with a synchronous square-wave signal generated by the lock-in amplifier input stage. It was used for accurate measurement of the frequency of the sinewave modulation used for impedance analysis.

SECTION 3:4 THE OPTICAL SYSTEMS

Throughout this work, U-V and visible illuminations were provided by a 150W high-pressure Xenon lamp (Wotan XBO/1) and stabilized d.c. power supply (Oriel). The spectral envelope of the light resembles that spectrum of solar light incident on the outer edge of the Earth's atmosphere (defined as Air Mass Zero (AM0) sunlight)²²⁹. For precise solar-conversion efficiencies, measurement is normally referred to that light incident on the Earth's surface after the passage through one thickness of the Earth's atmosphere (so-called AM1 sunlight) which absorbs the major fraction of the light in the U-V region. Thus the Xenon spectrum is richer in U-V than true surface sunlight, but this was of advantage for the study of the large bandgap semiconductors ($E_g > 3.0\text{eV}$). To provide more representative terrestrial sunlight-conversion efficiencies, U-V cut-off filters were available (Ealing).

The output of the lamp was directed through a fused silica lens (f 1.5) with variable focussing facility on the lamp housing. A number of options were then available for spectral selections before the light reached the electrode. For most long-term stability tests, the full spectra output of the lamp was directed at the electrode. However, various cut-off, bandpass, and interference filters were used as indicated appropriately in the results sections. For finer tuning of illumination wavelength, a high-radiance (f 4.0) monochromator (Applied Photophysics) was used with variable input and output slitwidth and gratings blazed at 300nm and 500nm. Further focussing of the beam with a fused silica lens (f 4.0) was used in some instances for maximizing irradiation intensity at the electrode.

Fig.3.12 Typical spectral envelope from Xenon lamp/monochromator combination



The relative incident light intensity from the lamp as a function of wavelength was measured on every occasion that a semiconductor action spectrum was taken. In such a way, lamp output profile and chromatic aberration created by the lenses were taken into account in the production of an absolute efficiency profile. These relative light-intensity measurements were made with a photodiode having a documented photoresponse. An example of a typical spectral envelope for the lamp/monochromator combination is shown in Fig.3.12.

In certain cases (see Section 3:2:3) it was found useful to apply a square-wave, pulsed illumination to the electrode. This was achieved with the assistance of a programmable light Chopper (Rofin 7503) placed between the lamp and electrode. The device provided for frequency readout and a synchronous square-wave output signal necessary as the reference for the lock-in amplifier.

SECTION 3:5 MECHANICAL DESIGN

3:5:1 Cell design

Three electrochemical cell designs were used in this work: two for stationary electrodes, the other for use with the R.R.D.E. The designs are shown in Figs. 3.13, 3.14, and 3.15. In common with all accurate electrochemical work, the systems provided for precise temperature control ($25^{\circ}\text{C} \pm 0.2^{\circ}\text{C}$ throughout) and solution degassing (using high-purity Argon unless otherwise stated). However, as required for photoelectrochemical work, the cells also provided for rectilinear passage of the light from the optical source to the electrode surface. Much of the work was carried out in transparent electrolytes for which cells I and III were used as shown. However, when absorbing electrolytes were used, these cells could be fitted with an alternative window arrangement (Fig. 3.16) allowing the optical flat to be brought as close as 0.5mm from the electrode surface. (As can be seen, cell II provided for this capability as a standard).

FIG. 3.13
PHOTOELECTROCHEMICAL
CELL ASSEMBLY 1

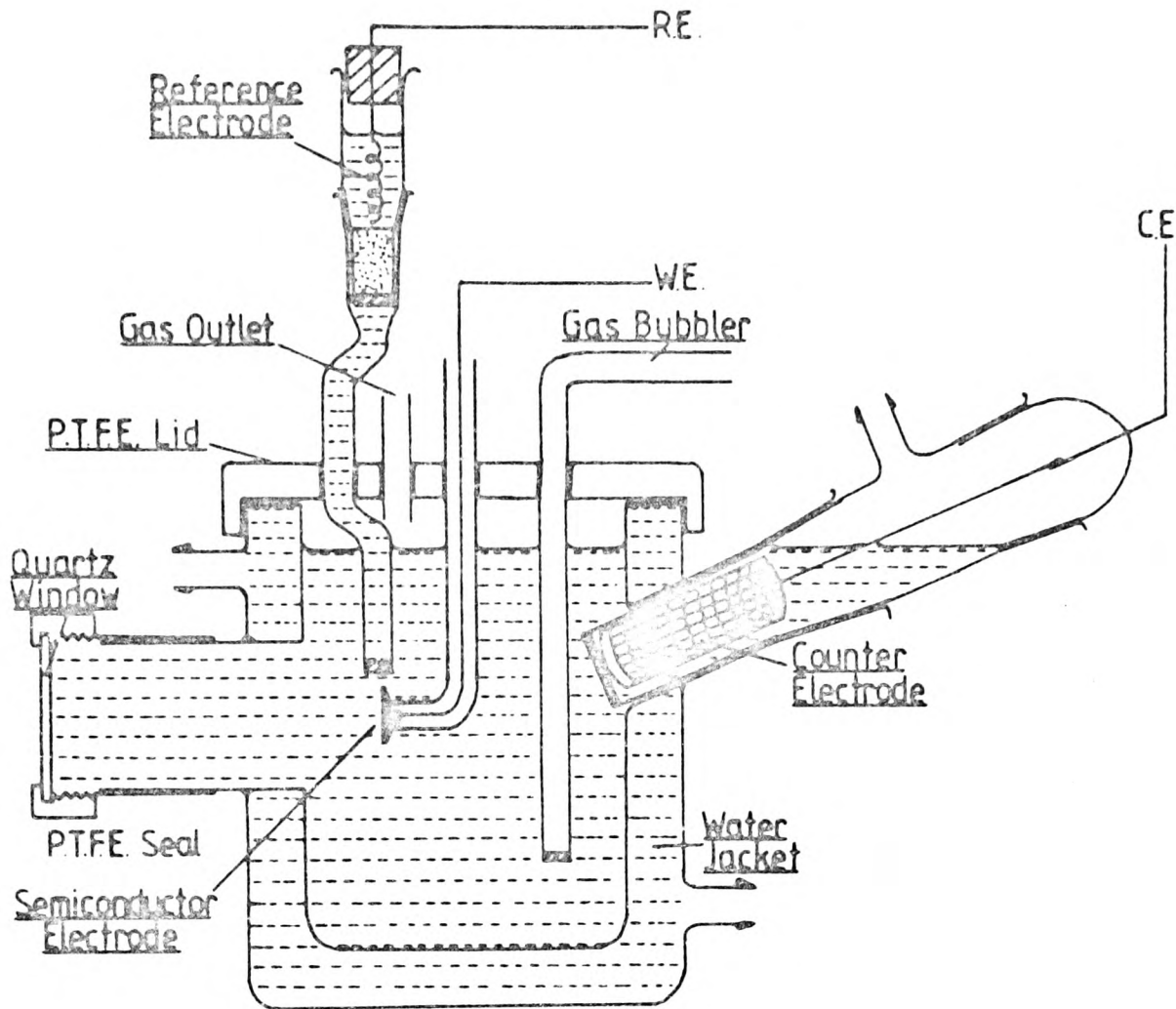


FIG 3.14
PHOTOELECTROCHEMICAL
CELL ASSEMBLY 2

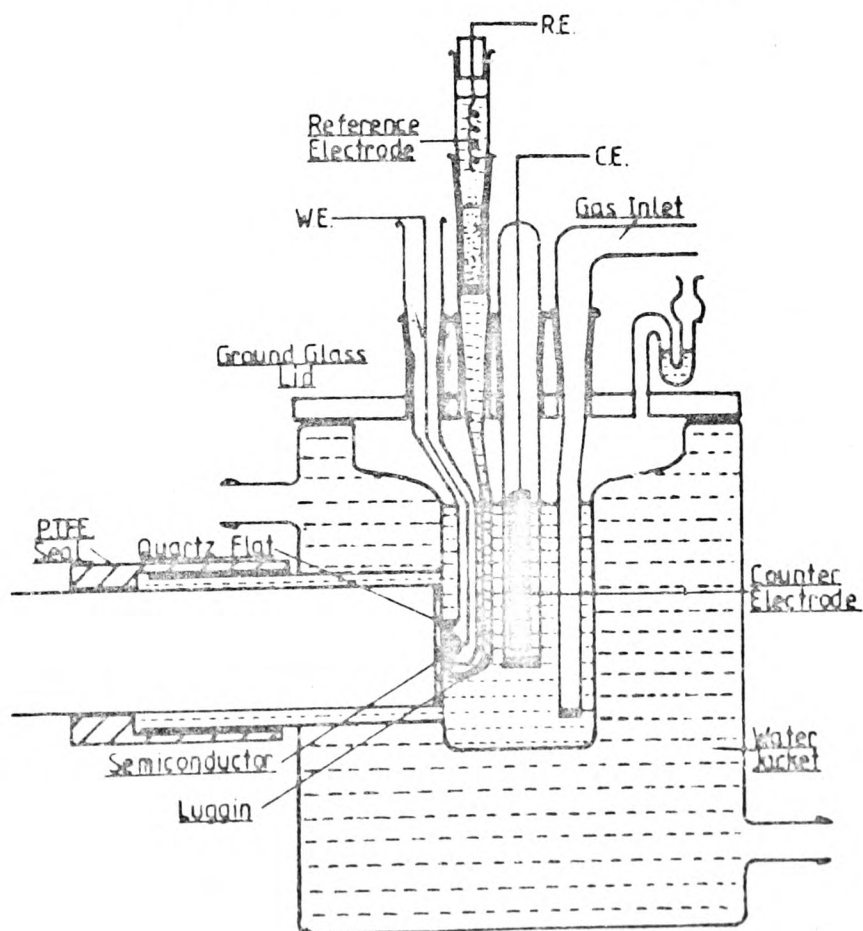
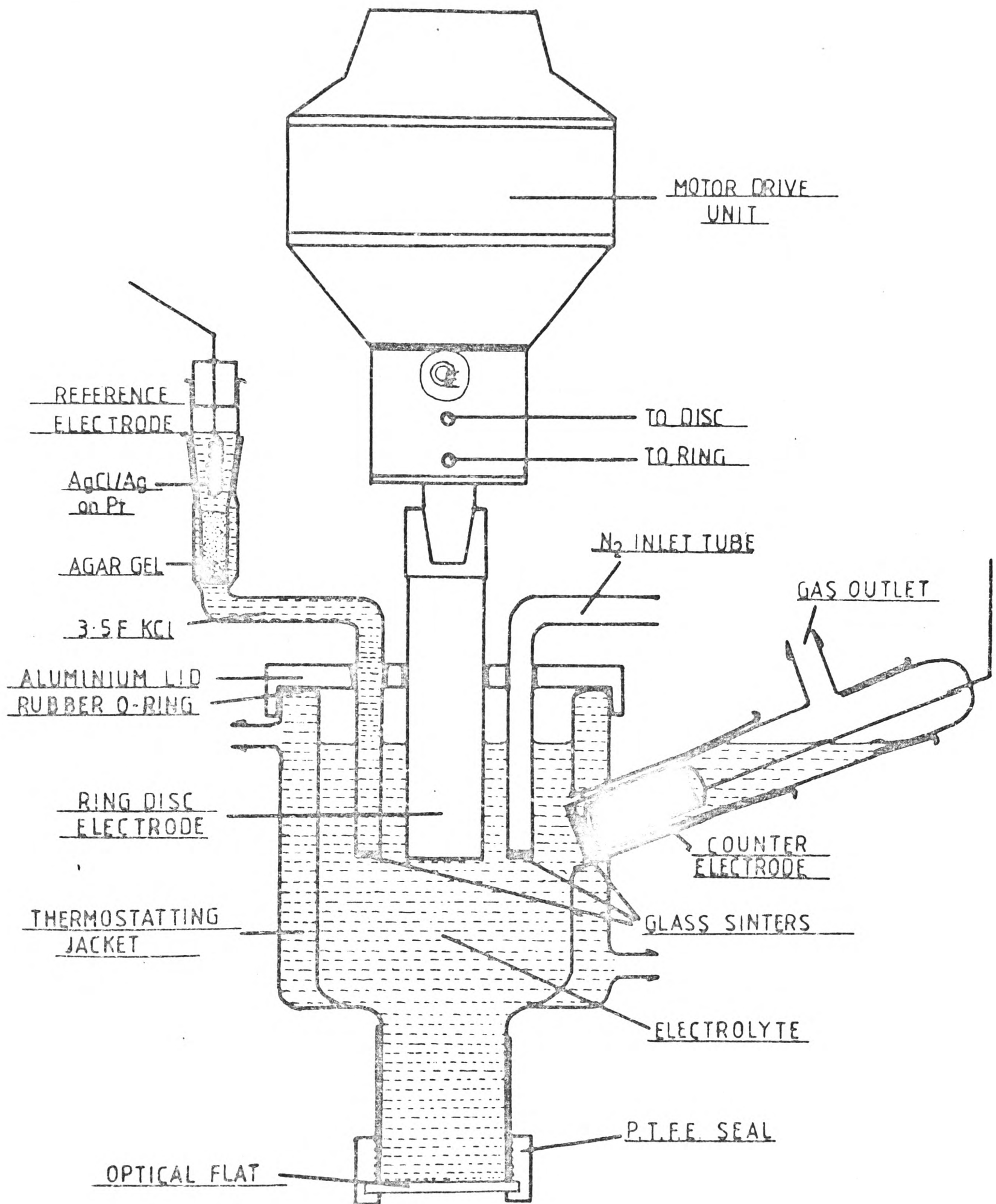


FIG 3.15

ROTATING RING-DISC ELECTRODE ASSEMBLY



Cell II was specifically designed for use in experiments where analysis of electrochemical products was required. It could also be used for electrochemical studies in non-aqueous solvents since it allowed for total isolation from the atmosphere. The other two designs only provided for partial sealing, but this was sufficient for solution purging providing a continuous overpressure was provided on the gas-inlet line.

3:5:2 Reference Electrode

In all experiments, the reference electrode used was a Pt|Ag|AgCl|3.5MKCl system (denoted S.S.E) prepared according to a literature procedure.²³⁰ Its potential was regularly checked against a Standard Calomel Electrode; when found to be outside the range $-0.040\text{V} \pm 5\text{mV}$ vs. S.C.E., it was discarded and replaced with a fresh electrode.

3:5:3 Counter Electrodes

For the majority of experimentation, the counter electrode was a platinum gauze fashioned into a cylinder and spotwelded to a length of platinum wire. Occasional cleaning was performed by electrolyzing as a cathode in concentrated HCl. In order to avoid reoxidation of any electrogenerated reduced carbon species in experiments on CO_2 reduction a graphite rod was used as counter electrode as suggested in a literature report.²³¹ To increase the mechanical strength of the rod, it was dipped in molten ceresin wax for 2-3 hours and then cooled.²³²

3:5:4 Working Electrodes - Stationary

The working electrode was in all cases a semiconducting material in the form of a single crystal chip or a polycrystalline sintered disc. Electrode fabrication required the discovery of a suitable ohmic-contact material (see Appendix 1). For the stationary electrodes, a copper wire was attached to the ohmic-contact material applied to the semiconductor sample (see Section 3:6) by use of a thermosetting silver preparation

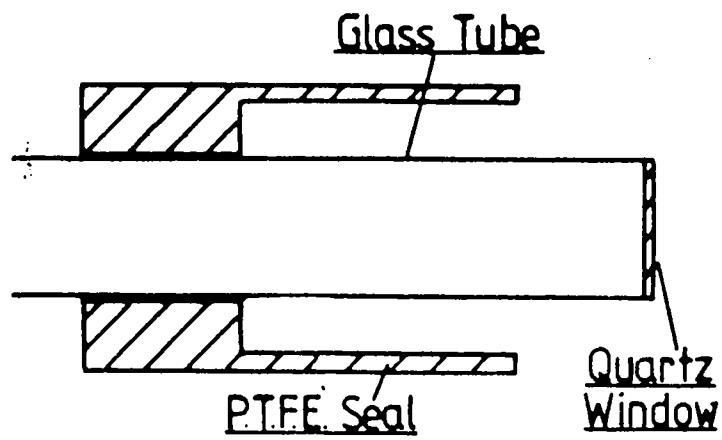


Fig.3.16
ALTERNATIVE
CELL WINDOW

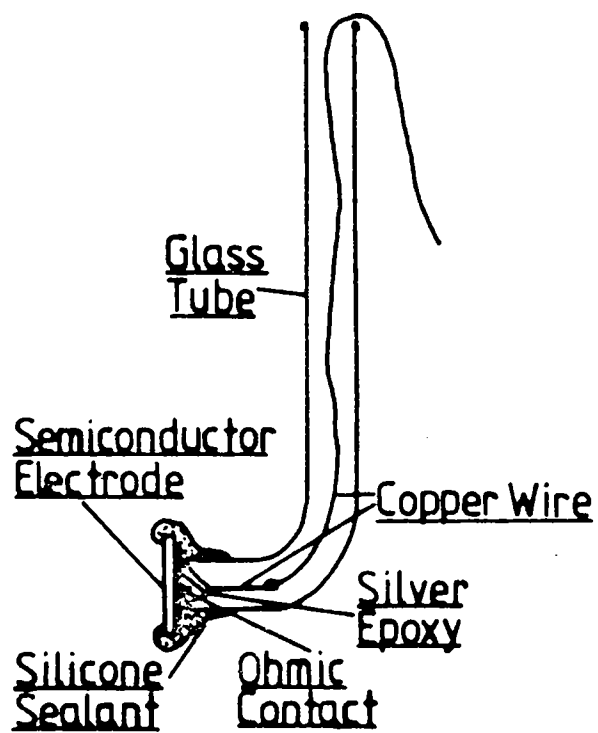


Fig. 3.17
STATIC
SEMICONDUCTOR
ELECTRODE
ASSEMBLY

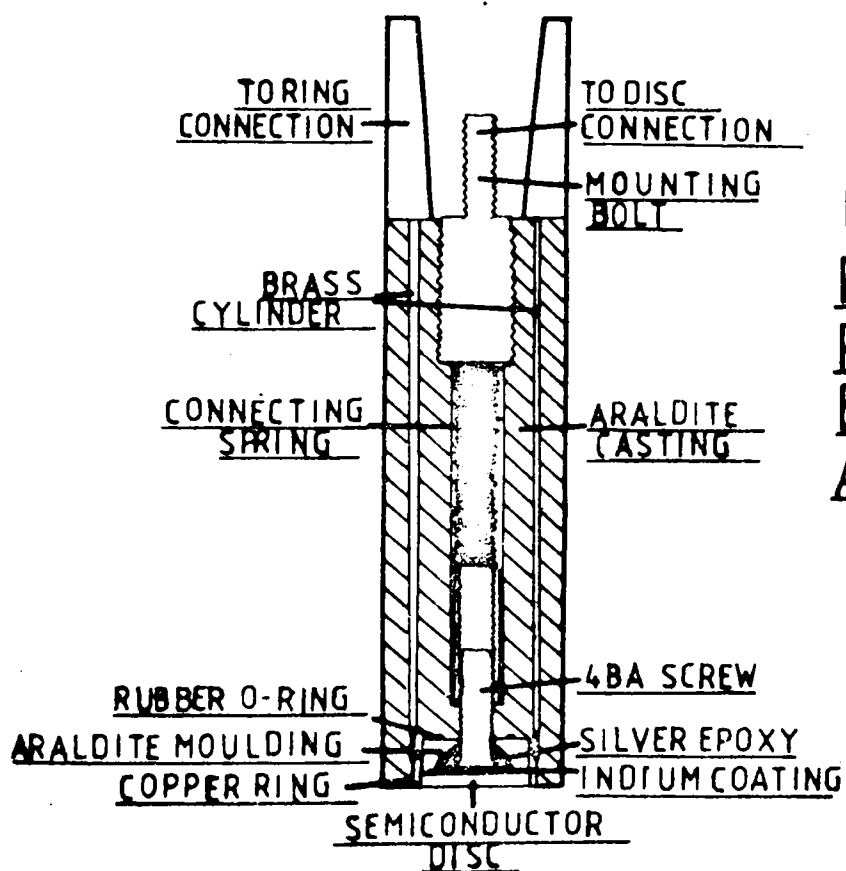


Fig. 3.18
ROTATING
RING-DISC
ELECTRODE
ASSEMBLY

(Johnson Matthey FSP49H and 49R). This preparation was cured at $\sim 100^{\circ}\text{C}$ for approximately one hour before a further flexible copper lead was soldered on. The electrode and lead were then mounted in a glass tube as illustrated in Fig. 3.17. The electrode was finally sealed into its mounting with a silicone-rubber adhesive (Dow Corning) to insulate the back and sides of the electrode from the solution. Earlier experimentation with a Pt electrode had ensured that the rubber glue contained no electroactive ingredients.

3:5:5 The Rotating Ring Disc Electrodes

The RRDE is illustrated in Fig. 3.18. In a similar manner to the stationary electrodes, a length of brass studding (4BA) was attached to the electrode via the ohmic contact with the silver epoxy. This combination was then set in an insulating and transparent epoxy compound (Ciba Geigy MY753 and HY951) in a disc-shaped P.T.F.E mould. After curing at room temperature for 24 hours, the disc was removed from the mould and located in the space provided at the centre of the RRDE. By means of the screw attachments and more silicone sealant, the disc could be rigidly held in position in the assembly. Prior to use, the whole of the base of the Rotating electrode was polished mirror flat ($\pm 1\mu\text{m}$) with disc and ring electrodes assumed to be coplanar as required for quantifiable hydrodynamics in solution.

The additional requirement for the RRDE experiment was the rotary motor and velocity-control box. These were provided ready built; they possessed capability for internal and external rotation-speed control between 0 and 50Hz. Continuous electrical contact to the rotating disc and ring was achieved through the use of liquid-mercury contacts.

It should be emphasized at this stage that considerable difficulty was found in the operation of the preparation procedure for single-crystal RRDE's. The major reason for this was the tendency for the transparent epoxy to contract on hardening, often causing sufficient strain on the single crystal chip to shatter or crack it. The design of the supposedly

replaceable disc RRDE was also not entirely satisfactory since alignment of disc and threaded bolt with the location in the RRDE was found to be extremely difficult. In the end, it proved simpler for a highly experienced technician to purpose-build a separate electrode for each single-crystal chip required than for me to attempt to redesign another replaceable disc RRDE.

SECTION 3:6 ELECTRODE MATERIALS, OHMIC CONTACTS, AND CHEMICALS

3:6:1 III-V Materials

The III-V electrodes used throughout this work were single-crystal wafers 0.5mm thick with the crystal axes oriented such that the (100) or (111) faces were exposed. The details of the crystals used are shown in Table 3.I.

Table 3.I

<u>Material/Orientation</u>	<u>Dopant and Concentration</u>	<u>Resistivity</u>
GaP(100)	Zn:2.1- 9.3x10 ¹⁷ cm ⁻³	0.315 - 0.091Ωcm
GaP(111)	Zn:6.3- 7.1x10 ¹⁷ cm ⁻³	0.111 - 0.102Ωcm
GaAs(100)	Zn : 1.0x10 ¹⁷ cm ⁻³	0.27Ωcm
InP(111)	Cd : 7.4x10 ¹⁷ cm ⁻³	0.103Ωcm
GaSb(100)	Undoped, Carrier Conc. 1.4-1.6x10 ¹⁷ cm ⁻³	0.0687 - 0.0617Ωcm

3:6:2 Oxide Semiconductors

(a) TiO₂. The materials used was cut from a single-crystal boule of TiO₂ (supplied by Dr. Scheele of Zurich.) with a diamond saw; it was oriented so as to leave the front face of the electrode perpendicular to the c axis. To ensure good n-type conductivity and optimum photoresponse, the electrode was reduced in H₂ at 630°C for 3 hours.²³³

(b) SrTiO₃. This material was cut from a single-crystal boule of SrTiO₃ with a diamond saw; it was oriented so as to leave the front face of the electrode perpendicular to the (010) axis. To achieve n-type conductivity, the crystal wafers were reduced in H₂ at 900°C for 3 hours.

(c) p-NiO. The detailed preparation of this electrode material has been discussed at length elsewhere.⁸³ For most reproducible results, single-crystal slices were used (supplied by B.M. Wanklyn of Oxford)²³⁴ and doped with lithium by heating to 1450°C with lithiated Nickel Oxide powder in a Platinum foil.

(d) Other Titanates and doped SrTiO₃. These sintered-pellet electrodes were prepared by G. Campet²³⁵ and G.S. Bin-Daar²³⁶ as described in recent articles.

3:6:3 Surface Preparation

All electrodes were polished to a mirror finish with 6µm and 1µm diamond paste followed by etching according to the procedures outlined in Table 3.II.

SECTION 3:6:4 OHMIC CONTACTS

(a) III-V materials - p-type

Ohmic contacts were made to GaP, GaAs, InP and GaSb electrodes with 5% Zn-doped Indium annealed into the crystal in a Hydrogen atmosphere at 550°C, 350°C, 450°C and 400°C respectively.²³⁷ The apparatus used (Fig. 3.19) provided for continuous flow through Hydrogen gas and very rapid heating and cooling cycles (25-500°C in 2 minutes, 500-80°C in 10 minutes). The procedure adopted was to place a minimum of six small pieces of the In/Zn alloy (≈0.1mm³) onto the surface of each single-crystal chip (20-25mm²). After placing on a quartz microfurnace plate, the system was flushed with H₂ for 5 minutes. The first stage of heating was up to 200°C; at this temperature the bypass system (see Diagram) was used for passage of gaseous HCl flux over the sample to clean the oxide layers in the metal and semiconductor (15 secs). Rapid heating to the required temperature followed

Table 3.II

<u>Material</u>	<u>Etch</u>	<u>Conditions & Duration</u>	<u>Results & Comments</u>
GaP	$\text{HNO}_3\text{:HCl}$, 3:1 ²³⁸	25°C, 15s	Smooth shiny surface
GaP	$\text{K}_3\text{Fe(CN)}_6$ (1.0M) / KOH 0.5M ²³⁹	95°C, 3 min	Differentiates ($\bar{1}\bar{1}\bar{1}$) and (111)Ga surfaces ($\bar{1}\bar{1}\bar{1}$)Smooth P surface (111) 'Orange Peel' mottled Ga surface
GaAs	5% Br ₂ in methanol ^{238,240}	25°C, 60s	Smooth shiny surface
GaAs	$\text{H}_2\text{O}_2\text{:H}_2\text{SO}_4\text{:H}_2\text{O}$ 3:1:1 ²⁴¹	25°C, 15s	Grayish smooth surface (not used generally)
InP	$\text{HCl:HNO}_3\text{:HClO}_4\text{:CH}_3\text{COOH}$ ²⁴² 1 : 6 : 1 : 1	25°C 30s	Differentiates ($\bar{1}\bar{1}\bar{1}$) and (111)In surface ($\bar{1}\bar{1}\bar{1}$) Smooth P surface (111)Triangular Etch Pits in In surface
GaSb	5% Br ₂ in CH ₃ OH ²³⁸	25°C, 15s	Smooth shiny surface
TiO ₂	H_2SO_4 ²³³	265°C, 3 hours	Smooth matt surface
SrTiO ₃	H_2SO_4 ²³⁵	130°C, 1 hour	Smooth surface
NiO	HCl ⁸³	25°C, 15 min	Smooth surface
Other titanates	H_2SO_4 ⁶⁰	25°C, 5 min	-
	HNO_3 ⁶⁰	25°C, 5 min	-

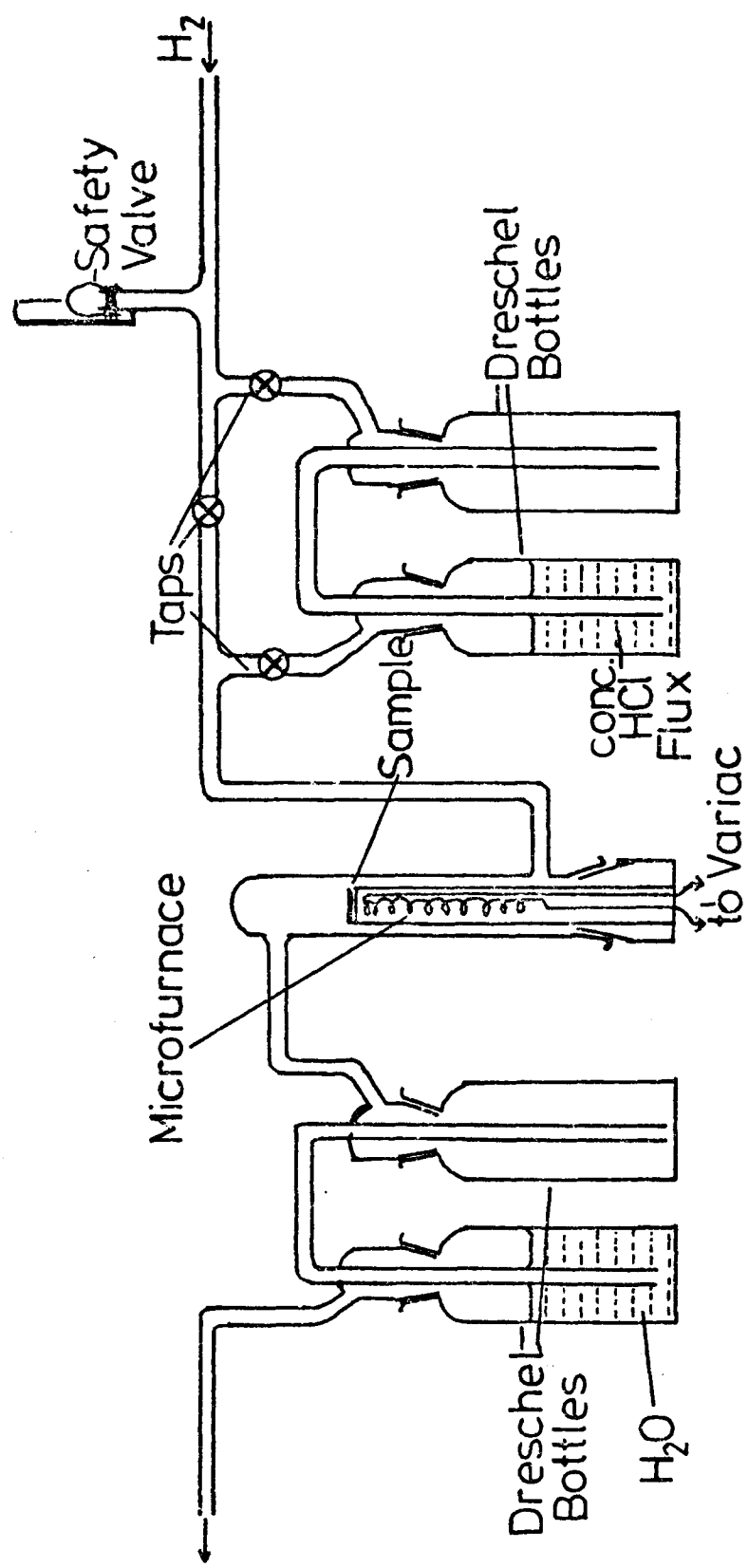


Fig.3.19 Apparatus used for the annealing of ohmic contacts into p-type III/V semiconductors

after return to the pure H_2 flow, and a five minute annealing period was allowed before cooling to $80^\circ C$, at which temperature the crystals could be removed.

This technique provided for ideal ohmic contacts tested up to $\pm 2V$ across the samples. Lower temperatures and use of pure Indium both failed to produce such ideal contacts. Instead, classical Schottky barrier diode response was obtained. The theory behind this technique of alloy regrowth and other general principles for producing ohmic contacts to semiconductors are discussed in Appendix 1.

(b) All n-type oxide materials

The Ohmic-contact material used universally for these materials was a Ga/In eutectic, applied mechanically to the back surface of the electrodes. The 'semiliquid' eutectic wetted the surface of these oxide materials, so no further annealing treatment was necessary.

(c) p-NiO

For this material, either In/Zn alloy applied at $\sim 200^\circ C$ in air or graphitic carbon applied at room temperature produced satisfactory ohmic contacts.

SECTION 3:6:5 SOLUTIONS AND DEOXYGENATION

The solutions for all the electrochemical work were prepared from ANALAR grade or better materials made up in deionized, double distilled water. Pre-electrolysis of solutions prior to use with the semiconductor electrodes was not found necessary since no significant changes in results were noted when this procedure was applied.

The gas purge used for deoxygenation of the solution was always high-purity argon deoxygenated using a Zinc/anthraquinone oxygen absorber as described previously. For the CO_2 reduction experiments, the CO_2 purge was supplied by a cylinder of high-purity CO_2 not further purified in any way.

CHAPTER FOUR

THE PHOTOELECTROCHEMISTRY OF

p-TYPE GALLIUM PHOSPHIDE

A. RESULTS

SECTION 4:1 CYCLIC VOLTAMMAGRAMS (C.V.'s) IN VARIOUS MEDIA.

4:1:1 0.5M H₂SO₄

Figs. 4.1-4.3 depict typical cyclic voltammograms taken under dark and illuminated conditions (henceforth referred to as dark and illuminated C.V.'s) for p-type GaP electrodes with the (100), ($\bar{1}\bar{1}\bar{1}$) and (111) faces exposed respectively (see Section 4:7:3 for explanation of differences). The plots taken in darkened conditions (henceforth referred to as dark C.V's) are characterized by very low cathodic currents ($< 1\mu\text{A cm}^{-2}$) for a considerable voltage range (-1.4 to 0.4V). At higher cathodic potentials, the cathodic current does increase, but its magnitude appears to be sensitive to the purity of the electrode surface. An electrode used directly after etching and washing reveals more cathodic dark current than an electrode washed in a dilute acid (e.g. HCl) for five minutes prior to use. Further reduction in dark current is obtained on repeated cycling of the electrode within the potential ranges shown in the plots 4.1 to 4.3.

Although there appears to be no correlation of the magnitude of the cathodic dark current with electrode orientation, there is some variation of anodic dark current, for potentials $> +0.4\text{V}$, between the three surfaces investigated. In general, at any given voltage $> +0.4\text{V}$, the anodic current appears to increase in the order (111) $<$ (100) $<$ ($\bar{1}\bar{1}\bar{1}$). At higher anodic potentials ($> +1.0\text{V}$, not shown in Figs. 4.1-4.3) passivation behaviour is observed, but no detailed investigations were undertaken of these phenomena.

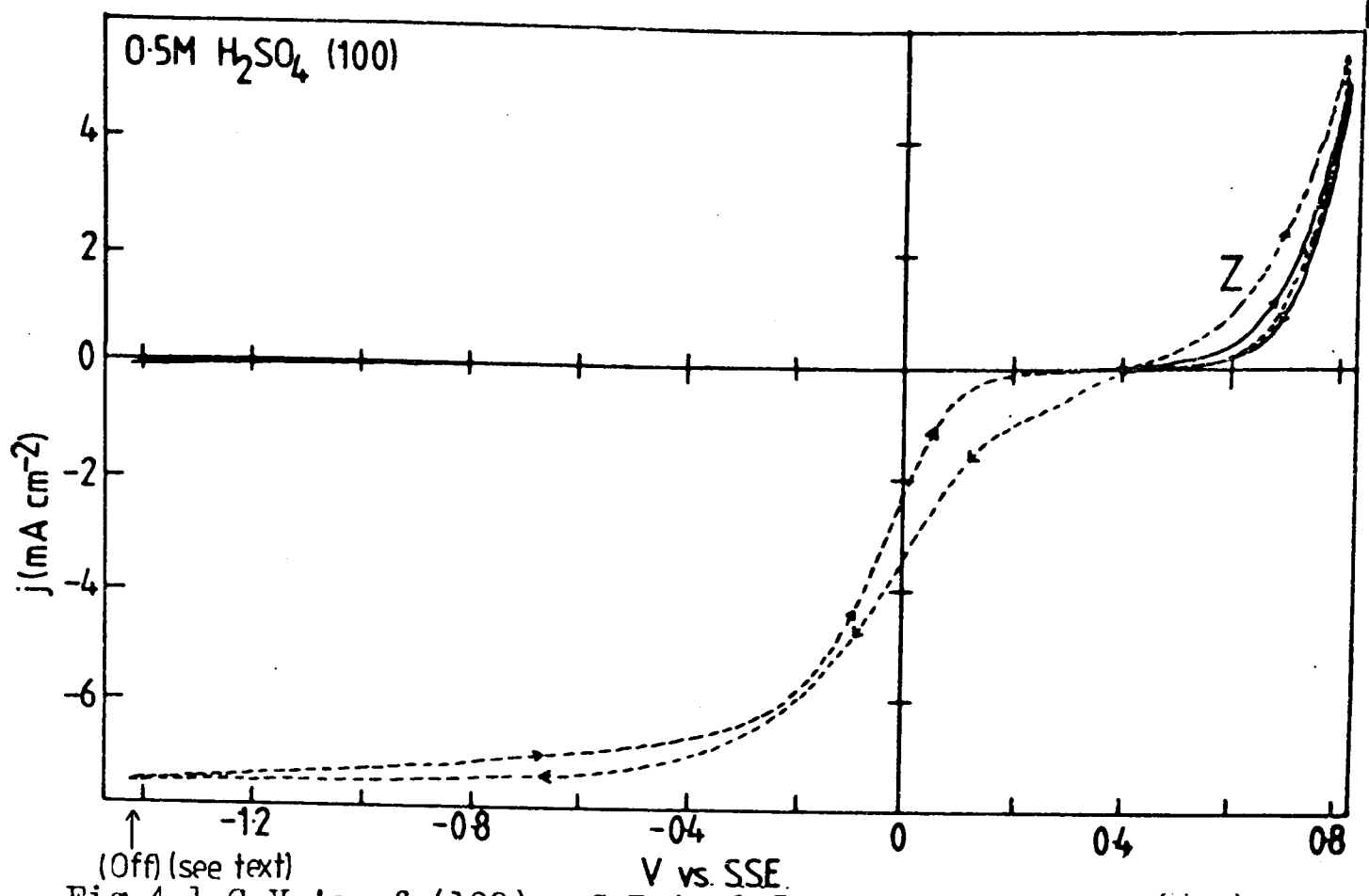


Fig.4.1 C.V.'s of (100) p-GaP in 0.5M H_2SO_4 under dark(—) and illuminated(---)(white light) conditions. Sweep rate = 250mV s^{-1} .

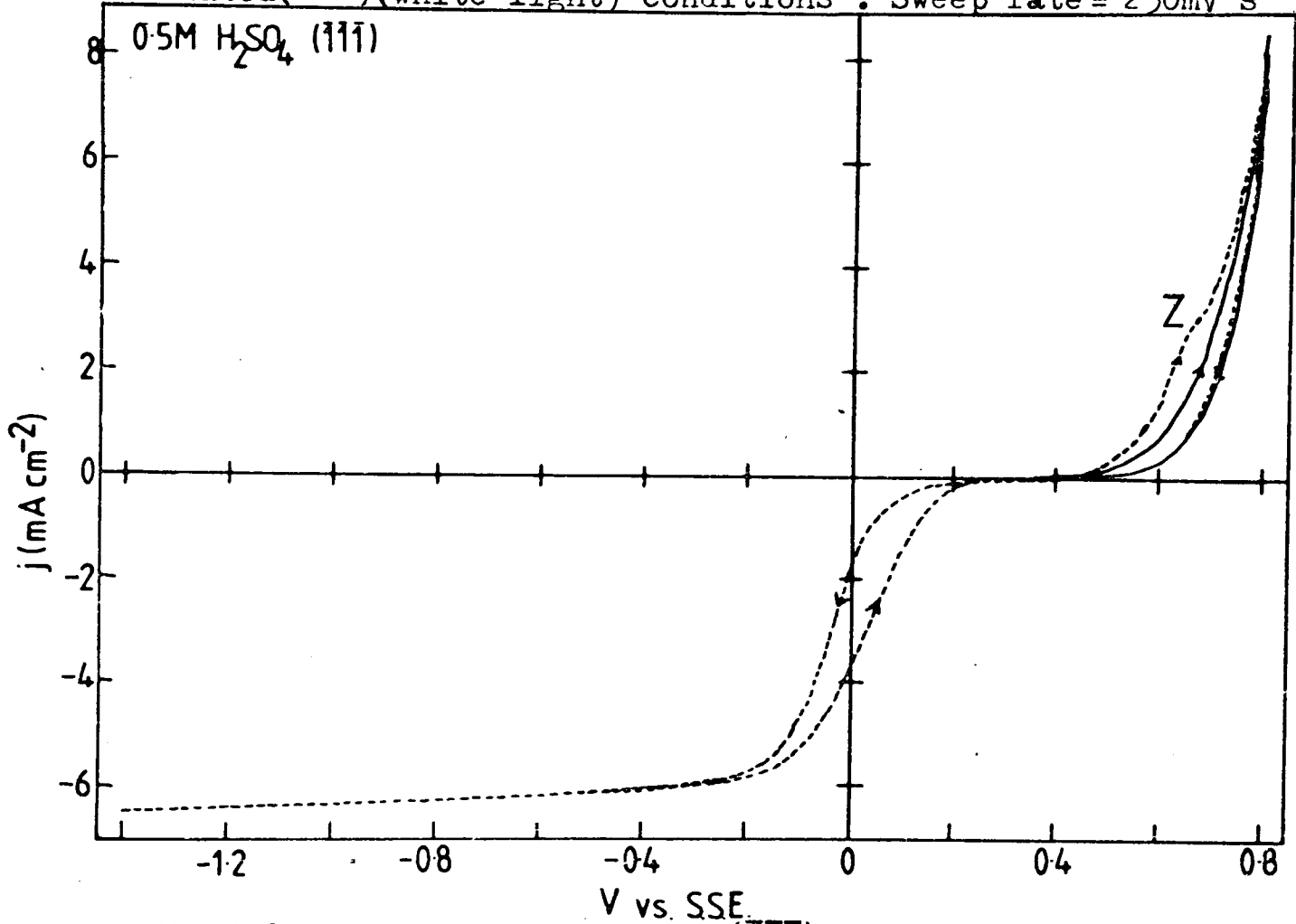


Fig.4.2 As in Fig.4.1 but for (111) p-GaP

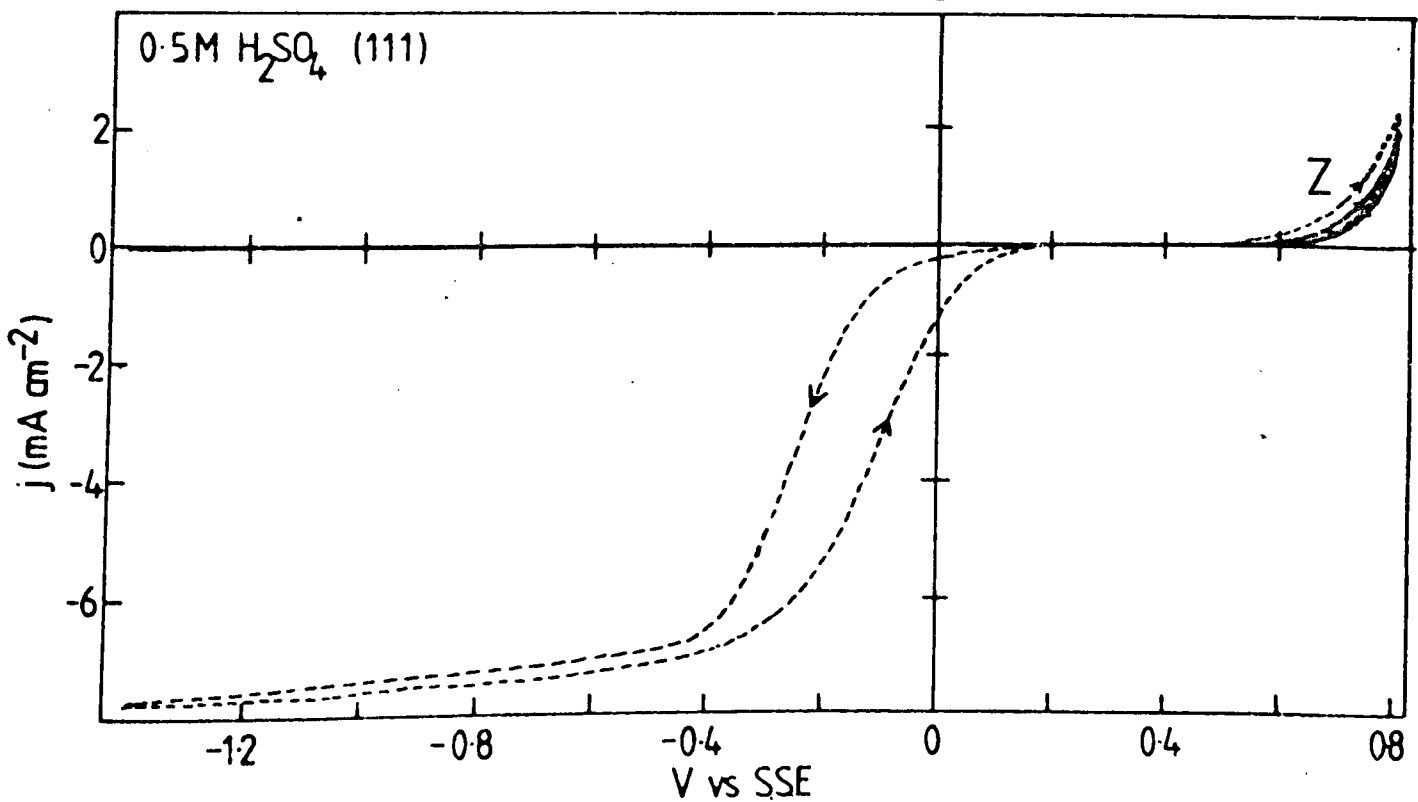


Fig.4.3 As in Fig.4.1 but for (111) p-GaP

On illumination with radiation of energy greater than the bandgap of GaP, the C.V.'s of all surfaces revealed cathodic photocurrents that, for well etched electrodes, revealed saturation behaviour for potentials negative of -0.4V . Poorly etched electrodes did not reveal this current saturation, but only a slow rise in photocurrent proceeding in a cathodic direction from $+0.2\text{V}$. The maximum quantum efficiency was found to be approximately 30%, virtually independent of crystal orientation. However, the photocurrent onset potential (p.o.p.) and hysteresis behaviour do show some reproducible variation with electrode surface. There is only a small difference between the behaviour of the (100) and $(\bar{1}\bar{1}\bar{1})$ surfaces, but the p.o.p. for the (111) surface is significantly more cathodic than that of the other two. This is found to be unrelated to the smaller magnitude of anodic current flowing at the anodic limit of the sweep. Indeed, no difference is seen in the p.o.p. if the anodic sweep limits are allowed to become more positive with consequent large anodic current flow.

For all surfaces, illuminating the electrodes appears to enhance the anodic current ahead of the main irreversible wave (labelled Z). This enhancement is not a directly induced anodic photocurrent since it is still present for the first anodic sweep even if the light is switched off at the beginning of the anodic run (at the point labelled 'Off'). Its size is found to be related to the total magnitude of the cathodic charge passed by the electrode since last entering the region of the irreversible anodic wave (positive of $+0.3\text{V}$). Faster sweep rates also tend to reveal greater enhancements, and there is a decay in magnitude if an increasing time interval is allowed between extinguishing the illumination and starting the anodic potential sweep through this region. Moreover for similar sweep rates and photocurrent densities, there is a considerable diversity in the magnitude of the anodic enhancement, being in the order (111) < (100) < $(\bar{1}\bar{1}\bar{1})$.

4:1:2 1.0M NaOH

Figs. 4.4-4.6 show dark and illuminated C.V.'s for the (100), ($\bar{1}\bar{1}\bar{1}$) and (111) surfaces in 1.0M NaOH. The general shapes of the waves are very similar to those in 0.5M H_2SO_4 although shifted by approx. 0.6-0.7V in the cathodic direction. Saturation photocurrent efficiencies are insignificantly different from those obtained in 0.5M H_2SO_4 . The only noticeable difference is that the anodic enhancements produced following illumination can become sufficiently clear to appear as a separate peak, being particularly clear for the ($\bar{1}\bar{1}\bar{1}$) surface. Again, passivation phenomena were observed at higher anodic potentials.

One additional feature observed in 1M NaOH is that C.V.'s noticeably deteriorate with time. This occurs for both the (100) and ($\bar{1}\bar{1}\bar{1}$) surfaces; degradation of the (111) surface is much slower. After many hours of potential cycling, the cathodic dark current begins to increase and anodic passivation appears to set in at much less positive potentials (see Fig. 4.7). It seems as if an insoluble, poorly conducting layer is formed on the surface, and this hypothesis is supported by an increase in interfacial capacitance observable in separate a.c. experiments and also by virtue of the considerable hysteresis of this plot. Concurrent with this dark current behaviour, the photocurrent efficiency also falls quite dramatically. Optical microscopic studies of the electrode revealed no major surface degradation.

4:1:3 Other Blank Solutions

For solutions with $\text{pH} < 4$, behaviour was very similar to that found in 0.5M H_2SO_4 . However, C.V.'s in solutions of $\text{pH} 4-10$ all demonstrated passivation behaviour at more anodic potentials (see Discussion Section). In addition, photocurrent efficiencies were markedly reduced, and in some cases no approach to photocurrent saturation was observed even at cathodic potentials in excess of -2.0V vs. S.S.E. Some results for acetate, phosphate, triethanolamine and borate buffers (for composition see

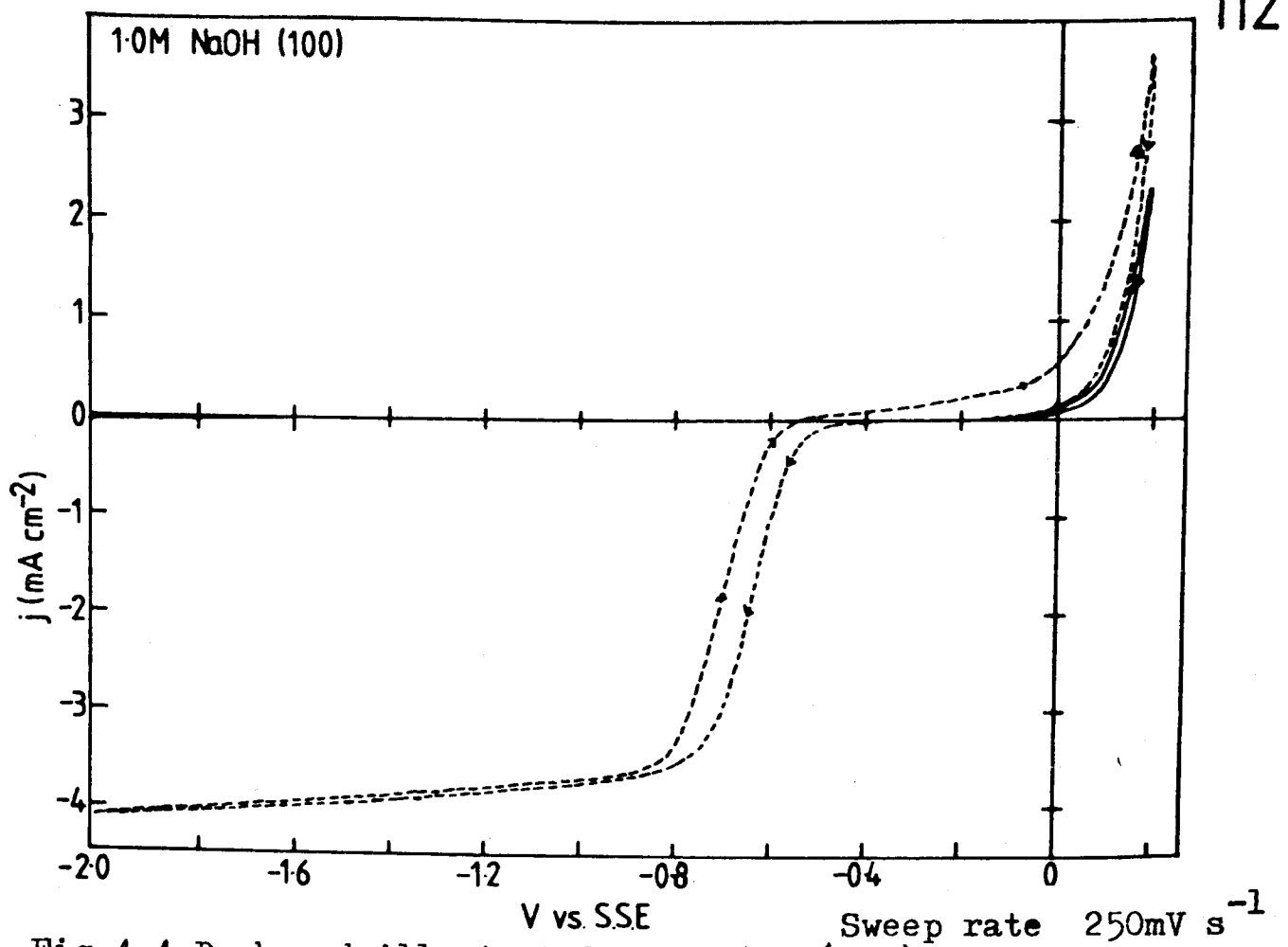


Fig.4.4 Dark and illuminated C.V.'s of (100) p-GaP in 1.0M NaOH

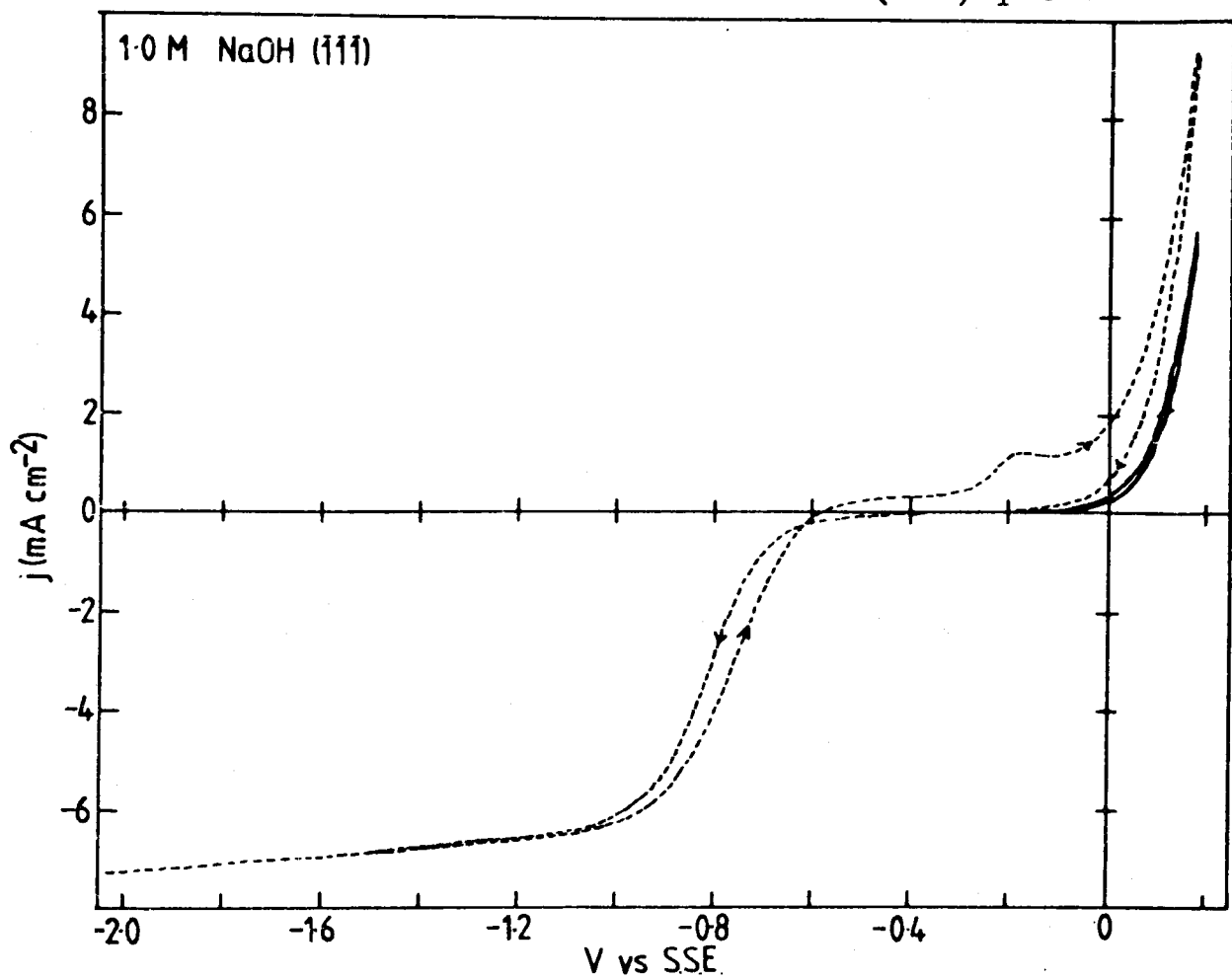


Fig.4.5 As in Fig.4.4 but for (111) p-GaP

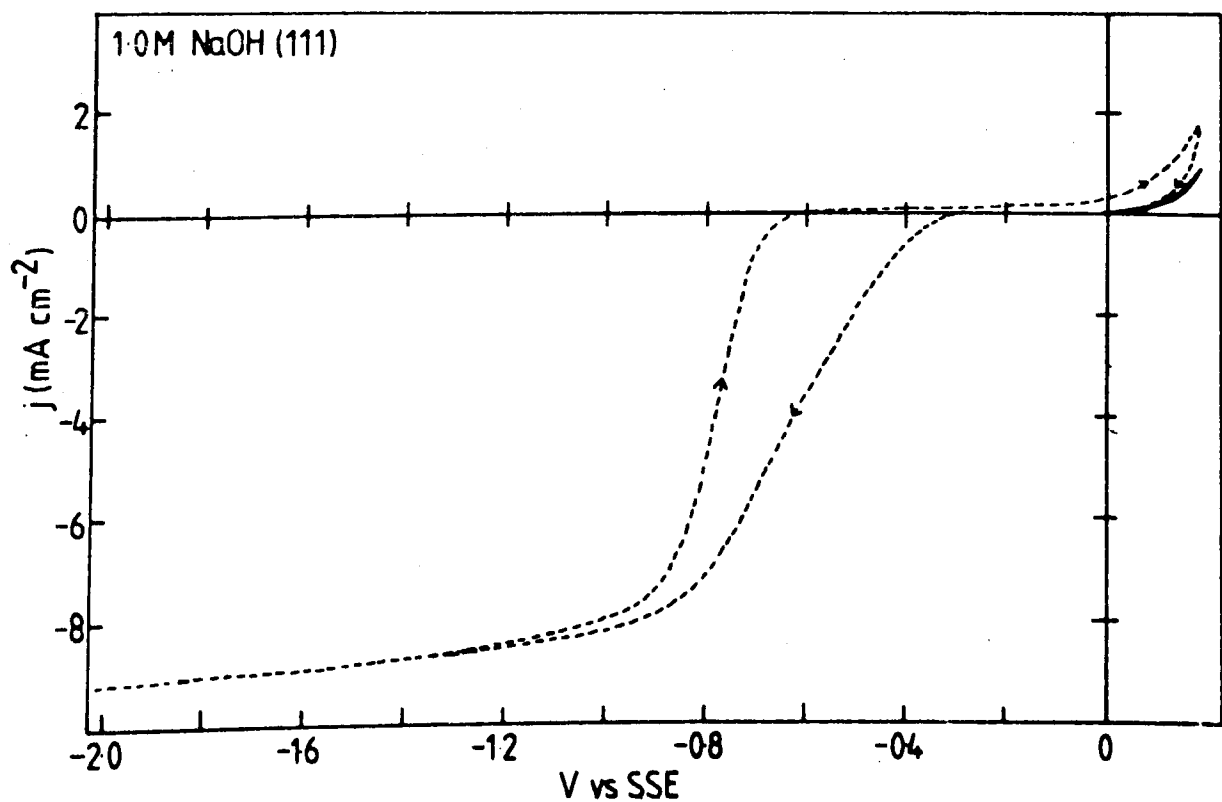


Fig.4.6 As in Fig.4.4 but for (111) p-GaP

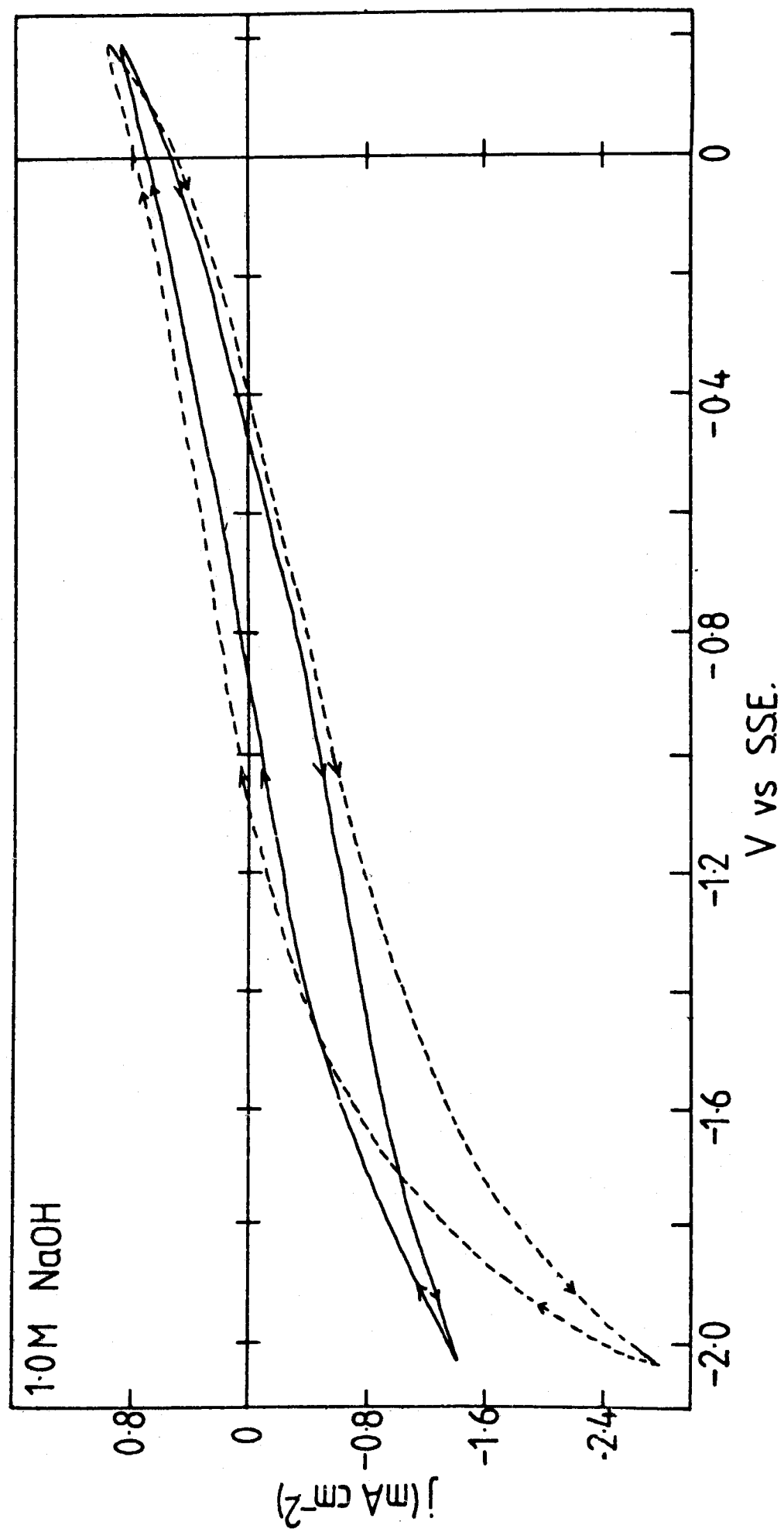


Fig.4.7 C.V.'s of p-GaP (100) under dark(—) and illuminated (---) conditions after 4 hours of potential cycling over the range as shown.

Figure 4.27 Section 4:2) are presented in Figs. 4.8-4.11. Little reproducible variation in behaviour was found for different crystal orientations since a major factor governing the response was the time spent by the electrode in solution and the magnitude of anodic charge passed.

SECTION 4:2 PHOTOCURRENT-VOLTAGE PLOTS (P.C.V.'s)

4:2:1 0.5M H₂SO₄

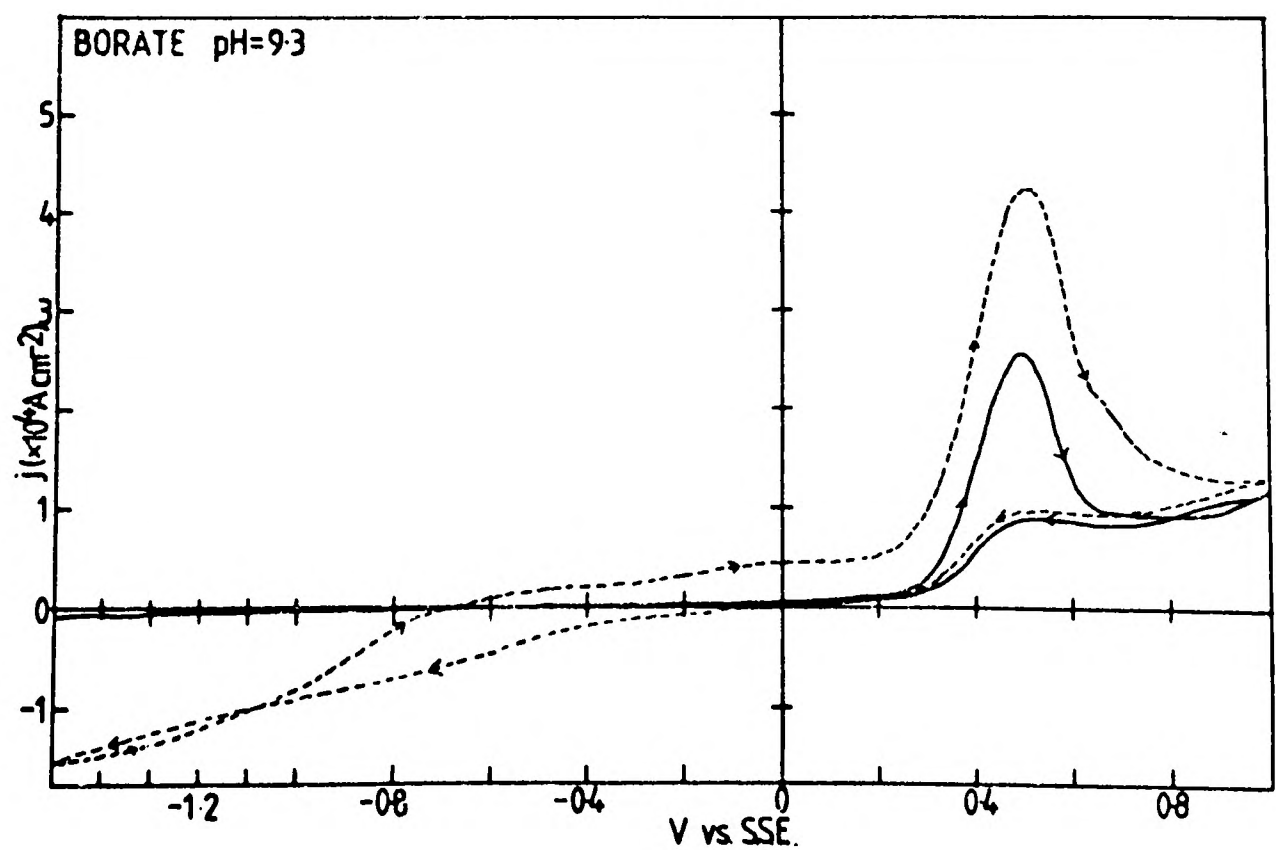
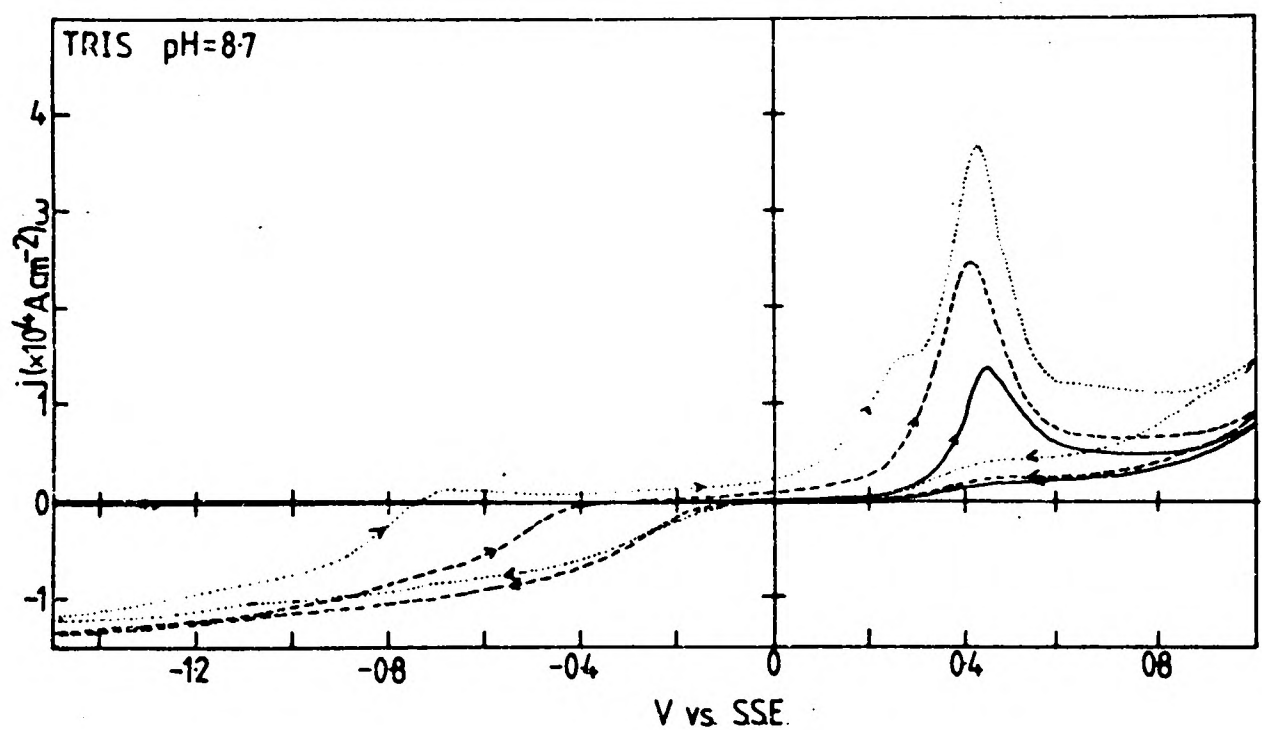
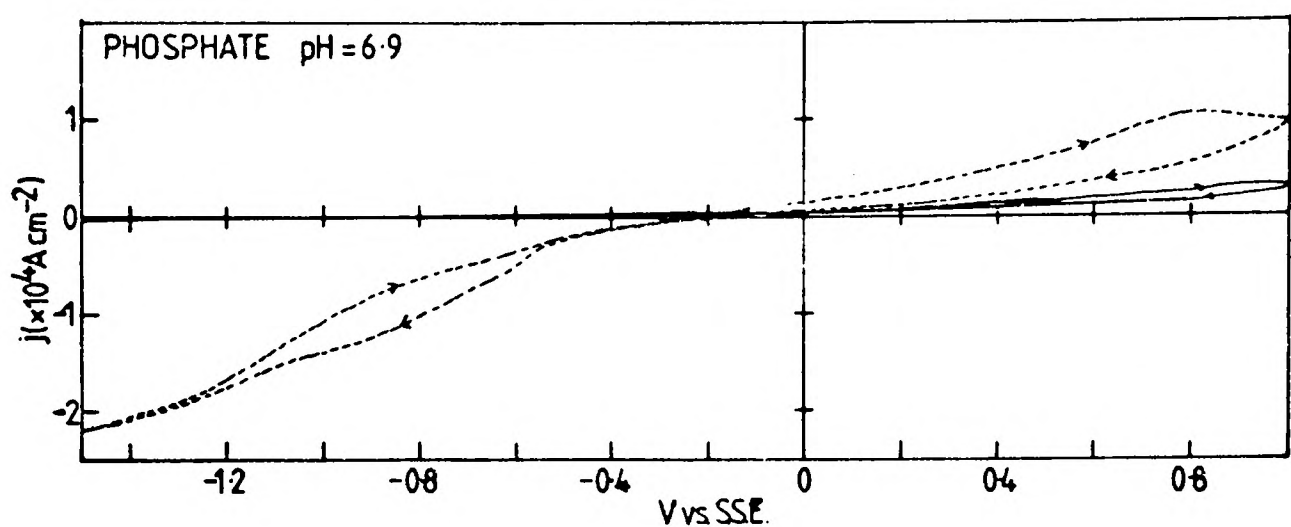
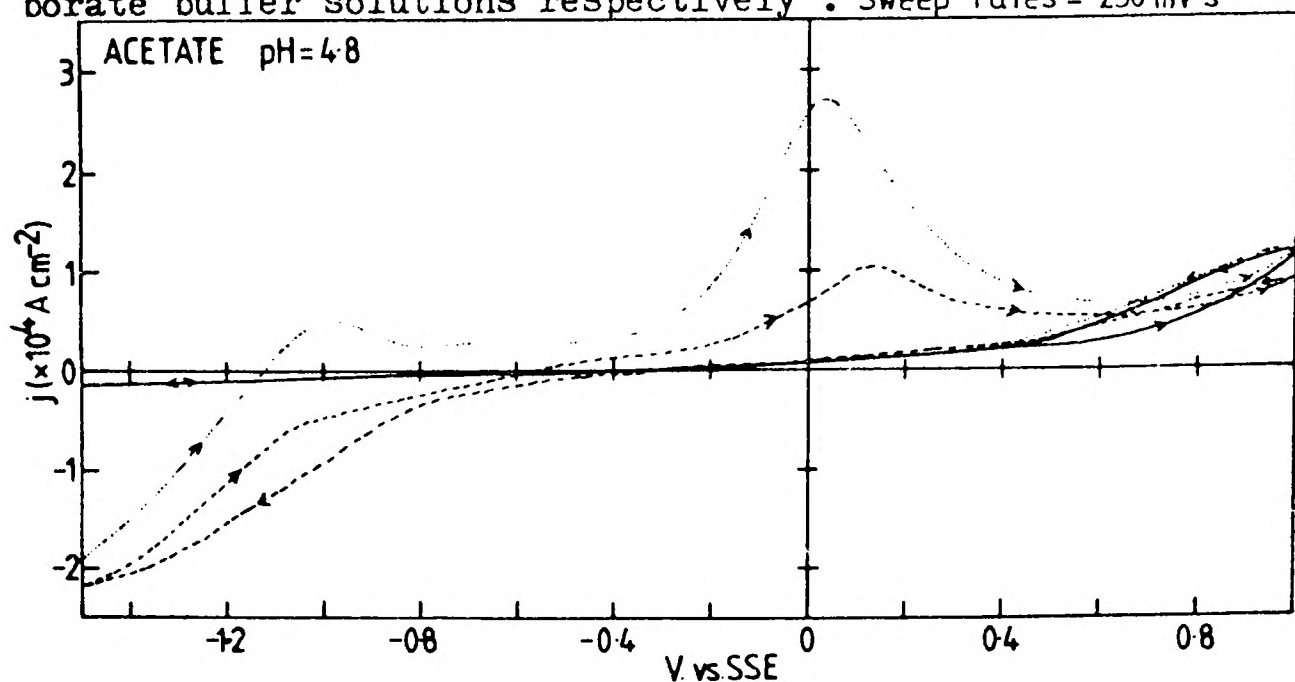
Using chopped light and phase sensitive detection (see Section 3:2:3) the photocurrent may be separated from ongoing dark currents, thus making possible measurements of photocurrent at much lower light intensities than d.c. methods allow. Typical results from experiments on the three crystal faces are presented in Figs. 4.12-4.14. The p.o.p.'s and hysteresis observed are quite typical of the three surfaces providing consistent polishing and etching procedures are adhered to. Although considerable dark anodic current flows at the positive limit of these sweeps, there is no significant change in the shape of these curves providing the electrode is taken at least to potentials anodic of +0.4V.

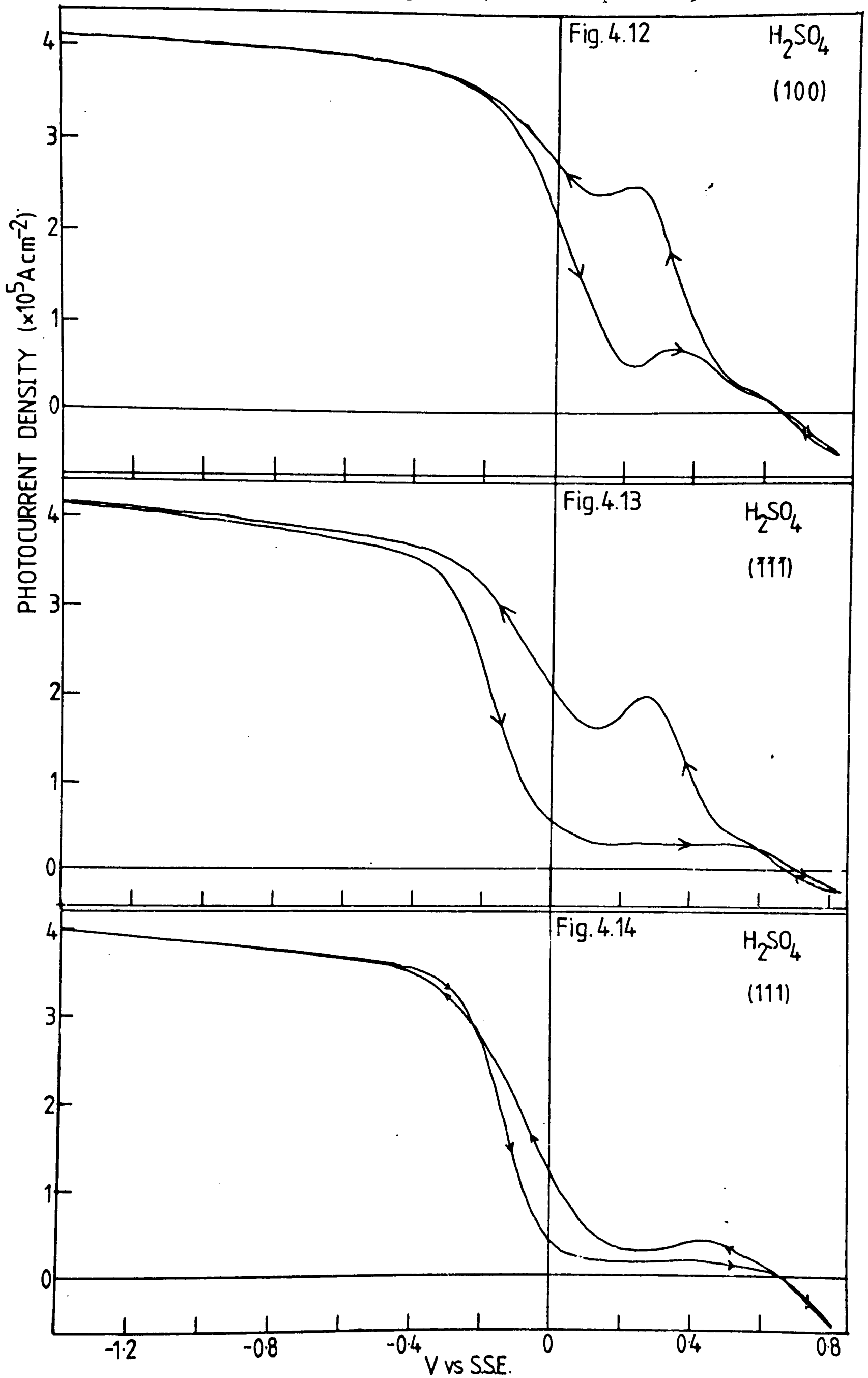
It is observable that, at the anodic limit of these sweeps, a small but real anodic photocurrent does flow. There is no correlation of this real photocurrent with the photo-induced anodic enhancement observed in the d.c. measurements. The former only shows up the lock-in technique since the magnitude of dark current flowing at these potentials (> +0.65V) is many orders of magnitude greater than the anodic photocurrent.

Note also that the cathodic/anodic crossover potential in the P.C.V.'s is exactly the same as the flat-band potential in this medium as found from interfacial capacitance measurements (see Section 4:4) i.e. +0.65V for all crystal orientations in 0.5M H₂SO₄.

Figs. 4.8 - 4.11 C.V.'s of (100) p-GaP under dark (—) and illuminated (---) conditions in :- acetate , phosphate , triethanolamine (tris) and borate buffer solutions respectively . Sweep rates = 250 mV s^{-1}

115





4:2:2 1.0M NaOH

Similar P.C.V.'s taken in 1.0M NaOH are shown in Figs. 4.15-4.17. Similar variations of behaviour for the three surfaces, as seen in 0.5M H_2SO_4 , are also in evidence in the alkaline medium. Again anodic photocurrents are observed at the anodic limit and the cathodic/anodic crossover agrees well with the measured flat-band potential, i.e. +0.05V vs. S.S.E.

4:2:3 Other media

Photocurrent voltage plots for pH's < 4 and > 10 reveal similar behaviour to that shown in strong acid and alkali. However, P.C.V.'s taken in the range of pH4-10 reveal low photocurrent efficiencies, poor saturation behaviour and also deterioration with time.

4:2:4 Effect of light intensity on P.C.V. plots

The P.C.V. behaviour of all crystal orientations is qualitatively similar with respect to varying light intensity. A typical set of results for the (100) surface is shown in Fig. 4.18 where each successive plot represents an increase in light intensity of a factor of 10. The saturation limiting photocurrents remain approximately linear with respect to light intensity, but the hysteresis region shows considerable variation; the p.o.p. becomes increasingly more cathodic as the light intensity is increased.

SECTION 4:3 STEADY-STATE MEASUREMENTS

4:3:1 Action Spectrum

Steady-state, action spectra show no significant variation as a function of crystal orientation or electrolyte composition. Also no significant difference in response was found for the small variation in dopant densities available with the crystals used. Typical corrected spectral response curves are shown in Figs. 4.19 and 4.20. Despite difficulties in obtaining satisfactory correction curves for wavelengths < 350nm, no fall-off

Figs.4.15-4.17 Cathodic photocurrent-voltage plots for (100), ($\bar{1}\bar{1}\bar{1}$) and (111) p-GaP (respectively) in 1.0M NaOH under reduced white light illumination . Chopper speed 87Hz . Sweep rate 50mV s⁻¹. 118.

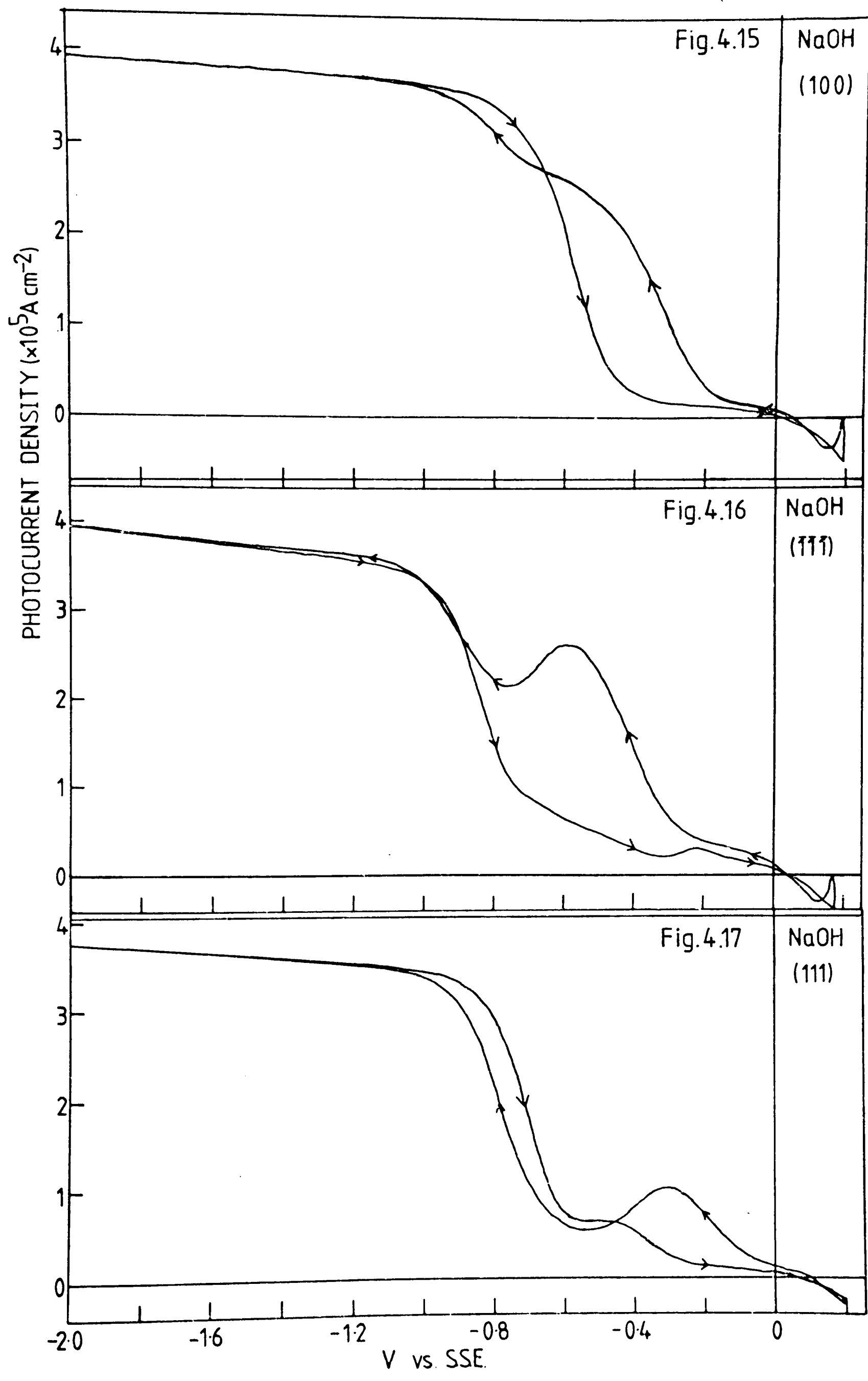
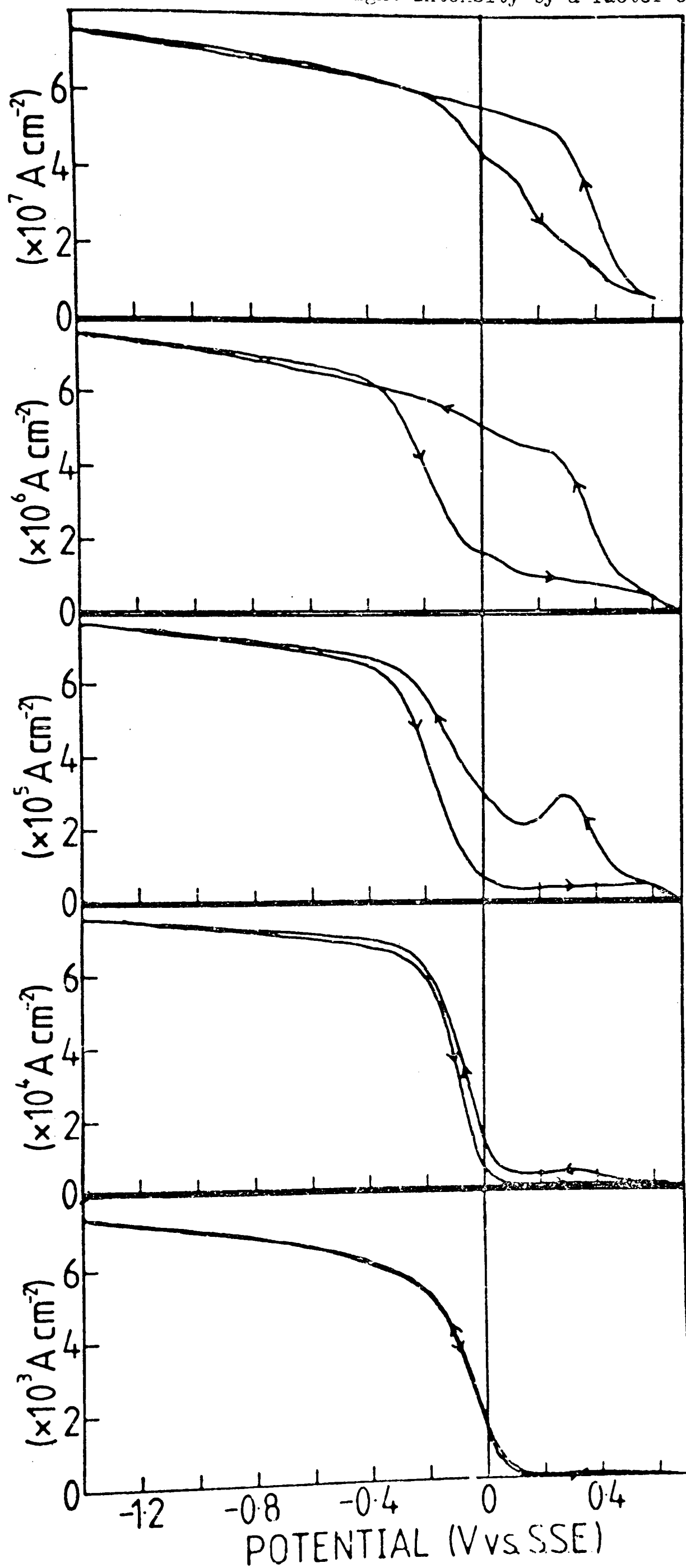


Fig.4.18 Cathodic photocurrent-voltage plots for (100) p-GaP in 0.5M H_2SO_4 under white light illumination . Each successive plot represents an increase in light intensity by a factor of ten .



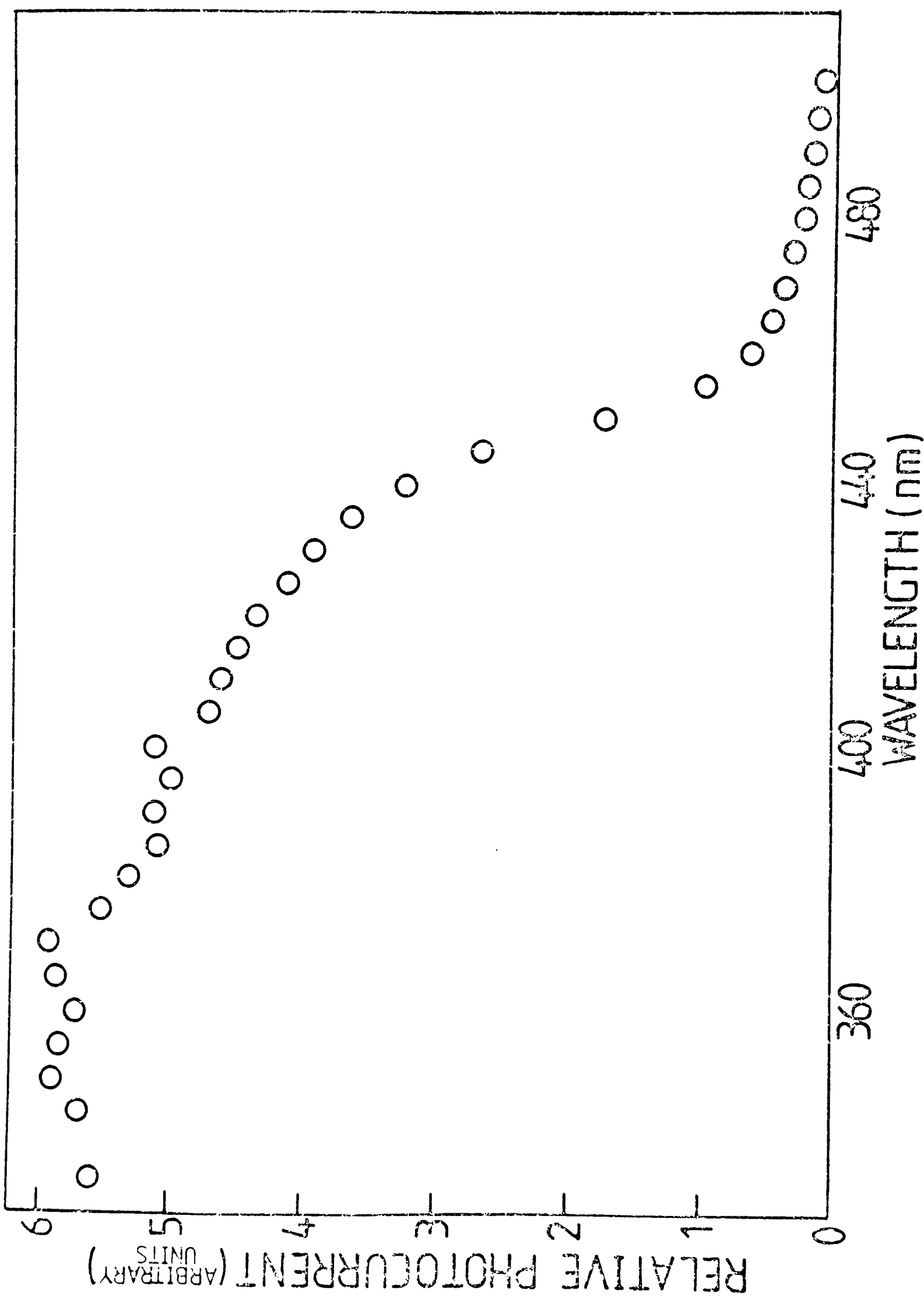


Fig.4.19 Corrected action spectrum for (100) p-GaP in 0.5M H₂SO₄ .
Electrode potentiostatted at -0.5V vs. S.S.E.

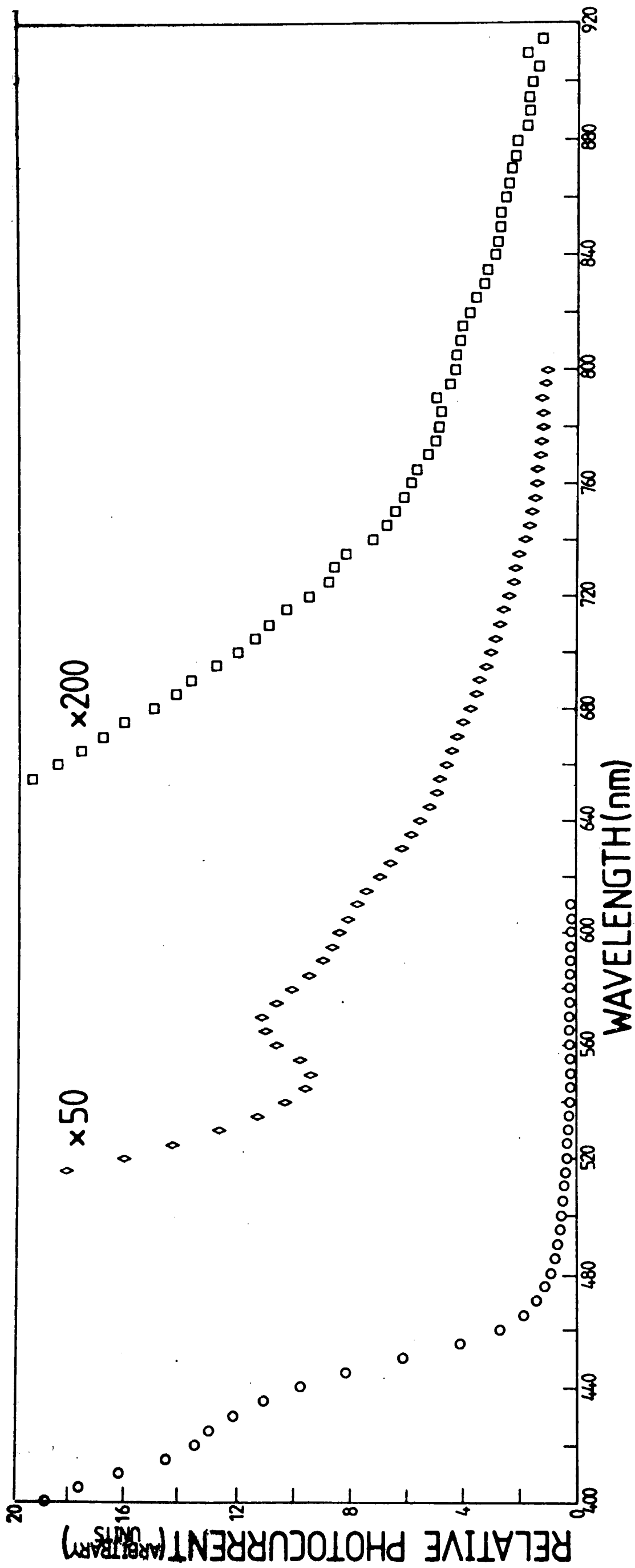


Fig. 4.20 Corrected action spectrum for (III) p-GaP in 0.5M H₂SO₄.
Electrode potentialistattd at -0.5M vs. S.S.E.

in photocurrent was seen at very short wavelengths, contrary to some previous reports. As Fig. 4.20 shows, there is a considerable spectral response for GaP with photon energies less than the reported bandgap of 2.24eV ($\approx 553\text{nm}$). The sub-bandgap response is not a transient current, in contrast to that found for the sub-bandgap response for materials such as TiO_2 and SnO_2^{243} . Fast-response, continuous, photocurrent is in fact observed right up to the limit of the transmission of the monochromator used (i.e. up to 950nm).

4:3:2 Intensity dependence of Photocurrents

In the photocurrent saturation region i.e. $< -0.5\text{V}$ for p-GaP in 0.5M H_2SO_4 , photocurrent response has been shown to be linear over some 4 orders of magnitude of light intensity. However measurements taken in the onset region ($0 \rightarrow +0.6\text{V}$) reveal distinct departure from ideality, as was also demonstrated in the P.C.V.'s of Fig. 4.18. Typical intensity vs. photo-response curves are shown in Figs. 4.21 and 4.22.

SECTION 4:4 STATIC A.C. MODULATION EXPERIMENTS

4:4:1 Equivalent circuit impedance analysis

In these experiments, a small a.c. potential modulation was applied to the controlling electrode potential of the potentiostat. The a.c. current at 0° (in phase) and 90° (out of phase) were measured and the admittance of the cell was calculated as a function of voltage and frequency. Preliminary analyses of the results were made according to a simple equivalent circuit consisting of a series resistor + capacitance. Typical Mott-Schottky plots using the derived capacitance values are shown in Fig. 4.23. Considerable dispersion of the gradient is observed as a function of modulation frequency. In some cases, dispersion in the x-intercept was also found, but this could generally be eliminated by careful

Figs. 4.21 and 4.22 Relative cathodic photocurrent vs. light intensity plots for (100) p-GaP in 0.5M H_2SO_4 at -1.0 and 0.4V respectively. 123

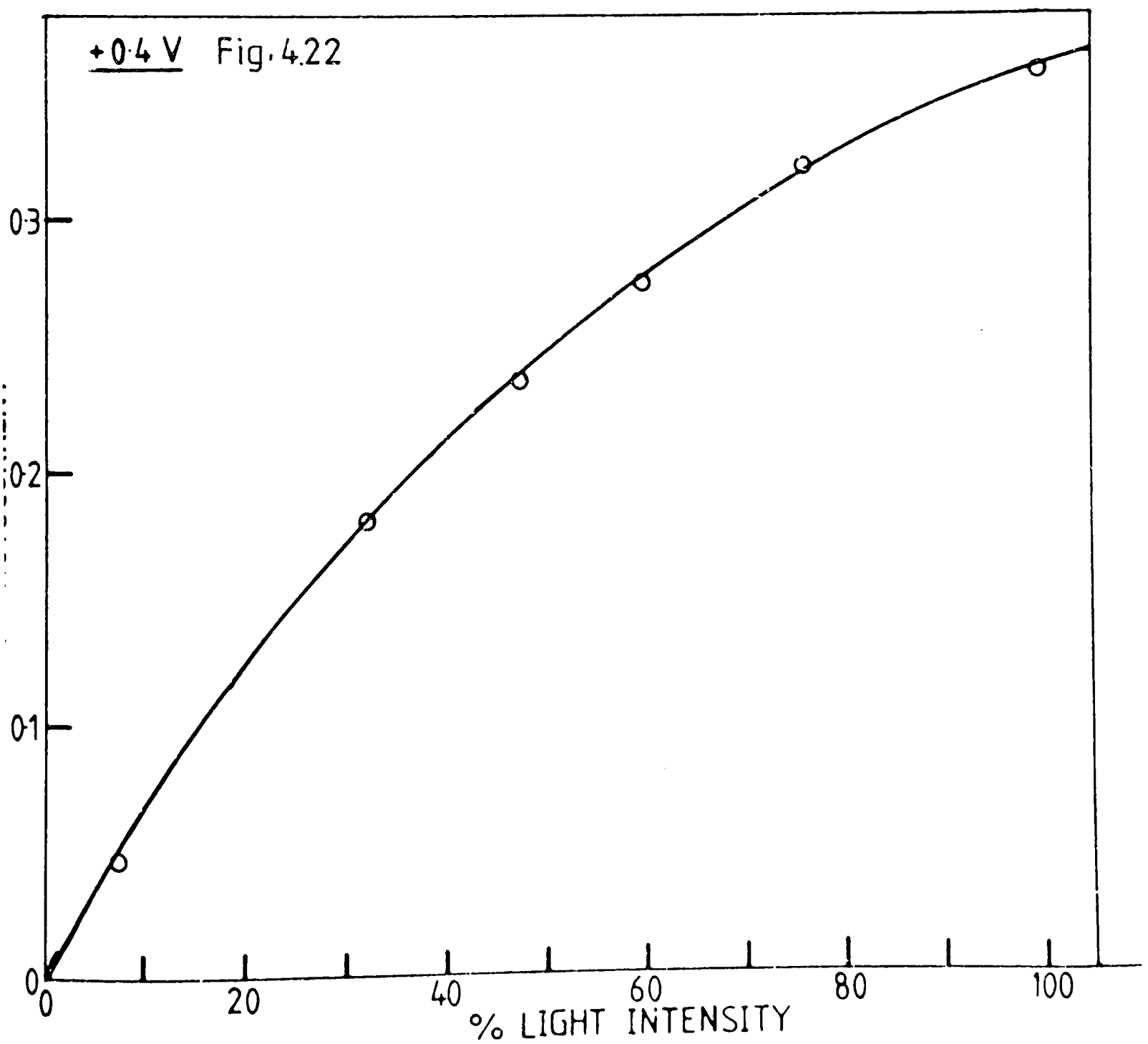
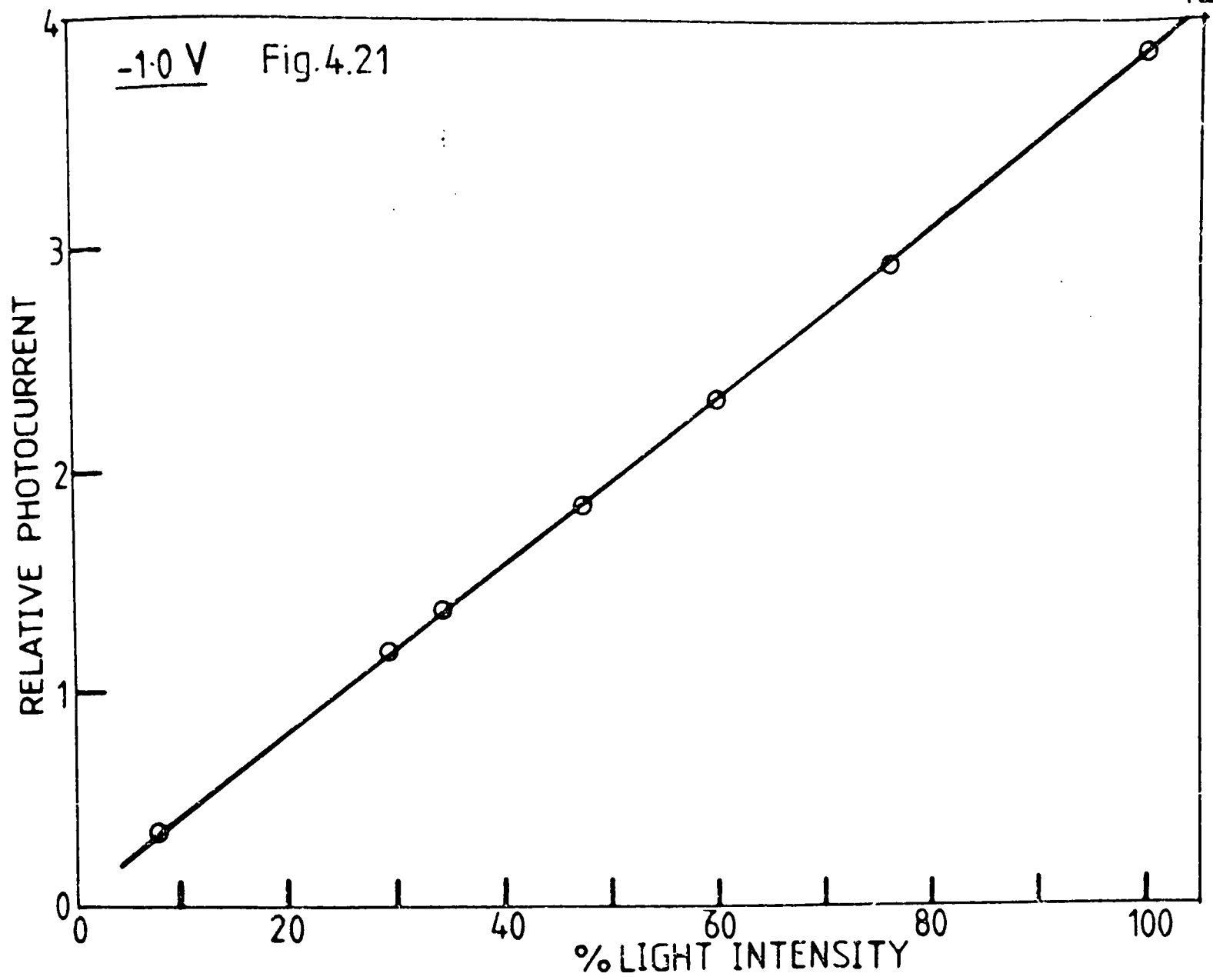
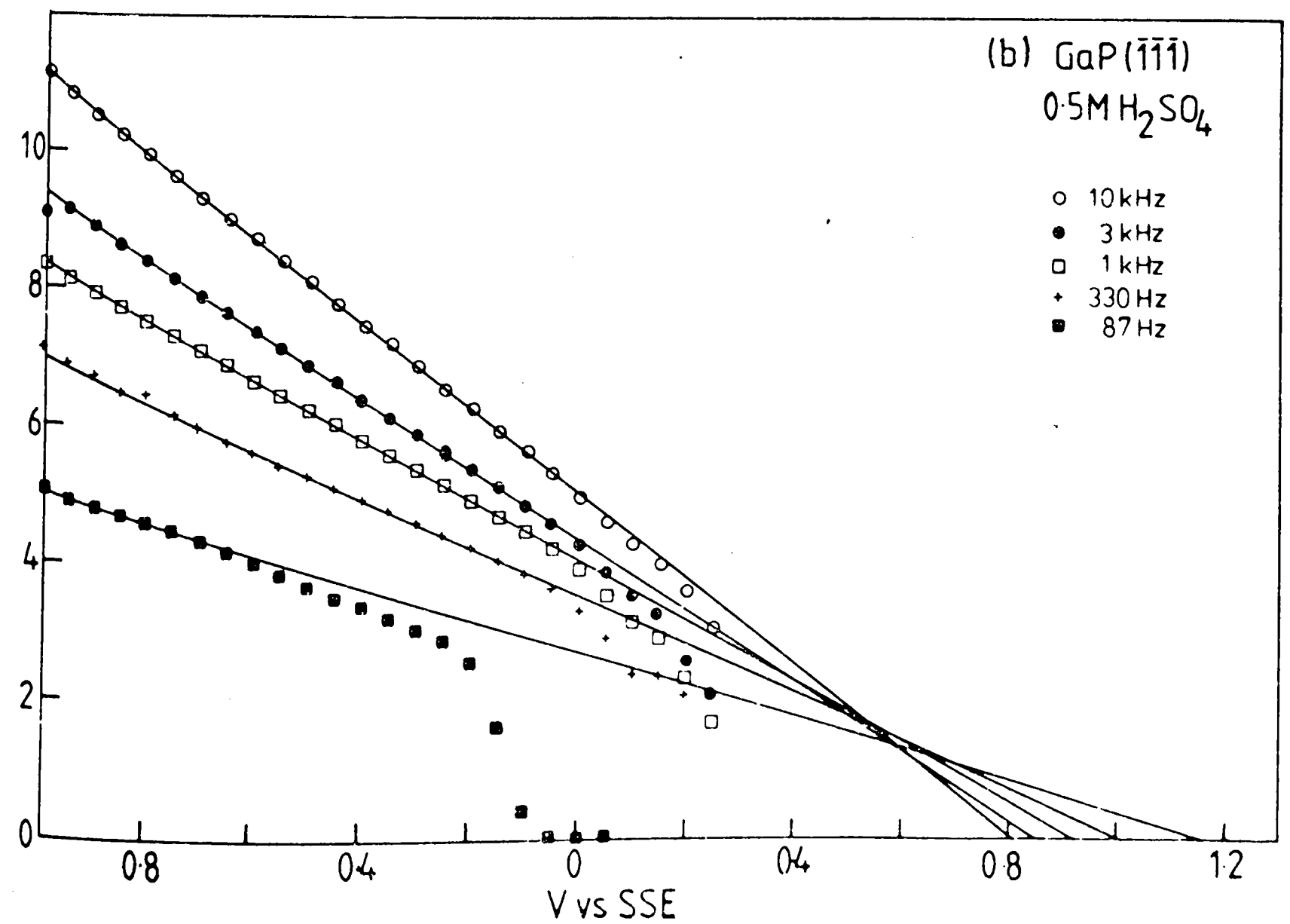
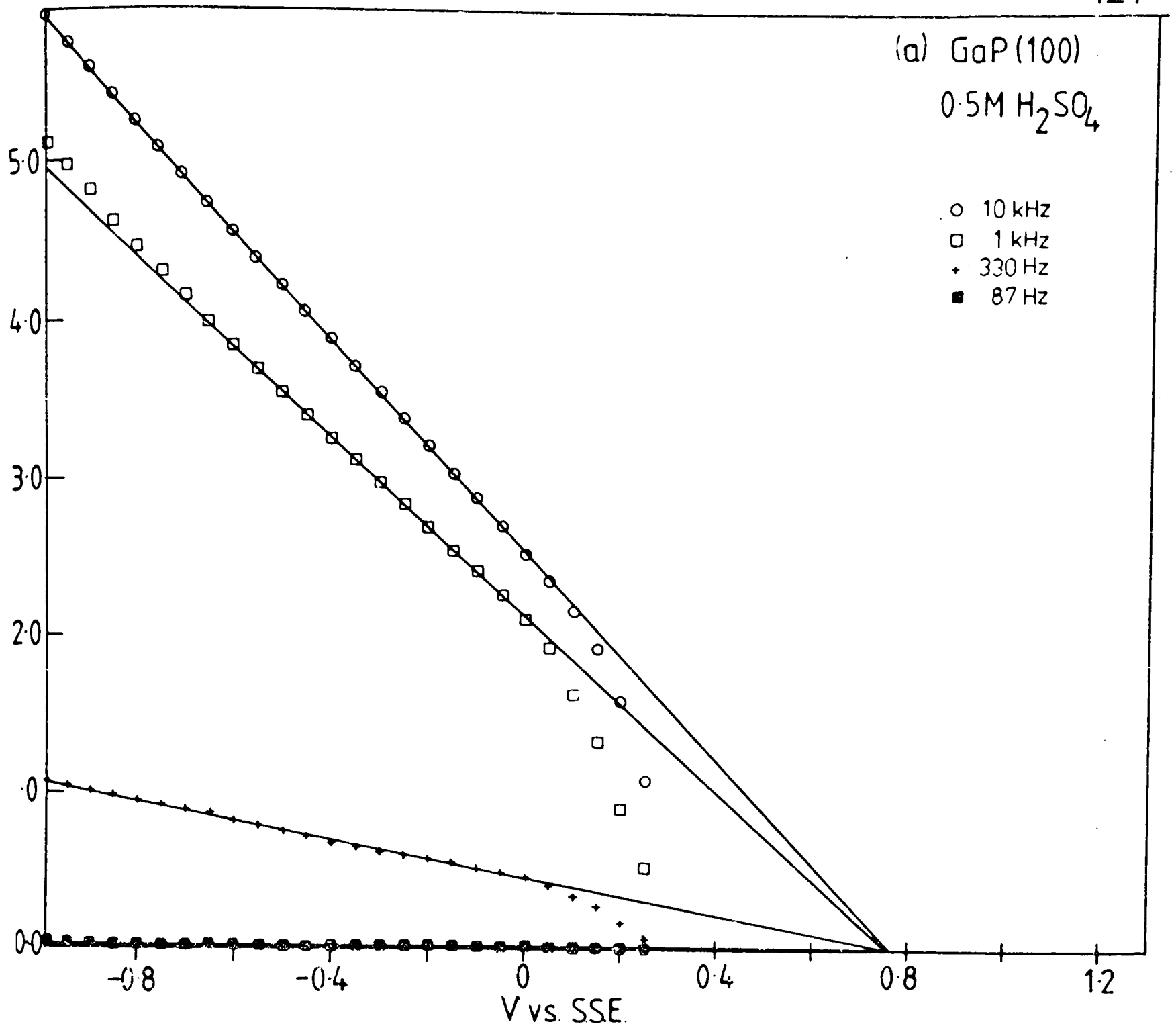


Fig. 4.23 Mott-Schottky plots for (a) (100) p-GaP and (b) ($\bar{1}\bar{1}\bar{1}$) p-GaP in 0.5M H_2SO_4 using data analyzed according to a series resistor capacitor² model circuit .



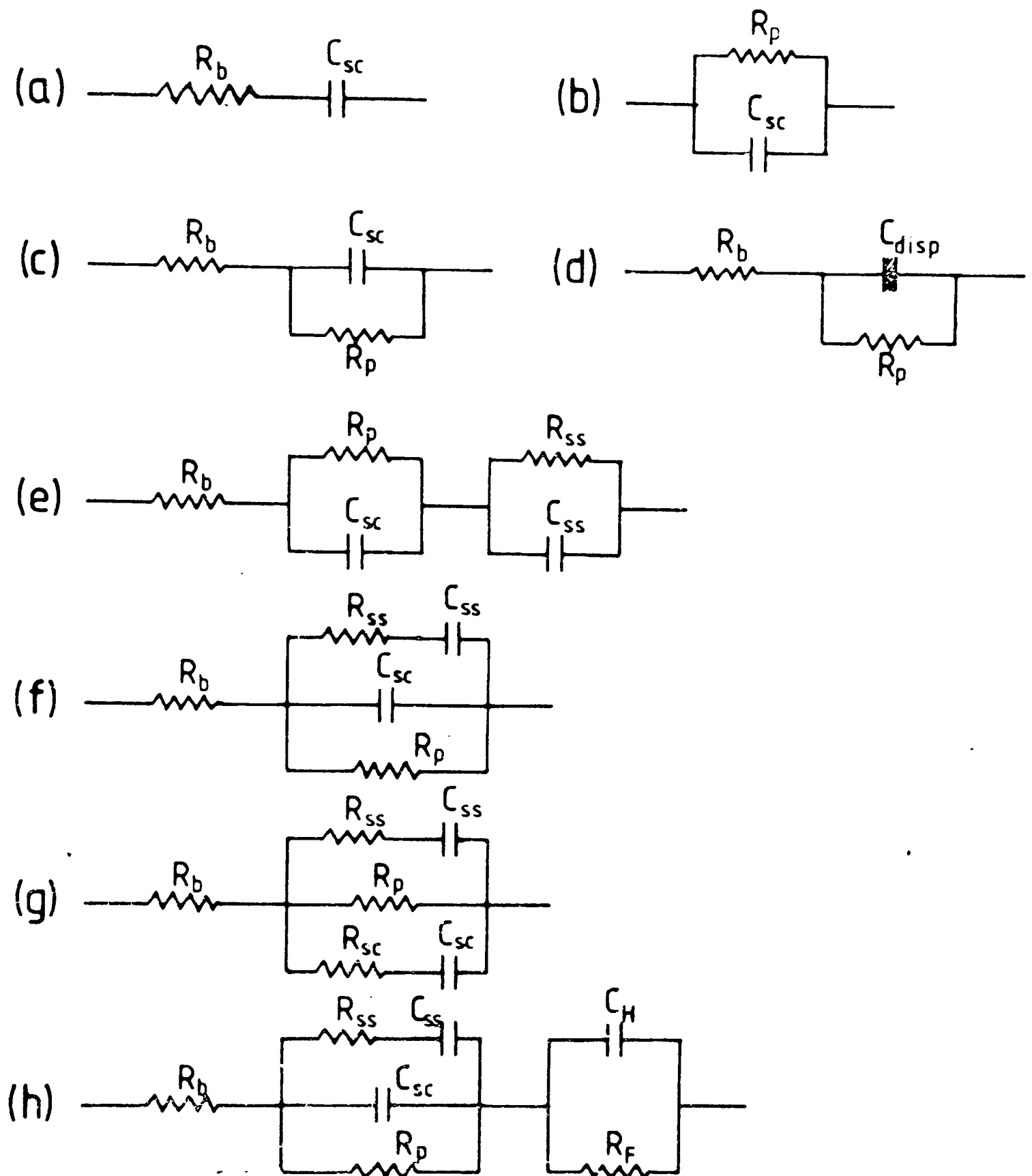
etching of the polished electrode prior to experimentation. By taking such care, reproducible results were obtained; and by choice of a suitable fixed frequency, a compilation of Mott-Schottky x-intercepts could be made as a function of electrolyte pH. (See Section 4:4:2).

In order to discover the origin of the frequency dispersion of the Mott-Schottky gradients, a number of alternative equivalent circuits were tried (see Figs. 4.24a-h). Analyses of the results taken at varying frequencies were performed with the aid of an iterative fitting programme run on the computer and using the complex-plane analysis of each circuit given in Appendix 2. The deciding factor governing the choice of the appropriate equivalent circuit was the value of the error function (see Appendix 2) obtained from the best computer fit to the experimental results. However, it was also found that increasing the number of components, in the model circuit, beyond a certain point was counter-productive resulting in appreciably longer run-times for the computer fit and also appreciable computation problems from numerical instabilities and the degeneracy of certain model components (notable for circuits (g) and (h)). The minimum error values were found for circuits (e) and (f), and indeed the errors were precisely the same. However, Mott Schottky plots using the derived values for C_{sc} for the two equivalent circuits gave appreciably different results (see Fig. 4.25 and 4.26). Analysis according to circuit (e) failed to produce a reasonable straight line whereas the results from circuit (f) gave good straight plots as expected for Mott-Schottky behaviour. For this reason attention was focussed on the analyses according to circuit (f). A further discussion of the relevance of the various equivalent circuits is given in the Discussion Section 4:8:1

4:4:2 The pH dependence of Flat Band Potential

With the simple two-component circuit of Fig. 4.24(a) and a fixed frequency (330Hz), flat-band potentials (V_{fb} 's) for p-GaP (100) pre-etched

Figs. 4.24(a-h) Various alternative equivalent circuits tested to model the p-GaP/electrolyte interface .



R_b = bulk (solution + semiconductor) resistance .

R_p = combined faradaic and space charge resistance .

R_{ss} = surface state resistance

R_{sc} = space charge resistance

R_F = faradaic resistance

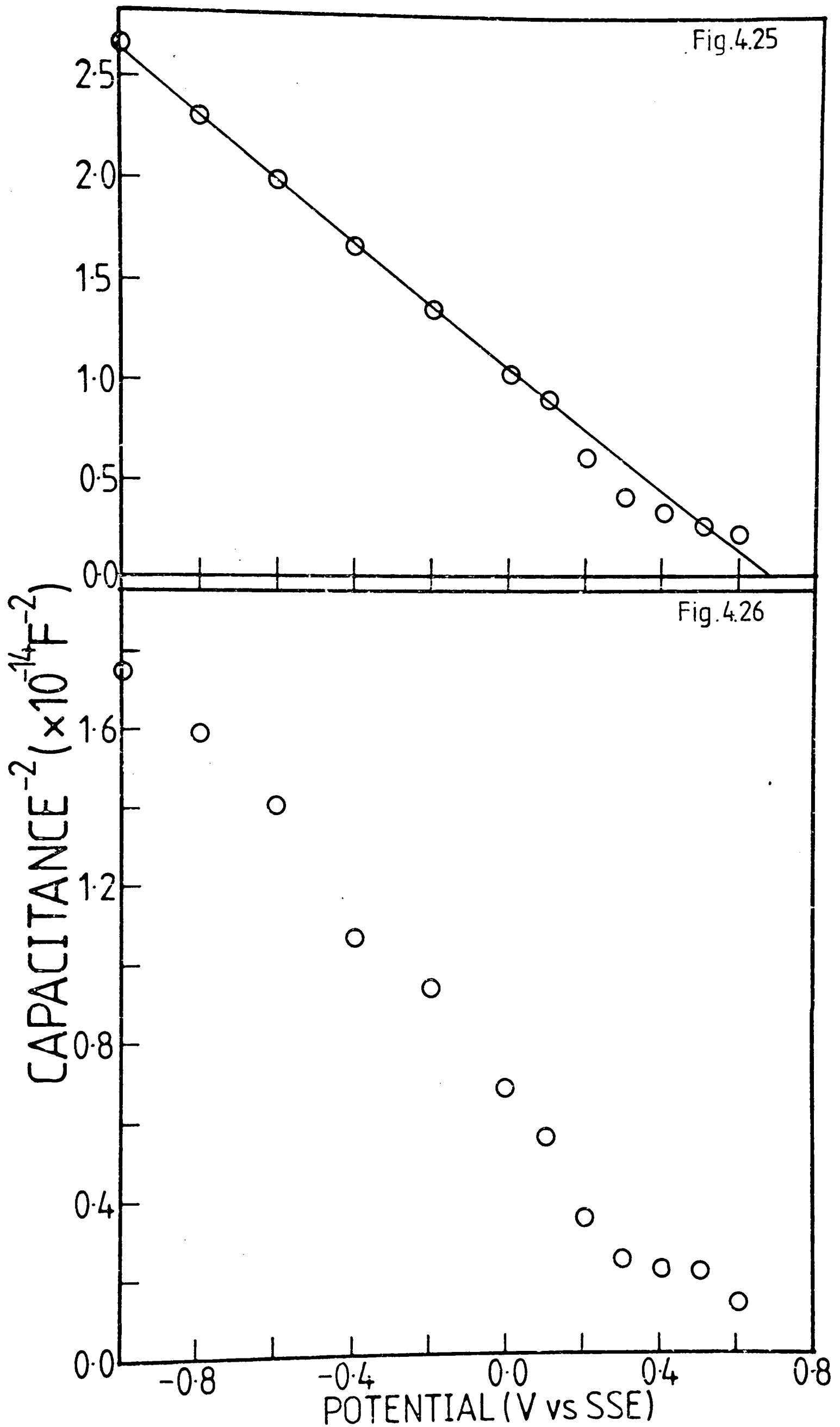
C_{sc} = space charge capacitance

C_{ss} = surface state capacitance

C_H = Helmholtz capacitance

C_{disp} = frequency dependent capacitance

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Figs. 4.25 and 4.26 Mott-Schottky plots for ($\bar{1}\bar{1}\bar{1}$) p-GaP in 0.5M H_2SO_4 using data analyzed according to equivalent circuits 4.24(f) and 4.24(e) respectively .



in aqua-regia were obtained from Mott-Schottky plots for electrodes immersed in solutions of pH 0.5-13.3. The results are presented in Fig. 4.27. For results taken in the intermediate and higher pH ranges (pH 4-10 and 10-14), any period of illumination of the electrodes was found to cause a significant effect of V_{fb} . A typical result is that found for the phosphate buffer pH 6.9. A perfectly clear electrode fresh from etching gave V_{fb} of +0.44V; but following a 10 minute period of illumination at -0.775V, the apparent V_{fb} had shifted to +0.75V.

In addition to this pre-illumination dependence, Mott-Schottky plots for the higher pH range revealed very poor reproducibility on consecutive experiments. There was some indication, in fact, that there was a direct relationship between the magnitude of anodic current passed and the extent of the variation of V_{fb} . This behaviour was particularly noticeable for the (100) electrode in 1M NaOH and may relate to the degradation in response, of the cyclic voltammograms for this crystal orientation (Section 4:1:2).

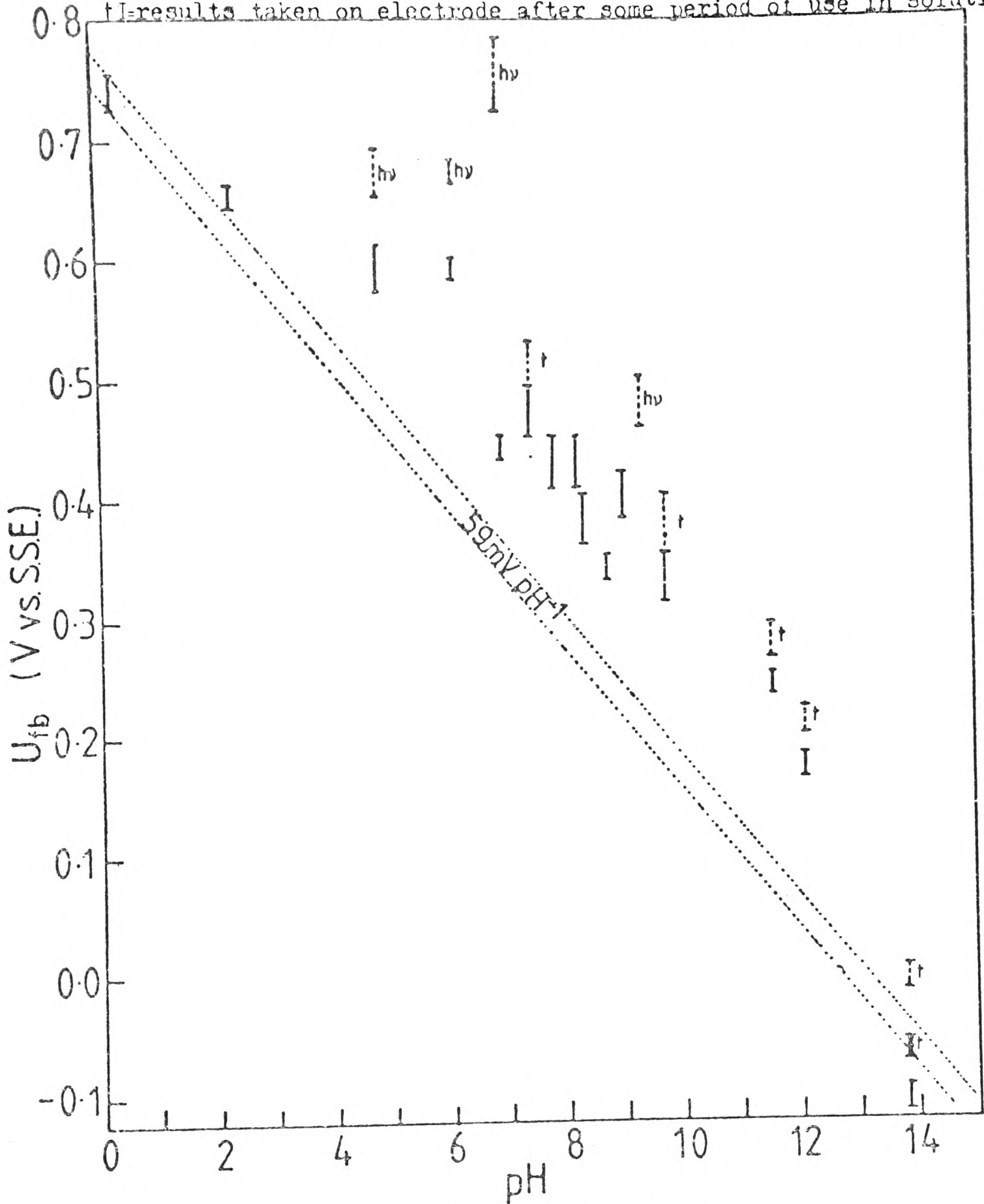
Analysis using the more complex, five-component circuit of Fig. 4.24(f) on results from the $(\bar{1}\bar{1}\bar{1})$ and (111) surfaces gave much more reproducible results for the Mott-Schottky plots, even in the phosphate medium. The problems associated with the above two-component results in the (100) surface in fact seem more related to an inherent chemical instability of this surface (see Section 4:6) rather than the failure of this more simple circuit analysis.

Compilations of results of typical five-component impedance analyses for electrodes immersed in H_2SO_4 , phosphate and NaOH electrolytes are given in Figs. 4.28-4.30.

The flat-band potentials obtained from these complex analyses can be plotted as a function of pH, and a good straight line results (Fig. 4.31). Note also that there is good agreement between these values of V_{fb} obtained in this manner and the cathodic/anodic photocurrent crossover obtained from the P.C.V. plots (see Table 4.1).

FIGURE 4.27 Compilation of flat band potentials as obtained from extrapolation of Mott-Schottky plots taken in various media .

I=results taken on fresh electrodes
hv=results following a period of illumination cathodic of flat-band
tI=results taken on electrode after some period of use in solution .



Buffer Solution	pH	Buffer Solution	pH
0.5M H ₂ SO ₄	0.3	Tris/HCl, 1M KCl	8.3
0.01M HCl, 1M KCl	2.3	" " " "	8.7
0.05M KHphthalate/NaOH, 1M KCl	4.8	" " " "	9.0
acetic acid/NaOH, 1M KCl	4.8	Borate, 1M KCl	9.3
1.0M KCl	6.1	Bicarbonate, 1M KCl	9.7
KH ₂ PO ₄ /Na ₂ HPO ₄ 0.5M	6.9	Triethanolamine/HCl, 1M KCl	9.7
Tris/HCl, 1M KCl	7.4	Phosphate, 1M KCl	11.5
" " " "	7.8	0.012M NaOH, 1M KCl	12.1
Triethanolamine/HCl 1M KCl	8.2	1M NaOH	13.3

Fig. 4.28 Compilation of results of typical five-component impedance analyses for $(\bar{1}\bar{1}\bar{1})$ p-GaP in $0.5M H_2SO_4$.

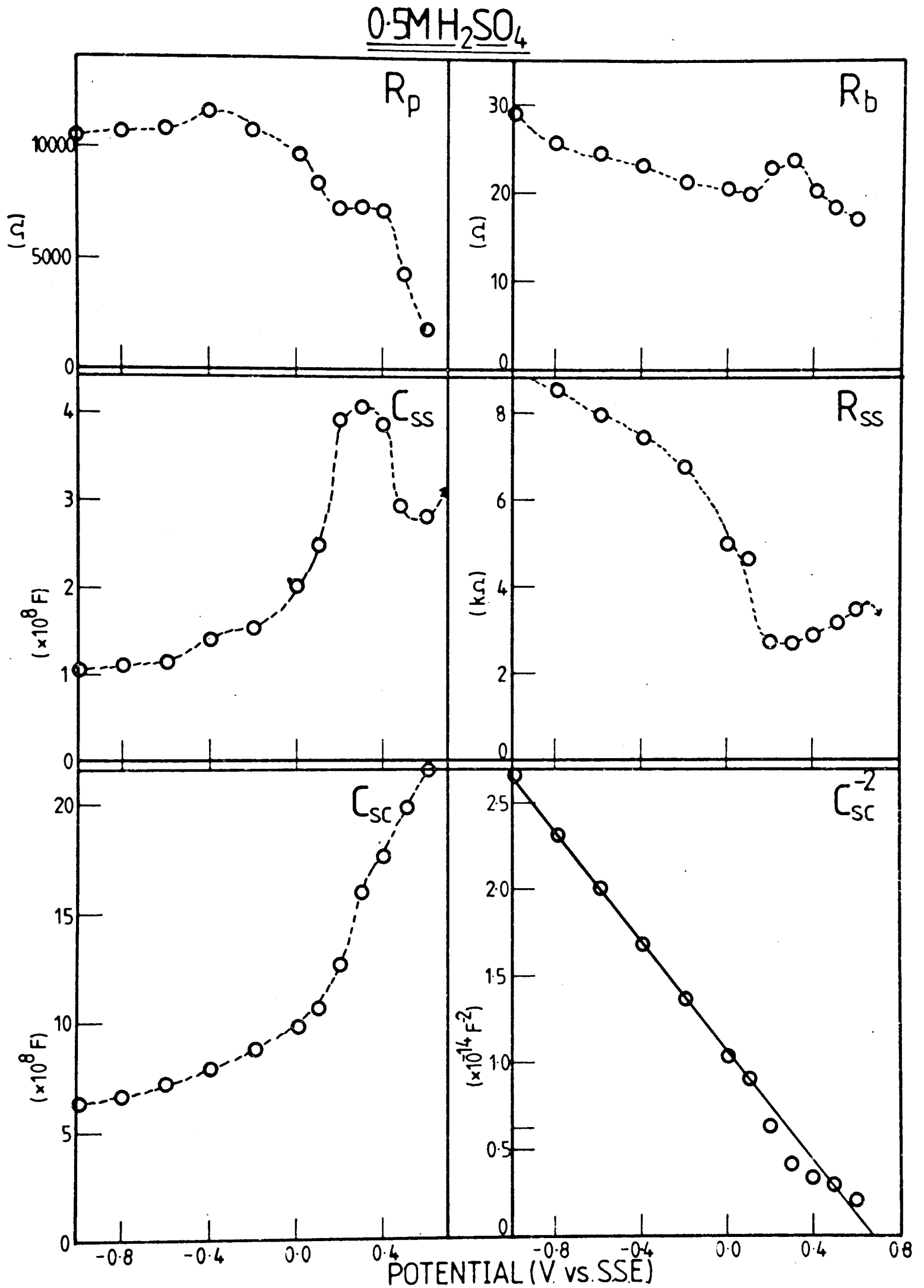


Fig. 4.29 Compilation of results of typical five-component impedance analyses for $(\bar{1}\bar{1}\bar{1})$ p-GaP in pH 6.9 phosphate buffer .

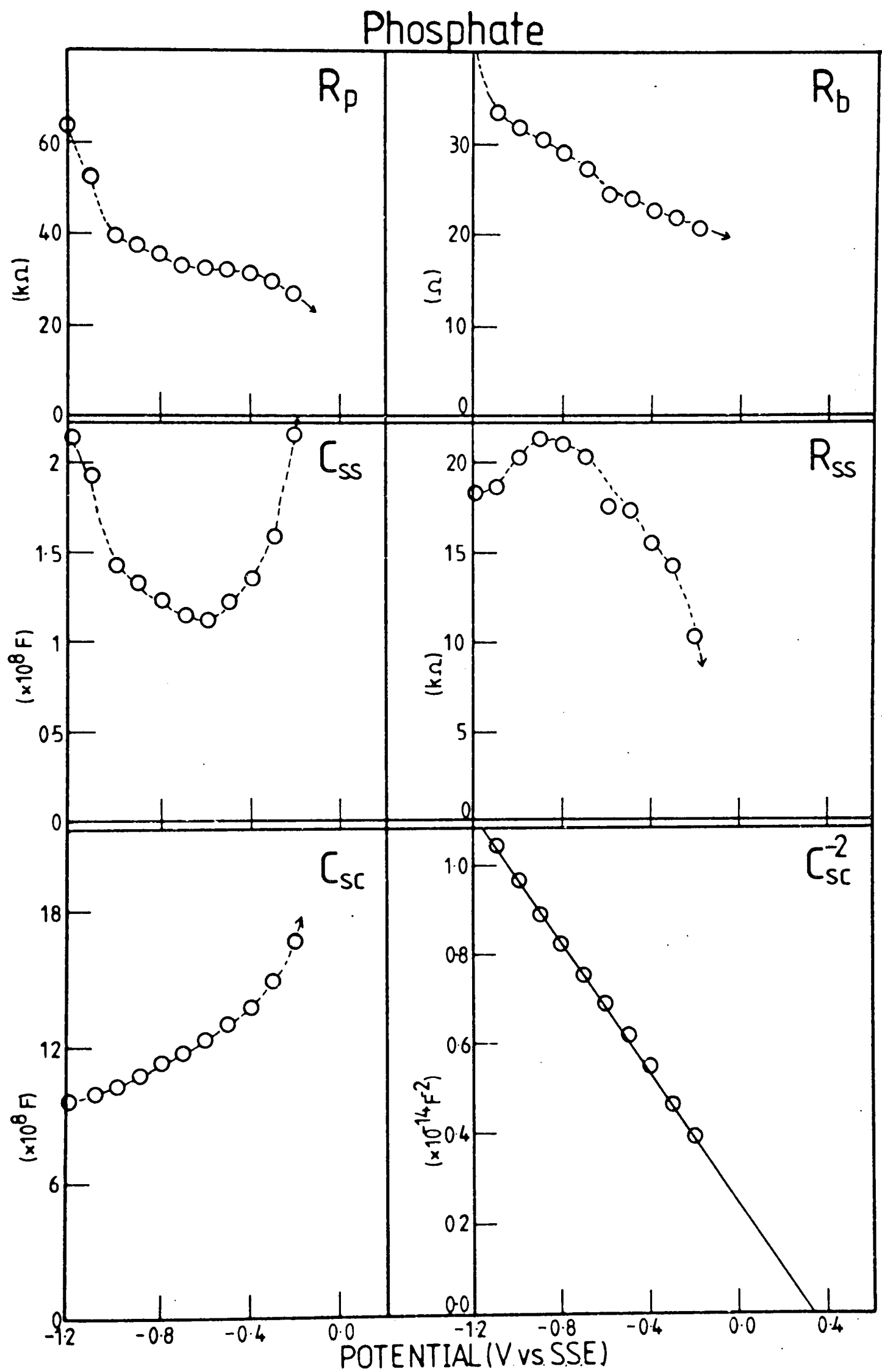


Fig. 4.30 Compilation of results of typical five-component impedance analyses for ($\bar{1}\bar{1}\bar{1}$) p-GaP in 1.0M NaOH .

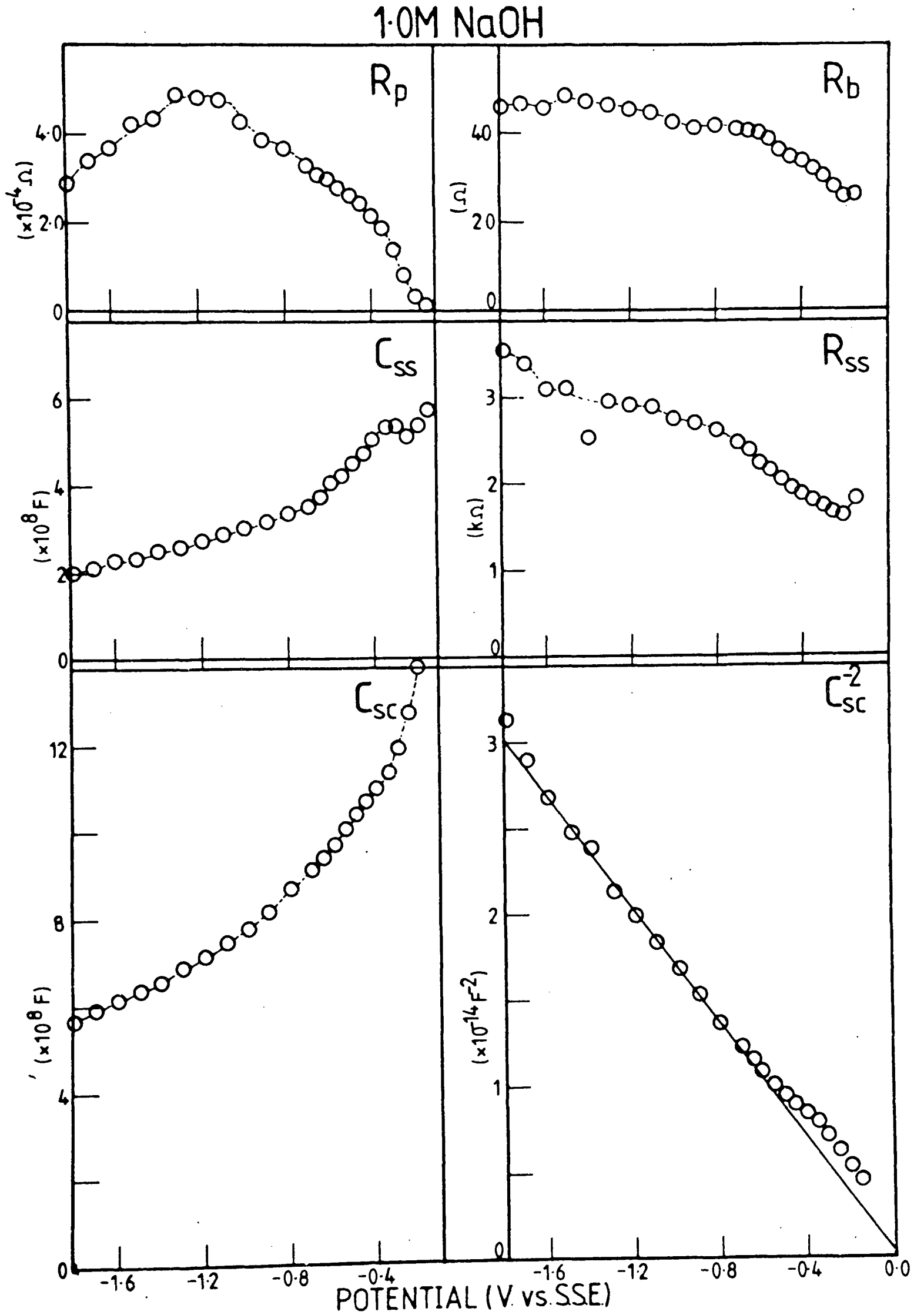


Fig. 4.31 Plot of flatband potential vs. solution pH for (111) p-GaP 133
 taken from the data compilations of Figs. 4.28-4.30 .

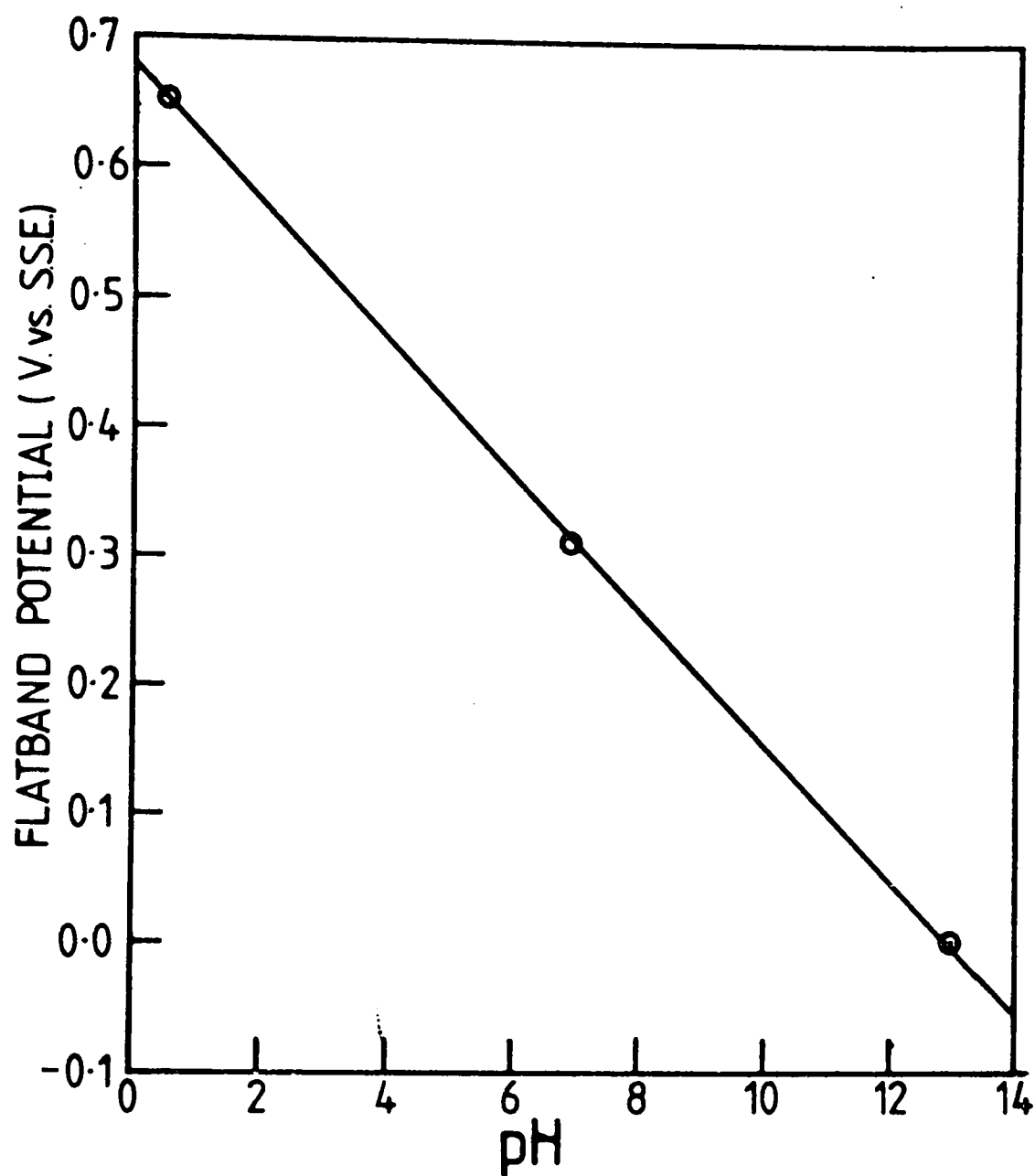


TABLE 4.1 Correlation of flatband potential determined by the five-component analysis with the cathodic/anodic photocurrent crossover obtained from the P.C.V. plots .

Solution pH	Flatband Potential	Cathodic/Anodic Crossover
0.5	0.65 V	0.65 V
6.9	0.32 V	0.30 V
13.3	0.00 V	0.05 V

SECTION 4:5 DYNAMIC A.C. MODULATION EXPERIMENTS

4:5:1 A.C. Cyclic Voltammograms (ACCV's)

The technique of a.c. cyclic voltammetry has more commonly been applied to the study of interfacial phenomena at metal electrodes. However, much interesting qualitative information could be gained by applying the technique to the study of semiconductor electrochemistry. In this technique, no attempt is made to analyze quantitatively the admittance data in terms of an equivalent circuit. Instead, 0° in phase and 90° out of phase signals are plotted directly as a function of electrode voltage during the course of a cyclic potential sweep.

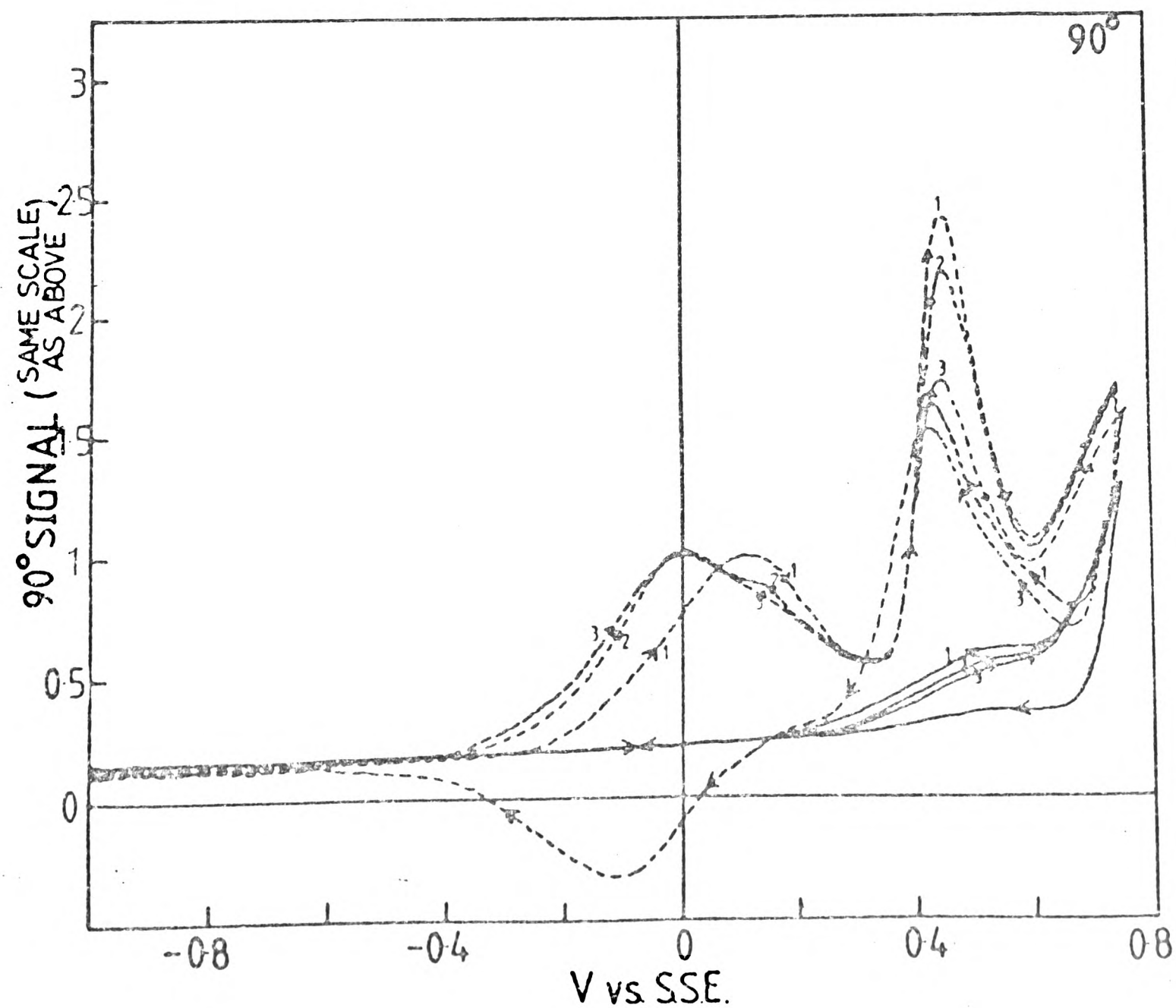
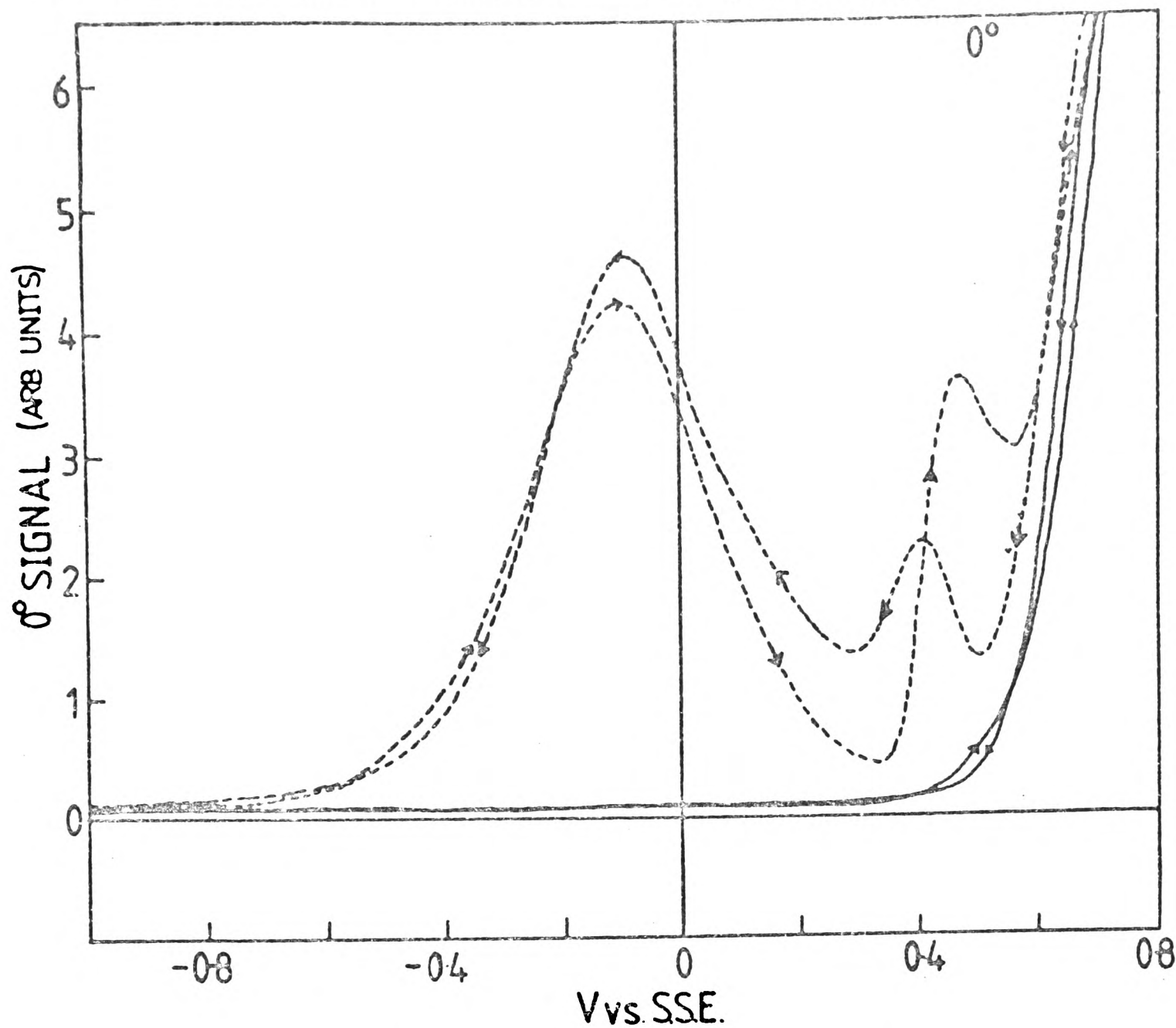
One additional variable, available for the investigation of semiconductor (as opposed to metal) electrode using this technique, is the magnitude of illumination on the electrode surface. Detailed impedance analyses of illuminated electrodes is precluded due to the added complication to the equivalent circuit. The presence of a voltage-dependent current generator in the space-charge region of the semiconductor complicates the necessary equivalent circuit to a degree where it is no longer practical to attempt the detailed complex-plane analysis (see Discussion Section). Despite this drawback, changes in a.c. cyclic voltammograms brought about by the illumination of the electrode can provide further insight into the interfacial processes.

4:5:2 0.5M H₂SO₄

Typical a.c. cyclic voltammograms of p-GaP in 0.5M H₂SO₄ are shown in Fig. 4.32. It was found that the precise details of the plots were highly dependent on the recent history of usage of the electrode, but some general observations can be made concerning the basic features. In the dark, the 0° plot bears a striking resemblance to the dark d.c. C.V. (cf. Fig. 4.1). The dark 90° plot, however, has a small feature just negative of the large irreversible anodic wave. This feature is the major cause of the deviation from linearity on approach to flat band seen in the

Fig. 4.32 A.C.Cyclic Voltammograms for (100) p-GaP in 0.5M H_2SO_4
 (—)dark, (---)illuminated. Modulation=3mV rms, 330Hz. Sweep rate $50mVs^{-1}$

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Mott-Schottky plots of capacitance as analyzed according to the two-component circuit (see Fig. 4.23). With the more complex circuit of Fig. 4.24(f) the C_{ss} plot shows a peak at this potential ($\sim 0.4V$) and the majority of this deviation is lost from the $\frac{1}{C_{sc}^2}$ plot.

It is found that the magnitude of the small feature in the ACCV is particularly dependent on electrode past history. Long periods potentiostatted at potentials negative of $+0.3V$ cause an initial enhancement of this feature on restarting the cycle even if the electrode is maintained strictly in the dark. Conversely, any passage of anodic current through the electrodes causes a diminution of the feature. Finally, if left open circuit for some time, the feature also increases in magnitude although, as with the cathodically potentiostatted case, it decays on restarting the cycling.

When unfiltered white light - or indeed any light of energy greater than the bandgap of p-GaP - is allowed to illuminate the electrode, radical alterations occur in both the 0° and 90° plots. The additional peaks appear in both phases. The more cathodic peak shows a direct correlation with the potential and which the rise in photocurrent is observed in the d.c. illuminated C.V. Confirmation for this correlation comes from studies on the various crystal orientations; the onset potential varies from one orientation to another, and this more cathodic peak moves analogously. The second, more anodic peak, however, shows no correlation with any significant change in dark current; however, studies at varying light intensities point to some relationship between the dark 90° enhancement and this illuminated 0° and 90° peak.

4.5.3 1M NaOH

Work on a clean, freshly etched, (100) electrode in 1M NaOH can again provide reasonable results although reproducibility using this crystal face is more suspect in this medium. However, more reproducible results can be obtained from the other ($\bar{1}\bar{1}\bar{1}$) and (111) faces, and in general results are precisely analagous to the results taken in H_2SO_4 .

4:5:4Other media

Qualitatively similar results are obtained for work in other electrolytes. Two major features are always observed for illuminated ACCV's:

1. One peak in the 0° signal always correlates with the rise of d.c. photocurrent.
2. The feature observable in the 90° plots ahead of the large anodic wave becomes dramatically enhanced on illumination and indeed remains enhanced for the first dark sweep through this region even if the illumination is cut off at the cathodic limit.

SECTION 4:6 LONG TERM STABILITY UNDER ILLUMINATION AND CO_2 -REDUCTION EXPERIMENTS

4:6:1 (100) Surfaces

Some preliminary long-term experiments were performed on this surface in deoxygenated, CO_2 -free solutions. It was discovered that this surface was not stable over long periods (> 24 hours) of illumination in both acidic and neutral solutions. Long-term tests in 1M NaOH, even in the dark, had shown some instability, so no long-term tests were performed with illumination for this solution. For H_2SO_4 tests, bubbles of Hydrogen were observed to stick to the surface of the electrode; and after long periods, it was noted that a grey colouration had appeared on the electrode surface directly under the bubble. If the electrode was removed from solution, taking care not to disturb the bubbles, the grey patches were clearly observable. On reimmersion in the acid gas evolution was observed from the grey regions. Qualitative tests following these experiments confirmed the presence of small quantities of Gallium in solution.

Similar tests were performed in CO_2 -free phosphate buffer prior to experiments run on CO_2 reduction. During these experiments, it was observed that the photocurrent decreased steadily with time; and at the end of the tests, the surface of the electrodes was found to be coated

with a coherent metallic layer. This metallic layer was apparently insoluble in the phosphate buffer solution- but on immersing it in dilute acid, gas was immediately evolved, and the metallic colouration disappeared.

When work was carried out in CO_2 -saturated phosphate solutions, similar surface degradation occurred. Standard spot tests were used to detect CO_2 reduction products in the solutions (notably HCOOH , HCHO and CH_3OH). However, these tests all proved negative even after the passage of $\sim 120\text{mC}$ of cathodic charge (over 24 hours). The maximum sensitivity of the tests for HCHO and HCOOH was $\sim 5 \times 10^{-5}\text{M}$. Thus, if CO_2 reduction had taken place, its current efficiency must have been less than 1%.

Long-term experiments in a bicarbonate solution (1.0M) with similar charge flow again produced no detectable CO_2 reduction products. However, the electrode again became coated in a very thin layer of metallic appearance, and the solution became slightly clouded with a white precipitate. The precipitate was collected, and spot tests revealed the presence of Gallium. However, X-ray powder diffraction failed to give any identifiable pattern.

As a final experiment on this surface, a short-term (6 hours) experiment was run to ascertain whether p-GaP was capable of reducing acetic acid to ethanal or ethanol. The result was very complex. The surface of the electrode became extensively corroded, and there was evidence for the presence of a grey metallic material that evolved gas on immersion in dilute acid. In addition, there was a black deposit on the surface of the electrode that could not be analyzed.

4:6:2 $(\bar{1}\bar{1}\bar{1})$ and (111) Surfaces

Long-term (> 48 hours) experiments carried out on the $(\bar{1}\bar{1}\bar{1})$ and (111) surfaces in 0.5M H_2SO_4 produced stable generation of Hydrogen and cathodic photocurrent. No change in surface morphology was detectable and also no

trace of Gallium could be found in solution (to a limiting concentration of $\sim 10^{-5}$ M, corresponding to a maximum current efficiency for dissolution of $< 0.02\%$). Also, weight change in the electrode could not be detected.

An experiment on the $(\bar{1}\bar{1}\bar{1})$ surface in degassed phosphate buffer also maintained the initial current density over a longer period than for the (100) surface. However, after ~ 49 hours there was an approximate 25% decrease in photocurrent, and there was a slight discolouration of the electrode surface. In particular, the specular-reflection properties of the surface appeared to have been altered as if the originally flat surface had become faceted in some photoetching process. The apparent discoloration, unlike the grey metallic layer on the (100) face, did not disappear on immersion in dilute acid.

Similar tests using CO_2 -saturated solutions again failed to produce any detectable formic acid, formaldehyde or methanol; but, unlike the CO_2 -free experiment, the photocurrent fell away much more rapidly (by about 90% of the initial value after 24 hours). At the end of the test, the electrode was removed from solution, and a distinct black deposit was found on the surface. This black material appeared quite inert, and again chemical analysis failed to elucidate its constitution. Since it could not be dissolved off, mechanical means had to be used to remove it; but this turned out to be a relatively simple process since it readily came off on the application of a paper tissue.

According to Halmann, higher CO_2 -reduction efficiencies could be attained using CO_2 -saturated 0.1M Li_2CO_3 . After 61 hours, the GaP electrode was slightly blackened, and formic acid was detected with a chromotropic-acid spot test (see Reference 244) Quantitative analysis (alkaline permanganate titration) revealed that the formic acid had been formed at an approximate 6.5% current efficiency. Again no lower oxidation states of Carbon were detected, and formaldehyde was undetectable up to a maximum

concentration of $5 \times 10^{-5} \text{M}$. This $\text{Li}_2\text{CO}_3/\text{CO}_2$ result was found to be quite reproducible with both Carbon and platinum counterelectrodes.

Finally, since no HCHO had been detected in all other work, a 1.0M solution of formic acid was photoelectrolyzed with a $(\bar{1}\bar{1}\bar{1})$ p-GaP cathode and carbon anode for 40 hours at about 10mA cm^{-2} (0.25cm^2 electrode area). The current remained fairly stable for this period. HCHO was detectable after 24 hours at about the 10^{-4}M level (chromotropic acid test), but no change in concentration was detectable after a further 16 hours. Any CH_3OH present remained undetected to a maximum concentration of 10^{-4}M . The current efficiencies represented by these conversions were $\sim 3\text{--}5\%$ for HCHO and $< 1\%$ for CH_3OH .

Alternative analysis techniques were also used on the solution resulting from these long-term reduction experiments. In particular, gas chromatography using a column of Poropak Q was attempted. Positive tests were obtained with standard solutions of known concentrations down to 10^{-4}M in CH_3OH and 10^{-4}M in HCHO. However, tests on the electrolyte solutions only succeeded in detecting the HCHO at a level similar to that obtained from a colourimetric analysis. CH_3OH again remained undetected.

The results of all long-term reduction experiments are summarized in Table 4.2.

TABLE 4.2 Summary of long-term reduction experiments on p-CaP

Electrode	Purge	Electrolyte	Period	Comments
(100)	Ar	0.5M H_2SO_4	24hrs.	Grey colouration under H_2 bubbles - weight loss .
(100)	Ar	Phosphate Buffer	24hrs.	Coherent metallic layer formed ,soluble in acid .
(100)	CO_2	Phosphate Buffer	24hrs.	Similar surface degradation to CO_2 free soln. No detectable CO_2 reduction .
(100)	None	1.0M NaHCO_3	24hrs.	No CO_2 reduction products Surface metallisation and white ppt. formed .
(100)	Ar	1.0M CH_3COOH	6hrs.	Extensive electrode corrosion Black deposit on surface .
($\bar{1}\bar{1}\bar{1}$) or(111)	Ar	0.5M H_2SO_4	60hrs.	Stable H_2 generation . No surface degradation .
($\bar{1}\bar{1}\bar{1}$)	Ar	Phosphate Buffer	49hrs.	25% decrease in photocurrent Some surface faceting .
($\bar{1}\bar{1}\bar{1}$)	CO_2	Phosphate Buffer	24hrs.	90% decrease in photocurrent. Inert black deposit on electrode surface .
($\bar{1}\bar{1}\bar{1}$)	CO_2	0.1M Li_2CO_3	61hrs.	Some surface blackening . HCOOH detected 6.5% current efficiency .
($\bar{1}\bar{1}\bar{1}$)	CO_2	1.0M HCOOH	40hrs.	HCHO (10^{-4}M) detected at 24hrs. No change in conc. ⁿ after 40hrs. No CH_3OH detectable .

B. DISCUSSION

SECTION 4:7

4:7:1 Dark Current

The dark C.V.'s for all electrolytes and electrode surfaces (Figs. 4.1-4.10) are characteristic of a near-ideal p-type semiconductor/electrolyte interface, which, itself would be expected to closely resemble the behaviour of a p-type semiconductor/metal Schottky barrier. There is only a very small "leakage" current through the barrier when the semiconductor is reverse-biased (i.e. biased cathodic of the flat-band potential which is found to be +0.65V vs. S.S.E.). However, as shown in Figure 4.33, this reverse current, if plotted at higher sensitivity, may be seen to increase in an approximately exponential fashion. Indeed as Figure 4.34 shows, the dark cathodic current closely follows a Tafel-like relationship.

$$i(V) = i_o \exp [\alpha e_o (V - V_o) F / RT]$$

i_o = exchange current at $V = V_o$, V_o = flat-band potential

V = electrode potential and α = transfer coefficient.

However, unlike a true Tafel slope obtained on metal electrodes where $\alpha \approx 0.5$, the slopes found for p-GaP are generally in the range 600-1200mV per decade, which would correspond to a very small transfer coefficient $\alpha = 0.05$ to 0.1 . No simple explanation exists to explain such an observation and so the following theory was developed. It makes use of the idea of electron injection into a Gaussian distribution of acceptor states in the solution at the electrode interface.

The model used is shown in Fig. 4.35.

Fig.4.33 Dark C.V. of ($\bar{1}\bar{1}\bar{1}$) p-GaP in 0.5M H_2SO_4 plotted at high sensitivity . Sweep rate 50mV s^{-1} .

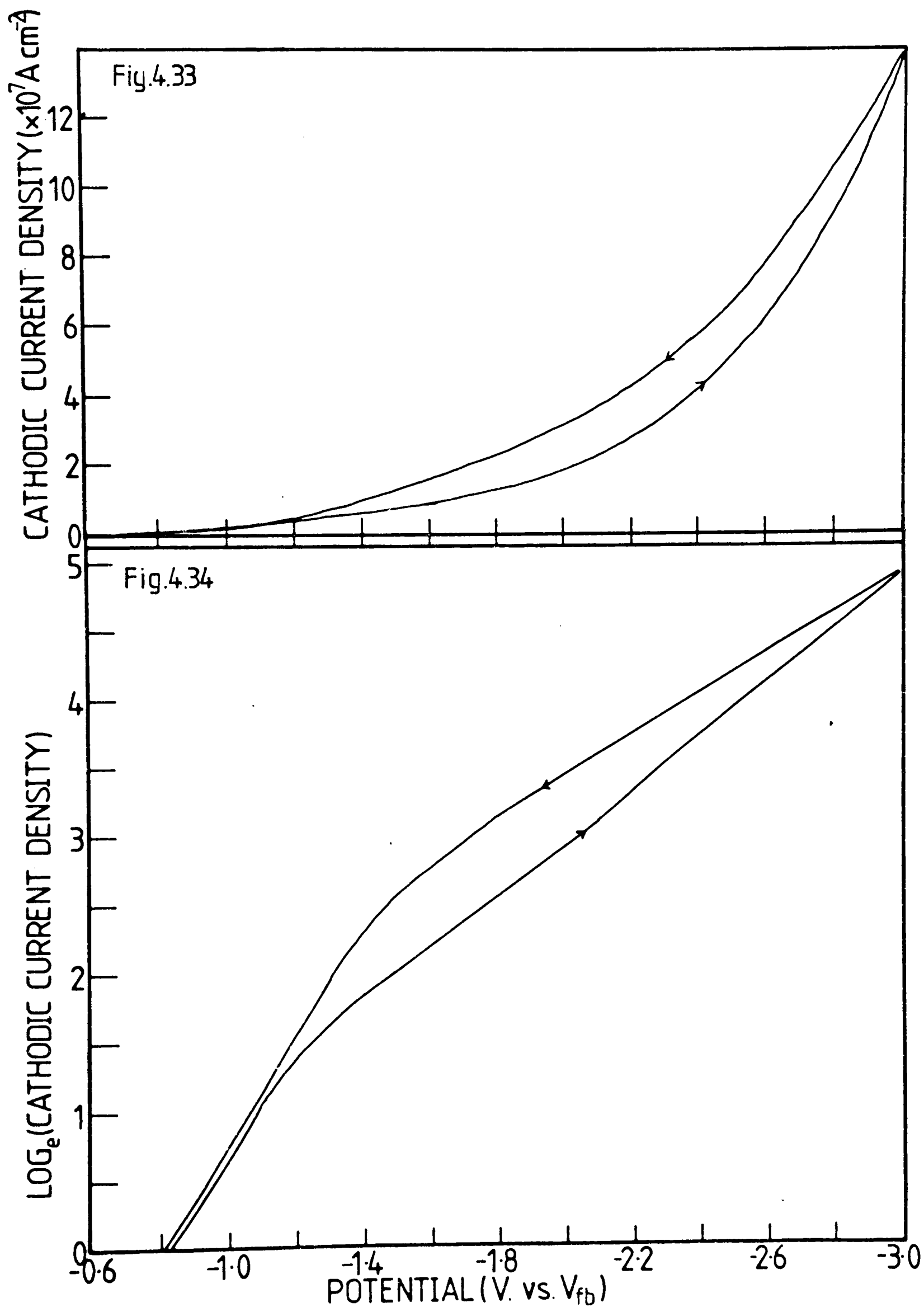
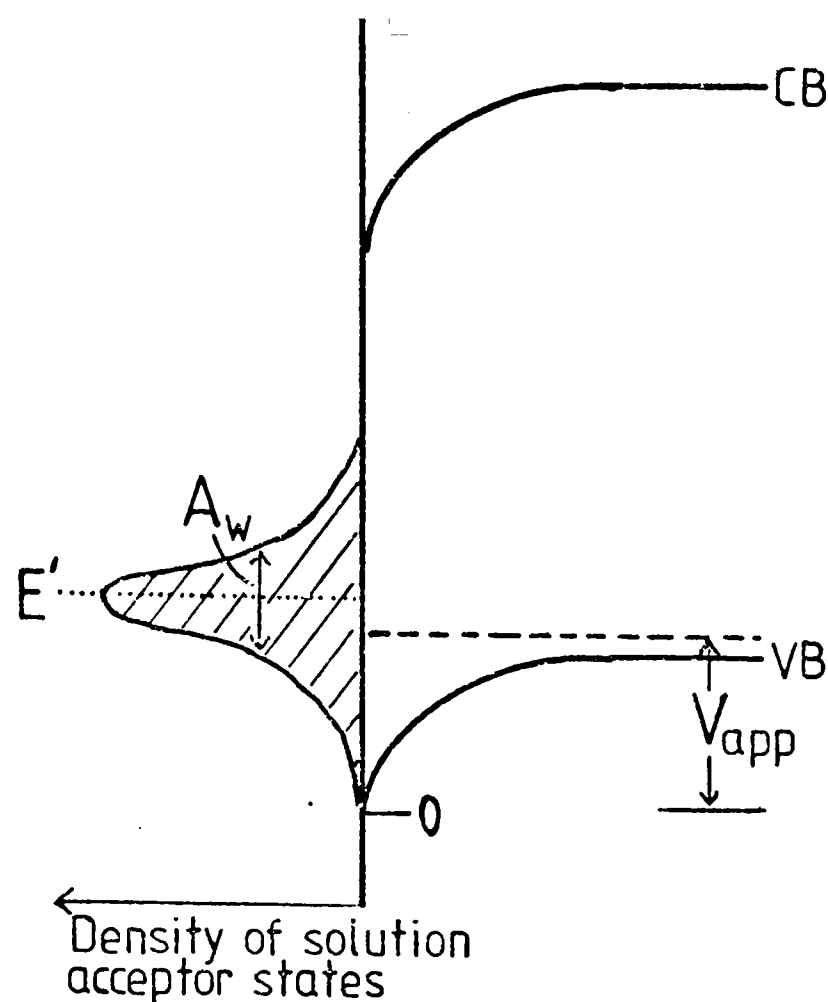


Fig.4.34 Data of Fig.4.33 plotted on a logarithmic current scale .



- where
- V_0 = Potential of Valence Band edge at the electrode surface
 - V_{app} = Applied voltage versus flat-band potential
 - V = Running variable voltage
 - E' = Potential of Maximum of Gaussian distribution of acceptor states in solution
 - A_w = Width of Gaussian

To calculate the reverse current we must integrate the contributions to the current over two different regions.

1. Below the valence band edge at the surface $V < V_0$

Here, the electron injection will be purely limited by the overlap of the distribution functions for the occupied valence band states and occupied solution states.

i.e.

$$J \propto \int_{-\infty}^{V_0} \frac{\exp\left(-\frac{(E' - V)^2}{A_w^2}\right)}{A_w \sqrt{\pi}} dV$$

2. Above the valence band edge $V_{app} > V > V_0$

Here, the injection current will be limited by the tunnelling probability through the depletion layer as well as being determined by the overlap of the distribution functions in the semiconductor and solution.

i.e.

$$J \propto \int_{V_0}^V Q_A \exp \left(\frac{-(E' - V)^2}{A_w^2} \right) \frac{dV}{A_w \sqrt{\pi}}$$

where Q_A is the tunnelling probability as calculated with the W.K.B. approximation

$$Q_A = \exp(-A \times S)$$

$$A = (V \times V_{app})^{\frac{1}{2}} - (V_{app} - V) \times \ln \left(\frac{(V_{app} - V)^{\frac{1}{2}}}{(V_{app}^{\frac{1}{2}} - V^{\frac{1}{2}})} \right)$$

$$\text{and } S = \frac{4\pi(8_m^* e_o)^{\frac{1}{2}}}{2h.(K)^{\frac{1}{2}}}$$

$$K = \left(\frac{eN_D}{2\epsilon\epsilon_o} \right)$$

These integrals may be calculated numerically with a small computer program.

A typical log J vs. V plot generated with this program is shown in Fig. 4.36 for a Gaussian positioned 1.5V above the valence-band edge and with a width of 0.2V. As can be seen, there is a considerable similarity to the experimental data of Fig. 4.34.

A number of very similar plots were generated with differing E' 's and A_w 's but the plot shown in Fig. 4.36 represents the approximate best-fit. Further experimentation with the program revealed that the majority of electron transfer takes place at energies very close to the valence-band edge - at least with materials of moderate to low doping levels where depletion-layer thicknesses are quite large (> 100nm).

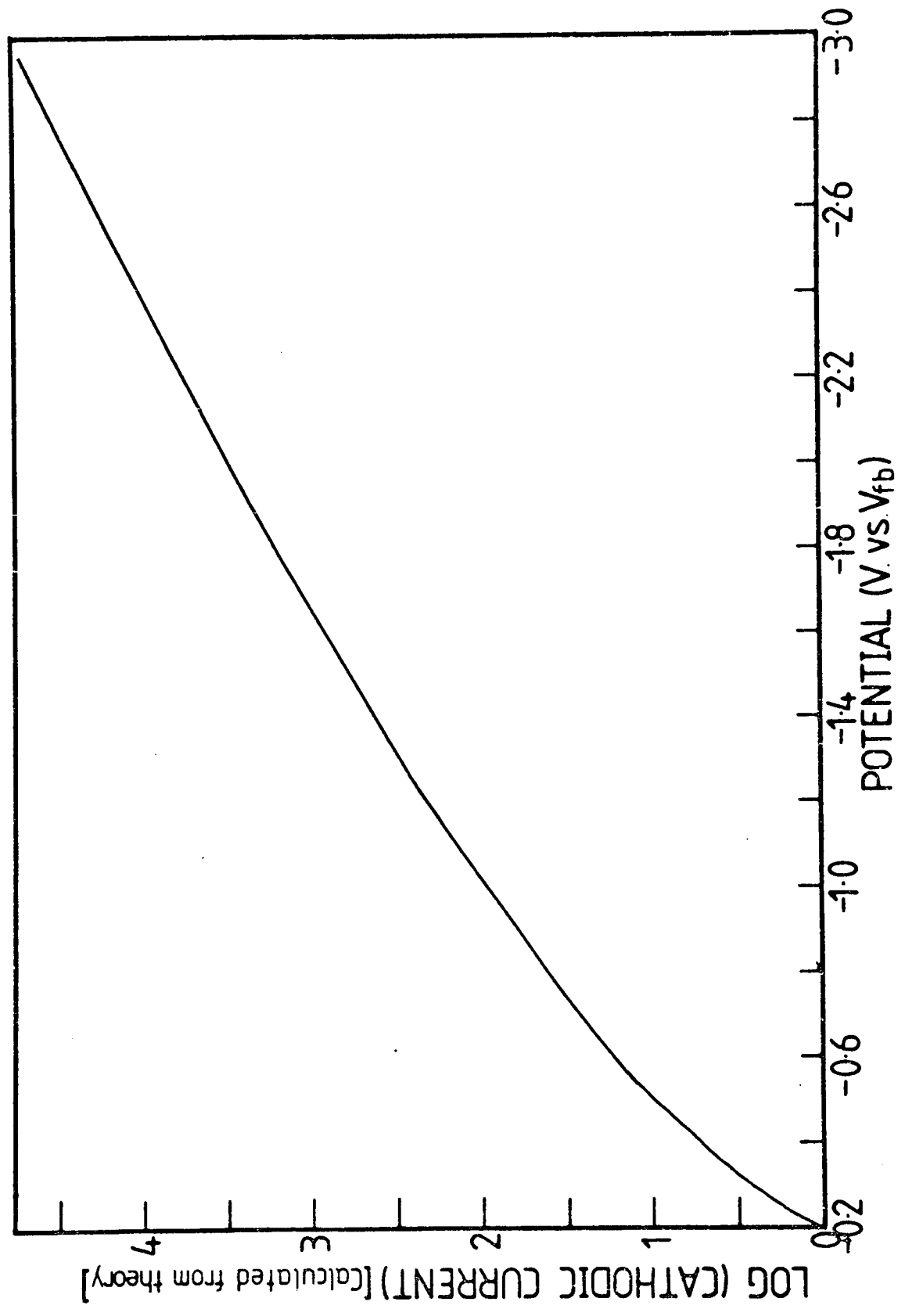
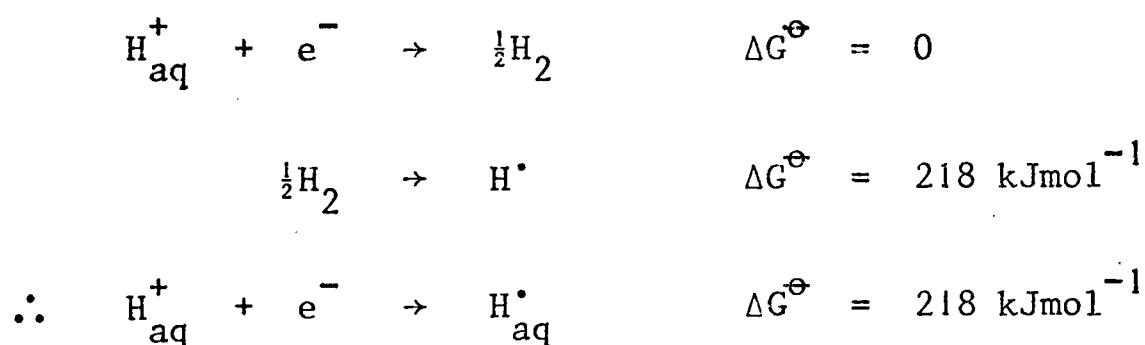


Fig. 4.36 Approximate best theoretical fit to the high sensitivity dark C.V. shown in Fig. 4.34 . For theory see text .

One very important point to note is that this theory does not include forward current, i.e. injection from solution donors into semiconductor acceptors (holes) and consequently the downturn ^{cathodic} in current observed in the experimental data at about +0.5V vs. S.S.E. is not matched well by the theoretical curve. A more detailed model is under investigation, but its application will be of only limited practical value since the dark current measurements on p-GaP are highly time and surface dependent.

In the absence of dissolved oxygen or other added oxidizing agents and no observed decomposition of the electrode the only available solution species that could support the continuous cathodic current is the aquated proton. However, the single electron redox potential for creation of an intermediate $H^{\bullet}_{aq}$ can be shown to be significantly cathodic of the overall two electron redox potential $E^{\circ}_{H^+/H_2}$.



$$E^{\circ}_{H^+/H^{\bullet}_{aq}} = \frac{-\Delta G}{2F} = \frac{218}{96500} = \underline{-2.25V}$$

However, with the flat-band potential of GaP lying at +0.65V (S.S.E), the energy of the conduction band at the surface of GaP is at -1.25V vs. S.H.E. [$E^{\circ}(H^+/H_2)$] (See Fig. 4.37). Thus creation of an aquated Hydrogen atom, even using a conduction-band electron (only present on illumination for p-GaP) would be impossible. However, the intermediate Hydrogen atom may be considerably stabilized by adsorption onto the surface of the GaP electrode. As a very rough approximation, we could consider the GaP surface to consist of Gallium or Phosphorus atoms with dangling bonds.

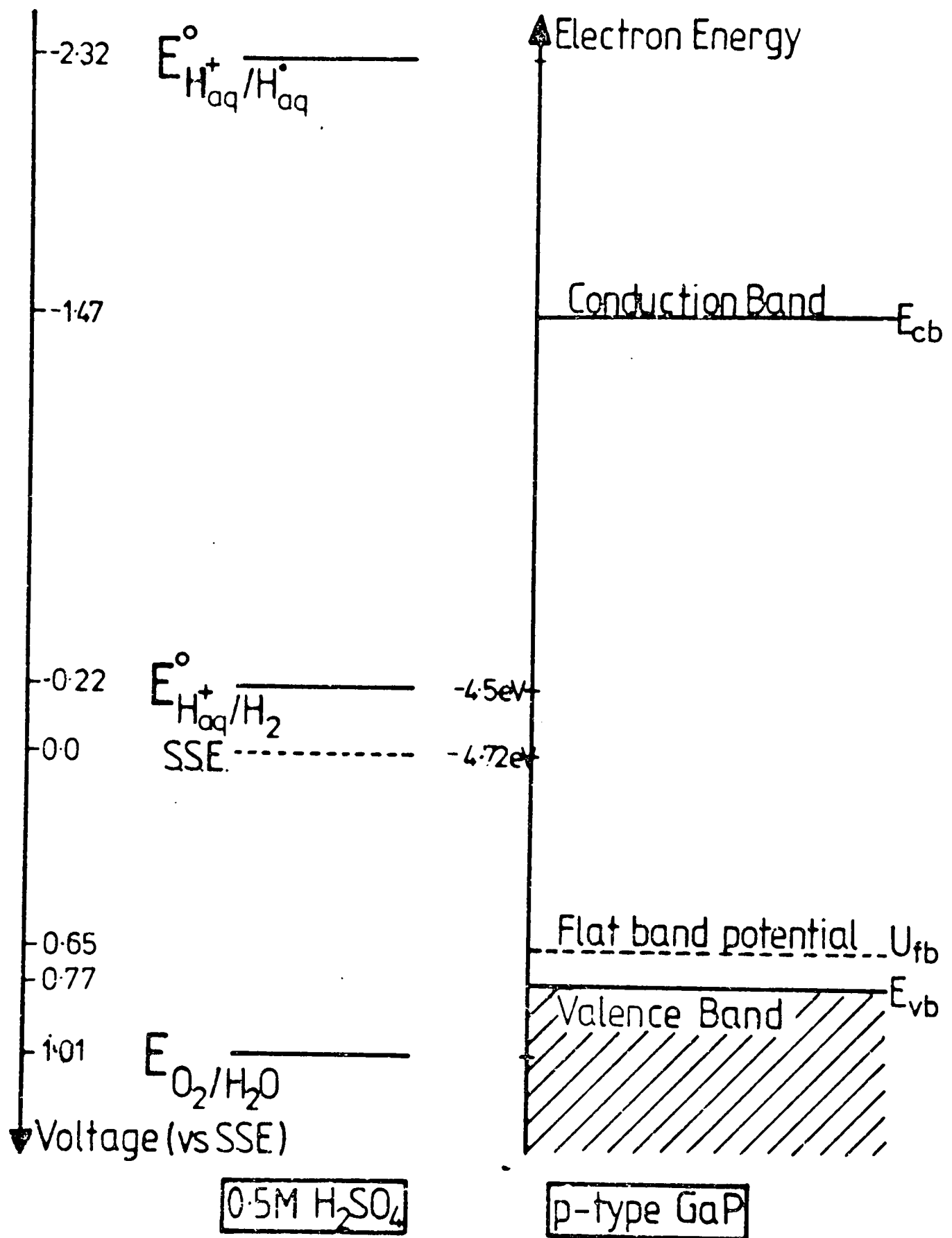
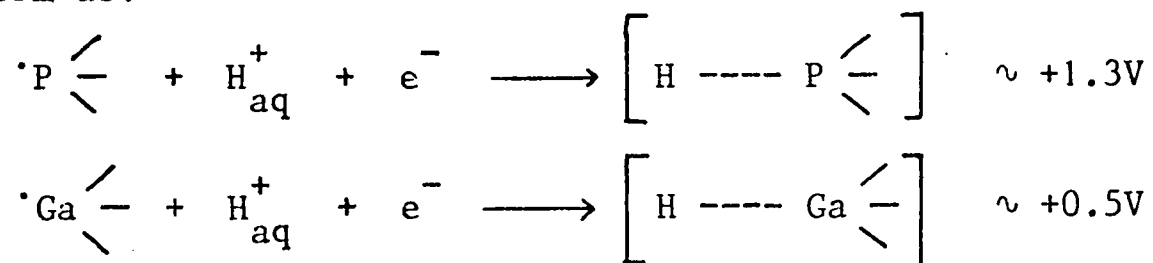
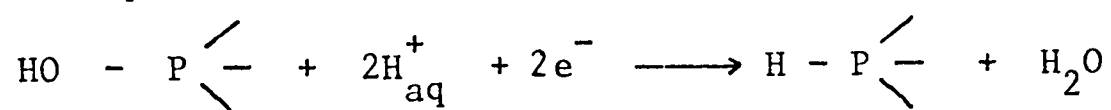


Fig..4.37 Energy level diagram for the p-GaP/aqueous electrolyte interface including thermodynamic redox potentials for appropriate aqueous redox couples .

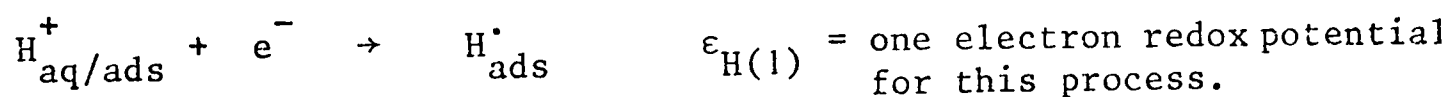
Under these circumstances, using bond strength data for Ga-H and P-H bonds we may predict limiting redox potentials for creation of an adsorbed Hydrogen atom as:-



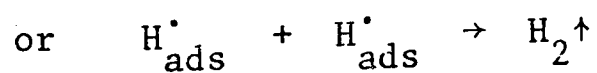
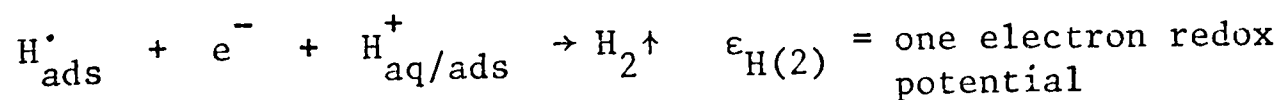
In reality, true dangling bonds would not exist at the surface of a real semiconductor in aqueous solution and it is most likely that at anodic potentials the surface will be covered with hydroxyl groups. Indeed, following the findings of a number of other groups; it may be suggested that the appropriate redox couple responsible for the observed dark cathodic currents would be:-



It is not possible to estimate a theoretical redox potential for the process but it is known that the E^0 's for similar processes e.g. $\text{H}_3\text{PO}_3/\text{H}_3\text{PO}_2$ are $\sim -0.59\text{V}$ ²⁴⁵. Since the true nature of the intermediate remains unknown, we shall continue to refer to the initial single electron process as:-



The adsorbed Hydrogen atom so formed may then be removed in one of three ways in order to allow for a continuous flow of cathodic current.



The redox potential for the first process ($\epsilon_{\text{H}(2)}$) will be, from a thermodynamic consideration, given by:-

$$\epsilon_{\text{H}(2)} - E^0_{(\text{H}^+/\text{H}_2)} = E^0_{(\text{H}^+/\text{H}_2)} - \epsilon_{\text{H}(1)}$$

and similarly, the free energy change for the atom recombination process is given by:-

$$\Delta G_{2\text{H} \rightarrow \text{H}_2} = 2F \cdot \epsilon_{\text{H}(1)}$$

The relative contribution of these two processes will thus be markedly determined by the value of the redox potential for the creation of the adsorbed Hydrogen atom. However the third possibility also deserves consideration since it is known that, in the case of Germanium, with a similar lattice parameter to GaP, Hydrogen atoms can incorporate deep into the Ge lattice following periods of cathodic polarization.²⁴⁶ Indeed, this type of process might explain the observation of the considerable hysteresis in the dark current C.V.'s of p-GaP (see Fig. 4.33). The incorporation of Hydrogen atoms into the surface region of the electrode may create additional electronic states within the space charge region of the semiconductor. This in turn could cause an enhancement in the rate of electron transfer through the depletion layer by the process of resonance assisted tunnelling, as discussed at length by Schmickler for Pt atoms incorporated into the surface of TiO_2 electrodes²⁴⁷ (see Fig. 4.38(a)).

It is also observed for the dark C.V.'s that the concentration of surface defects (arising from polishing procedures) or surface impurities (remaining from etching procedures) can significantly increase the magnitude of the cathodic dark current. It has been suggested that such imperfections may increase the density of electronic states within the bandgap of the semiconductor at the surface - such states being termed as "surface states".²⁴⁸ The probability of electron transfer through the space charge barrier may be enhanced by the presence of these surface-localized states. Electron transfer into solution (or hole injection) may then be enhanced by the mediation of these surface states²⁴⁹ (see Fig. 4.38(b)).

An alternative simpler explanation may be suggested whereby the increased concentration of surface defects itself increases the concentration of sites available for bonding to Hydrogen atoms. For example, at step dislocations the carrier atom would possess a greater affinity for bonding to solution species than those on a planar face due to the coordinative unsaturation in the former. Unfortunately no simple method exists to choose between these alternatives.

Fig. 4.38(a) Diagram illustrating the mechanism of resonance assisted tunnelling in the enhancement of cathodic dark current on p-GaP in aqueous solution .

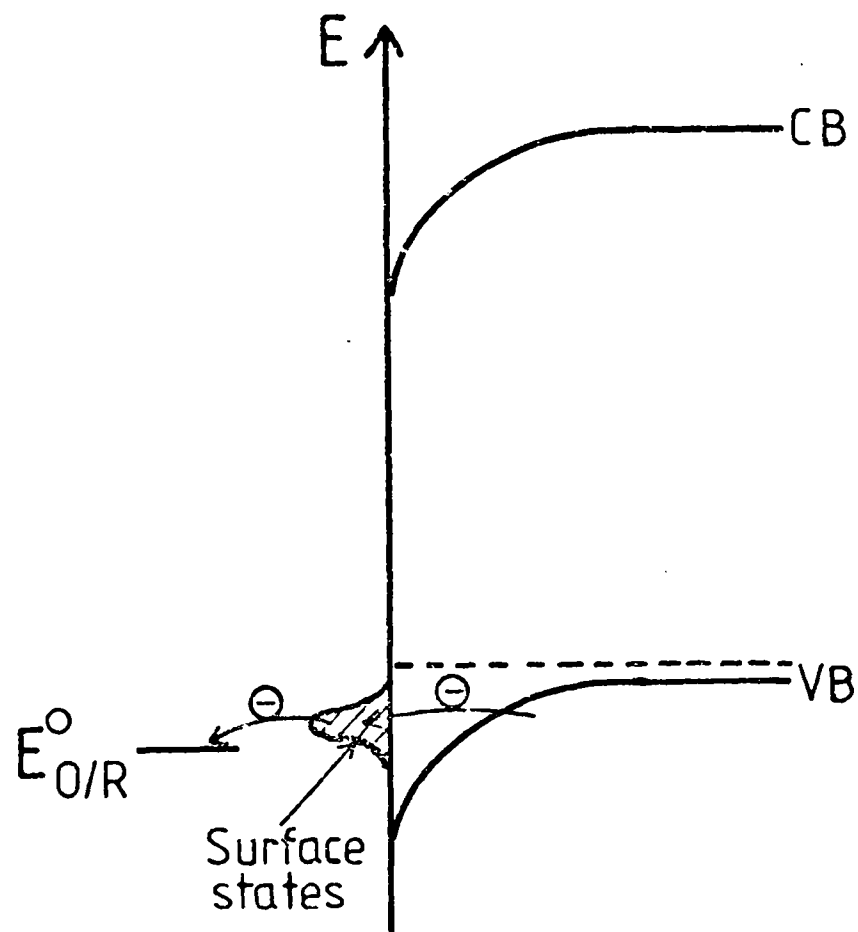
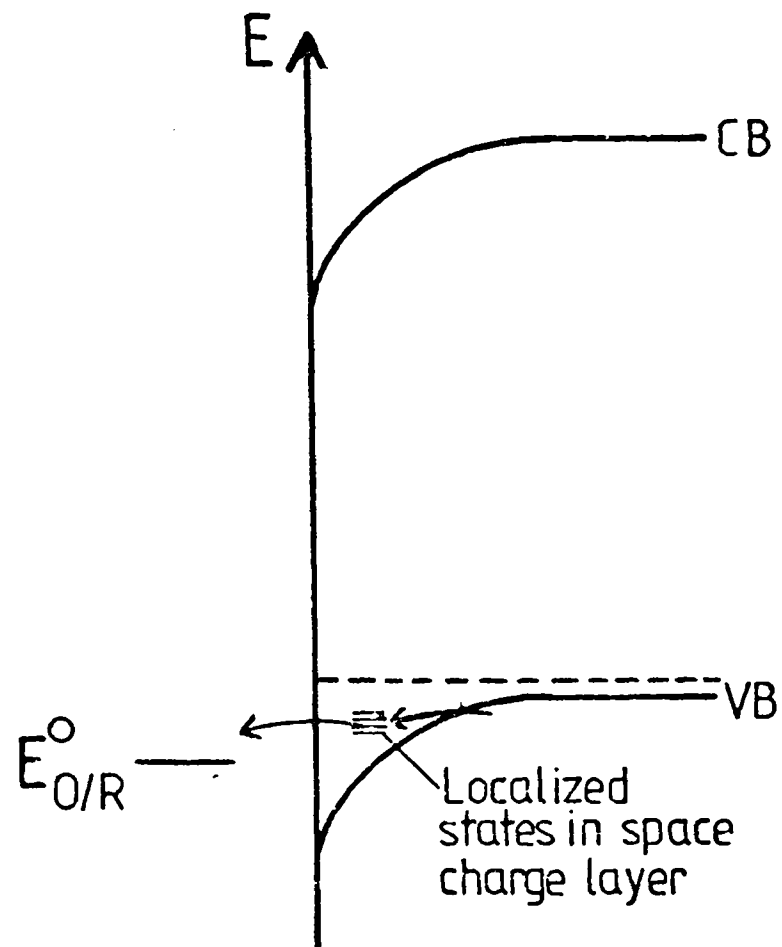
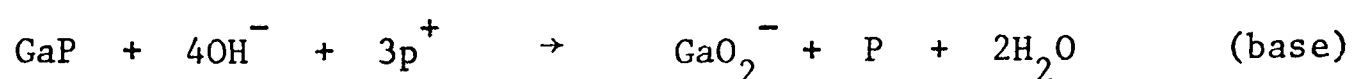
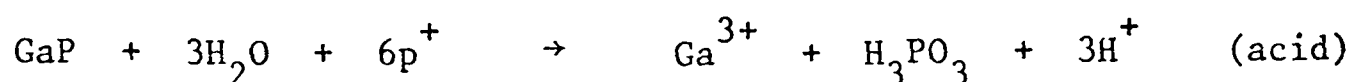
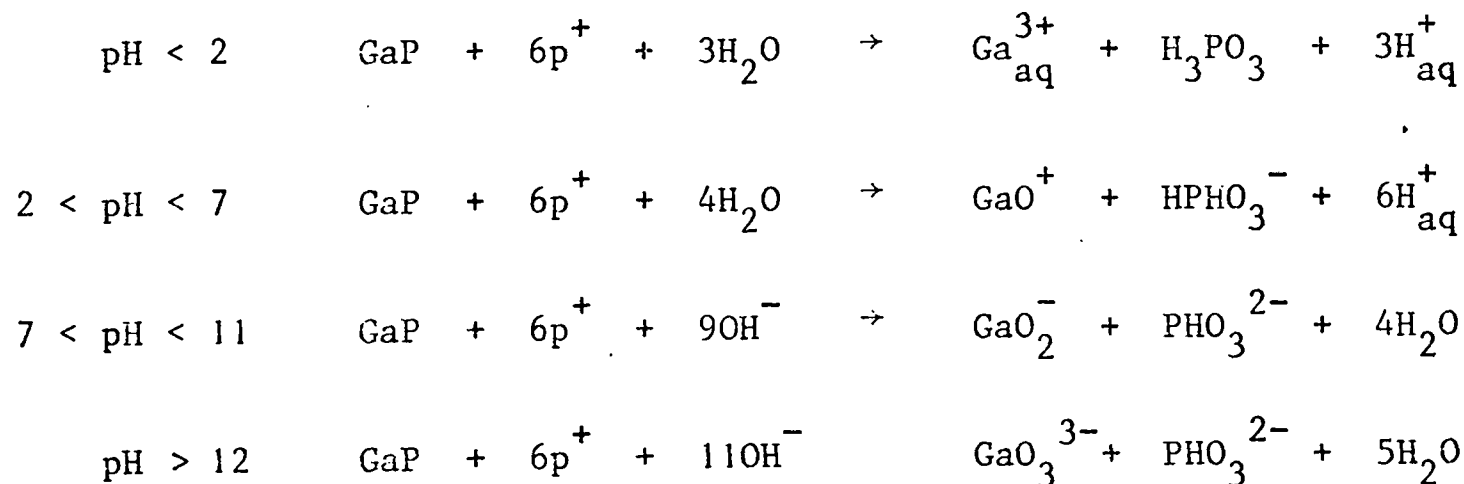


Fig. 4.38(b) Diagram illustrating the mechanism of electron transfer into solution as enhanced by the mediation of surface states .

In all solutions, there appears to be an irreversible anodic wave starting at about 0.25V cathodic of the flat band potential (e.g. at $\approx +0.4V$ in 0.5M H_2SO_4). These waves have been shown to correspond to anodic oxidation of the electrode. According to early work by Memming and Schwandt,⁹³ colorimetric determination of Gallium in solution indicated that the processes, in acid and base, respectively, were:-



More recent calorimetric determinations by Kohayakawa et al.,²⁵⁰ however, found that for acid and base, six holes were consumed per GaP unit dissolved. They concluded that for all pH's, anodic dissolution was due to an electrochemical oxidation involving the formation of the oxide of both elements present.

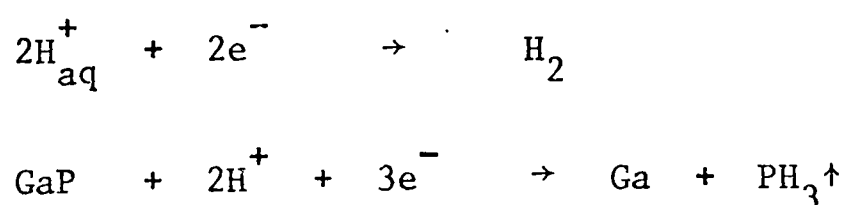


For all pH ranges passivation phenomena were observed at high anodic potentials although the potential of passivation was most cathodic, and the peak anodic current flow smallest, in the media of intermediate pH (2 < pH < 11). The reason for this is that for this intermediate pH's the solubility of the gallium oxidation products falls dramatically. Passivation occurs when the electrode oxidation currents increase to a point where the rate of dissolution of the products (in this Ga_2O_3 or $Ga(OH)_3$) becomes less than the rate of their formation. Under these circumstances, a coherent film of non-

conducting oxide is built up at the surface and further oxidation becomes limited by the transport of H_2O and/or metallic ions through the surface oxide. The latter ionic transport gives rise to the small but still continuously flowing anodic currents anodic of the passivation peak. The phenomenon was not further investigated in any detail since at these passivation potentials the electrode was biased anodic of flat band where the semiconductor was displaying the metal like properties of a degenerate semiconductor. The subject of the passivation of the III-V semiconductors has been discussed at length by workers investigating the formation of thick oxide films on semiconductors for use in MOS or MIS devices.²⁵²⁻²⁵⁴

4:7:2 Photocurrents

On illumination of the p-GaP/electrolyte interface, it is observed that there is a limiting cathodic photocurrent at the more negative potentials. This is to be expected for a p-type semiconductor reverse biased and in contact with a solution that contains a high concentration of acceptor species. In the absence of dissolved oxygen or added redox species, the only possible cathodic reactions are Hydrogen evolution or cathodic decomposition of the electrode.



Despite some evidence from the measurement of electrode weight loss and solution analysis of cathodic instability of the GaP electrodes (see Section 4.5), particularly the (100) face, the majority of the current appears to be directed into the H^{+}/H_2 couple to evolve Hydrogen gas.

However, there is a very important point to note about all the illuminated cyclic voltammograms. For example, although the measured flat-band potential of p-GaP has been measured (see Section 4:3) to be at +0.65V vs. S.S.E. in 0.5M H_2SO_4 , the photocurrent does not rise significantly until some 0.6-0.8V

cathodic of that potential. As discussed in Chapter 2 for an ideal semiconductor we should expect to see a rise in photocurrent as soon as the bands are bent to create a reverse bias. By biasing negative of +0.65V, the field created at the surface of p-GaP should separate the photogenerated electron/hole pair, sending the electron to the surface and the hole into the bulk of the electrode.

The theoretically predicted current voltage curve, calculated with the Albery/Hamnett equation of Chapter 2 (see Section 2:11), is presented in Fig. 4.39 for comparison with the results of Fig.4.2. The parameters used in this equation represent the experimentally observed values taken for p-GaP Schottky diodes and the measured dopant density as found in this work. In the saturation region negative of -0.2V, agreement is very good; but nearer to flat-band potential there is a marked deviation between predicted and measured values. In case the literature values of the various parameters are not applicable to the material used in these experiments, an iterative best-fit programme (similar to that used for the impedance analysis Appendix 2) was run on the computer in an attempt to improve the agreement. However it was still not found possible to obtain a good fit even allowing for significant recombination rates within the space-charge region (i.e. $k/k' = 5 \times 10^8$).

The Albery/Hamnett equation represents the most thoroughgoing approach to date to the quantification of the kinetics at the semiconductor/electrolyte interface based solely on the bulk properties of the semiconductor. Unfortunately it does take into account any loss processes other than those occurring within the semiconductor and thus ignores the possibility of surface recombination via localized surface states. In a paper by Wilson,²¹⁴ it was found possible to account for the deviation from the simplistic ideal photocurrent/voltage response (i.e. not allowing for recombination in the depletion layer) by the inclusion of some additional parameters relating to such surface state recombination processes. This approach was applied

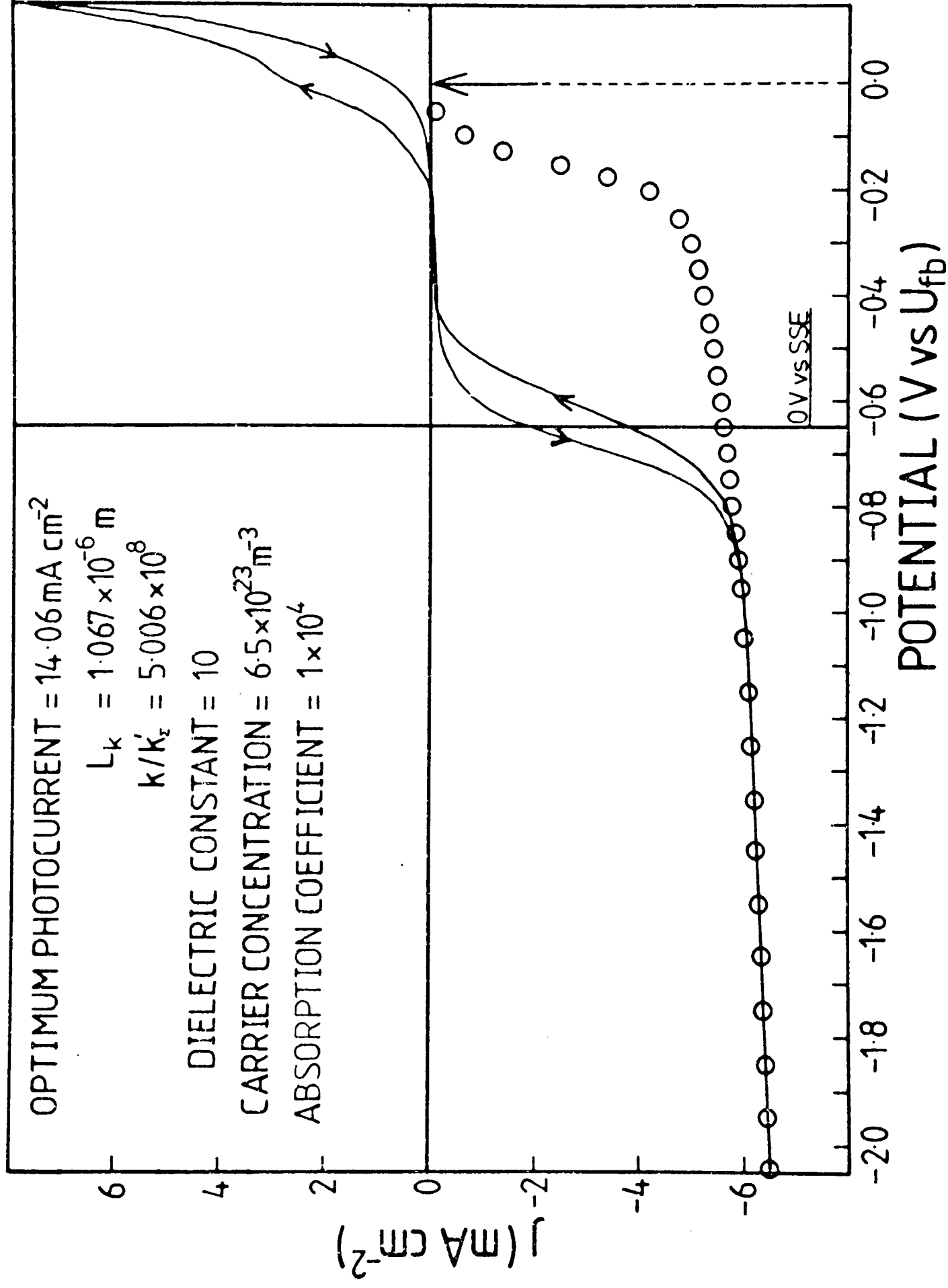


Fig. 4.39 Comparison of theoretically predicted current voltage curve calculated according to the Albery/Hamnett equation with the results of Fig.4.2 .

to the particular case of $n\text{-TiO}_2$ but the value of quantifying the recombination process was found to be limited. Nevertheless such surface state recombination may readily be qualitatively applied to an explanation of the photocurrent/voltage behaviour of p-type Gallium Phosphide.

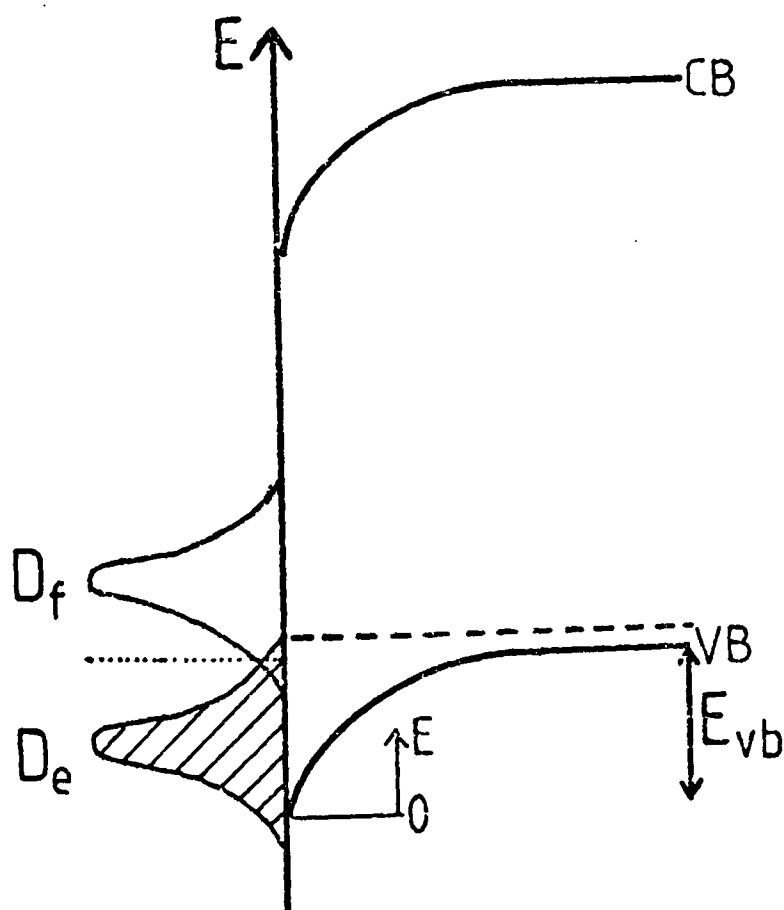
If there were a high density of surface states on the surface of p-GaP with energies just above the valence band edge, these surface states may act as parasitic recombination centres at low values of band bending as shown in Fig. 4.40.

The ability of these surface levels to act as recombination centres relies on the semi-transparent nature of the depletion layer with respect to tunnelling by the valence band holes. We may consider the distribution of holes in the valence band to be Boltzmann-like with decreasing occupancy as we proceed away from the valence band edge. Using Fig. 4.41 we may write:-

$$i_T^f = \int_{-\infty}^{\infty} N_s(E_{vb}-E) e^{-V_o-V/kT} A^* \exp[-Q(E_{vb}-E)] D_f(E) dE$$

and
$$i_T^r = \int_{-\infty}^{\infty} N_s(E_{vb}-E) A^* \exp[-Q(E_{vb}-E)] D_e(E) dE$$

Fig. 4.41



D_f = density of filled states

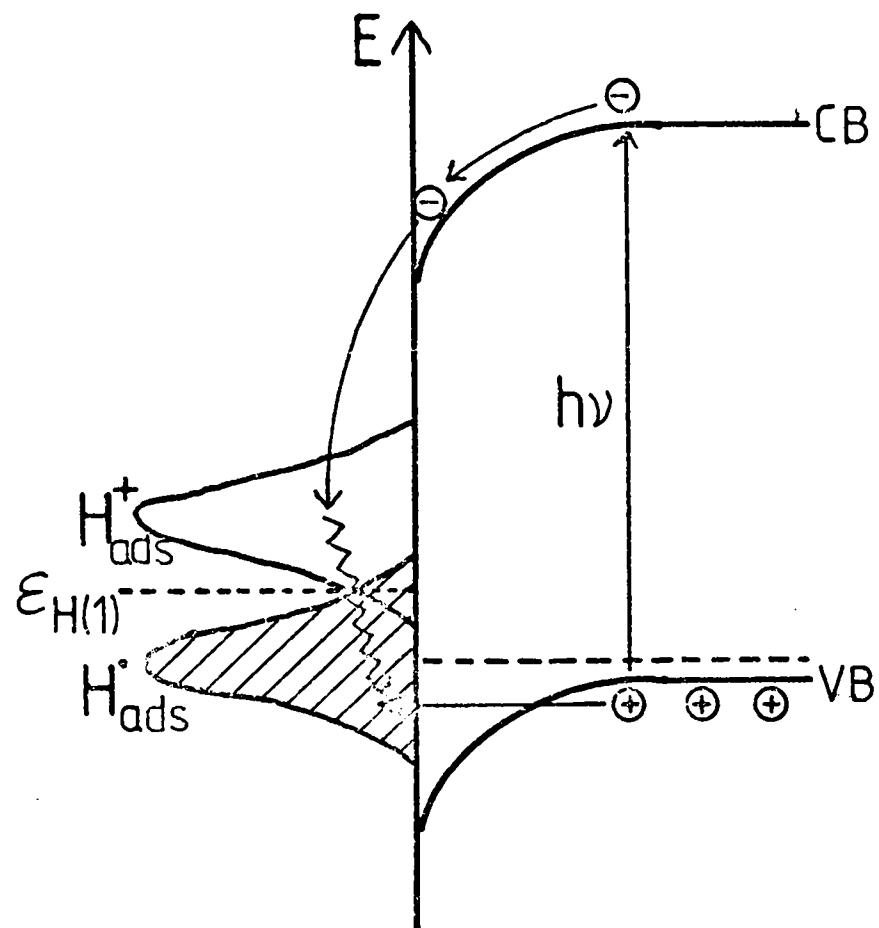
D_e = density of empty states

N_s = density of states in semiconductor

A^* = Richardson Constant

$\exp(-Q(V))$ = WKB tunnelling probability.

Fig. 4.40 Diagram illustrating mechanism of parasitic surface recombination on p-GaP via high density of surface adsorbed Hydrogen atoms .



As the semiconductor potential (E_{vb}) is made increasingly more cathodic, there will be three competing effects on the tunnelling probability for holes through the depletion layer.

1. An increase in tunnelling probability at any given energy above the valence band edge at the surface caused by the decrease in the width of the barrier at any given energy.
2. A decrease in the number of holes at any given energy brought about by the decreasing hole population of that energy level.

[Note that this is different from the variation in electron tunnelling probability responsible for the cathodic reverse current discussed in Section 4:6:1. In that case there is no competition from effect 2 above since the density of filled electron states in the semiconductor may be assumed to be approximately constant as we move away from the band edge.]

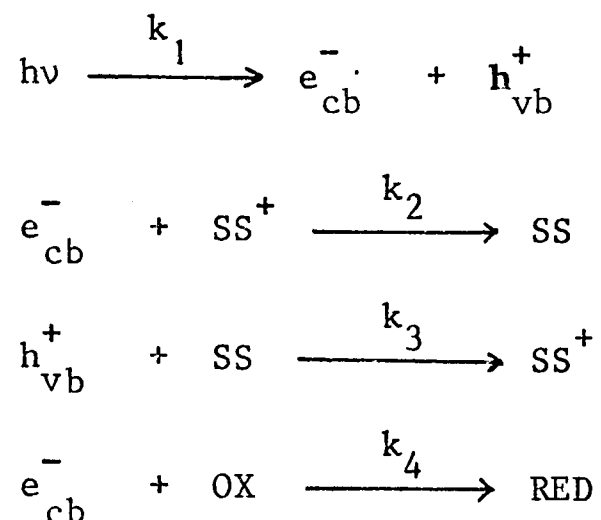
3. A third contributing factor may be the variation in density of the states of the filled levels in solution. This density of states might be expected, from the Marcus theory²⁵⁵, to have an approximately Gaussian distribution. Thus on the higher energy side there would be a fall-off in the density of states and as E_{vb} increases relative to the surface valence band level E_s , there would be a consequent decrease in forward (hole injection) current as we increase the cathodic bias in the semiconductor.

The question now arises as to whether these surface states are inherent to the surface of the polished and etched GaP electrode or are in some way induced by the electrochemical reactions proceeding at the electrode interface. Optical microscopy and electrode weight loss studies seem to indicate that no significant change in surface morphology is induced by the photo-processes over a short time scale.

Thus major changes in surface structure and consequent generation of surface recombination caused by electrode dissolution do not appear to explain the poor efficiencies near flat-band. The variation of photocurrent/

voltage response as a function of light intensity does however provide the required information for settling the above problem.

Let us take a simple kinetic model.



where e_{cb}^- = electron in the conduction band

h_{vb}^+ = hole in the valence band

SS = Surface state

OX = Oxidised solution species

RED = Reduced solution species

[] = Concentration

$$\begin{aligned}
 \frac{d[RED]}{dt} &= j \text{ (electron flux)} \\
 &= k_4(e_{cb}^-) [OX]
 \end{aligned}$$

Taking steady state approximations for the concentration of electrons at the surface and the concentration of reduced surface states we have

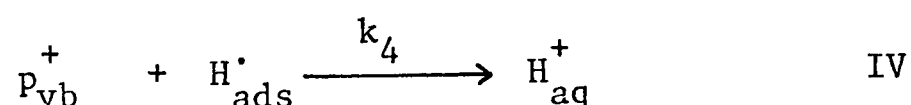
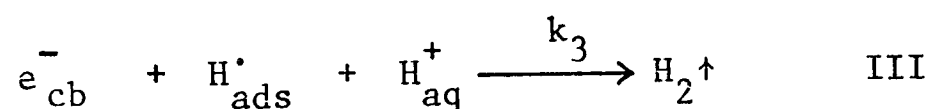
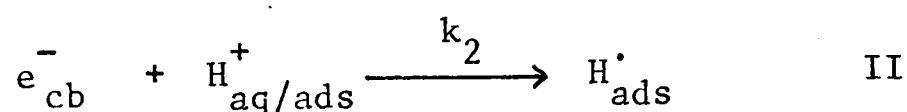
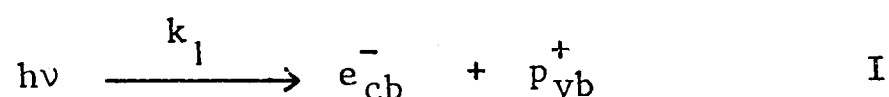
$$\frac{d[RED]}{dt} = k_1[hv] - k_3[p_{vb}^+][SS]$$

With a fixed concentration of surface states [X], we would expect that as $k_1[hv]$ increases (i.e. the light intensity increases), the photocurrent efficiency

$$\phi = \frac{k_1 - k_2[p_{vb}^+][X]}{k_1}$$

will approach 100%, i.e. the surface-state recombination process becomes saturated. This is the state of affairs familiar to solid state physicists in the operation of Schottky barrier and p-n junction solar cells. In these cases, optimum efficiency is found for the highest light intensities (hence reports of 23% solar conversion efficiency from GaAs-based solid-state devices measured in solar-focussing arrays).

If, however we consider the situation where the surface state is itself a photogenerated intermediate in the overall redox process the predictions are further complicated. For the case of Hydrogen evolution on GaP we may propose



Unfortunately no simple solution exists for this kinetic structure, so discussion is forced to remain qualitative only. As mentioned previously the redox potential for the generation of Hydrogen atoms will be extremely unfavourable unless the Hydrogen atom is strongly adsorbed on the electrode surface. In addition we require the one electron redox potential for this first step $\epsilon_{H(1)}$ to be approximately equal to the reversible two-electron redox potential for H_2 evolution ($\approx -0.24V$ vs. S.S.E.) This is to avoid the necessity for excess overpotential for rapid kinetics of either the first or second steps in the Hydrogen evolution reaction.

The Hydrogen evolution reaction may then be completed by the combination of a surface Hydrogen atom, solution proton and conduction band electron where the one electron potential for this process $\epsilon_{H(2)}$ is given by

$$E_{H^+/H_2} - \epsilon_{H(1)} = \epsilon_{H(2)} - E_H.$$

The creation of surface-bound Hydrogen atoms, however, may create filled electronic levels at the surface of the electrode. As shown in Fig. 4.40 valence band holes may then tunnel to these surface states (Reaction IV). The combination of processes II and IV is to create an alternative surface recombination route for the photogenerated electron-hole pair resulting in severe loss of photo-efficiency. According to the above reaction sequence, the net photocurrent flowing is

$$i = 2FA_e k_3 [e_{cb}^-] [H_{ads}^\bullet] [H_{aq}^+]$$

where A_e is the electrode area and reaction k_3 is assumed rate determining

Moreover:-

$$\frac{d[H_{ads}]}{dt} = k_2 [e_{cb}^-] [H_{aq}^+] - k_3 [e_{cb}^-] [H_{ads}^\bullet] [H_{aq}^+] - k_4 [p_{vb}^+] [H_{ads}^\bullet]$$

$$\frac{d[e_{cb}^-]}{dt} = \eta k_1 - k_2 [e_{cb}^-] [H_{aq}^+] - k_3 [e_{cb}^-] [H_{ads}^\bullet] [H_{aq}^+]$$

where η is the efficiency of transport of a photogenerated hole to the surface (as given by Alberly/Hamnett equation for an ideal semiconductor)²¹⁸. Therefore the net photocurrent depends sensitively on the light intensity, I_0 through k_1 and the density of occupied surface states $[H_{ads}^\bullet]$. At higher light intensities, we may expect a build-up in the concentration of Hydrogen atoms at the surface leading to a greater efficiency loss through the hole tunnelling recombination process (IV).

The data of figures 4.18 and 4.22 provide strong evidence in support of this model since it is seen that in the range of potential (0-0.6V) there is a strongly non-linear variation of photocurrent efficiency as a function of light intensity. Cathodic of this range, the photocurrent increases linearly as a function of light intensity over four orders of magnitude. In this saturation region, efficiency is purely a function of the bulk properties of the semiconductor as is confirmed by the good theoretical fit shown previously in Fig. 4.39.

Using this model we may also explain the hysteresis observed in the photocurrent voltage plots run at low light intensities (e.g. Figs. 4.12 to 4.17). At the completion of an anodic sweep, reaction IV has essentially cleared the surface of all $H_{ads}^{\bullet}$ since, as flat-band is approached, the thermal barrier to hole injection into the surface approaches zero. At low coverage of $H_{ads}^{\bullet}$, but with a negative band bending (i.e. small reverse bias), the rate of photogeneration of $H_{ads}^{\bullet}$ is initially greater than the rate of elimination through reactions III and IV. A net creation of $H_{ads}^{\bullet}$ provides a component to the cathodic photocurrent that is not directly correlated to the evolution of Hydrogen gas. At sufficiently low light intensities (I_0), the cathodic sweep rate may be fast enough for this component to make a major contribution to the photocurrent until the potential is raised to a point where the tunnelling rate through the surface barrier falls significantly such as to prevent the surface state recombination reaction (k_4). In this case, the photocurrent will appear to saturate at potentials only a little cathodic of flat-band as predicted for the ideal semiconductor/electrolyte interface.

However, at greater light intensities and/or lower sweep rates, reaction IV becomes increasingly competitive in the voltage range immediately cathodic of flat-band. Fig. 4.18 reveals the steady transition from apparent ideal photocurrent/voltage behaviour at very low light intensities to the highly non-ideal behaviour at high light intensities similar to the d.c. cyclic voltammograms. At lower light intensities, the non-ideality in the PCV plot is in evidence only for the anodic-going sweep, caused by the build-up of $H^{\bullet}$ atoms whilst the electrode potential is in the cathodic saturation region (0 to -1.0V). At higher light intensities the rate of $H^{\bullet}$ generation is much faster so that the recombination pathway (IV) becomes significant at a much earlier stage of the sweep. Indeed with sufficient light intensity, the photocurrent efficiency can consequently fall on the cathodic-going sweep giving rise to the unique hysteresis seen in the third and fourth PCV's of Figure 4.18.

It is particularly important to be clear that the observations of Fig. 4.18 are only apparent for non-steady state measurements. Potentiostatic photocurrent measurements over the same potential range are far less revealing than the results taken from cyclic potential sweeps. Similarly any quantitative theoretical fit to the shapes of the photocurrent curves would strictly speaking require non-equilibrium kinetics. At this present stage due to the complex nature of the photoprocesses on the surface of p-GaP no detailed attempt will be made to obtain such a quantitative fit without appreciable further work.

One further piece of evidence from the photocurrent measurements remains to be explained. That is the magnitude of the anodic enhancement seen in the d.c. C.V.'s just cathodic of the main dissolution wave. To date we have only considered that the Hydrogen atoms would be likely to build up to a maximum of one monolayer. However, if one integrates the magnitude of reoxidation charge corresponding to the anodic enhancements, one finds that it varies from about $10^{-4} - 2 \times 10^{-3} \text{C}$. This is equivalent to $10^{-9} - 2 \times 10^{-8} \text{F}$ i.e. 10^{14} to 2×10^{15} electrons. With a surface atomic density of $\approx 10^{14} \text{cm}^{-2}$ we see that these current enhancements can be greater than one monolayer of surface reoxidation even for these continuously cycling C.V.'s.

However, if we potentiostat the electrode $\sim 1\text{V}$ negative of flat-band for periods of 1 min - 1 hour, the anodic enhancements can then approach an equivalent of 20-200 monolayers of one electron redox agent (dependent on crystal surface orientation). The reproducibility of these sweeps and the non-appearance of Gallium in solution following long periods of cathodic photocurrent verifies that these reoxidations cannot correspond to reoxidation of electrode dissolution products.

This may only be explained if Hydrogen atoms can actually penetrate the surface of the GaP crystal. In the case of Germanium with a lattice parameter of $5.45\text{\AA}$, evidence was found for Hydrogen atom incorporation into the lattice following periods of cathodic polarization.²⁴⁶ It would

thus be expected for GaP with a cubic lattice parameter of $5.65\text{\AA}$ that a similar absorption of the Hydrogen atoms may take place. Since the $\text{H}^\bullet$ atom is uncharged, the only driving force for its diffusion into the lattice will be the concentration gradient set up at the surface. When the electrode is returned to anodic potentials once more following a period of cathodization, the surface becomes depleted of $\text{H}^\bullet$ atoms by reoxidation at the electrolyte interface and so the concentration gradient is reversed resulting in a net $\text{H}^\bullet$ migration to the surface. It may be possible, by following the anodic current transient of $\text{H}^\bullet$ reoxidation to determine the diffusion constant of the Hydrogen atoms. However, no simple model has yet provided a satisfactory fit with the results.

To complete our kinetic model for H_2 evolution in GaP we must therefore include one further reaction



There may be two consequences of this surface equilibrium. Perhaps the most important is that the Hydrogen atoms within the space charge region may actually mediate the hole tunneling process resulting in increased rates of recombination. Such resonance assisted tunneling through the mediation of localized states in the space charge region has been suggested by Schmickler et al. for Pt doped TiO_2 films and has also been treated theoretically by him.²⁴⁷ In that case the concentration of space charge states is constant, but in our case it appears that this is not so since the $\text{H}^\bullet$ atoms are so mobile. Hence in our system considerable further complications will be necessary to utilize the Schmickler theory.

4:7:3 Surface variations in Dark Currents, Photocurrents and

Electrode stability

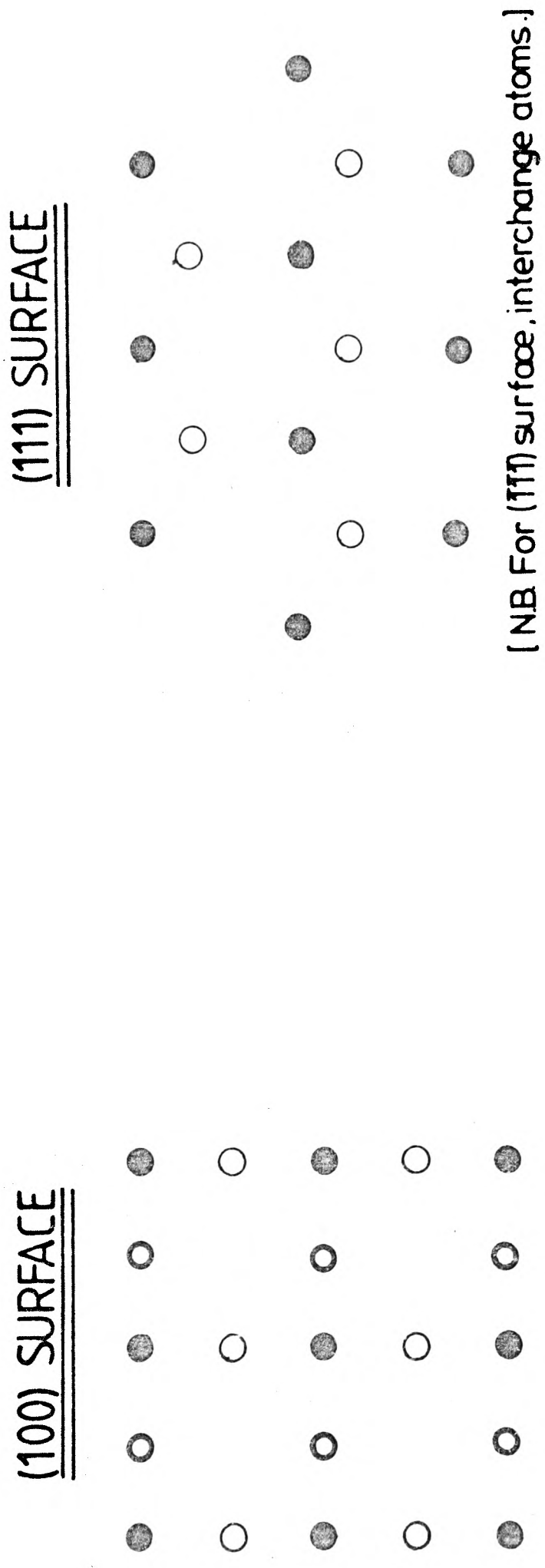
It was noted in the results section that there was considerable variation in four features of the electrochemistry of p-GaP as a function of crystal orientation.

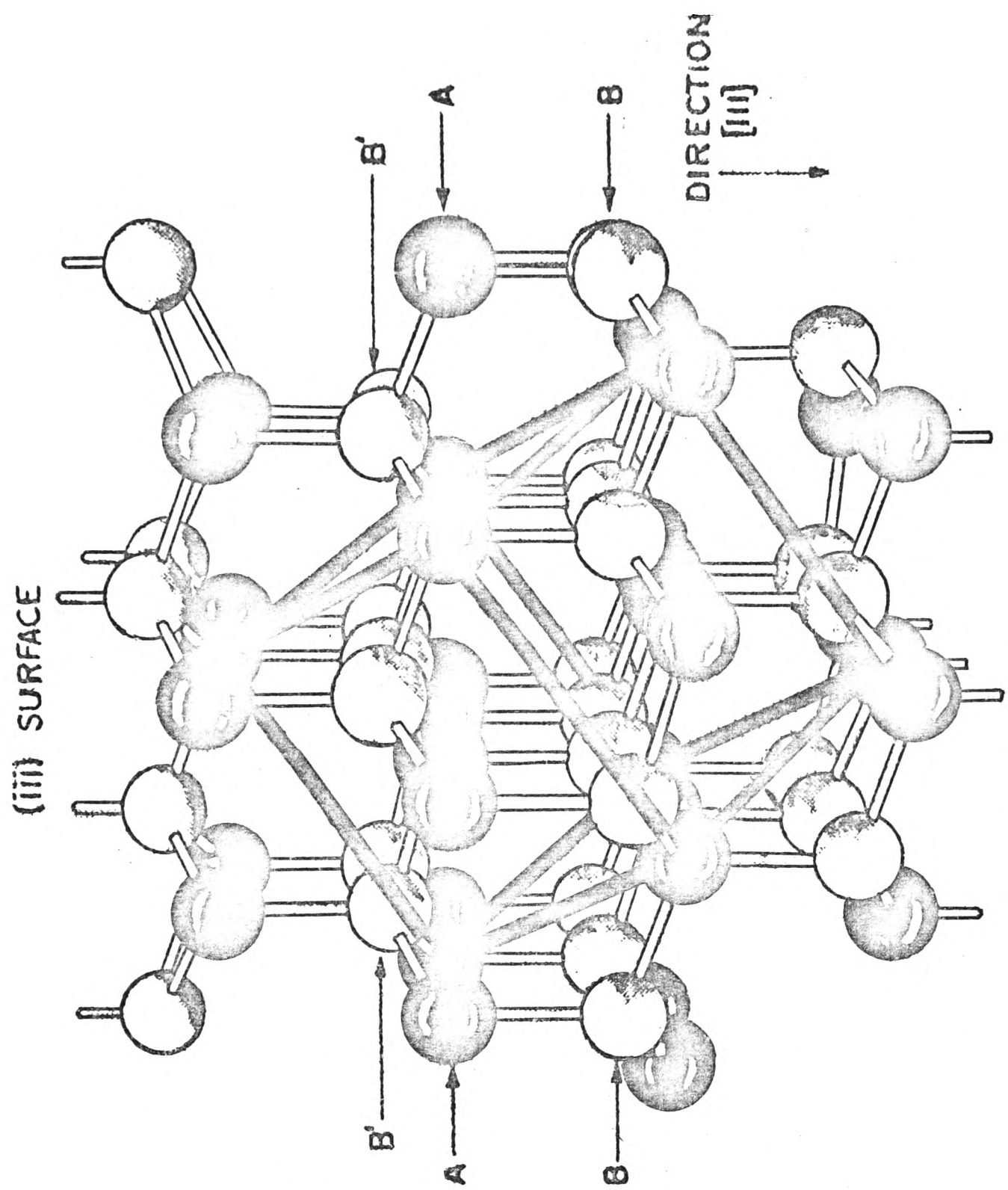
- (a) anodic dark current at a given voltage (due to electrode anodic dissolution)
- (b) magnitude of 'anodic enhancement' on illumination (H^+ reoxidation)
- (c) photocurrent onset potential (with continuous and chopped illumination)
- (d) long-term cathodic stability.

Figure 4.42 shows the nature of the ideal (and unrearranged) crystal faces for the three orientations used. It can be seen that ideally, the (100) surfaces can consist of either A or B atoms. However, since we can be fairly certain that real surfaces will not be atomically flat(!), real (100) surfaces will consist of equal numbers of A and B atoms each doubly bonded to the rest of the lattice. However, for the (111) orientation we will find that there is a difference between parallel (111) surfaces, designated (111) and $(\bar{1}\bar{1}\bar{1})$ in the diagram. The outermost atom layer in each surface consists of either group III or Group V atoms which are triply bonded to the lattice. This results from the fact that the (111) surfaces can be created only by cuts between planes such as AA and BB (Fig. 4.42b) where atoms are singly bonded to one another. A surface configuration containing atoms only singly bonded to the lattice, resulting, for instance, from a cut AA-B'B' is not stable. The origin of the differential etching characteristics used to distinguish the two (111) faces has been shown to be related to the differing mechanisms and rates for dissolution around dislocations in the lattice. Indeed it is the enhanced etched rates around dislocations at the Ga(111) surface that gives rise to the etch pits seen as the "orange peel" effect observed from the $K_3Fe(CN)_6$ etch^{239, 256} (see Section 3:6:3)

The influence of surface orientation is most pronounced in relatively slow reactions where the surface atoms partake in the rate-determining step such that kinetic considerations are more pertinent than the thermodynamic considerations. Indeed very little variation is to be expected for surface free energies as a function of crystal orientation. The

Fig. 4.42(a) Schematic diagram showing the idealized nature of the atomic composition for the (100) , (111) and (111) surfaces of GaP .





(iii) SURFACE

Fig. 4.42(b) The crystal structure (zincblende) of GaP , the unit cell is indicated . group III atom ; group V atom . Layers A,B and B' referred to in text .

etching rates of the various faces in oxidizing media have been shown to lie in the order $(\bar{1}\bar{1}\bar{1})P > (100) > (111)Ga$. In fact, and not surprisingly for the electrochemical oxidation (dissolution), the ordering of the magnitude of anodic dark currents at any given potential is also $(\bar{1}\bar{1}\bar{1})P > (100) > (111)Ga$. It is most likely to be related to the fact that the Group V element possesses an unshared pair of electrons and so attack by the oxidizing agent will be most rapid at this point. The matter has been discussed at greater length by Gatos and Lavine.^{238,256}

For the anodic enhancement following illumination, one would expect that the relative ordering would relate to the relative concentrations of sites that strongly adsorb the Hydrogen atom. Since we expect the P-H bond to be the stronger ($P-H = 343 \text{ kJ mol}^{-1}$ and $Ga-H < 274.1 \text{ kJ mol}^{-1}$) the ordering $(\bar{1}\bar{1}\bar{1})P > (100) > (111)Ga$ is again in agreement with the predictions. Although once the H atom enters into the electrode surface, crystal orientation is no longer important, electrodes with higher surface H_{ads}^* concentration will possess steeper concentration gradients for building up the bulk H^* concentration. Thus the nature of the surface will still be the governing factor.

Variations from acid to base (Figs. 4.1-4.6) and in particular the larger anodic enhancements in base rather than in acid are not readily explained and in any case may relate to microscopic variations in surface chemical composition (presence of oxide etc.). This would require considerable further investigation.

The ordering of d.c. photocurrent onset potential is complicated by the variation in hysteresis behaviour from surface to surface and from one electrolyte to another. It must therefore suffice to realize that the highly complex nature of the competition between the various rate constants for Hydrogen evolution and tunneling rates would be expected to reveal itself in considerable variation of photocurrent onset as a function of electrode surface. Indeed potentials of photocurrent onset from electrodes with same crystal orientations reveal considerable diversity.

Finally on the subject of variations in behaviour for different electrode surfaces, it was noted in Section 4:5 that the (100) surface revealed extensive cathodic corrosion in acid and neutral solutions during long-term illumination tests. Some surface roughening effect was also seen for the $(\bar{1}\bar{1}\bar{1})P$ surface, but no Gallium was observed on the surface or detected in aqueous solution. It thus appears that the (100) surface is the most unstable with respect to cathodic corrosion. This would be expected on the basis that atoms on the (100) surface are only bonded to two lattice atoms whereas surface atoms on (111) are bonded to three other lattice atoms.

SECTION 4:8 DISCUSSION OF A.C. RESULTS

4:8:1 Impedance Analysis of the p-GaP/electrolyte interface

For an ideal reverse biased semiconductor/electrolyte interface one might hope to model the a.c. impedance of the junction by a simple two-component model (Fig. 4.24a).

Here R_b represents the total resistance of solution, electrode and contacts and C_{sc} is the space charge capacitance of the semiconductor. As discussed in Chapter 2 Helmholtz capacitance and contributions to capacitance from the counter electrode will not be significant since for the series combination of capacitors the smallest capacitance (in this case the space charge capacitance) dominates. No account is taken in this circuit for any passage of d.c. current through the system as the ideal diode-like semiconductor/electrolyte interface passes no reverse current.

As seen in section 4:4 and figure 4.23 the Mott Schottky graphs, constructed using admittance data analyzed according to the above model circuit, do not show ideal behaviour particularly within 0.8V of the extrapolated flat-band potential. There is also considerable frequency dispersion in the gradient of the straight line portions such that doping

densities cannot be accurately estimated. Allowance for passage of Faradaic current by the inclusion of a parallel resistance R_f as in circuit 4.24(c) produces no improvement in the fit. Gomes et al.²⁰⁶ have suggested the inclusion of a frequency dependent capacitance 4.24(d) in place of C_{sc} which did improve the theoretical fits to the experimental impedance response of the p-GaP electrode. However, there is no simple way of attaching any physical significance to such a frequency dependent capacitance so this model was not further investigated.

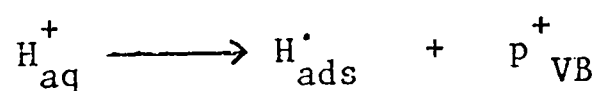
The circuit 4.24 (e) was suggested as a good model representing the semiconductor space charge and electrolyte double layer capacitances in series. With the increased number of variable components the fits were improved but unfortunately the secondary requirement that the squared reciprocal capacitance should follow the Mott-Schottky relationship failed with the results analyzed according to this circuit structure. A further problem arose with this circuit such that the degeneracy of components in the system caused computer fitting oftento leadto oscillations within the programme.

Circuit 4.24(f) provided the best fits to the experimental data and some physical significance can be attributed to the various components. As before R_b represents the solution + bulk semiconductor resistance. C_{sc} also represents the space charge capacitance (assumed to be much smaller than the capacitance of the Helmholtz layer). R_p then represents a combination of the resistance of the space charge region and the resistance to passage of current across the interface (Faradaic resistance), the latter inversely relating to the rate constant for electrochemical reactions at the electrode interface. The additional two components in parallel with the space charge capacitance R_{ss} and C_{ss} can be related to the presence of localized states at the semiconductor surface which also may store charge and hence contribute to capacitance. In this manner C_{ss} relates to the

number of surface states present and the product $R_{ss} C_{ss}$ relates to the time constant of the surface states - i.e. the kinetics for transfer of electrons to and from the surface states.

As we have already seen analyses using the simple two-component model revealed considerable frequency dispersion. This may now be accounted for by the varying contribution to interfacial capacitance from the surface states at different frequencies. Supporting this concept of constant kinetics for the surface states it is found that as a function of voltage the product $R_{ss} \cdot C_{ss}$ does indeed remain approximately constant to within 10%.

Perhaps most important to arise from this five-component analysis is that the surface state capacitance reveals a peak at around 0.3-0.4V but with a width of about 0.4V. This shows a striking correlation with the earlier prediction of a band of surface states lying just above the valence band which cause the high recombination rates at potentials between 0.6 and 0V vs. S.S.E. Of course it must be remembered that these detailed impedance analyses are made on results taken in dark conditions. Thus it would be expected that the density of surface states found from the a.c. data would not correlate with that predicted from the photocurrent measurements. Nevertheless we would still expect surface states due to Hydrogen atoms to be present in the dark because of the small ongoing dark current



4:8:2 The 'true' meaning of surface states on p-GaP

When surface states have been discussed previously in the literature they have been referred to and pictured as electronic energy levels localized at the surface of the semiconductor at a semiconductor/electrolyte interface. As has been shown with this work these so-called surface states should really be pictured as chemical entities since addition or removal of electrons from localized states must correlate with a reduction or

oxidation of some singular chemical species - in this case an adsorbed proton or hydrogen atom. To what then does the peak in surface state capacitance really refer? In order to observe a differential capacitance effect of the surface states there must be both oxidized and reduced species present to allow for simultaneous electron injection and removal. This is analagous to the observation of a peak in a.c. cyclic voltammetry of metals corresponding to the product of the probabilities for reducing and oxidizing the solution redox couple. To make this clearer in Fig. 4.43 the hypothetical density of states plots are shown for the acceptor species H_{ads}^+ and donor species H_{ads}^* on the same energy diagram as the semiconductor valence and conduction bands.

Thus, we will see a peak in surface state capacitance at a certain potential when we have the maximum joint concentration of H^+ states and H^* states adiabatic with the top of the valence band (the most probable energy of valence band holes) at that potential. Thus to use a concept introduced by Gerischer in 1975²⁵⁷ the surface state peak really corresponds to an energy spectrum of joint electron exchange density for oxidation and reduction reactions.

Supporting this interpretation for the peak in surface state capacitance is the observation that after long periods of dark cathodic bias ($< -1.0V$ vs. S.S.E. in H_2SO_4) and return to $\sim +0.4V$ the admittance signals actually increase for a while before coming to equilibrium over about 10-15 minutes. Diagram 4.44 illustrates the explanation. After biasing cathodically for long periods the surface will become rich in H_{ads}^* and relatively poor in H_{ads}^+ . Initially the joint density of states adiabatic with the electrode Fermi level is small and dark current must flow corresponding to the reoxidation of the H_{ads}^* before the two surface concentrations become more equivalent and the joint density of states becomes larger.

Fig.4.43 Diagram illustrating hypothetical density of states for surface bound H_{ads} and $H_{ads}^{\bullet}$ relative to the semiconductor band edges. Also shown is the "energy spectrum of joint electron exchange density". For explanation, see text.

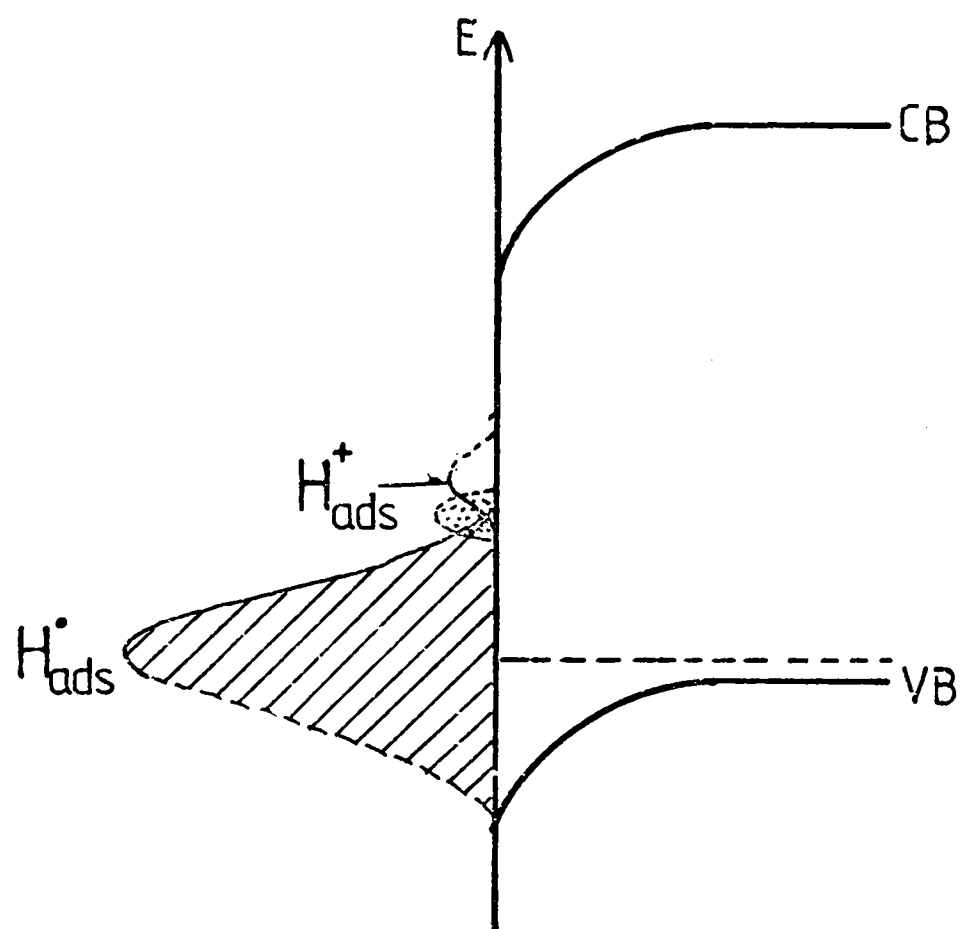
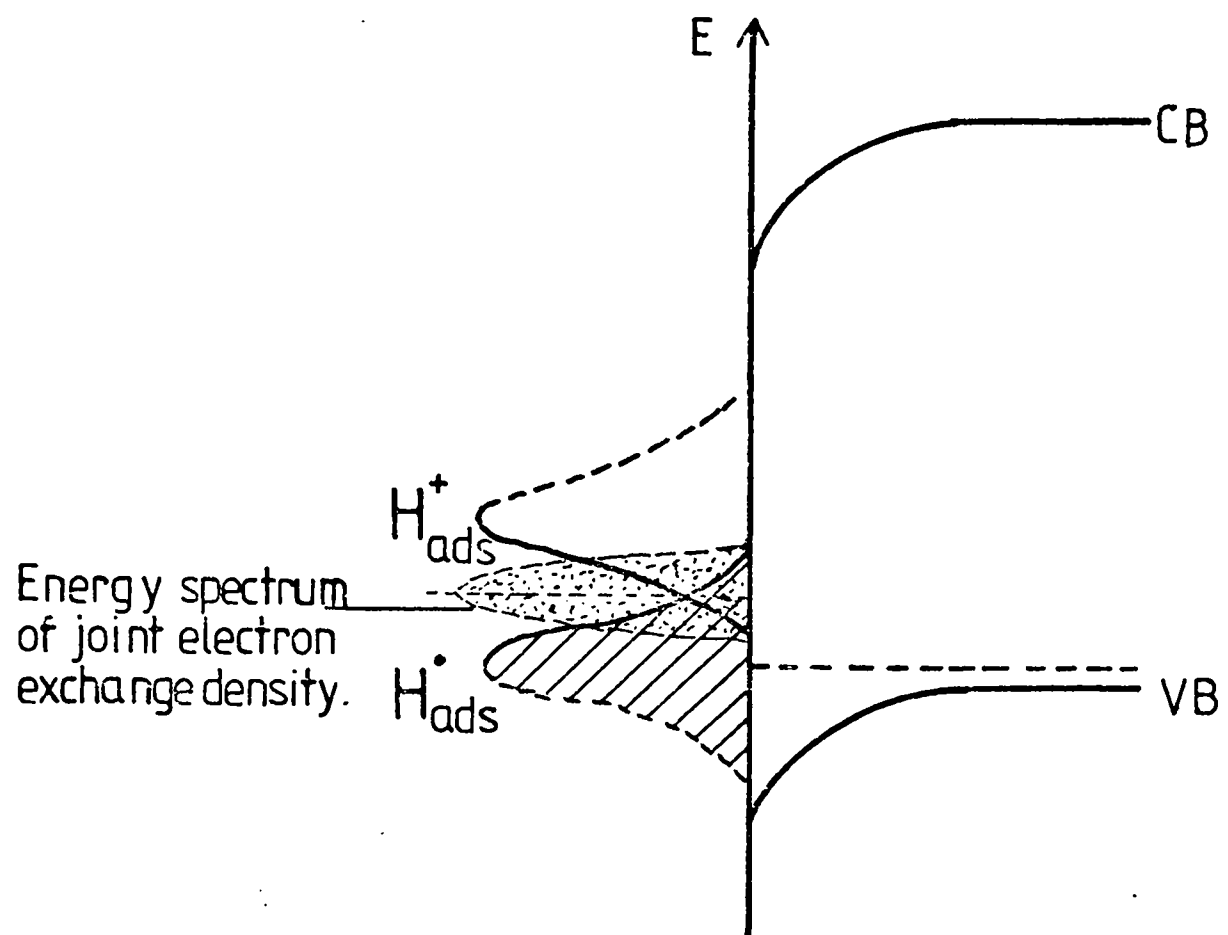


Fig.4.44 Diagram illustrating the hypothetical density of states for surface bound H_{ads} and $H_{ads}^{\bullet}$ after electrode has been biased at very cathodic potentials for a long period. See text. Energy spectrum of joint electron exchange density represented by stippled area.

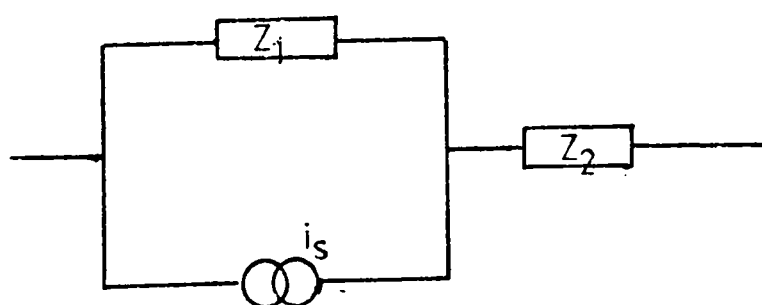
4:8:3 A.C. Cyclic voltammograms

With this technique the surface concentrations of adsorbed species on the electrode are no longer allowed to come to equilibrium at each voltage since sweep rates are quite fast (typically $10\text{--}50\text{mV s}^{-1}$). Detailed impedance analysis cannot be performed since the data on the 0° and 90° admittances can no longer be taken for a number of frequencies in precisely similar conditions. In addition, when the technique is used under illumination the complexity of introducing additional current generating components into the model circuit precludes quantitative interpretations.

Dark A.C.C.V's on p-GaP are essentially similar to the raw data obtained from steady state measurements taken point by point at a single frequency for impedance analysis. In this way it appears that there is a 1:1 correspondence between the appearance of a peak in the A.C.C.V plot and the presence of a peak in surface state capacitance at the same potential. Necessarily though because the 0° signal also involves terms including C_{ss} some crosstalk occurs such as to enhance the magnitude of the 0° signal at this same potential.

The illuminated dynamic a.c. response reveals much more structure but in particular there appear to be two peaks in the 0° and 90° plots.

A simple semi-quantitative model may be proposed incorporating a voltage dependent current generator $i_s(V)$ in the depletion layer to represent the photocurrent. If Z_1 is then the depletion layer impedance and Z_2 represents the combine faradaic impedance and bulk resistance, the illuminated electrode may be represented by the equivalent circuit.



where i_s is strictly a function of V'_0 the potential dropped across the depletion layer.

If we write for V , the total potential drop across the circuit

$$V = V'_o + i_{dc}Z_2 + V_1 \exp(i\omega t)$$

then we may expand i_s as a Taylor series in V or V'_o

$$i_s = i_s(V_o) + V_1 \exp(i\omega t) (\partial i_s / \partial V_o)$$

$$i_s = i_s(V'_o) + (V_1 - i_s Z_2) \exp(i\omega t) (\partial i_s / \partial V'_o)$$

The admittance of the circuit may now be written:-

$$A = [1 + Z_1 (\partial i_s / \partial V_o)] / (Z_1 + Z_2)$$

or

$$A = [1 + Z_1 (\partial i_s / \partial V_o)] / [Z_1 + Z_2 + Z_1 Z_2 (\partial i_s / \partial V'_o)]$$

In a reverse biased Schottky barrier, where $Z_1 \gg Z_2$ the admittance changes from $\sim 1/Z_1$ to a substantially higher value if $(\partial i_s / \partial V_o)$ changes from a small to a large value. The sharp change in photocurrent with applied potential V_o near 0.0V (S.S.E.) (see Fig. 4.1) in acid media thus accounts for the maximum near this voltage in the 0° and 90° photoresponses of Fig. 4.32 (and analogously for the 1M NaOH results). On the other hand, if $(\partial i_s / \partial V_o) \approx 0$ as in the saturation region of Fig. 4.1 the admittance will remain unchanged on illumination, as indeed is observed at high cathodic potentials. Since $(\partial i_s / \partial V_o)$ in Fig. 4.1 is also very small in the range $0.2 < V_o < 0.6V$ (S.S.E), it follows that a marked change in $(Z_1 + Z_2)$ must occur in this voltage range to produce the sharp enhancement of the shoulder a.c. response at 0.45V (S.S.E). The simplest assumption is to assume that the surface state capacitance C_{ss} of Fig. 4.24f increases substantially with illumination in this voltage range. Such a finding is again entirely consistent with the photogeneration of the H^+_{ads} generating surface states as predicted from the variation of photocurrent voltage plots with increasing light intensity (Fig. 4.18 and discussion Section 4:7:2)

4:8:4 A.C. Cyclic voltammograms following long periods cathodic in dark or illuminated conditions

Figures 4.45 and 4.46 illustrate respectively the a.c. admittance response of electrodes following periods of potentiostating at cathodic potentials in the dark and under illumination (sufficient to give 4mA cm^{-2} photocurrent). It is apparent that the magnitude of both the 0° and 90° signals are radically altered by this treatment. Only very minor changes are observed in the d.c. cyclic voltammograms so it is apparent that the a.c. technique provides much greater sensitivity for detecting surface changes at the electrode. In the 90° plot (Figure 4.45c) an additional peak is seen at $\sim 0.1\text{V}$ (S.S.E) as well as the expected enhancement of the peak at 0.45V attributed to increased $[\text{H}_{\text{ads}}^*]$. However the major differences are in the 0° plots. Interestingly the results taken after dark and illuminated periods at cathodic potentials differ significantly in the structure of the peak.

No attempt will be made in this work to interpret these peaks since much more data is required concerning dependences on electrolyte, crystal orientation etc. Nevertheless these results reveal that the simple model presented to date does not account for all the detailed features of the electrochemistry of p-GaP. Obviously much further work will be required before a thorough understanding is available and in particular the theory of a.c. cyclic voltammetry needs much attention. This sensitive technique must surely provide much valuable information concerning the interfacial behaviour of semiconductor electrodes but so far a satisfactory complete interpretation is far from available.

SECTION 4:9 SPECTRAL RESPONSE

The action spectra for p-GaP presented in Figures 4.19 and 4.20 demonstrate clearly the indirect nature of the GaP band edge. Significant photocurrent does not appear until wavelengths much shorter than the quoted

Figs. 4.45a-c A.C. Cyclic voltammograms of p-GaP in 0.5M H_2SO_4 177
 (a) 0° and 90° plots of freshly etched electrode .
 (b) 0° plots taken after electrode potentiostatted at -1.0V for $2\frac{1}{2}$ hrs.
 in dark conditions .
 (c) 90° plots taken simultaneously with those in (b)

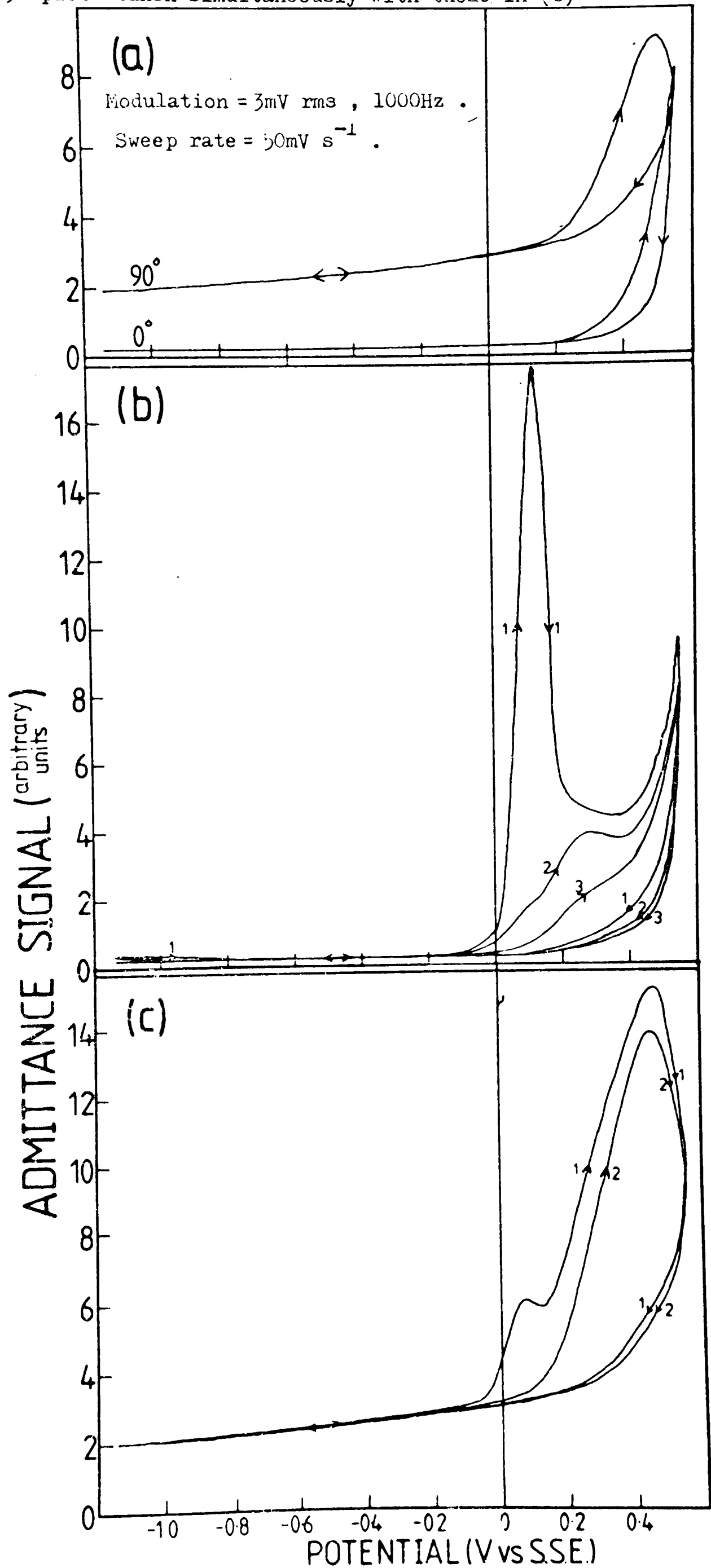
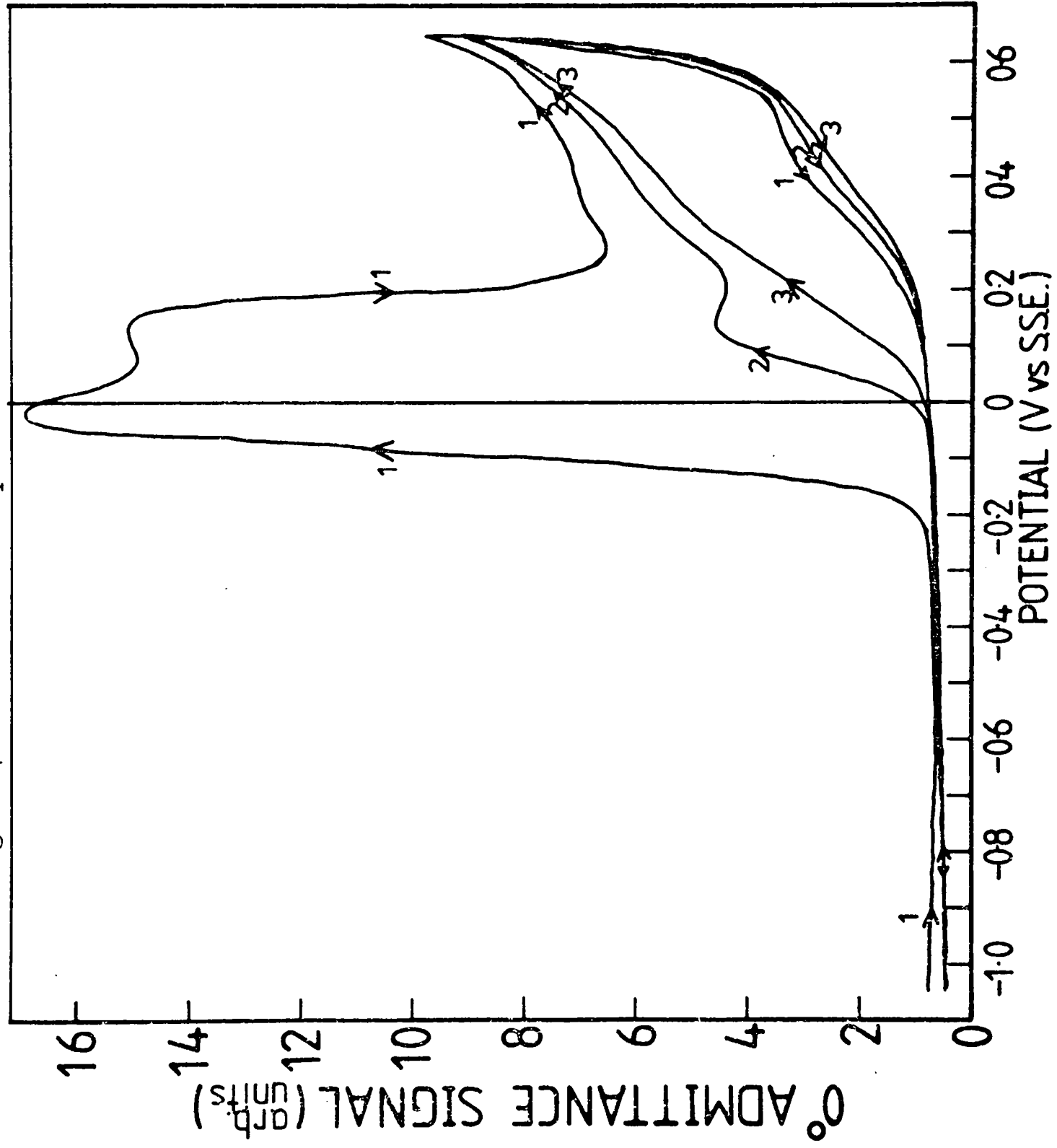


Fig. 4.46 A.C.C.V.'s of p-GaP in 0.5M H₂SO₄ (0° plot only) taken after 30 mins. potentiostatted at -1.0V under white light illumination sufficient to give 4mA cm⁻² cathodic photocurrent. Modulation as in 4.45

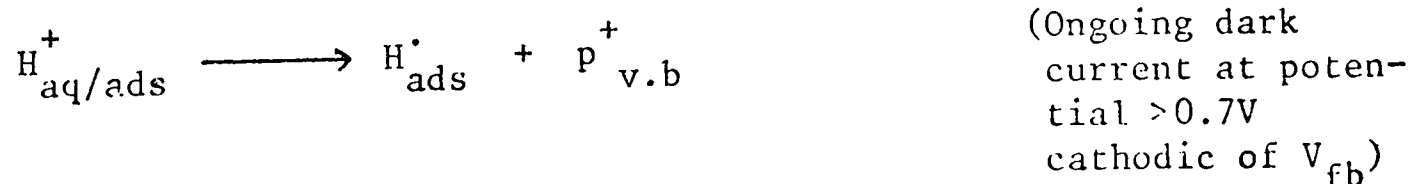
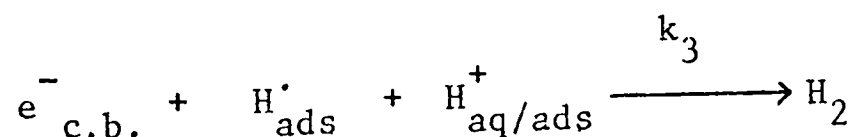
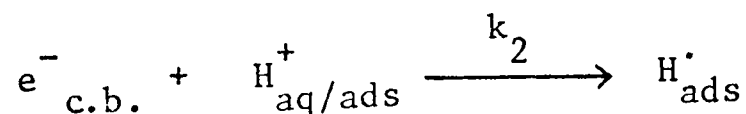
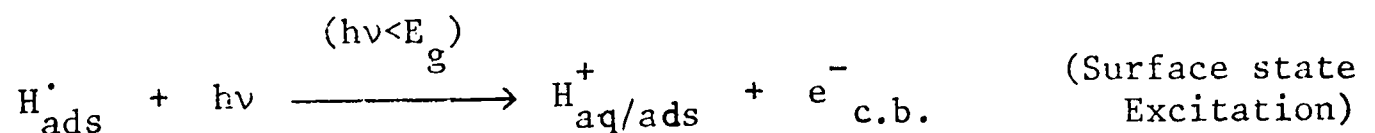


bandgap of 2.24eV. Theoretical analysis of an interband transition suggests that at the band edge the intensity of the photocurrent should vary as $(h\nu - E_g)^{1/n}/Ih\nu$ where $n = 0.5$ for an indirect transition, 0.67 for a direct forbidden and 2.0 for a direct allowed transition.²⁵⁸ Unfortunately the graphical plots used to test the nature of the transition all failed to give straight lines although the best fit was obtained for the indirect transition.

Two additional features are to be noted in the action spectra.

1. There is significant sub-bandgap photocurrent (i.e. $h\nu < E_g \sim 2.24\text{eV}$) trailing off very slowly into the infra-red ($> 900\text{nm}$). The sub-bandgap response is also non-transient (i.e. continuous) for potentials more than 0.7V cathodic of flat-band.
2. There is a small peak in photoresponse at approximately 570nm (2.175eV).

Since, no optical absorption exists for GaP single crystals at wavelengths greater than 553nm, the sub-bandgap photocurrents must be associated with surface state excitations at the electrode/electrolyte interface. It is surprising, however, to note the continuous nature of this photocurrent, unless an ongoing dark current is maintaining an approximately constant occupancy (or concentration) of surface states. The following mechanism may provide an interpretation (see also Fig. 4.47).



The surface state excitation may also take place within the surface of the electrode due to the presence of bulk $H^\bullet$ species which have diffused from the surface. The creation of an electron in the conduction band by sub-bandgap irradiation may then allow passage of net cathodic current only if there is a net change in surface state concentration. The second reaction above is essentially a surface recombination process for the sub-bandgap photon and produces no net current. However the third reaction causes charge transfer to occur across the electrode/electrolyte interface which may be observed as net photocurrent. This photocurrent would however be transient unless, the ongoing cathodic dark current were able to maintain a reasonably constant concentration of surface adsorbed Hydrogen atoms. In support of this theory, it is to be noted that at all times, the sub-bandgap photoresponse produced photocurrents at least one-order of magnitude below the ongoing dark current. Thus the constancy of the sub-bandgap photocurrent may be explained by the slow nature of k_3 above and the constant surface concentration of $H^\bullet_{ads}$.

No definite assignment may be made as to the origin of the peak in photoresponse at 570nm. A reasonable possibility is that the peak is due to excitation from the filled acceptor levels in the depletion layer of p-GaP. Alternatively, since an excitonic state has been determined below the band edge of GaP, the photocurrent peak may result from excitation of this state followed by electron injection into solution as with the conduction band electrons.

SECTION 4:10 CONCLUSIONS: THE PROSPECTS FOR USING p-GaP AS A PHOTO-ELECTRODE IN SOLAR PHOTOELECTROCHEMICAL CELLS

With a bandgap of 2.24eV, GaP has a potential of obtaining about 16% solar energy collection efficiency in a photovoltaic cell, or 9-10% conversion efficiency in a solar photoelectrolysis cell. The indirect nature of the band-edge of GaP would, however, lower these two efficiencies

to $\sim 10\%$ and 4% respectively since the effective bandgap (associated with the rapid rise in the absorption spectrum) would be closer to 2.7eV (460nm).

The results of this chapter have revealed that when used as a Hydrogen evolution electrode, the electrode has to be biased well over 0.6V cathodic of flat-band before rapid H_2 evolution occurs. This is contrary to the superficial expectation for a conduction band edge lying well above the H^+/H_2 level in solution and the required bias creates an unacceptable loss in efficiency for any proposed solar photoelectrolysis cell. If allowance is made for the two-step nature of the Hydrogen evolution reaction, it becomes clear that the major cause of the inefficiency at potentials immediately cathodic of flat-band is strong adsorption of the intermediate Hydrogen atom and consequent enhanced surface recombination rate. In essence it appears that the adsorbed Hydrogen atoms acts as a photogenerated surface states, creating efficiency vs. light intensity relationships which are entirely unknown with solid-state semiconductor photo-devices.

The problem is further exacerbated since the surface bound Hydrogen atom appears to be mobile and can diffuse quite rapidly into the semiconductor lattice. The presence of bulk Hydrogen atoms may increase the rate of recombination in the space-charge layer as well as enhancing the surface recombination rate through quantum mechanical processes such as resonance-assisted tunnelling.

The problems associated with strong Hydrogen adsorption on p-GaP do not appear to be limited to the Hydrogen evolution reaction. Indeed, use of p-GaP in wet-type photovoltaic devices is also severely limited since the desired photo-reduction process has to compete with the very rapid creation and surface recombination of Hydrogen atoms. Indeed to effectively compete with this latter loss process the kinetics of the desired reduction process (k_R) must be much faster than k_2 such that there is no build-up

in concentration of adsorbed Hydrogen atoms. A number of rotating ring-disc studies using p-GaP have confirmed the magnitude of this problem since even rapid one-electron redox couples such as $\text{Fe}^{3+}/\text{Fe}^{2+}$ have reduction rates $k_R \sim k_2^{228,259}$.

For p-type GaP, the binding strength of the Hydrogen atom appears to be a little less than the bond-strength between the Ga and P atoms such that cathodic photo-decomposition is not rapid (although crystal-orientation dependent). However, an operational solar photo-cell must be stable for a minimum of 10 years so minor competing side-reactions involving electrode decomposition must be completely eradicated.

To improve the potential response and durability of p-GaP in photo-electrolysis cells will necessarily require some surface modification or protection. The next chapter will deal with one particular approach which has been applied to p-type GaP. From the first paragraph of this conclusion however, it is clear that GaP is not the optimum candidate for use in solar cells due to its large and indirect bandgap. Nevertheless, a detailed understanding of this material should provide valuable information directly applicable to the studies on some smaller bandgap materials covered in Chapters 6 and 7.

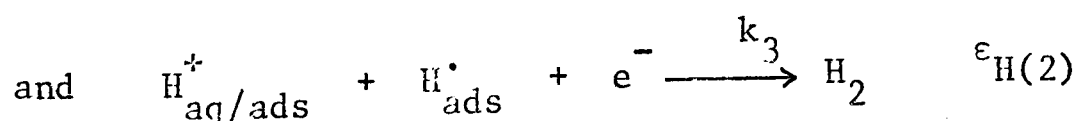
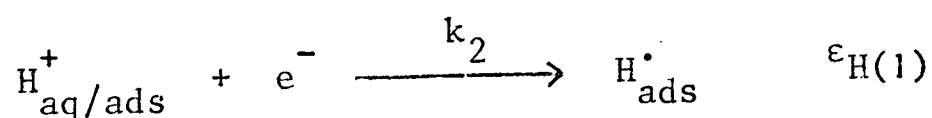
CHAPTER 5

SURFACE MODIFICATION OF P-TYPE GALLIUM PHOSPHIDE

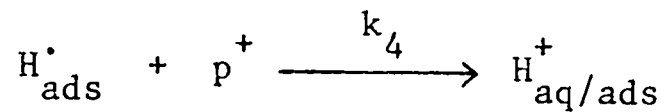
SECTION 5:1 INTRODUCTION

We have discovered in Chapter 4 that the major loss in efficiency of photoelectrolysis devices utilizing the p-GaP electrode is caused by adsorbed intermediates in the Hydrogen evolution reaction. These intermediates create recombination centres at the surface of the electrode. To achieve high quantum efficiencies for Hydrogen evolution, one has to bias the electrode over 0.8V away from the flat-band potential, with consequent severe loss in overall conversion efficiency (see Appendix 3). To improve on this conversion efficiency whilst still using p-GaP as the photoactive electrode we must find ways of modifying the surface of the electrode to remove the deleterious surface properties of the unaltered material. Such surface modifications would be required to bring about any one, or probably some combination, of the following changes:-

1. Reduce the affinity of the electrode surface for the Hydrogen atom (i.e. lower the free energy of formation of the $\downarrow\cdots\dot{\text{H}}_{\text{ads}}$ bond). This, in turn would alter the two separate one-electron redox potentials for the overall two-electron process for the evolution of Hydrogen:-

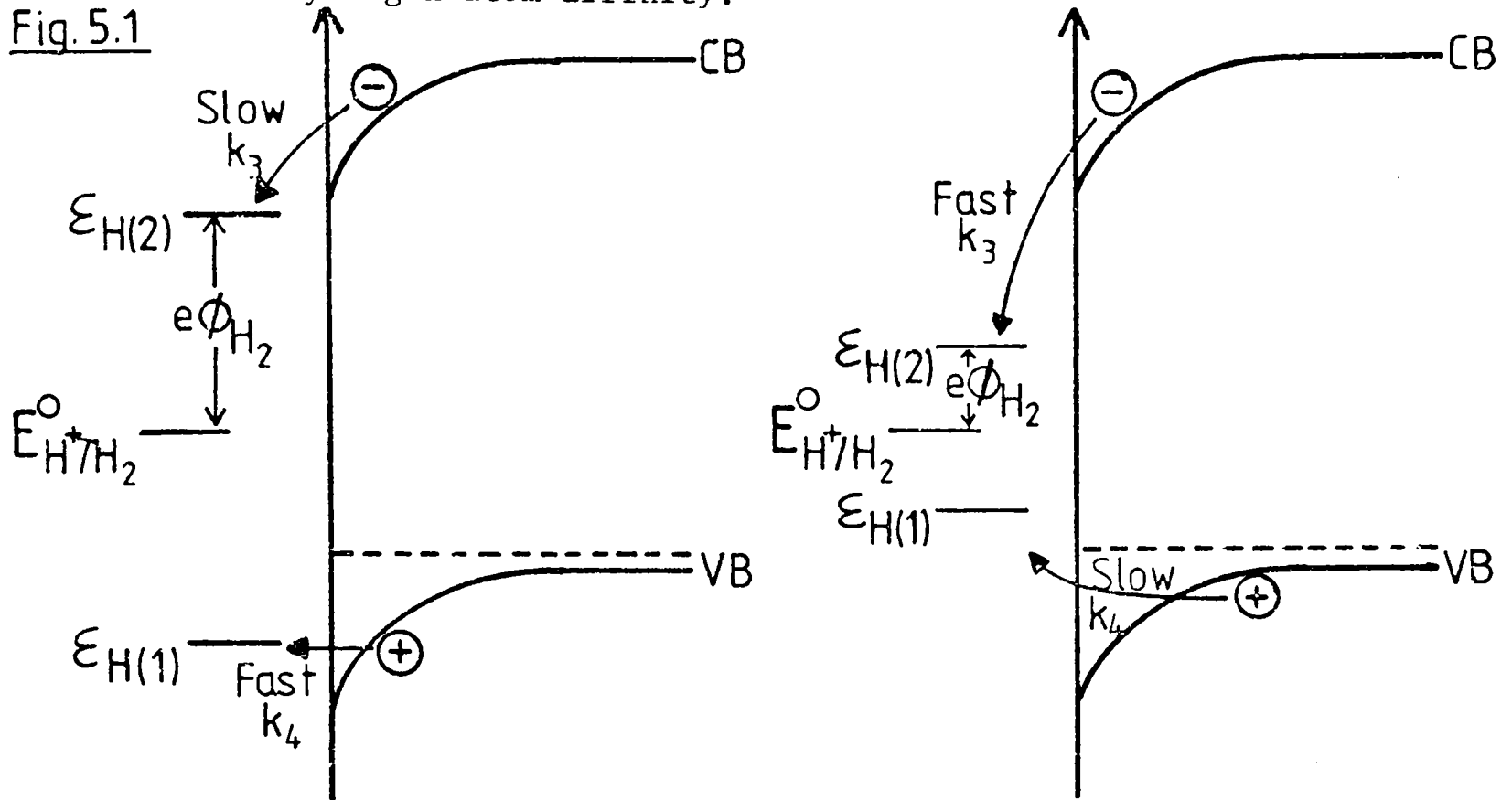


In such a manner, we may reduce the overvoltage (ϕ_{H_2}) necessary for Hydrogen evolution ($e\phi_{\text{H}_2} = -E^0_{\text{H}^+/\text{H}_2} + \epsilon_{\text{H}(2)}$) and consequently increase k_3 so as to compete more effectively with the surface recombination pathway



Indeed as Fig. 5.1 shows we may both increase k_3 and reduce k_4 by altering the surface Hydrogen atom affinity.

Fig. 5.1

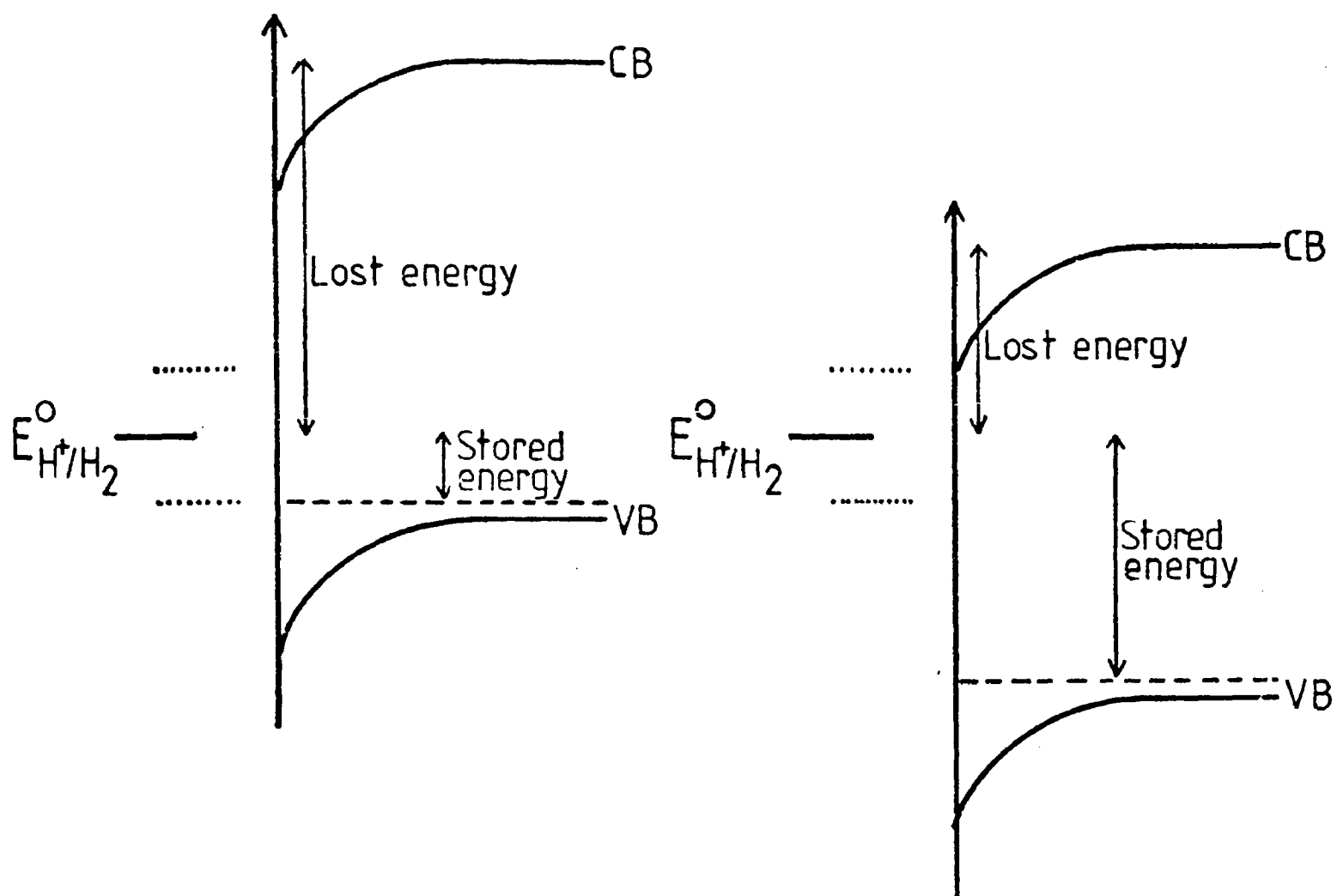


POOR H_2 EVOLUTION EFFICIENCY
LARGE OVERVOLTAGE (ϕ_{H_2})

GOOD H_2 EVOLUTION EFFICIENCY
SMALL OVERVOLTAGE (ϕ_{H_2})

2. Increase the electron affinity of the semiconductor surface and thus alter the flat band potential of the electrode. Neglecting complications arising from the two-step nature of the Hydrogen evolution reaction, this semiconductor surface modification may provide for a better matching of conduction band energy with the $E_{\text{H}^+/\text{H}_2}^0$. As Fig. 5.2 shows, this could result in a higher fraction of energy being stored in any operational solar cell.

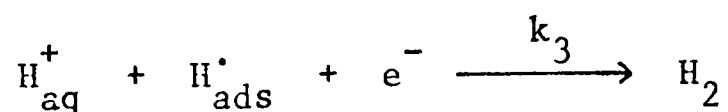
Fig. 5.2 Diagram illustrating improved photoefficiency for H_2 evolution on p-GaP by increasing the surface electron affinity.



It is obvious that concurrent with this flat band shift we require a smaller Hydrogen overvoltage (ϕ), else the more cathodic of the two one-electron redox potentials $\epsilon_{H(1)}$ and $\epsilon_{H(2)}$ may be above the semiconductor conduction-band edge resulting in no net Hydrogen reduction.

3. Prevent Hydrogen atom migration into the surface of the electrode by physically blocking the surface to atom transfer across it, yet retaining rapid electron transfer. In this manner it would be hoped to prevent build up of $[H_{ads}^*]$ to greater than one monolayer and also reduce the resonance assisted tunnelling mechanism mediated by the depletion-layer Hydrogen atoms.

4. Increase the rate of the second step in the Hydrogen-evolution reaction.

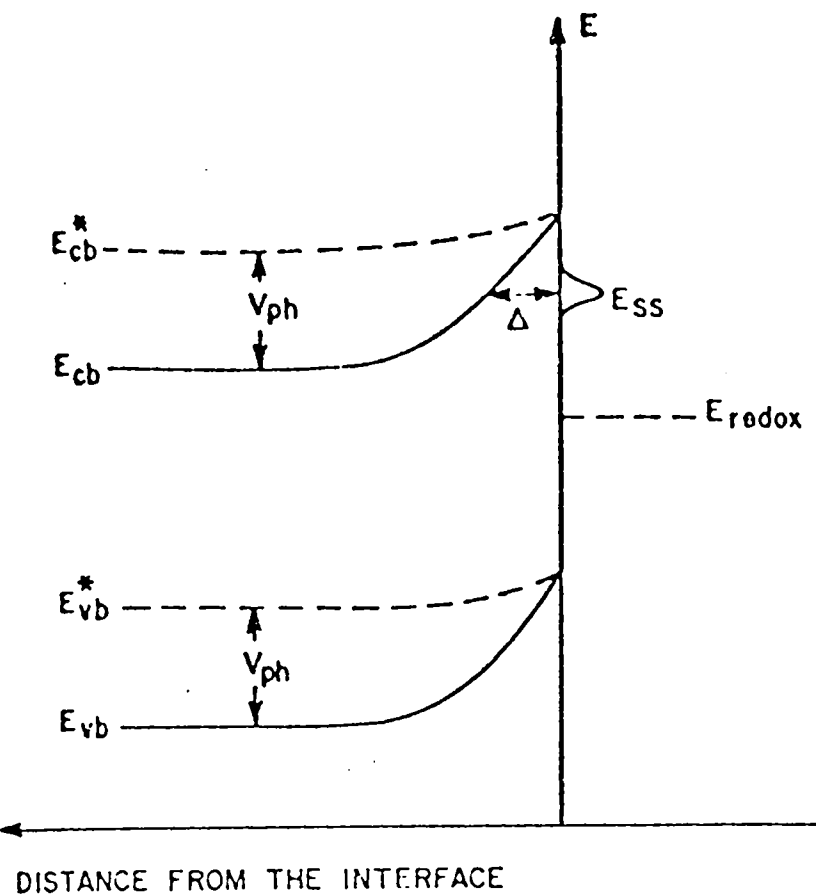


such that it may more effectively compete with the Hydrogen atom-reoxidation process (k_4). (This of course may be related to 1 above, but could also be purely a kinetic effect - there being no change in the positions of $\epsilon_{H(1)}$ or $\epsilon_{H(2)}$.)

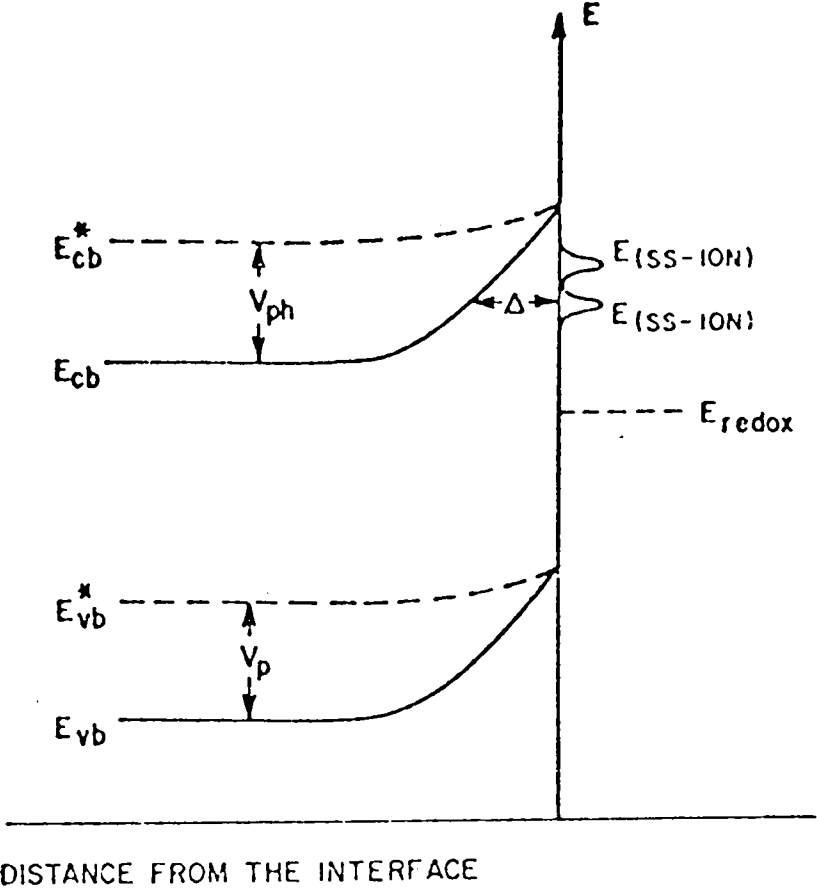
In practice, any surface modification may cause a combination of these individual effects, but nonetheless it may be possible to determine the dominating factor by careful choice of experiment.

A successful surface modification of a semiconductor electrode has been demonstrated for n-GaAs in the nGaAs|K₂Se, K₂Se₂, KOH|C photovoltaic cell.^{134,260} In this case it was found for clean GaAs surface that the fill factors of the cell were very poor. Translated into terms relevant to these studies a large potential bias away from flat-band potential was required on the semiconductor before saturation photocurrent was achieved. Adsorption of Ruthenium species from a solution of RuCl₃ was found to improve dramatically the cell's fill factor although having no effect on the

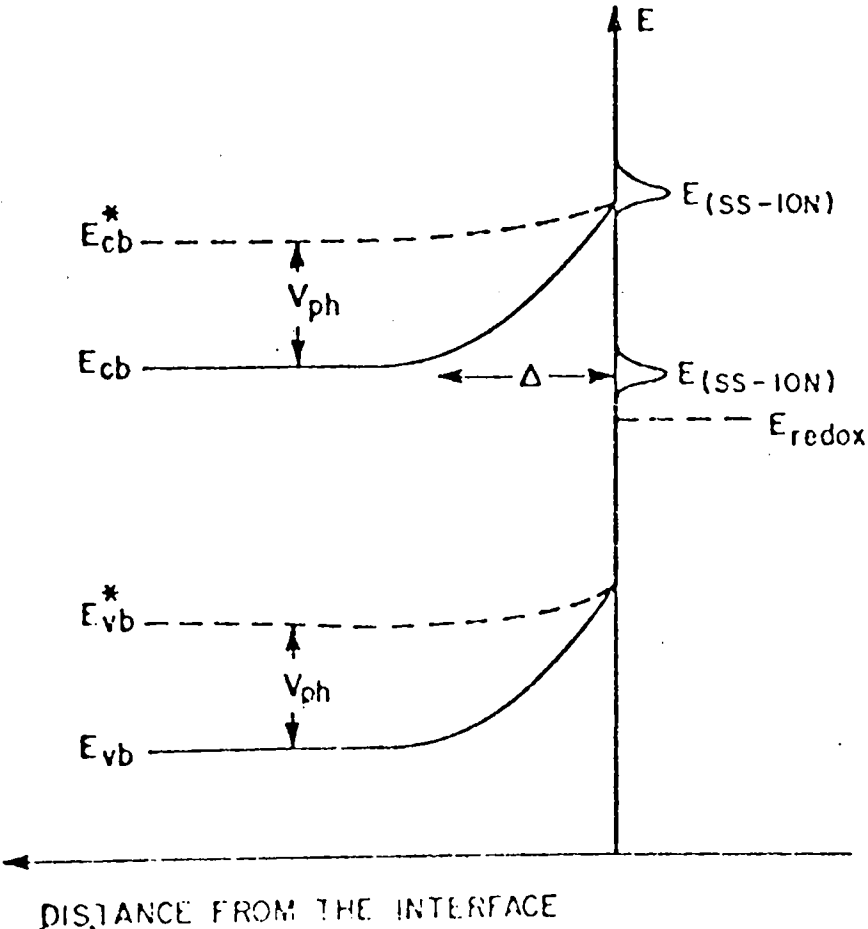
Figs.5.3(a-c) Diagrams illustrating a possible mechanism whereby adsorbed metal ions can interact with a surface state responsible for a surface recombination pathway²⁶⁰.



(a) Shunting of a liquid junction solar cell by a surface state near the conduction band. CB, VB, ss, and redox refer to the conduction band, valence band, surface state and solution redox potential, respectively. The positions of the energy levels in an intensely illuminated cell are shown in dashed lines and are marked by an asterisk. V_{ph} is the highest photovoltage that can be reached in the absence of a surface state.



(b) Weak interaction of a surface entity with an ion splits the original state into two new states with energies $E'_{(ss-ion)}$ and $E_{(ss-ion)}$. If tunneling from the conduction band to E_{ss} is possible, the fill factor is reduced and the photovoltage is limited to $E_{(ss-ion)} - E_{cb}$, a value lower than $E_{ss} - E_{cb}$ by $\sim 1/2$ of the splitting.



(c) Strong interaction of a surface entity with an ion splits the original state to $E'_{(ss-ion)}$ and $E_{(ss-ion)}$. Electrons cannot tunnel to $E_{(ss-ion)}$ because the barrier is too thick. $E'_{(ss-ion)}$ is above the conduction band edge, and cannot capture electrons. The split surface state no longer reduces the photovoltage or the fill factor.

maximum cell current. The explanation put forward by Heller et al. was that adsorbed metal ions interact with the surface state responsible for the surface recombination pathway. As shown in Figs. 5.3(a-c), weak interaction could in fact reduce the fill factor whilst strong interaction effectively removed the shunting ability of the surface state. Indeed Bi(III) adsorption was found to reduce the fill factor of the cell. However, no further experimental evidence could be found to support their claims.

Following on the success of the simple surface treatment on n-GaAs, it was decided to investigate the effect of similar treatments on p-GaP and, in particular, to search for materials that might improve the Hydrogen-evolution efficiency from this material. Given that any differences were observed, it was hoped to apply the novel techniques, developed for the study of the unmodified electrode, to the modified material and thus provide experimental evidence for the theory of operation of surface-modifying agents.

SECTION 5:2 RESULTS AND DISCUSSION

For each given metal-ion treatment, a 0.01M solution was made up by dissolving either the nitrate or chloride in 0.1M HNO_3 as tabulated in Table 5:1. The electrode pre-treatment consisted of the following steps:-

1. Removal of the electrode from the cell and washing in H_2O .
2. Dipping the electrode into the metal-ion solution for 20 seconds.
3. Washing thoroughly in H_2O and returning to the cell.

Much effort was taken to ensure equal illumination intensity before and after the electrode dip. This was generally possible to within $\pm 5\%$.

In general, no significant difference could be discerned between the dark cyclic voltammograms taken before and after the dip process. Two exceptions were found: notably with Hg(II) and Pt(II) dips, which

TABLE 5.1 List of Metal-ion solutions used for electrode pretreatment of p-GaP along with their source materials

Metal-ion	Source	Metal-ion	Source
"Ru(III)"	Crude $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$	Ru(III)	$\text{K}_2\text{RuCl}_5 \cdot \text{H}_2\text{O}$
Bi(III)	$\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$	Sb(III)	SbCl_3
$\text{Ru}(\text{bpy})_2\text{Cl}_2$	$\text{Ru}(\text{bpy})_2\text{Cl}_2$ (purified)	$\text{Ru}(\text{bpy})_3(\text{II})$	$\text{Ru}(\text{bpy})_3\text{Cl}_2$
Rh(III)	$\text{RhCl}_3 \cdot x\text{H}_2\text{O}$	Pb(II)	$\text{Pb}(\text{NO}_3)_2$
Cu(II)	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	Ni(II)	$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$
Fe(II)	$\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$	Fe(III)	$\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$
Pt(II)	K_2PtCl_4	Eu(III)	EuCl_3
Hg(II)	$\text{Hg}(\text{NO}_3)_2$		

TABLE 5.2 Responses of p-GaP electrodes to various metal-ion dips .

Positive Effect	Null Effect	Negative Effect
"Ru(III)" Bi(III), Sb(III) Cu(II), Pb(II) Rh(III), Ru(III) $\text{Ru}(\text{bpy})_2\text{Cl}_2$, Ni(II)	Fe(III), Fe(II) Eu(III), $\text{Ru}(\text{bpy})_3(\text{II})$	Pt(II) Hg(II)

caused an increase in the cathodic dark currents along with a slight blackening of the surface from deposition of small particles of Hg and Pt metal respectively.

For electrodes under high intensity illumination, some very small and insignificant effects were observed following the majority of solution dips. Exceptionally, after a dip in crude RuCl_3 solution, the cyclic voltammograms revealed a considerable shift in the potential of the photocurrent onset (see Fig. 5.4). However, there was no detectable change in the value of the saturation photocurrent at the more cathodic potentials.

To study the effect of metal ion dips at lower light intensities, the Photocurrent-Voltage plots were recorded for saturation photocurrents of $\approx 10^{-5} \text{ A cm}^{-2}$. The results are tabulated in Table 5:2. A "positive" effect relates to an anodic shift in photocurrent onset potential, "null" to no significant change, and "negative" to either a decrease in saturation current or a cathodic shift in onset potential. The two modifications that provided the largest positive effects were "Ru(III)" and Bi(III) dips, with the former demonstrating the most significant improvement. Fig. 5.5 depicts the Photocurrent-voltage plots of clean, Ruthenium and Bismuth modified surfaces of GaP. As with the high intensity data, it is found that, if the electrode potential is taken anodic of +0.4V, the photocurrent improvement deteriorates steadily with successive sweeps - see Fig. 5.5(b). It seems likely that this is caused by the ruthenium complex entering solution as the electrode surface dissolves at these more anodic potentials.

In consequence, all further investigations were concentrated on the "Ru(III)" modification. Firstly an attempt was made to elucidate the nature of the active species (labelled "Ru(III)") contained in the crude RuCl_3 solutions. It is well known that the so-called crude Ruthenium(III) chloride is actually composed of a wide range of Ruthenium complexes with oxidation states varying from II to IV.

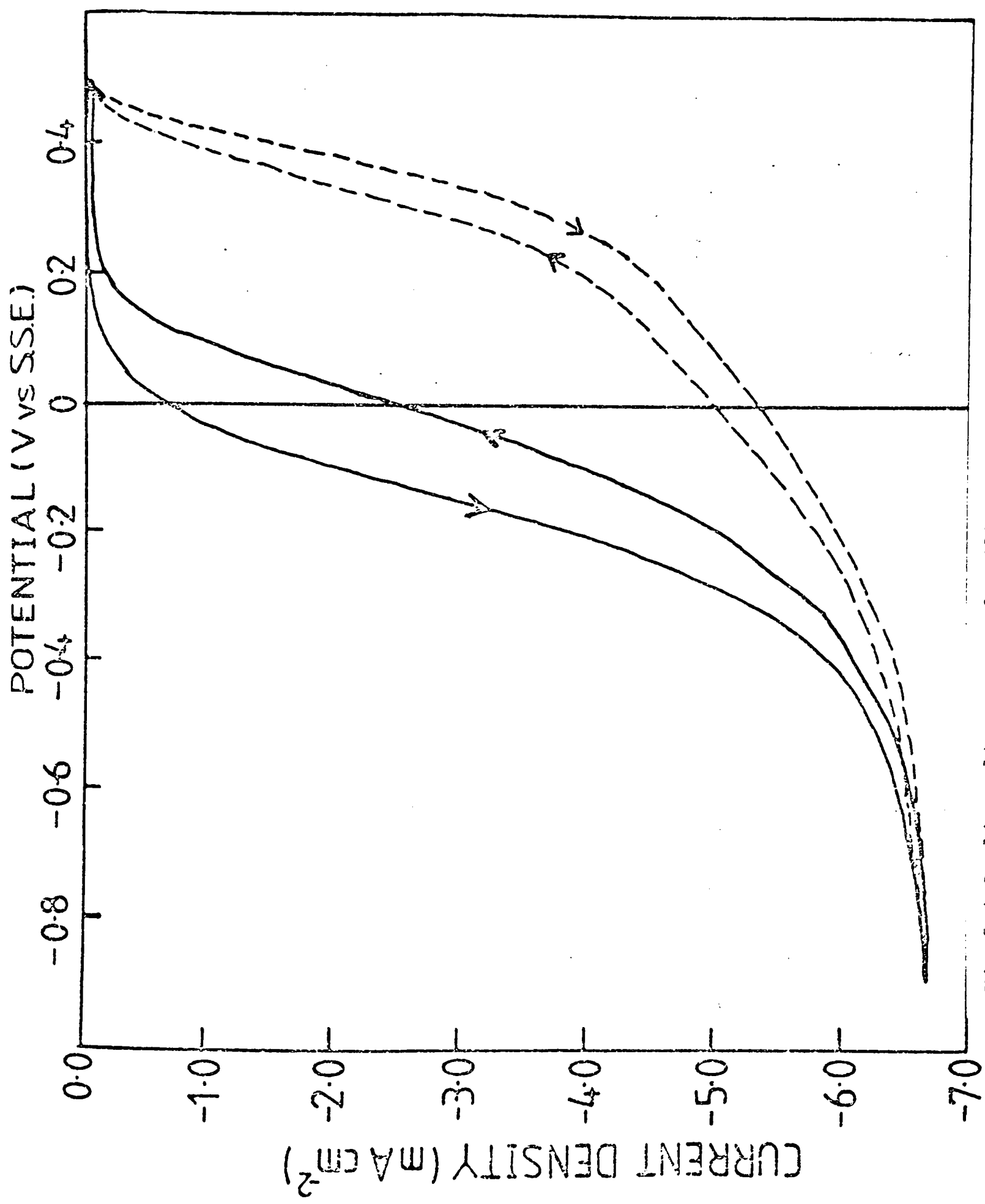
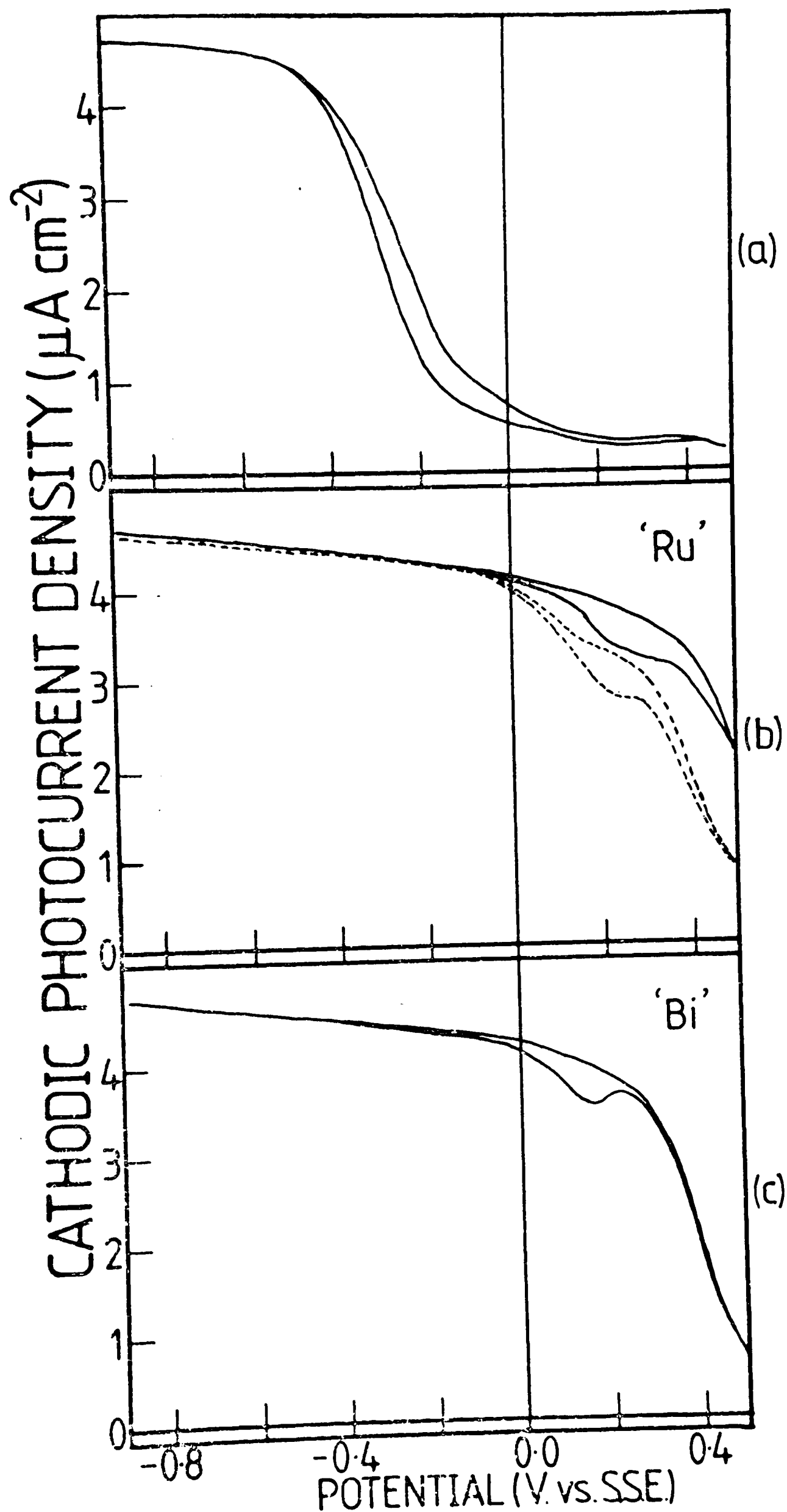


Fig.5.4 Cyclic voltammograms for illuminated p-Gap in 0.5M H₂SO₄ solution. (—) clean surface, (---) surface following dip in crude RuCl₃ solution. Sweep rate 250mV s⁻¹

Figs.5.5(a-c) Photocurrent-voltage plots for clean , Ruthenium and Bismuth modified surfaces of p-GaP in 0.5M H_2SO_4 , respectively . 192
 Fig.5.5(b) depicts the response from a freshly dipped electrode (—) and that obtained after 20 sweeps over the potential range shown (---)

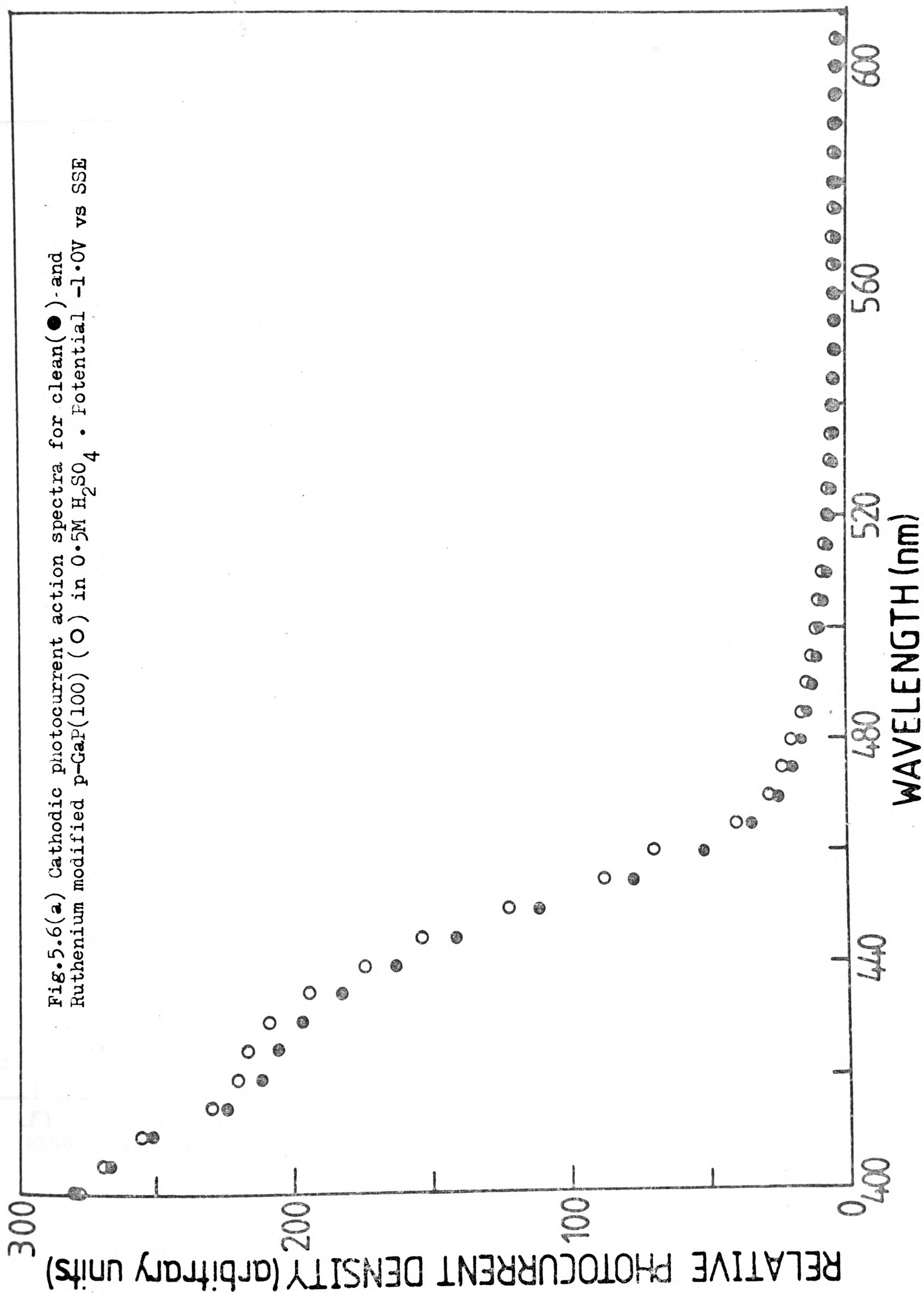


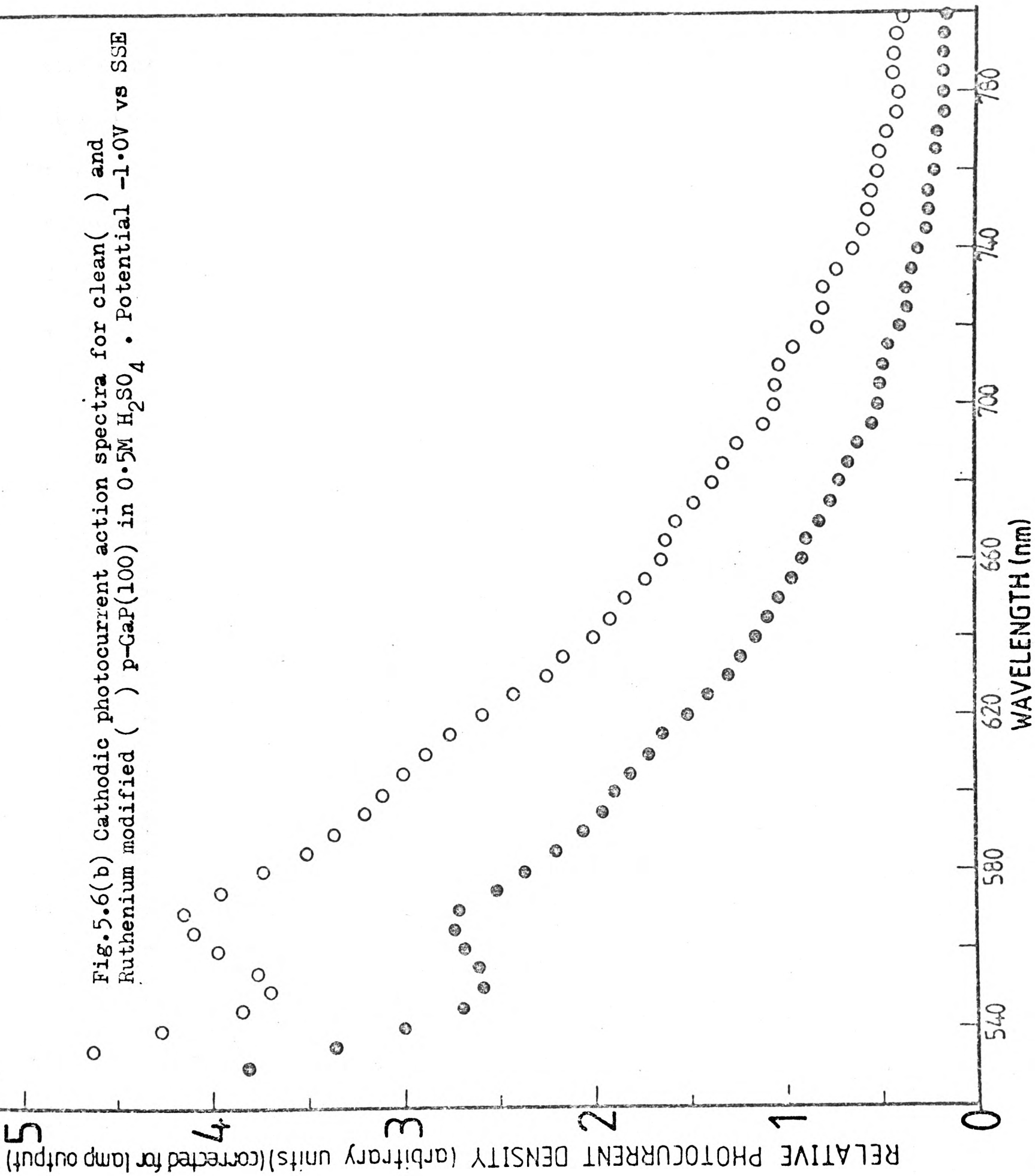
Some pure Ru(III) was obtained as the $K_2RuCl_5 \cdot H_2O$ salt and dissolved in 0.1M HCl. The improvement in photoresponse was far smaller than with the crude $RuCl_3$ solutions. However, when dissolved in 0.1M HNO_3 , $K_2RuCl_5 \cdot H_2O$ is slowly converted to a wide range of ruthenium nitro and nitrosyl complexes. On repeated dips in this solution during the course of its conversion, it was found that there was some distinct (though non-linear) correlation between the fractional decomposition of the $[RuCl_5 \cdot H_2O]^{2-}$ species (determined spectrophotometrically) and the shift in onset potential for the p-GaP electrode.

Chemical analysis has revealed that the crude $RuCl_3$ contains substantial concentrations of nitrosyl complexes resulting from its method of preparation. It is known also that there exist many stable phosphine derivatives of these ruthenium nitrosyl complexes, and it may thus be suggested that the ruthenium nitrosyl moieties may strongly bond with the surface Phosphorus on the GaP electrodes. To verify this suggestion will require a surface spectroscopic analysis using ESCA, Auger or preferably an in situ technique such as ellipsometry.

The question remains as to the mechanism for the shift in photocurrent onset potential. The action spectrum of the modified electrode (see Fig. 5.6) is found to differ from that of a 'clean' surface only in the sub-bandgap region. The photocurrents produced in this region were, however, too small to account for the change in overall photoresponse. Simple two-component impedance analysis of the modified electrode revealed no change in the extrapolated flat band potential (+0.65V vs SSE). Thus the situation discussed as case 2, Section 5:1 cannot account for the observed improvements. However deviations from the extrapolated straight line at potentials close to flat band were even greater than for 'clean' electrodes.

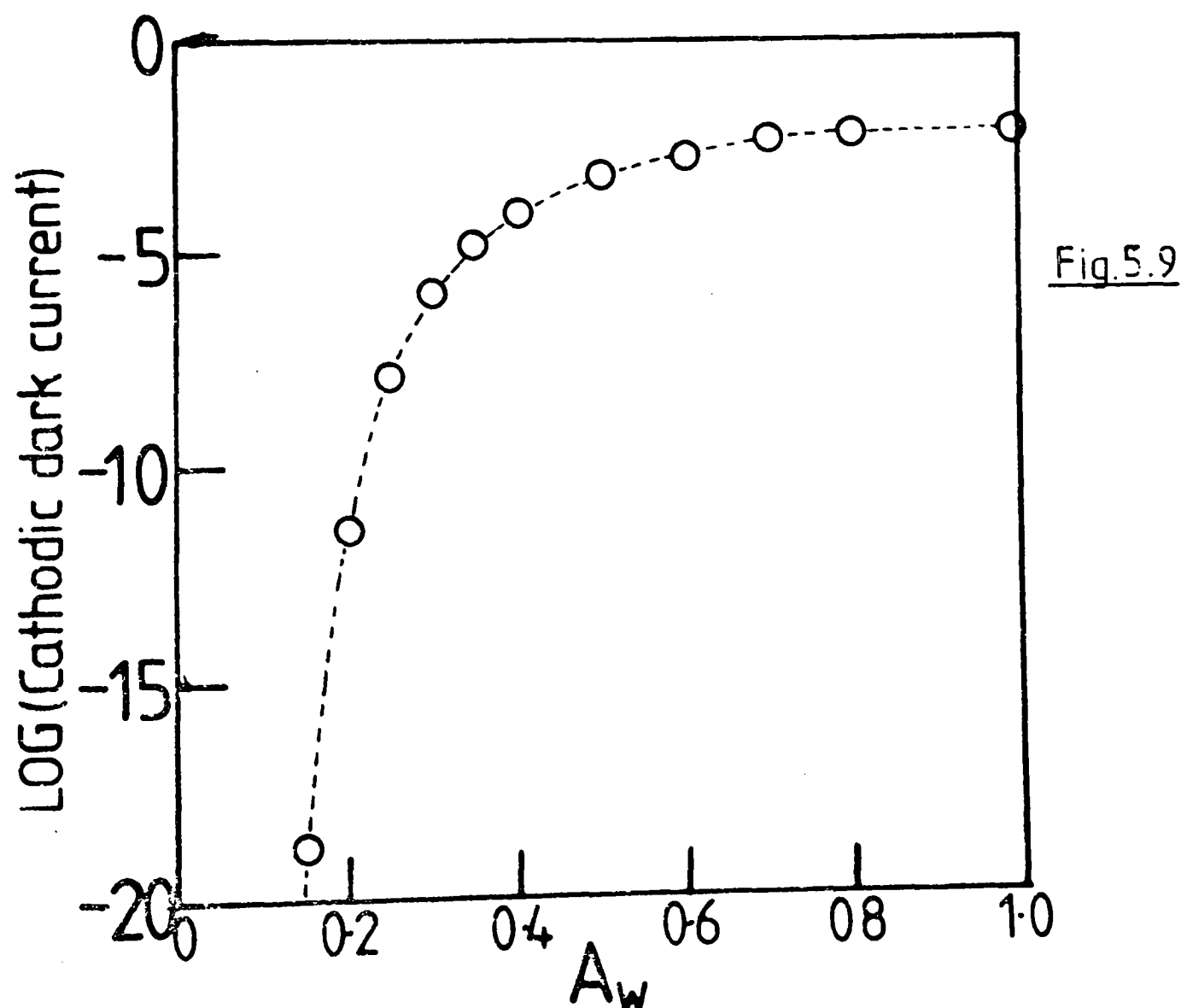
The detailed impedance analysis was more revealing. Again, no appreciable change could be discerned for the plots of C_{SC}^{-2} as a function



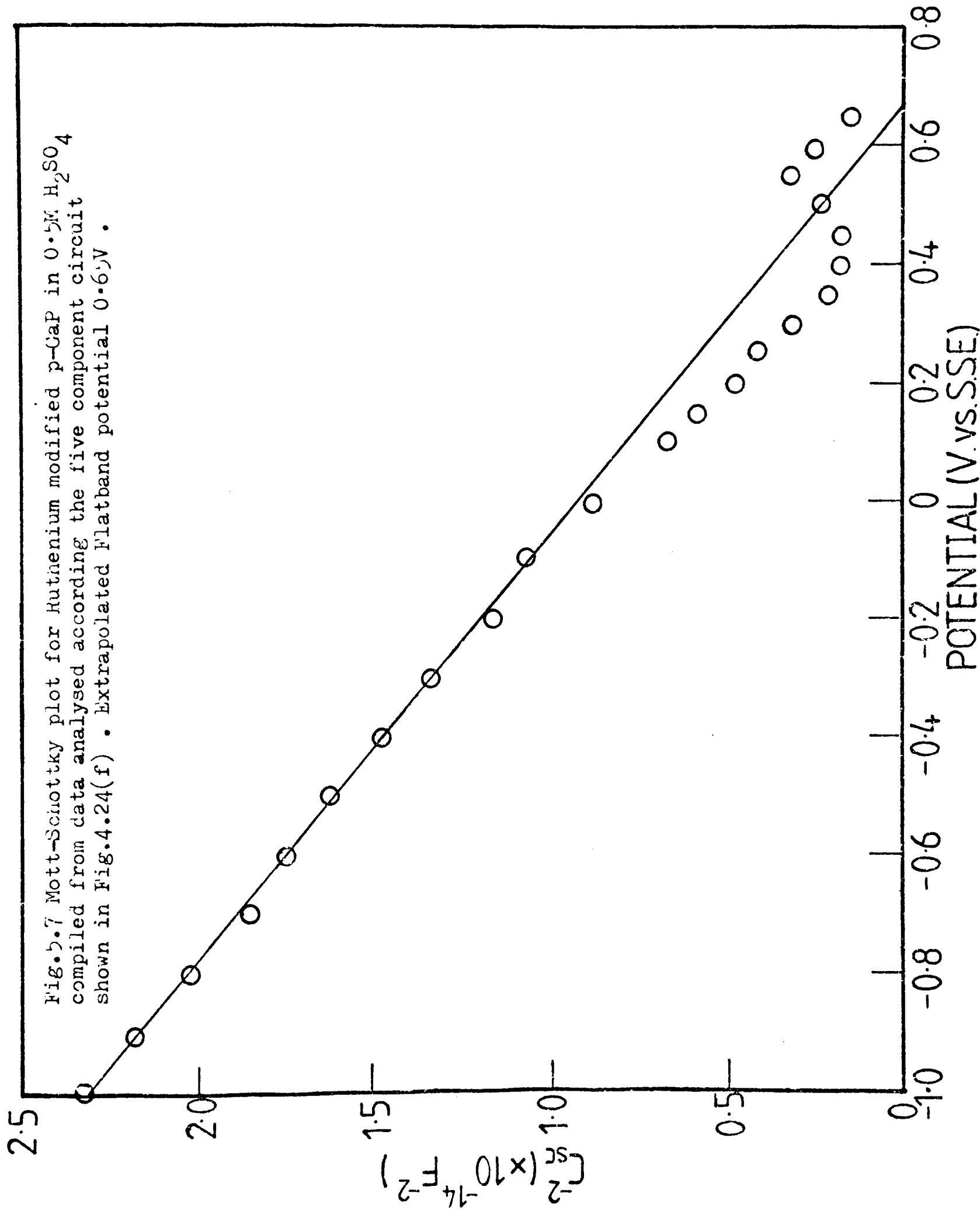


of voltage (Fig. 5.7); but the C_{SS} plots displayed a strikingly enhanced peak at 0.3-0.4V (see Fig. 5.8).

Two possible explanations for an enhanced (dark) surface state capacitance involve changes in the overlap of surface acceptor and donor states brought about by Ruthenium adsorption. With the model presented in Chapter 4, Section 4:7 it may be shown that the majority of hole transfer to and from surface redox levels will take place at energies at or just above the valence band edge. In particular with a fixed position (E') for the solution acceptor Gaussian, but variable width A_w , Fig. 5.9 depicts that the electron-transfer rate increases extremely rapidly and initially exponentially as a function of that width.



If this is true for the electron transfer rate from the solution donor Gaussian to the acceptor levels (holes) in the valence band, then we might predict that any species, that when adsorbed on the surface of a semiconductor, increases the apparent size of the surface state density, might actually be increasing the width of the energy distribution functions for the surface adsorbed redox couple. (Fig. 5.10)



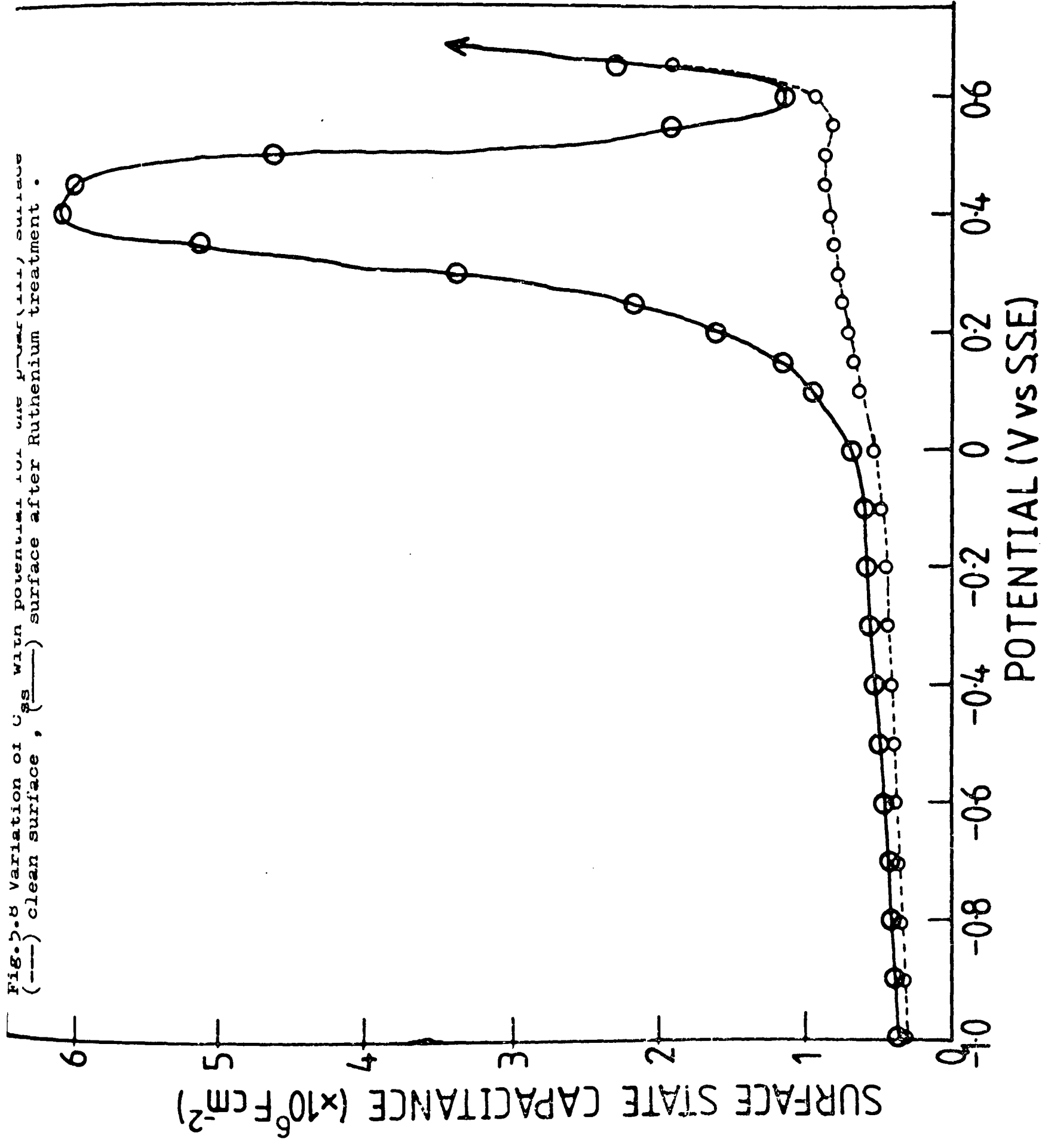


Fig. 5.8 Variation of C_{ss} with potential for the pure (---) surface (---) clean surface, (---) surface after Ruthenium treatment.

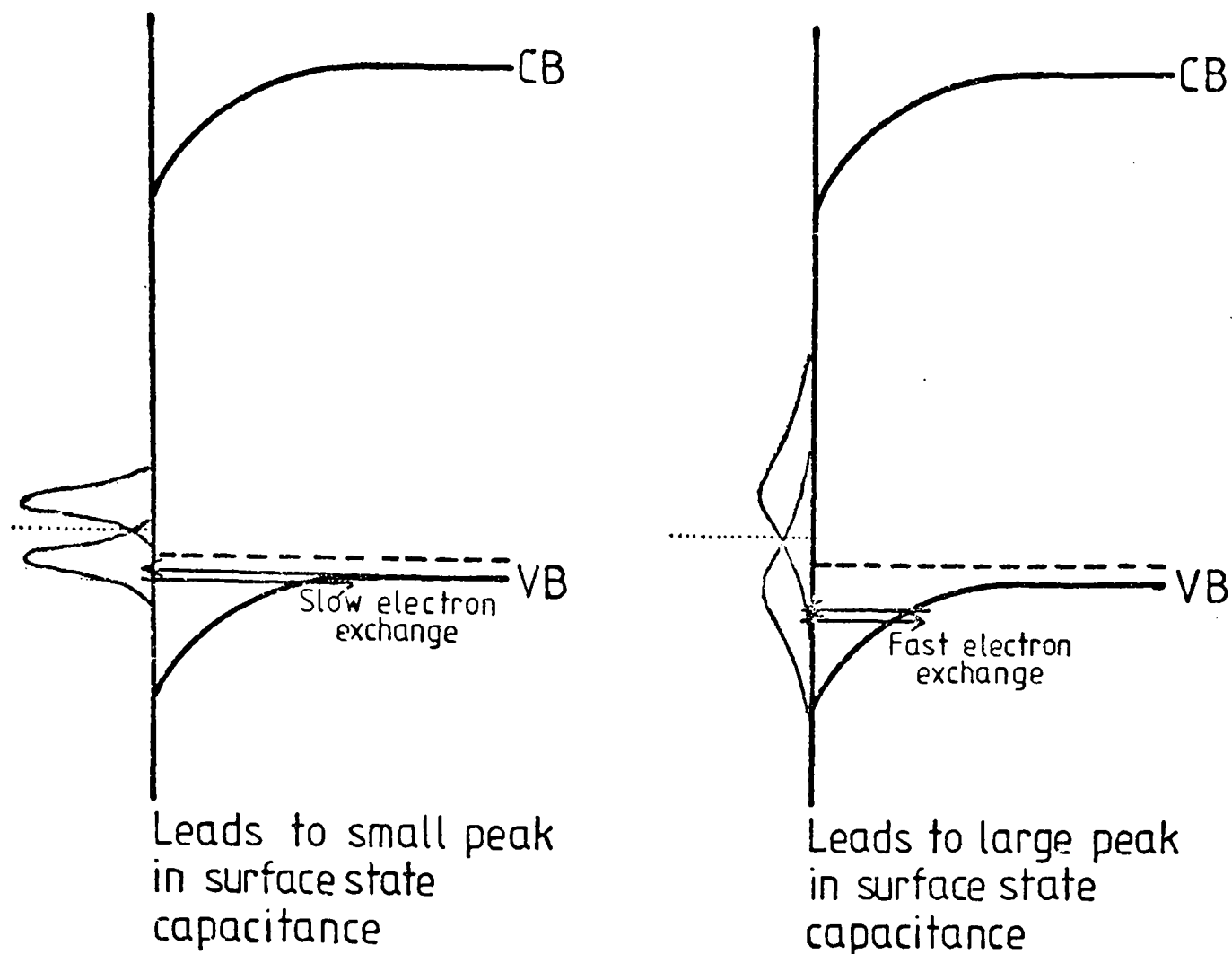


Fig.5.10 Diagrams illustrating the possible correlation between the width of the energy distribution functions for surface adsorbed redox couples and the apparent size of the surface state density .

However, this is the case for the strictly classical case of tunnelling directly through the space-charge region. On the other hand, it is worth noting that when the impedance measurements are taken, very long periods are required for the electrode to come to equilibrium in the potential region $0.0 \rightarrow +0.6V$. This observation is not simply explained using this purely classical model since concentrations of surface bound species would be expected to attain equilibrium quite rapidly even with exchange current densities $< 1 \mu A cm^{-2}$.

The matter may be explained by the presence of the fifth equilibrium process occurring at the surface of p-GaP, notably



The only driving force for this equilibrium is that of the concentration gradient set up at the surface of the electrode when adsorbed. Hydrogen atoms are generated by electron transfer from the electrode. The limiting concentration of Hydrogen atoms in the surface region appears quite high since anodic waves due to reoxidation of the Hydrogen atoms can exceed 2000 monolayer equivalents following even short periods of illumination.

Now, following on from the theory developed in Chapter 4, it was suggested that the bulk Hydrogen atoms may assist the process of resonance assisted tunnelling of charge carriers through the space-charge region in the manner first proposed by Schmickler. Under these circumstances, the space-charge layer will no longer present a classical energy barrier to electron transfer to and from surface bound redox species, and indeed the behaviour of the electrode may approach that of a metal. Thus, the model put forward in Chapter 4 Section 4:7 may break down at this point.

For a metal electrode in contact with various redox couples it is found that the electron exchange current increases as the distribution functions for the redox species become narrower (i.e. as the reorganization energy λ becomes smaller)^{257,261}. Thus the observation of enhanced surface-state capacitance on Ruthenated p-GaP may be explained by the narrowing of the distribution functions for the adsorbed species. In particular, this may occur for stronger adsorption of both donor and acceptor species.^{257,261} (See Fig. 5.11).

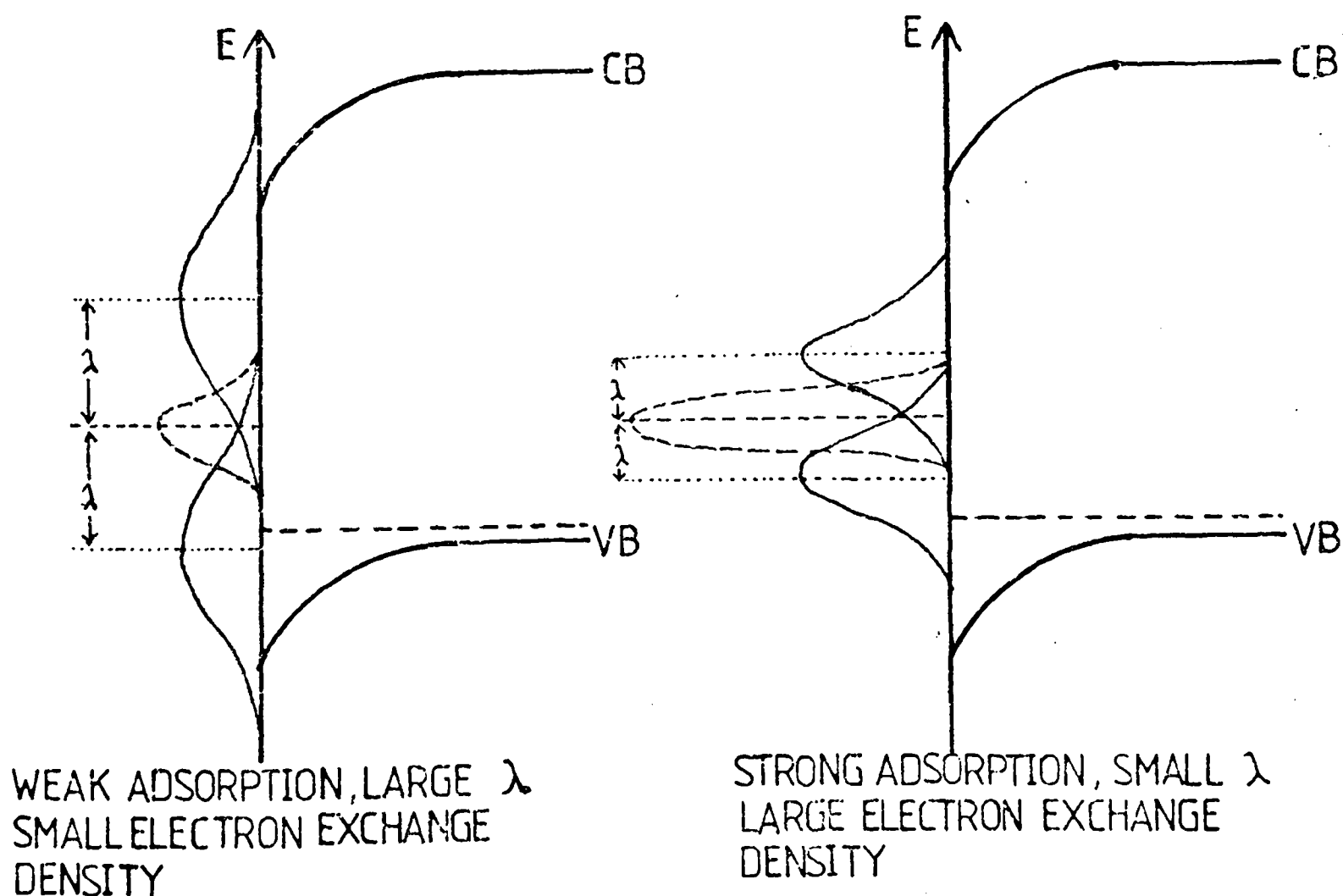
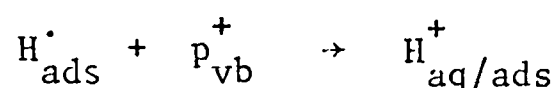


Fig.5.11 Diagram illustrating the correlation between the strength of adsorption of the surface bound redox couples and the magnitude of the joint electron exchange density. λ = the reorganisation energy for the adsorbed redox couples.

The model of Heller et al.²⁶⁰ does not seem applicable to these GaP results since there does not appear to be any significant shift in energy of the surface-state maximum. Similarly there is no evidence of a shift in the flat band potential as determined by extrapolation of the capacitance data taken at the more cathodic potentials. In theory it can be shown that uncompensated surface-state densities in excess of 10^{12} cm^{-2} would create a significant shift in flat band potential.²⁰⁸⁻²¹⁰ The evidence from these results points to the fact that the additional surface states induced by 'Ruthenation' are either neutral or that their charge is neutralized by compensating ionic charge in the Helmholtz layer.

The following theory may be suggested to explain the increased photoefficiency at potentials approaching flat band. As the electrode potential is made more positive ($>0\text{V}$), the initially neutral surface states may become oxidized by hole injection from the valence band, and the concentration of charged surface states may then rise above 10^{12} cm^{-2} . This in turn can cause an apparent shift in the energies of the semiconductor band edges, thus retaining the wide depletion layer to more anodic potentials. In the case of the unmodified electrode, these oxidized species will be protons and so they may diffuse rapidly away from the surface of the electrode producing no resulting shift in flat band potential. For the 'ruthenated' electrode it would appear that the oxidized Ruthenium species are retained on the electrode to more anodic potentials since the improved photoresponse can be maintained even at potentials up to $+0.4\text{V}$ (vs SSE). Thus on oxidizing these ruthenium moieties a net positive charge may build up at the surface of the electrode causing the semiconductor band edges to shift anodically. Note that the small anodic current required to oxidize the Ruthenium species will be very much less than the overall cathodic photocurrents which will be passing through the interface simultaneously via the conduction band.

With this anodic shift in flat band potential comes a corresponding retention of depletion layer width as the electrode potential is taken more anodic. Thus the rate of the back reaction

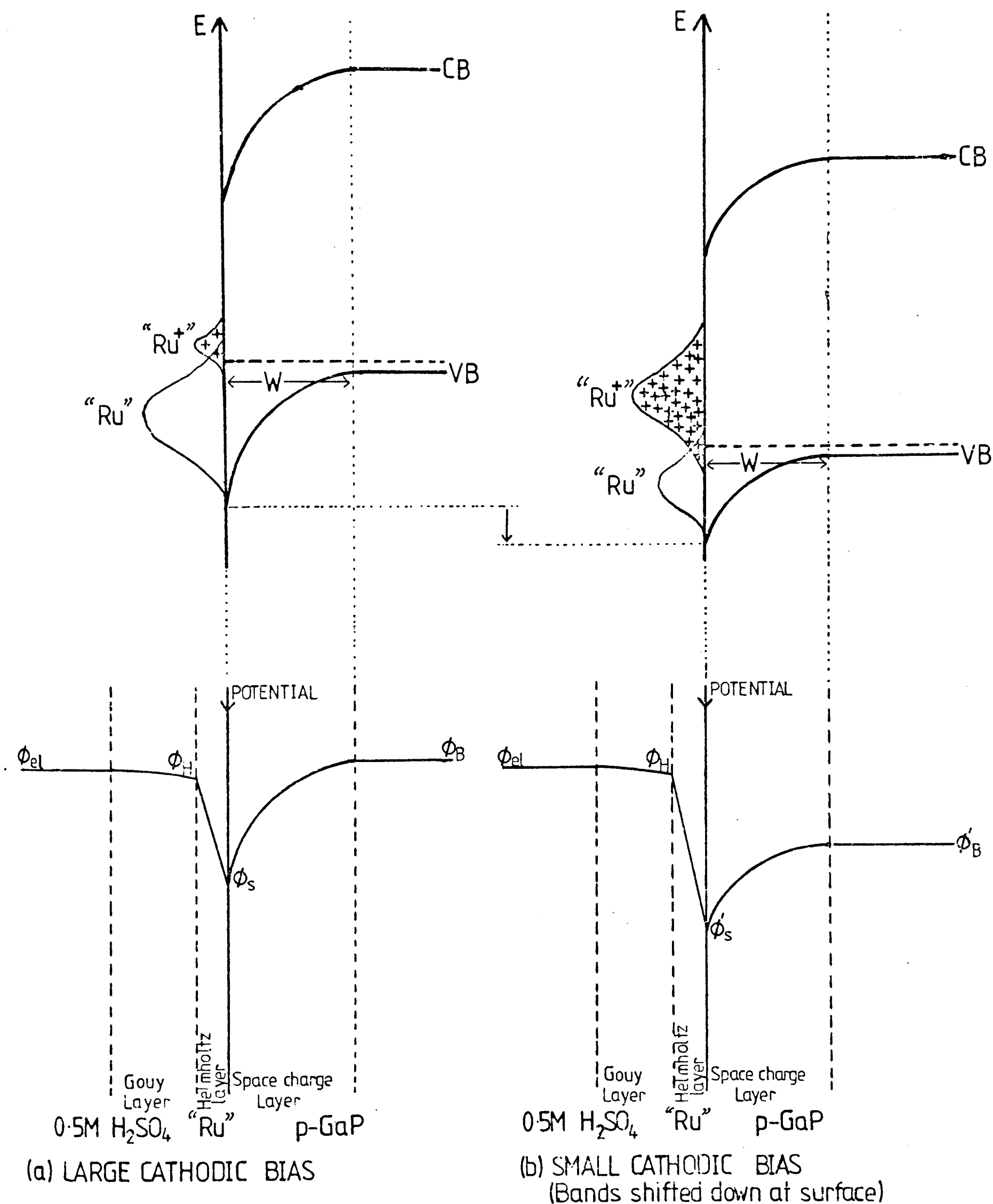


is kept low (since the tunnelling probability is reduced) until more anodic potentials. The sequence of events is illustrated in the diagrams 5.12a & 5.12b.

Taking the electrode potential anodic of +0.4V results in irreversible loss of the enhanced photoefficiency, but this may be explained by electrode dissolution carrying the adsorbed Ruthenium species out into solution. The very small resulting concentration for the Ruthenium species in solution prevents effective re-adsorption of the Ruthenium moieties onto the electrode surface.

It must be stressed that this theory has no strong experimental evidence in its favour since impedance data taken over the potential range 0.1-0.6V cannot be fitted accurately according to the simple 5 component model used in these investigations. Thus Mott-Schottky plots based on the space-charge capacitance data taken in this potential range are quite unreliable and do not show any signs of revealing the predicted flat-band shift. Despite this criticism it is important to note that the experimental data provide strong evidence against all the other theories that have been suggested to date. The particular interpretative problem presented in this chapter reveals the necessity of discovering some additional experimental technique for determining the band edge positions of non-ideal semiconductor surfaces. A detailed electroreflectance study may provide further useful information.

One further fact should be noted concerning the different behaviour of impedance data on unmodified and modified electrodes. For so-called 'clean electrodes' with relatively low surface state densities the product

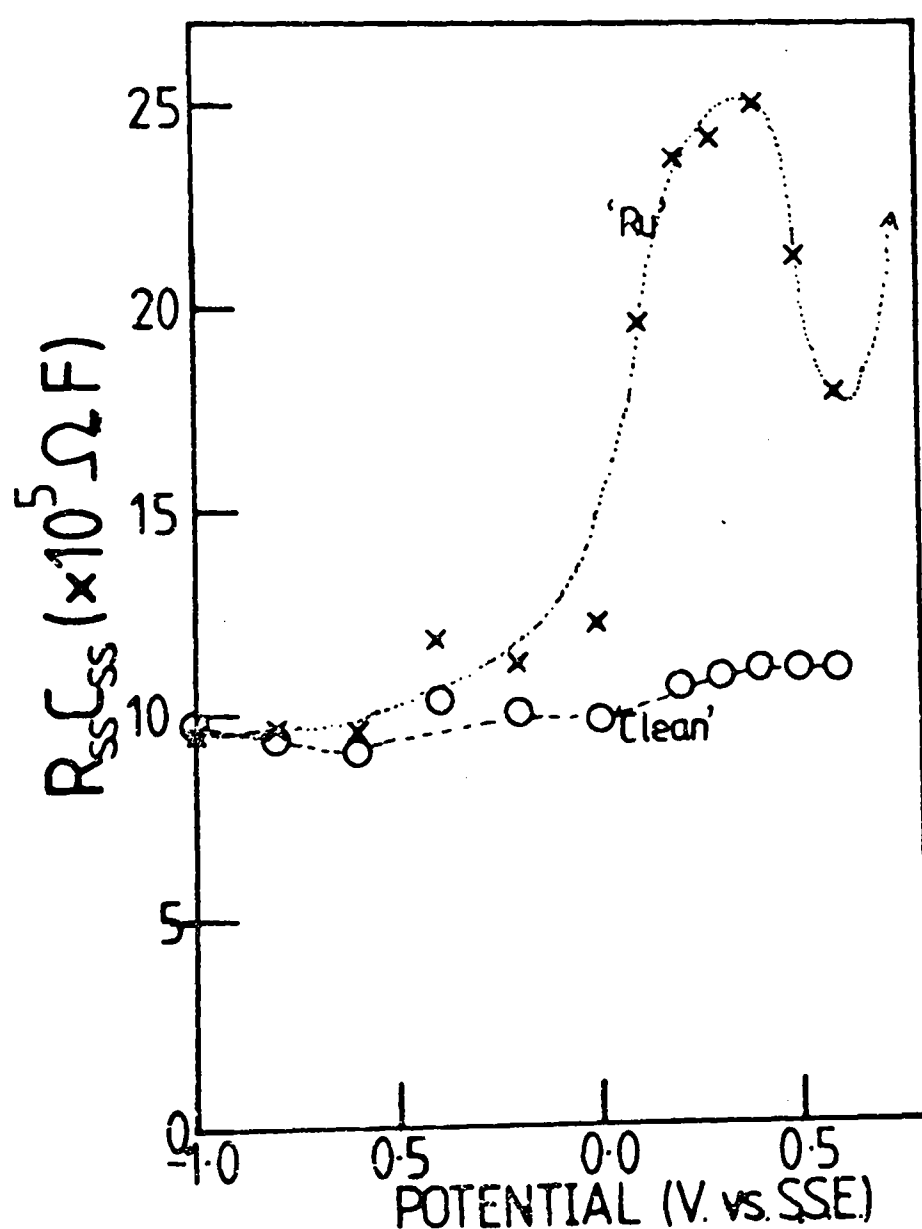


Figs.5.12(a) and (b) . Energy level and potential distribution diagrams for the Ruthenium-modified p-GaP electrode in 0.5M H₂SO₄ at large cathodic and small cathodic biases . The progression from (a) to (b) illustrates how the depletion layer width (W) is retained to more anodic potentials by the charging of the Helmholtz layer and consequent band-edge shifting.

"Ru" = uncharged adsorbed Ruthenium species .

"Ru⁺" = positively charged Ruthenium species .

$R_{SS} \times C_{SS}$ is effectively constant ($\pm 3\%$) over the whole potential range. Indeed the impedance data can be fitted quite accurately with a Warburg impedance²⁶² in place of the $R_{SS} + C_{SS}$ combination. This itself is indicative of the majority of the variation in the interfacial potential difference occurring across the semiconductor. For the modified electrode there is a considerable loss in constancy for this $C_{SS} \cdot R_{SS}$ product in the range 0-0.6V (SSE) (see Fig. 5.13)



Also impedance fits using the Warburg impedance in place of $R_{SS} + C_{SS}$ are considerably poorer over this same potential range. Such a breakdown in this Warburg-like model implies that there may be a considerable potential drop across the Helmholtz layer as would occur if the semiconductor band-edges became unpinned relative to the solution energy levels.

A method was sought for improving the photoefficiency of Hydrogen Evolution on p-GaP at potentials approaching flat-band. Following the work of Heller et al.^{134,260} on n-GaAs a Ruthenium species adsorbed from 0.01M solutions of $\text{RuCl}_3 \cdot \text{H}_2\text{O}$ also appears to be effective on p-GaP. Contrary to expectations, further detailed experiments lead to the conclusion that the Ruthenium adsorption actually increased surface state density. This finding also rules out application in this instance of the theory suggested by Heller et al.²⁶⁰ for the Ruthenium modification of n-GaAs. A complex theory has been put forward which at present remains the only one compatible with all the results. However, strong positive evidence for this theory is not forthcoming as yet although the failure of any other model does lend some credibility to the suggestions.

The surface of p-type Gallium Phosphide in contact with aqueous solution is an extremely complex system and in many ways deviates from the ideal behaviour of a semiconductor electrolyte function as expressed in the present literature. Surface modification of semiconductor electrodes, however, remains a rewarding study since further detailed information may result about both the 'clean' and modified surfaces, and the nature of chemical interactions at solid/liquid interfaces.

The future of this study undoubtedly lies with the application of in-situ spectroscopic techniques such as Electroreflectance, Ellipsometry and others still to be developed. Until the advent of the serious application of these techniques to semiconductor electrodes, these purely electrochemical studies will no more than touch at the surface of the wealth of information and knowledge to be gained about the interfacial processes taking place at semiconductor/electrolyte junctions.

CHAPTER SIX

THE PHOTOELECTROCHEMISTRY OF

p-TYPE GALLIUM ARSENIDE

SECTION 6:1 INTRODUCTION

The exchange of phosphorus for its next lower congener, arsenic might lead one to expect many similarities between the electrochemistry of GaAs and GaP. However despite their many chemical and physical similarities, there is one striking physical difference immediately apparent from the appearance of the single crystal material and that is their colour: GaP is orange and GaAs is black. The origin of this colour difference lies in the magnitude of their bandgaps. GaP possesses an indirect edge of 2.24eV (at 300K), whilst GaAs has a much smaller bandgap of 1.43eV with a direct transition at the band-edge. The magnitude of these bandgaps and the detailed band structures of the III-V compounds have been discussed at length elsewhere.²⁶³⁻²⁶⁶

The difference in the bandgaps of GaP and GaAs has a great significance for the likely application of these materials for solar energy conversion. The maximal efficiency of any device utilizing GaP as the sole energy absorbing material would be expected to be <15% (ignoring the indirect nature of the band-edge). However, with GaAs, efficiencies could be attained as high as 28%, close to the theoretical limit for an optimal single threshold absorbing system (29%).²⁶⁷

Indeed GaAs has found applications in solid-state solar-energy conversion devices such as Schottky barriers, M.I.S. devices and p-n junctions. With some of these systems, conversion efficiencies have exceeded 20%, but only through the use of single crystal materials and at high irradiation intensities ($\sim 10-20 \times \text{AM1}$). The main disadvantage of these devices is thus that the fabrication costs are prohibitive at the present time although

much work continues in the search for the new technologies needed to prepare efficient devices utilizing polycrystalline or thin-film material.

More recently, n-type GaAs has also been utilized in wet-type photovoltaic devices (see Chapter 1) with some quite encouraging results. Heller et al. have reported 14% solar conversion efficiencies for a cell based on the single crystal n-GaAs | 0.8M K_2Se , 0.1M K_2Se_2 , 1M KOH | C¹³⁴ (graphite) cell and have even obtained $\approx 8\%$ ¹³⁵ for a cell based on polycrystalline material. The major problems with the commercial development of this cell are expense, toxicity and the extremely high extinction coefficient of the selenide solution through which the light must pass in order to reach the electrode surface.

n-type GaAs is of no use as an anode for the photoelectrolysis of water since photoinduced anodic decomposition of the electrode takes place preferentially in the absence of a suitable electron donor (e.g. Se^{2-} or Te^{2-}) in the solution. The p-type material has, however, been shown to evolve Hydrogen when used as the cathode in a photoassisted electrolysis cell, but its stability and efficiency remain under question.

The purpose of this study was to carry out a thoroughgoing electrochemical and photoelectrochemical study of p-GaAs in order to establish:-

1. The band positions of p-GaAs.
2. The kinetics of Hydrogen Evolution.
3. The effect of adsorbed metal ions on those kinetics.
4. The stability of the electrode under dark and illuminated conditions.

In particular, for each of these aspects, comparisons were sought between the behaviour of p-GaAs and p-GaP. Some prospects for the use of p-GaAs as a photoelectrode in solar-energy conversion devices are also briefly discussed.

SECTION 6:2 THE BAND POSITIONS OF p-GaAs AND IMPEDANCE MEASUREMENTS

There is some controversy in the literature regarding the flat-band potential V_{fb} of p-GaAs in acid solutions. Bockris and Uosaki⁹¹ found it to be +0.19V vs. S.S.E. (corrected from data using the S.C.E.) and Laflère et al., obtained a value of 0.2V vs. S.S.E.¹⁰⁷ However, Memming,²⁶⁸ in some much earlier work gave a value of +0.6V, that has been quoted by many authors along with his data on p-GaP,⁵ which is also high relative to the value of V_{fb} found in this work and by a number of other workers.

Admittance data for the p-GaAs electrode immersed in 0.5M H_2SO_4 were taken for use in the simple two-component circuit (R+C series network) and five component circuit (see Fig4.24(f)) analyses. However, the latter analysis requires many more results at each potential, taken at a number of frequencies, and an inherent time-dependence in the admittance readings between -0.5 - +0.2V. rendered the results in this potential range of little value. Despite these problems, straight-line portions were obtained for the C_{sc}^{-2} vs. Voltage plots with both analyses (see Figs. 6.1 & 6.2). As with p-GaP, the two-component analyses showed signs of being incomplete due to the considerable deviations from ideal Mott-Schottky behaviour at potentials approaching flat-band.

Comparing these results with the findings on p-GaP, we may attribute the deviations from linearity, for the two component C_{sc}^{-2} vs. Voltage plots, to an additional capacitance contribution from surface states accessible in the potential range -0.5 - +0.2V.

Despite these problems of interpretation for results taken near to V_{fb} , it is interesting to note that for potentials cathodic of -0.6V, there is virtually no frequency dispersion in the capacitance data taken from the two-component analysis (Fig. 6.1). However, this was found to be true only for electrodes etched in 5% Br_2 in CH_3OH prior to use. An alternative etch (H_2O_2 , H_2SO_4 , H_2O) suggested by Gatos and Lavine,²³⁸ produced a more

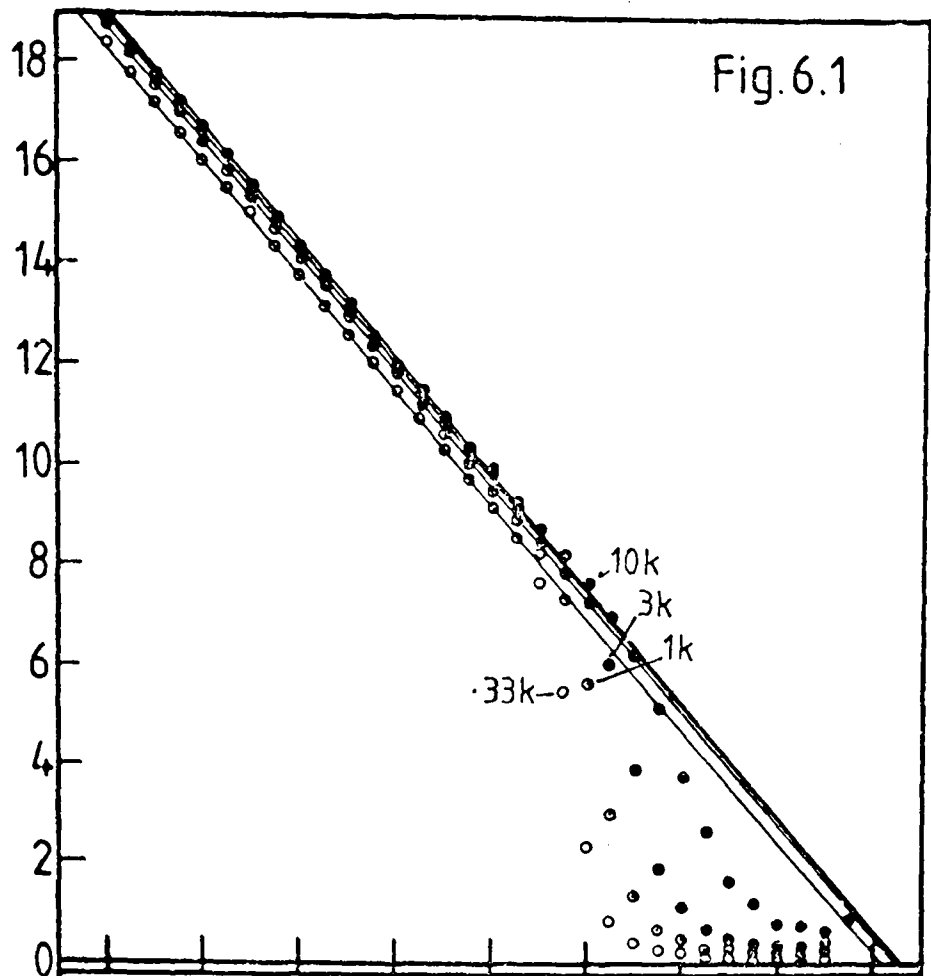


Fig.6.1 Mott-Schottky plots for (100) p-GaAs in 0.5M H_2SO_4 . Data analysed according to simple R+C model. The data shown were compiled at 10kHz, 3kHz, 1kHz and 330Hz in order of increasing capacitance. Electrode pre-etched in Br_2/CH_3OH .

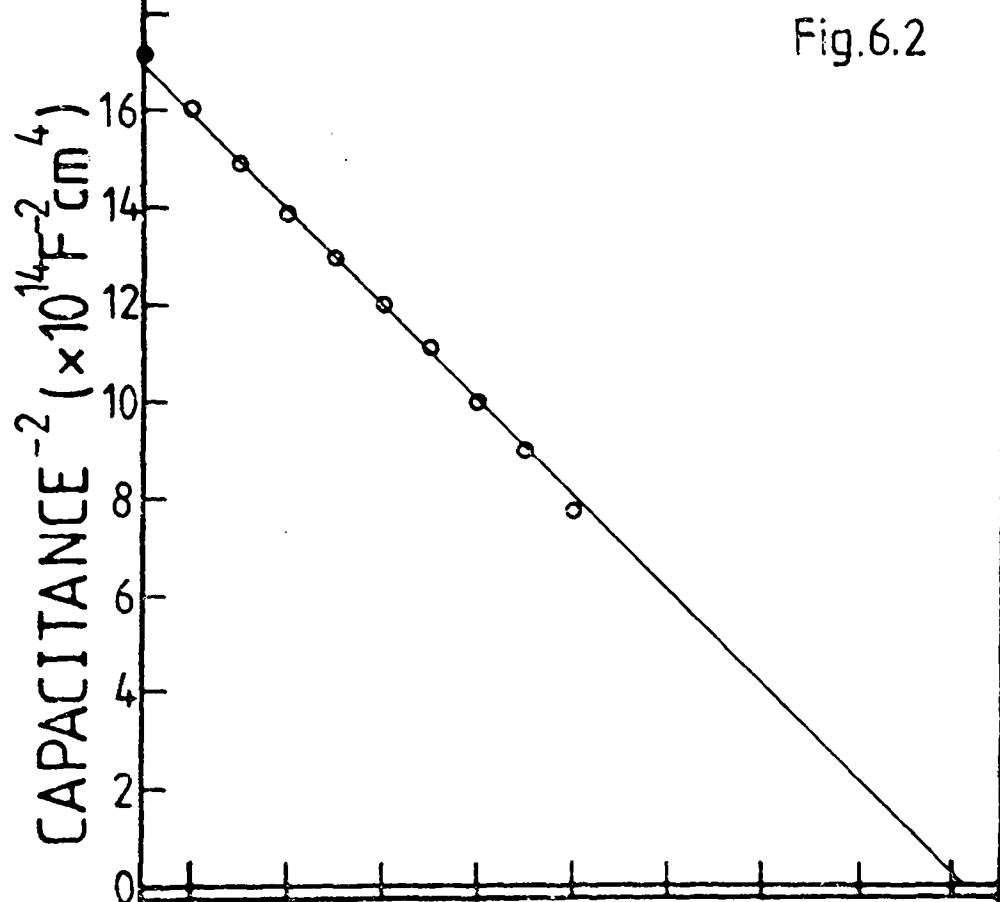


Fig.6.2 Mott-Schottky plot for (100) p-GaAs in 0.5M H_2SO_4 . Data analysed according to five component (Fig. 4.24f) circuit. Electrode pre-etched in Br_2/CH_3OH .

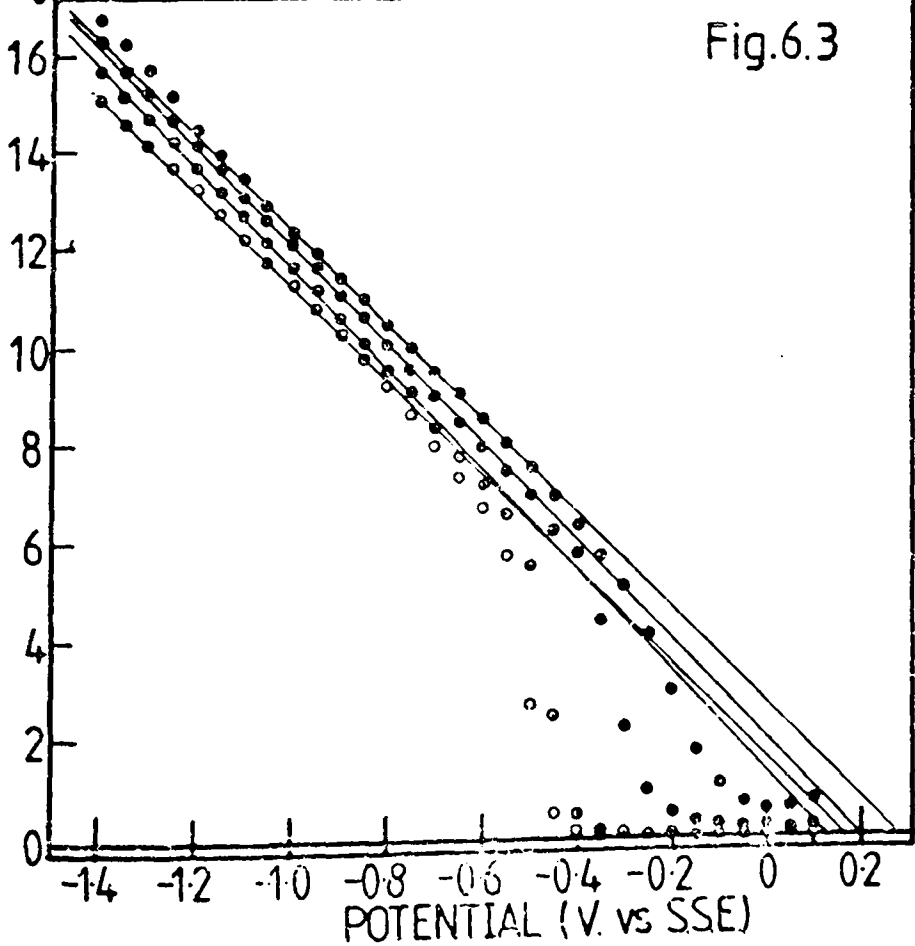


Fig.6.3 Mott-Schottky plots for (100) p-GaAs in 0.5M H_2SO_4 . Data analysed according to simple R+C model. Ordering of capacitance data as in Fig. 6.1. Electrode pre-etched in $H_2O_2/H_2SO_4/H_2O$.

marked frequency dispersion of capacitance (see Fig. 6.3), similar to that discussed by Gomes et al. as a Type B behaviour in their nomenclature.²⁰⁶ However, no attempt was made to interpret this result seriously and all further work used electrodes pre-etched in the $\text{Br}_2/\text{CH}_3\text{OH}$ solution.

As a consequence of this negligible frequency dispersion under the two-component analysis, surface state capacitances (C_{ss}) obtained with the five-component analysis for the potential range cathodic of -0.6V were found to be typically $\approx 10^{-10}$ – 10^{-9}F cm^{-2} . This is to be compared with a C_{ss} value of $\sim 10^{-8}$ – 10^{-7}F cm^{-2} for p-GaP electrodes where frequency dispersion of capacitance data was a far greater problem (see Fig. 4.23). Since the $\text{Br}_2/\text{CH}_3\text{OH}$ etch produced a perfectly shiny finish to the p-GaAs electrodes, the varying behaviour between the two etches and that for p-GaP may well reflect a difference in the density of surface step and dislocation sites for the various electrodes. It has been suggested that these imperfections introduce additional interband surface states that contribute to capacity dispersion.

The flatband potential for p-GaAs in $0.5\text{M H}_2\text{SO}_4$ can be seen to be $+0.2\text{V}$ vs. S.S.E. based on the results from both analyses. This is in good agreement with the findings of Bockris et al.⁹¹ and Laflère et al.¹⁰⁷ and must cast further doubt on the validity of Memming's data.²⁶⁸

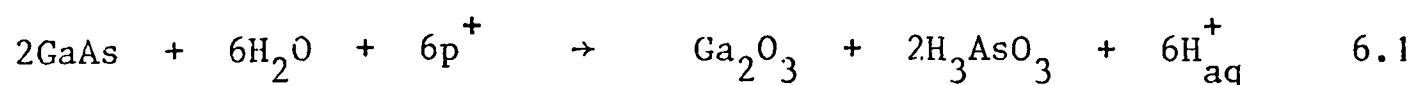
Attempts were also made to obtain the flat band potentials of p-GaAs electrodes in other media, in particular 1M KCl ($\text{pH} 6.3$) and 1M NaOH ($\text{pH} 13.3$). However, Mott-Schottky plots generated from the results analyzed according to a two-component equivalent current failed to produce satisfactory straight-line regions. In addition, it was found that all admittance readings were dependent on the time that the electrode had been immersed in solution (for neutral and alkaline pH's), so that five-component analysis was rendered impossible. Nevertheless, from a compilation of results taken in 1M NaOH immediately after immersion in the solution, a flat band potential was estimated as $V_{fb} \approx -0.6\text{V}$. Extrapolation from the known value of

+0.2V in 0.5M H_2SO_4 according to a variation of -60mV per pH unit gives a predicted value in 1M NaOH of -0.55V. Only one published result may be quoted for comparison, and that is from Bockris and Uosaki who claim a value of -0.26V (vs. S.S.E)⁹¹.

Fig. 6.4 depicts the band edge of p-GaAs relative to the H^+/H_2 and $\text{O}_2/\text{H}_2\text{O}$ redox potentials in 0.5M H_2SO_4 . It is apparent that the valence band of GaAs lies well above the $\text{O}_2/\text{H}_2\text{O}$ level, which makes n-GaAs of no use as an anode for the photoelectrolysis of water. However, the conduction band lies well above the H^+/H_2 level; with this high hydrogen overvoltage ($\sim 0.8\text{V}$), it would be expected that p-GaAs should be an efficient cathode for the photoevolution of Hydrogen.

SECTION 6:3 CURRENT-VOLTAGE BEHAVIOUR OF p-GaAs IN VARIOUS ELECTROLYTES

Figs. 6.5-6.8 depict dark and illuminated cyclic voltammograms (C.V.'s) of p-GaAs in 0.5M H_2SO_4 , 1M HCl, 1M KCl and 1M NaOH respectively. Similar illumination intensities were used for the three former media; but for the NaOH results, an illumination intensity of about one quarter of the others was used. In all media, the dark C.V.'s are characterized by small cathodic currents at the more cathodic potentials and an irreversible anodic wave at the anodic limits of the sweeps. As with p-GaP, this is the typical behaviour of an ideal p-type semiconductor. The anodic wave corresponds to dissolution of the electrode according to



At higher potentials ($\sim 1.0\text{V}$ vs. S.S.E) passivation behaviour is observed, but this was not further studied in this work. The subject of passivation and oxide growth on GaAs has received much attention in the literature of MOS and MIS devices.²⁵²⁻²⁵⁴

The illuminated C.V.'s in H_2SO_4 and HCl are quite similar, although there is some difference in the hysteresis behaviour at potentials -0.5 to

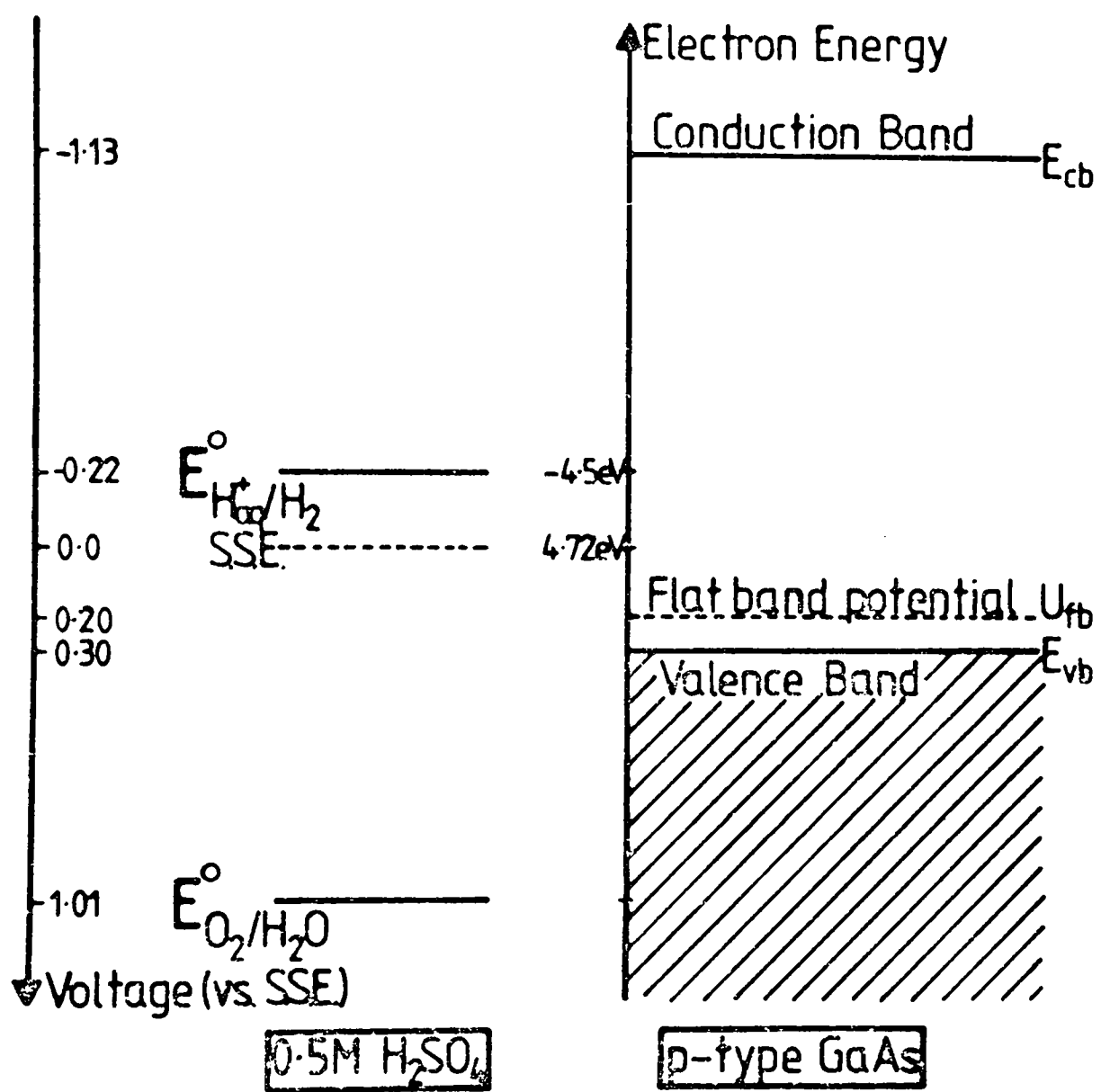


Fig.6.4 Energy level diagram for p-GaAs in 0.5M H₂SO₄, shown relative to the H⁺/H₂ and O₂/H₂O levels in aqueous solution .⁴

Figs.6.5 and 6.6 Cyclic voltammograms of p-GaAs in 0.5M H_2SO_4 and 1.0M HCl respectively in dark (—) and illuminated (---) conditions Sweep rate 250mV s^{-1} .

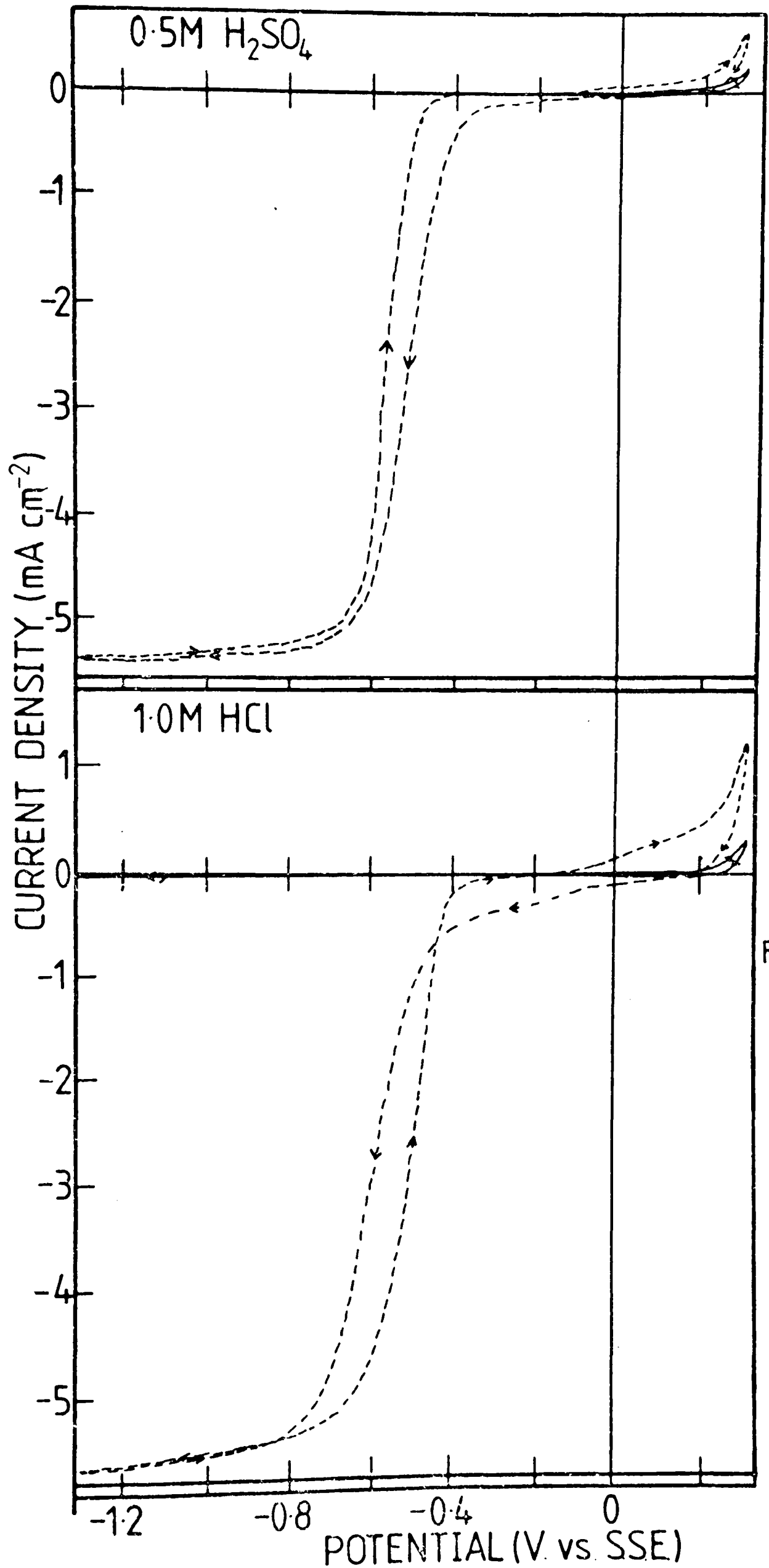


Fig.6.5

Fig.6.6

Fig.6.7 Cyclic voltammogram of p-GaAs in 1.0M KCl in dark (—) and illuminated (---) conditions . Sweep rate 250mV s^{-1} .

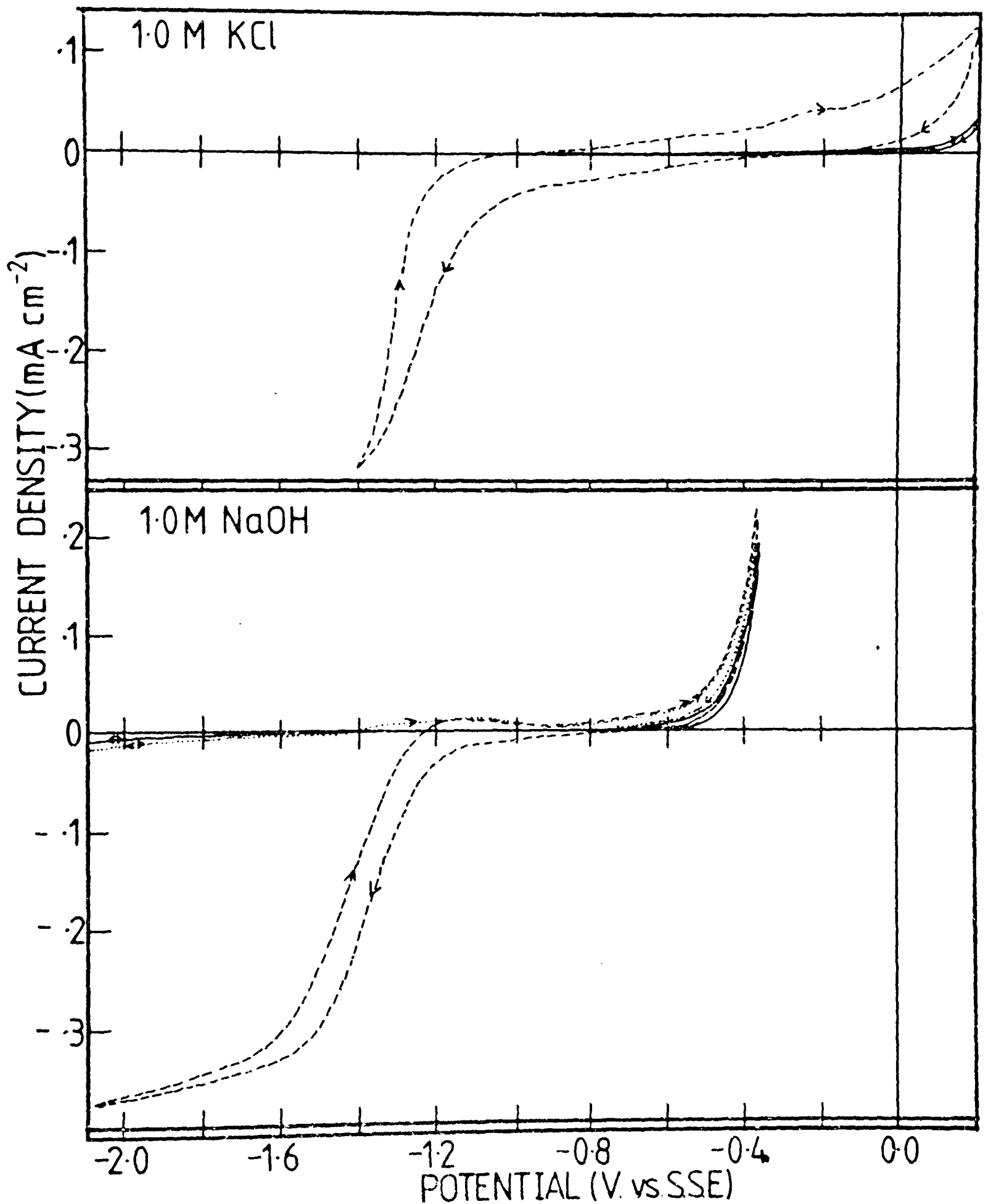
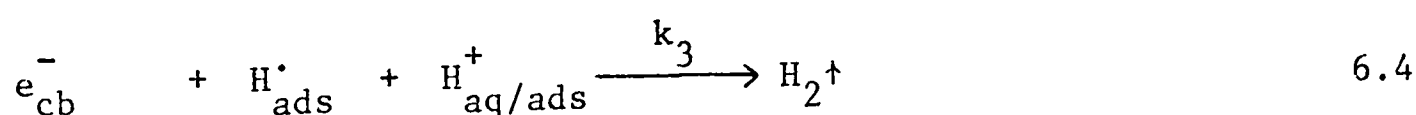
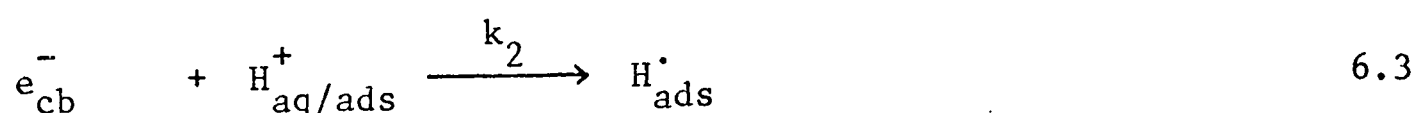


Fig.6.8 Cyclic voltammogram of p-GaAs in 1.0M NaOH in dark (—) and illuminated (---) conditions . (Light intensity approx. one quarter that used for Figs.6.4-6.7 .) Dotted plot (....) created by extinguishing the illumination at the cathodic limit . Sweep rate 250mV s^{-1}

-0.6V. Short-term quantitative tests indicate that >95% of the photocurrent is directed towards the evolution of Hydrogen gas. However, these two results reveal a strong similarity to the situation with p-GaP; the onset of efficient Hydrogen evolution fails to occur until the electrode is biased some 0.6 to 0.7V cathodic of the flat-band potential. It is also observed that following the passage of cathodic photocurrent there is an enhancement of the irreversible anodic wave for potentials anodic of -0.1V. This enhancement, as for p-GaP, is not a direct anodic photocurrent, but reflects the reoxidation of species electrogenerated by the cathodic photocurrent. Integration of the total additional charge under the anodic enhancement can lead to figures corresponding to greater than one monolayer of one-electron redox species. This is particularly apparent if the electrode is potentiostatted at negative potentials under illumination for several minutes before the cycle is continued.

Thus, we may suggest that a similar Hydrogen evolution mechanism to that proposed on p-GaP is also in operation on p-GaAs, notably:-



In addition, the presence of $H^\bullet$ atoms in the bulk of the electrode may have two further consequences

1. The rate of tunnelling of holes to the surface of the electrode (e.g. in reaction 6.5) will be enhanced by the process of resonance-assisted

tunnelling. Thus photocurrent efficiencies will fall for potentials at which there exist states at the surface to which these holes might tunnel adiabatically.

2. The H^+ atoms within the surface may act as electron/hole-pair recombination centres resulting in **poor** photocurrent efficiencies even at very cathodic potentials where the surface recombination pathway through 6.5 may no longer be important.

Support for this differentiation of two separate effects of bulk H^+ atoms comes from the far slower decay in the magnitude of the cathodic photocurrent for potentials cathodic of $-0.8V$ than anodic of this point.

In NaOH (Fig. 6.8), the photoefficiency appears to be appreciably lower and saturation of the cathodic photocurrent at more cathodic potentials is less marked than in acidic media. Fig. 6.8 also demonstrates that the passage of cathodic photocurrent increases the magnitude of the dark current flowing at the cathodic limit. The anodic reoxidation waves in this electrolyte are also considerably larger than in acid solutions. As noted from the steady decay of the a.c. admittance data for p-GaAs in 1M NaOH, there appears to be a general degradation of the electrode in the alkaline medium. There is no literature citation for the chemical dissolution of p-GaAs in alkali; but the passage of continuous, small anodic or cathodic dark currents ($<1\mu A\text{ cm}^{-2}$) may lead to the formation of oxidized or reduced material in the surface of the electrode. The apparent short-term stability of p-GaAs in acid solutions may reflect the solubility of these surface films at low pH's.

If in NaOH the surface layer of the electrode becomes coated in a layer of insoluble or partially soluble mixed Gallium and Arsenic oxides, the electrochemistry and a.c. admittance of the electrode will be severely affected. Attempts have been made to determine the precise chemical nature of oxide films formed on the surface of GaAs used in M.I.S. solid-state devices. However, even with accurate depth profiling using Argon-ion

etching and ESCA/Auger techniques, the chemical composition of the electrode surface cannot be described in terms of single chemical compounds.²⁶⁹ Rather, the results show very complex and depth-dependent mixtures of Gallium and Arsenic Oxides. Detailed electrochemical studies of these films appear fruitless since the surface chemical composition will be continuously dependent on the past history of experiments on the electrode. Thus all the intensive studies on p-GaAs were concentrated on work in acidic solutions where the rate of formation of such films was very much slower, if not entirely eradicated.

In KCl (Fig. 6.7), despite nearly ideal dark-current behaviour, the photoefficiencies are strikingly decreased relative to both the acidic and alkaline solutions, particularly at potentials approaching flat-band. Anodic reoxidation waves are also very large; they may reflect a very slow k_3 (Equation 6.4 above) in this medium, since there appears to be a large build-up of readily reoxidisable material (possibly adsorbed Hydrogen atoms) on the surface of the electrode. Since results in 0.5M H_2SO_4 and 1M HCl are very similar, effects due to specific chloride-ion chemisorption in KCl may be ruled out. As with NaOH, potentiostatic results in 1M KCl appear to be highly time-dependent at all potentials. At cathodic potentials this may be explained by the steady incorporation of Hydrogen atoms into the surface regions of the electrode. The $H^\bullet$ atoms, as well as assisting hole transfer to the surface in the surface-recombination reaction, may assist electron tunnelling to the surface to increase the magnitude of the cathodic dark current. Illumination increases the rate of incorporation of the $H^\bullet$ atoms, and so dark currents are further enhanced by periods of illumination.

At anodic potentials, time-dependent behaviour reflects the continuous surface oxidation of the electrode. In the neutral pH's (and apparently in alkali) the surface oxides are insoluble, so irreversible degradation of the electrode response results.

Figure 6.9 shows the cathodic photocurrent action spectrum for p-GaAs in 0.5M H_2SO_4 . The results have quite large standard deviations (as depicted by the error bars) since very small illumination intensities had to be used to prevent significant time-dependent behaviour of the photocurrent. Nevertheless the overall shape of the spectrum is quite clear; the steady decrease in photocurrent efficiency on approaching the direct band edge at about 900nm is caused by the decreasing absorption coefficient of GaAs with increasing wavelength. From the Albery/Hamnett equation of Chapter 2, the fraction of light absorbed in the field-free region increases as the absorption coefficient decreases and consequently the overall photocurrent efficiency falls.

SECTION 6:4 LOW LIGHT INTENSITY PHOTOCURRENT/VOLTAGE PLOTS FOR p-GaAs IN VARIOUS MEDIA

Photocurrent voltage (PCV) plots for p-GaAs electrodes in 0.5M H_2SO_4 , 1M HCl, 1M KCl and 1M NaOH are shown in Figs. 6.10-6.13, run at maximum photocurrents of approximately $10^{-5} \text{ A cm}^{-2}$ in 830nm light. Considerable hysteresis is observed for all media, but saturation at higher cathodic bias is only apparent for the H_2SO_4 , HCl and NaOH cases. Also, as one approaches flat-band, the photocurrents become increasingly transient for all the solutions. Focussing attention initially on the results in H_2SO_4 and HCl, it is notable that it is not possible to see any change-over from cathodic to anodic transient photocurrent near the flat-band potential. This is in contrast to p-GaP where the cathodic/anodic photocurrent crossover agreed to within 0.025V with the flat-band potential derived from impedance measurements. Indeed the apparent crossover seen at $\sim 0.35\text{V}$ in 0.5M H_2SO_4 may be shown to be instrumental in origin as at this potential the lock-in amplifier becomes no longer capable of separating out the small in-phase photocurrent from the very large varying background of anodic dissolution current.

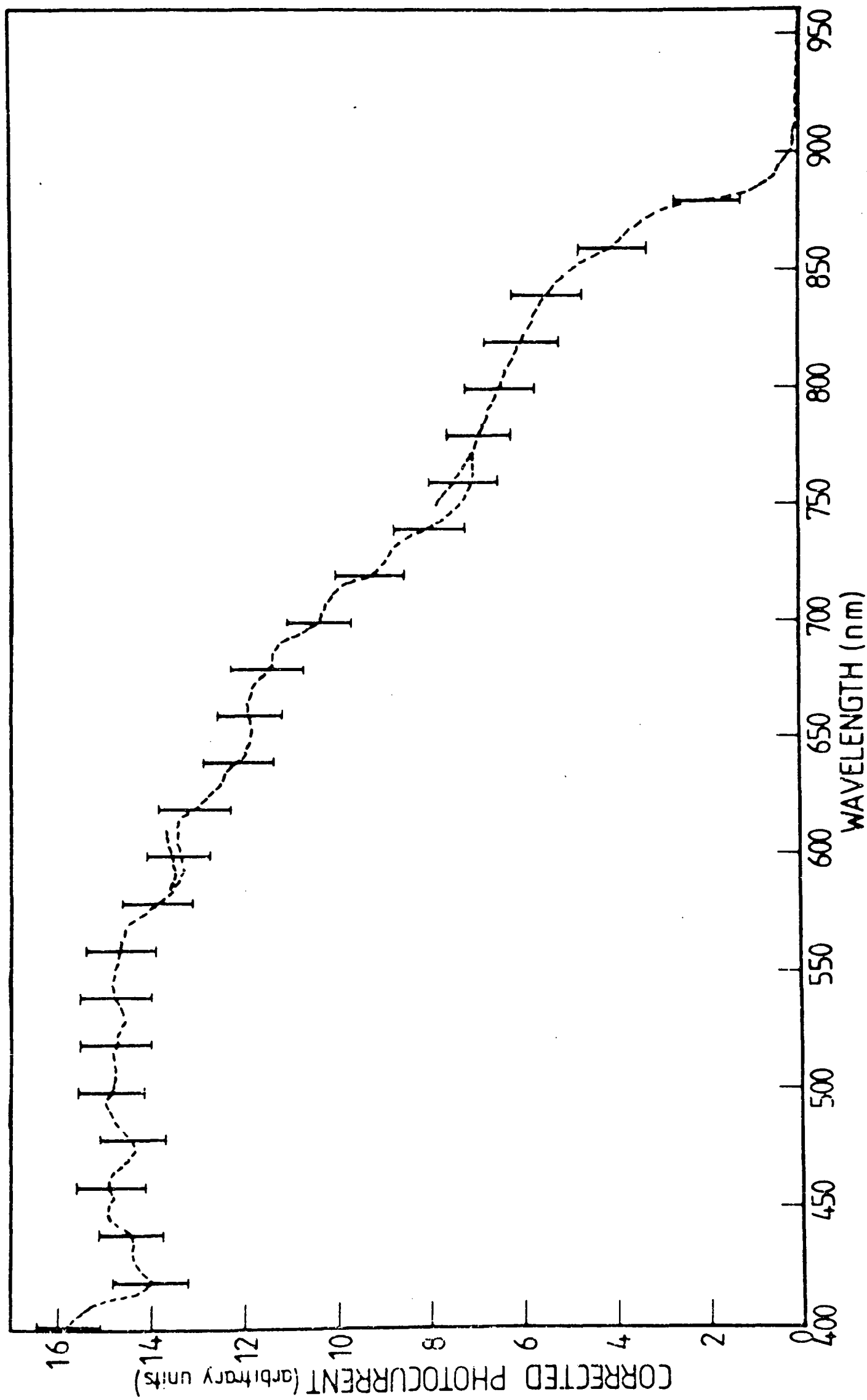
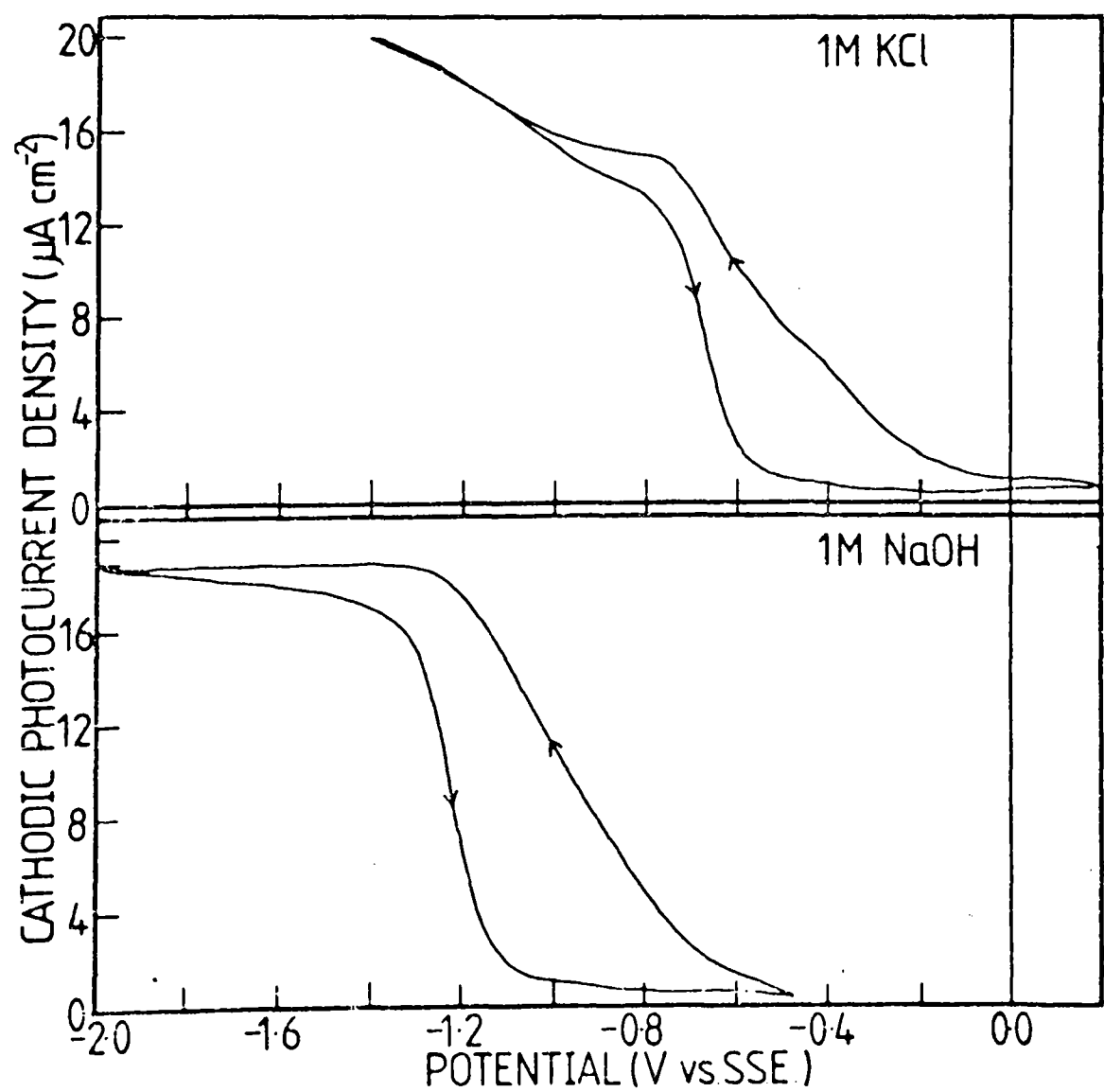
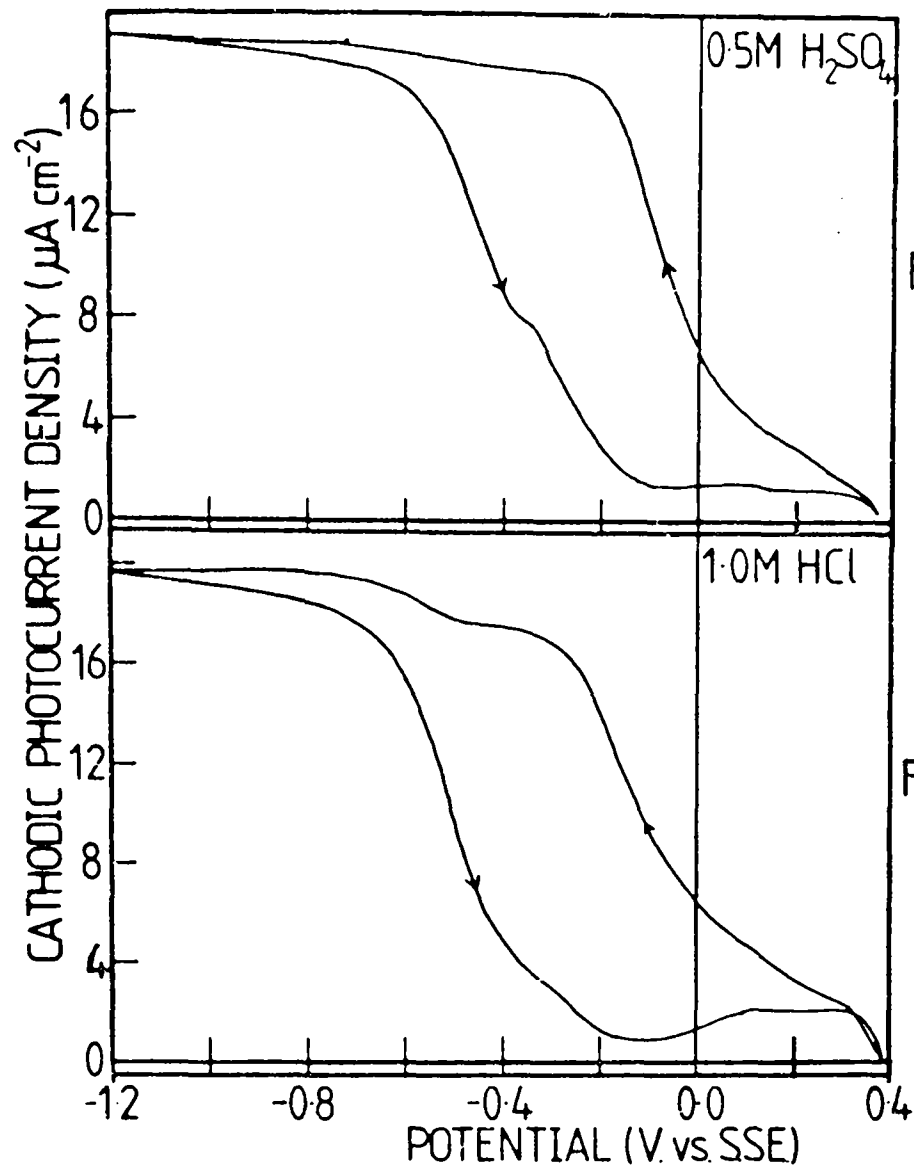


Fig.6.9 Cathodic photocurrent action spectrum (corrected for lamp output) of p-GaAs in 0.5M H_2SO_4 . Very low light intensities were used to avoid time dependent behaviour of the photocurrent. Hence signal to noise ratio was low resulting in large standard deviations for photocurrents.

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Figs.6.10-6.13 Photocurrent-voltage plots for p-GaAs in 0.5M H_2SO_4 , 1.0M HCl, 1.0M KCl and 1.0M NaOH respectively. 830nm illumination. Approx. four times intensity required to generate Fig.6.12. Sweep rate $50mV s^{-1}$.



Some explanation for this contrasting observation may be sought in the differing mobilities and effective masses for the mobile carriers in GaP and GaAs (see Table 6.1)¹⁹².

Table 6.1

	Mobility at 300K (cm ² /Volt sec)		Effective Mass ($\frac{m^*}{m_0}$)	
	Electrons	holes	Electrons	holes
GaP	110	75	0.5	0.5
GaAs	8500	400	0.068	0.5

The magnitude of the cathodic photocurrent is seen to be related to the mobility (or diffusion coefficient) of the minority-carrier electrons (see Albery / Hamnett equation Section 2:11). In GaP with approximately equal mobilities for the electrons and holes, we find a crossover from cathodic to anodic photocurrent at an 'expected' potential very close to flat-band. In GaAs, on the other hand, the electron mobility is much greater than that of the holes, and the cathodic photocurrent continues to much more anodic potentials, even anodic of the flat-band potential. Now the approximations and limitations made to reach Equation 2.131 of Chapter 2 are not applicable in the potential range near flat-band. Also allowance for non-equilibrium effects due to the passage of very large anodic dark currents would be necessary so any theory designed to explain the detailed behaviour of transient photocurrents near flat-band would be very complicated. No further attempt will be made here.

Although not clear from the results as shown, the photocurrent efficiency of the p-GaAs electrode in 1M KCl is about 25% of that in the other

media, since approximately four times as much light intensity had to be used to generate the curve of Fig. 6.12 as the other PCV plots. The surface oxide produced by the anodic current when the electrode is at potentials $>0.0V$ (S.S.E) does not dissolve in the neutral KCl solution; and the surface oxide may increase the density of surface recombination states or, possibly, reduce the rate of the proton reduction and Hydrogen evolution reactions.

The photocurrent-onset hysteresis appears to be very similar to that observed for p-GaP and similar to the results of Fig. 4.12 ; p-GaAs also shows a very similar dependence of the PCV plots on illumination intensity. It thus seems quite reasonable to suggest that the problems of strong Hydrogen-atom adsorption and bulk migration at the surface of p-GaAs are responsible for the very poor photocurrent efficiencies at potentials within 0.7V of the flat-band potential.

SECTION 6:5 EFFECT OF METAL IONS ON CATHODIC PHOTOCURRENT EFFICIENCY OF p-GaAs ELECTRODES

As with p-GaP, it was thought that adsorption of various metal ions onto the surface of p-GaAs might have an advantageous effect on the efficiency of Hydrogen evolution on illumination. The first and obvious adsorption material tried was crude $RuCl_3$ in HNO_3 . Photocurrent efficiencies were indeed improved at potentials approaching flat-band, although as Fig. 6.14 shows the effect is not all that marked in the PCV plot measured at low light intensity. There is little improvement in the photocurrent onset for the cathodic sweep, but the anodic sweep shows significant improvement. This is to be expected from the model since, on the cathodic, sweep, the surface concentration of Hydrogen atoms is initially quite small so the surface recombination pathway of equations 6.3 and 6.5 will make little contribution to loss of efficiency. However, on the anodic sweep for the clean surface, the Hydrogen-atom concentration has now increased sufficiently to allow for significant back reaction of the Hydrogen atoms

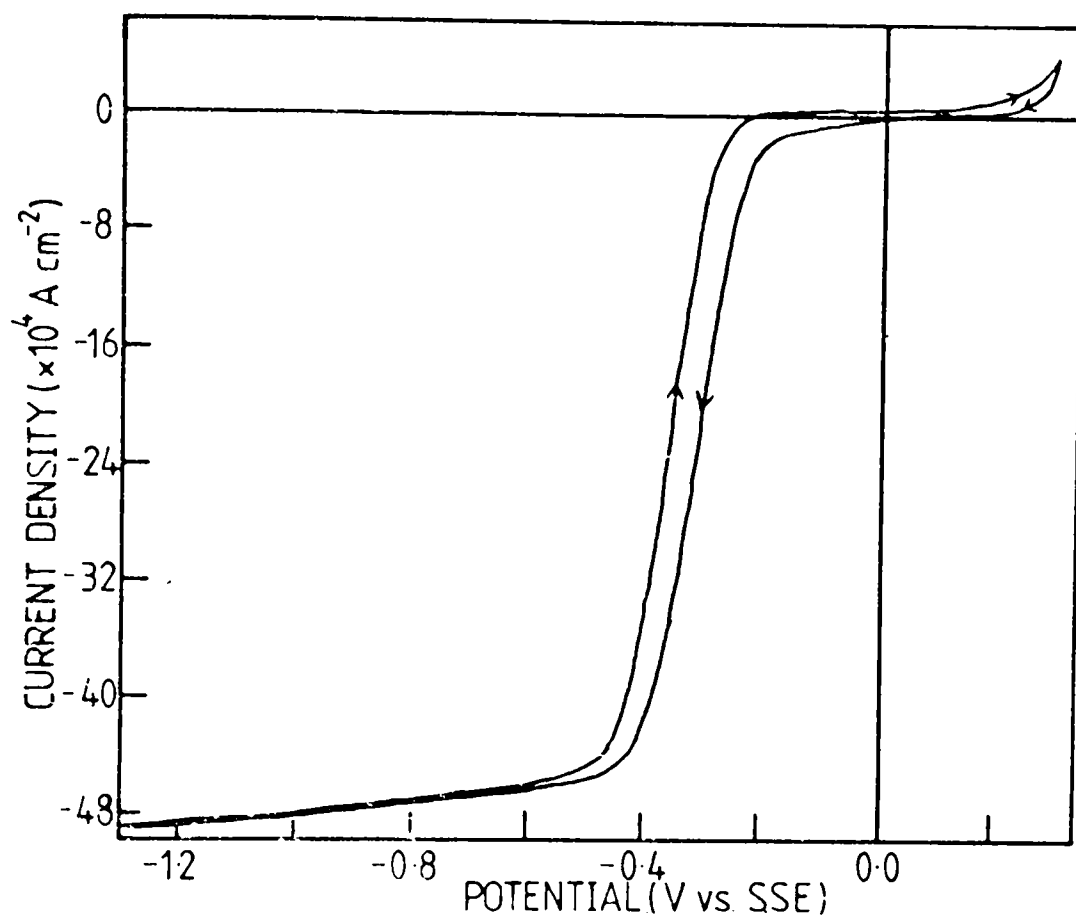
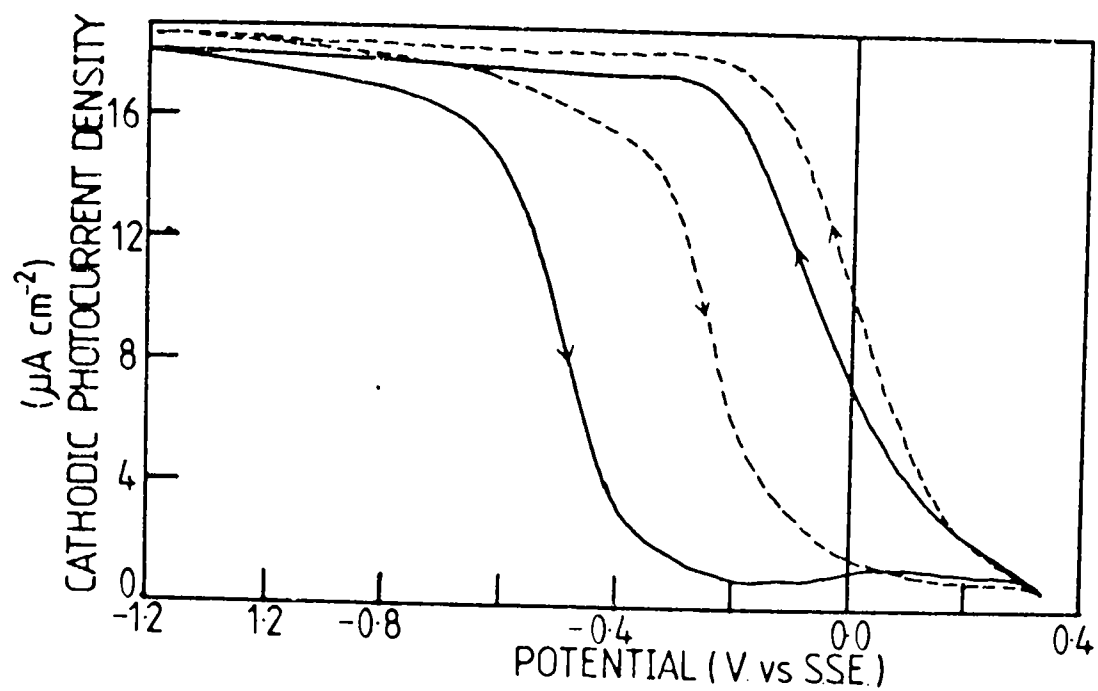


Fig.6.15 Cyclic voltammogram for Selenium and Ruthenium modified p-GaAs under white light illumination in 0.5M H_2SO_4 . Sweep rate 250mV s^{-1}

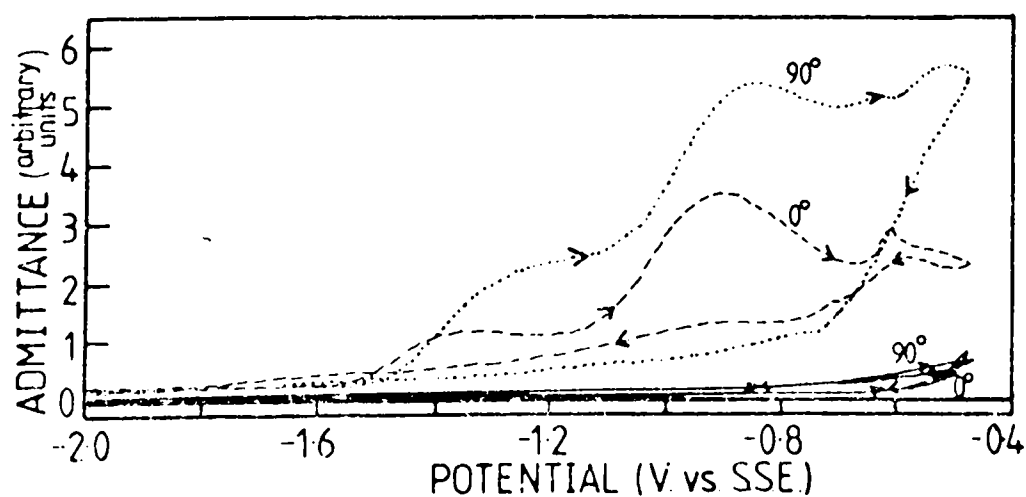


Fig.6.16 A.C. cyclic voltammograms of p-GaAs in 1.0M NaOH before (—) and after (---) dipping into a 0.01M solution of Bi(III) . Modulation 3mV ,1kHz . Sweep rate 50mV s^{-1} .

with valence-band holes (possibly assisted by resonance tunnelling via Hydrogen atoms which have penetrated the surface region of the electrode). For the Ruthenated surface, however, it appears that the rate of the back reaction is in some way decreased. From the mechanism put forward in Chapter 5, this may occur by a temporary shift in the flat-band potential of the electrode caused by the charging up of a surface bound ruthenium redox couple. This will act such as to increase the width of the depletion layer and thus reduce the rate of non-classical hole transfer through the space-charge region. Further evidence for this comes from capacitance measurements, in particular A.C.C.V's where it is found that Ruthenium-ion adsorption causes a tenfold increase in interfacial admittance near flat-band, traceable on more detailed analysis to an increase in surface-state capacitance. It is apparent, therefore, that again the theory of Heller ²⁶⁰ et al. used for n-GaAs is not applicable in this instance for p-GaAs. Unfortunately, no complete impedance analysis is possible for this material since the admittance readings for all potentials were very unsteady. In consequence the data could not reveal the position of any peak in surface state density on the p-GaAs electrode.

Following, the suggestion by Heller ¹³⁴ that a combination of Selenium and Ruthenium adsorption has a greater effect on the photoefficiency of n-GaAs than Ruthenium alone, the same combination was tried on p-GaAs. The additional effect of Selenium adsorption was very small but Fig. 6.15 illustrates the best photocurrent voltage curve for p-GaAs in the photoevolution of Hydrogen gas, obtained to date.

There is an apparent greater stability for the Ruthenium modified GaAs surface than with the p-GaP:Ru treatment. However, this may be related to the differing sweep limits that were used as standard for p-GaAs and p-GaP. Thus, for p-GaAs, the standard voltage sweep reached the anodic limit at +0.3V (cf. p-GaP $\sim$ +0.7V). Although this potential is sufficient to cause surface oxidation of the p-GaAs electrode, it does not seem to cause

irreversible degradation of the Ruthenium modification. Further tests seemed to indicate that the adsorbed Ruthenium complex was only removed by biasing the electrode anodic of +0.5V.

A number of other metal ions were tested for their effects on the cathodic photocurrent efficiency of p-GaAs near flat-band in both acidic and alkaline solutions. The results are presented in Table 6.2; none of the other metal ions tested produced a positive increase in photoefficiency, the majority producing a negative response. Evidence for actual adsorption of some of these ions (as indicated in Table 6.2) comes from the observation of significant changes in the A.C.C.V of the electrodes following the metal-ion dip, (e.g. see Fig. 6.16 for Bismuth adsorbed on p-GaAs used in 1M NaOH).

No detailed mechanistic conclusion could be reached about the effect of metal-ions on p-GaAs. However it is apparent that the strength of adsorption of the Hydrogen atoms on the p-GaAs surface is sufficiently large to nullify any small catalytic effects induced by metal-ion adsorption. On p-GaP, the success of the Ruthenium treatment was thought to be due to the shifting of the energy bands caused by oxidation of the surface adsorbed Ruthenium complex at potentials approaching flat-band (see Chapter 5). Assuming the same complex to be adsorbed on the p-GaAs surface, the smaller enhancement effects seen with this latter material may be related to the more cathodic flat-band potential of p-GaAs. Thus, rather than "pinning the Fermi level" (relative to the band edges) with a large degree of band bending, as the electrode is made more anodic, the p-GaAs bands may become almost flat before the Ruthenium complex may be oxidized. To discover a more effective surface modification for p-GaAs may entail finding an adsorbed complex with a more cathodic redox potential than that produced by the Ruthenium treatment.

TABLE 6.2 Responses of p-GaAs electrodes to various adsorbed ions .
Those marked with an asterisk correspond to cases where there is
strong evidence from A.C.C.V.'s that adsorption has taken place .

Positive Effect	Null Effect	Negative Effect
"Ru(III)"*	Sn(II)*,V(IV) Co(II) ,Ni(II) Eu(III)	Bi(III)*,Cu(II)* Ag(I)*,Hg(II)* Pb(II)*,Rh(III)* Sb(III)*,Pt(II)*

For composition and method of treatment , see Chapter 5 ,Section 5:2

SECTION 6:6 THE LONG TERM STABILITY OF p-GaAs

6:6:1 Dark Conditions

An application by Park and Barber²⁷⁰ of Pourbaix diagrams²⁵¹ to the understanding of the thermodynamic stability of a number of semiconductor materials has shown that GaAs is expected to be unstable with respect to both anodic and cathodic dissolution in aqueous solution. Indeed a number of experimental reports have recently suggested some confirmation of cathodic instability, although Fan et al., have maintained that p-GaAs is stable after prolonged use in solutions containing various oxidizing agents.

Early studies using d.c. cyclic voltammetry indicated that after prolonged usage at cathodic potentials under dark and illuminated conditions the dark cathodic current was increased (see Fig. 6.8). However, this was found to be a fairly insensitive method for detecting changes in the surface of the p-GaAs electrode. The more sensitive technique of a.c. cyclic voltammetry is particularly suited to a study of the deterioration of the p-GaAs surface.

Figures 6.17 and 6.18 illustrate, respectively, A.C.C.V's of p-GaAs in 0.5M H_2SO_4 for a clean, fresh electrode and the same electrode after potentiostating at -1.0V for $2\frac{1}{2}$ hours under dark conditions. For the clean electrode (Fig. 6.17), the results are quite typical of a near ideal p-type electrode except for some slight deviations, probably associated with surface states, between -0.2 and +0.2V. Indeed the general behaviour is similar to the A.C.C.V's of clean p-GaP electrodes (see Fig. 4.32). However, following long periods at cathodic potentials there was considerable change in both the 0° and 90° A.C.C.V's for the first cycle after the hold. In particular, the 90° plot shows an extremely large increase in signal nearer to flat-band and the 0° plot reveals considerable structure in the form of three peaks (labelled (1)(2) and (3)) in the same region. The

result shown is quite typical of such A.C.C.V's following long periods at cathodic potentials; they generally show three peaks although the relative heights of these peaks vary from one electrode to the next.

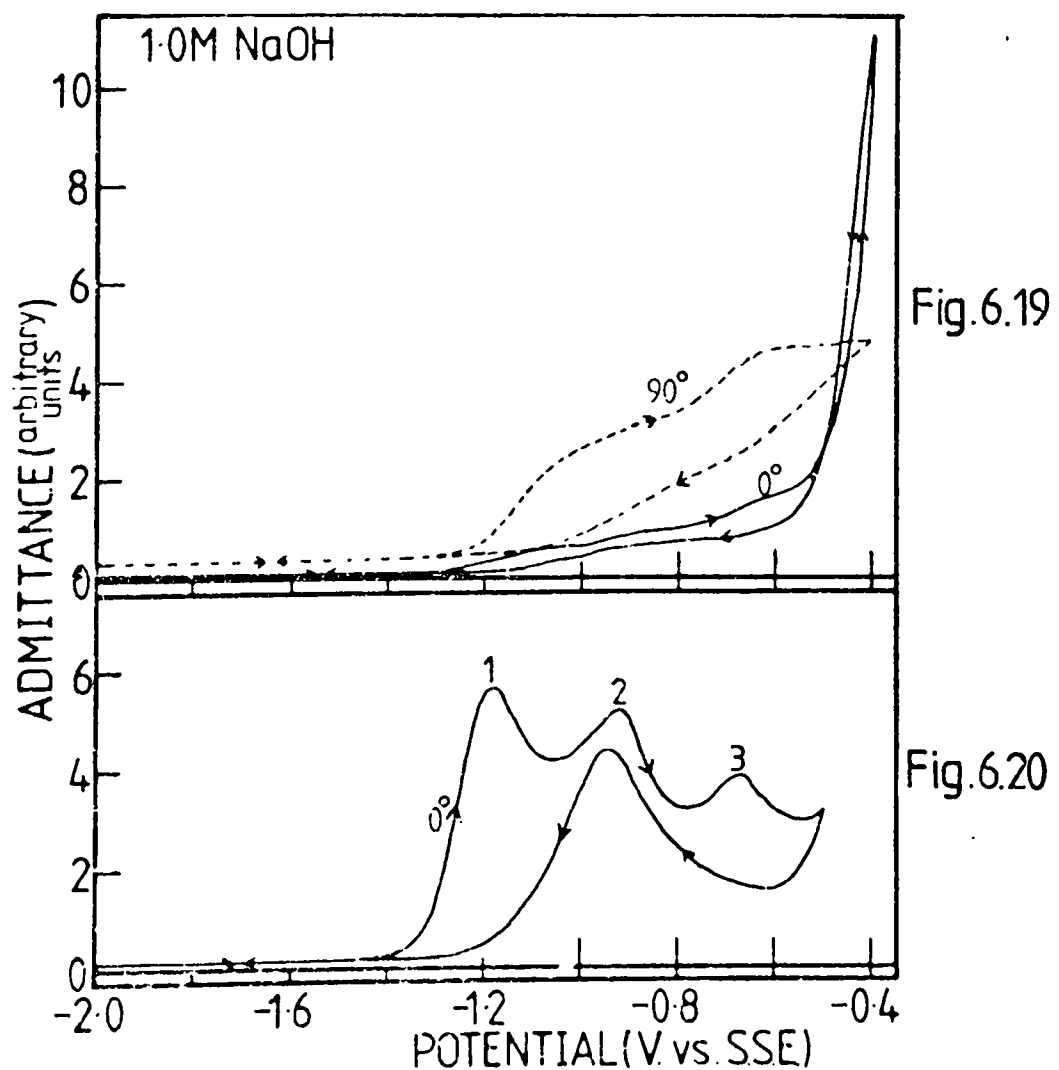
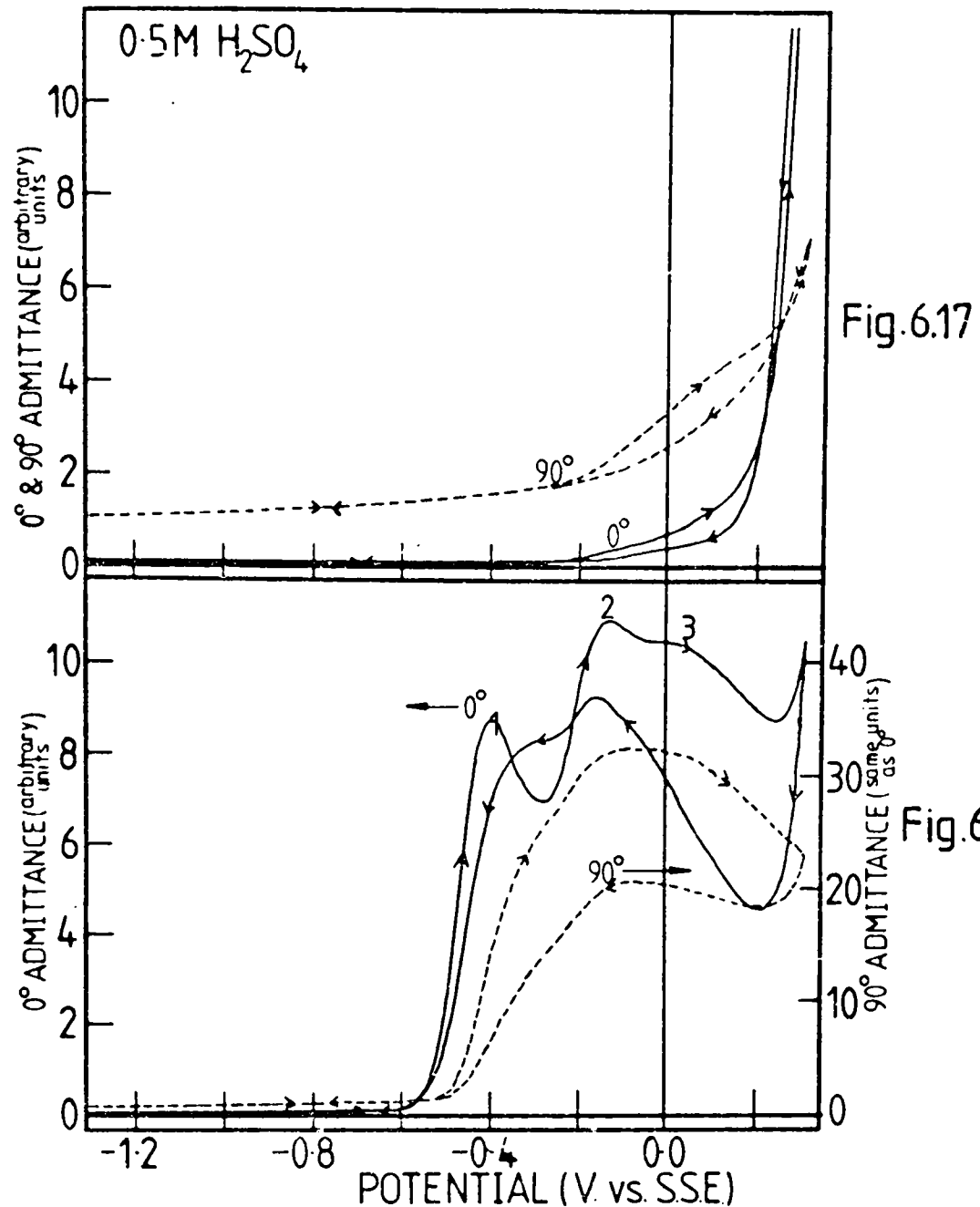
As Figures 6.19 and 6.20 show, similar behaviour is also in evidence in NaOH solutions- again three peaks are clearly seen for the first 0° plot after the long-term hold. All further consecutive sweeps do not reveal such structure providing the electrode is taken to potentials at which anodic dark current flows. Attempts to reproduce these curves (6.19 and 6.20) by holding the electrode at negative potentials under illumination have failed. Some changes are seen in the A.C.C.V's; but in general no structure is observed in the plots, only a general increase in 0° and 90° signals near flat-band.

Similar tests were then run on electrodes immersed in solutions containing 0.01M Gallium(III). It was again found possible to generate curves very similar to Figs. 6.17 and 6.18 (see Fig. 6.21) but following much shorter periods of potential hold at cathodic potentials. With this latter finding, it is reasonable to suggest that the major species responsible for the anomalous A.C. and d.c. - C.V's is Gallium metal on the surface of the electrode. Some appropriate E° 's are given in Table 6.3.

Table 6.3

<u>Redox Couple</u>	<u>E° (vs. S.S.E)</u>
Ga^{3+}/Ga	-0.74
$\text{Ga}^{3+}/\text{Ga}^{2+}$	-0.87
GaO^+/Ga	-0.6
$\text{H}_2\text{GaO}_3^-/\text{Ga}$	-1.44

Figs.6.17 and 6.18 A.C.cyclic voltammograms for a fresh and a 2½ hour aged p-GaAs electrode under dark conditions . Aging carried out by potentiostatting electrode at -1.0V in 0.5M H_2SO_4 . Sweep rate 50mV s^{-1}



Figs.6.19 and 6.20 A.C.Cyclic voltammograms for a fresh and 2 hour aged p-GaAs electrode in 1.0M NaOH . Aging carried out by potentiostatting electrode at -1.8V vs S.S.E. Sweep rate 50mV s^{-1} .

From the Figures of Table 6.2, reduction of Gallium(III) on p-GaAs requires a greater cathodic potential than that thermodynamically predicted for evolution of Hydrogen. However, as has already been discovered in this Chapter, the kinetics of Hydrogen evolution on p-GaAs are very slow; there is predicted to be a surface redox couple associated with the first step of Hydrogen Evolution (Equation 6.3) about 0.4V positive of $E^0_{(H^+/H_2)}$. In consequence, the evolution of Hydrogen requires for the second step of the process (Equation 6.4) a redox potential $\epsilon_{H(2)}$ at least 0.4V negative of $E^0_{(H^+/H_2)}$ resulting in at least a 0.4V overpotential with respect to H_2 evolution.

Recent studies on p-GaAs in solutions containing high concentrations of Zn^{2+} ions have revealed that Zinc metal may be electroplated onto the electrode surface at potentials cathodic of -1.0V even in strongly acidic media. Given the far more cathodic E^0 for Zinc deposition (-0.98V vs. S.S.E) than the thermodynamic value for Hydrogen evolution (-0.22V vs. S.S.E), this result suggests a Hydrogen overpotential of over 0.7V. The enhanced rate of Gallium metal deposition is only observed for potentials cathodic of the thermodynamic E^0 for Ga^{3+} reduction (-0.74V). However, the slower evolution of the A.C.C.V's may be observed for less cathodic potentials, suggesting an apparent underpotential formation of Gallium metal.

For the bulk deposition of Ga and Zn metals in acidic media, the apparent stability of the metallic layer may reflect a local pH at the electrode surface that is considerably higher than in bulk solution. This would be the case if the electrode surface became totally covered in $H^{\bullet}$ atoms. The implication is that the kinetics for the adsorbed $H^{\bullet}$ -atom formation are exceedingly rapid whilst all the secondary processes, such as $H^{\bullet}$ -atom migration, Hydrogen evolution and Gallium or Zinc deposition are far slower. Thus for all potentials cathodic of flat-band p-GaAs will be totally covered with adsorbed Hydrogen atoms.

Fig.6.21 A.C.cyclic voltammograms for a p-GaAs electrode after potentiostating at -1.0V in a solution containing 0.01M Ga(III) for 15 mins under dark conditions .

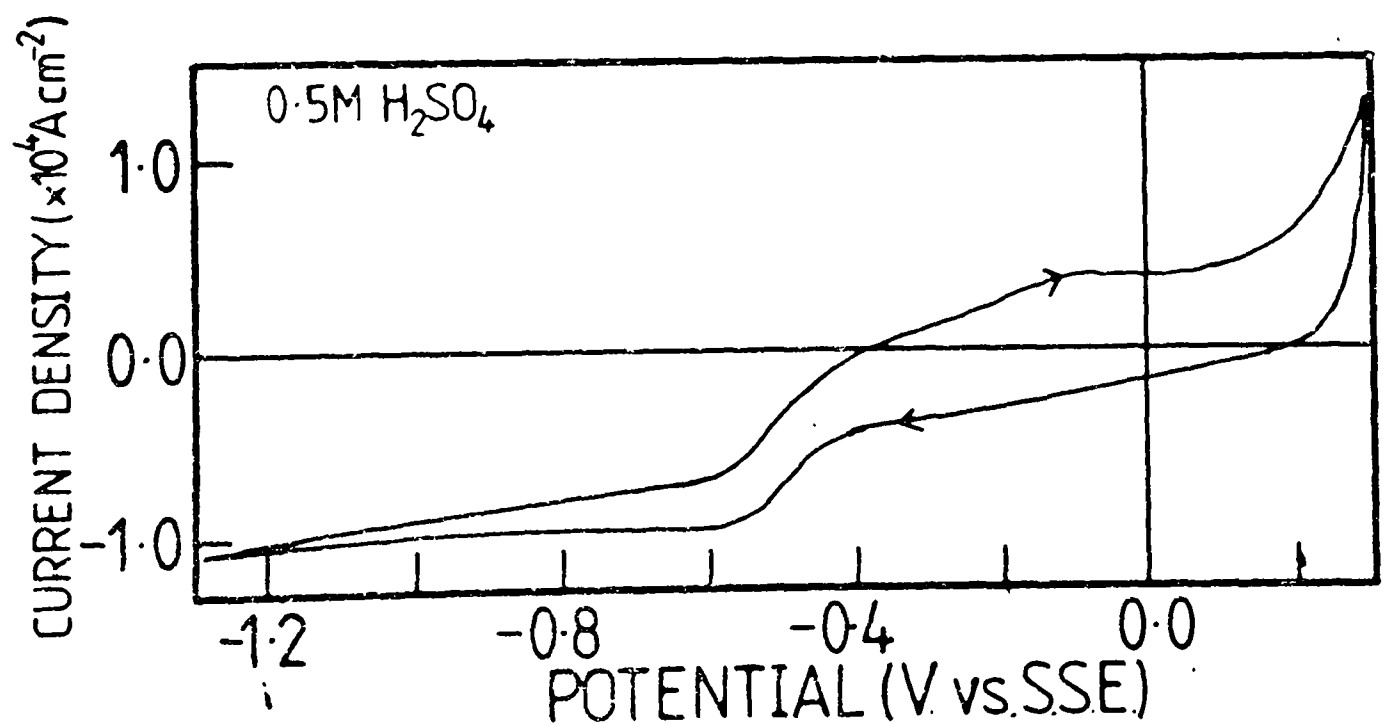
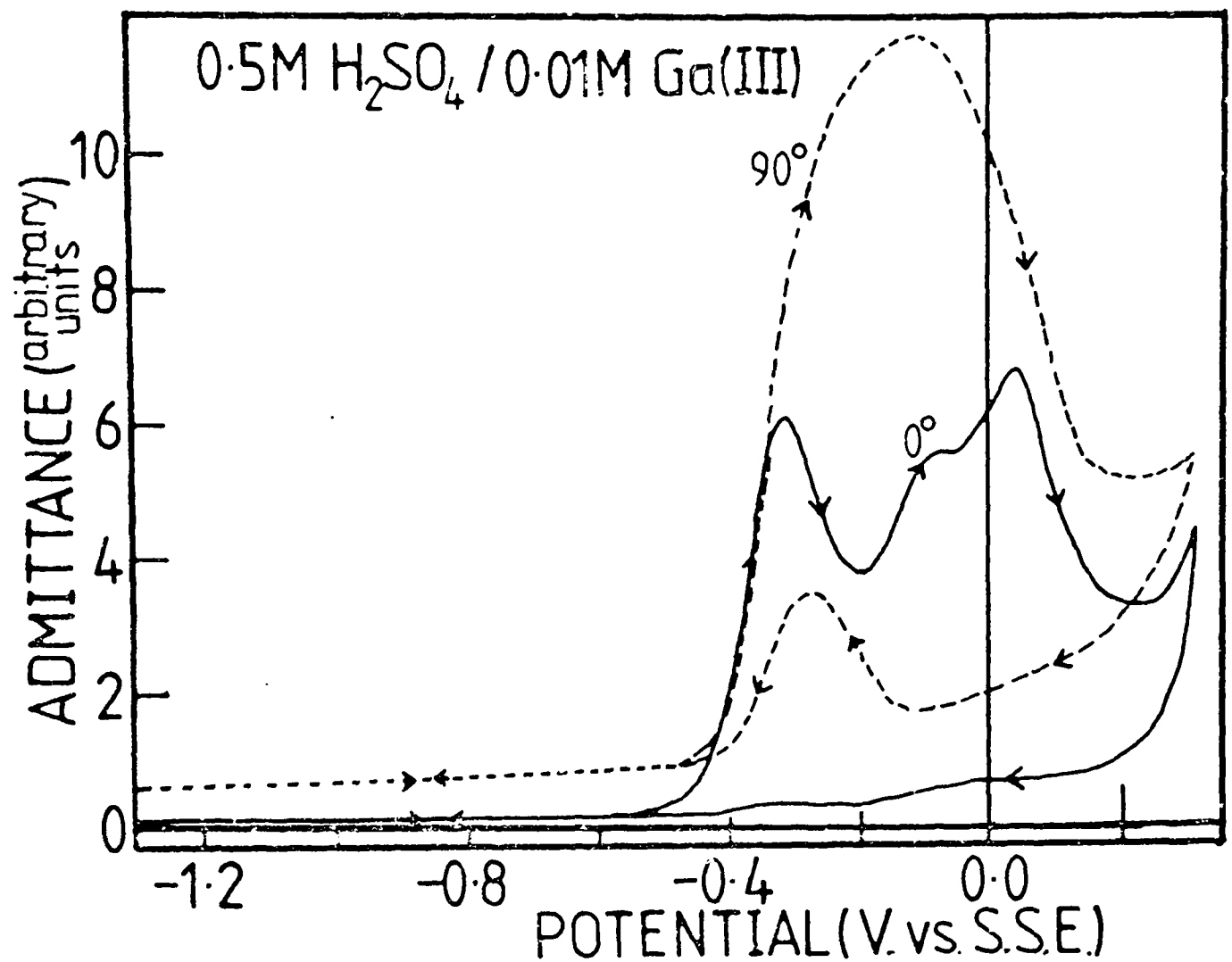


Fig.6.22 Cyclic voltammogram for a p-GaAs electrode previously aged for $2\frac{1}{2}$ hours at -1.0V in $0.5\text{M H}_2\text{SO}_4$ (c.f. Fig.6.18). Sweep rate 50mV s^{-1} .

As to the origin of the three peaks in the ACCV's one possible clue was from results in Gallium metal electrodes where considerable structure has been observed in d.c. CV's over a similar potential range.²⁷¹⁻²⁷⁴ In this case, the structure was attributed (without detailed chemical identification and analysis) to the formation of suboxides of Gallium on the surface of the metal electrode. Despite the fact that simple theories do exist for the general form of ACCV's on semiconductor electrodes, no theory has been put forward that can explain the detailed structure observed in this instance on p-GaAs. Many further experiments were carried out to attempt a deeper understanding of the electrochemical behaviour responsible for the complex ACCV's, but no further conclusions could be reached.

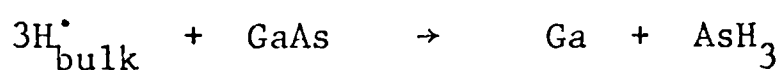
However, some explanation is possible for the general nature of the d.c. CV as shown in Fig. 6.22. It can be seen that at about -0.5V the cathodic dark current sharply rises and then appears to approach a saturation region. A mechanism may be proposed whereby the saturation cathodic current is limited only by the concentration of Gallium metal at and possibly within the surface region of the electrode; i.e. the mechanism for electron transfer to the surface is non-classical in origin, occurring by the process of resonance-assisted tunnelling. If the saturated cathodic current were all due to reduction of the electrode according to



then one might expect to see the cathodic current rise rapidly as a function of time. The creation of additional surface Gallium would increase the probability for electron transfer to the surface. Since this is not observed experimentally, we may propose that the majority of cathodic current is due to Hydrogen gas evolution and thus will not greatly affect the rate of the ongoing cathodic process by the creation of surface states.

We have not yet discussed how Gallium metal might be produced for potentials anodic of $\text{E}^0(\text{Ga}^{3+}/\text{Ga})$. Indeed it is found that, even if the

electrode is maintained at potentials as anodic as -0.2V (in $0.5\text{M H}_2\text{SO}_4$), the complex behaviour seen in the ACCV's still steadily evolves over a period of time. At -0.2V , the only thermodynamically feasible cathodic processes are the creation of surface Hydrogen atoms and their migration into the bulk of the electrode. It is conceivable that the bulk H atoms may act as chemical reducing agents within the surface of the electrode to decompose it according to:-



The thermodynamic driving force for this reaction would be the formation of three stable As-H bonds per Ga atom. The Ga atoms may then act as sites for resonance-assisted tunnelling providing suitable redox energy levels are available at the electrode surface to which electrons may be transferred. Referring to Fig. 6.22, this seems to be possible only for potentials cathodic of -0.4V , where the cathodic dark current does indeed rise.

6:6:2 Long-term stability to Illumination

Fig. 6.23 depicts a typical current/time plot for p-GaAs potentiostatted at -1.0V under strong white-light illumination. An initial fall in current is followed by a consequent rise to saturation. Further more careful studies revealed that the overall shape of the plot is due to the super-imposition of a continuous decrease in photocurrent and a continuous rise in dark current.[Fig.6.24]

At the end of the long-term illumination test (~ 24 hours), the cyclic voltammograms in the dark and under illumination were as shown in Fig. 6.25. Initially, at the cathodic end of the sweep there is a very large cathodic dark current, but this steadily decays on successive sweeps. The photocurrent efficiency is dramatically reduced relative to the value before the long-term test was initiated. After repeated cycling, the CV evolves into that shown in Fig. 6.26, and the photocurrent efficiency also returns

Fig.6.23 Typical cathodic current/time plot for p-GaAs potentiostatted at -1.0V under strong white light illumination in $0.5\text{M H}_2\text{SO}_4$.
 Fig.6.24 Breakdown of Fig.6.23 to illustrate that overall shape is due to a superimposition of varying photocurrents and dark currents.

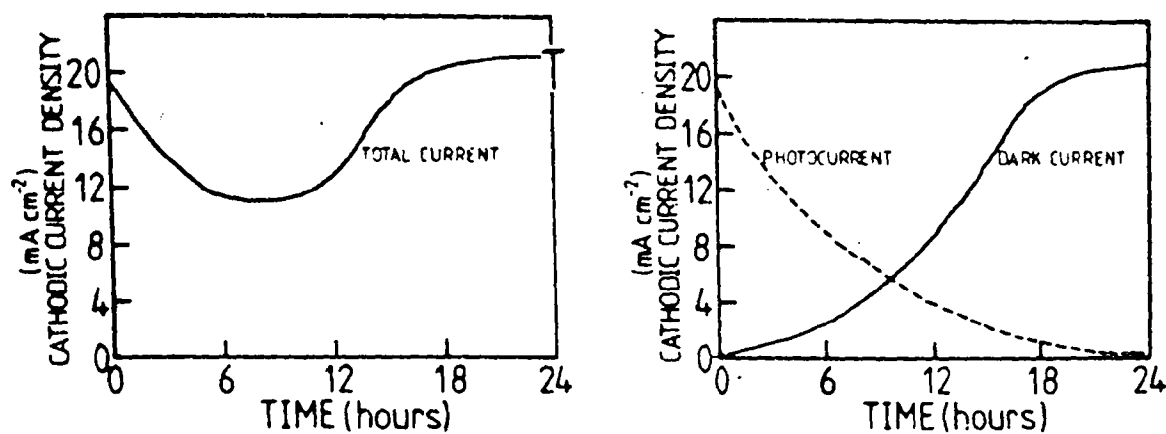


Fig.6.25 Cyclic voltammogram of p-GaAs following the long-term stability test recorded in Fig.6.23. The numbers refer to successive cycles. Sweep rate 250mV s^{-1} . Light intensity as for Fig.6.23.

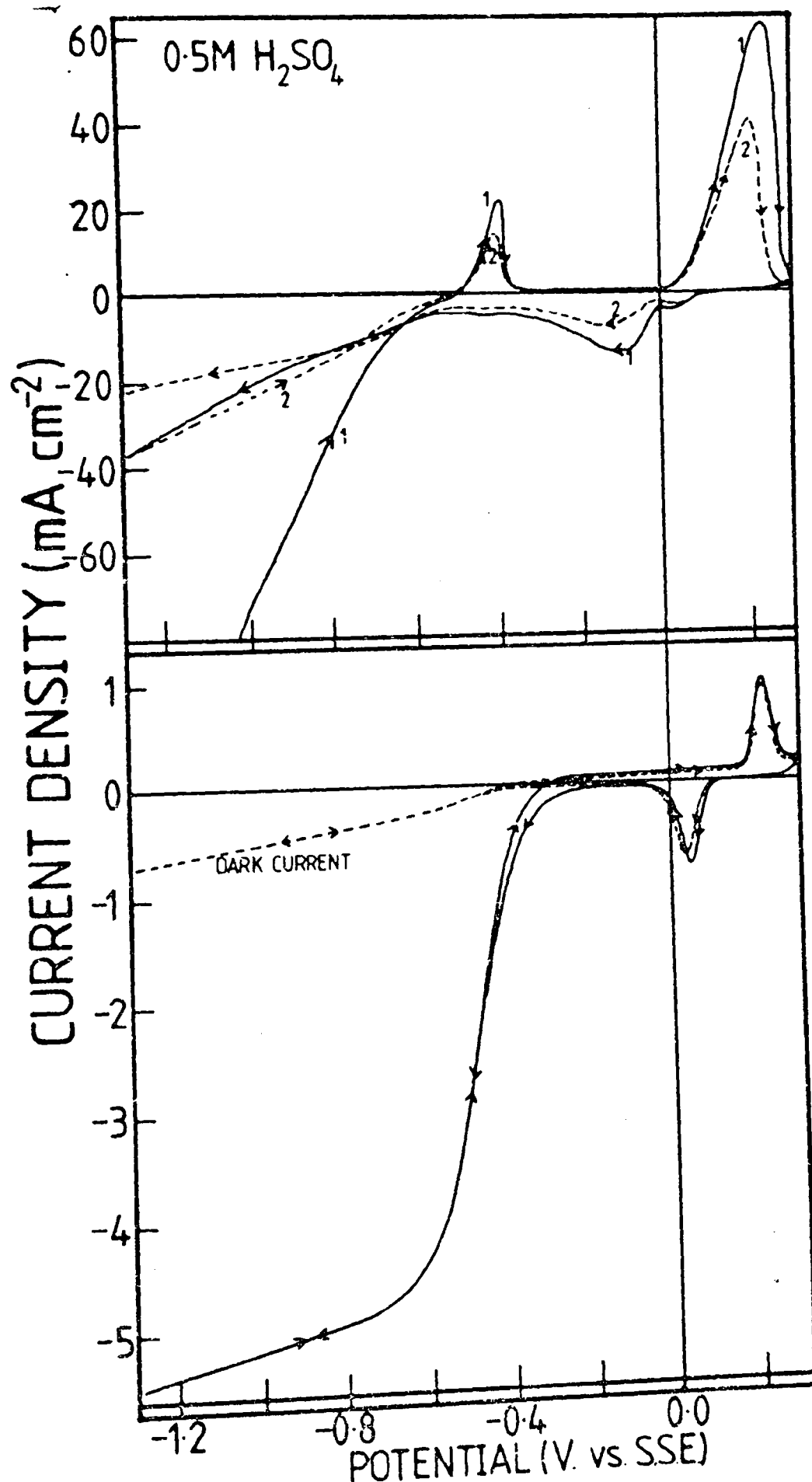


Fig.6.26 Dark and illuminated cyclic voltammograms of p-GaAs in $0.5\text{M H}_2\text{SO}_4$ following on from Fig.6.25 after five minutes of repeated cycling over the range shown. Sweep rate 250mV s^{-1} .

to a value very similar to that of the clean electrode. Tests were made to ensure that the peaks at +0.04 and +0.23V were not due to dissolved species in solution. Further complications in the shape of the CV (not shown here) also arose following periods of anodization. Shorter-term cathodic photocurrent tests were then run in 0.01M Ga(III) solutions, following which it was possible to show that bulk Gallium metal was formed on the electrode. Also peaks similar to those found for the longer tests in Gallium-free solutions were observed. However, it is important to note that the CV response was quite different from that found after long-term tests in dark conditions. This variation may be due to the difference in the nature and depth of the Gallium metal formed in the two cases. Under strong illumination, the photogenerated conduction-band electrons are thermodynamically capable of producing bulk Gallium metal at the surface of the electrode. However, in the dark this is not possible thermodynamically (although Gallium formation is observed at potentials positive of $E^0(\text{Ga}^{3+}/\text{Ga})$ and instead the Gallium is formed from chemical reduction of GaAs, within the surface of the electrode, by $\text{H}^\bullet$ atoms.

These observations are an entirely novel discovery for p-type III-V materials; they require extensive further electrochemical study in conjunction with various surface spectroscopic and analytic techniques. Until these are done the above conclusions must remain as calculated conjecture! Whatever the true nature of the surface of p-GaAs after long-term usage (in the dark or light), it is apparent that p-GaAs will have little value for solar photoelectrolysis cells unless some way can be found to stabilize the surface. This may be by polymer protection or the discovery of a method of reducing the large Hydrogen overpotential on the GaAs surface.

SECTION 6:7 PHOTOELECTROCHEMISTRY OF p-GaAs IN CONTACT WITH SOLUTIONS CONTAINING WELL-DEFINED REDOX COUPLES

Fan and Bard have made a study of p-type GaAs in aqueous solutions containing several redox couples (I_3^-/I^- , Fe(III)/Fe(II), Sn(IV)/Sn(II), Eu(III)/Eu(II)) in the dark and under irradiation.²⁷⁵ They observed a constant difference between the photocurrent onset potential and the standard electrode potential for the redox couple, independent of the nature of that couple. They claim that this behaviour represents an example of Fermi-level pinning of a semiconductor due to a large density of surface states with energies within the bandgap. In such a surface controlled system, the Fermi level of the semiconductor is pinned at the surface-state level and change in the potential of the semiconductor or solution lead only to changes in the potential drop across the surface state layer or Helmholtz layer (see Chapter 2 Section 2:8).^{208,209}

To follow up the validity of this report, a short study was made of the behaviour of p-GaAs in contact with two solutions: Fe(III)/Fe(II)/ H_3PO_4 (0.5M/0.5M/1.0M) and $I_3^-/I^-/H^+$ (0.25M/0.75M/1.0M). These two solutions possess very similar redox potentials of 0.22 and 0.31V vs. S.S.E respectively. On the basis of the generalized theory due to Fan and Bard,²⁷⁵ it would be predicted that there would be very similar electrochemical behaviour for the p-GaAs electrode in the two electrolytes.

6:7:1 Fe(III)/Fe(II) Solutions

Figure 6.27 depicts three dark C.V.'s of p-GaAs in the Fe(III)/Fe(II) electrolyte taken with differing sweep rates (25, 100 and 500 $mV s^{-1}$). The variation in the magnitudes of the cathodic currents flowing at each point on the sweeps is a consequence of a strong time dependence of the dark currents when measured at potentials cathodic of +0.3V. Thus if the electrode is potentiostatted negative of 0.3V, the cathodic current will rise steadily over a period of many hours. The rate of increase is however far greater initially as can be seen from the three C.V.'s.

Fig.6.27 Cyclic voltammograms of p-GaAs in Fe(III)/Fe(II) electrolyte under dark conditions . Sweep rates 25 , 100 and 500 mV s⁻¹ .

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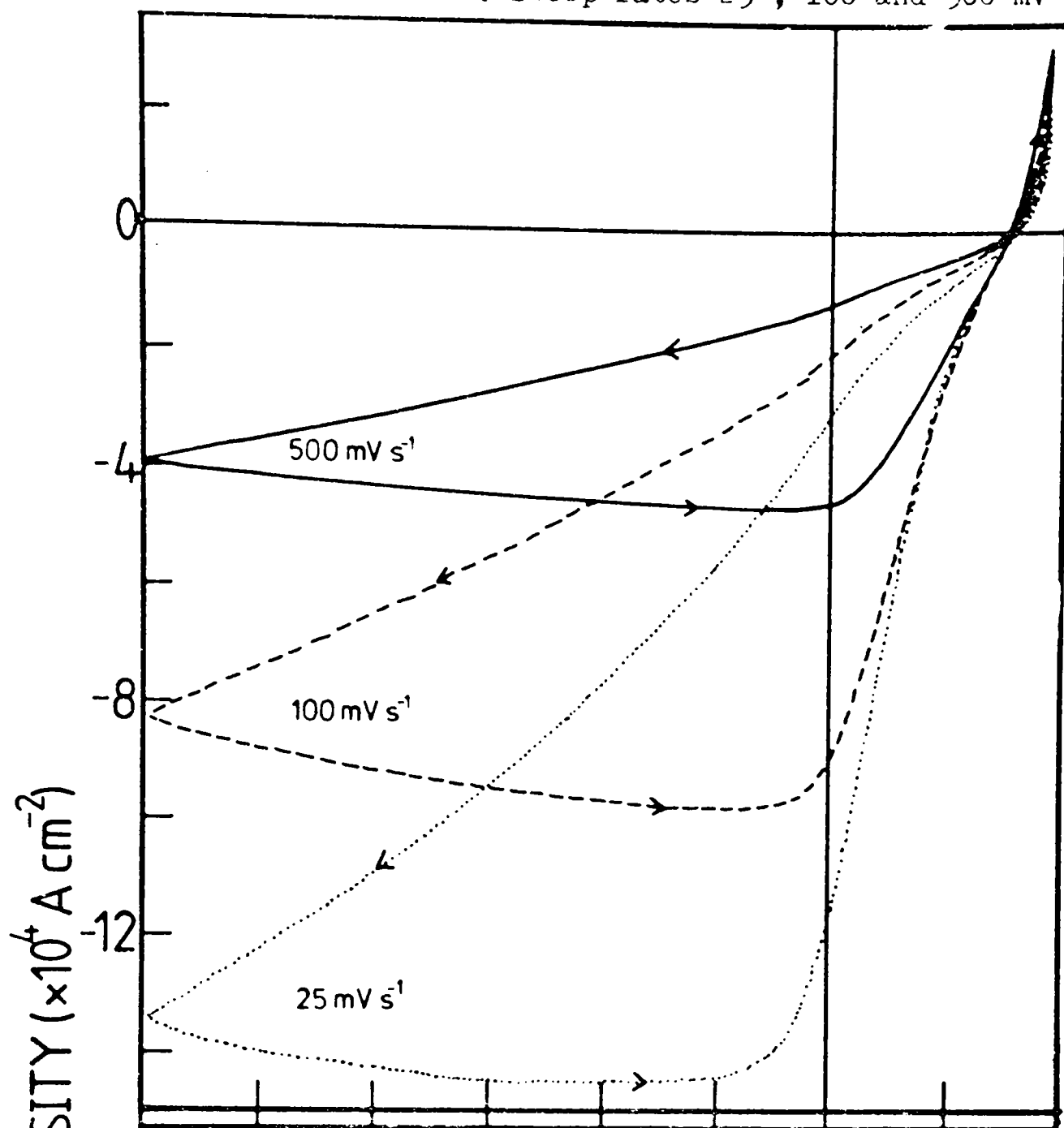
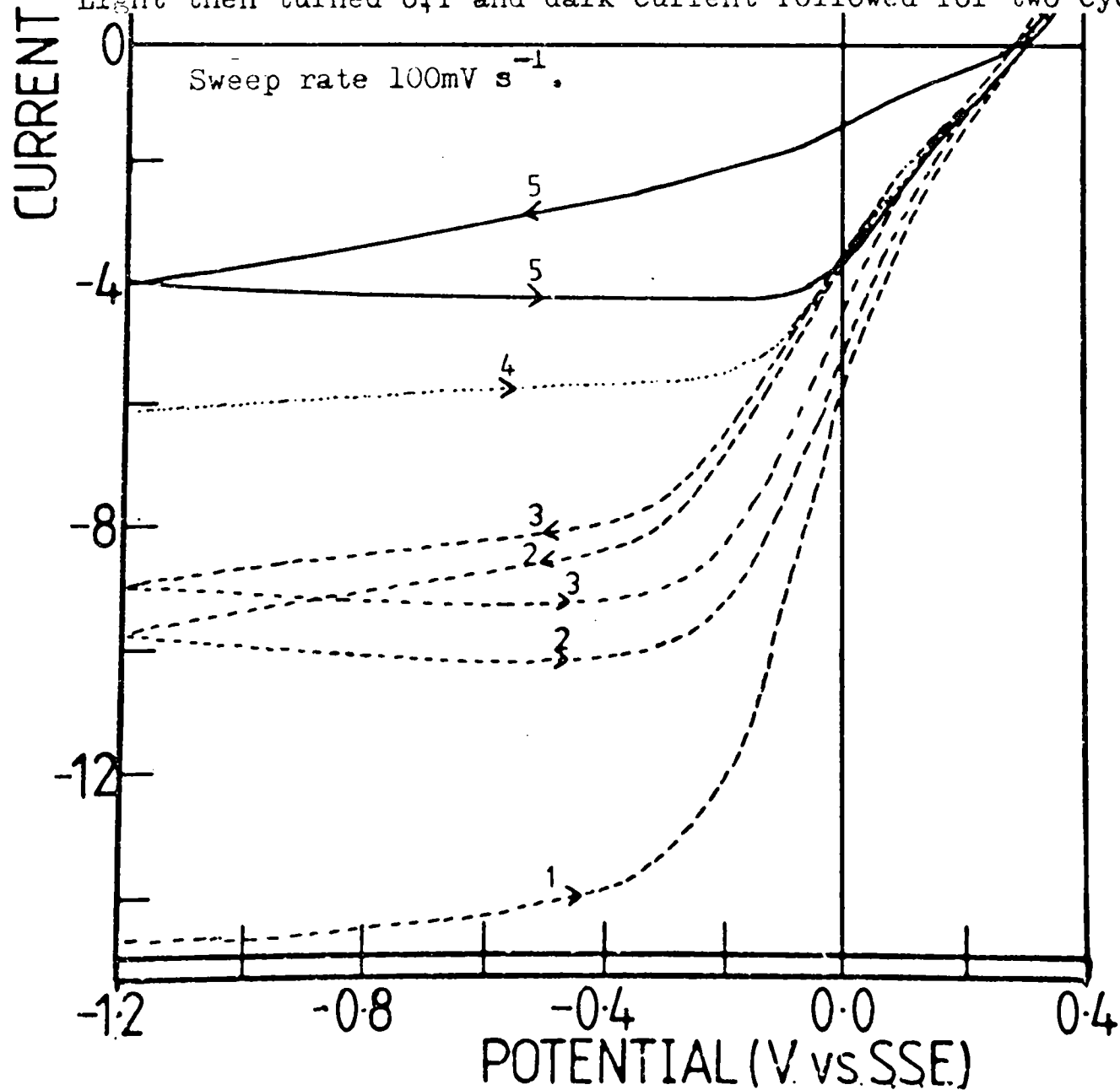


Fig.6.28 Cyclic voltammograms of p-GaAs in Fe(III)/Fe(II) electrolyte under dark (—), (...) and illuminated conditions (---) . Light turned at cathodic limit and current followed for three cycles (as numbered). Light then turned off and dark current followed for two cycles (4 and



There is also a strong time dependence for the cathodic photocurrent (see Fig. 6.28) although in this case the photocurrent decreases as a function of time. (No evidence exists that this is caused by concentration polarization since stirring the solution has no significant effect on the photocurrent). The passage of cathodic photocurrent further enhances the rate of increase in the cathodic dark current; also illustrated in Fig. 6.28. The two opposing effects are clearly illustrated in Fig. 6.29 where the time dependence of the cathodic photo- and dark-currents are monitored at the same time using a slow light chopping technique (<3Hz). These are instrumental difficulties involved in following accurately both the photo and dark response within the first 10 seconds after commencing the sweep. Following this initial period, the graph shows quite clearly that, after an initial peak in photocurrent the photoresponse steadily decays away whilst the dark current steadily increases. The total current flowing (photo + dark-currents) then seems to approach a steady value after about 5 minutes.

A fast PCV plot (Fig. 6.30) fails to reveal this interesting transient behaviour although there is a degree of hysteresis in the plot suggesting a decay in photocurrent over a period of time. Fan and Bard only use such chopped light PCV plots to measure the behaviour of their p-GaAs electrodes. It is thus clear that they are missing much of the information available in studies that incorporate a wide range of experiment-type.

No Mott-Schottky plots were obtainable for the electrode in this medium due to the rapid time dependence of all the admittance readings. The PCV intercept may bear some relation to the flat-band potential and the value of 0.47V would indicate a positive shift of V_{fb} of about 0.25-0.3 Volts.

Some similar dark current behaviour has been observed in some recent results on static p-GaP electrodes in Fe^{3+}/Fe^{2+} solutions and has also been investigated in detail for rotating disc electrodes with a view to determining

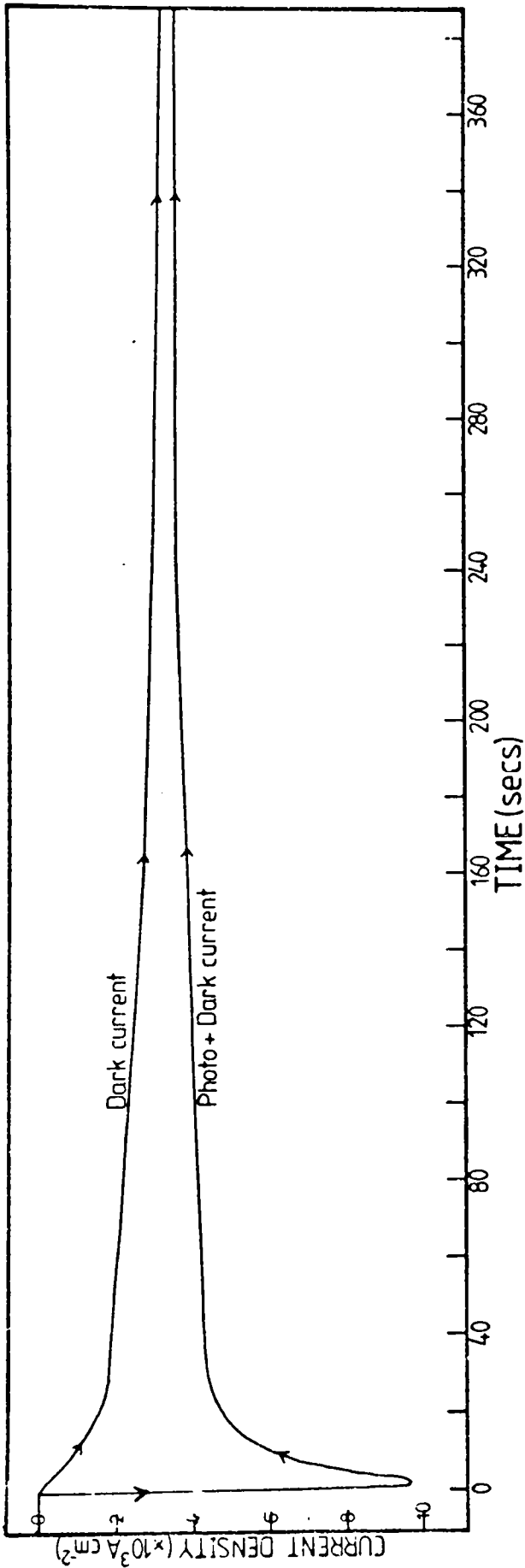


Fig.6,2> Diagram illustrating time dependence of cathodic photo- and dark currents of p-GaAs in Fe(III)/Fe(II) electrolyte . To achieve this a slow (3Hz) light chopping technique was used .

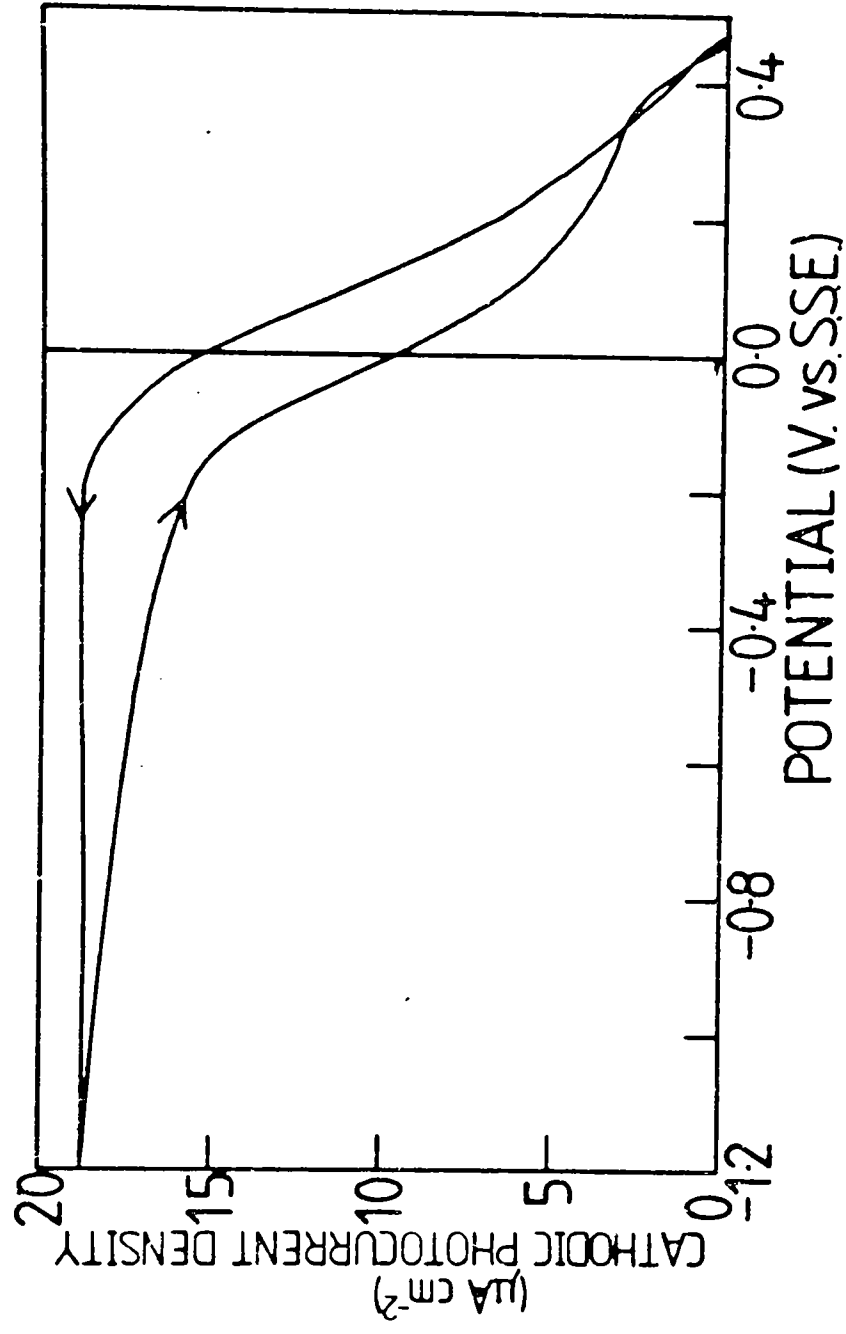
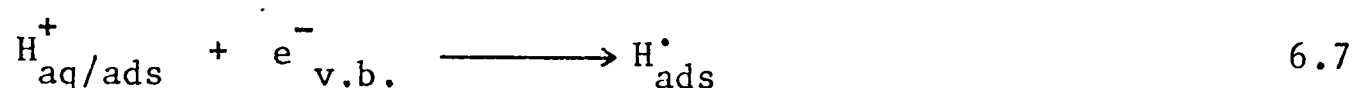


Fig.6.30 Photocurrent-voltage plot for p-GaAs in Fe(III)/Fe(II) solution. Chopping rate 87Hz . Sweep rate 50mV s⁻¹.

quantitatively the kinetics and mechanisms of the interfacial processes. However, the quantitative study had to be performed on deliberately abraded electrode surfaces to ensure that the intrinsic surface state concentration exceeded those photogenerated under illumination. Thus much of the transient behaviour was avoided in these rotating disc studies.

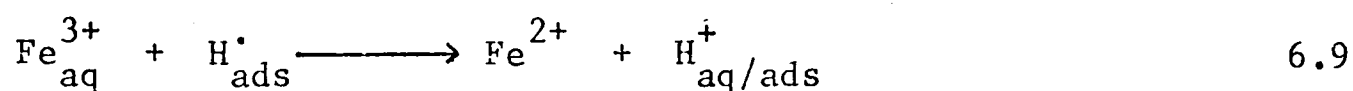
The following model may be suggested to explain the dark current behaviour. Once the electrode is biased negative of +0.3V then the surface edge of the electrode will rapidly become covered with Hydrogen atoms



There are then two possible fates for these surface $\text{H}^{\bullet}$ atoms, migration into the electrode bulk



or they may reduce Fe^{3+} in the solution



This only explains the origin of a constant cathodic dark current. One further reaction will be necessary and that is the use of depletion layer Hydrogen atoms as mediating agents for the resonance assisted tunnelling of valence band electrons into solution to reduce either more solution protons or to directly reduce Fe^{3+} .



It is not possible to distinguish between these two latter processes since the net reduction of Fe^{2+} may result either directly from equation 6.11 or

indirectly from a combination of 6.10 with 6.9. The increase in the cathodic current may now be explained by the ever-rising concentration of Hydrogen atoms within the depletion layer of the electrode. The catalytic nature of the depletion layer $H^\bullet$ states will increase the rate of electron injection into solution.

The decrease in photocurrent may also be explained by use of the same model proposed above. Illumination increases the rate of Hydrogen atom formation which in turn creates more depletion layer Hydrogen atoms via equation 6.8. However the presence of these states within the depletion layer will increase the rate of recombination of the photogenerated electron/hole pairs thereby reducing the photocurrent efficiency. If the light is switched off again, the cathodic dark current is also enhanced by the increased concentration of bulk Hydrogen atoms.

The limiting value of cathodic dark current will only be attained when either the surface region of the electrode is totally saturated with $H^\bullet$ atoms, or the rate of diffusion of oxidized species (Fe_{aq}^{3+} or H_{aq}^+) to the electrode surface becomes limiting. By the very slow nature of the dark current saturation, the former suggestion seems the more likely. To test this theory more carefully rotating disc studies would be necessary. Due to the extensive technological difficulties of mounting single crystals in such electrodes, no such experiments could be carried out at this time.

6:7:2 I_3^-/I^- solutions

Figure 6.31 depicts dark and illuminated C.V.'s for p-GaAs in an I_3^-/I^- solution. Despite the similarity in redox potential for the $Fe^{3+}/Fe^{2+}(H_3PO_4)$ and I_3^-/I^- couples, there is a totally different behaviour for the C.V.'s 6.31 and 6.27. There is very little hysteresis observable in either the dark or illuminated curves of Fig. 6.31 although there is a small enhancement in the magnitude of the dark current following illumination. The PCV plot (Fig. 6.32) also reveals very little hysteresis and

Fig.6.31 Dark and illuminated cyclic voltammograms for p-GaAs in I_3^-/I^- solution . (—) dark , (---) white light illumination , (...) dark following illuminated cycle . Sweep rate 100mV s^{-1} .

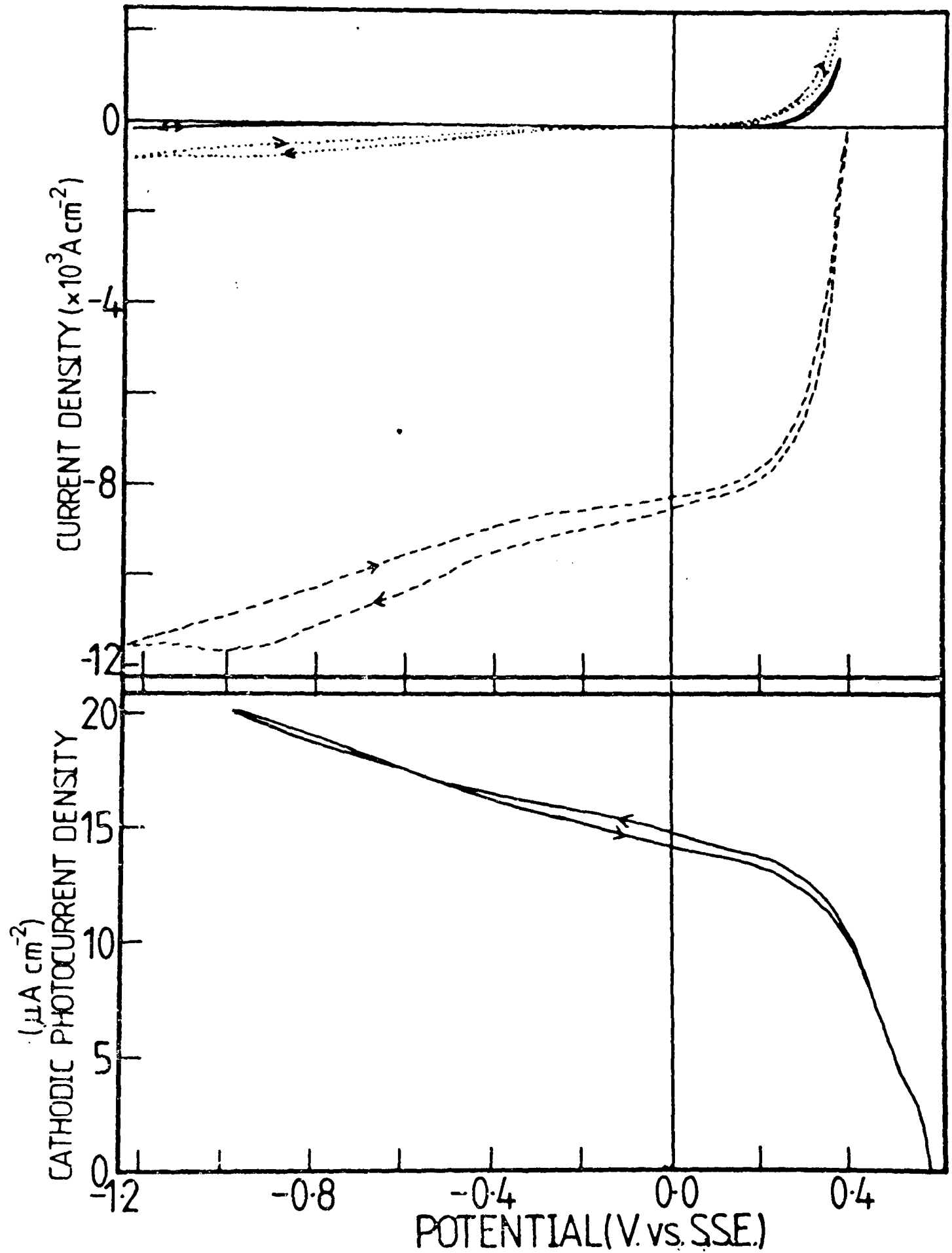


Fig.6.32 Photocurrent-voltage plot for p-GaAs in I_3^-/I^- solution . Chopping rate 87Hz . Sweep rate 50mV s^{-1} .

a photocurrent intercept at $\approx 0.55V$. There was no significant transient behaviour found for the photocurrents and also little time dependence in the magnitude of the photocurrent over short periods (≈ 10 minutes).

One very interesting observation which could very easily have been missed was a transient variation in the admittance response of the electrode when first dipped onto the I_3^-/I^- solution. The initial 0° and 90° admittance signals were found to be approximately (phase angle 53° at 999Hz) equal but over a period of about 3 minutes the phase angle of the output a.c. current shifted rapidly towards 90° with an eventual value of around 84° . Despite careful checks no such rapid transient behaviour was discovered in Fe^{3+}/Fe^{2+} solutions where output phase angles were generally around 72° (1000Hz). In addition to this above observation, it was found that after experimentation with a p-GaAs single crystal electrode for about 4 hours, on removal of the electrode from solution, a translucent film could be seen on the surface which removed the originally perfectly reflective mirror-like appearance seen for freshly polished and etched electrodes. Again no such changes were found after long experiments in the Fe^{3+}/Fe^{2+} solutions.

6:7:3 Brief Conclusions to be drawn on the photoelectrochemistry of p-GaAs in Iron and Iodine containing Solutions

The conclusions of Fan and Bard²⁷⁵ were that there was a constant relationship between photocurrent onset potential and potential of the redox couple contained in the solution. From this work, there appears to be some grounds for confirmation of this behaviour providing that one only uses results obtained from chopped illumination PCV plots (see Table 6.4)

Table 6.4

Redox Couple and Potential		p.o.p. (from PCV plots)	Difference
Fe^{3+}/Fe^{2+}	0.22V	0.46	0.24
I_3^-/I^-	0.31V	0.56	0.25

However, it is apparent that such a generalized-rule is not applicable to the continuous current measurements, detailed short term transient studies (< 1 sec), long term (> 1 minute) variations in photoresponse, or interfacial impedance. It is therefore very necessary to consider not only a generalized theory dealing with a hypothetical distribution of charge and potential through a surface covered with surface states of unknown origin. Instead it is far more valuable to make an attempt at discussing the precise nature of the chemical and electronic interactions at the interface.

In the case of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ solutions it is possible to explain much of the behaviour on the basis of surface state and near surface-states associated with a particular chemical entity - probably adsorbed and adsorbed Hydrogen atoms respectively. In this particular instance the observed behaviour has little to do with specific interactions between the electrode and the added redox couple. However for the I_3^-/I^- solutions, the transient effect on p-GaAs caused by the presence of surface Hydrogen atoms are no longer present. Instead there appears to be a specific interaction between the electrode and the added redox couple observable by the rapid change in electrode impedance after initial immersion in solution and in the form of the translucent film after long periods of experimentation. Indeed the behaviour of the electrode p-GaAs in the I_3^-/I^- solution is far closer to the ideal behaviour of a p-type semiconductor electrode than that observed in any other medium used to date even for solutions containing no added redox couple.

However long-term photocurrent tests in I_3^-/I^- solutions still indicate a slow rise in background dark current probably due to slow incorporation of Hydrogen atoms into the surface or slow cathodic decomposition to generate AsH_3 and Gallium metal at the surface of the electrode. Nevertheless it is encouraging that a material has been found that can slow this degeneration and it probably reflects the strong adsorption characteristics of iodine or triiodide onto semiconductor electrodes as was previously observed on materials

such as MoS_2 , MoSe_2 , WS_2 , WSe_2 etc.²⁷⁶⁻²⁸⁰ Prevention of strong adsorption of the Hydrogen atoms at the electrode surface may decrease the rate of $\text{H}^\bullet$ incorporation into the electrode bulk thereby decreasing back recombination by resonance assisted hole tunnelling to the electrode surface and the decomposition of the electrode according to:-



SECTION 6:8 CONCLUSION ON THE APPLICATION OF p-GaAs TO SOLAR ENERGY CONVERSION

From the results revealed in this chapter, it would appear that p-GaAs suffers generally from the same problems with respect to poor efficiencies of Hydrogen evolution as were made apparent for p-GaP in Chapter 4. Adsorbed and interstitial Hydrogen atoms which are intermediates in the Hydrogen evolution reaction create surface and bulk recombination centres that severely reduce the photoefficiencies at potentials immediately cathodic of flat-band. Attempts to improve efficiencies by surface metal-ion treatments were of rather limited success. The greater problem with respect to the application of p-GaAs in photoelectrolysis devices is the considerable instability enhanced by illumination.

In p-GaP the redox potential for the formation of the adsorbed Hydrogen atom ($\epsilon_{\text{H}(1)}$) appeared to lie above the valence band edge such that the Gallium-Phosphorus binding energy (effectively responsible for the bandgap) was stronger than the Phosphorus-Hydrogen binding energy relevant to the cathodic decomposition into $\text{Ga} + \text{PH}_3$. Thus p-GaP possessed a modicum of stability to illumination over periods of several days. However, with p-GaAs, the failure to resolve a surface-state maximum in the potential range adjacent to flat-band, along with the observed cathodic instability, suggests that the redox potential for the formation of adsorbed Hydrogen is either much closer to or possibly even below the valence band edge. In

this case one is lead to believe that the Gallium-Arsenic binding energy is thus weaker than the Arsenic-Hydrogen binding energy. Indeed, calculations taken from Pourbaix diagrams have suggested that GaAs should be thermodynamically unstable with respect to cathodic dissolution. However a number of 'experimentally stable' materials are also predicted to be thermodynamically unstable on illumination (e.g. SrTiO_3) so kinetic factors should also be taken into consideration.

As with p-GaP, the use of p-GaAs in wet-type photovoltaic cells in aqueous solutions, still suffers from the extreme rapidity of the creation of the adsorbed Hydrogen species. The work shown in the reduction of Fe^{3+} has revealed the extent of this problem as well as some recent studies in Cr^{3+} and V^{3+} solutions. However, some specific ion adsorption effects in the I_3^-/I^- solutions appear to nullify the effects of strong Hydrogen adsorption. This lends some encouragement therefore to the possibility of discovering a surface treatment of p-GaAs which may both protect the electrode from corrosion and enhance the kinetics for the desired faradaic process. Some preliminary work on p-GaAs electrodes coated in polypyrrole demonstrates some considerable improvements in electrode durability and response although the precise mode of operation of this surface treatment remains unclear.²⁸¹

CHAPTER 7

THE PHOTOELECTROCHEMISTRY OF P-TYPE InP AND P-TYPE GaSb

SECTION 7:1 INTRODUCTION

To complete the story of the photoelectrochemistry of the p-type III-V semiconductors, a brief study was undertaken on Indium Phosphide (Bandgap 1.29eV) and Gallium Antimonide (Bandgap = 0.67eV). Though of course this does not cover all the known III-V materials, it does include the four materials that possess bandgaps between 0.5eV and 3.0eV and which are known to be stable, at least in ambient conditions. On the basis of the bandgap criteria, imposed to limit consideration of materials with remote applicability to solar energy conversion, there would remain only one further III-V compound not studied, viz. AlSb ($E_g = 1.63\text{eV}$). However, this material is rapidly decomposed by water and moist air at room temperature producing $\text{Al}_2\text{O}_3 + \text{Sb} + \text{H}_2$, thereby ruling it out from further consideration.

The few previous reports of studies performed on single-crystal p-InP have, in general, revealed a considerable cathodic instability for the material when used in aqueous solution. Two very recent papers due to Heller et al. have, however, completely contradicted the previous findings and have reported stable systems using p-InP for the photoassisted electrolysis of HCl and H_2O with quoted overall solar efficiencies of 6% and 3% respectively. To date, there does not appear to have been any study of the photoelectrochemistry of GaSb, but based on thermodynamic calculations and on the observed trends in the results from GaP, and GaAs, it would appear that GaSb would suffer markedly from cathodic instability. Nevertheless, it was felt that the material was worthy of a brief study to investigate the nature of photoeffects on a small-bandgap semiconductor.

SECTION 7:2 p-InP

A notable feature of the results obtained on p-InP are the considerable difference seen for electrodes used directly after the preparation of the ohmic contact (Zinc-doped Indium at 550°C in H_2) and following either a period of anodic oxidation or a further etch in $\text{CH}_3\text{OH}/\text{Br}_2$ (5%). Figs. 7.1 and 7.2 illustrate this difference for dark cyclic voltammograms taken before and after a 60-second period of anodic oxidation at +0.8V. There is a significant contrast in the magnitude of the cathodic current flowing at the cathodic end of the sweep. This would suggest, on the basis of the findings on p-GaAs and p-GaP, that there is a considerably lower concentration of surface states on the anodized material than for electrodes freshly placed into solution. Such surface (or near-surface) states can assist the transport of electrons from the valence band into the solution through non-classical and resonance-assisted tunnelling modes as discussed at greater length for p-GaP.

It has been suggested recently that anodization of InP creates an impervious oxide film at the surface that may also serve to protect the material from cathodic corrosion.¹⁷⁸ It has been shown that continuous passage of the cathodic dark current on new InP electrodes leads to irreversible degradation of the electrode. Electrode weight loss, the odour of PH_3 and observable surface corrosion becomes apparent after many hours at currents exceeding 1mAcm^{-2} .

Attempts were made to elucidate the band positions of InP relative to solution redox levels. Five-component impedance analysis was rendered impracticable by the considerable time dependence of the admittance readings. However, analysis according to the two-component circuit over a range of set frequencies was possible, although considerable frequency dispersion was found for the gradients of the derived Mott-Schottky plots. Nevertheless reasonable constancy was found for the potential intercepts

Fig.7.1 Cyclic voltammagram of p-InP in 0.5M H_2SO_4 under dark conditions. The electrode was used without further preparation directly after annealing in the ohmic contact to the reverse side. Sweep rate 250mV s^{-1} .

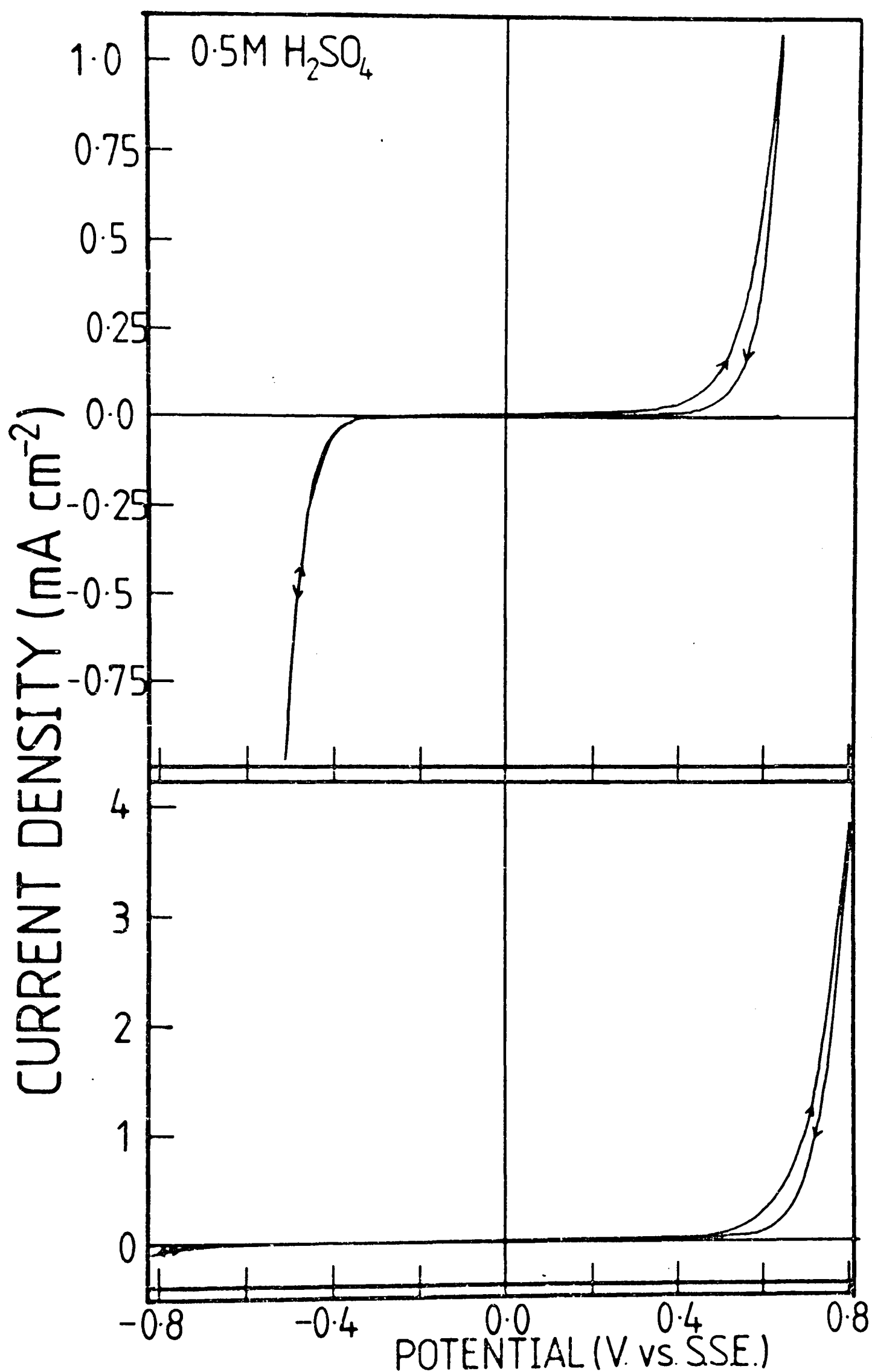


Fig.7.2 Cyclic voltammagram of p-InP in 0.5M H_2SO_4 under dark conditions. The electrode was the same as that used for Fig.7.1 but following a 60 second period of anodic oxidation at 0.8V vs S.S.E. Sweep rate as above

of these plots. In general, it was found that the extrapolated flat-band potentials (V_{fb}) for fresh and anodized electrodes were respectively +0.175V ($\pm 0.025V$) and +0.6V ($\pm 0.02V$). This variation may reflect the differing electron affinities in solution of the fresh, and probably real, InP surface when compared with the oxide surface created by the anodizing treatment. Surface analysis techniques would again seem appropriate for further detailed study of this material.

Reproducible results could not be obtained in an alkaline medium for either C.V's or impedance measurements, so all further work was carried out in the 0.5M H_2SO_4 acidic medium.

The photoresponse of p-type InP was found to be very poor compared to the expected potential dependence based on the band positions determined in the a.c. experiments. Fig. 7.3 illustrates the best illuminated cyclic voltammogram obtained for an anodized surface, but on successive cycles the response deteriorates quite rapidly, approaching the much poorer response shown by fresh electrodes. At higher light intensities, this deterioration is made even more rapid, and a considerable reoxidation wave is seen on the anodic sweep (see Fig. 7.4). Further studies indicate that this wave corresponds to reoxidation of Indium metal created by the photo-assisted cathodic dissolution in the cathodic potential region.

Even with much lower light intensities, the PCV plots on p-InP still are remote from the ideality of significant photocurrent onset immediately cathodic of the flat band potential. As Fig. 7.5 shows significant photocurrent onset does not occur until some 0.8V cathodic of the flat-band potential. Additional PCV's taken at varying light intensities reveal an intensity dependence for the photocurrent similar to that obtained on p-GaP. However, even at the lowest illumination intensity used (giving saturation photocurrents of $10^{-9}A$), there is still no real approach to the ideal response, which is seen for p-GaP at the lowest

Fig.7.3 Dark and illuminated cyclic voltammograms of p-InP in 0.5M H_2SO_4 (—) dark, (---) illuminated with one-tenth maximum white light output of Xenon lamp. Sweep rate 250mV s^{-1} .

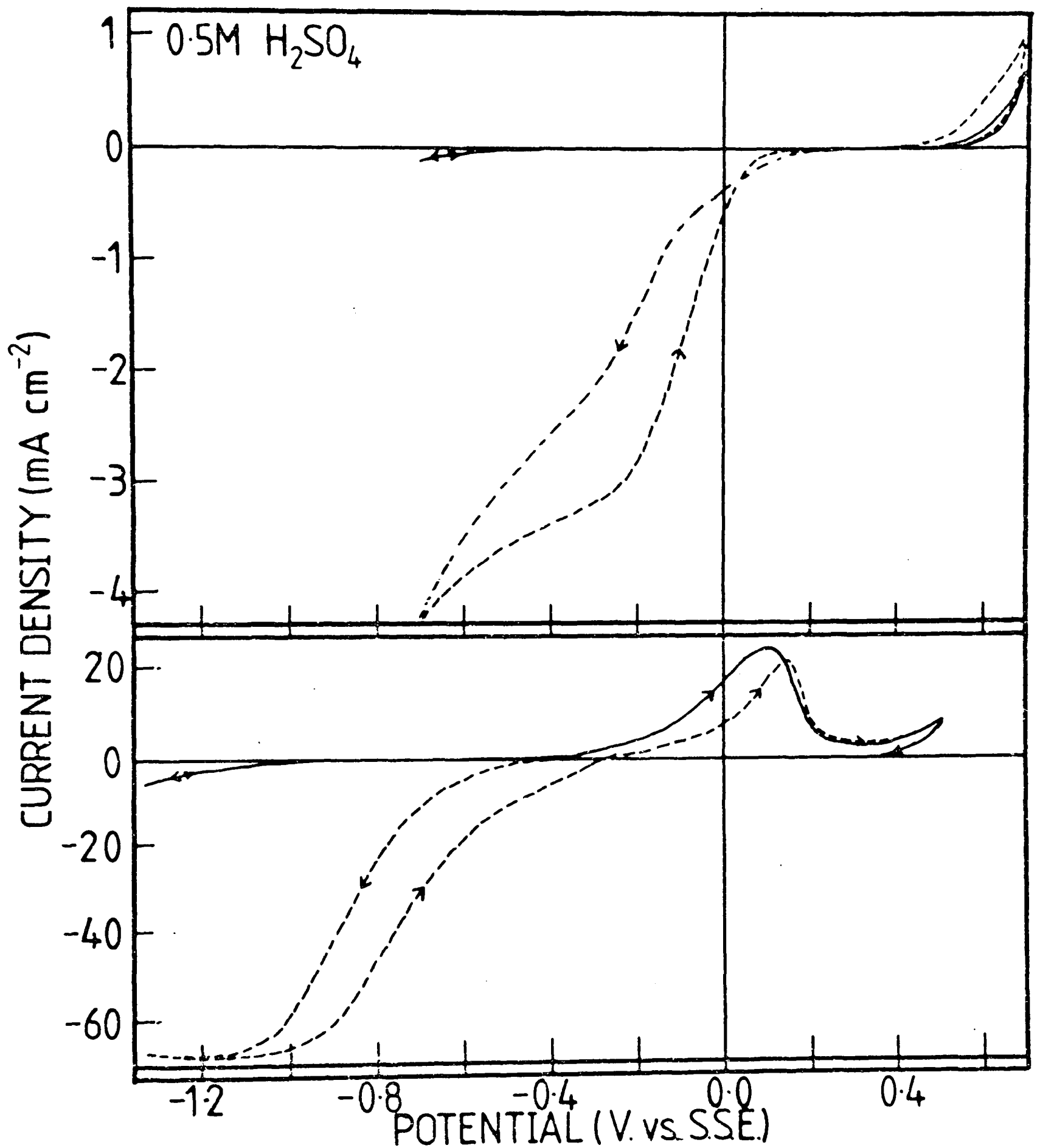
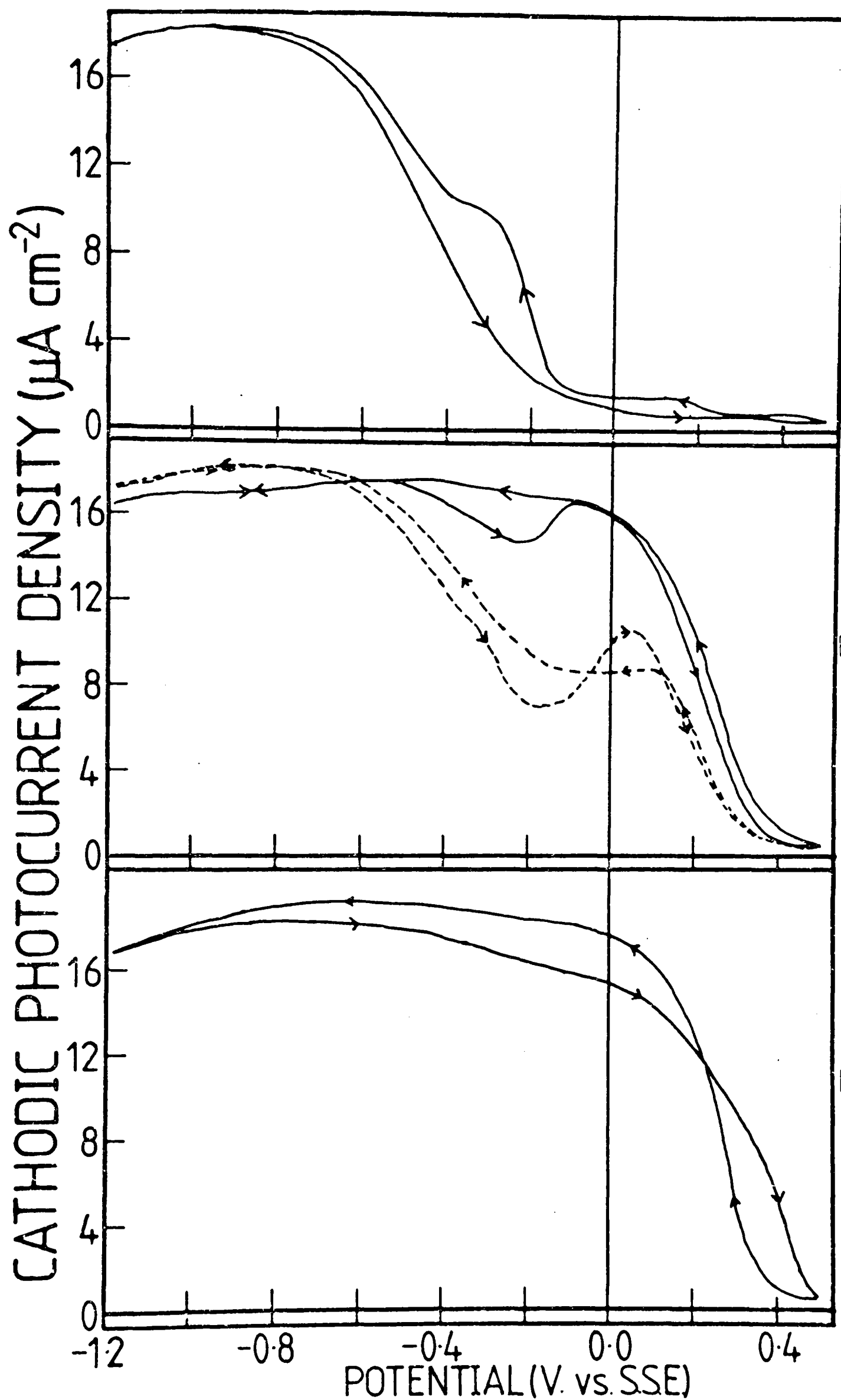
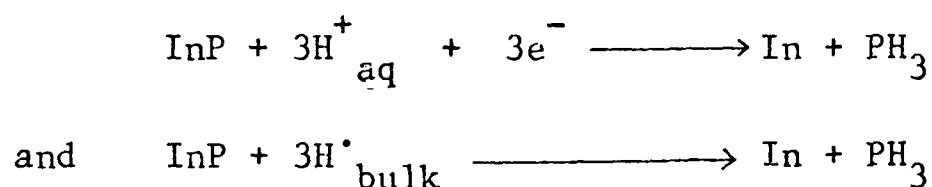


Fig.7.4 Dark and illuminated cyclic voltammograms of p-InP in 0.5M H_2SO_4 (—) dark, (---) illuminated with maximum white light output of 150W⁴ Xenon lamp. Sweep rate 250mV s^{-1} .

Figs.7.5-7.7 Photocurrent-voltage plots for p-InP in 0.5M H_2SO_4 (clean surface, 7.5) ; following a Bismuth(III) treatment (7.6) ; and in a dilute (0.001M) Bi(III) solution in 0.5M H_2SO_4 (7.7) . All light intensities equal and approx. 0.04% maximum Xenon lamp output . Chopping frequency 87Hz . Sweep rate 50mV s^{-1} .



light intensities (c.f. Fig. 4.18) If we accept a similar model for Hydrogen evolution at p-InP and p-GaP (see page 160) it follows that the competition between kinetics of the second step in the Hydrogen evolution reaction and the surface recombination reaction are even more in favour of the latter for InP than GaP. In addition, from the considerable instability of p-InP, it is apparent that reactions such as



are far more prevalent than with GaP. This probably reflects the weaker bond strengths of the InP lattice (seen as the lower bandgap $\sim 1.3\text{eV}$) such that the considerable strength of the P-H bond makes the above reactions highly favourable thermodynamically.

Despite extensive efforts, no realistic photocurrent action spectrum could be obtained on this material. All photocurrent readings suffered from a steady decrease and, due to the time required to obtain all the points on the spectrum, there was little correlation between the measurements taken at the beginning and end of the experiment. Nevertheless, it was clear that the major photocurrent onset occurred at about 960nm (1.29eV) and was a direct transition such that the photocurrent efficiency rose rapidly for wavelengths shorter than this onset value.

Following the success of metal ion adsorption in improving the Hydrogen evolution kinetics on p-GaP, similar tests were run on p-InP. In general, little or no improvements could be seen for higher intensity cyclic voltammograms, but some improvements were visible at lower light intensities. In this instance the crude RuCl_3 treatment had little effect, but dips in Bi(III) solution produced quite significant improvements (see Fig. 7.6). Unfortunately these improvements were quite short-lived on repeated cycling. Some experiments were carried out in a dilute (0.001M) Bi(III) solution in 0.5M H_2SO_4 . As Fig. 7.7 shows, the photoresponse curve is

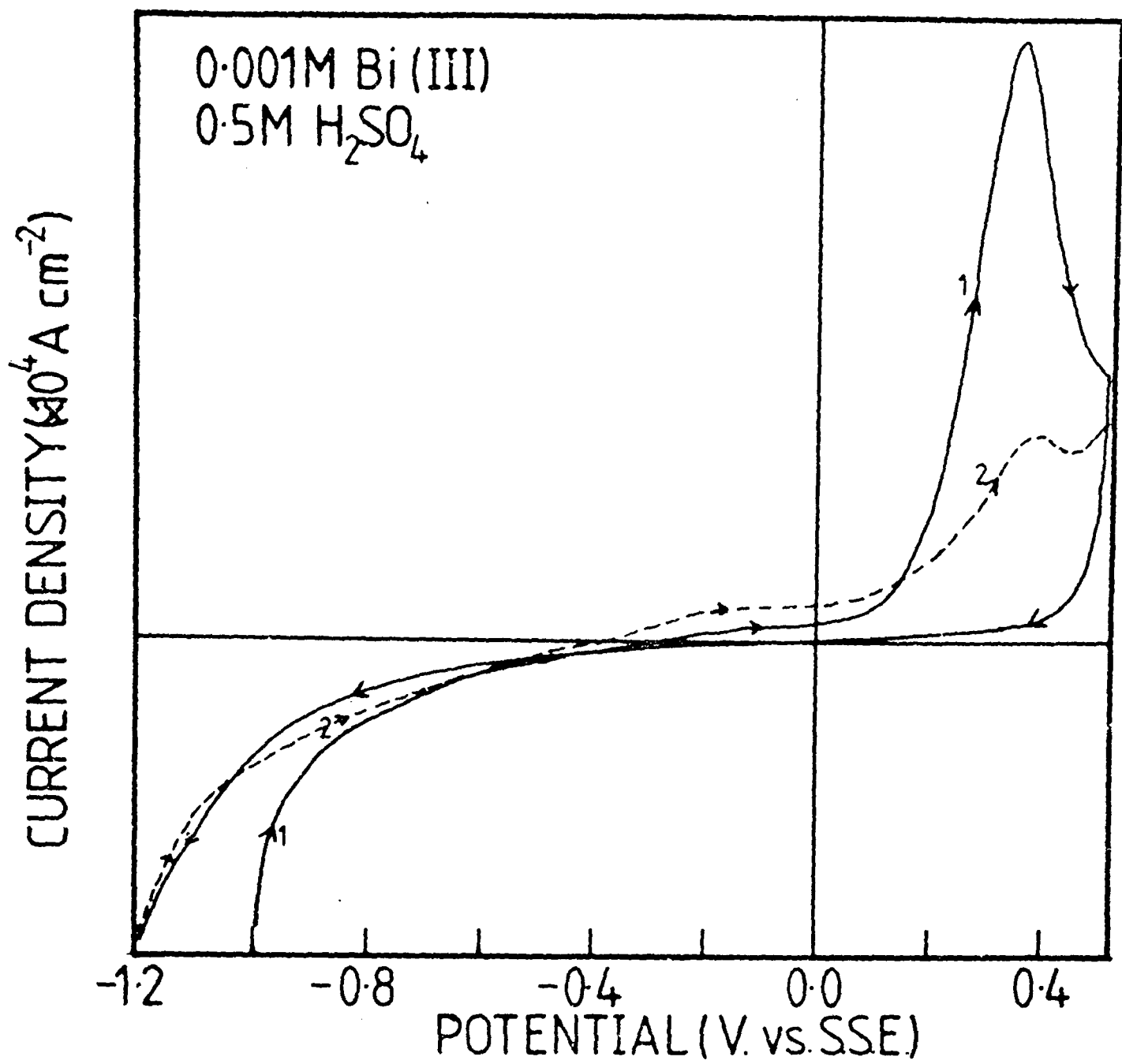


Fig.7.8 Dark cyclic voltammogram for p-InP in 0.001M Bi(III)/0.5M H₂SO₄. Sweep (1) directly follows period of illumination at -1.0V. Sweep (2) follows on directly. Sweep rate 250mV s⁻¹.

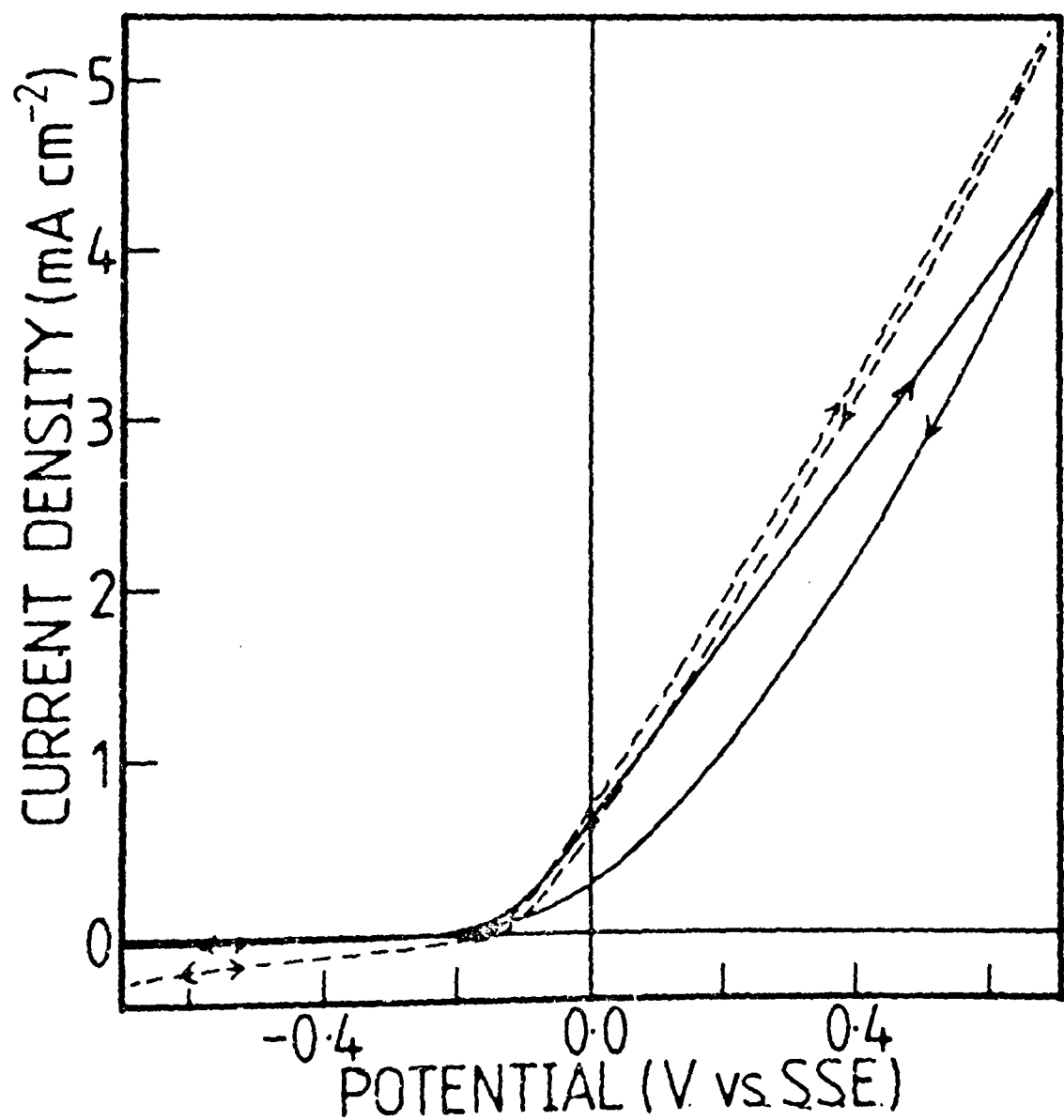


Fig.7.9 Cyclic voltammograms of p-InP electrode under dark (—) and illuminated conditions (---) following a 15 hour cathodic photocurrent test with initial photocurrent 40mA cm⁻². Sweep rate 250mV s⁻¹.

considerably improved and also reasonably stable. However, additional peaks in the dark cyclic voltammogram (Fig. 7.8) made it clear that the majority of this improvement resulted not from improved rates of Hydrogen evolution, but from Bismuth-metal deposition on the surface of the electrode. The magnitude of the additional anodic wave (at 0.36V) was directly related to the Bi(III) concentration in the solution.

Long-term durability tests on p-InP in dark and illuminated conditions, with and without the anodic pretreatment or metal-ion adsorption, all gave similar results. ACCV's were able to detect small surface changes even following short periods at potentials cathodic of 0V (SSE). A CV of an electrode that had been illuminated at cathodic potentials ($\sim -1.0\text{V}$) for about 15 hours (initial photocurrent $\approx 40\text{mAcm}^{-2}$) is shown in Fig. 7.9. The cathodic photoresponse has now been reduced to about 1% of the initial value, and there is a very large and irreversible anodic wave starting at about -0.1V (c.f. Fig. 7.3). At the end of the test the electrode appears to be coated in a grey material, and it seems clear that the irreversible anodic wave corresponds to the re-oxidation of macroscopic quantities of surface Indium metal. Similar surface appearances of InP electrode after prolonged usage have been observed previously, but no detailed surface analysis has yet been reported.¹¹⁴

The one literature report due to Heller et al.¹⁷⁸ thus remains as the only claim for cathodic stability of p-type InP. Despite intensive efforts to reproduce his conditions of anodized and Ruthenium treated electrodes, the p-InP electrodes were still found to be unstable. From the findings of this present work, it is certain that p-InP would be unlikely to find a use for the solar photoelectrolysis of water unless some way can be found to protect the electrode surface from the cathodic corrosion reactions. For the present, the anomalous result of Heller must remain a mystery until he publishes a more detailed experimental paper. To date his papers on the subject have concentrated more on the solar efficiencies of his devices than the actual electrochemical results.

SECTION 7:3 p-GaSb

Consecutive cyclic voltammograms of p-GaSb reveal a slow, steady charge; but the initial response (Fig. 7.10) is close to the expected ideal behaviour for a p-type III-V material: little cathodic current and a large, irreversible anodic wave representing the anodic oxidation and dissolution of the electrode according to:-



After prolonged cycling and experimentation, the CV approaches that shown in Fig. 7.11 with a sharp anodic wave at about -0.02V and a sharp and slightly structured cathodic wave at about -0.3V. However, at an intermediate age the structure at -0.3V is very clear and indeed displays a very complex time dependent behaviour as shown in Fig. 7.12. On the scale of 7.11 there is virtually no observable cathodic photocurrent in this potential range, but illumination does increase the rate of evolution of the wave in consecutive cycles. Only at potentials cathodic of -1.0V does any significant photocurrent become apparent, but photocurrent efficiencies remain very low <1% and are highly time-dependent, deteriorating rapidly with continued illumination (see PCV plot of Fig. 7.12). No photocurrent action spectrum could be obtained due to this rapid determination, but the onset wavelength was found to be beyond the range of the monochromator used (i.e. >1000nm).

All attempts to determine the flat-band potential of the material by a.c. measurements failed since all the readings were unsteady even over periods less than 1 second. On the basis of comparison of the onset of the anodic dissolution wave between the three III-V Gallium compounds studied, an estimate of about 0.0V could be made for the flat-band potential.

Prolonged cathodization (in dark or illuminated conditions) caused a metallization of the surface, presumably due to formation of Gallium metal

Fig.7.10 Initial cyclic voltammogram for p-GaSb in 0.5M H_2SO_4 under dark conditions. Sweep rate 250mV s^{-1} .

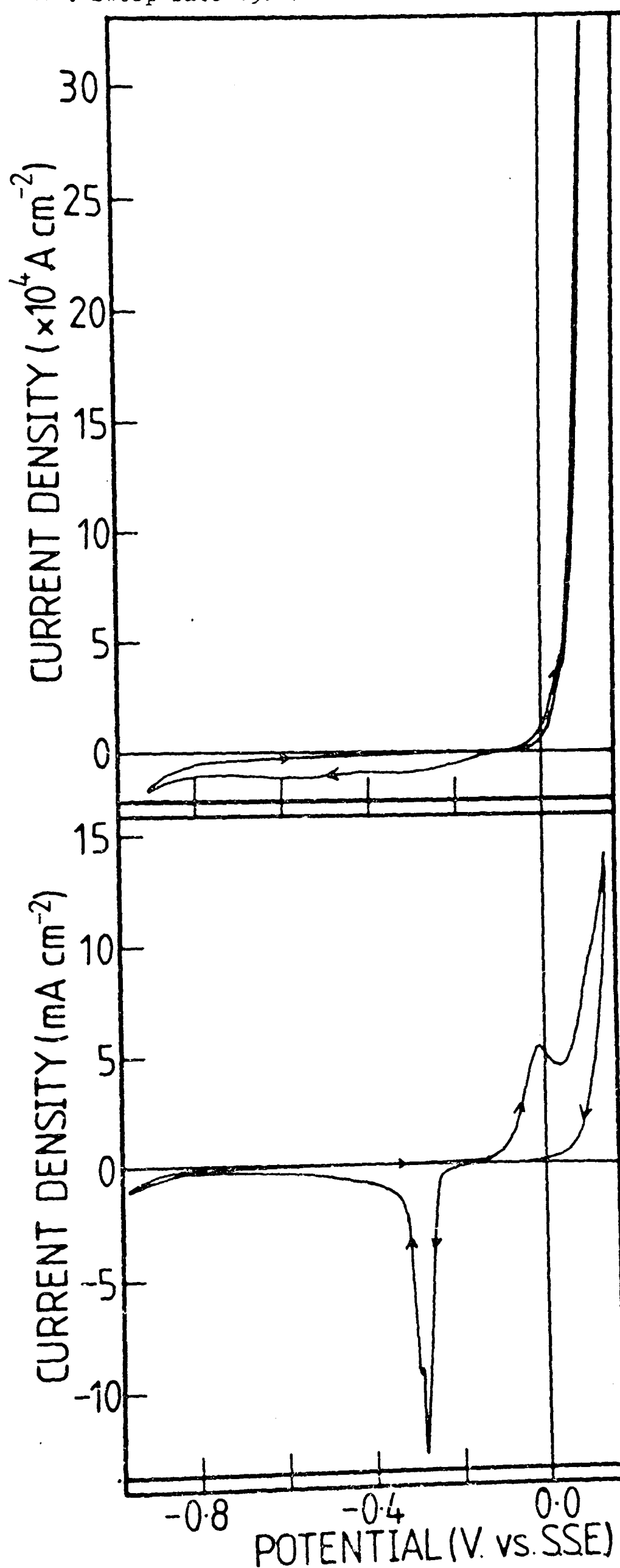


Fig.7.11 Cyclic voltammogram for p-GaSb in 0.5M H_2SO_4 following three hours of cycling between potential ranges as shown. Sweep rate 250mV s^{-1} .

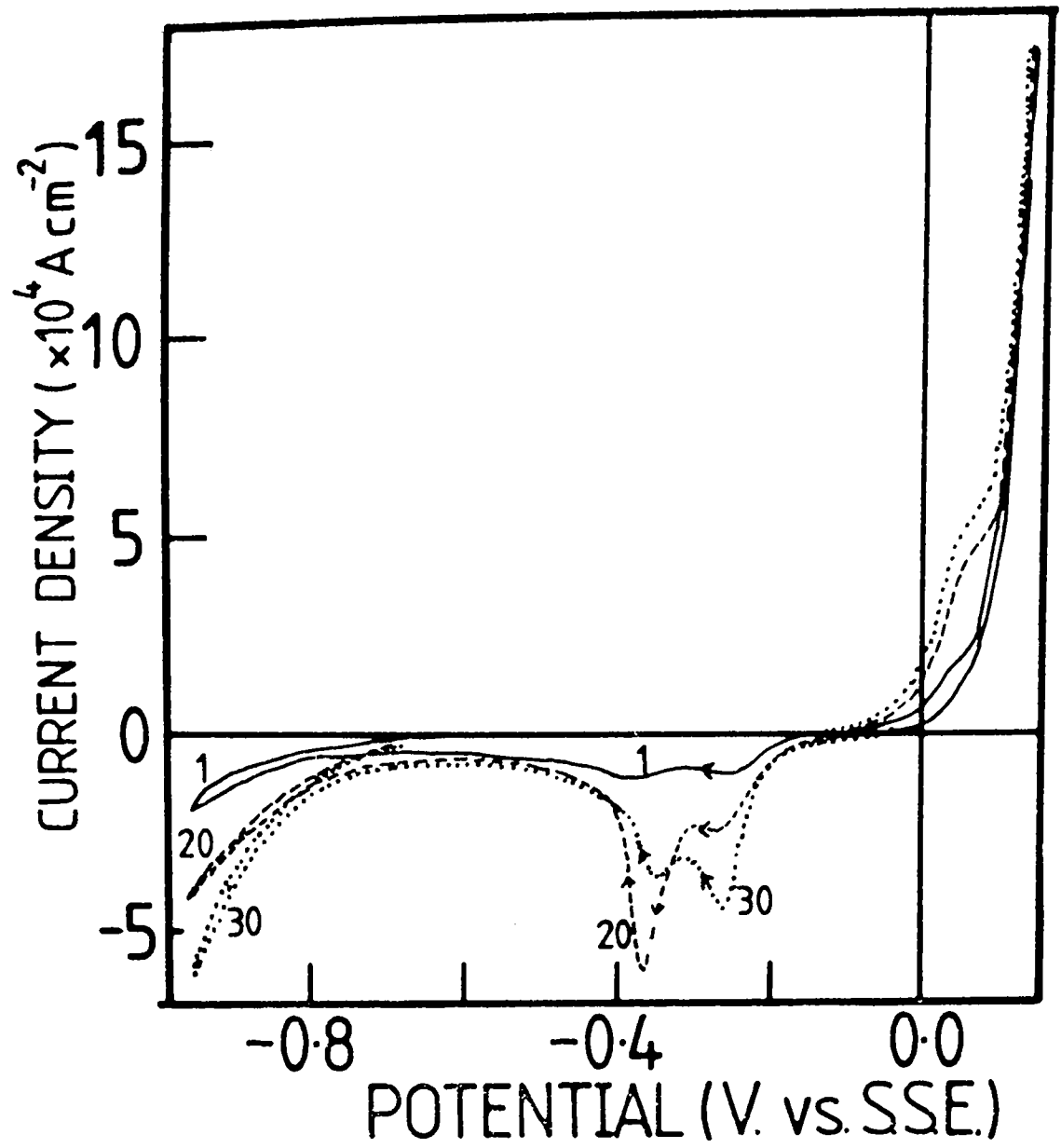


Fig.7.12 Cyclic voltammogram for p-GaSb in 0.5M H₂SO₄ at an age intermediate between that shown in Figs. 7.10 and 7.11 . The numbers correspond to the number of cycles over which the electrode is aged .

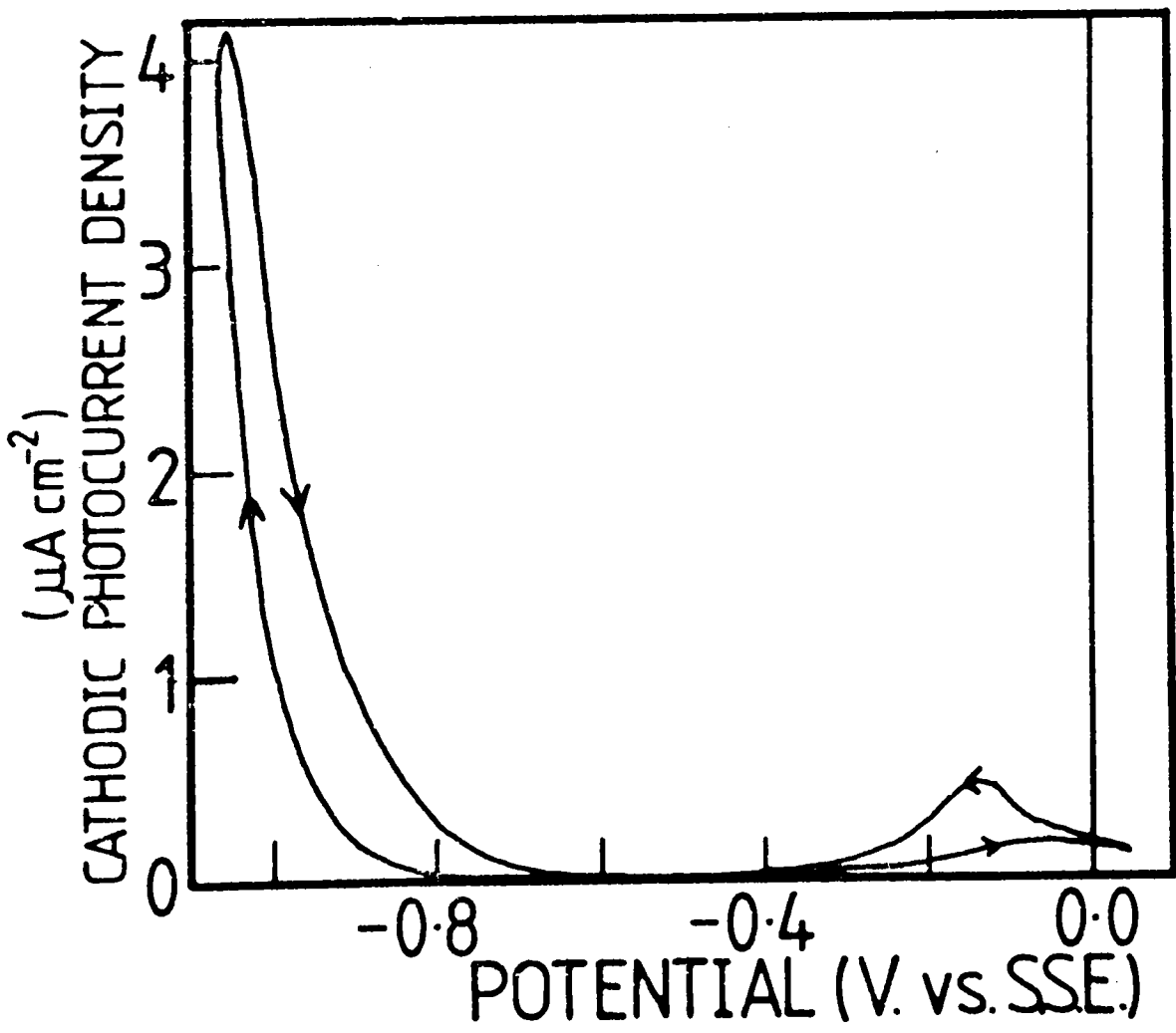
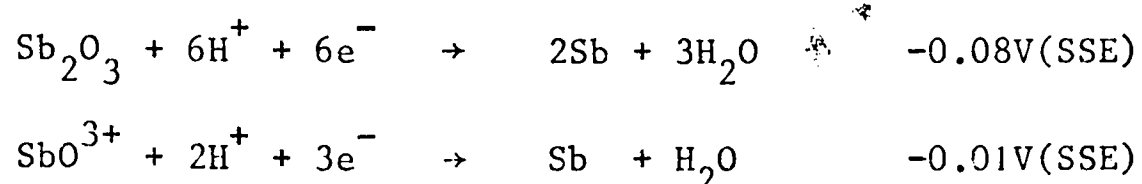


Fig.7.13 Photocurrent-voltage plot for p-GaSb in 0.5M H₂SO₄ for complete output of 150W Xenon lamp illumination . Sweep rate 50mV s^{-1} .

by cathodic dissolution. The considerable structure of the CV's may be related to the reduction and oxidation of antimony oxides created on the surface of the electrode during the irreversible anodic wave. Despite the expected additional complexities for variation of the standard redox potentials for species created at and adsorbed on solid electrodes, the E^0 's for a number of antimony couples show approximate correlation with the peak positions in the CV's:-



The origin of the evolution of the complex waves can only be guessed at; without further detailed surface analysis and depth profiling, there is little value in further conjecture. It is, however, apparent that GaSb by no means behaves as an ideal p-type electrode on illumination. Surface defects and the creation and rapid annihilation of surface-bound intermediates are the dominating recombination pathways for photogenerated electrons created in the electrode surface. As with InP, before further study is made on GaSb some method must be sought for stabilizing the electrode surface possibly by polymer coating. Alternatively studies may be restricted to work in non-aqueous aprotic solvents where protons are no longer present to assist the cathodic decomposition reactions. Nevertheless, as has already been found by Kohl and Bard^{282,283}, the difficulties in drying solvents to make them truly non-aqueous present an almost insurmountable problem. Kohl and Bard continually discovered surface films formed on their electrodes over quite short periods of experimentation; they were generally attributable to very small concentrations of H_2O in their solvents even below the 0.1p.p.m. level. Some attempts were made at studies of GaSb in CH_3CN , but problems with satisfactory water-tight cell design precluded the acquisition of any meaningful results. Extensive development in the technological design of water seals on the electrochemical cells is necessary before any further serious attempt is made in this field.

CHAPTER EIGHT

FURTHER APPROACHES TO THE PHOTOELECTROLYSIS OF WATER

SECTION 8:1 INTRODUCTION

Hydrogen is an important chemical fuels, except where abundant hydropower itself a fuel representing a convenient method of long-term energy storage. Utilization of solar energy with its inherent seasonal and diurnal variation is plagued by the need for long-term storage. Therefore conversion of solar energy into Hydrogen via the electrolysis of water must be considered as a high-priority technical objective.

Future Hydrogen production from water using solar energy will probably utilize photovoltaic cells (solid-state or wet-type: see Chapter 1:3) coupled to a conventional electrolysis plant. The cost of efficient photovoltaic devices will be expected to come down by at least an order of magnitude over the next 10 years as the technology of polycrystalline or amorphous thin-film materials becomes further advanced. In addition, progress in the field of low-overvoltage oxygen electrodes should make electrolysis cells more feasible. The advantage of such a dual system are flexibility, allowing multiphoton processes via the series connection of cells, and greater efficiency of energy concentration.

Nevertheless, the announcement by Fujishima and Honda^{16,17} of a one-photon photoelectrolysis of water with ultra-violet light and a working anode of TiO_2 stimulated investigation of the direct photoelectrolysis of water by sunlight. Chapter One introduced the basic operation of the semiconductor photoelectrolysis cell, along with the three major cell configurations used and a list of the materials studied to date. Sections 8:2 - 8:4

of this Chapter will consider the details of the energetic constraints and materials properties required for efficient photoelectrolysis cells operating in each of the three configurations mentioned in Chapter 1.

In addition, a brief resumé will be given of the results obtained on novel materials for use in photoelectrolysis cells that have been designed and tested in parallel with the major research topic of this thesis covered in Chapters 4-7. One novel approach, not discussed in Chapter One, has been the use of inorganic dye molecules for the photosensitization of semiconductor photoelectrolysis cells for operation in the visible region of the spectrum. This will be discussed briefly in Section 8:5.

SECTION 8:2 STRATEGY I: THE DESIGN OF NOVEL SEMICONDUCTING ANODES FOR THE PHOTOELECTROLYSIS OF WATER.

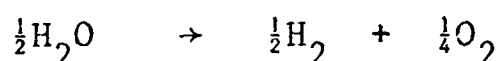
In Configuration I (see Fig. 1.1), the light is absorbed by an n-type semiconductor that is short circuited to a metallic counter electrode. In operation, Oxygen gas is evolved at the semiconductor surface and Hydrogen is evolved at the metal electrode. To minimize iR potential losses through the external circuit, it is essential that the semiconductor should be adequately conducting with a resistivity of $<100\Omega$ cm. The optimum doping level for a given semiconductor is, however, a subject for careful investigation with each new material. Early workers suggested that the width of the space-charge layer should be made approximately equal to the penetration depth of the light. A number of exceptions to this rule have since been discovered, and a combination of absorption coefficient, minority-carrier diffusion length and various interfacial kinetic parameters can affect the value of the optimum doping density. This may be seen by studying the Albery-Hamnett equation of Chapter 2.

In practice it is found that unless the n-type O_2 electrode is an oxide, oxidation of the surface anions rapidly occurs, leading to either electrode

dissolution or the formation of an impervious and insulating surface-oxide film. Thus our requirement in Configuration I is for an n-type, conducting oxide semiconductor. Fig. 8.1 shows the detailed energetics expected for an ideal photoelectrolysis cell operating in Configuration I.

For operation without the assistance of an external bias, it is necessary for the conduction-band in the semiconductor to lie at least 0.7eV above the $E^0(\text{H}^+/\text{H}_2)$ level in solution: This figure arises from a 0.4V band bending to achieve adequate charge separation of electron hole pairs in the space-charge layer plus an estimated 0.3eV separation between the base of the conduction band and the Fermi level (E_F) (a typical value in most n-type oxide semiconductors).

A further loss may arise from the overvoltage required for Hydrogen evolution. However, a number of metallic cathode materials are now known that can efficiently evolve Hydrogen with overvoltages $<0.1\text{eV}$, so this loss may be minimized quite effectively. The actual energy stored by the photoelectrolysis of water is 1.23eV per photon - this being the energy required for:-



Finally an additional loss will come from the overvoltage required for Oxygen Evolution. On the basis of the minimum values obtained on presently-known materials, this value can be estimated at $\sim 0.4\text{eV}$.

Thus the minimum band-gap, with which one can expect to obtain efficient photoelectrolysis of water, may be calculated from the sum of the above figures

$$\begin{aligned} \text{i.e. } E_g &\sim 1.23 + \epsilon_{cf} + \eta_{\text{O}_2} + \eta_{\text{H}_2} + \epsilon_{bb} \\ &\sim 1.23 + 0.3 + 0.4 + 0.1 + 0.4 \\ &\sim \underline{2.4\text{eV}} \end{aligned}$$

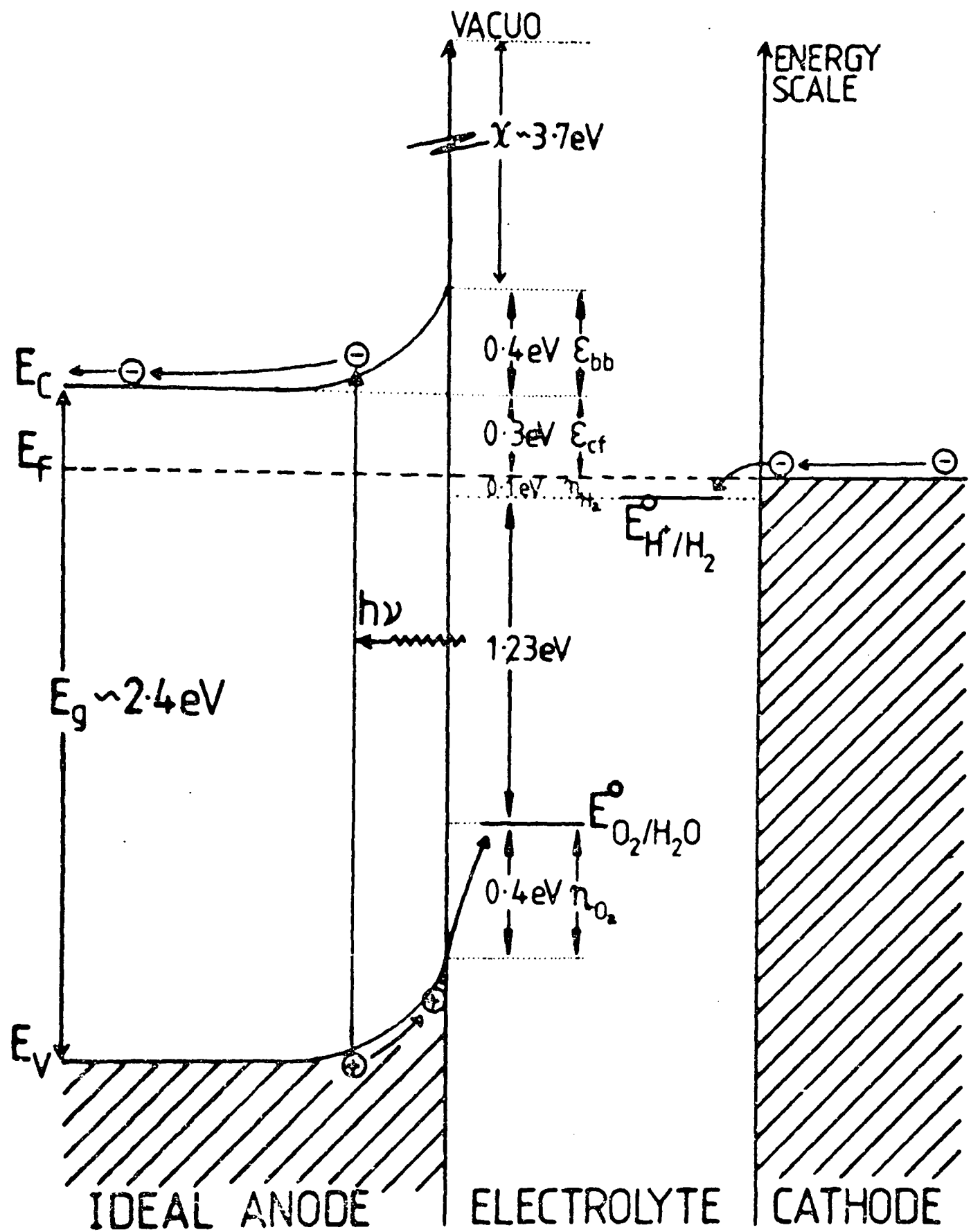


Fig.8.1 Detailed energetics for an ideal semiconductor/electrolyte photoelectrolysis cell operating in Configuration I .
 ϵ_{bb} =band bending required for efficient electron/hole separation .
 ϵ_{cf} =separation between base of conduction band and the Fermi level .
 η_{O_2} =overvoltage for oxygen evolution on semiconductor.
 η_{H_2} =overvoltage for hydrogen evolution on metal counter electrode .

In addition the material must possess a conduction band which lies at least 0.7eV above the H^+/H_2 level. Given the estimated value of $E^0(H^+/H_2)$ vs. vacuum as 4.5eV, this requires the semiconductor to have an electron affinity <3.7 eV. For semiconducting oxide materials, conduction bands based on the octahedral site $Ti^{4+}:3d$ or the $Nb^{5+}:4d$ energy levels possess the required energies: $\chi(TiO_2) \approx 4.2eV$ ²¹ $\chi(SrTiO_3) \approx 4.0eV$ ²³⁵ $\chi(Nb_2O_5) \approx 4.2eV$ ⁴⁷. A number of materials can be found with smaller electron affinities (e.g. ZrO_2), but in general these oxides are not reducible and remain highly insulating, which makes them of little use in photoelectrolysis devices. TiO_2 does not operate in Configuration I without the application of an external bias²¹, and even $SrTiO_3$ does not attain its maximal efficiency under short-circuit conditions. It is thus clear that a method must be sought for further reducing the electron affinity of these compounds. An obvious method would be to add a small quantity of a cation with an even smaller electron electronegativity than Ti^{4+} , e.g. Zr^{4+} . On the basis of Butler and Ginley's empirical formula²⁸⁴, there is a direct relationship between the flat-band potential (or the electron affinity) of a compound and the geometric mean of the atomic electronegativities of the constituent elements. Given this prediction, polycrystalline sintered pellets of reduced $SrTiO_3$ and $SrTi_{0.75}Zr_{0.25}O_3$ were prepared and electrochemical measurements performed on them to discover the flat-band potentials of these materials in aqueous solution.

Table 8:1

Material	Flat-Band potential in 1.0M NaOH vs. S.S.E	Electron Affinity	Band gap
$SrTiO_3$	-1.4	4.0	3.1
$SrTi_{0.75}Zr_{0.25}O_3$	-1.55	3.85	3.3

The desired reductionⁱⁿ electron affinity has thus been achieved, and the position of the $O^{2-}:2p^6$ valence band is little affected by the Zr^{4+} substitution. However, some additional unexpected discoveries arose from the study of the $SrTi_{0.75}Zr_{0.25}O_3$ electrode.^{61,62} The dark CV's revealed quite a significant structure (Fig. 8.2) not expected from a material possessing such electroinactive constituents and not seen for pure $SrTiO_3$. Further studies revealed that the presence of surface Zr could reduce the overpotential for oxygen evolution to less than 0.4eV, signalling greater facility at surface zirconium for the formation of peroxy intermediates. This is consistent with the greater tendency for Zr versus Ti to accept higher oxygen-ion coordination.

The problem with all the above materials (TiO_2 , $SrTiO_3$, $SrTi_{1-x}Zr_xO_3$) is that their band-gaps are far too large for effective use of the solar spectrum. As Fig. 8.3 shows, there is a rapid fall off in efficiency as the semiconductor bandgap increases above the optimum 1.1-1.2eV. Materials with bandgaps between 3.0 and 3.2eV can operate only with overall conversion efficiencies <1%. The minimum operational bandgap of 2.4eV can, however, still attain ≈8-9%; with cheap materials and fabrication costs this may still be economically viable given the direct solar → storable energy nature of the photoelectrolysis cell. In the titanate materials above, the valence band originates from the $O^{2-}:2p^6$ energy levels; for a majority of compounds the band lies in the region of 7.0-7.5eV below the vacuum level i.e. ≈1.3-1.8eV below the O_2/H_2O level (5.73eV vs. vacuum). To further reduce the bandgap in these compounds, an additional valence band must be sought that lies only ≈0.4eV below the O_2/H_2O level. This may only be satisfactorily achieved by the synthesis of compounds possessing an additional cation (other than Ti^{4+} or Nb^{5+}) whose non-bonding orbitals overlap, either directly or via an intervening oxygen (in a more covalent system), to create an energy band within the titanate bandgap, but without strongly perturbing the $Ti:3d$ conduction band.

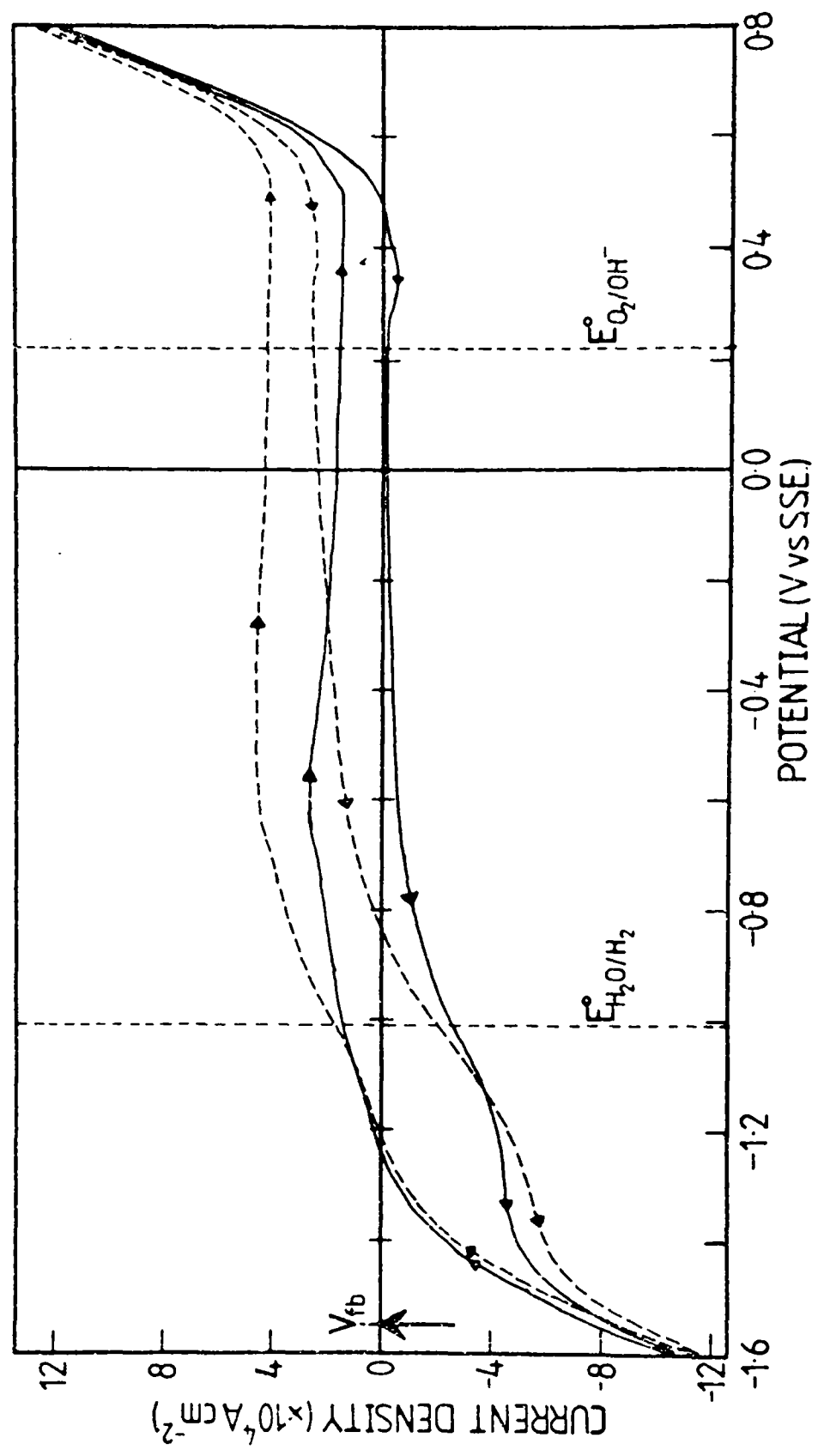


Fig.8.2 Cyclic voltammograms for $\text{SrTi}_{0.75}\text{Zr}_{0.25}\text{O}_3$ in 1.0M NaOH under dark(—) and illuminated (---)(white light) conditions . Sweep rate 250mV s⁻¹ . V_{fb} = flatband potential for this material .

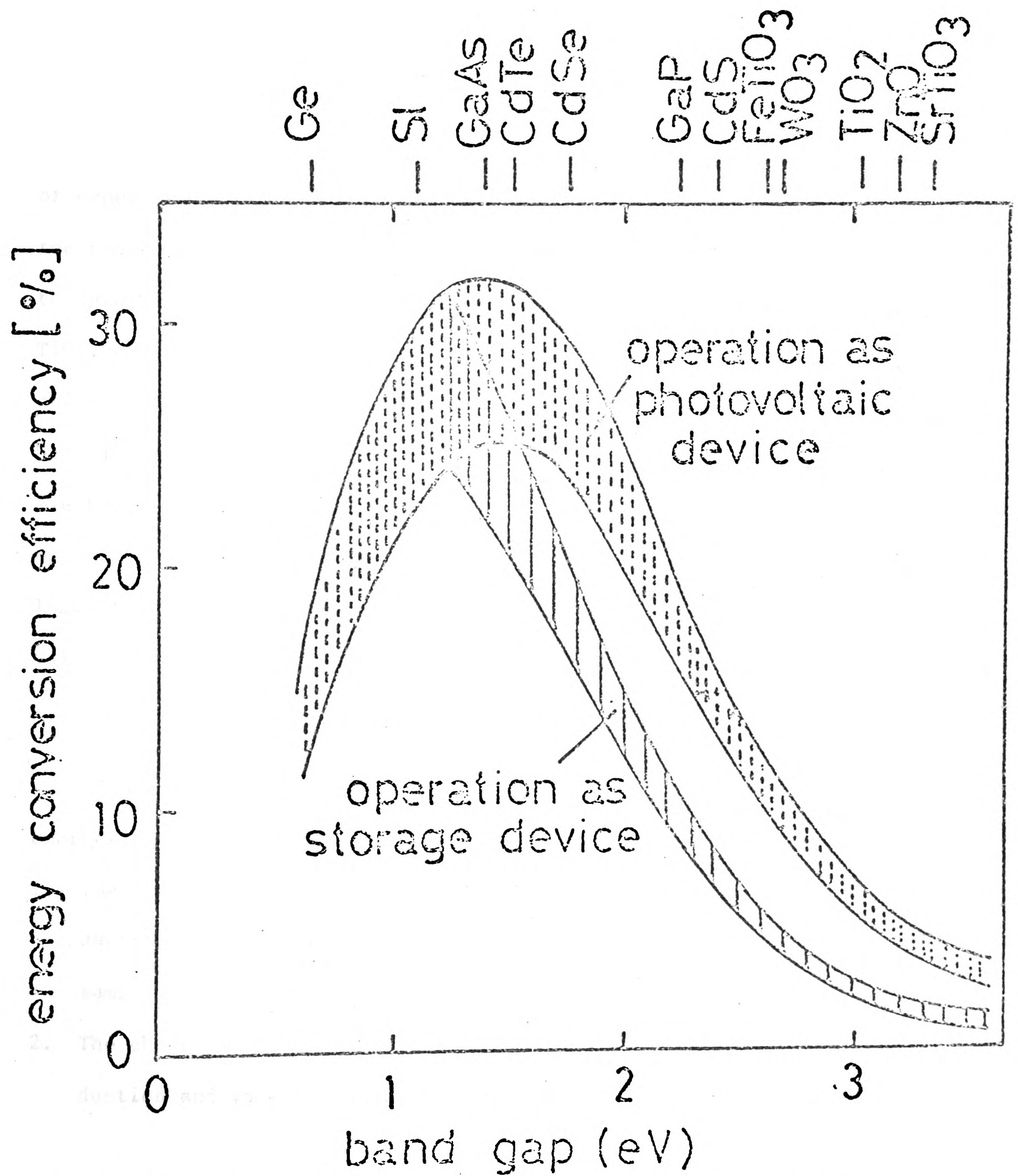
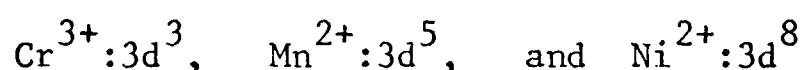


Fig.8.3 Plot of energy conversion efficiency vs. semiconductor bandgap
Upper curve represents optimum efficiency for photovoltaic cell ; lower
curve represents optimum efficiency for photoelectrolysis cell .

Basing the choice of suitable cation on the known energies of non-bonding orbitals in a wide range of oxide materials, the only candidates as 'dopant' ions are those that possess either $3d^n$, $4d^n$, $5d^n$, $4f^n$ or $5s^2$ manifolds. However economic criteria restrict the d block element choice to the 3d elements.

Considering ions possessing the $3d^n$ manifold initially; a further narrowing of the choice of transition-metal ion may be made on the basis of experimentally determined energy levels. Mizushima et al.²⁸⁵ used a technique based on photoconductivity and photosensitive E.S.R. measurements to determine the energy levels of various transition metal ions doped into TiO_2 . The results are presented in Fig. 8.4 with the energies of $E^0(H^+/H_2)$ and $E^0(O_2/H_2O)$ shown for reference. For the additional valence band to be able to assist in the photoelectrolysis of water, the valence band must lie below the $E^0(O_2/H_2O)$ level. Also it is necessary to be able to prepare an n-type conducting compound from any proposed material. Given these limitations, the only $3d^n$ manifolds likely to be suitable for an additional valence band in the titanate structure are



Two alternative structural strategies may now be used given the energetic considerations above:-

1. The chosen ions may be doped into TiO_2 or $SrTiO_3$ such that the conduction and valence bands result from two different cations on the same sublattice.
2. The chosen ions may be used in structures that provide for the conduction and valence bands to arise from overlap of the two different cations on two separate sublattices.

The former approach might appear to be doomed to failure since problems of sufficient overlap with the single mixed sublattice would be expected to severely reduce the charge carrier mobility in both the conduction and

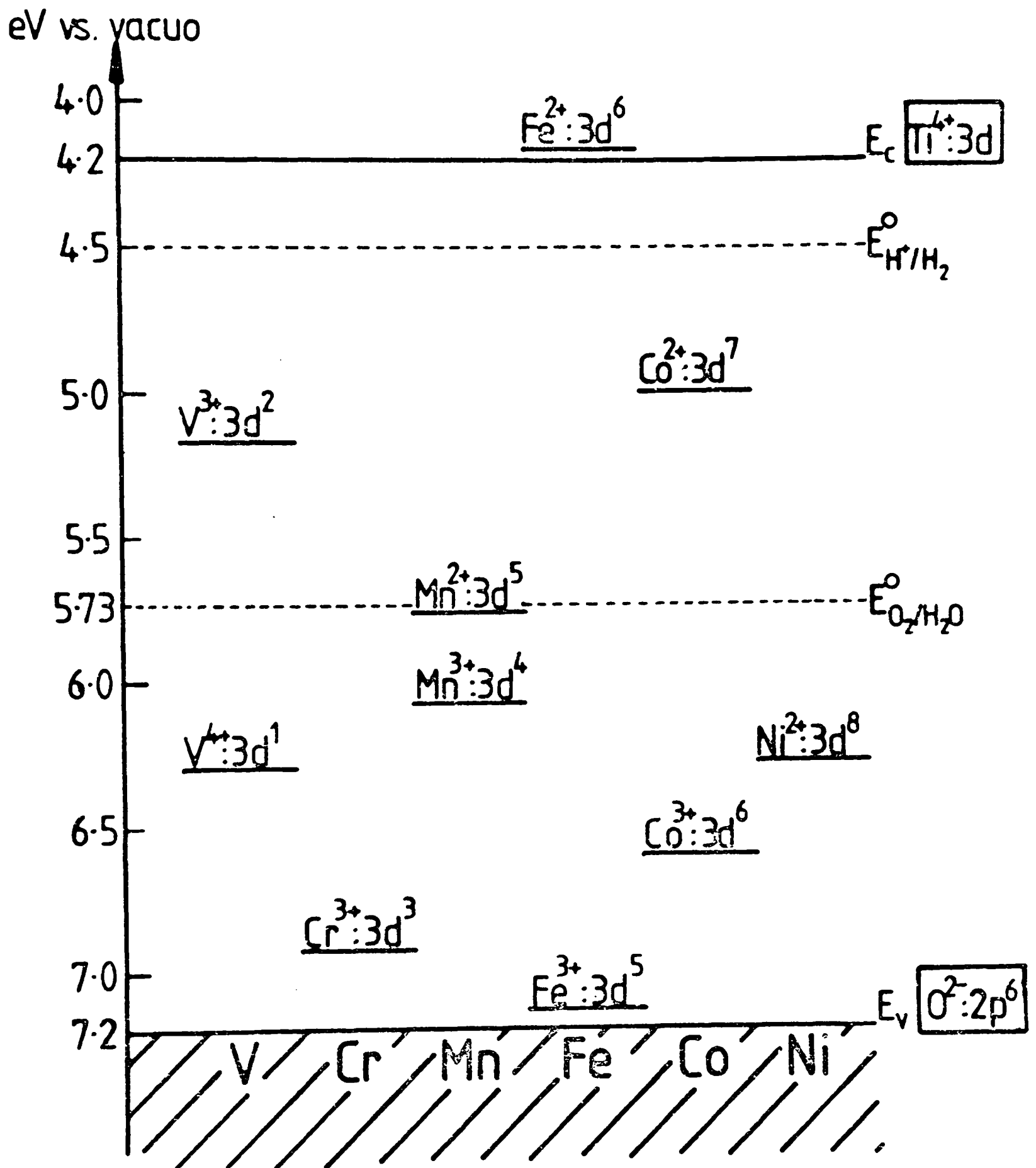


Fig.8.4 Energy levels of various first row transition metal ions doped into TiO_2 as determined by Mizushima *et. al.* (Ref.285)

valence bands. In general, efficient photocurrent response seems to require high charge carrier mobility for both minority and majority carriers, (see Albery and Hamnett Equation, Section 2:11), favouring the second approach above.

Nevertheless a study was made of the photoelectrochemical properties of Chromium doped SrTiO_3^{235} . Even with quite small concentrations of Cr^{3+} , (<10% substituted for Ti^{4+}), absorption in the visible region of this spectrum was quite significant - as determined from diffuse reflectance spectra. In addition photosensitization of the anodic photocurrents was also quite impressive at large anodic bias and/or under a.c. irradiation. However, under the d.c. conditions of a normally working cell, little improvement in the photoelectrolysis of water was achieved. The major problem appeared to be the very slow water oxidation kinetics for the holes created in the $\text{Cr}^{3+}:3d^3$ valence band. Because of these slow hole-transfer kinetics across the interface, the holes become trapped at the surface in Cr^{4+} states. The result of this is a slow readjustment of the charge distribution at the interface in such a way as to reduce the photocurrent. The second difficulty is that the same sublattice is being used to transport both electrons and holes and the diffusion lengths of both will be reduced by recombination. However, one discovery from this study was that the problem of poor mobility in the narrow valence bands may be overcome by field-assisted transport mechanisms in the space-charge layer.

Many other workers have also studied the photosensitization effect of metal ions doped into TiO_2 and $\text{SrTiO}_3^{286-300}$. However, all but one of these attempts has actually decreased the overall solar conversion efficiency of the photoelectrolysis cells employing these novel methods. One basic problem appears to dog further progress in this field: the dopant ion cannot be dissolved in sufficient quantity into the TiO_2 lattice to effect sufficient visible light absorption whilst preventing the formation of

macroscopic defect structures (e.g. shear planes) that enhance electron hole recombination. The only successful dopant ion has been Be^{2+} ³⁰⁰ and in this case, sensitization of photocurrent response into the visible is not achieved, but rather the photocurrent response as a function of voltage seems to be considerably improved. Other dopants ions tested now include Al^{3+} , Sr^{2+} , Ga^{3+} , Eu^{3+} , B(III) , Ni^{2+} , Co^{2+} , Mn^{2+} , Fe^{2+} , Cu^{2+} , Ru^{4+} , Cr^{3+} , V^{3+} , Y^{3+} , Ta^{5+} , Nb^{5+} , Mo^{6+} , Pd^{2+} , Zn^{2+} .

On the second approach above, two titanate structures are suitable for compounds possessing a valence band resulting from overlap of ions on a separate sublattice: the ilmenite and perovskite (both MTiO_3) structures. Given the choice of cations made above, MnTiO_3 or NiTiO_3 were considered appropriate for study. The latter compound could not be prepared n-type without the total reduction of Ni^{2+} to Ni metal.⁶⁰ This in fact suggests the Ni^{2+}/Ni level lies very close to the Ti^{4+} conduction band edge. Successful studies have, however, been claimed on Nb doped NiTiO_3 ²⁸⁹ but the conversion efficiencies are not interesting. MnTiO_3 was prepared as a polycrystalline sintered pellet and made n-type by H_2 reduction.⁶⁰ Reflectance spectra revealed absorption to wavelengths as long as 480nm (2.6eV). However, when used as an anode in aqueous solutions, negligible photocurrents were seen in the range 400-480 nm (2.6-3.0eV). In addition, the visible light photocurrents possessed a transient behaviour similar to that seen in Cr doped SrTiO_3 .²³⁵ Two main conclusions arose from more detailed studies of the photoelectrochemistry of MnTiO_3 .⁶⁰⁻⁶²

1. The $\text{Mn}^{2+} \rightarrow \text{Ti}^{4+}$ charge transfer absorption has a very low oscillator strength and so photosensitization into the visible even for transient photocurrents is very poor. This finding may be understood from the geometry of the ilmenite structure and d-electron configurations at the cations. Transition with excitation energies <3.0eV involve $\text{Mn}^{2+} : e_{\sigma}$ electrons in Mn-O σ bonding orbitals transferring to $\text{Ti}^{4+} : e_{\pi}$

orbitals of t_{2g} parentage; the overlap integrals for these orbitals in the ilmenite structure is very small.

2. Holes photogenerated in the $Mn^{2+}:3d^5$ band are about 0.5eV too high to provide rapid oxidation of water with visible light. Hence the $Mn^{2+} \rightarrow Ti^{4+}$ transition leads only to transient photocurrents when high anodic biases are used.

In addition to studies on $MnTiO_3$, some work was done on other ilmenite materials.⁶⁰ Preparation difficulties and electrochemical instability rendered the results to be of little interest save a general confirmation of the energy level diagram of Fig.8.4.

Given the failure of compounds possessing $3d^n$ valence bands, the next approach was to investigate the use of materials containing $4f^n$ bands. In practice, the only $4f^n$ levels that lie in the titanate ($O^{2-}:2p^6 \rightarrow Ti:3d$) bandgap are the $4f^1$ and $4f^2$ levels of Ce^{3+} and Pr^{3+} . The compound chosen for detailed study was $NaCeTi_2O_6$ possessing a perovskite structure.^{61,62} Cyclic Voltammetry revealed the surface $E^0(Ce^{4+}/Ce^{3+})$ to lie at about 0.5V cathodic of the O_2/H_2O level in the electrolyte. With thermal broadening of over 0.5eV, the $Ce^{4+}4f^0$ level is well above the O_2/H_2O level, which means that holes arriving at the surface in the $Ce^{2+}:4f^1$ valence band does not oxidize water. Instead they charge the surface so as to lower the semiconductor band energies. Only if the added surface charge is large enough to lower the band energies by over 0.5eV can oxidation of water by surface Ce^{4+} ions occur. Nevertheless, the electrolyte displacement currents that accompany accumulation of surface Ce^{4+} ions do produce a transient photocurrent. Photosensitization in $NaCeTi_2O_6$ is seen to extend to 700nm (see Fig. 8.5) and the onset of charge-transfer excitation from the $O^{2-}:2p^6$ valence band appears only below 400nm. The intensity of the transient photocurrent is about 50% due to $Ce^{3+}:4f^1$ to $Ti^{4+}:3d$ transitions. This observation demonstrates that photogenerated holes in the $Ce^{3+}:4f^1$ band

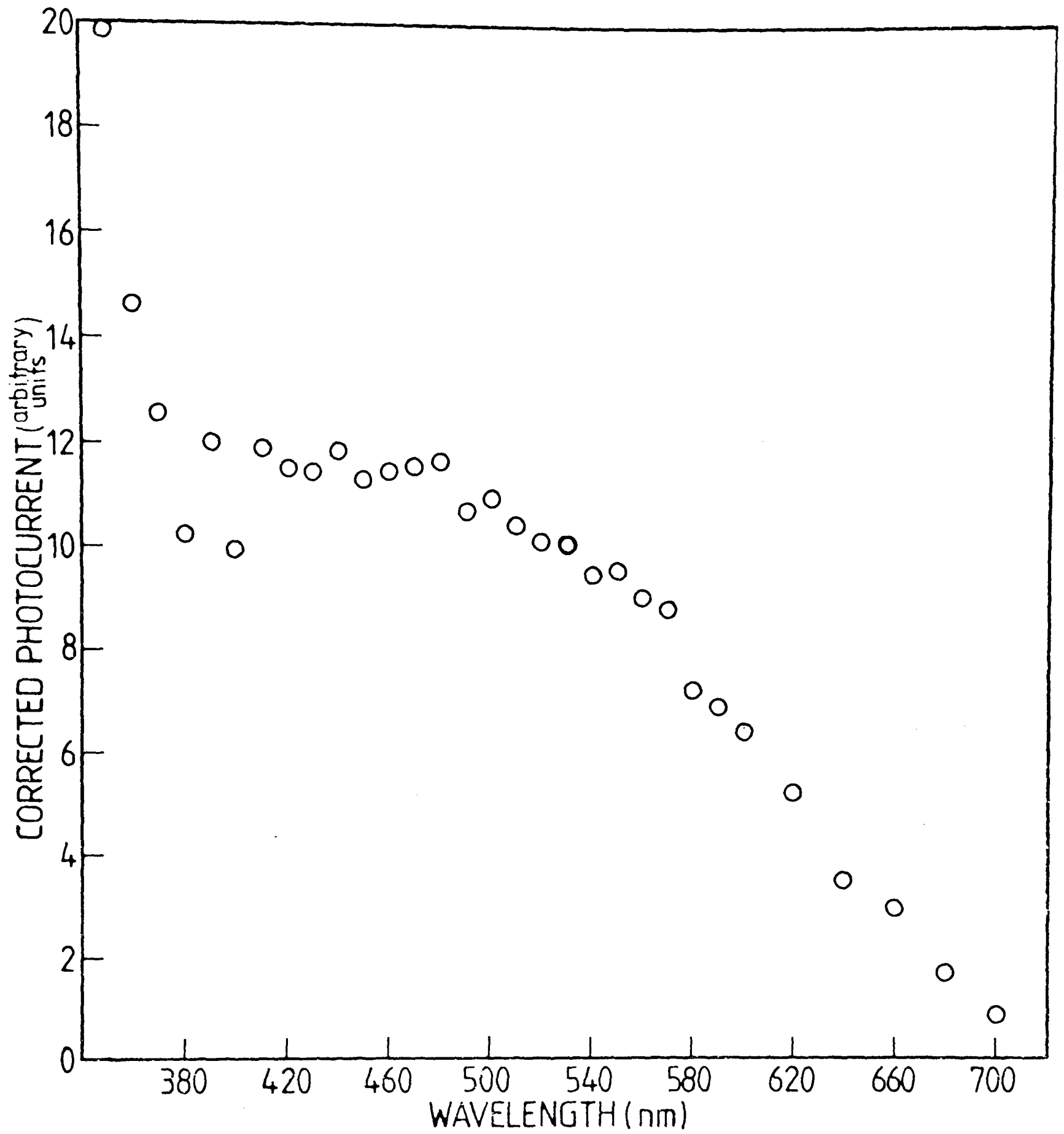


Fig.8.5 Corrected action spectrum for reduced $\text{NaCeTi}_2\text{O}_6$ in 1.0M NaOH .
Electrode potentiostatted at 0.0V vs.S.S.E.

have adequate mobility to reach the surface with high probability, at least if generated within the depletion layer. In addition, the oscillator strength for charge transfer excitations from Ce^{3+} to Ti^{4+} ions is high enough for an important fraction of the visible light to be adsorbed within the depletion layer.

The results from this compound are still discouraging since the Ce^{3+} energy levels are still too high to support efficient water oxidation. However, the energetic problems created by the large reorganization of the surface $\text{Ce}^{4+}/\text{Ce}^{3+}$ couple calls attention for the first time to the reorganization energy of surface cations as an additional source of loss. Further detailed studies are required to discover the likely extent of this loss for a given system.

A final possibility, which as yet has not been studied in any great depth, is to study titanate compounds possessing a $5s^2$ valence band. In particular $\text{Sn}_2\text{Nb}_2\text{O}_7$ and $\text{Sb}_2\text{Ti}_2\text{O}_7$ have been suggested, and the former has even been prepared.⁶⁷ However, there is a great difficulty in preparing a sufficiently n-type conducting sample without enhancing cation site exchange or the production of Sn metal in the material.⁶⁷

SECTION 8:3 STRATEGY II. THE ENERGETIC REQUIREMENT FOR A SEMICONDUCTING CATHODE FOR THE PHOTOELECTROLYSIS OF WATER.

Fig. 8.6 illustrates the optimal energetics for a semiconducting cathode for use in the Configuration II photoelectrolysis cell. As a first approximation there is no restriction on the type of compound to be used; oxide, chalcogenide, or pnictide although it must be stable in the presence of the Hydrogen gas evolved from its surface. The overall energy gap again may be shown to be necessarily $>2.3\text{--}2.4\text{eV}$ from a summation of the energy losses and overvoltages as depicted in Fig. 8.6. The conduction band must lie just above the $E^0(\text{H}^+/\text{H}_2)$ level given an optimal H_2 evolution overvoltage of $\approx 0.1\text{eV}$. Meanwhile the valence band must lie some 1.0V positive of the

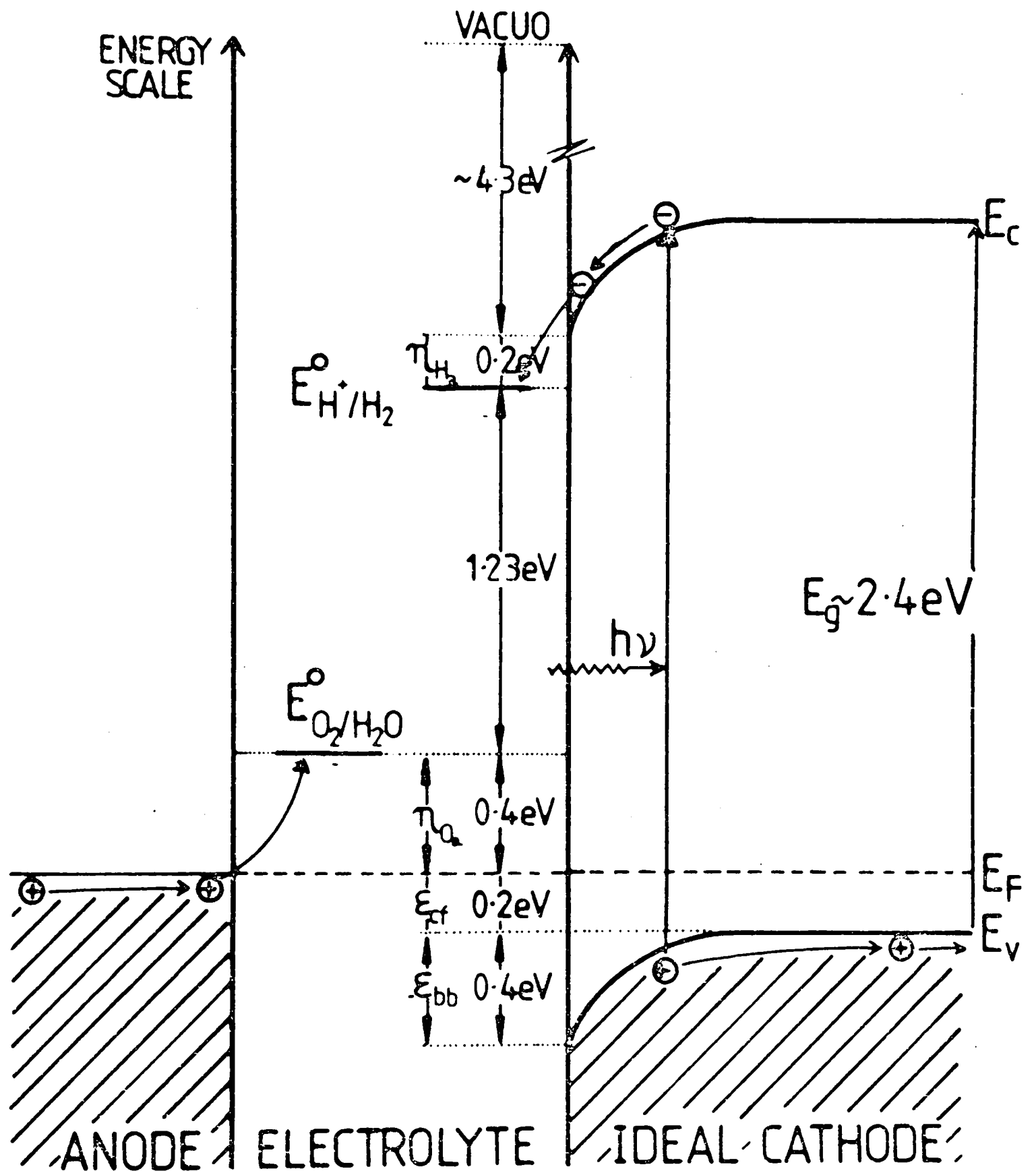


Fig.8.6 Detailed energetics for an ideal semiconductor/electrolyte photoelectrolysis cell operating in Configuration II .

E_{bb} =Band bending required for efficient electron/hole separation .

E_{cf} =Separation between top of valence band and the Fermi level .

η_{H_2} =overvoltage for hydrogen evolution on semiconductor .

η_{O_2} =overvoltage for oxygen evolution on metal counter electrode .

$E^0(\text{O}_2/\text{H}_2\text{O})$ level to provide for sufficient band bending in the semiconductor surface and oxygen evolution overvoltage in the metal anode.

Many p-type materials are known which satisfy the former constraint on the conduction band. However, no p-type semiconductors are known that possess such a deep valence band. In general, the valence band is likely to originate from the filled anionic orbitals. Phosphide, Arsenide, Sulphide, Selenide and Telluride valence bands all lie too high to meet the requirements, and so p-GaP, p-InP, p-GaAs, p-CdTe will be of no use for Configuration II. The only known p-type materials that can provide the necessary valence band are oxides. A very small number of p-type oxide materials are known, and in general they suffer from a problem of poor mobility for the majority carriers the holes in the valence band. In these materials, the valence band finds origin in the overlap of filled metal d orbitals rather than from the $\text{O}^{2-}:2p^6$. p- Cu_2O had been investigated previously and was found to be photodecomposed in aqueous solution.^{4,86-88} p-NiO had, however, received little attention as a photoelectrode although some work had been performed on the 'dark' electrochemistry of the material. A project was commenced to study the photoelectrochemistry of single-crystal, lithiated NiO for possible use as a p-type photoelectrode in Configuration II.⁸³

The use of the electrochemical data so obtained along with p.e.s. data permitted the development of a phenomenological model for the electronic energies in NiO.⁸³ The band edges were determined relative to the solution H^+/H_2 level by use of Mott-Schottky analyses and photocurrent action spectra. Through the electrochemical measurements, it was possible to establish that the valence and conduction bands are respectively $\text{Ni}^{2+}:3d^8$ and $\text{Ni}^+:3d^9$ (Fig 8.7) bands, the top of the $\text{O}:2p$ valence band lying some 1.4eV below the top of the $\text{Ni}^+:3d^9$ band and the bottom of the $\text{Ni}:4s$ band lying near, but above the bottom of the $\text{Ni}^+:3d^9$ conduction band. Cyclic voltammetry augmented

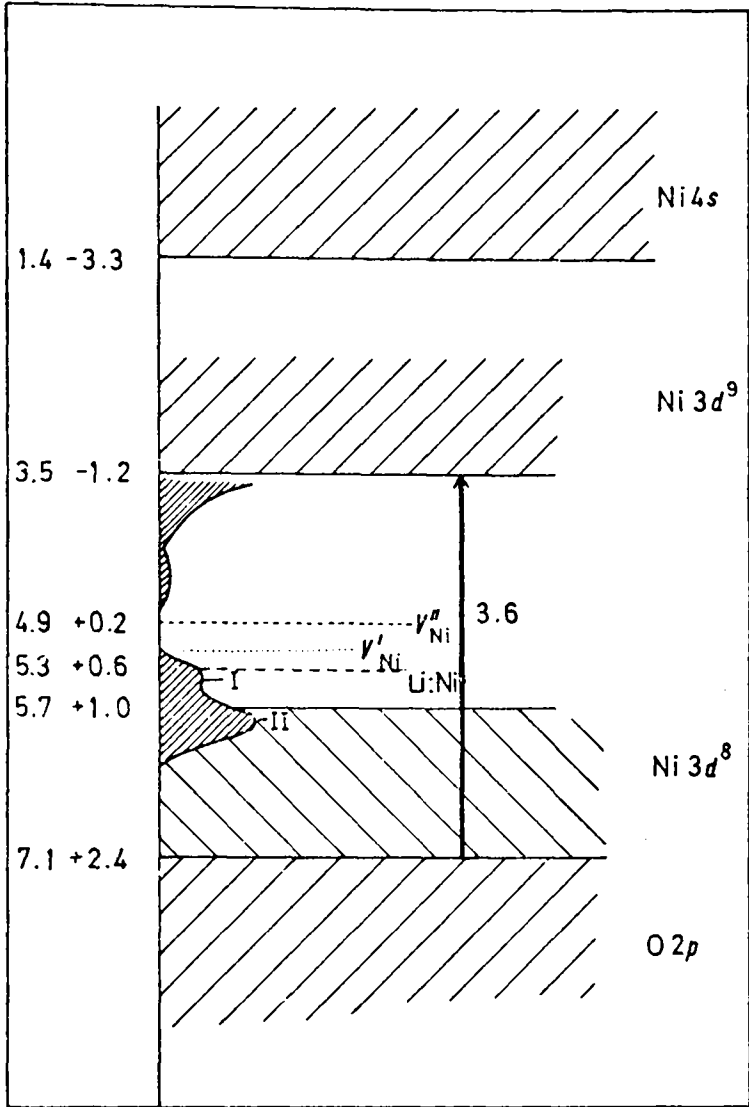


Fig. 8.7 —Semi-empirical band structure for NiO. The first optical transition is marked. Surface states derived from capacitance and d.c. c.v. measurements are shown with narrow hatching. Not shown are fast states in the region 0.0–0.5 V (SSE). All potentials are given relative to SSE. The energies on the left are referred to vacuum assuming the absolute electrode potential for the standard hydrogen electrode is 4.5 V. The electrolyte is 0.5 mol dm⁻³ H₂SO₄.

by a.c. capacitance measurements permitted a mapping of the surface density of states through which the d.c and a.c photocurrents could be interpreted. However, despite the success of the study as a tool for understanding the p-NiO:Li band structure, the photoconversion efficiencies were found to be very low ($\sim 1\%$ quantum efficiency) and the bandgap very large ($356\text{nm} \approx 3.5\text{eV}$)⁸³. The very poor efficiencies were identified as being partly due to the surface states, but primarily associated with a narrow depletion layer due to necessarily large doping concentrations (to achieve adequate conductivity) and a very small electron diffusion length of $\sim 10^{-7}\text{cm}$ that reflects efficient electron-hole recombination at the deep Li^+ acceptor centres.

Only one other p-type oxide has received any attention, and that is p-LuRhO₃^{89,90}. This material, however, possesses a valence band of low spin t_{2g}^6 which lies too high in energy (above $E^0(\text{O}_2/\text{H}_2\text{O})$) for use in Configuration II.

SECTION 8:4 STRATEGY III. THE REQUIREMENTS OF A TWO-SEMICONDUCTOR PHOTOELECTROLYSIS CELL.

Referring to Fig.8.8, it may be seen that the energetic requirements for this configuration are far less stringent than for Configurations I or II. The essential requirements may be summarised as follows:

1. The n-type material must possess a valence band below the solution $\text{O}_2/\text{H}_2\text{O}$ level such that holes photogenerated in the valence band are sufficiently energetic to oxidize water at the electrode surface.
(0.4eV O_2 overvoltage)
2. The p-type material must possess a conduction band above the solution H^+/H_2 level such that electrons photogenerated in the conduction band are sufficiently energetic to evolve H_2 at the electrode surface.
(0.2eV H_2 overvoltage)
3. The conduction band of the n-type material must lie sufficiently above the valence band of the p-type material to provide adequate band bending - in practice $\approx 1.2\text{eV}$.

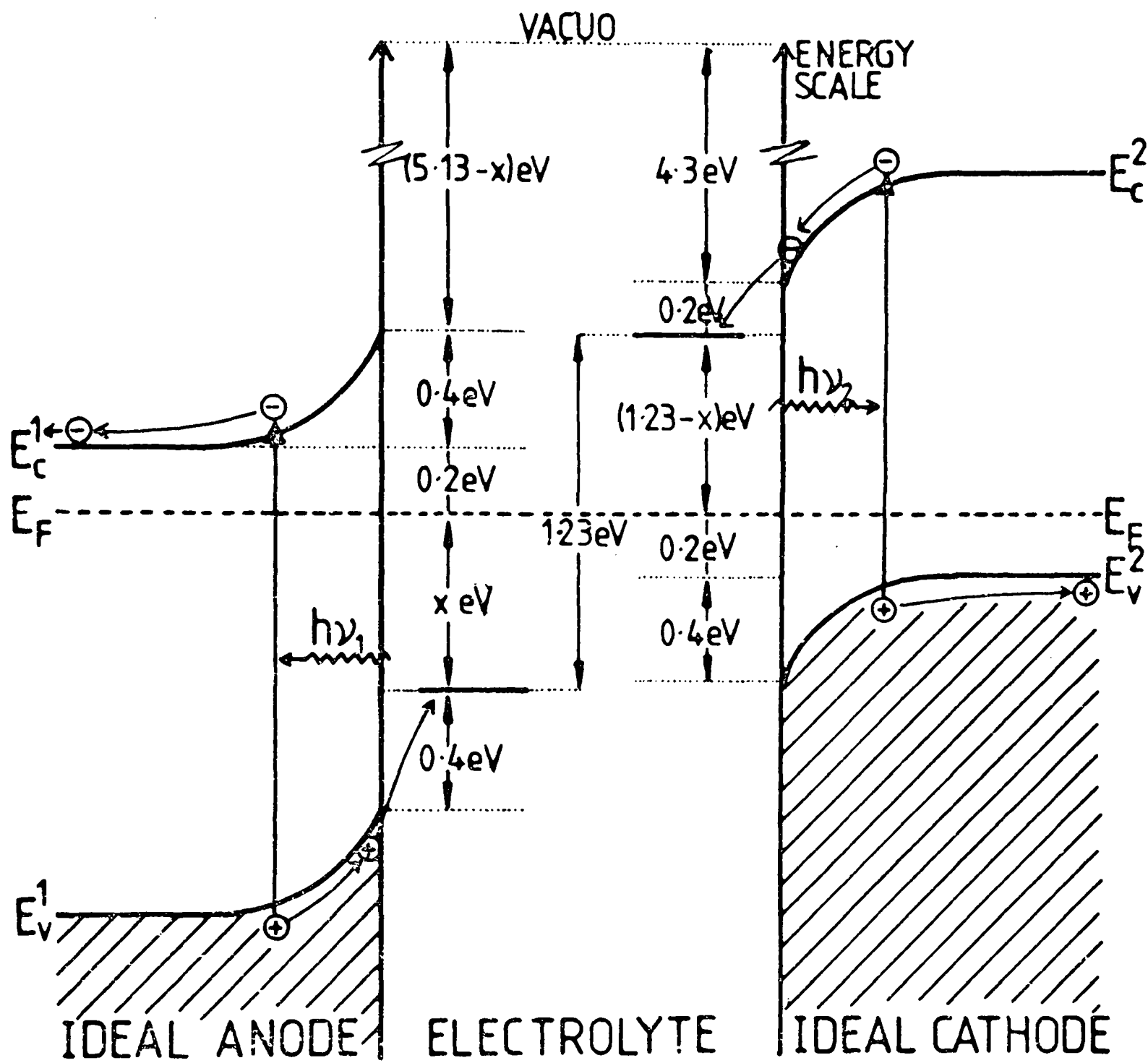


Fig.8.8 Detailed energetics for an ideal dual semiconductor/electrolyte photoelectrolysis cell operating in configuration III .

To cater for these requirements, the sum of the bandgaps in the two semiconductors must exceed 3.2eV, but neither material should possess a bandgap <1.0eV, see Fig. 8.3. Given the series nature of this cell, the overall solar conversion efficiency of the device will be limited by the least efficient photoelectrode.

Two further variations in design are feasible:-

- a. There is a single light path such that light not absorbed by the first semiconductor passes on to be absorbed by the second material. This strategy requires the two semiconductors to possess different bandgaps, the material possessing the largest E_g lying closest to the source of illumination. The optimum bandgaps need to be carefully chosen such that the short circuit current densities at each electrode are approximately equal. No operational design has yet been devised for this species of photoelectrolysis cell. Indeed many technological problems would seem to limit the development of this cell.
- b. There are two separate light paths to the two semiconductor electrodes. In this case the optimum bandgaps would be likely to be both as low as possible i.e. $\sim 1.6\text{eV}$.

A number of p-type materials are known that possess bandgaps of approximately this magnitude, e.g. p-GaAs 1.43eV, InP 1.29eV, CdTe 1.4eV. It was for this reason that the detailed study was initiated on the III-V materials (see Chapters 4-7) with a view to possible use in photoelectrolysis cells of Configuration III. The poor H_2 evolution kinetics, high H_2 evolution overvoltages and poor stability of these materials, however, limit their realistic application at the present time although surface modification agents and corrosion protecting films may re-enhance their applicability. However, on the n-type side there remains a major problem. As yet no n-type materials are known that possess bandgaps <2.2eV and which are stable to the conditions of Oxygen evolution. As discussed in Section 8:2, the material will necessarily be an oxide and the only stable candidate material is Fe_2O_3 .

($E_g = 2.2\text{eV}$ which would be particularly attractive economically) Poor minority-carrier mobility and small recombination pathlength renders the photoresponse very poor³⁰¹, since the valence and conduction bands derive from the same Fe^{3+} sublattice.

Despite these criticisms, little attention has been paid to the design of materials for use in Configuration III. Much further research is necessary on materials design, precise energetic constraints and device contribution before a true appraisal can be made of this strategy.

SECTION 8:5 DYE SENSITIZATION OF SEMICONDUCTORS FOR USE IN THE PHOTOELECTROLYSIS OF WATER.

One further approach to the photoelectrolysis of water employs solution-based or surface-bound dye molecules for the so-called photosensitization of wide-bandgap semiconductors.³⁰²⁻³⁰⁴ Fig. 8.9 illustrates the energy-level scheme for an oxygen electrode photosensitized by a dye molecule having a ground state energy E_D , a ground state energy E_D^+ for the oxidized state D^+ , and excited state energies $E_D^{*'}$ and E_D^* corresponding to the unrelaxed and relaxed excited states $D^{*'}$ and D^* . With this configuration, sub-bandgap radiation of energy $h\nu = (E_D^{*'} - E_D) < E_g$ excites the dye, and separation of photogenerated electron-hole pairs requires injection of the excited electron to the semiconductor conduction band (CB) and capture by D^+ of an electron from the electrolyte to evolve O_2 and return the dye to D . The energy losses in this scheme are $E_D^{*'} - E_o(\text{H}^+/\text{H}_2)$ and $E_o(\text{O}_2/\text{H}_2\text{O}) - E_D$. The energy difference $E_c^s - E_o(\text{H}^+/\text{H}_2) > 0.7\text{eV}$ required for an adequate depletion layer field is a built-in loss as for the Configuration (I) (Section 8:2). In the more likely event that excited electrons are injected into the CB from D^* rather than $D^{*'}$ (given the short lifetime of the unrelaxed excited dye molecule) the energy difference $\Delta^* = (E_D^{*'} - E_D^*)$ becomes an additional loss that must be minimized. Since electron capture

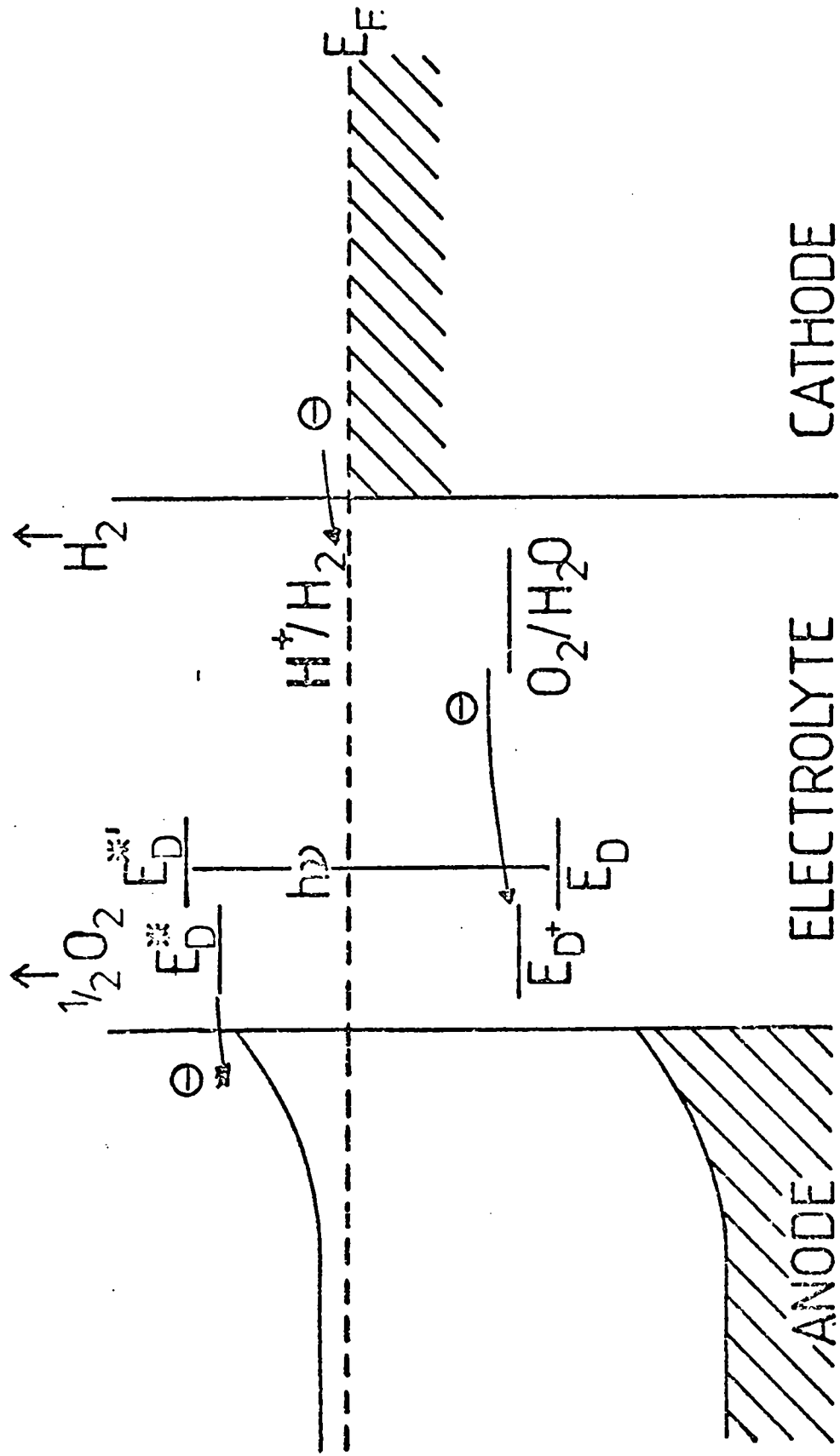


Fig.8.9 Energy level diagram for a dye sensitized semiconductor / electrolyte photoelectrolysis cell .

by D^+ occurs with the dye at the energy E_D^+ , the energy loss $\Delta = (E_D^+ - E_D)$ must also be minimized. Unless we can find $\Delta + \Delta^* < [E_O(O_2/H_2O) - E_V^S - \epsilon_O - \epsilon_H]$, where ϵ_O is the energy loss for O_2 evolution at an oxygen electrode and ϵ_H is the energy loss for H_2 evolution at the metal cathode, use of a dye seems to be of little value. In addition, separation of the photogenerated electron-hole pair must compete against luminescent decay of the dye back to its ground state as well as the recapture of a CB electron (probably via a surface state).

The general system shown in Fig. 8.9 was investigated for two different arrangements of dye and electrode.

1. Solution-based dye molecules³⁰⁵
2. Dye molecules chemically attached to the surface of the electrode.^{306,307}

In both cases, inorganic dye systems were chosen, based on the $Ru(bipy)_3^{2+}$ molecule. These inorganic dyes are far more stable over prolonged periods of use than purely organic systems and also the lifetimes of the excited states of the inorganic dyes are significantly longer so that energy loss through luminescence is reduced.

Photosensitization in solution requires that the lifetime τ of the excited state D^* be sufficiently long that the majority of excited complexes are within a diffusion length $(D\tau)^{\frac{1}{2}}$ of the electrode surface, D being the chemical diffusion coefficient. Clark and Sutin first observed anodic sensitization of TiO_2 by using $Ru(bipy)_3Cl_2$ in acidic aqueous solution.³⁰⁸ Work performed in Oxford demonstrated that this was purely a transient phenomenon at potentials near flatband.³⁰⁵ Instead, as the potential of the electrode is made more cathodic (closer to flatband), photoexcitation of surface state electrons to the CB was observed to occur, which ensured modulation of an ongoing cathodic dark current such as to produce a net cathodic d.c. photocurrent. A detailed analysis of this response was undertaken, but it was clear that solution sensitization was unable to provide effective photosensitization into the visible.³⁰⁵

The requirement $(D\tau)^{\frac{1}{2}}$ may be relaxed to $k_e\tau \gg 1$, where k_e is the rate constant for inspection of an electron from D^* to the CB, if D is either adsorbed or chemically attached to the electrode surface. Our approach was to photosensitize $n\text{TiO}_2$, $n\text{SrTiO}_3$ and $n\text{SnO}_2$ by a chemically attached derivative of $\text{Ru}(\text{bipy})_3^{2+}$ shown in Fig. 8.10. The two possible methods for the derivatization of the electrode are discussed elsewhere.³⁰⁶

The chemically attached dyes gave long-term photosensitization although the photocurrents were very small. A detailed kinetic analysis was performed with the solution-based-dye studies.³⁰⁷ The essential conclusions were as follows:

1. For any electrode possessing a monolayer coverage of dye with an extinction coefficient $\alpha \approx 10^7 \text{ cm}^2 \text{ mol}^{-1}$ the maximum photocurrent generated by an incident light intensity of approximately solar power would be ca. $1 \mu\text{A cm}^{-2}$. Thus, to achieve efficient solar collection efficiencies, multiple dye layers would be essential. However, based on the experience of Albery et al. with thionine coated electrodes, self-quenching mechanisms may contribute severe losses to overall conversion efficiency.
2. Strong direct interaction between the semiconductor conduction band and the dye excited state wavefunctions can generate bonding and anti-bonding electronic states at the electrode surface. The bonding state will then act as an electron trap at the surface such that the efficiency of injection of electrons from D^* into the CB becomes very poor. Thus the measured photocurrents were far below those expected from a 100% current collection efficiency from excited dye molecules. Typically photocurrents were in the range 10^{-8} – $10^{-7} \text{ A cm}^{-2}$, representing a collection efficiency of 1–10%. Weaker interaction between dye and semiconductor may eliminate the formation of deep surface traps and thus improve on this collection efficiency. Following the

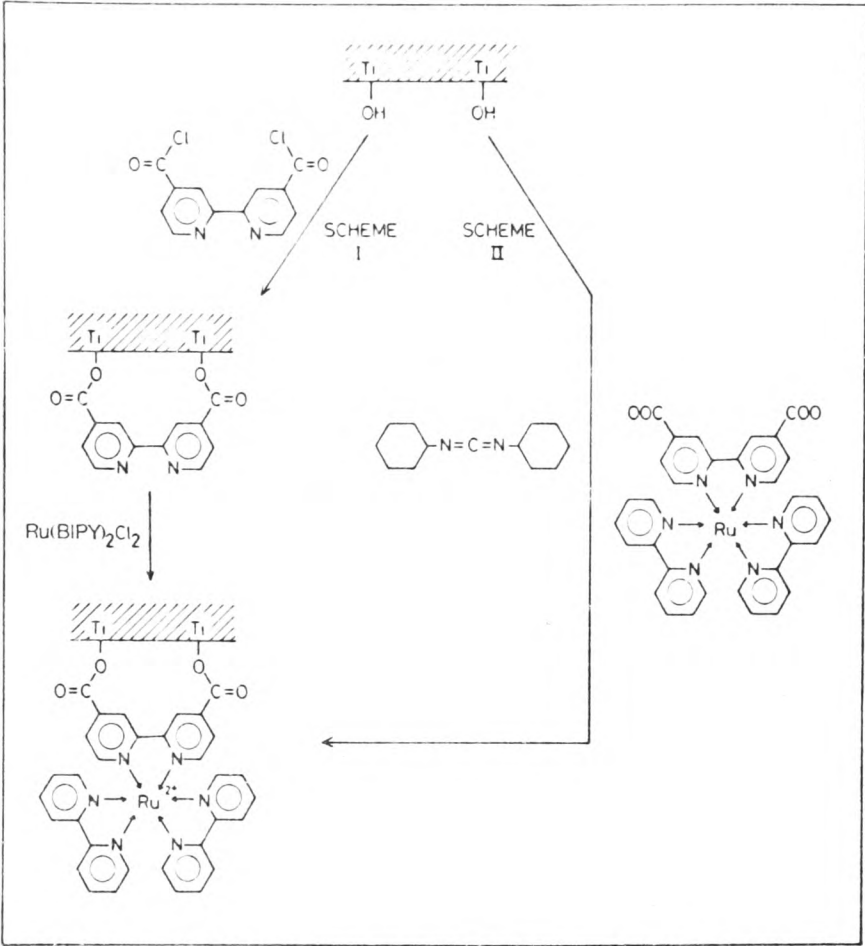


Fig. 8.10 Two reaction schemes for the derivatisation of TiO₂ with a monolayer of a [Ru(BIPY)₃]²⁺ derivative.

the discovery by Memming and Schröppel³⁰⁹ of much higher collection efficiencies for surfactant functionalized dye molecules adsorbed on TiO_2 , work is in progress in Oxford to find a chain length that optimizes the rapidity of charge injection whilst reducing surface loss processes through recombination.

3. The long term stability of the chemically attached $\text{Ru}(\text{bipy})_2\text{bpca}$ was investigated with high-intensity illumination applied over a period of many hours. A slow deterioration in performance was observed; it was quite irreversible, and the calculated quantum efficiency for this decay is ca. 10^{-5} . The reason for this instability has been suggested to be due to the instability of the carboxyl linkage under illumination, and work with other modes of attachment or adsorbed dyes may eliminate this decay.

APPENDIX ONEA1:1 The Theory and Technology of Ohmic Contacts to Semiconducting Materials

The phenomenon of rectification at a metal-semiconductor contact was first discovered by K.F. Braun in 1874.³¹⁰ Since that observation, these contacts have served man for use in rectifiers, photodetectors and also more recently as injectors and collectors for the first transistors. However since the discovery of the p-n junction with more reproducible properties than the metal-semiconductor rectifier, metal-semiconductor junctions have played a more subservient role as so-called ohmic contacts for transporting current into and out of the p-n junction devices.

Unlike the rectifying metal-semiconductor contact (Schottky barrier), p-n junction and semiconductor-oxide interfaces, the metal semiconductor ohmic contact has received far less scientific attention. This problem is in part due to the unexciting performance of a satisfactory ohmic contact and to the rather notorious history of the metal-semiconductor interface. It is fairly reasonable to admit, therefore, that ohmic contact technology has developed to date more in the form of alchemy than as pure science.

The term "ohmic" apparently implies that the interface shows a linear current-voltage characteristic. However, from a practical point of view, a satisfactory ohmic contact is one that does not significantly perturb device performance. One infers, therefore, that the contact is generally acceptable if it can apply the required current density with a voltage drop that is small compared to the voltage drop across the active region of the device, even though the current-voltage behaviour of the contact itself may not be strictly linear.

The contact resistance of any two materials can be completely defined theoretically if operating parameters (temperature and bias) and physical parameters (contact area, impurity concentration profile, barrier height, effective mass and dielectric constant) are known. However, in practice a number of other factors may seriously affect the contact resistance, e.g. interface layers due to oxide formation or contamination, surface damage, minority carrier injection, and energetically deep-lying impurity levels or traps. Hence correlation of theory and experiment is often difficult. Therefore the study of ohmic contacts is generally restricted to the examination of processing techniques that lead to low impedance metal-semiconductor contacts.

In the following sections, the qualitative description of current-transport mechanisms at metal-semiconductor contacts will be discussed briefly, and a few general methods of approach to obtaining ohmic contacts will be presented.

Al:2 Theoretical Considerations

(a) Schottky barriers. The metal-semiconductor interface is not the only interface at which an energy barrier is presented to current flow. If two metal plates are placed in vacuum with a voltage between them, very little current flows. The reason is not that there are no electrons in the metal; nor is it that, if the electrons were free, they could not cross the vacuum from one plate to another. Instead there is an energy barrier between the highest electron energy in the metal (at $T = 0K$) and the lowest energy in the vacuum where an electron can exist. This energy difference is called the work function of the metal. A similar barrier is developed at the semiconductor-metal interface (and semiconductor-electrolyte interface). If the metal and semiconductor are brought into contact, the Fermi

levels of the two materials equilibrate by transient electron flow. For example, for most n-type materials the conduction band lies above the Fermi-level of the metal, and electron flow is from semiconductor to metal. The energy difference at the interface between the Fermi level of the metal and the conduction band edge is known as the barrier energy of the particular metal-semiconductor interface.

To date no theory exists for accurately predicting the barrier heights, but much experimental data exists. Two main classes of barrier energies are distinguished:

- (1) Barrier heights to covalent semiconductors such as Si, Ge and GaAs are very nearly independent of the metal contact used.
- (2) Barrier heights to ionic semiconductors such as CdS, ZnS and ZnO are a function of both the work function (or electronegativity) of the metal and of the particular semiconductor.

There has been some discussion of this transition being representative of a more fundamental transition in the electronic nature of solids.³¹¹ However, in general one finds that, except for one or two materials, the barriers for Au contacts are given quite well by the expressions applicable for all metals with covalent semiconductors.

$$\phi_B = \frac{2E_g}{3} \text{ for n-type materials}$$

and

$$\phi_B = \frac{E_g}{3} \text{ for p-type materials}$$

where ϕ_B = Barrier height

and E_g = Semiconductor bandgap

(b) Modes of current flow. We shall now consider in particular the metal interface with an n-type semiconductor. The arguments all hold for the p-type case as well. The situation at zero bias is

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 Figs.A1(a-c) Schematic diagrams representing electron energy distributions in a metal and an n-type semiconductor for a Schottky junction at zero, forward and reverse bias respectively. Also depicted are qualitative rates of electron diffusion represented by the arrows.

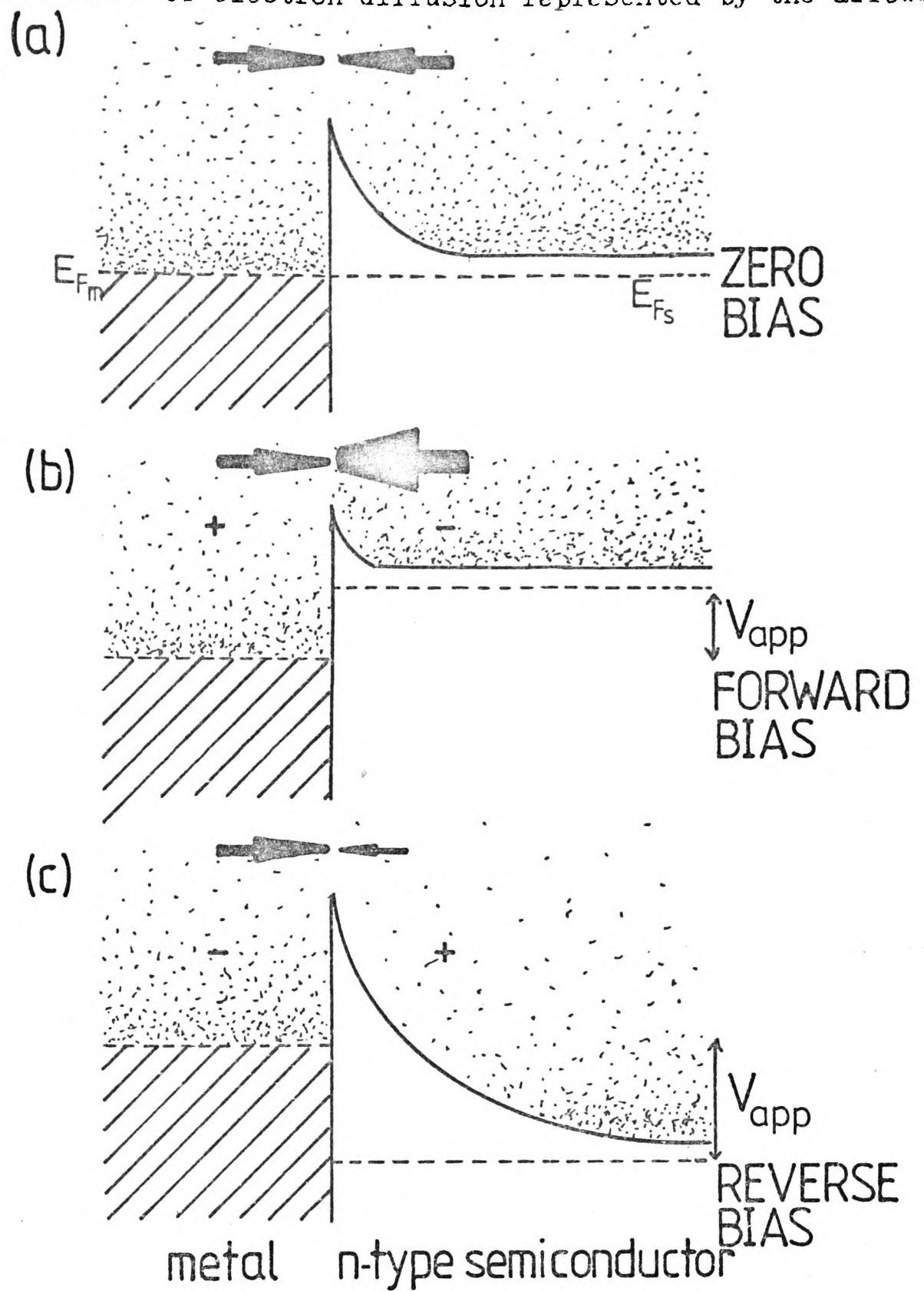


Fig.A2

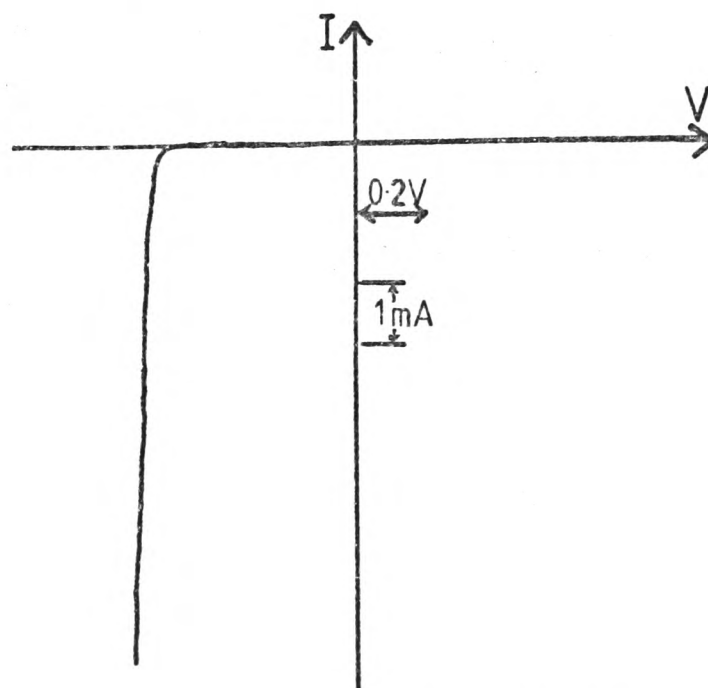


Fig.A2 Current-voltage response for ideal Schottky diode.

illustrated in Fig.A1a. For both metal and semiconductor, the electron energy distribution is Boltzmann-like for energies higher than the Fermi level and conduction band edge respectively, the electron density decreasing rapidly as we increase in energy. If a negative voltage is applied to the semiconductor (Fig.A1b) the electron distribution is raised in the semiconductor relative to in the metal, so there are now more electrons in the semiconductor at energies higher than the peak of the barrier. These electrons will thus flow by diffusion into the metal. With the opposite bias, Fig.A1c, net current flow from the metal into the semiconductor now results because of the fewer electrons on the semiconductor side with energies greater than the barrier height. However, this current is very small and does not increase appreciably with reverse bias.

The situation leads to the familiar diode current-voltage characteristic (Fig.A2). In the forward direction we find from theory and experiment³¹²

$$J = A^* T^2 \exp(-e\phi_B/kT) [\exp(eV/kT) - 1]$$

(J = Current density, A^* = Richardson constant, k = Boltzmann constant, T = Absolute temperature, V = Bias)

giving a straight line plots of $\log J$ vs voltage (Fig.A3) and reciprocal temperature (Fig.A4).

From either of these plots, the barrier can be determined and the thermal nature of the current established. This temperature-dependent mode of current transport is referred to as thermionic emission. However, there are two other modes of current transport that involve quantum-mechanical tunnelling through the barrier.

As the impurity concentration in the semiconductor is increased, the width of the depletion layer is decreased (see Chapter 2); initially

Fig.A3 Plot of log(current density) vs. voltage for an ideal Schottky diode .

Fig.A4 Plot of log(current density) vs reciprocal temperature for an ideal Schottky diode .

Fig.A3

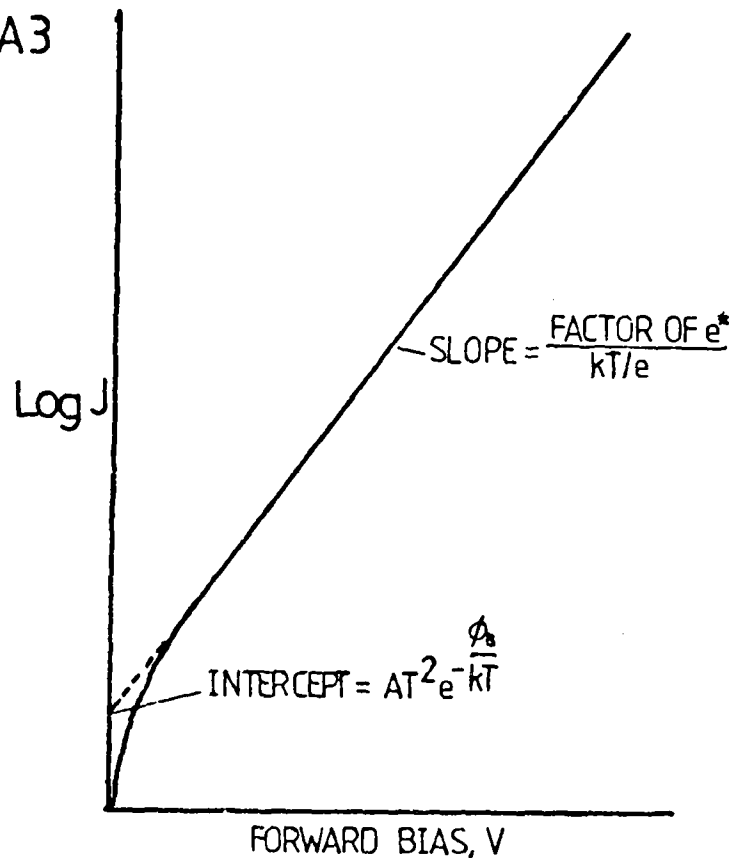


Fig.A4

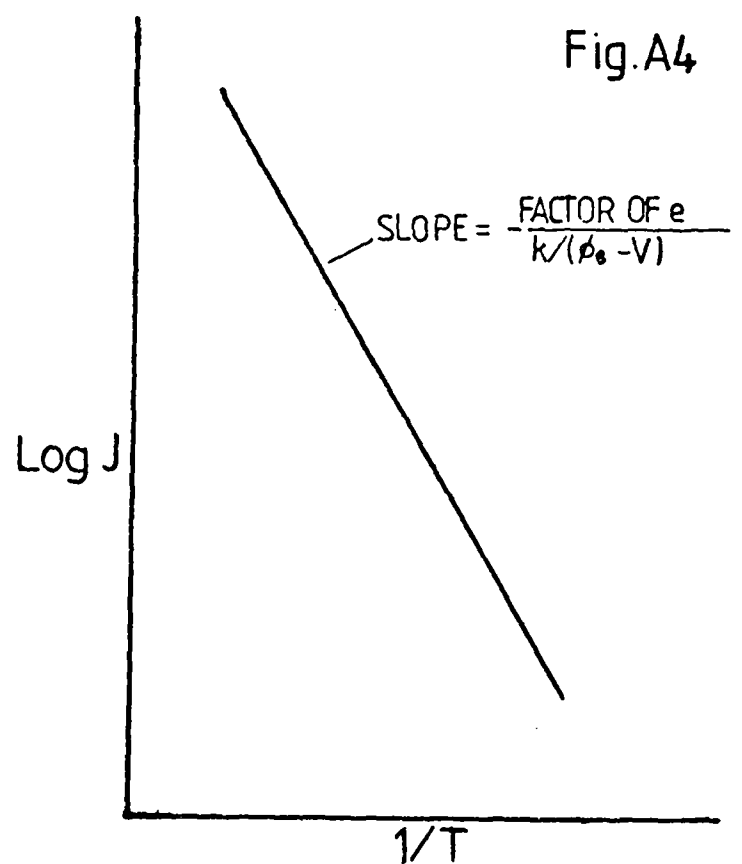


Fig.A5

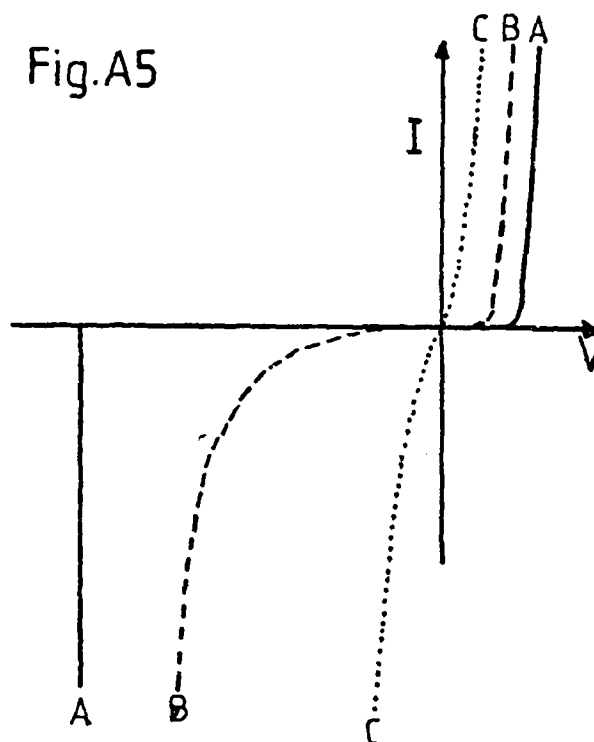


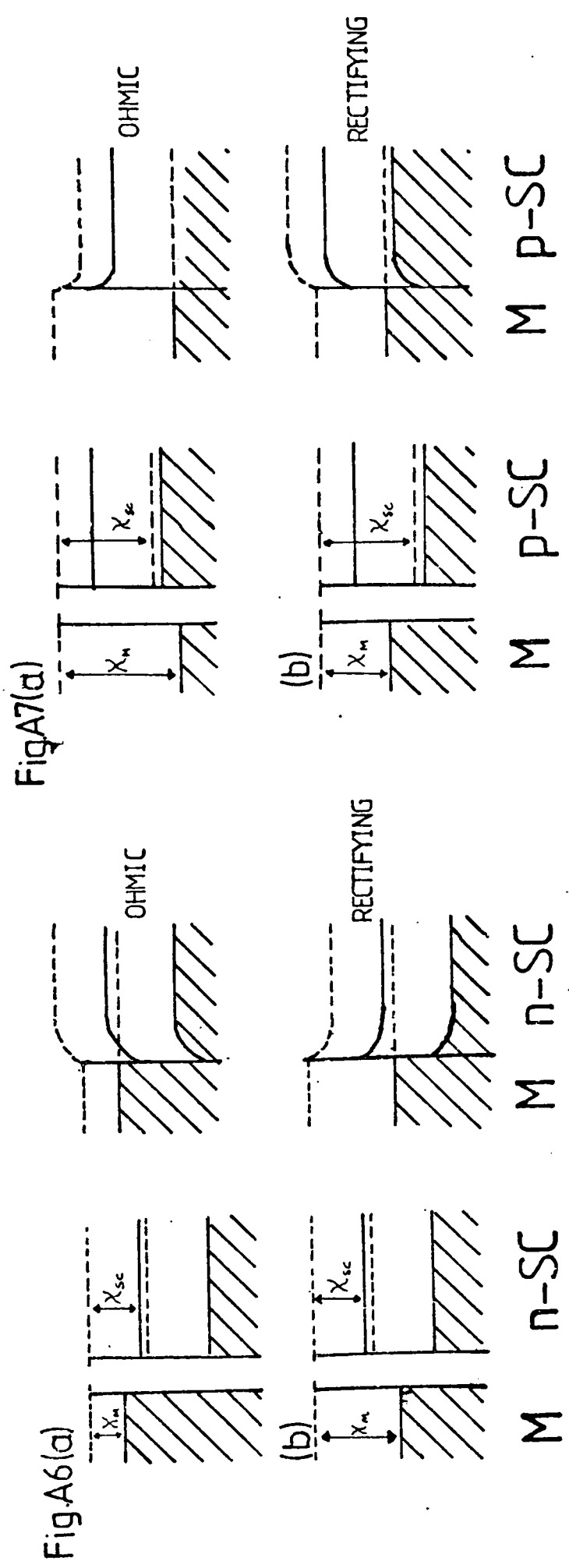
Fig.A5 Current voltage relationships for Schottky barriers with semiconductors of increasing doping concentration (From A to C) showing the transition from thermionic-field to field dominated conduction .

the barrier becomes thin enough that thermally excited electrons can tunnel through near the top of the barrier. The thermally assisted mode of current transport is referred to as thermionic field emission or thermally excited tunnelling. As the impurity concentration is increased even further, the barrier becomes so thin that significant numbers of carriers can tunnel through even at the base of the barrier. This mode of current transport is called field-emission tunnelling and is temperature independent. The transition from thermionic to thermionic-field to field dominated conduction is shown schematically in Fig.A5.

A1:3 Ohmic Contact Formation

If thermionic emission were the entire story, the only possible way of making an ohmic contact to a semiconductor with a metal would be to decrease the barrier energy so that the thermal current that flowed in the reverse direction is large enough for the particular device application. Ideally, of course, one can create a barrierless contact to an n-type semiconductor by using a metal of work function equal to or less than that of the semiconductor, see Figs.A6 and A7. However, for many wide band-gap semiconductors such a work function match is not possible. For example, as mentioned above for covalent materials, the barrier height is generally found to be $\approx 2E_g/3$ for n-type materials and $E_g/3$ for p-type materials and does not change appreciably with the metal used. Also with some highly ionic materials, metals do not exist with electronegativity sufficiently small (for n-types) or large (for p-types) to make the resulting barrier heights low enough to form ohmic contacts with current flow solely from thermionic emission

However as Fig.A5 shows, increasing the carrier concentration sufficiently will result in both forward and reverse currents increasing in a rapid exponential fashion. At very low voltages, this behaviour becomes essentially ohmic. The general approach used in making ohmic contacts



Figs.A6 and A7 Energy level diagrams showing the formation of ohmic and rectifying contacts between n- or p-type semiconductors and metals of differing work function .
 χ_M = Work function of metal .
 χ_{SC} = Work function of semiconductor

to the traditional semiconductors is therefore as follows: place a metal contact on a region of very high dopant concentration and rely on tunnelling through the resulting narrow barrier to carry the essentially ohmic current.

Al:4 Specific cases

1. If a semiconductor as used is required to have a high carrier concentration and can be doped heavily without difficulties, it is of little consequence whether the contacting material forms a barrier or not. The high bulk doping in itself will provide for a narrowing of the contact barrier and communication between semiconductor and external circuit will occur via tunnelling through the narrow barrier. Examples of such semiconductors are the conducting oxides SnO_2 , TiO_2 , ZnO and In_2O_3 (all when highly doped). It is well known that SnO_2 can be used as a transparent metal when coated in a thin layer on glass. During its formation from an alcoholic solution of SnCl_4 , it is doped by inclusion of a small quantity of SbCl_3 , which creates a concentration of n-type carriers of about $10^{20} - 10^{21} \text{ cm}^{-3}$. A metal pressure contact or a strip of silver paste is then normally sufficient to form an ohmic contact to this material.³¹³

2. Contacts to almost all medium and low-doped n-type semiconductors are generally obtainable with Indium as the contacting metal. As can be seen from Fig. 8, Indium has the lowest work function of the common metals not corroding in the atmosphere. Indeed, for most of the n-type materials, Indium has a work function less than the electron affinity of the semiconductor conduction band so no barrier is created at the metal-semiconductor interface (e.g. TiO_2 , Fe_2O_3 , WO_3 and CdS etc.). However, for materials with very low electron affinities such as SrTiO_3 , BaTiO_3 , $\text{KTa}_x\text{Nb}_{1-x}\text{O}_3$ and KTaO_3 , in theory a barrier should exist at the Indium/semiconductor interface. For these materials, it is believed that n-type conductivity is derived from defects based on oxygen deficiency. Hence conditions during contact formation that deprive the crystal surface of oxygen are beneficial in creating ohmic contacts to these materials in

n-type form; they are deleterious for p-type crystals. Accordingly, metal contacts with a strong affinity for oxygen (Cr, Al, Ti and even In) lead to form ohmic contacts on n-type materials whereas the best contacts for p-type oxides are obtained by contacting with metals like Au, Pd or Pt in an oxygen atmosphere. The simplest method of obtaining a room-temperature contact to an n-type material has been found to be the application of a Ga/In eutectic to the surface of semiconductors. This alloy has virtually zero surface tension and so readily 'wets' the semiconductor surface to maximize the contact area and which aids the formation of the ohmic contact.

3. The favourite method of achieving a high doping density under a contact is the technique of alloy regrowth.³¹⁵ In this technique, the metal dissolves some of the semiconductor during heating. Upon cooling, the semiconductor will come out of the solution and regrow on the underlying crystal. The regrown region will contain a substantial concentration of the contact metal which is thought to act as a dopant (e.g. Au for n-type GaAs³¹⁶). If lower alloying temperatures or higher doping levels are required, it is often advantageous to utilize another dopant impurity in addition to the majority contact metal (e.g. Au-Zn, In-Zn or In-Cd for pGaAs, pGaP and p-InP, Zn has a very high diffusion coefficient at the alloying temperatures used). The wetting action of many metals on the III-V semiconductors is very low, and contact material has a tendency to separate into islands (mounding or balling-up). This difficulty can be alleviated by the evaporation or co-evaporation of a metal overlay such as Ni, Pt or Au which does not form a eutectic with the contacting metal at temperatures below the alloying temperature.³¹²

With p-type materials for high current density, the Au-Zn contact is most successful;³¹⁷ but care must be taken with this material not to be re-evaporate the Zinc at the alloying temperature - so a very short temperature pulse is required. For the experimentation presented in this

thesis, contact currents are all relatively low. Therefore the balling-up problem with In-Zn contacts created no difficulties; and lower alloying temperatures could be used thus avoiding Zn evaporation within the fairly slow heating and cooling times of the microfurnace.

For some III-V materials, in particular the As and Sb-based compounds, satisfactory ohmic contacts are provided by Indium alone. It has been suggested that In may form an InSb or InAs layer on alloying.³¹² Since the bandgap of these two compounds are relatively low (0.35 and 0.17eV respectively), the resultant small bandgap to wide-bandgap heterojunction may serve as the ohmic contact. Although feasible, no evidence exists for proof or disproof of this hypothesis.

Note that surface cleanliness is essential for reliable and reproducible ohmic contacts. AlAs has a significant interfering oxide layer in air at room temperature and even GaAs can form a 20Å Gallium oxide layer within one hour in air.³¹² For this reason alloying is usually performed in vacuum or in an inert (Ar) or mildly reducing atmosphere (H_2/N_2 or H_2).

4. A substantial number of wide-bandgap semiconductors present contacting problems because they cannot be doped heavily enough. This may not be due to limited solubility of suitable dopants, or to compensation of the intentionally added dopants by native defect centres. This is particularly common with p-type materials such as ZnS or ZnSe; the problems encountered with contacting to p-NiO are of a similar nature. For the latter material, literature methods quote the use of evaporated and annealed layers of silver acting as the contacting material. This may have proved successful for the highly doped, single crystal material used by these workers. However, the high-temperature annealing process (960° in inert atmosphere) failed to provide sufficient mobility for Ag diffusion and possibly some compensating oxygen loss from the sample

at high temperatures contributed as well to the poor ohmicity of contacts that resulted. The method used finally to achieve good quality ohmic contacts was to apply a soft graphite pencil with considerable physical pressure to the surface of the polycrystalline NiO. It seems likely that this process achieved a metallographic microstructure under the contact that created a multitude of sharp spikes. At the tip of each spike, there would be a very high field gradient, which promotes injection of charge carriers.³¹⁵ However, because the total voltage drop at each spike would be small - and there would be many spikes of different geometry, orientation and field gradient, the contact as a whole behaves more like an ohmic than an injecting contact. Although there is no experimental proof for this explanation, the lack of high-temperature anneal or likely dopant seems to support the above argument.

Al:5 Conclusions

The subject of ohmic contacts is at best a pragmatic art rather than a science, and consequently it tends to be rather an unglamorous area of research. Nevertheless, active studies are still being conducted on the surface and contact properties of many wide-bandgap semiconductors, and a deepening understanding is appearing of the fundamental details of the metal-semiconductor interface. However for the ohmic contact user rather than researcher, the general guidelines outlined above permit ohmic contacts to be achieved to most materials. The electrochemist probably has the simpler task since his commonly encountered current densities seldom cause contact resistance to exceed the overall device impedance. Improvements in the understanding of the metal-semiconductor contact may however, have significant relevance to the semiconductor-electrolyte interface - and vice versa, so the two subjects should retain a healthy family relationship.

APPENDIX 2

COMPLEX IMPEDANCE ANALYSIS AND COMPUTER FITTING PROCEDURES

As discussed in Chapter 4, a number of equivalent circuits have been suggested to model the semiconductor/electrolyte interface. If the model circuit consists of only two components (e.g. 4.24a and b), an analytical solution can be derived from the two pieces of data available, namely the in-phase and quadrature admittances (measured with the lock-in amplifier). However, once the proposed circuit contains more than two components, an analytical solution is no longer possible and the various components in the equivalent circuit must be fitted to the experimental data by an iterative method. A series of admittances is obtained from the electrochemical cell over a range of modulation frequencies and the final values derived should be those which gave the best overall agreement with the data.

A computer program is obviously essential for this process and the algorithm used is shown in Fig. A2.1.³¹⁸ The error was defined as the average value for both 0° and 90° admittances at all frequencies of the formula:-

$$\left(\frac{\text{Experimental Admittance}}{\text{Calculated Admittance}} \right)^2 + \left(\frac{\text{Calculated Admittance}}{\text{Experimental Admittance}} \right)^2$$

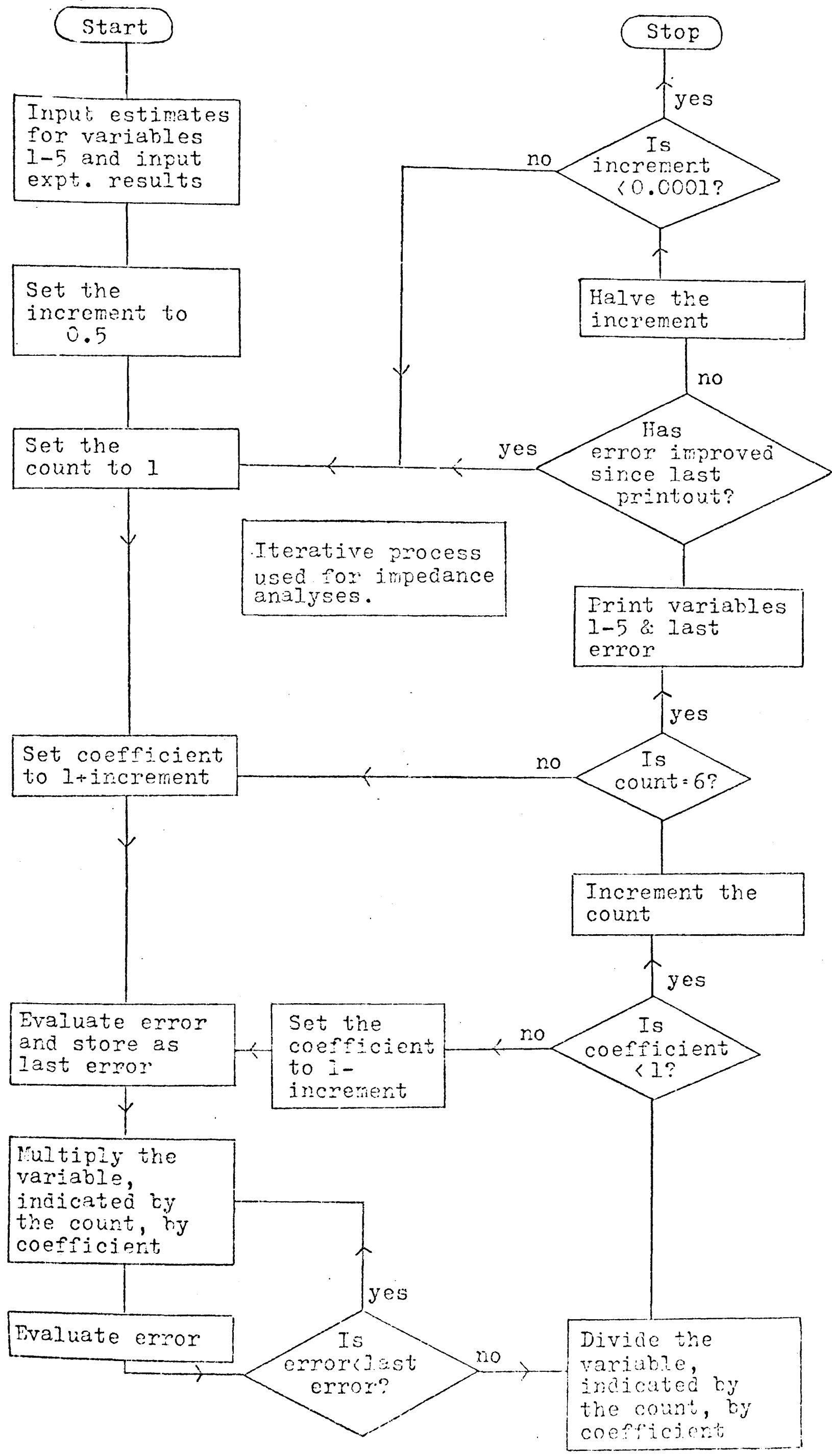
All results will thus be positive, so this formula has a single minimum at

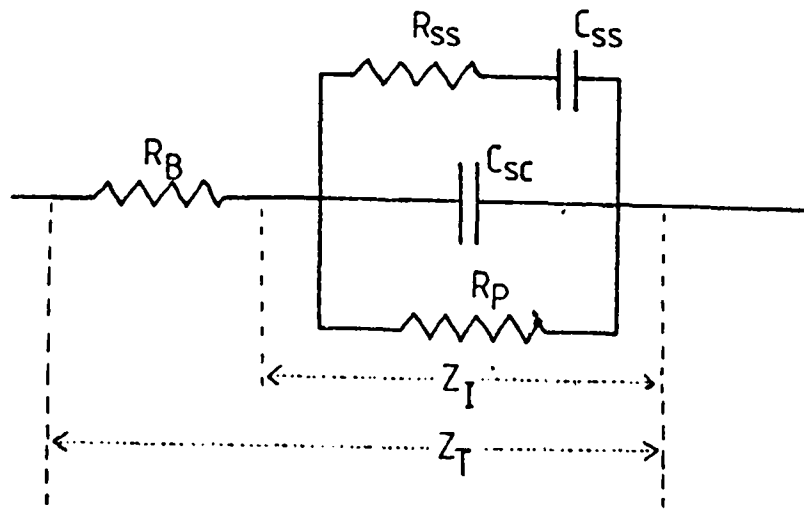
$$(\text{Experimental Admittance}) = (\text{Calculated Admittance})$$

In this manner, a least-squares fit was obtained.

To determine the calculated admittance values for each chosen equivalent circuit, complex algebraic analysis of the circuit components was necessary. The results from this analysis as performed on the favoured circuit representation are given below :

Fig.A2.1 Algorithm used in computer program for the calculation of the components of the equivalent circuit of the semiconductor/electrolyte interface³¹⁸.





R_B = Bulk Resistance of Semiconductor and Solution

R_p = Space Charge + Faradaic Resistances

C_{sc} = Space Charge Capacitance

C_{ss} = Surface State Capacitance

R_{ss} = Surface State Resistance (or $R_{ss} \cdot C_{ss}$ = Surface State Time Constant)

Z_I = Interfacial Impedance

Z_T = Total Impedance

A_T = Total Admittance

$$\frac{1}{Z_I} = \frac{1}{R_p} + i\omega C_{sc} + \frac{i\omega C_{ss}}{i\omega C_{ss} R_{ss} + 1}$$

$$Z_T = \frac{R_p(i\omega C_{ss} R_{ss} + 1)}{i\omega C_{ss} R_{ss} + 1 + i\omega C_{sc} R_p - \omega^2 C_{sc} C_{ss} R_{ss} R_p + i\omega C_{ss} R_p} + R_B$$

$$A_T = \frac{1 + i\omega C_{ss} R_{ss} + i\omega C_{sc} R_p + i\omega C_{ss} R_p - \omega^2 C_{sc} C_{ss} R_{ss} R_p}{(R_p + R_B - \omega^2 C_{sc} C_{ss} R_{ss} R_p R_B) + i\omega(C_{ss} R_{ss} R_p + C_{ss} R_{ss} R_B + C_{sc} R_p R_B + C_{ss} R_p R_B)}$$

The numerator and denominator must now be multiplied by the complex conjugate of the denominator. The resulting expression may then be divided into the real (0°) and imaginary (90°) components of the total admittance.

$$A_T(\text{real part}) = \frac{\left\{ (R_P + R_B)(1 + \omega^2 C_{ss}^2 R_{ss}^2) + 2\omega^2 C_{ss} R_P R_B (R_{ss} C_{ss} + C_{sc} R_P) + \right. \\ \left. 2R_P^2 R_B (C_{sc}^2 + C_{ss}^2) + \omega^2 C_{ss}^2 R_P^2 R_{ss} (1 + \omega^2 R_{ss} R_B^2 C_{sc}^2) \right\}}{\left([R_P + R_B - \omega^2 C_{sc} C_{ss} R_{ss} R_P R_B]^2 + \omega^2 [C_{ss} R_{ss} (R_P + R_B) + R_P R_B (C_{sc} + C_{ss})]^2 \right)}$$

$$A_T(\text{imaginary part}) = \frac{i R_P^2 (\omega^2 C_{sc} C_{ss}^2 R_{ss}^2 + C_{ss} + C_{sc})}{\left([R_P + R_B - \omega^2 C_{sc} C_{ss} R_{ss} R_P R_B]^2 + \omega^2 [C_{ss} R_{ss} (R_P + R_B) + R_P R_B (C_{sc} + C_{ss})]^2 \right)}$$

More complex circuits than that shown above produced still more lengthy algebraic solutions. Despite increasing the difficulty of obtaining such a solution, the additional complexity of the circuit was found to be non-productive. In certain cases, the degeneracy of certain components (e.g. in circuit 4.24) created computational difficulties with oscillations between equivalent minima. However, even where degeneracy was avoided, the accuracy demanded of the experimental data, in order to distinguish between the various error minima for circuits containing > six components, exceeded that which was technically feasible on the available instrumentation. The upper limit on the number of circuit components which could be distinguished accurately thus appeared to be about six.

As a necessary check on the accuracy of this computer fitting procedure, particularly on the chosen circuit discussed above, a model circuit was built containing resistors and capacitors of predetermined values. The standard data acquisition and computer analysis was then performed over a range of d.c. biases with frequencies ranging from 87-10,000Hz. The computer calculated values were found to be accurate in relation to the known values to within 5% for a number of alternative sets of components.

APPENDIX 3

ENERGY CONVERSION EFFICIENCIES

A3:1 Ultimate Efficiency

It was first pointed out by Trivich and Flynn³¹⁹ that direct converters of solar energy can transduce only a calculable fraction of incident broad band light to useful work, because they can only make use of photons with more energy than a threshold value E_g . In the photovoltaic or photo-electrolysis system, E_g is the semiconductor bandgap. For the sensitized photocurrent treated as a separate entity, E_g would be the energy of the first excited singlet state of the light absorbing molecule.

Photons of energy $E < E_g$ are not absorbed by the converter, or if they are, they are not convertible into useful work. Photons of energy $E > E_g$ are not entirely efficient even if they are completely absorbed, since vibrational relaxation almost inevitably occurs in the upper excited state before the charge transfer process can take place: the fraction $(E - E_g)/E$ of the photon energy is therefore dissipated as heat, and only the fraction E_g/E can be converted to useful work. If such a quantum converter is irradiated with white light, the spectral irradiance of which is described by the function $P(E)$ and the flux density of photons by the function $N(E)$, then the fraction of incident radiant energy available for conversion (η_{ult}) is given by:

$$\eta_{ult} = \frac{E_g \int_{E_g}^{\infty} P(E) d(\ln E)}{\int_0^{\infty} P(E) dE} \quad (A3.1)$$

$$= \frac{E_g \int_{E_g}^{\infty} N(E) dE}{\int_0^{\infty} E N(E) dE} \quad (A3.2)$$

This factor is a function of both the irradiating spectrum and of E_g . η_{ult} for AM0 and AM1 (AM stands for Air Mass and AM0 is the sunlight spectral intensity for just outside the Earth's atmosphere and AM1 for the sun directly overhead at sea level i.e. one vertical Earth's atmosphere absorption length) has a maximum of 0.45 and the optimal value of E_g shifts from 1.1eV to slightly higher values as the air mass increases. (N.B. obviously 1.1eV is of no use for a photoelectrolysis device as we require a minimum of 1.23eV for water splitting. These figures above are for a general solar energy conversion device).

A3:2 Light Absorption Efficiency

The calculation of ultimate efficiency assumed the system was perfectly absorbing for all photons of $E > E_g$. This is a somewhat unrealistic situation and equations A3.1 and A3.2 should be modified by a factor of A_E , the optical absorbance of the device for photons of energy E , giving a modified efficiency factor η'_{ult} :

$$\eta'_{ult} = \frac{E_g \int_{E_g}^{\infty} A_E P(E) d(\ln E)}{\int_0^{\infty} P(E) dE} \quad (A3.3)$$

$$= \frac{E_g \int_{E_g}^{\infty} A_E N(E) dE}{\int_0^{\infty} E N(E) dE} \quad (A3.4)$$

η'_{ult} may be made to approach η_{ult} by making the device sufficiently optically dense; this may however increase other loss factors considerably.

A3.3 Overall Conversion Efficiency

Expressions similar to A3.3 and A3.4 have been used by several workers in calculations of solar cell efficiencies.³²⁰⁻³²² The advantage of this form on η'_{ult} is that it is readily combined with the other efficiency factors to produce an overall conversion efficiency. For example, the overall power conversion η_{pv} of a photovoltaic solar cell is expressible as the product of four major factors.

$$\eta_{pv} = \eta'_{ult} \eta_{V_o} \eta_i \eta_{i_v} \quad (A3.5)$$

η_{V_o} is the open circuit voltage efficiency, η_i , the short circuit current efficiency or photon efficiency and η_{i_v} , the fill factor or current-voltage efficiency.

A3.4 Open Circuit Voltage Efficiency

Let the change in open circuit potential that occurs on illumination of the Photoelectrochemical (PEC) half cell be ΔV_o . The open circuit voltage efficiency is defined by

$$\eta_{V_o} = \frac{e\Delta V_o}{E_g} \quad (A3.6)$$

This open circuit potential of the illuminated PEC electrode is determined by the requirement that the electron-hole pairs are eliminated as rapidly as they are produced, there being no net current flow in the circuit. The generation rate depends on the light density and on the optical density of the half cell; thermal generation is ignored by comparison. The recombination rate is the sum of the rates of radiative recombination and of such non-radiative physical and chemical quenching processes as may occur in the system. η_{V_o} is therefore only partly determined by unalterable properties and is not a fundamental parameter of the system but simply an indication of the extent to which light absorption

produces charge transfer in the system. The dependence of V_o and hence η_{V_o} upon light intensity depends on the nature of the particular device but a relationship of the type $\Delta V_o = k \ln I$ not uncommonly holds for moderate light intensities. (Similar behaviour is found in p-n junction photovoltaic devices).

A3.5 Short Circuit Current Efficiency or Photon Efficiency

This factor and the following one describe the behaviour of a PEC half cell under closed circuit conditions.

The photon efficiency η_i is defined as the ratio of the number of electrons flowing per photon absorbed:

$$\eta_i = \frac{i_{lim}/e'}{\int_{E_g}^{\infty} A_E N(E) dE} \quad (A3.7)$$

e' is the electronic charge in Coulombs. This factor has low values if the energy of the optically excited state is quenched before charge separation occurs, or if the electroactive species is produced by photolysis in solution and is so unstable that only a small proportion survives long enough to diffuse to the electrode; even if the electroactive species is stable, concentration polarization may severely limit i_{lim} . The value of η_i is therefore dependent on solution concentration, cell geometry and other factors affecting mass transfer within the cell.

A3.6 Fill Factor or Current - Voltage Efficiency

The nominal power a PEC half cell delivers by transducing the light irradiance P into a flow of electrons is $\eta'_{ult} \eta_{V_o} \eta_i P$ and the nominal power efficiency $\eta'_{ult} \eta_{V_o} \eta_i$. The actual power conversion efficiency depends on the photocurrent - voltage characteristic of the half cell. If this were rectangular the half-cell would deliver the nominal power; if the characteristic were linear, implying an Ohmic internal resistance, the maximum

deliverable power would be one quarter of the nominal power. In general, the ratio of power delivered to nominal power is given by

$$\eta_{iv} = \frac{i\Delta V}{i_{lim}\Delta V_o} \quad (A3.8)$$

η_{iv} is not constant and its variation with V is determined by the sum of the internal losses due to ohmic resistance, charge transfer overpotential and concentration polarization in the half cell as in a conventional electrochemical half cell. Equation A3.8 is applicable to the whole PEC system only if the counter half cell is non polarizable so no power loss occurs in it.

The ohmic resistance of a PEC half cell is substantial if a semiconducting electrode of poor conductivity is employed. The maximum photon flux that a PEC cell has to handle in unconcentrated sunlight is $15 \times 10^{21} \eta_{ult} = 2.5 \times 10^{21} \text{ photons s}^{-1} \text{ m}^{-2}$ (corresponding to a maximum photocurrent density of 40 mA cm^{-2}). The scale up of a resistive device which has good efficiency when small may result in an unacceptable increase in resistive loss.

A3.7 Storage Devices

If the cell operates as an energy source with optional adjustment for power generation (as in photovoltaic devices), but as a storage device, the efficiencies are further reduced. We can approximate this by the relation

$$\eta_{storage} = \frac{E_{storage}}{E_{gap}} \cdot \eta_{photovoltaic} \quad (A3.9)$$

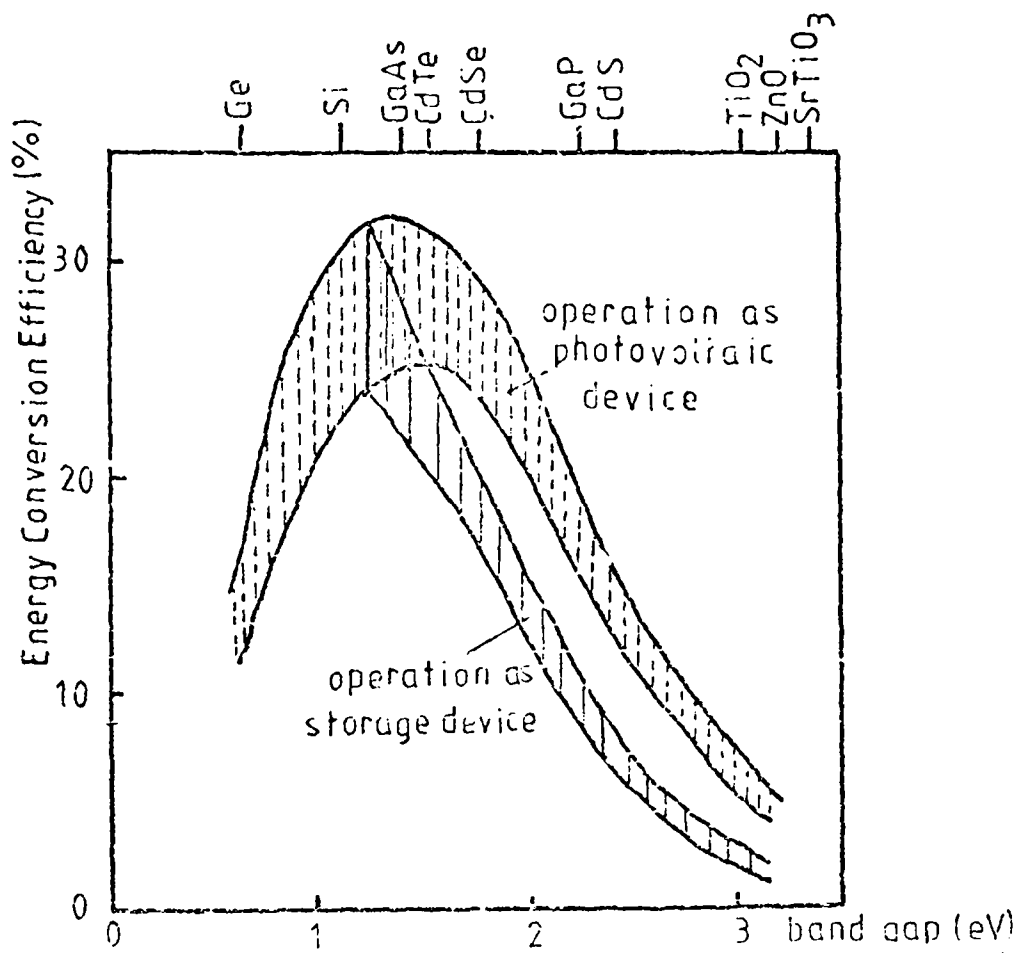


Fig. A3:1

Theoretically predicted optimal efficiencies for solar energy conversion by semiconductor photocells as photovoltaic power source or as storage device by electrolytic water decomposition.

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A Thesis submitted in Michaelmas Term 1981 by M.P. Dare-Edwards, Wolfson College, for the degree of Doctor of Philosophy.

A study has been undertaken of the detailed photoelectrochemistry of a number of III-V and oxide semiconductors. In particular, the work has been aimed at obtaining a material which can act as a stable and efficient photoelectrode for the solar photoelectrolysis of water. However to achieve this aim, it was considered essential to obtain a far deeper understanding of the mechanisms of the electrochemical reactions taking place at the semiconductor/electrolyte interface.

The mechanism for Hydrogen evolution from the surfaces of the p-type III-V materials has represented a particular problem. P-type GaP was chosen as the representative member of the III-V materials and a mechanistic study has been made of the material using a.c. and d.c. experiments in addition to a detailed interfacial impedance analysis. A model for the Hydrogen evolution reaction has been proposed invoking surface bound Hydrogen atoms as both intermediates in the desired reaction and also as photogenerated surface states in parasitic recombination reactions. With the experience of the work on p-GaP, the analagous mechanisms to those found on p-GaP have been found to be consistent with results obtained on p-GaAs, p-InP and p-GaSb. However for these latter materials, additional complexities have arisen from their greater instability with respect to cathodic corrosion.

A method has been sought for modifying the surface of the III-V materials in order to obtain improved Hydrogen evolution efficiencies. Such a modification has been discovered for p-GaP by the adsorption of a Ruthenium species from solutions of crude $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$. Its mode of operation is discussed at length.

For the oxide materials, a semiconducting oxide has been sought that possesses the ideal band energies and bandgap to obtain optimum photo-efficiencies for the photoelectrolysis of water. The design constraints for such a material are presented and some results on a number of novel oxide semiconductors are discussed in relation to their use in such photo-electrolysis cells.