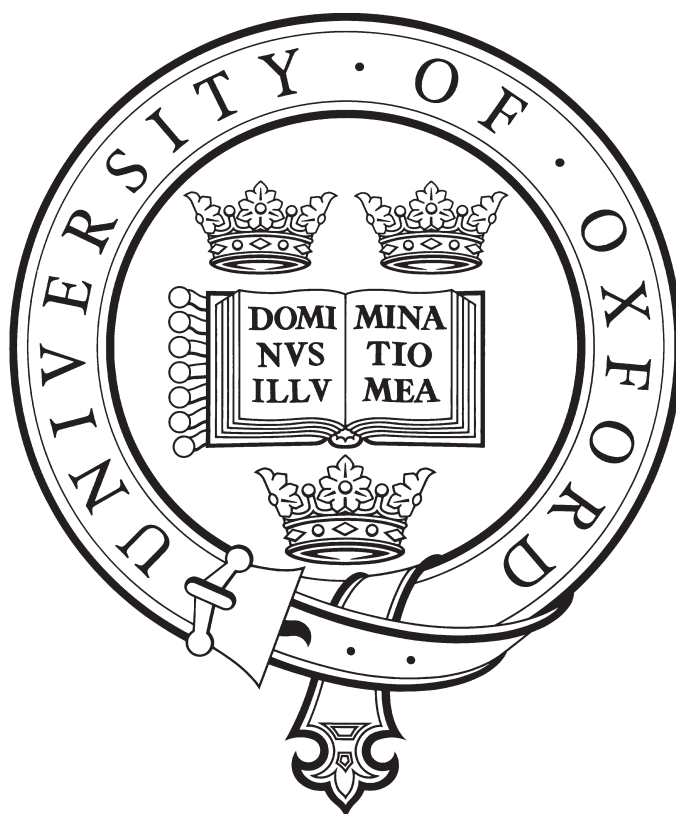


The properties of nitrogen and oxygen in silicon

J.D. Murphy



Thesis submitted for the Degree of Doctor of Philosophy

Trinity Term 2006

Supervisor: Dr P.R. Wilshaw

Abstract

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A novel dislocation locking technique is used to study the behaviour of nitrogen and oxygen in silicon. Specimens containing well-defined arrays of dislocation half-loops are subjected to isothermal anneals of controlled duration, during which nitrogen or oxygen diffuses to the dislocations. The stress required to move the dislocations away from the impurities is then measured. Measurement of this unlocking stress as a function of annealing time and temperature allows information on the transport of nitrogen and oxygen to be deduced.

Despite being present in a concentration of just $3 \times 10^{14} \text{cm}^{-3}$ in some specimens, nitrogen is found to provide substantial benefits to the mechanical properties of float-zone silicon (FZ-Si). The segregation of nitrogen at dislocations is stable to at least 1200°C and the unlocking stress measured at 550°C is of similar magnitude to that found previously for oxygen in Czochralski silicon (Cz-Si). The unlocking stress initially rises linearly with annealing time, before it takes a constant value. The rate of the initial rise is dependent on temperature and the 1.5eV activation energy found agrees with that found previously. The rate of the initial rise also depends on nitrogen concentration. In the 500 to 700°C temperature range, the unlocking stress is found to decrease linearly as the temperature at which the unlocking process takes place increases.

The results of a pre-annealing experiment confirm that oxygen monomers and dimers in Cz-Si exist in thermodynamic equilibrium at 550°C . Numerical simulation of oxygen diffusion to dislocations allows values of the effective diffusivity of oxygen in Cz-Si with four different oxygen concentrations to be deduced. At 500°C , the effective diffusivity depends upon oxygen concentration in a way which is consistent with oxygen dimers being responsible for transport. The transport of oxygen in Cz-Si at 550 to 600°C is found to be unaffected by nitrogen doping at a level of $2.1 \times 10^{15} \text{cm}^{-3}$.

The dislocation locking technique has also been used to study the effect of high concentrations of shallow dopants on oxygen transport in Cz-Si in the 350 to 550°C temperature range. Oxygen transport has been found to be unaffected by a high antimony concentration ($\sim 3 \times 10^{18} \text{cm}^{-3}$), but is found to be enhanced by, on average, a factor of approximately 44 in Cz-Si with a high boron concentration ($\sim 5 \times 10^{18} \text{cm}^{-3}$).

Furthermore, deep-level transient spectroscopy (DLTS) and high-resolution DLTS (HR-DLTS) are used to study the electrical activity of defects in silicon. A deep-level with an enthalpy of 0.50eV and a concentration of order 10^{11}cm^{-3} is found in n-type nitrogen-doped FZ-Si and n-type nitrogen-doped neutron transmutation doped FZ-Si. No additional deep-levels are found in either material, for which the detection limit is $6 \times 10^{10} \text{cm}^{-3}$. No deep-levels are found in p-type nitrogen-doped Cz-Si, for which the detection limit is approximately 10^{12}cm^{-3} . DLTS and HR-DLTS are also used to investigate the electrical activity of oxygen-decorated dislocations in Cz-Si and states associated with oxygen at dislocation cores have been identified.

Preface

This thesis is an account of the work carried out by the author in the Department of Materials, University of Oxford, under the supervision of Dr P.R. Wilshaw from Michaelmas Term 2003 to Trinity Term 2006. No part of this thesis has previously been submitted for a degree at this University or elsewhere. The work of other authors has been freely drawn upon and is duly acknowledged in the text. A list of references is given at the end of the thesis.

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3. A. Giannattasio, **J.D. Murphy**, S. Senkader, R.J. Falster, P.R. Wilshaw, “Oxygen and nitrogen transport in silicon investigated by dislocation locking experiments”, *Journal of the Electrochemical Society*, **152** G460 (2005).
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The DLTS results presented in this work were obtained in collaboration with Prof. J.H. Evans-Freeman and D. Emiroglu at the Materials and Engineering Research Institute at Sheffield Hallam University. I am very grateful to the EU-funded CADRES Consortium for funding my visit to Sheffield, during which the results presented in Chapter 7 were obtained.

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Chapter 1

Introduction

1.1 Background

As electronic devices become smaller and integration gets larger, previously tolerable defects in silicon now have a catastrophic impact on device yields. The need for faster devices is placing more stringent demands on the basic silicon substrate, which must be increasingly “perfect”. At present this level of perfection can generally only be achieved by expensive epitaxial growth or annealing schedules to remove oxygen precipitates and crystal originated particles (COPs).

Since the late 1990s there has been a drive to improve silicon substrates by the intentional addition of nitrogen. Most importantly, nitrogen is known to affect oxygen precipitation [1–7]; a process of vital importance to device manufacturers, who use oxide precipitates for collecting unwanted fast-diffusing metallic contaminants in a process known as *intrinsic gettering*. Nitrogen also reduces the size of voids [8–10] and improves mechanical strength [11–14]. For the full benefits of nitrogen to be exploited, the properties of nitrogen in silicon must be fully understood. The understanding of nitrogen in silicon has progressed mainly on an empirical basis to date and many questions remain to be answered about its fundamental properties.

The material of choice for the vast majority of electronic devices, Czochralski silicon (Cz-Si), has a high residual concentration of oxygen ($\sim 10^{18}\text{cm}^{-3}$). As well as forming precipitates during certain thermal treatments, oxygen impurities improve the

mechanical strength of Cz-Si by immobilizing dislocations [15, 16]. A large amount of research has been carried out into oxygen in silicon, although there are several key areas in which problems are unresolved. For instance, it is known that at temperatures below approximately 650°C, oxygen transport occurs at rates far higher than expected from the extrapolation of accepted diffusivity data [17–24]. It has been suggested that a different oxygen species, the dimer, is responsible for this enhanced transport [25–27], although more experimental evidence is needed before this is known for certain. Additionally, it has been shown that oxygen transport is affected by a high concentration of certain shallow dopants [28–30], although no clear picture of the doping dependence of oxygen transport has yet emerged.

In this Chapter, an overview of modern silicon is presented, including a detailed account of the current understanding of the behaviour of nitrogen and oxygen impurities. A brief review of dislocations and their interaction with impurities is then given. Finally, a dislocation locking technique is introduced and earlier experimental results obtained by using it are discussed.

1.2 Growth of silicon crystals

1.2.1 Czochralski method

A method invented by Czochralski in 1916 to determine the crystallization velocity of metals [31] is used today to grow the silicon on which most electronic devices are fabricated. The silicon crystals pulled in the early years were not dislocation free. The method was refined by Dash in 1958, who introduced a crystal neck, which allowed crystals with negligible dislocation densities to be grown [32]. Modern silicon grown in this way is completely free of dislocations.

To produce Cz-Si, a seed crystal is dipped into a melt of electronic grade silicon and is slowly withdrawn vertically, as shown in Figure 1.1. The liquid crystallizes at the seed. Typical growth velocities exceed 1mm per minute for 200mm diameter wafers. The silicon ingot drawn from the melt is then sliced into wafers, which are mirror polished on at least one side.

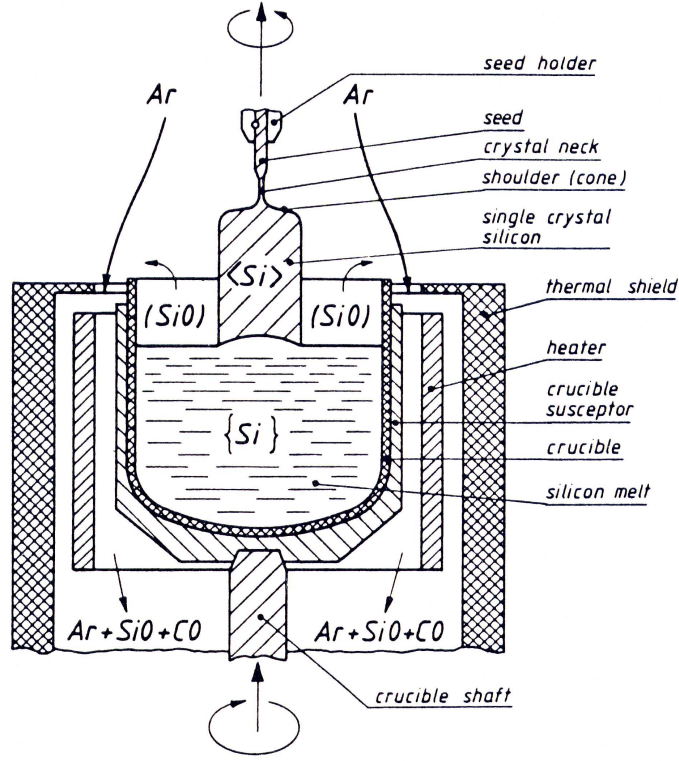


Figure 1.1: Czochralski method for pulling silicon single crystals (after Zulehner [33]).

Impurity	Al	As	B	C	Cu	Fe	N	O	P	Sb
k_0	0.002	0.3	0.8	0.07	4×10^{-4}	8×10^{-6}	7×10^{-4}	1.25	0.35	0.023

Table 1.1: Segregation coefficients for common impurities in silicon (after Pearce [34], except for N which is after Yatsurugi *et al.* [35]).

Generally, the main impurity present in silicon grown by the Czochralski method is oxygen, which is introduced because the walls of the silica (SiO_2) crucible dissolve into the melt. The segregation coefficient, defined as the ratio between the concentration of an impurity in the solid to the melt, of oxygen is greater than unity [34]. This means that oxygen preferentially partitions into the ingot during growth and consequently Cz-Si has a high concentration of oxygen (approximately 10^{17} to 10^{18}cm^{-3}). As can be seen from Table 1.1, most impurities have a much lower segregation coefficient than oxygen and so unwanted impurities are often present in low concentrations. For example, the concentration of carbon in Cz-Si is often below the detection limit ($< 10^{15} \text{cm}^{-3}$).

The vast majority of very large scale integration (VLSI) devices are fabricated on Cz-Si. The reason for this is not only that Cz-Si is relatively cheap to produce, but Cz-

Si generally has higher mechanical strength at high temperatures compared to silicon grown by other methods. It has long been known that Cz-Si wafers are less susceptible to slip than wafers grown by the floating zone method [15,36]. The oxygen in Cz-Si is responsible for this and this is discussed further in Section 1.3. Cz-Si wafers are the largest in regular production today and 300mm diameter wafers are rapidly becoming the standard size for device fabrication. The International Technology Roadmap for Semiconductors states that 450mm diameter wafers will be used for high volume device fabrication by 2013 [37].

1.2.2 Floating zone method

To grow silicon of the highest purity, it is necessary to reduce or eliminate totally contact between the melt and contaminant sources (such as a crucible). Zone refining of crystals takes advantage of the low segregation coefficients for most impurities at the solid-liquid transition. In the freely floating zone refining method, the floating zone is suspended between the melting and the freezing interfaces, as is shown in Figure 1.2. The floating zone is created by radio-frequency induction heating and the silicon ingot again forms on a seed crystal. The whole apparatus is contained in vacuum, or an inert gas or nitrogen atmosphere.

The high purity of the silicon grown by the floating zone method (FZ-Si) allows its electrical properties to be controlled carefully. One way of doing this is by neutron transmutation doping. Neutron transmutation doped (NTD) FZ-Si is produced by irradiating intrinsic FZ-Si with neutrons. Some of the silicon undergoes a nuclear reaction and is converted to phosphorus, making the material n-type. By controlling the dose and the width of the irradiating neutron beam, the resistivity variation can be kept at low values over a large range of bulk resistivity ranging from 10 to 4000 Ωcm . A particular application NTD FZ-Si is for producing drift detectors [38].

FZ-Si is significantly more expensive than Cz-Si and the largest wafers currently in high volume production have a diameter of just 200mm. Additionally, because of its negligible oxygen content ($\sim 10^{15}\text{cm}^{-3}$ or lower), FZ-Si experiences none of the beneficial effects that oxygen provides, which are discussed in the next Section. It is

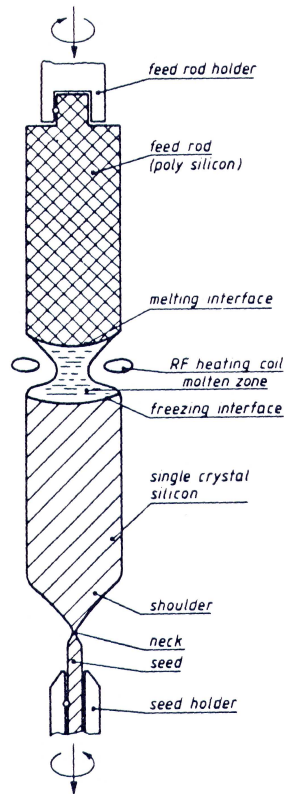


Figure 1.2: Floating zone method of silicon growth (after Zulehner [33]).

thought that doping FZ-Si with nitrogen will provide some of these beneficial effects and this is part of the motivation for the work presented in Chapter 4. Due to its high cost and lack of mechanical strength, FZ-Si is generally only used when absolutely necessary. FZ-Si is generally used for high power solid-state devices, high efficiency solar cells and photodetectors. High resistivity FZ-Si is used for radio frequency devices and micro-electromechanical systems (MEMS).

1.3 Oxygen in silicon

1.3.1 Introduction

Oxygen is an unavoidable impurity in Cz-Si, as it results from the dissolution of the walls of the silica crucible which contains the melt. Perhaps surprisingly, oxygen impurities actually provide significant benefits to Cz-Si. Oxygen precipitates are able to trap fast-diffusing unwanted metallic impurities (see Section 1.3.2) and oxygen is

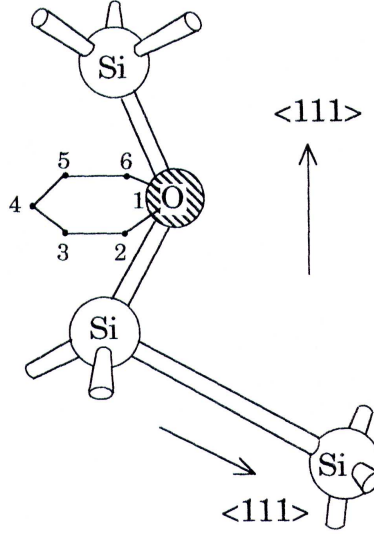


Figure 1.3: Interstitial position of oxygen atom in silicon lattice, covalently bonded with two neighbouring silicon atoms. The equivalent interstitial positions are indicated (1-6) (after Borghesi *et al.* [39]).

known to improve the mechanical stability of the material by immobilizing dislocations (see Section 1.6.2). With a few exceptions, the properties of oxygen in silicon are well understood. A summary of these properties, particularly those relevant to transport, is given in this Section. Oxygen in silicon has been reviewed from the perspective of transport and precipitation by Borghesi *et al.* [39] and Newman [40], and for its electrical properties by Michel and Kimmerling [41].

The majority of oxygen atoms in silicon exists in the form of interstitial monomers. Interstitial oxygen atoms are electrically neutral and occupy bond-centred sites in the silicon lattice (see Figure 1.3), as revealed by high resolution cryogenic Fourier transform infrared (FTIR) absorption measurements [42] and by small increases in the silicon lattice parameter compared to FZ-Si [43].

At temperatures typical for device processing (less than 1200°C), oxygen is present in Cz-Si as a supersaturated solid solution. The phase diagram in Figure 1.4 shows that at temperatures less than approximately 1200°C the equilibrium state of the Si-O system in Cz-Si is reached by means of oxygen precipitation. That is, at equilibrium, oxygen precipitates (SiO_2 particles) exist in the silicon crystal.

Oxygen in silicon also exists in the form of other species, including interstitial

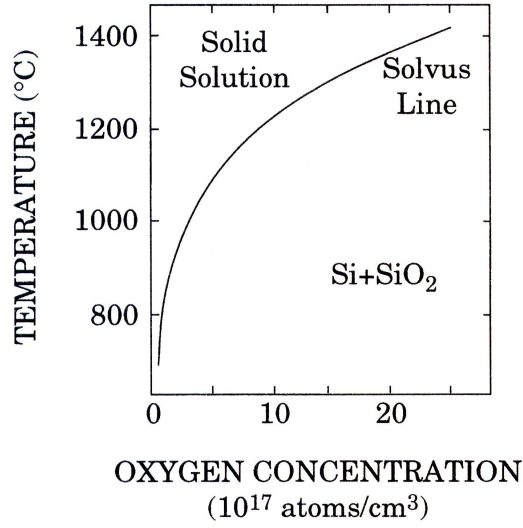


Figure 1.4: Phase diagram for Si-O system (after Borghesi *et al.* [39]).

dimers and thermal donor defects (see Section 1.3.4). These species are important at temperatures below approximately 650°C and it is at these temperatures where the understanding of oxygen in silicon is incomplete.

The transport of oxygen is the rate-limiting factor for the formation of oxide precipitates and thermal donor defects, and so a full understanding of oxygen transport from room temperature to the melting point of silicon is desirable. At high temperatures (650°C and above) the transport of oxygen is well understood (see Section 1.3.3). At lower temperatures the transport of oxygen has been shown to be a more complicated process and more research is required in this area (see Section 1.3.4).

1.3.2 Oxygen precipitation

Oxide precipitates play a vital role in modern silicon, as they trap unwanted metallic impurities [44]. Oxide precipitates are one tool used in a process known as *gettering*, which has been reviewed extensively by Myers *et al.* [45]. Carefully controlling the formation of oxygen precipitates in Cz-Si is of utmost importance. If the precipitate formation is not carefully controlled, oxide precipitates can punch-out dislocation loops [46] and these can ruin devices.

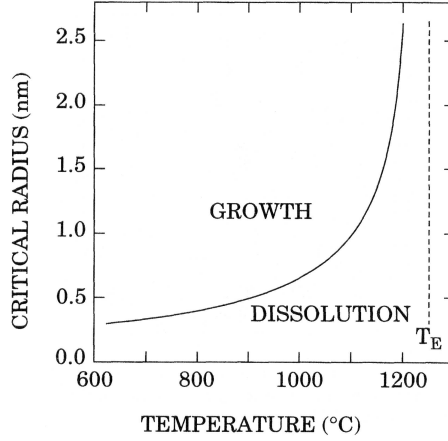


Figure 1.5: The temperature dependence of the critical radius, r_c , as determined from simple theory (after Inoue *et al.* [49]).

Mechanism

Oxide precipitates develop from nuclei which form during annealing in the 600 to 900°C temperature range and are then grown by annealing from 1000 to 1200°C [39].

Nucleation occurs when a few oxygen atoms aggregate within the silicon lattice and form the so-called *nuclei*. Once formed, the precipitate nuclei either dissolve or grow into oxide precipitates. The fundamental parameter for nucleation is the degree of supersaturation of the oxygen in the silicon crystal, *i.e.* the ratio of the concentration of oxygen in the crystal to the (temperature-dependent) solubility limit (see Figure 1.4). The radius of the nucleus, r , is also an important parameter, insofar as nuclei with r greater than a critical value, r_c , tend to grow into precipitates and those with $r < r_c$ tend to dissolve. The critical radius for oxygen nuclei in silicon depends on several parameters: the self-interstitial and vacancy concentration, the impurity type and content, the elastic properties and the temperature [47,48]. The dependence of the critical radius on temperature is shown in Figure 1.5. The dependence of the nucleation rate on the oxygen content in the crystal and the annealing temperature is shown in Figure 1.6.

If the conditions are favourable for nuclei growth, oxygen precipitation occurs during further annealing. It is widely accepted that precipitation is driven by diffusion kinetics over a wide temperature range. A theory of diffusion-limited precipitation was

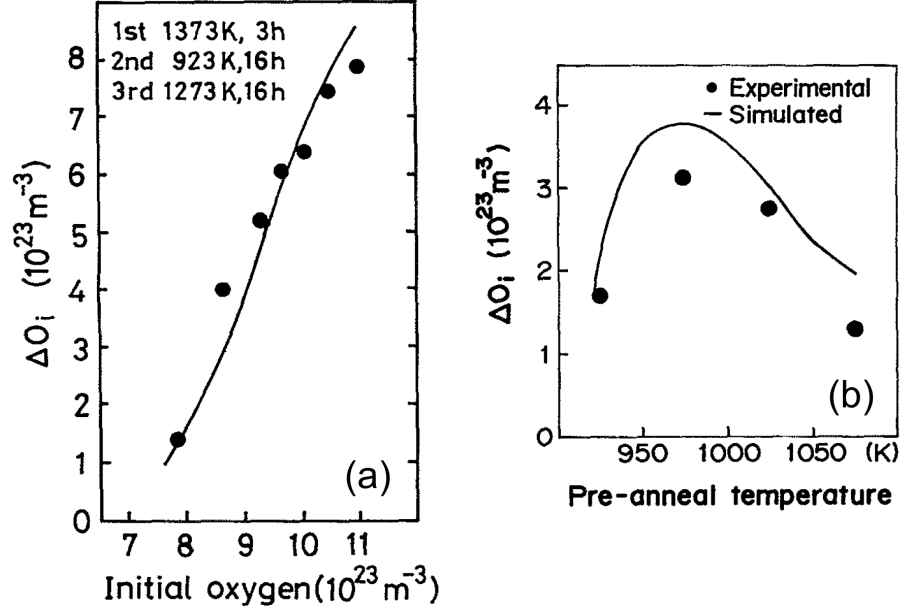


Figure 1.6: Dependence of the precipitated oxygen concentration, ΔO_i , on (a) the initial oxygen concentration in a three-step annealing process and (b) pre-annealing temperature for a 2 hour pre-anneal in Cz-Si with an initial oxygen concentration of $9.7 \times 10^{17} \text{ cm}^{-3}$ (after Isomae [50]).

published by Ham in 1958 [51]. The theory is general insofar as it applies to diffusion-limited precipitation of any substance in any material. The theory involves the solution of Fick's equation:

$$\frac{\partial \rho(\mathbf{x}, t)}{\partial t} = D \nabla^2 \rho(\mathbf{x}, t) \quad (1.1)$$

where $\rho(\mathbf{x}, t)$ is the solute concentration as a function of position $\mathbf{x}$ and time t , and D is the diffusion coefficient, which is independent of time. The equation is solved with appropriate boundary conditions to give the impurity concentration as a function of distance from a precipitate. In the case of spherical precipitates, amongst other things, the temporal evolution of the precipitate radius can be deduced from Ham's theory.

The validity of the model has been verified experimentally at certain temperatures. In 1983, Binns *et al.* studied the kinetics of oxygen precipitation using infrared (IR) spectroscopy, cold neutron scattering and chemical etching [52]. Their results confirmed Ham's model in the 650 to 1050°C temperature range. However, recent evidence exists for the classical theory of nucleation being violated at temperatures less than approxi-

mately 600°C. Work by Kelton *et al.* [53] showed agreement with the classical theory at temperatures above 600°C, but at lower temperatures the precipitate density in their specimens was found to be orders of magnitude higher than expected. Rather than simply concluding that the precipitation was due to the anomalous oxygen diffusion referred to in Section 1.3.4, the authors noted that this alone was not enough to explain their results. They suggested that the kinetic model needed refining to explain the enhanced precipitation that they observed.

Effects

SiO₂ precipitate particles, which can be produced at random sites in dislocation-free Cz-Si during post-growth anneals, can act as sinks for fast-diffusing metallic atoms (such as iron, nickel and copper) that are unintentionally introduced during device processing in concentrations of 10¹⁰ to 10¹³cm⁻³ [44, 54]. Although extreme care is taken to avoid such metallic impurities, such a small contamination level is presently unavoidable. Metal atoms are very harmful to devices. For example, iron can react with dopant atoms [55] and precipitate as iron silicide which causes short circuits [56].

Wafer manufacturers recognize the importance of gettering in modern device processing, so wafers are produced with that in mind. Manufacturers of Cz-Si often use a thermal treatment after wafer production to allow oxygen near the surface of the wafer to out-diffuse, hence creating a small oxygen-free layer on the top of the wafer. This so-called *denuded zone*, where devices are fabricated, is guaranteed to be free of precipitates and so no metallic elements trapped at precipitates can interfere with devices.

On average, for every two oxygen atoms that are added to a precipitate, one interstitial atom, I, is required to accommodate the local increase in volume [57, 58]. Thus, there are two parallel process; O_i diffusion and I diffusion. The diffusion of interstitial atoms can lead to their clustering. This can lead to the formation of small punched-out dislocation loops adjacent to the precipitates [59] and oxidation-induced stacking faults [60].

1.3.3 “Normal” diffusion of oxygen in silicon

Diffusion of interstitial single oxygen atoms, O_i , occurs from a bond-centred site to one of the six equivalent adjacent sites (see Figure 1.3) with a jump distance $d = \sqrt{2}a_0/4 = 1.92\text{\AA}$, where $a_0 = 5.42\text{\AA}$ is the lattice constant for silicon [40]. This is referred to as diffusion by single atomic jumps. Many studies have been performed to deduce the diffusivity of O_i , which is thought to be well known for temperatures in the 350 to 1325°C temperature range.

Early work at high temperatures used acoustic waves to generate an oscillating stress in a heated block of silicon [61]. At high temperatures the damping of the waves occurred with a broad superposed resonant peak. Analysis of this curve allowed the diffusivity to be deduced. These experiments also validated proposals that interstitial oxygen atoms occupied bond-centred sites with $\langle 111 \rangle$ axes.

More recently, secondary ion mass spectrometry (SIMS) has been used to measure oxygen transport in silicon at high temperatures. The distribution of in-diffused $^{18}O_i$ [62,63] and out-diffused $^{16}O_i$ [64,65] was fitted to error function profiles and the derived values of the diffusivity were in agreement with the earlier work done by monitoring damping of acoustic waves [61]. These values are plotted in Figure 1.7.

Diffusivity values for the low temperature range (330 to 400°C) were determined by stress-induced dichroism [66,67]. The technique involves subjecting a sample to a static uniaxial stress of $\sim 100\text{MPa}$, usually along a $[111]$ direction, for 15 to 30 minutes at the investigation temperature and then cooling the sample to room temperature with the stress still applied. The oxygen concentration at certain interstitial sites, but not others, is changed and is “frozen in”, so that IR spectroscopy experiments at room temperature reveal a difference in absorption between light polarized with its $\mathbf{E}$ -vector perpendicular ($\alpha_{\perp}$) and parallel ($\alpha_{\parallel}$) to the direction of the stress axis. The magnitude of the dichroism can be measured as $\frac{\alpha_{\perp} - \alpha_{\parallel}}{\alpha_{\perp}}$. By performing a further isothermal anneal and monitoring the dichroism’s exponential decay, the diffusion coefficient can be deduced. The stress-induced dichroism results of Corbett *et al.* [67], Stavola *et al.* [68] and Newman *et al.* [69] are also plotted in Figure 1.7.

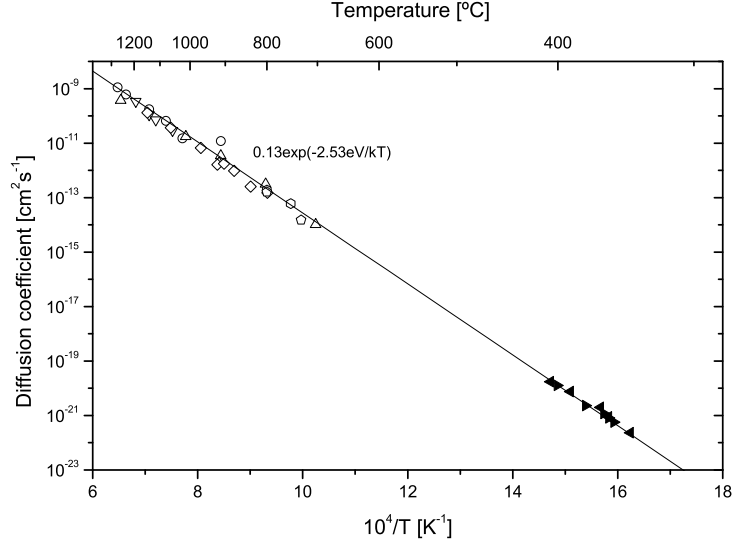


Figure 1.7: Diffusivity measurements of oxygen in silicon. High temperature measurements are made by SIMS. Low temperature measurements are measured by stress-induced dichroism (after Mikkelsen [70]).

The data from SIMS and stress-induced dichroism lead to the following expression for the diffusion coefficient of O_i in the 350 to 1325°C temperature range [40]:

$$D_{\text{normal}} = 0.13 \exp\left(-\frac{2.53\text{eV}}{kT}\right) \text{cm}^2\text{s}^{-1} \quad (1.2)$$

It is important to realize that unlike stress-induced dichroism, SIMS diffusion studies do not simply measure the diffusion of O_i , but in fact measure total oxygen transport. In the case that the transport is dominated by the majority species (*i.e.* O_i) then these values are approximately the same. However, if the species that dominates oxygen transport is a minority species, then the data obtained by SIMS need to be analyzed more carefully if they are to be expressed in terms of the diffusivity of a single species.

Techniques such as SIMS and stress-induced dichroism are unable to measure oxygen transport in the 430 to 650°C temperature range easily. The diffusivity was initially thought to be too small to be measured by SIMS and is too large to be measured by stress-induced dichroism. Thus, to investigate transport in this temperature range the use of more indirect techniques needs to be considered.

1.3.4 “Anomalous” diffusion of oxygen in silicon

The diffusivity measurements plotted in Figure 1.7 appear to imply that oxygen transport in silicon is well understood. However, investigations on a particular class of electrically-active defects in silicon, known as thermal donors, revealed that this is not the case. Before describing the experimental evidence for this anomalous diffusion, it is necessary to introduce the thermal donor defects themselves.

Thermal donors

Oxygen in its usual interstitial configuration is electrically inactive. It was discovered in 1954 by Fuller *et al.* that upon heat treatment in the 300 to 550°C temperature range, electrically active centres were formed in oxygen-rich silicon [17]. It was established that these centres are donors [18] and because they were generated by thermal treatment they were termed *thermal donors* (TDs). In 1977, a second type of electrically active centre in silicon was found, which was also associated with oxygen [71]. These so-called *new donors* (NDs) are formed in the temperature range from 650 to 850°C. Formation rates of oxygen-related donors as a function of annealing temperature are plotted in Figure 1.8. The Figure shows two peaks; one for TDs and one for NDs.

Early experiments on TDs used resistivity measurements to determine the added electron concentration and hence determine the TD concentration. Kaiser *et al.* showed that the formation rate and maximum TD concentration were dependent on the fourth and third powers of the oxygen concentration respectively [18]. They assumed that a TD was one specific defect centre; a $[\text{SiO}_4]$ donor complex. However, later, Hall effect measurements showed that a single specimen subjected to a particular set of annealing conditions produced two ionization energies [73], hence implying that TDs are actually double donors. Also, by subjecting specimens to different annealing conditions it was possible to deduce the existence of several different TD species.

The use of IR spectroscopy allowed for the identification of nine TDs with slightly different binding energies [74, 75]. More have been identified since and a list is given in reference [76]. The binding energy was found to decrease with annealing time,

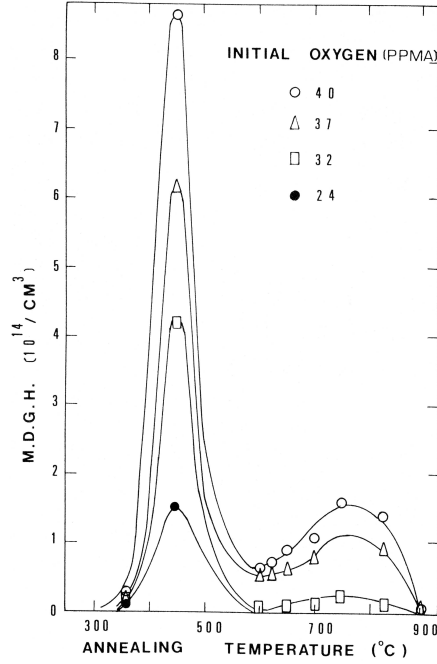


Figure 1.8: Maximum donor generation per hour of annealing at given temperatures in a nitrogen ambient. The peak at approximately 450°C is due to thermal donors (TDs); the peak at approximately 750°C is due to new donors (NDs) (after Cazcarra and Zunino [72]).

which is explained by TD complexes growing in size by the addition of more and more oxygen impurities with increasing annealing time. Experiments using deep-level transient spectroscopy (DLTS) [77] have also revealed donor levels [78].

Magnetic resonance techniques have been used to study the symmetry and local environment of the TDs. Electron paramagnetic resonance (EPR) showed the existence of certain TD states [79]. However, the technique is unable to resolve the different TD species. It was found that a technique that detects the hyperfine interactions between the paramagnetic electron and the nuclei surrounding the defect, known as electron nuclear defect resonance spectroscopy (ENDOR), could distinguish between the different TD species [80]. ENDOR measurements proved the existence of oxygen as part of the defect for the first time from the nuclear g -factor of the nuclei surrounding the defect [81,82]. Photoluminescence (PL) has also been used to study thermal donors [83–85], as have emission transient spectroscopy and excitation spectroscopy [86].

TDs annihilate at above approximately 550°C, whereas NDs are created above this

temperature. NDs are found to exhibit significantly different annealing behaviour to TDs and their generation depends on either a pre-anneal at 470 to 550°C or a high carbon concentration in the material ($[C] > 2 \times 10^{16}$) [87]. Cazcarra and Zunino found that the formation kinetics of NDs are closely related to the formation of oxygen precipitates [72]. They therefore suggested that NDs are Si_yO_x clusters of a few hundred atoms of oxygen that act as nucleation centres for oxygen precipitates. From DLTS experiments it became evident that NDs are actually a collection of different defects [88]. Currently, it is generally agreed that NDs are due to extended defects [41] whether as oxygen clusters or precipitates, but there is no agreement on the structure of the donors. Techniques such as ENDOR have not yet been applied successfully to NDs.

“Anomalous” diffusion measurements

The formation kinetics of TDs present a significant difficulty for the direct involvement of oxygen. At 450°C the effective diffusivity of oxygen extracted from the TD formation rate is $2 \times 10^{-16} \text{cm}^2 \text{s}^{-1}$ [17, 18], whereas the diffusivity of O_i as determined by stress-induced dichroism is $6 \times 10^{-19} \text{cm}^2 \text{s}^{-1}$ [68]; a difference of more than two orders of magnitude. Additionally, several other experiments have indirectly indicated enhanced oxygen transport [19–22]. The inferred enhancement in transport is shown in Figure 1.9.

Oxygen diffusivity in the 430 to 650°C temperature range was originally thought to be too small to be measured by SIMS. For SIMS to provide reliable results it was thought that the depletion depth from the surface had to be in the range 5 to 10 μm . However, reports of observed out-diffusion have been reinvestigated [23] and the measured profiles are strange because their depths ($\sim 5 \mu\text{m}$) are essentially independent of the anneal temperature and increasing the anneal time only leads to slightly larger reductions in the surface concentration. A consequence of this is that the derived diffusion coefficient is essentially constant over the temperature range investigated: increasing from the expected value (Figure 1.7) to a factor of up to approximately 3×10^5 as the temperature falls from 650 to 450°C.

In 1983, Gösele and Tan proposed the existence of a fast-diffusing oxygen dimer,

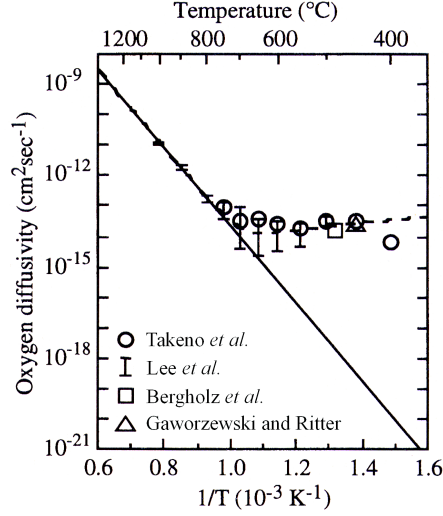


Figure 1.9: An Arrhenius plot of the oxygen diffusivity showing an enhancement in oxygen diffusivity below approximately 700°C. The data are taken by different authors using oxygen precipitation experiments. The solid line is the widely accepted expression of $D = 0.13 \exp(-\frac{2.53\text{eV}}{kT}) \text{cm}^2\text{s}^{-1}$ [70]. The dashed curve indicates a calculated result using a molecular oxygen model (after Takeno *et al.* [19]).

O_2 , to explain the enhanced oxygen transport [25]. It has also been proposed that enhanced rates of oxygen transport result from an interaction between oxygen and another highly mobile species. It was suggested by Newman *et al.* [89] that hydrogen, vacancies, self-interstitials and metallic impurities, such as copper or nitrogen, could be candidates because of their high diffusion coefficients. However, new evidence indicates that the oxygen dimer is the mostly likely candidate [24, 27].

Various investigations looking at the local vibrational modes of oxygen species [27, 90] have shown experimental evidence for the oxygen dimer in silicon. From these investigations, the binding energy of the oxygen dimer was found to be approximately 0.3eV [27]. From the formation kinetics of thermal donor formation, it was possible to deduce the activation energy for transport to be 1.3eV at low temperatures [90], which is consistent with theoretical investigations which give 1.33eV [91] and 1.5eV [92].

Further evidence for the dimer was provided by Senkader *et al.* who studied the locking of dislocations by oxygen in the 350 to 650°C temperature range [24]. An activation energy for transport of approximately 1.5eV was found. Their technique, which is used extensively in this present work, is discussed in Section 1.7.

1.3.5 Electrical doping dependence of oxygen transport

The findings presented for the transport of oxygen in the previous Sections only apply to Cz-Si with a low concentration of shallow dopants (approximately 10^{15}cm^{-3} and lower). It is known that oxygen transport is modified in the presence of a high concentration of certain shallow dopants. The effect of the material's electrical doping level on oxygen transport in Cz-Si has been studied by SIMS [28–30]. The experimental results for the effect of high concentrations of antimony, boron and arsenic on oxygen transport in Cz-Si are summarized in Table 1.2. High concentrations of all three elements have been found to provide a retardation effect on oxygen transport at temperatures less than 800°C [29,30]. In the study of Takeno *et al.* a high boron doping level was found to slow oxygen transport at 600 and 700°C [30]. Since in the same work it was also found that oxygen transport is not affected by a high boron doping level at 500 and 800°C , the authors attribute the retardation to the formation of immobile oxygen complexes at 600 to 700°C .

None of the studies on as-grown material show an enhancement in oxygen transport being associated with a high concentrations of dopants. However, there is indirect evidence for a high concentration of boron enhancing oxygen transport. The precipitation of oxygen in Cz-Si, a process which is limited by oxygen transport, has been found to be enhanced in highly boron doped material [93]. Additionally, a SIMS study on oxygen transport in Cz-Si into which boron had been diffused showed enhanced oxygen out-diffusion at 1100°C [94].

Diffusion of the oxygen dimer has been investigated theoretically by Adey *et al.* who used density functional theory calculations [91]. They proposed that the oxygen dimer diffuses by alternating between square and staggered states, as illustrated in Figure 1.10. According to their model, the electrical doping level makes a difference to the activation energy for diffusion of the oxygen dimer. The diffusion pathways are illustrated in Figure 1.11. The model predicts that in Cz-Si with a high concentration of shallow acceptors, the activation energy for diffusion is reduced to 0.86eV, compared to 1.33eV in material with a low concentration of shallow acceptors.

Dopant	Dopant concentration [cm^{-3}]	Temperature range	Effect on oxygen transport	Reference(s)
Sb	2.3×10^{17} to 2.1×10^{18}	950 to 1100°C	None	[28, 29]
Sb	5×10^{17}	800°C	None	[29]
Sb	1.3×10^{18}	500 to 800°C	Slows (E_A increased by 1.40eV)	[30]
B	8×10^{18} to 1.2×10^{19}	1050°C	None	[29]
B	8×10^{18} to 1.2×10^{19}	800°C	Slows (factor of ~ 5)	[29]
B	4.4×10^{18}	500 and 800°C	None	[30]
B	4.4×10^{18}	600 to 700°C	Slows (factor of ~ 2 to 3)	[30]
As	1.1×10^{19}	1050°C	None	[29]
As	1.1×10^{19}	800°C	Slows (factor of ~ 2.5)	[29]
As	4×10^{18} to 1.3×10^{19}	500 to 800°C	Slows (E_A increased by 0.64 to 0.68eV)	[30]

Table 1.2: The effect of high concentrations of various shallow dopants on the transport of oxygen in as-grown Cz-Si.

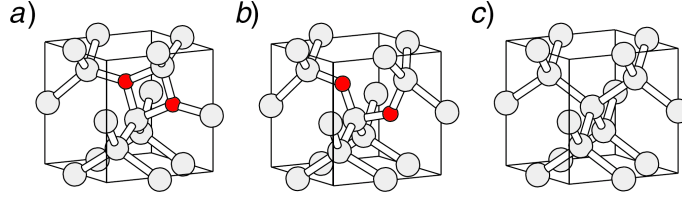


Figure 1.10: The structures of the oxygen dimer as proposed by Adey *et al.* [91]. O_{2i}^{sq} (structure a) is the stable form of the dimer in the double positive charge state. The stable form of the dimer in the neutral and single positive charge states is labelled O_{2i}^{st} (structure b). Also shown is a piece of equivalent bulk material (structure c). Grey circles represent silicon and red circles represent oxygen (after Adey *et al.* [91]).

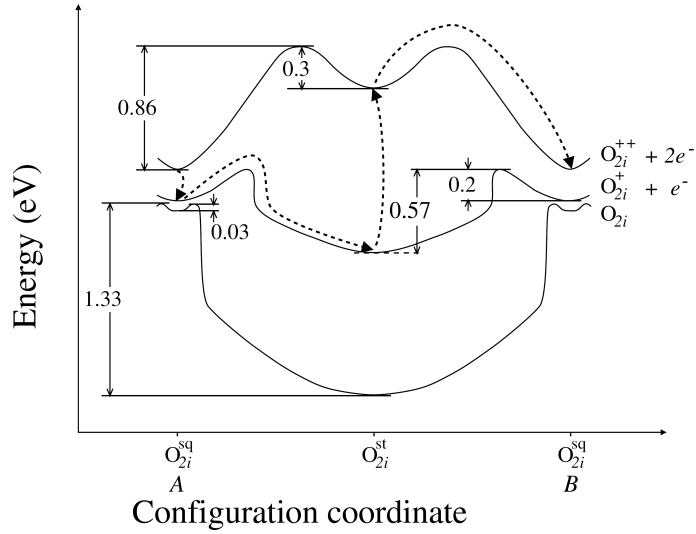


Figure 1.11: The configuration-coordinate diagram for the oxygen dimer proposed by Adey *et al.* [91]. Arrows show the proposed thermally assisted Bourgoin diffusion mechanism with a thermal barrier of 0.3eV. O_{2i}^{++sq} at A first captures a photogenerated or injected electron and, after overcoming a 0.2eV barrier, changes its configuration to O_{2i}^{+st} . It then traps a hole becoming O_{2i}^{++st} , and executes a diffusion jump to O_{2i}^{++sq} at B after overcoming a thermal barrier of 0.3eV (after Adey *et al.* [91]).

New experimental results which further the understanding of oxygen transport in Cz-Si with high concentrations of antimony and boron dopants are presented in Chapter 6.

1.3.6 Determination of oxygen concentration

IR spectroscopy measurements on Cz-Si at room temperature revealed the broad absorption line for bond-centred interstitial oxygen at 1106cm^{-1} with an absorption coefficient of $\alpha \sim 3\text{cm}^{-1}$ [18]. A considerable amount of effort has been put into establishing calibration factors to convert the value of the peak absorption coefficient, α_{max} , of the 1106cm^{-1} line to the concentration of isolated oxygen atoms present in the sample. Calibrations have different labels according to their origin (*e.g.* ASTM (USA), New ASTM (USA) or DIN 50438/I (Germany)) and the different standards are discussed in reference [95]. Care must be taken when analyzing experimental results, as different manufacturers and researchers use different calibration standards.

1.4 Nitrogen in silicon

1.4.1 Introduction

Very little nitrogen exists in as-grown wafers produced by either the Czochralski or the floating zone methods. Nitrogen is added to Cz-Si by the addition of silicon nitride (Si_3N_4) to the melt and to FZ-Si by growing the crystal in a nitrogen atmosphere.

Nitrogen in silicon is considerably less well understood than oxygen. The first research on nitrogen in silicon was performed almost fifty years ago [96], but accurate data on the chemical and physical properties of nitrogen in silicon are still lacking. One reason for this is that nitrogen can only be present in as-grown silicon in very low concentrations; making experimental measurements difficult. Another is that the standard technique for measuring impurity transport in silicon, SIMS, is particularly insensitive to nitrogen. The solubility of nitrogen in molten silicon is significant ($\sim 6 \times 10^{18}\text{cm}^{-3}$), yet the segregation coefficient is very small (7×10^{-4}) [35]. By extrapolation to zero growth velocity, the maximum nitrogen concentration in solid silicon is just

$4.5 \times 10^{15} \text{cm}^{-3}$. This value is much smaller than oxygen ($1.70 \times 10^{18} \text{cm}^{-3}$ [97]), carbon ($\sim 10^{18} \text{cm}^{-3}$ [98]) or group V elements (*e.g.* antimony, $6.6 \times 10^{18} \text{cm}^{-3}$ [99]). The nitrogen concentration in silicon can be increased by ion implantation. This brings with it a whole host of associated effects and problems which are generally not considered here.

Whilst nitrogen in silicon is difficult to study experimentally, it poses fewer problems to computational physicists, who make *ab initio* calculations to deduce some of its fundamental properties. A large proportion of current knowledge regarding nitrogen in silicon is based on the results of their calculations.

1.4.2 Effects of nitrogen in silicon

Silicon manufacturers have started doping their wafers with nitrogen because, in spite of its low concentration, it brings many beneficial effects. It is found that nitrogen affects oxygen precipitation in Cz-Si, which is necessary for internal gettering (see Section 1.3.2). It is also found that nitrogen can increase mechanical strength and suppress interstitials and vacancy-related defects, as well as bringing other minor benefits such as retarding the growth of oxide films on nitrogen implanted substrates [100]. The principal effects of nitrogen in silicon are considered in this Section.

Enhancement of oxygen precipitation

Manufacturers of Cz-Si are particularly keen to add nitrogen to their wafers, since it has been found that nitrogen enhances the precipitation of oxygen that is necessary for gettering fast-diffusing metallic contaminants. The enhancement was first discovered by Shimura and Hockett who used a preferential etching technique to reveal the precipitates and SIMS [1]. Many others have shown the enhancement since by IR spectroscopy [2–4], light scattering tomography [5, 6] and by electroluminescence [7]. A high-resolution transmission electron microscopy (TEM), scanning TEM (STEM) and electron energy loss spectroscopy (EELS) investigation has revealed that precipitates formed in nitrogen-doped Cz-Si are in fact oxynitride precipitates with a nitrogen content of 6 to 17% [101].

Increase in mechanical strength

The first research on the influence of nitrogen on the mechanical strength of silicon was conducted by Sumino *et al.* in 1983 [11]. They found that nitrogen significantly increased the yield stress by immobilizing the dislocations (see Figure 1.22). Many other studies have found that nitrogen is beneficial to the mechanical properties of silicon, including Giannattasio *et al.* who studied nitrogen by its interaction with dislocations [12] (see Section 1.7.2), Orlov *et al.* who found that nitrogen increased the yield stress in nitrogen-doped Cz-Si [13] and Brinkevich *et al.* who found that nitrogen increased the microhardness of Cz-Si [102]. In a recent work Yonenaga suggests that by enhancing the precipitation of oxygen at dislocations in Cz-Si, nitrogen acts to increase the mechanical strength of the material [14]. However, the technique he uses is very indirect and it is doubtful whether the explanation he provides can be justified without more direct evidence, as it could be that the nitrogen itself is responsible for the extra strength.

Suppression of interstitials and vacancy-related defects

In nitrogen-doped FZ-Si, nitrogen can suppress interstitials and vacancy-related defects [8–10]. The dominant reaction for vacancy suppression in FZ-Si is suggested to be [103]:



and the reaction that suppresses interstitial aggregation is suggested to be:



In nitrogen-doped Cz-Si the oxygen content favours the formation of NO complexes at high temperatures [103]:



Unfortunately, this implies that no N_2 is available to react with vacancies, and the

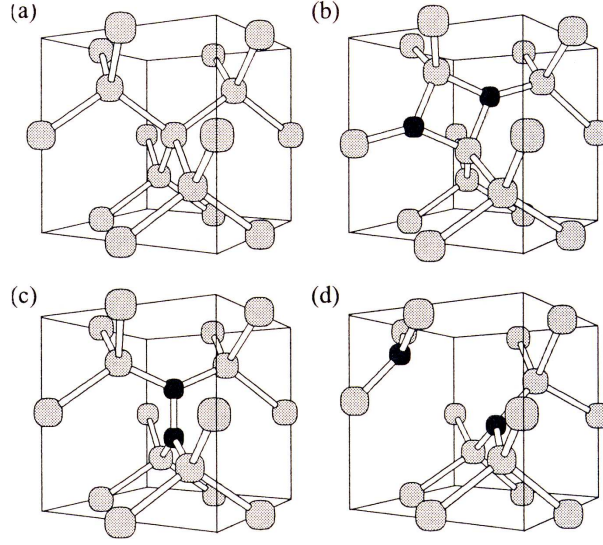


Figure 1.12: Schematic representation of defects containing two N impurities. Black and grey circles represent the N and Si atoms, respectively. (a) Fragment of Si lattice, (b) the $C_{2h}(N_i - N_i)$ complex, (c) the D_{2d} molecule-like split-interstitial ($N_i - N_s$), and (d) ($N_s - N_s$) (after Jones *et al.* [107]).

desirable defect suppression effect is reduced. At lower temperatures the equilibrium of Equation 1.5 shifts to the left-hand side and N_2V complexes can form again, hence suppressing vacancy aggregation.

1.4.3 Nitrogen species in silicon

Perhaps the simplest nitrogen defect in silicon is substitutional nitrogen, N_s , and this has been detected by EPR [104] and localized vibrational mode (LVM) spectroscopy [105]. The EPR spectrum is consistent with the nitrogen atom lying off site along $\langle 111 \rangle$. However, the majority of nitrogen in silicon takes the form of a dimer, N_2 . This is known from an IR study by Stein on silicon doped with different nitrogen isotopes [105]. Using a combination of IR spectroscopy and *ab initio* density functional theory calculations, Jones *et al.* [106] were able to show that this pair consisted of two neighbouring $\langle 100 \rangle$ oriented N - Si split interstitials, arranged in an antiparallel configuration, and with four N - Si bonds forming a square lying on $\{011\}$. This configuration is shown in Figure 1.12 (b); other possible configurations are also shown in Figure 1.12.

Interstitial monomeric nitrogen, N_i , is also known to exist in silicon. The stable

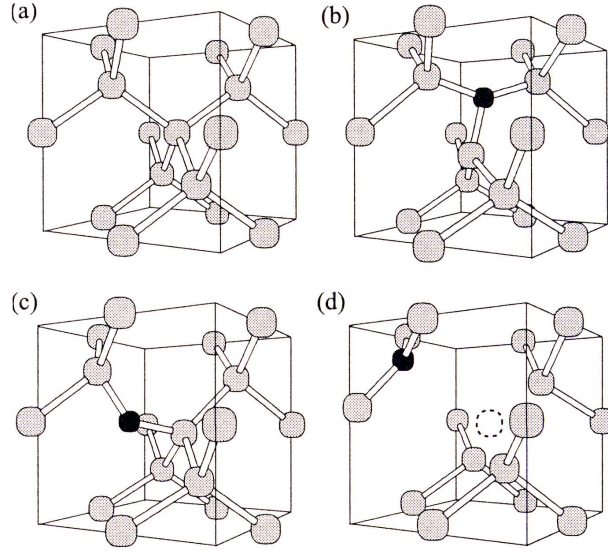


Figure 1.13: Schematic representation of defects containing a single N impurity. Black and grey circles represent the N and Si atoms respectively. (a) Fragment of the Si lattice, (b) the C_{1h} approximately $\langle 001 \rangle$ split-interstitial structure for N_i , (c) the puckered bond-centred structure for N_i and (d) the (N_sV) complex. The vacant site in (d) is represented schematically by a dashed circle (after Jones *et al.* [107]).

configuration for neutral N_i is a slightly distorted $\langle 001 \rangle$ split-interstitial [107], as shown in Figure 1.13 (b). Other possible configurations of monomeric nitrogen are also shown in Figure 1.13.

It is thought that the nitrogen dimers, N_2 , will partially dissociate into nitrogen monomers, N_1 , upon increasing temperature, according to:



The dissociation constant, k_d , for this reaction is given by:

$$k_d = \frac{[N_1][N_1]}{[N_2]} = \exp\left(-\frac{\Delta G}{kT}\right) \quad (1.7)$$

where ΔG is the variation in free energy after the dissociation.

The binding energy of the nitrogen dimer has been calculated by different authors using *ab initio* methods to be 1.7eV [108], 3.86eV [109] and 4.3eV [110]. The first value implies a strong dissociation above a certain temperature. The last value implies that the nitrogen dimer is stable up to the melting point of silicon. Because of the large

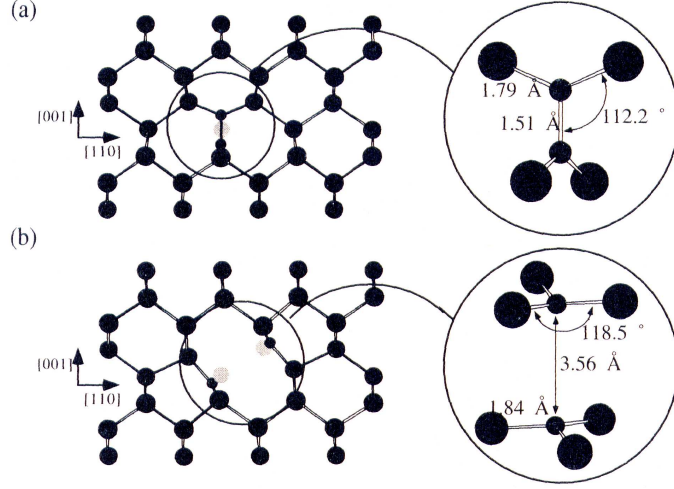


Figure 1.14: Optimised atomic configurations for (a) the defect complex constructed by one Si vacancy and two N atoms, and (b) that constructed by two Si vacancies and two N atoms shown in the (100) plane. Large filled circles denote Si atoms, and small filled circles denoted N atoms. Grey circles indicate Si vacancy sites (after Kageshima *et al.* [109]).

variation in theoretical values, experimental evidence is urgently needed to resolve the question of the thermal stability of the nitrogen dimer.

Nitrogen can also exist in the form of nitrogen-vacancy complexes. N_2V (or $N_s - N_i$) and N_2V_2 (or $N_s - N_s$) are particularly stable [107, 109], and are depicted in Figure 1.14. The existence of nitrogen-oxygen complexes in Cz-Si has also been shown experimentally [111, 112] and theoretically [113].

1.4.4 Nitrogen diffusion in silicon

According to numerical simulations, the majority nitrogen species in silicon, the interstitial dimer, has a large activation energy for migration (of order 2.5eV [114–116]) and is therefore practically immobile at low temperatures. By contrast, the nitrogen monomer, whose concentration is much lower than the dimer at low temperatures, is thought to have an activation energy for migration of just 0.4eV [117, 118] and so would rapidly diffuse at room temperature. Because of the large differences in mobilities and abundances of the two species, it is not straightforward to state which is responsible for transport at a particular temperature. This is still a matter of open debate [119–122].

The diffusion coefficient of nitrogen in silicon is more difficult to measure experi-

mentally than that of oxygen. This is because nitrogen is generally present in a concentration that is at least two orders of magnitude lower than oxygen and because SIMS is particularly insensitive to nitrogen in silicon. Additionally, nitrogen has limited electrical activity and no suitable radioactive isotopes for depth profile measurements. SIMS studies of nitrogen in silicon are difficult, but possible, and usually require a specifically modified apparatus. Therefore, in contrast to oxygen, experimental measurements of the diffusivity of nitrogen in silicon are limited in number.

The first attempt at measuring the diffusion coefficient of nitrogen was made by Clark *et al.* in 1968 [123]. They implanted N_{14}^+ ions into 100 Ω cm p-type silicon. Hall effect measurements indicated that the samples had formed a n-type surface layer. The depth of this layer was then measured as a function of annealing time and temperature. The diffusion coefficient of the nitrogen in the irradiated silicon was determined as:

$$D_N^{Clark} = 0.87 \exp\left(-\frac{3.29\text{eV}}{kT}\right) \text{cm}^2\text{s}^{-1} \quad (1.8)$$

However, this expression is thought to be unreliable for general nitrogen transport in silicon, since it probably refers to substitutional nitrogen complexes and the proportion of nitrogen in a substitutional position in the lattice is thought to be very small.

In 1975, Denisova *et al.* heated 300 Ω cm p-type FZ-Si in a nitrogen ambient at temperatures between 700 and 1200°C [124]. The depth to which the nitrogen diffused into the sample was assessed by irradiating the sample with 50KeV neon ions followed by a 800°C anneal. This resulted in the formation of an inversion layer that was assumed to be coincident with the nitrogen diffusion layer. The depth of the inversion layer was measured by successive oxidation etching and resistivity measurements. After making corrections for the 800°C anneal, they deduced the diffusivity to be:

$$D_N^{Denisova} = 3 \times 10^{-2} \exp\left(-\frac{2.63\text{eV}}{kT}\right) \text{cm}^2\text{s}^{-1} \quad (1.9)$$

However, the formation of a SiO_2 or Si_3N_4 film inhibited diffusion at temperatures greater than 800°C, so the reported expression is only valid in the 700 to 800°C temperature range. Additionally, the technique used is so indirect that it is not clear that it

is the nitrogen that has the effect on the inversion layer. The measurement is therefore not thought to be reliable.

More recently, in 1988, out-diffusion profiles of nitrogen in silicon were measured by SIMS in the 800 to 1200°C temperature range by Itoh and Abe [119]. By comparison with error function profiles, the concentration profiles gave what is widely considered to be the most reliable transport measurement for nitrogen in silicon, which is:

$$D_N^{Itoh} = 2.7 \times 10^3 \exp\left(-\frac{2.8\text{eV}}{kT}\right) \text{cm}^2\text{s}^{-1} \quad (1.10)$$

In the same work, Itoh and Abe confirmed that the total amount of out-diffusion was equal to the change in IR absorption at the nitrogen dimer peak. Itoh and Abe therefore concluded that their transport measurement given by Equation 1.10 was in fact the diffusivity of the nitrogen dimer. The diffusivity measurement of Itoh and Abe was confirmed by Hara *et al.* [125] who deduced a value for the diffusion coefficient of $2 \times 10^{-6} \text{cm}^2\text{s}^{-1}$ at 1270°C. Work by Willems and Maes [126] also confirms the diffusivity measured by Itoh and Abe.

Theoretical investigations imply that the activation energy for diffusion of the nitrogen dimer is large. The value of the activation energy deduced by Itoh and Abe was confirmed by *ab initio* calculations made by Sawada *et al.* [114]. A more recent theoretical investigation by Fujita *et al.* [115] has calculated the activation energy for diffusion to be 2.69eV and Stoddard *et al.* have used *ab initio* calculations to obtain a full expression for the diffusivity of nitrogen in silicon [116]:

$$D_N^{Stoddard} = 67 \exp\left(-\frac{2.38\text{eV}}{kT}\right) \text{cm}^2\text{s}^{-1} \quad (1.11)$$

Thus, it would appear that the diffusivity of nitrogen in silicon is well understood, as recent experimental and theoretical results agree well. However, as was the case for oxygen, the diffusivity of nitrogen in silicon is more complicated than it was first thought. Hockett observed anomalous diffusion of nitrogen ion implanted specimens [120]. He suggested that nitrogen dimers may not be the only species responsible for transport. His SIMS depth profile is shown in Figure 1.15. The stationary peak at a

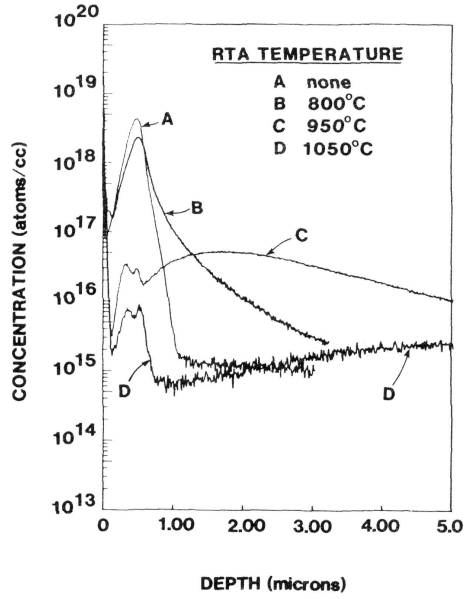


Figure 1.15: SIMS depth profiles of nitrogen implanted into $\langle 100 \rangle$ FZ-Si followed by rapid thermal annealing for 10s in argon (after Hockett [120]).

depth of approximately $0.6\mu\text{m}$ is believed to be associated with the nitrogen dimer and the other peak shown on curve C could be associated with fast-diffusing monomers or nitrogen-oxygen complexes.

Recently Mannino *et al.* performed similar experiments to Hockett using silicon grown by the Czochralski method and epitaxially-grown silicon [127]. Their SIMS depth profile is shown in Figure 1.16. Their work showed different effects in the two different types of material and consequently they concluded that oxygen was necessary for the anomalous nitrogen transport to occur.

Further evidence for anomalous nitrogen transport was proposed by Giannattasio *et al.* who measured nitrogen transport to dislocations [12]. They suggested that the transport was due to the nitrogen dimer and they measured its activation energy for transport to be 1.45eV; half of that predicted by the theorists. This work, on which the results presented in Chapter 4 of this thesis build, is discussed further in Section 1.7.2.

Voronkov and Falster recently published a theory that explains nitrogen diffusion in terms of a dissociative mechanism [122]. Nitrogen transport is postulated to occur by the dissociation of practically immobile dimers, N_2 , into mobile monomers, N_1 , which

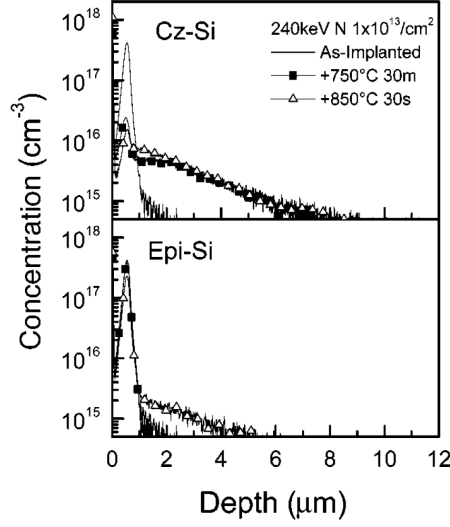


Figure 1.16: SIMS depth profiles of nitrogen-implanted Czochralski (top) and nitrogen-implanted epitaxially-grown (bottom) silicon. The different profiles correspond to different post-implantation annealing schedules (after Mannino *et al.* [127]).

diffuse some distance and then produce a new N_2 species by a pairing reaction. The model assumes that the dissociation reaction is catalyzed by oxygen. The dissociative model gives the following expression for the diffusivity of nitrogen:

$$D_N^{Voronkov} = 6.3 \times 10^{-2} \exp\left(-\frac{1.38\text{eV}}{kT}\right) \text{cm}^2\text{s}^{-1} \quad (1.12)$$

The model of Voronkov and Falster combines data from many different studies [119,120,127–130]. However, there is a distinct lack of nitrogen diffusivity data available at low temperatures ($< 750^\circ\text{C}$). In Chapter 4 of this thesis, results from a dislocation locking technique obtained in the 500 to 1200°C temperature range are presented, which are discussed in terms of nitrogen transport.

1.4.5 Electrical activity

The majority nitrogen species in silicon, the dimer, is thought to be electrically inactive. However, many of the minority nitrogen species are likely to exhibit electrical activity, *i.e.* give rise to states in the band gap. Several studies have found deep-levels which have been attributed to nitrogen [104,131–134]. Other studies have found nitrogen containing TDs in Cz-Si [130,135,136].

Most of the current knowledge about nitrogen in silicon comes from DLTS experiments. A limitation of DLTS is that it is often difficult to associate a peak with a particular defect. Furthermore, impurities introduced during specimen preparation can also give rise to deep-levels and it is possible that the silicon used in the early studies [133,134] was not as pure as that used in the later studies [104,131,132]. Thus, the experimental results presented in this Section should be treated with extreme caution.

A summary of the DLTS results for nitrogen-related defects in silicon is given in Table 1.3. In 1982, Tokumaru *et al.* associated levels at $E_c - 0.19\text{eV}$ and $E_c - 0.28\text{eV}$ with nitrogen [133]. In 1985 Nauka *et al.* found that two nitrogen-related levels were formed during annealing at high temperatures ($\geq 900^\circ\text{C}$) at $E_c - 0.58\text{eV}$ and $E_c - 0.5\text{eV}$ [134]. Both sets of researchers concluded that the levels were associated with complexes rather than isolated nitrogen atoms. The level at $E_c - 0.5\text{eV}$ was found by Kakumoto and Takano [132] in 1996, who also found a nitrogen-related deep-level with an enthalpy of $E_v + 0.55\text{eV}$ p-type silicon. Kakumoto and Takano attributed both of these levels to the same defect: an N_2 vacancy complex (*e.g.* N_2V or N_2V_2). In 1996 Fuma *et al.* found a deep-level at $E_c - 0.42\text{eV}$ in float-zone silicon into which N_2 was in-diffused [137]. Because of the correspondence of depth profile of the level and the complementary error function, they concluded that the level was nitrogen-related and attributed it to an N_2 -vacancy complex.

Also stated in Table 1.3 are the capture cross-sections of the traps. It is noted that Nauka *et al.* suggest that the capture cross-section of the $E_c - 0.19\text{eV}$ defect is $\sim 4 \times 10^{-15}\text{cm}^2$ [134], two orders of magnitude less than the value measured in the original work [133].

Density functional theory calculations are also able to predict energy positions of certain traps. Table 1.4 provides a summary of the work of Goss *et al.* [138]. There seems to be a reasonable agreement between four of the states predicted by Goss *et al.* and the experimental values presented in Table 1.3. The calculations may help in the assignment of the experimentally observed levels to specific nitrogen-related defects.

New experimental results obtained by using DLTS on nitrogen-doped silicon are presented in Chapter 7 of this thesis.

Activation energy [eV]	Cross-section [cm ²]	Reference
$E_c - 0.19$	$\sim 8 \times 10^{-17}$	[133]
$E_c - 0.19$	$\sim 4 \times 10^{-15}$	[134]
$E_c - 0.28$	$\sim 5 \times 10^{-16}$	[133]
$E_c - 0.42$	$\sim 10^{-17}$	[137]
$E_c - 0.5$	not measured	[134]
$E_c - 0.5$	$\sim 7.6 \times 10^{-16}$	[132]
$E_c - 0.58$	$\sim 5 \times 10^{-14}$	[134]
$E_v + 0.55$	$\sim 10^{-15}$	[132]

Table 1.3: Nitrogen-related deep-levels in silicon found by DLTS.

Defect	Energy [eV]
$N_s N_s$	$E_c - 0.2$
N_s	$E_c - 0.4$
$N_s V$	$E_c - 0.5$
$N_2 I$	$E_v + 0.2$
N_s	$E_v + 0.5$

Table 1.4: Nitrogen-related deep-levels in silicon predicted by density functional theory calculations by Goss *et al.* [138].

1.4.6 Determination of nitrogen concentration

Determining the nitrogen concentration in silicon is not as straightforward as determining the oxygen concentration. Firstly, nitrogen is often present in concentrations of over two orders of magnitude lower. Secondly, there are calibration issues to consider.

In Cz-Si, a method for determining the nitrogen concentrations has been developed by Voronkov *et al.* [139]. This involves measuring depth profiles of nitrogen containing shallow thermal donors and deducing the nitrogen concentration from these. Since this technique requires the presence of oxygen it cannot be used in FZ-Si.

In FZ-Si, the content of nitrogen can be measured by IR absorption measurements. Nitrogen is known to exhibit an IR absorption peak at 963 cm^{-1} [140], which has been assigned to the nitrogen dimer [112,141]. However, nobody has yet devised an accurate method for calibrating the absorption to an absolute concentration, but due to the technological importance of nitrogen in silicon, the Japanese Electronics and Information Technology Association (JEITA) has established a working group for this purpose [142]. The consequence of no generally accepted nitrogen calibration standard being available is that manufacturers are using their own standards. Thus, nitrogen

concentrations measured by different manufacturers cannot be easily compared.

1.5 Dislocations in silicon

1.5.1 Introduction

The role of dislocations in silicon technology and the mechanisms responsible for dislocation propagation and multiplication are reviewed in this Section. For an introduction to dislocations, the reader is referred to the book by Hull and Bacon [143]. The works of Hirth and Lothe [144] and Nabarro [145] provide a more detailed overview. Additionally, Sumino has published a review of dislocations specific to semiconductor materials [146].

Dislocations in semiconductors give rise to several important effects in electronic devices; some of which are beneficial, most however, are detrimental. Impurities and defects can be removed from the junction regions of devices by a gettering mechanism. In combination with oxide precipitates and associated defects, dislocations can provide favourable trapping sites for fast-diffusing transition metal species. Impurities trapped in these dislocated areas become electrically harmless, provided that such areas are sufficiently far from the active regions of devices.

Dislocations can be extremely harmful to electronic devices. If a dislocation decorated with metal atoms crosses a junction, then the the junction characteristics and the device quality are degraded. In shallow junction transistors, for example, emitter-collector shorts (pipes) increase the leakage current and constitute the dominant failure mechanism. Several models have been proposed to be responsible for the pipes, as shown in Figure 1.17.

The presence of dislocations in semiconductors also leads to a reduction in the material's mechanical strength. High temperature treatments during device fabrication can produce considerable gravitational and thermal stresses, which in turn can lead to dislocation generation. The associated wafer warpage is a very significant problem for lithography and wafer bonding. A sufficient applied shear stress can cause dislocations to propagate to the surface of a wafer where they form microscopic steps, known as *slip*

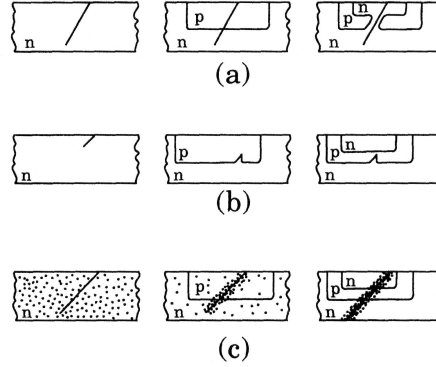


Figure 1.17: Scheme of various models proposed to explain emitter-collector shorts: (a) Enhanced diffusion of emitter dopant along crystal defect; (b) locally retarded base-dopant diffusion; (c) precipitation of fast-diffusing impurities (after Lawrence [147]).

lines, on the surface. It has been discovered that the failure of built-in MOS devices is clearly correlated with the presence of slip lines on the wafer surface [148].

Modern silicon wafers are produced free of dislocations, so any dislocations that arise are created during device processing. Unintentional damage at the wafer surface is one such way in which dislocations can be created. However, the device isolation process itself may build up a large enough lattice strain to cause the formation of dislocations. Additionally, the misfit strain around oxide precipitates (see Section 1.3.2) can also be relieved by the creation of punched-out dislocation loops [59].

Dislocations can move by crystallographic glide, which consists of slipping of a part of the crystal as a unit across an adjacent part. The glide takes place on a surface known as the glide (or slip) plane and the direction of motion is the glide direction. Glide occurs along crystallographic planes of low Miller index in the direction of densely packed atomic rows. Therefore in a crystal subjected to a stress, the direction of glide and the glide plane are not determined by the loading, but are fixed by the structure of the lattice.

1.5.2 Structure of dislocations in silicon

Silicon has a diamond lattice structure and the dislocations glide in $\{111\}$ planes [149]. Dislocations in silicon can be present in the form of hexagonal loops [150], as shown in Figure 1.18. The Burgers vector for a perfect dislocation in silicon was determined to

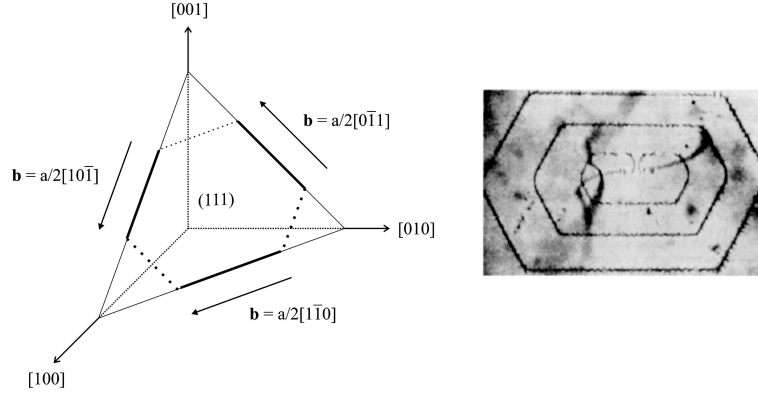


Figure 1.18: Three possible Burgers vectors for a hexagonal dislocation loop lying in the (111) plane, although only one of them is allowed in a real loop. Each of the three Burgers vectors associated with the (111) plane defines a different glide system in silicon. The famous micrograph (after Dash [32]) shows copper-decorated dislocation loops in a real silicon crystal.

be $\mathbf{b} = \frac{a}{2}\langle\mathbf{110}\rangle$, where a is the lattice constant, by an X-ray topographic study [151]. The character of a dislocation in silicon is usually screw, 60° or edge.

In silicon, a dislocation in the glide set dissociates into two partial dislocations having Burgers vector $\frac{1}{6}a\langle\mathbf{112}\rangle$, which bound a strip of 4 to 8nm of stacking fault [152]. By dissociating into partials in this way, the elastic strain energy is reduced. A dislocation in such a dissociated state is called an extended dislocation and the two partial dislocations are known as *Shockley partials*. Figure 1.19 shows a 60° dislocation which has dissociated into 30° and 90° partials.

1.5.3 Dislocation motion and multiplication

A characteristic applied shear stress is required for dislocation motion. To quantify the strength of materials, Schmid introduced the concept of *critical resolved shear stress* (CRSS) [153], which is the applied shear stress, τ , resolved on to the slip plane in the slip direction required for slip. If τ is greater than the CRSS then dislocations move with an average velocity given by [154]:

$$v = v_0 \tau^m \exp\left(-\frac{U}{kT}\right) \quad (1.13)$$

where v_0 is a phenomenological mobility coefficient, U is the activation energy for

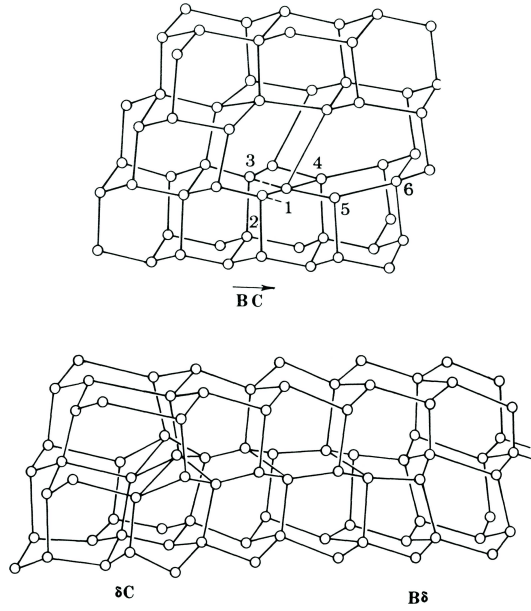


Figure 1.19: The 60° dislocation **BC** (top) and the dissociation of **BC** into the partial dislocations $\delta\mathbf{C}$ and $\mathbf{B}\delta$. On the left hand side is the 30° partial and on the right hand side is the 90° partial (after Hirth and Lothe [144]).

dislocation glide and τ is the applied stress resolved on the glide plane along the glide direction. The values of m and U depend on the class of dislocations (edge, screw or mixed), but in silicon the difference between these values for the different classes is only approximately 10%. In the case of 60° dislocations in silicon, the values are $v_0 = 1 \times 10^{-2} \text{MPa}^{-1} \text{s}^{-1}$, $m = 1$ and $U = 2.2 \text{eV}$ [146].

Dislocations can multiply by the Frank-Read mechanism [155], as depicted in Figure 1.20. The segment DD' is held at both ends by an unspecified barrier. Possible barriers are dislocation intersections, composite jogs or precipitates. An applied resolved shear stress, τ , exerts a force τb per unit length of line and tends to make the dislocation bow out. Thus, as τ increases the radius of curvature, R , decreases and the line bows out until the minimum value of R is reached in Figure 1.20 (b), where the slip plane is represented by the plane of the paper. As the line continues to expand at this stress, R increases and the dislocation becomes unstable. Subsequent events are shown in Figure 1.20 (c) to (e). The dislocation forms a large kidney-shaped loop and parts of the loop annihilate, since they have the same Burgers vector but opposite line senses. The result is that the outer loop continues to expand and a regenerated loop in the centre

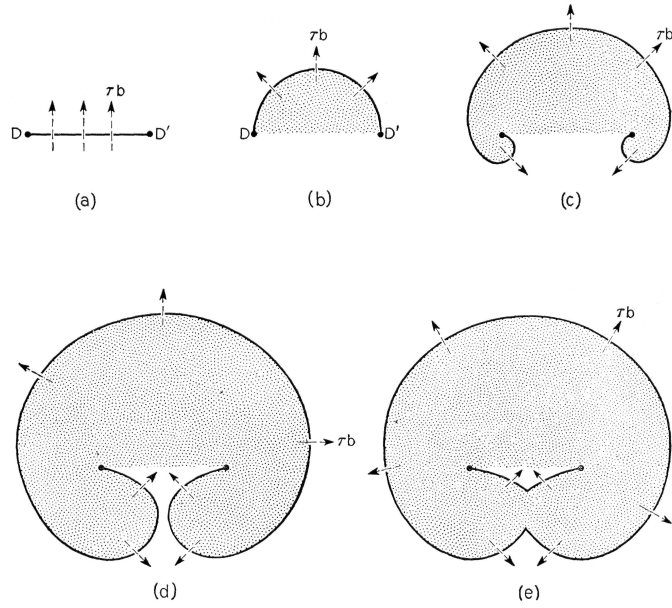


Figure 1.20: Diagrammatic representation of dislocation multiplication by a Frank-Read source (after Read [156]).

repeats the process. The micrograph shown in Figure 1.18 is an excellent example of a Frank-Read source.

1.6 Interaction of impurities with dislocations

Dopants in silicon are known to significantly affect dislocation motion. The effect of shallow dopants on the mechanical properties of silicon has been studied using a simple indentation technique by Hirsch *et al.* [157] and Roberts *et al.* [158]. It has also been found that non-electrically active dopants, such as nitrogen and oxygen, have an effect on dislocation motion. In this Section, general concepts applicable to impurity-dislocation interactions are first discussed, before the discussion moves on to the interaction of oxygen and nitrogen with dislocations.

1.6.1 An overview of dislocation locking

Accumulation of impurity atoms at a dislocation core during annealing at high temperature may render the dislocation immobilized. This effect is known as *dislocation locking*. To move a locked dislocation, a stress, referred to as the *unlocking stress*, must

be applied. The magnitude of this stress depends on the number of and nature (*e.g.* atoms, precipitates) of the impurities segregated to the dislocation core.

Cottrell [159] and Eshelby [160] developed a theory for the effect of a solute atom atmosphere on dislocations in the early 1950s. An impurity in a crystal produces a strain field and this strain field may interact with the dislocation to increase or decrease the elastic energy of the crystal. This energy change contributes to the interaction energy, E_i , of the impurity atom and the dislocation. If the impurity occupies a site on the dislocation where E_i is large and negative, then $|E_i|$ of work is required to separate the impurity and the dislocation core. In this case, because it is energetically favourable for the impurity to be at the dislocation core rather than in the bulk, the concentration of impurity at the dislocation will be greater. In covalent crystals, such as silicon, interactions of an electrical and chemical nature, as well as this elastic interaction, can contribute to the total interaction energy, E_i . The electrical and chemical interactions are less well understood than that due to the strain fields.

The chemical interactions between impurity atoms and dislocation cores in silicon have been investigated theoretically by Heggie, Umerski, Jones *et al.* [161–163] using a cluster method with a local-density-functional pseudo-potential theory. An elastic interaction can take place if conduction electrons are captured by dangling bonds which may exist near the dislocation core.

According to Boltzmann statistics, the equilibrium concentration, $C(\mathbf{r})$, of an impurity at a position $\mathbf{r}$ relative to the dislocation is given as:

$$C(\mathbf{r}) = C_0 \exp\left(-\frac{E_i(\mathbf{r})}{kT}\right) \quad (1.14)$$

This assumes that the impurities do not interact with one another because there are a large number of vacant sites at the dislocation core. E_i can be expressed in terms of the variation in the binding energy (Gibbs free energy), ΔG , according to $-E_i = \Delta G = \Delta H - T\Delta S$ and so in cylindrical polar coordinates the concentration profile is:

$$C(\mathbf{r}, \theta) = C_0 \exp\left(\frac{-\Delta G(\mathbf{r}, \theta)}{kT}\right) \quad (1.15)$$

Impurities tend to agglomerate in the cores of dislocations, where ΔG is larger. As the temperature increases, the impurities become more mobile and a greater number of impurity species are able to segregate to the dislocation core. Above a certain temperature, impurities have enough energy to evaporate off the dislocation, which reduces the overall impurity concentration at the dislocation.

1.6.2 Dislocation locking by oxygen

It was thought since the 1950s that oxygen would lock dislocations, although the first experimental evidence from Hu and Patrick published in 1975 concluded that neither interstitial oxygen or SiO_2 precipitates had a pinning effect on dislocations [164]. Surprised by their results and by using a modified method based on indentation rosettes [165], Hu was finally able to prove the dislocation pinning effect two years later [15].

An *in situ* X-ray topographical technique developed by Sumino and Harada was used to study the interaction between dislocations and impurities in silicon [151]. In separate works published in 1983, Sumino and Imai showed that dislocations originally moving in an impurity-doped crystal are immobilized when the applied stress becomes lower than a certain value [166] and that oxygen is effective at locking dislocations [154]. Senkader *et al.* have since conducted a more thorough study of dislocation locking by oxygen [16,24,26,167–171] and their technique, which is used extensively in this present work, is discussed in Section 1.7.

It is possible for precipitates to form at the cores of dislocations as the result of particular annealing conditions. Yonenaga and Sumino found that the yield strength of Cz-Si increased during the early stages of oxygen precipitation [172]. They were able to prove that precipitation was occurring by the use of TEM and micrographs from their work are shown in Figure 1.21. They also found that the yield stress decreased remarkably in the later stages of precipitation. They explained this in terms of the creation of additional dislocations from the precipitates.

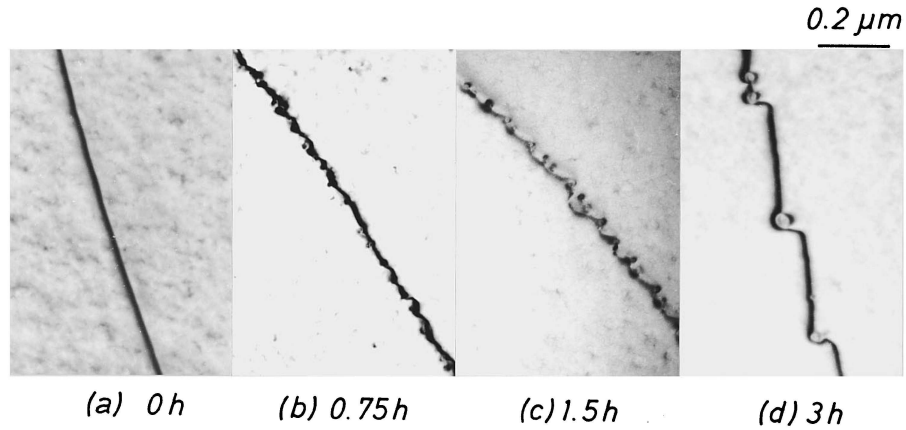


Figure 1.21: Variation in the configuration of an oxygen decorated dislocation in Cz-Si for increasing time of precipitation treatment of 900°C after solution treatment at 1300°C for 2 hours (after Yonenaga and Sumino [172]).

1.6.3 Dislocation locking by nitrogen

Using their *in situ* X-ray method, Sumino and Imai showed that nitrogen was extremely effective at immobilizing dislocations [154], as shown by the data presented in Figure 1.22. They noted that, under certain conditions, the locking in a crystal with a nitrogen concentration of $5.4 \times 10^{15} \text{cm}^{-3}$ was stronger than in a crystal with an oxygen concentration of $7.4 \times 10^{17} \text{cm}^{-3}$. Thus, according to their results, nitrogen can be more effective than oxygen at locking dislocations even though its concentration is more than two orders of magnitude lower. Further results on the locking of dislocations by nitrogen were obtained by Sumino *et al.* and these are presented in reference [11]. Recently, Giannattasio *et al.* have confirmed that nitrogen is highly effective at locking dislocations in FZ-Si and that the locking effect is similar to that due to oxygen in Cz-Si [12]. Additionally, Vedde and Gravesen have recently produced results that indicate that nitrogen improves the fracture strength of FZ-Si [173].

The mechanical properties of nitrogen-doped Cz-Si have also been studied. Three-point bending experiments by Wang *et al.* indicate that the addition of nitrogen increases the fracture strength of Cz-Si [174]. Yonenaga has recently studied the generation of dislocations from a surface scratch and found that the stress necessary to bring about dislocation generation increased with increasing nitrogen concentration [14]. He also found that nitrogen did not affect the velocity of dislocations in Cz-Si, which is in

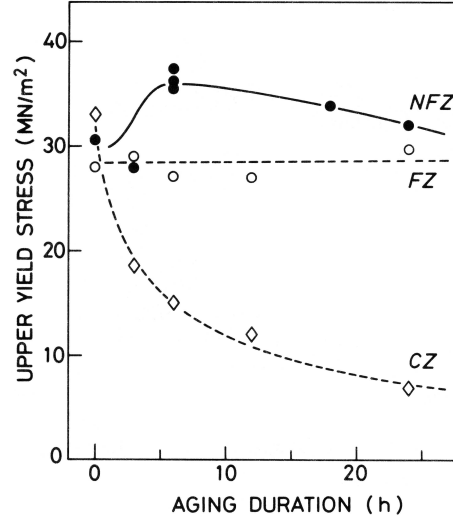


Figure 1.22: Variations of the upper yield stress against the duration of annealing at 1050°C for nitrogen-doped FZ-Si, FZ-Si without nitrogen and Cz-Si. The upper yield stresses are for [123] tensile deformation at 900°C under a strain rate of $1.1 \times 10^{-4} \text{s}^{-1}$ (after Sumino *et al.* [11]).

contrast to work done by Mezhenyi *et al.* [175].

Despite the fact that dislocation locking by nitrogen has been studied for over twenty years, some aspects of the nitrogen-dislocation interaction still remain unclear. For instance, the nature (*e.g.* atoms, precipitates) of the species responsible for dislocation locking and the binding energy of the nitrogen to the dislocation core are unknown. Additionally, the locking effect at high temperatures has not been fully investigated.

1.7 Transport investigated by dislocation locking

By measuring the stress required to move a dislocation immobilized by a particular impurity, information on the transport of the impurity can be deduced. A dislocation locking technique based on this has been developed in the Semiconductor Group of Dr P.R. Wilshaw. It has been used for over fifteen years to study the behaviour of oxygen and nitrogen impurities in silicon [12, 16, 24, 26, 167–171, 176, 176–179]. The key feature of the technique is that it enables very small values of effective diffusion coefficients to be measured. Consequently, the technique can be used to measure impurity transport in conditions under which more conventional techniques, such as SIMS, are unsuitable.

The technique involves introducing a controlled set of dislocation half-loops into a carefully produced bar of silicon. This bar is then subjected to an isothermal anneal, which allows impurities to diffuse to, and lock, the dislocations. By subjecting the different dislocation half-loops to different stresses by means of a three-point bend, the dislocation unlocking stress is measured by determining the least stress required for dislocation motion. Analysis of the unlocking stress as a function of annealing time and temperature can provide fundamental information on the behaviour of impurities in silicon. In Chapter 3, it is shown how the dislocation unlocking data can be analyzed to give the binding enthalpy of an impurity to a dislocation, the number of impurity atoms at a dislocation core, the diffusivity of an impurity and the composition of the species responsible for transport. In this Section, previous results obtained using the technique are summarized.

1.7.1 Oxygen in Cz-Si

Senkader *et al.* discovered that the unlocking stress for oxygen in Cz-Si obeyed five distinct regimes as a function of annealing time for all the annealing temperatures they investigated, as illustrated by Figure 1.23 [16, 26, 167]. In the first regime, oxygen accumulates at the dislocation core due to the diffusion process and the gradient of the initial rise is strongly dependent on temperature. The steady-state regime (regime 2) is due to the establishment of a local equilibrium between the oxygen at the dislocation core and the oxygen in the bulk. In this regime, the value of the unlocking stress is dependent on the annealing temperature and the oxygen concentration. In the next regime, the unlocking stress increases as a function of annealing time, which was explained by Senkader *et al.* as being due to precipitation at the dislocation core [16]. With increasing annealing time the unlocking stress saturates again (regime 4), before falling off rapidly as annealing time increases further (regime 5).

Describing oxygen diffusion to the dislocation core by:

$$\frac{\partial C_0}{\partial t} = D_0 \nabla (\nabla C_0 + \frac{C_0}{kT} \nabla (\Delta G)) \quad (1.16)$$

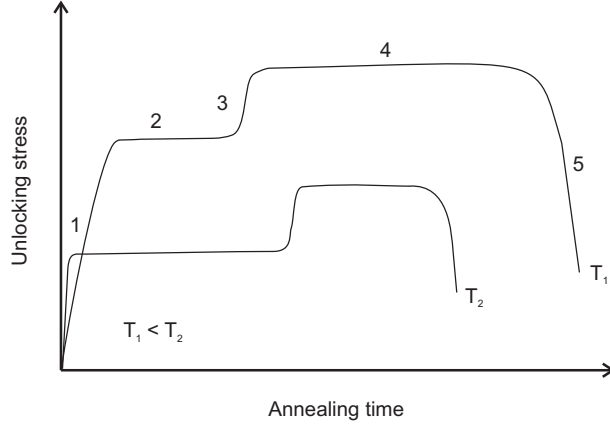


Figure 1.23: A schematic illustrating the variation in unlocking stress with annealing time and temperature (after Senkader *et al.* [167]).

where D_0 is the oxygen diffusivity, they were able to deduce values for the diffusivity of oxygen. In the high temperature regime ($\geq 650^\circ\text{C}$), the value of the activation energy for diffusion deduced by Senkader *et al.* was in good agreement with previous work done by the various authors whose work is shown in Figure 1.7 [70]. At low temperatures ($\leq 650^\circ\text{C}$), a lower value for the activation energy for diffusion of approximately 1.5eV was deduced from the dislocation locking experiments [24, 26, 167]. Thus, by investigating oxygen transport by measuring oxygen's locking effect on dislocations, they found more evidence for the enhanced diffusion discussed in Section 1.3.4.

Senkader *et al.* investigated specimens with different oxygen concentrations and labelled their specimens high ($1.04 \times 10^{18} \text{cm}^{-3}$), medium ($6.3 \times 10^{17} \text{cm}^{-3}$) and low ($2.6 \times 10^{17} \text{cm}^{-3}$). At temperatures below approximately 650°C , the values of the effective diffusivity of oxygen deduced from the dislocation unlocking data were:

$$D_{\text{low}} = 2.04 \times 10^{-7} \exp\left(-\frac{1.51\text{eV}}{kT}\right) \text{cm}^2 \text{s}^{-1} \quad (1.17)$$

$$D_{\text{medium}} = 7.33 \times 10^{-7} \exp\left(-\frac{1.52\text{eV}}{kT}\right) \text{cm}^2 \text{s}^{-1} \quad (1.18)$$

$$D_{\text{high}} = 2.16 \times 10^{-6} \exp\left(-\frac{1.55\text{eV}}{kT}\right) \text{cm}^2 \text{s}^{-1} \quad (1.19)$$

These values are plotted in Figure 1.24, on which data obtained by SIMS (at high temperatures) and stress-induced dichroism (at low temperatures) are also plotted (see

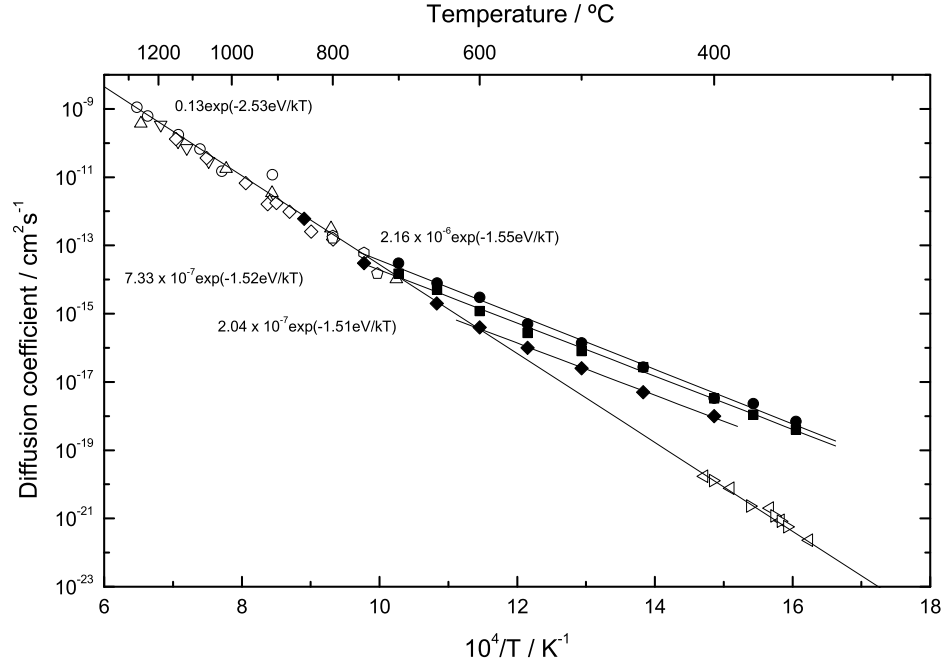


Figure 1.24: The effective diffusivity of oxygen in Cz-Si. The closed points are those obtained by the dislocation locking technique; the open points are those from SIMS and stress-induced dichroism as plotted in Figure 1.7 [70]. Specimens with a high oxygen concentration are circles, medium oxygen concentration specimens are squares and low oxygen-containing specimens are diamonds (after Senkader *et al.* [167]).

Section 1.3.3).

Additionally, by analyzing the second regime of the dislocation unlocking stress, it was possible for Senkader *et al.* to deduce the value of the binding enthalpy of the oxygen species to the dislocation core. This was done by assuming a Maxwell-Boltzmann distribution between the oxygen at the dislocation and oxygen in the bulk. From the Arrhenius plot in Figure 1.25, the binding enthalpy was found to take different values in the two temperature ranges. The fact that different binding enthalpies are deduced suggests that different oxygen species are responsible for the locking in the different temperature regimes.

An important feature of the dislocation locking technique is that it allows information on the composition of the diffusing species to be deduced. As described in detail in Chapter 3, by calculating the effective diffusivity as a function of impurity concen-

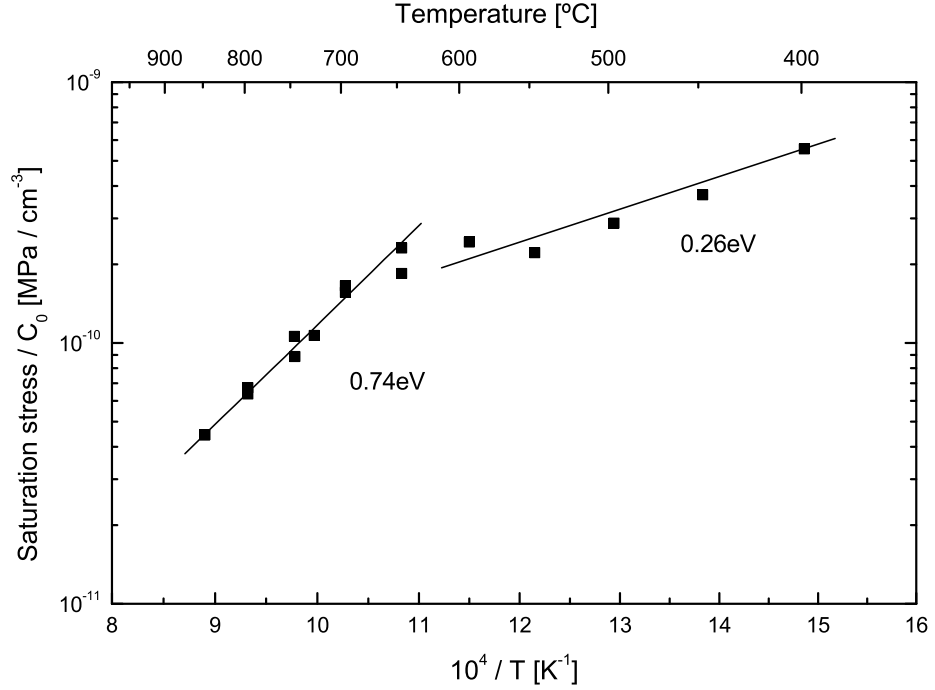


Figure 1.25: The saturation stress due to a local equilibrium between the oxygen at the dislocation core and the background oxygen concentration normalized by the oxygen concentration as a function of reciprocal temperature (after Giannattasio *et al.* [26]).

tration, it is possible to deduce information on the species responsible for impurity transport. The low temperature oxygen effective diffusivity measurements obtained by Senkader *et al.* were found to scale with oxygen concentration in a way consistent with transport by the oxygen dimer. Thus, the dislocation unlocking data may support the proposal of Gösele and Tan [25], who suggested that the oxygen dimer is responsible for the enhanced diffusion.

The value of the activation energy for diffusion at low temperatures was recently confirmed by Yarykin and Vdovin [180] who monitored oxygen loss by IR absorption techniques during annealing of Cz-Si with a high dislocation density. However, their value of the diffusivity pre-factor was approximately two orders of magnitude higher than those obtained by Senkader *et al.*. This discrepancy can be explained by the fact that the dislocation density in the work of Yarykin and Vdovin was not known accurately. This is because the dislocations in their work were not generated in a

particularly controlled way, in contrast to those in the work of Senkader *et al.*.

Recent work by Badylevich *et al.* [181] has used a technique similar to that used by Senkader *et al.* to investigate the effect of a magnetic field on the dislocation locking. They found that the effect of the locking could be strongly reduced by exposing the specimen to a 20kOe magnetic field for 2 to 3 hours [182]. They explained this in terms of spin-dependent reactions of oxygen accumulated at the dislocation core.

1.7.2 Nitrogen in FZ-Si

The dislocation locking technique used by Senkader *et al.* to investigate oxygen in Cz-Si has recently been used by Giannattasio *et al.* to investigate nitrogen in FZ-Si in the 500 to 830°C temperature range [12, 177].

The unlocking stress as a function of annealing time for certain annealing temperatures is shown in Figure 1.26. Two regimes were found for all annealing temperatures investigated. In the first regime, the unlocking stress increases approximately linearly and the gradient of the rise was found to be strongly dependent on the annealing temperature. In the second regime, the unlocking stress was found to take a constant value of approximately 50MPa for all annealing temperatures investigated. Giannattasio *et al.* explained the initial rise in terms of nitrogen diffusion to the dislocations and they explained the temperature independence of the saturation unlocking stress as being due to all the sites at the dislocation core being occupied. The consistently strong locking effect across the complete range of temperatures investigated enabled Giannattasio *et al.* to deduce that the binding energy of nitrogen to the dislocation must be at least 1.7eV.

From an Arrhenius plot of the gradient of the initial rises, Giannattasio *et al.* deduced the activation energy for the dislocation locking process to be 1.45eV. They also modelled the transport of nitrogen by using Equation 1.16, in the same way that Senkader *et al.* modelled the transport of oxygen in Cz-Si. Using the assumptions that the nitrogen dimer was responsible for the locking, and that all the states at the dislocation were full, the diffusivity of nitrogen in silicon was calculated to be:

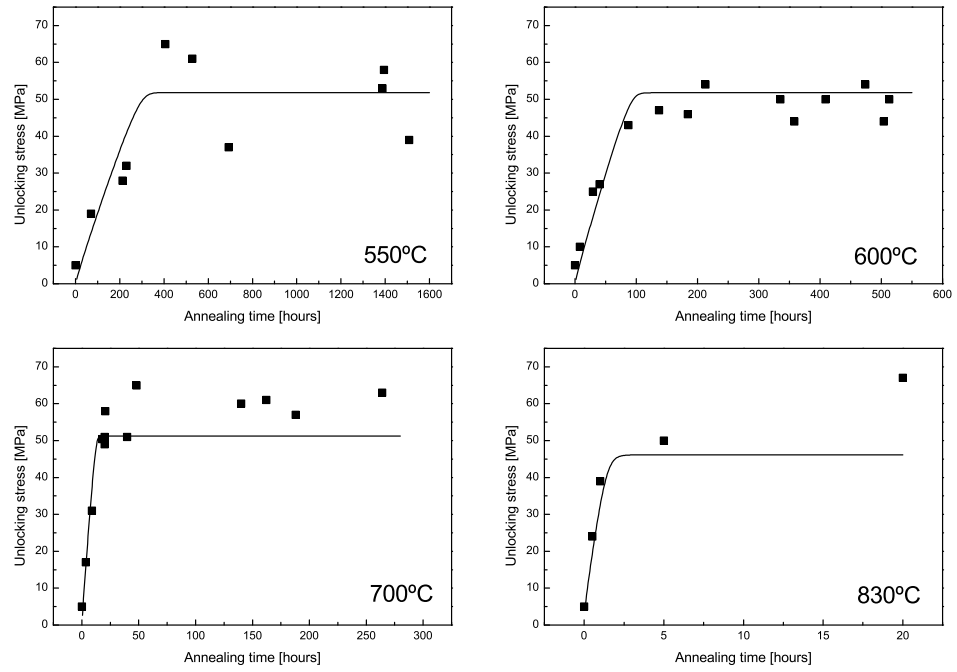


Figure 1.26: Unlocking stress as a function of annealing time for nitrogen-doped FZ-Si with a nitrogen concentration of $2.2 \times 10^{15} \text{cm}^{-3}$ (after Giannattasio *et al.* [26]).

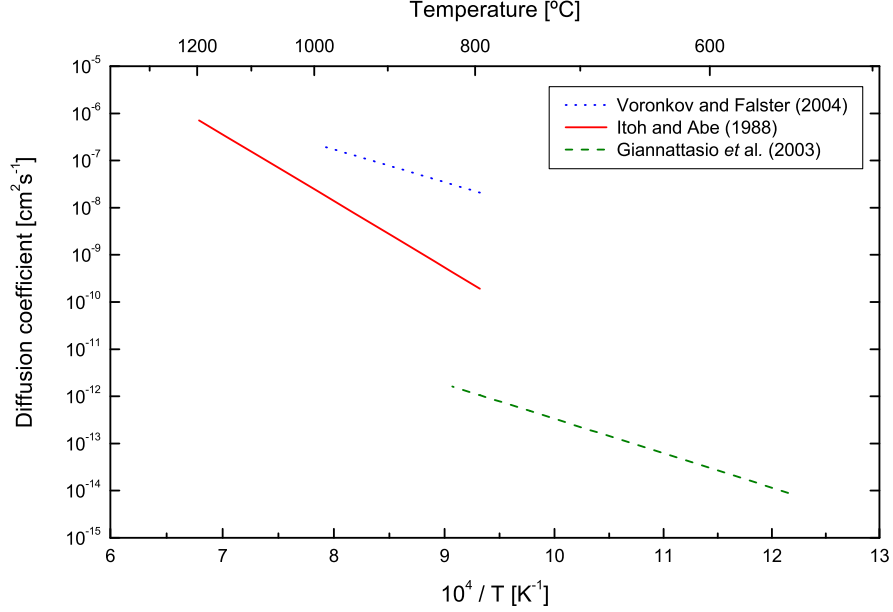


Figure 1.27: Diffusivity of nitrogen in silicon as determined by Itoh and Abe [119], Giannattasio *et al.* [12] and Voronkov and Falster [122]. It should be noted that the values of Itoh and Abe and Giannattasio *et al.* are effective diffusion coefficients, whereas the values of Voronkov and Falster are absolute diffusion coefficients.

$$D_N^{Giannattasio} = 6.8 \times 10^{-6} \exp\left(-\frac{1.45\text{eV}}{kT}\right) \text{cm}^2\text{s}^{-1} \quad (1.20)$$

This is plotted in Figure 1.27, along with the expression deduced from the SIMS out-diffusion measurements made by Itoh and Abe [119] and the value calculated by Voronkov and Falster assuming a dissociative mechanism [122]. The diffusivity deduced by Giannattasio *et al.* is significantly smaller than the other two measurements. Additionally, the activation energy for diffusion deduced by Giannattasio *et al.* is approximately half that found in *ab initio* calculations [114–116]. However, the dislocation locking results remain one of the few pieces of experimental evidence for the transport of nitrogen in silicon and the discrepancy indicates need for further research to be carried out using the technique.

This dislocation locking technique has only just started to be applied to nitrogen in silicon. The technique is certainly capable of providing more information on nitrogen in silicon, especially if different nitrogen concentrations and different temperature ranges are investigated. By applying the technique to FZ-Si with different nitrogen

concentrations, from the scaling of the unlocking stress it may be possible to deduce information on the composition of the species responsible for diffusion to the dislocation. Additionally, device manufacturers are interested in the interaction of nitrogen with dislocations at high temperatures. Oxygen is known to start to “boil off” dislocations at temperatures higher than about 800°C [16]. The dislocation locking technique will be able to determine whether nitrogen is able to maintain a strong dislocation locking effect at higher temperatures than oxygen. This would interest manufacturers of Cz-Si, who may be able to improve their products by doping them with nitrogen.

1.8 Objectives of this work

In this work, the dislocation locking technique described in Section 1.7 is applied to nitrogen-doped FZ-Si to give quantitative information on the locking of dislocations and on nitrogen transport. The technique is also used to provide information on the behaviour of oxygen in Cz-Si, including data on the transport of oxygen in Cz-Si with high concentrations of certain shallow dopants. Additionally, an investigation to determine the electrical activity of nitrogen- and oxygen-related defects is conducted using DLTS.

The aims of this work are:

1. To obtain information on the behaviour of nitrogen in FZ-Si using the dislocation locking technique (Chapter 4). The work of Giannattasio [12, 177] is extended by investigating dislocation locking by nitrogen in FZ-Si with a lower nitrogen concentration ($3 \times 10^{14} \text{cm}^{-3}$), over a wider range of temperatures (500 to 1200°C). The dislocation locking data at higher annealing temperatures allow the estimate of the binding enthalpy of nitrogen to dislocations to be refined. From analyzing the data in terms of nitrogen transport it will be possible to deduce information on the transport of nitrogen in silicon.
2. To obtain new information on the behaviour of oxygen in Cz-Si (Chapter 5). By using the dislocation locking technique, experiments will be carried out to investigate whether or not oxygen monomers and dimers exist in thermodynamic

equilibrium at approximately 550°C, to investigate the species responsible for oxygen transport at 500°C and to see how nitrogen affects dislocation locking by oxygen in Cz-Si at 550 and 600°C. Further experiments are carried out using DLTS and high-resolution DLTS (HR-DLTS) to investigate the electrical activity of oxygen at dislocations.

3. To investigate the transport of oxygen in Cz-Si with a high concentration of anti-mony and boron shallow dopants using the dislocation locking technique (Chapter 6). The dislocation unlocking data obtained are modelled by solving the diffusion equation for oxygen to a dislocation to give an experimental value for the effective diffusivity of oxygen in highly-doped silicon.
4. To investigate the electrical activity of nitrogen in the bulk of nitrogen-doped FZ-Si, nitrogen-doped NTD FZ-Si and nitrogen-doped Cz-Si using DLTS and HR-DLTS (Chapter 7).

The experimental methods used are described in the next Chapter.

Chapter 2

Experimental methods

The two experimental techniques that were used to obtain the results presented in this thesis are described in this Chapter. A mechanical dislocation locking technique was used to measure the stress required to move a dislocation pinned by nitrogen or oxygen. A capacitance-transient thermal scanning technique, known as deep-level transient spectroscopy (DLTS) and its close relative, high-resolution (Laplace) DLTS (HR-DLTS), were used to provide information on the electrical activity of nitrogen- and oxygen-related defects in silicon.

2.1 Introduction

2.1.1 Dislocation locking technique

The dislocation locking technique relies on the fact that certain impurities, including nitrogen and oxygen, diffuse to and immobilize stationary dislocations during an anneal. The stress required to unpin the dislocation from the impurity, known as the *unlocking stress*, is measured as a function of annealing time and annealing temperature. As well as providing useful information on the mechanical effects of impurities in silicon, the results obtained can be interpreted in terms of the fundamental properties of impurities in silicon. It is shown in Chapter 3 how the data obtained can be analyzed to give information on the effective diffusivity of the impurity to a dislocation, the composition of the diffusing species, its binding energy to a dislocation and the number of impurity

atoms or complexes that are at the core of the locked dislocation. The key feature of the technique is that it provides a method of measuring impurity transport over extremely small distances. It is therefore possible to measure impurity transport in conditions under which more conventional techniques (*e.g.* SIMS) are unsuitable.

The technique comprises many separate stages, as shown in Figure 2.1. A controlled set of dislocation half-loops is introduced into a carefully produced bar of silicon by indentation followed by a four-point bend at 400 to 600°C. This bar is then subjected to an isothermal anneal for a known time. After the removal of a surface layer by chemical etching, the dislocation half-loops are subjected to a range of stresses by three-point bending at a constant elevated temperature (usually 550°C). A preferential etch is used to reveal the dislocations and the critical resolved shear stress for dislocation motion is measured. The stages of the technique are discussed individually in more detail in Section 2.3.

Each iteration of the process illustrated in Figure 2.1 produces a single data point on a graph of annealing time versus unlocking stress at a particular annealing temperature. To obtain a useful set of data, it is necessary to perform the technique with a wide range of annealing times at a wide range of annealing temperatures. Many of the stages of the technique are extremely intricate in nature and there is a significant probability of specimen failure during the mechanical testing stages. Thus, obtaining a useful set of data can be a particularly time consuming process.

2.1.2 DLTS

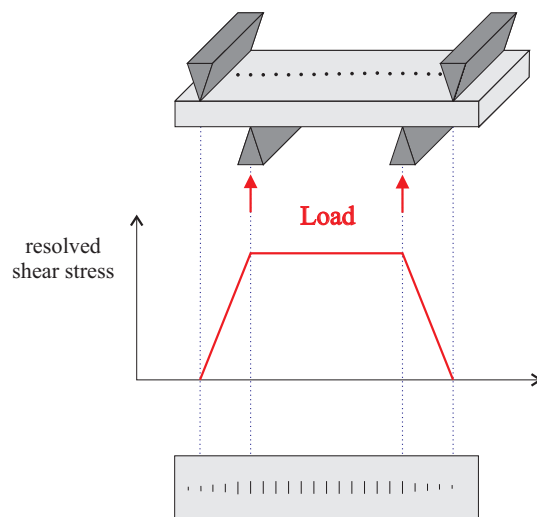
DLTS is an experimental technique developed by Lang [77] which is used in this work to deduce information on the electrical activity of nitrogen- and oxygen-related defects in silicon. In contrast to substitutional dopants which produce shallow states near the band edges, impurity complexes often give rise to deep states (or traps), defined as states which have an ionization energy of greater than approximately one tenth of the material's bandgap.

To carry out DLTS in this work, Schottky barriers are subjected to a non-equilibrium condition (a reverse bias) and the capacitance transient is measured as the system re-

1. **Indent** silicon bar with diamond tip



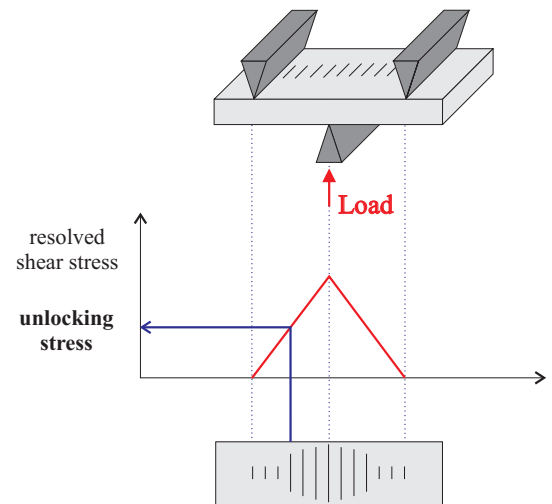
2. **Four-point bend** to grow dislocations



3. **Anneal** to allow impurities (such as oxygen or nitrogen) to diffuse to dislocations

4. **Planar etch** to remove indent damage and negate effects of impurity out-diffusion

5. **Three-point bend** to unlock dislocations



6. **Preferential etch** to reveal dislocations

Figure 2.1: The different stages of the dislocation locking technique used in this work.

turns to equilibrium. This is repeated many times as a function of temperature in the 70 to 320K range. Analysis of the experimental data allows for parameters such as the ionization enthalpy of the defect state, its concentration and its capture cross-section to be found. The theory and experimental techniques relating to DLTS are discussed in more detail in Section 2.6.

A problem with DLTS is that it is difficult to separate states which are closely spaced in energy. To overcome this problem a technique called high-resolution (Laplace) DLTS (HR-DLTS) [183, 184] is used. This technique, which uses the same experimental set-up as in conventional DLTS, involves averaging many capacitance transients at fixed temperature. By taking the inverse Laplace transform of the average transient, the same parameters of a trap as in conventional DLTS can be deduced. The HR-DLTS technique is described in more detail in Section 2.7.

2.2 Specimens

Silicon wafers produced by the float-zone and Czochralski methods containing different known concentrations of nitrogen and oxygen were used in this work. All the wafers were commercially grown. A summary of the key properties of all the wafers used is given in Table 2.1. The wafers used are described in more detail in this Section.

2.2.1 FZ-Si

Nitrogen-free FZ-Si

For control purposes, nitrogen-free p-type FZ-Si wafers provided by Wacker were used (reference: 047874). The wafers had a thickness of $525\mu\text{m}$, had a diameter of 100mm, were mirror polished on one side, were of (100) orientation and were boron doped to a concentration of approximately $9.6 \times 10^{16}\text{cm}^{-3}$. The concentration of oxygen and nitrogen were below the detection limits of FTIR; $< 10^{16}$ and $< 10^{14}\text{cm}^{-3}$ respectively.

Wafer (s)	Doping [cm^{-3}]	[O] $\times 10^{17} \text{cm}^{-3}$	[N] $\times 10^{15} \text{cm}^{-3}$	Technique in which used
FZ-Si	[B] = 9.6×10^{16}	< 0.1	< 0.1	Dislocation locking (Chapter 4)
NFZ-Si	[B] $< 1.3 \times 10^{12}$	< 0.1	0.3	Dislocation locking (Chapter 4)
NFZ-Si	[P] = 4.3×10^{13}	< 0.1	0.7	DLTS (Chapter 7)
NTD NFZ-Si	[P] = 2.9×10^{13}	< 0.1	~ 1.5	DLTS (Chapter 7)
Cz-Si	[B] $\approx 1.5 \times 10^{15}$	~ 6.4	< 0.1	Dislocation locking and DLTS (Chapters 5, 6 and 7)
Cz-Si with low [O]	not known	0.8	< 0.1	Dislocation locking (Chapter 5)
p ⁺ Cz-Si	[B] $\approx 5.4 \times 10^{18}$	~ 7.5	< 0.1	Dislocation locking (Chapter 6)
n ⁺ Cz-Si	[Sb] $\approx 3.4 \times 10^{18}$	~ 10.6	< 0.1	Dislocation locking (Chapter 6)
NCz-Si	[B] $\approx 8 \times 10^{14}$	~ 5.7	1.0 to 2.1	Dislocation locking and DLTS (Chapters 5 and 7)

Table 2.1: A summary of the key properties of the different types of silicon used in this work. Oxygen concentrations are quoted to the DIN 50438/I standard.

Nitrogen-doped FZ-Si

Two sets of nitrogen-doped FZ-Si (NFZ-Si) wafers provided by Topsil Semiconductor Materials A/S were used in this work.

For dislocation locking experiments, (100) orientation wafers with a nitrogen concentration of $3 \times 10^{14} \text{cm}^{-3}$ (determined by FTIR) were used (reference: 212820-3). The wafers were doped with boron (p-type) and their electrical resistivity was extremely high ($> 10,000 \Omega \text{cm}$). These 200mm diameter wafers were mirror polished on both sides and the thickness of the wafers was approximately $490 \mu\text{m}$.

A different set of nitrogen-doped FZ-Si wafers were used for the DLTS experiments (reference: 4110041). These were 100mm in diameter, of (111) orientation and doped with phosphorus (n-type) to give an electrical resistivity of $240 \Omega \text{cm}$ to $360 \Omega \text{cm}$. Whilst the manufacturer estimated the nitrogen concentration in these wafers from the growth conditions to be 1.5 to $2 \times 10^{15} \text{cm}^{-3}$ [185], a subsequent SIMS investigation on the same wafers by Charles Evans and Associates revealed that the nitrogen concentration was in fact $7 \times 10^{14} \text{cm}^{-3}$ [186].

The concentration of oxygen in both sets of nitrogen-doped FZ-Si wafers was below the detection limit of FTIR ($< 10^{16} \text{cm}^{-3}$).

Nitrogen-doped neutron transmutation doped FZ-Si

Nitrogen-doped neutron transmutation doped (NTD) FZ-Si was investigated using DLTS. The wafers were produced by Topsil Semiconductor Materials A/S, who bombarded a standard ingot of (100) orientation nitrogen-doped FZ-Si with neutrons from a nuclear reactor. The resulting wafers were phosphorus doped (n-type) with a resistivity of $150 \Omega \text{cm}$. The wafers were provided as-sliced, and so had to be polished on one side before use, and were approximately 120mm in diameter.

The nitrogen concentration of these wafers was not measured, but was thought to be around 1.5 to $2 \times 10^{15} \text{cm}^{-3}$ from the growth conditions [185]. The oxygen concentration was below the detection limit of FTIR ($< 10^{16} \text{cm}^{-3}$).

2.2.2 Cz-Si

Standard Cz-Si

For dislocation locking and DLTS experiments, wafers of nitrogen-free p-type Cz-Si provided by MEMC Electronic Materials Inc. were used (references: 8GGEF/57 and 8GGEF/113). The wafers were 200mm in diameter, were of (100) orientation and were mirror polished on one side. The wafers were doped with boron to a concentration of approximately $1.5 \times 10^{15} \text{cm}^{-3}$. The wafers had been subjected to an initial homogenization anneal carried out at 1000°C for 15 minutes known as a *tabula rasa* treatment [53]. This dissolved any grown-in precipitates and created a 3 to $4\mu\text{m}$ denuded zone at the surface.

The oxygen concentration of the wafers were determined by FTIR to be $6.59 \times 10^{17} \text{cm}^{-3}$ (DIN 50438/I) for 8GGEF/57 and $6.32 \times 10^{17} \text{cm}^{-3}$ (DIN 50438/I) for 8GGEF/113.

Cz-Si with low oxygen concentration

For dislocation locking experiments, a 100mm diameter wafer of Czochralski silicon with an oxygen $8 \times 10^{16} \text{cm}^{-3}$ was used. The wafer was obtained from Dr K. Bothe at Institut für Solarenergieforschung in Emmerthal, Germany.

Cz-Si with high electrical doping levels

Wafers of nitrogen-free Cz-Si with different concentrations of shallow dopants were provided by MEMC Electronic Materials Inc. and were investigated by the dislocation locking technique.

The highly-doped n-type material was doped with antimony to a concentration of 5.6 to $63 \times 10^{17} \text{cm}^{-3}$ (reference: 94FKA0H). The wafers were 200mm in diameter, had a (100) orientation and were mirror polished on one side.

The highly-doped p-type material was doped with boron to a concentration of 2.7 to $8.0 \times 10^{18} \text{cm}^{-3}$ (reference: 23FNA109). The wafers were 150mm in diameter, had a (100) orientation and were mirror polished on one side.

FTIR, the standard method of measuring oxygen concentrations in silicon, cannot

be used on highly-doped material because of free carrier absorption. Therefore, the oxygen concentrations in the wafers with a high concentration of shallow dopants was determined by gas fusion analysis. The oxygen concentration of the antimony doped material was approximately $1.06 \times 10^{18} \text{cm}^{-3}$ (DIN 50438/I) and the oxygen concentration of the boron doped material was approximately $7.5 \times 10^{17} \text{cm}^{-3}$ (DIN 50438/I).

Nitrogen-doped Cz-Si

Wafers of nitrogen-doped Cz-Si (NCz-Si) were provided by MEMC Electronic Materials Inc. (references: 27HPDI and 27HPDD). Both sets of wafers were (100) with 200mm diameter, had a thickness of approximately $700 \mu\text{m}$ and were mirror polished on one side. Both sets of wafers were doped with boron (p-type) to a concentration of approximately $8 \times 10^{14} \text{cm}^{-3}$.

The nitrogen and oxygen concentrations were determined by FTIR. The nitrogen concentration of the 27HPDI wafers was $2.10 \times 10^{15} \text{cm}^{-3}$ and the oxygen concentration was $5.73 \times 10^{17} \text{cm}^{-3}$ (DIN 50438/I). The nitrogen concentration of the 27HPDD wafers was $1.02 \times 10^{15} \text{cm}^{-3}$ and the oxygen concentration was $5.81 \times 10^{17} \text{cm}^{-3}$ (DIN 50438/I).

Both sets of wafers were used for DLTS experiments and the material with the higher nitrogen concentration was also used for dislocation locking experiments.

2.3 Dislocation locking technique

The dislocation locking technique introduced in Section 2.1.1 is used extensively in this work to investigate the properties of nitrogen and oxygen in silicon. As illustrated by Figure 2.1, the technique comprises many separate stages. These stages are described individually in this Section.

2.3.1 Cleaving and polishing

Specimen preparation had to be done with the utmost care as the smallest imperfection in the bar could lead to mechanical failure. Rectangular pieces of (100) silicon measuring 30mm by approximately 5mm were cleaved from wafers using a diamond-tipped

cutting tool. A set of these bars was mounted with wax in a slit cut into a cylindrical piece of aluminium with one of the long rough edges facing out of the slit.

The edges were then smoothed using a rotary pre-grinder with 600 and 1200 grit silicon carbide paper. A micrometer was used to measure the combined depth of the aluminium holder and the width of the bar and the edges of the bars were ground until both ends of the bar were the same width (to approximately $\pm 50\mu\text{m}$). They were then polished with $6\mu\text{m}$ followed by $1\mu\text{m}$ diamond pastes, until no scratches were visible. A final chemomechanical polishing stage was done using colloidal silica (“Syton”), the particle size of which was approximately 70nm [187]. The specimens were then remounted and the alternate edges of the bars were polished in the same way. After polishing the width of the bars measured $4\pm 1\text{mm}$.

The bars were removed from the holder and put into acetone. They were then cleaned in acetone in an ultrasonic bath. A cotton bud dipped in acetone was used to remove any stubborn wax. Bars were then etched in a planar etch solution (see Section 2.4.1), which removed any remaining damage to the edges. The bars were etched for two minutes before being turned over and etched for a further two minutes. The bars were rinsed in distilled water after the etch, prior to being cleaned in methanol.

Some specimens were mirror polished on both sides and hence the two sides of the bars were indistinguishable. A small scratch was made with a diamond scribe at one end of such specimens to ensure that the working side could be identified. This scratch was always made in a region of the specimen that was not subjected to high stresses and so did not lead to the generation of unwanted dislocations.

2.3.2 Indentation

Room temperature indentation was chosen as the method of creating a regular array of dislocation sources. Indentation introduces a residual stress into a localized region of the single-crystal silicon. This residual stress is frozen into the crystal structure until a certain transition temperature is reached, above which a stress-relieving mechanism takes place. The crystal minimizes its energy by punching out prismatic dislocation half-loops from the indent. The indentation geometry is shown in Figure 2.2.

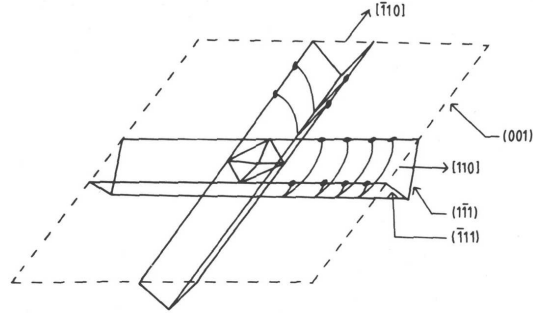


Figure 2.2: Geometry of indentation rosette on a (100) silicon surface (after Roberts *et al.* [158]).

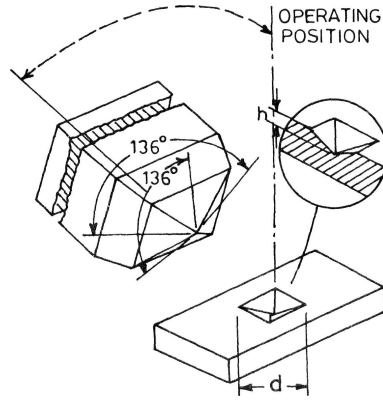


Figure 2.3: The geometry of a Vickers indenter (after Bhushan and Gupta [188]).

Microhardness tester

For the majority of specimens, a Vickers diamond tip mounted in a microhardness tester made by Matsuzawa Seiki Co. Limited, was used to make indents along the length of the bar. A Vickers diamond tip is a highly polished square-based pyramidal diamond with face angles of 136° , the geometry of which is shown in Figure 2.3. The depth of indentation is approximately one seventh of the diagonal length [188]. In this work, the microhardness tester was used to provide 10g loads for a dwell time of 5s. The Vickers diamond tip used in this work was supplied by UK Calibrations Limited and it was used solely for applying the small loads required for production of specimens used with the dislocation locking technique.

For indentation, the specimens were placed on the microhardness tester's adjustable stage and they were aligned to be parallel to the edge of the stage by the use of a glass microscope slide. The stage's micrometer screw gauge was adjusted so that indents

were placed at $250\mu\text{m}$ intervals along the length of the bar. Because of the geometry of the bending rig used, it was usually sufficient to place indents in the centre 18mm of the bar only.

Nanoindenter

In this work it was occasionally necessary to create arrays of indents which were not possible, or too time consuming, to make with the microhardness tester. In these cases indents were made using an MTS NANO Indenter XP, which could be pre-programmed to produce a complex array of precisely located indents. This used a three-sided pyramidal Berkovich tip to produce the indents.

The disadvantage of using this highly sophisticated piece of equipment is that it produces indents at a much slower rate than the microhardness tester. The rate of indentation was approximately one indent per 150s for the nanoindenter compared to one indent per 20s for the microhardness tester. However, a benefit of using the nanoindenter was that it also provided vast quantities of data relating to each indent. For instance, for each indentation it recorded load-displacement data, an example of which is shown as Figure 2.4. This clearly shows the pressure-induced phase transformation (from a diamond structure to an hexagonal closed packed structure) that silicon undergoes during indentation [189]. This has previously been observed using a much less sophisticated homemade nanoindenter by S.A. Galloway [176].

2.3.3 Bending set-up

Testing rig

The bending processes were carried out in the specially produced testing rig shown in Figure 2.5. Molybdenum was chosen as the material for rig as it has a low solubility in silicon and is stable at high temperatures.

The rig comprises two fixed knife-edges and three equally-spaced slots into which knife-edges can be inserted as required. The material chosen for these removable knife-edges was 1mm diameter molybdenum wire. On top of the knife-edges, a small piece

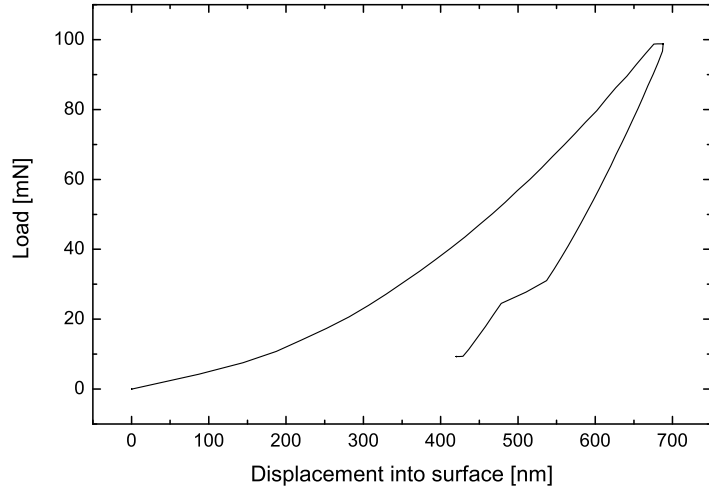


Figure 2.4: Load against displacement graph produced by the nanoindenter for a 10g indentation into the surface of silicon. The large change in gradient on unloading is due to a pressure-induced phase transformation.

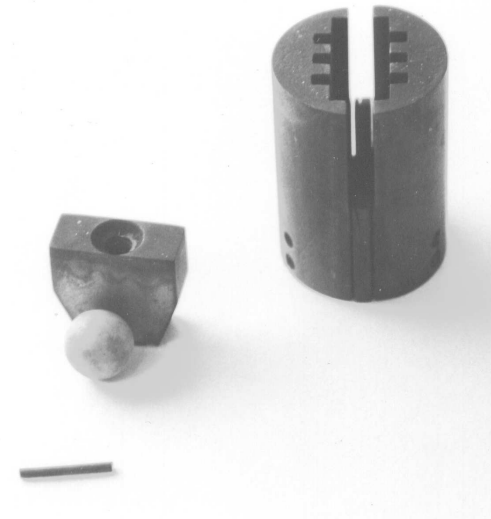


Figure 2.5: The molybdenum testing rig used for four- and three-point bending.

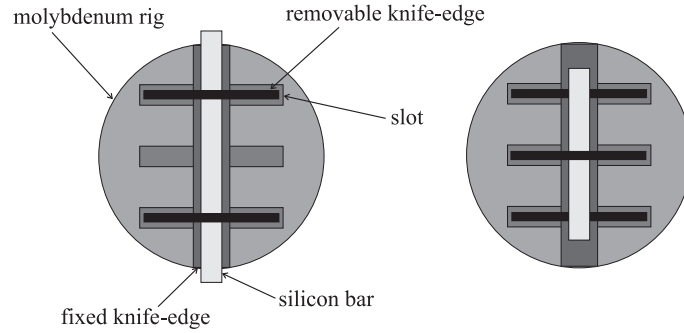


Figure 2.6: Top view of the testing rig in a four-point bend (left) and three-point bend configuration (right). The working side of the silicon bars faces the page. A grooved piece of molybdenum (not shown) is placed on top of the knife-edges.

of molybdenum with appropriately cut grooves was placed. The grooves were aligned with the knife-edges on top of the bar. The piece of molybdenum had a hemispherical shape cut into the top, in which a 7mm diameter steel ball could rest.

By varying the positions of the knife-edges used it was possible to use the same rig for both four- and three-point bending. The two knife-edge configurations used are illustrated in Figure 2.6. Note that approximately 5mm is cleaved from each end of the bar prior to three-point bending.

Periodically it was necessary to clean the rig to remove any oxide formed on its surface at elevated temperatures. This was done by placing all the molybdenum components in a solution of distilled water, hydrogen peroxide and ammonium hydroxide mixed in an approximate ratio of 8:1:1 for approximately five minutes. The cleaning process was only used when strictly necessary, as it also acted to etch the molybdenum and hence flattened the fixed knife-edges.

Mechanical testing set-up

The set-up used for mechanical testing of the silicon specimens is illustrated in Figure 2.7. The load was applied to a specimen by placing a steel rod with a hemispherical recess in it at one end in contact with the ball on top of the rig. This rod was used to transfer a load by one of two ways. For the application of high loads ($> 20\text{N}$), this rod was connected to the load cell of a mechanical testing machine. For low loads ($< 20\text{N}$), free weights were placed on top of the rod by hand.

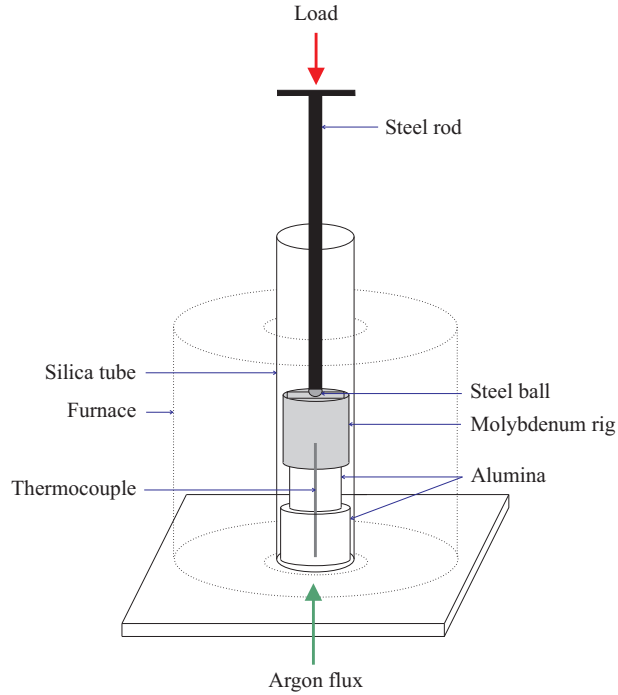


Figure 2.7: The mechanical testing set-up depicted schematically.

It was important to know accurately the temperature the specimen is at during bending. For the three-point bending stage this is critical, as the unlocking process for dislocations is known to be dependent on temperature [168, 190]. The tip of a type-K thermocouple was therefore arranged to pass through a circular hole in the bottom of the rig, so to be located just a few millimeters beneath the specimen. The temperature of the specimen in the rig is thought to be known to $\pm 5^\circ\text{C}$.

A cylindrical piece of quartz tubing was then placed over the rig and the thermocouple. A cylindrical furnace supplied by Severn Furnaces Limited was placed over the quartz tube. A seal was formed at each end of the quartz tubing by applying a small amount of high vacuum grease to the ends of the tubing. Small holes were drilled in the base of the testing frame so that argon gas could be pumped through the rig from the bottom. The seal above the rig was formed by a rubber glove, into which a hole had been cut for a tube carrying discharged argon.

High loads ($>20\text{N}$) Loads greater than approximately 20N were applied with an Instron 1195 mechanical testing machine. The steel rod that makes contact with the



Figure 2.8: Bending using the Instron 1195 mechanical testing machine.

ball on top of the testing rig was attached to the load cell with a screw attachment, as shown in Figure 2.8.

The load measured by the load cell was displayed on a digital voltage meter. The system was set up so that a load of 9.81N was recorded as 1V. Before making a measurement it was necessary to calibrate and zero the load cell. To do this, the calibration switch on the Instron controller was turned on and the full scale load dial was set to 20. The calibration knob was then turned to give an output voltage of 10.00V. The load cell was set to zero by turning on the zero switch and then adjusting the zero knob to give a voltage as close to zero as possible. The steel rod was then attached to the load cell, by fully tightening the screw attachment and then loosening by half a turn. During the course of the work it was noticed that for an accurate calibration it was necessary to switch on the Instron controller at least half an hour prior to making a measurement.

After attachment of the rod, the controller was programmed to apply the desired load. This was done by adjusting the load cell amplifier until the required load was displayed on the voltage meter. The maximum and minimum knobs on the load cycler were then adjusted to the point at which their respective lights were just on.

Calibration mass	Mean measured value	Discrepancy
100g	101.03mV	1.03%
1kg	1.0079V	0.79%
2kg	2.0025V	0.13%

Table 2.2: Values recorded by the load cell with different calibration weights attached. The voltage was recorded for the same weight hung from the load cell on ten separate occasions.

The load cell amplifier was then adjusted again to read zero and the Instron level was brought up at full speed to a pre-set stop just before the rod was able to make contact with the ball. At this point, time was allowed for the specimen to warm up to the required temperature. After release of the stop, the rig was initially brought up to the rod at a speed of 0.2mm/minute. As the voltage reading exceeded 500mV the speed was reduced to the slowest setting (0.05mm/minute). The load applied then increased slowly without further user intervention until the desired load was reached. At this point, the load cycler kept the applied load as close to the programmed load as possible by automatically making small adjustments to the position of the rig.

The load cell was calibrated in tension by hanging accurate calibration weights of different masses from the load cell, as shown in Table 2.2. Even with a load as low as 100g, the error in the load cell was approximately 1%; far less significant than other experimental errors.

It was found that the accuracy of making measurements with the Instron was questionable for loads less than 20N. This was because it was extremely difficult to zero the load cell amplifier accurately after selecting the desired load. Additionally, subsequent work by C.R. Alpass has revealed that the load cell reading can vary during the bend process [191]. The output voltage measured without the rod being attached to the load cell after the bend process was found to change by as much as 0.5V from the zero voltage programmed in prior to the bend process.

Low loads (<20N) For loads less than approximately 20N, the load was applied using separate free weights, as shown in Figure 2.9. These were carefully placed on top of the steel rod by hand.



Figure 2.9: Bending using free weights.

2.3.4 Four-point bending

A four-point bend was used to grow dislocations from each indent to form an array of dislocation half-loops with uniform diameter. The dislocation half-loops were grown to a diameter of 100 to 200 μm . In a four-point bend, the tensile stress between the centre two knife-edges is constant, as illustrated in Figure 2.10. This constant tensile stress is given by [192, 193]:

$$\sigma_{\text{constant}} = \frac{3Pa}{wh^2} \quad (2.1)$$

where σ_{constant} is the tensile stress between the central two knife edges (MPa), P is the load (N), a is the distance between an outer knife-edge and the nearest inner knife-edge (mm), w is the width of the beam (mm) and h is the thickness of the beam (mm). Typical values of these variables are given in Table 2.3.

For a dislocation to move, the resolved shear stress, τ , in its glide plane must be non-zero. To calculate the resolved shear stress, the tensile stress, given by Equation 2.1, must be multiplied by the appropriate Schmid factor. The Schmid factor is defined

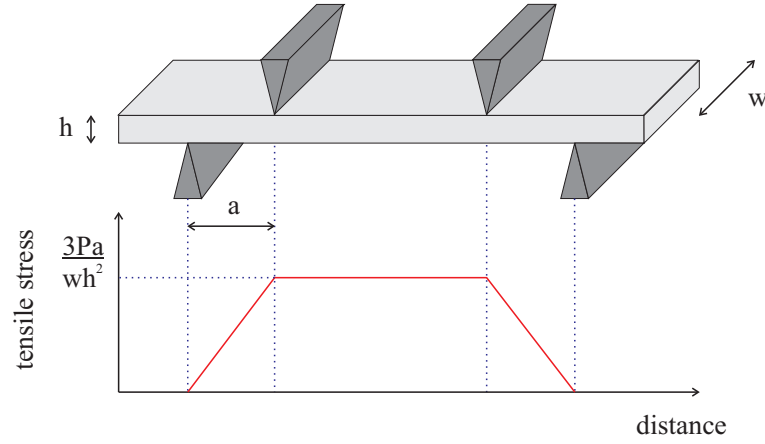


Figure 2.10: The stress distribution in a specimen subjected to a four-point bend.

Symbol	Description	Typical values
P	Applied load	$2\text{N} \leq P \leq 150\text{N}$
a	Loading span for four-point bend	6mm
b	Width of silicon beam	$2.5 \leq b \leq 4.5\text{mm}$
h	Thickness of silicon beam	$0.3 \leq h \leq 0.75\text{mm}$
l	Load span for three-point bend	6mm

Table 2.3: Typical values used in Equations 2.1 and 2.4.

as $\cos \theta \cos \phi$, where θ is the angle between the slip direction and the applied tensile stress and ϕ is the angle between the applied tensile stress and the normal to slip plane as shown in Figure 2.11. For the $a/2[10\bar{1}](111)$ slip system activated in this work, the Schmid factor is $\frac{1}{\sqrt{6}}$. Thus, in the four-point bending configuration:

$$\tau_{\text{constant}} = \frac{\sigma_{\text{constant}}}{\sqrt{6}} \quad (2.2)$$

To perform the four-point bend, the sample was placed with its working side in

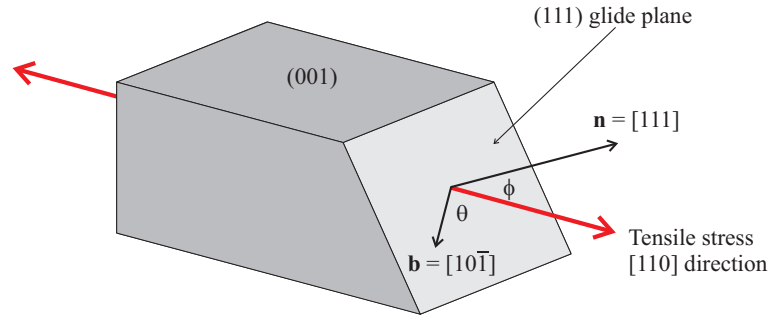


Figure 2.11: (111) glide plane activated during bending.

contact with the fixed knife-edges of the mechanical testing rig described in Section 2.3. Two pieces of molybdenum wire were placed in the outer slots in the rig above the sample, as illustrated in Figure 2.6. The grooved piece of molybdenum and the steel ball were placed on top. The load was then applied as the sample heated up from approximately 400 to 600°C, to grow the dislocation half-loops to the required diameter. The time required to grow the dislocations was calculated by using the following approximate expression for dislocation velocity found by Imai and Sumino [166]:

$$v = 10^{-2} \tau \exp\left(-\frac{2.2\text{eV}}{kT}\right) \text{ms}^{-1} \quad (2.3)$$

After the time required to grow the dislocation half-loops to the desired diameter at 600°C, the furnace surrounding the rig was switched off with the load still applied. The sample was then allowed to cool to below 400°C before the load was removed and the sample was removed from the rig. The reason for “cooling under load” in this way is to reduce the amount of unwanted dislocation locking that occurs when the sample is left at high temperatures for a short time. Nitrogen and oxygen impurities cannot accumulate at a moving dislocation and when the load is finally removed at below 400°C impurity diffusion occurs too slowly for significant locking to occur during the time the specimen is left unstressed in the rig.

Cooling under load is a modification to the dislocation locking technique used previously in the Semiconductor Group. The modification was found to significantly reduce the amount of dislocation locking in specimens which were not intentionally subjected to an anneal. For instance, in the case of Cz-Si with an oxygen concentration of approximately $6.3 \times 10^{17} \text{cm}^{-3}$, the unlocking stress measured in specimens which were not intentionally annealed was approximately 3MPa in specimens which were cooled under load, compared to 10MPa in specimens which were not cooled under load [16].

2.3.5 Annealing

After the controlled array of dislocations was introduced into the silicon bars, an anneal stage allowed nitrogen and oxygen impurities to diffuse to the dislocation cores. In this work, specimens were annealed at temperatures in the 350 to 1200°C temperature range for times of up to 4,345 hours.

Specimens were generally annealed under argon atmosphere in specially produced silica furnace tubes. Specimens were placed in silica furnace boats produced by St Gobain Glass, which could be pushed into or pulled out of the hot-zones of pre-annealed furnaces with a hooked silica rod. As the rate of accumulation of an impurity at a dislocation core is strongly dependent on the annealing temperature, it was imperative that the annealing temperature was strictly controlled. The temperature was measured as a function of position inside a furnace and care was taken to ensure that the specimens were always in the hottest part of the furnace, where the temperature was found to be most uniform. The furnace tubes were designed so that a type-K thermocouple could be positioned in the centre of the hot-zone of the furnaces, immediately above the specimens. To avoid any contamination of the sample from the metal thermocouple, its end was encapsulated in a silica sheath.

An experiment was performed to ensure that the thermocouple above the specimen provided a good measure of the actual temperature of the specimen. The tip of a type-K thermocouple was placed between two silicon specimens, which were tied together by thin pieces of wire. The specimens were placed in the hot-zone of a furnace in the usual way and the temperature was measured simultaneously from the thermocouple in contact with the specimens and the sheathed thermocouple above the specimens. At 450 and 550°C the thermocouples measured the same temperature to within 2°C. This does not represent the overall error in the annealing temperature measurement however, because it is also difficult to ensure that the specimens and thermocouples are located precisely in the part of the furnace where the temperature is most uniform. The magnitude of the error in annealing temperature depends on the particular annealing set-up used, as discussed below.

Anneals at temperatures of 750°C and lower were carried out in cylindrical furnaces of approximately 30cm in length produced by Severn Furnaces Limited or Instron SFL. The annealing temperature of the specimens in these furnaces was known to $\pm 5^\circ\text{C}$. Anneals at temperatures of 750 to 1000°C were performed in a cylindrical furnace produced by Lenton, which was approximately 55cm in length. The temperature of the specimen in this furnace was known to $\pm 10^\circ\text{C}$. The reason for the error being larger than for the other cylindrical furnaces is that because of the furnace's size it is more difficult to position the specimens and thermocouple accurately.

Anneals at 1100 and 1200°C were carried out by first sealing the specimens in evacuated silica ampules. These were then placed inside a pre-heated chamber furnace. After the required annealing time, the ampule was quickly removed with tongs and was dropped into a water bath. This quenching ensured that no substantial dislocation locking occurred during cooling. The annealing temperature of specimens annealed in this way was known to $\pm 20^\circ\text{C}$. The reason for the magnitude of this error is that the temperature distribution in the chamber furnace is not particularly uniform and it was not possible to arrange for the thermocouple to be in direct contact with the ampule. Additionally, to insert the specimens into the furnace, a large door at the front of the furnace had to be opened. This significantly reduced the temperature of the furnace and the time taken for the furnace to stabilize at the desired temperature represented a significant proportion of the total annealing time.

After annealing, a planar etch (see Section 2.4.1) was used to remove material from each specimen. Generally 30 μm of material was removed, however 50 μm of material was removed from specimens annealed at 900°C and higher. The purpose of this etch was two-fold. Firstly, it removed the damage associated with the indents and therefore it ensured that new dislocations were not grown from each indent at the subsequent three-point bend stage. Secondly, it removed material in which the nitrogen or oxygen concentration might be lower than that in the bulk, due to any out-diffusion that may have occurred.

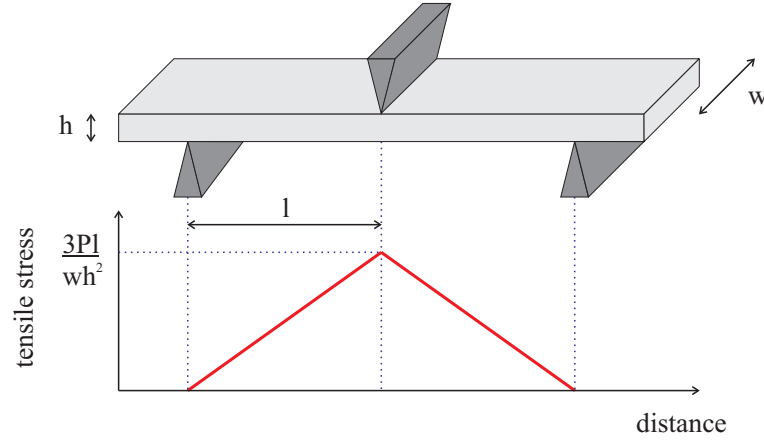


Figure 2.12: The stress distribution in a specimen subjected to a three-point bend.

2.3.6 Three-point bending

After the annealing stage the same amount of nitrogen or oxygen is segregated to every set of dislocations in a particular specimen. The amount of the impurity at the dislocation core was measured by finding the stress required to bring about dislocation motion. This was done by subjecting the silicon bar to a three-point bend at elevated temperature (usually 550°C). A three-point bend is used as it subjects the specimen to a stress distribution that varies approximately linearly from the outer knife-edges to the centre, as illustrated in Figure 2.12. Each set of dislocation half-loops arising from a particular indent is therefore subjected to a different stress. The maximum tensile stress in a three-point bending configuration is given by [192, 193]:

$$\sigma_{\max} = \frac{3Pl}{wh^2} \quad (2.4)$$

where l is the distance between the outer knife-edge and the central knife-edge (mm) and the other symbols are as defined in Equation 2.1. Typical values of these variables are given in Table 2.3, although they were measured individually for each specimen.

It is again necessary to resolve this shear stress on to the glide plane of the dislocation. The peak resolved shear stress on the dislocations in a sample subjected to a three-point bend is therefore given by:

$$\tau_{\max} = \frac{\sigma_{\max}}{\sqrt{6}} \quad (2.5)$$

The ends of the silicon bar were cleaved off to leave a bar with a length of 20mm and the inner three knife-edges of the testing rig were used, as illustrated in Figure 2.6. The applied load was chosen appropriately for the expected unlocking stress so that the unlocking takes place approximately half way between the outer and central knife-edges. The three-point bend was performed using the methods described in Section 2.3.3.

The standard method was to perform the three-point bending process at 550°C. This temperature was chosen so that the dislocations moved at a convenient speed, and so the results obtained could be directly compared to earlier work [12, 16, 24, 26, 167–171]. It was found in earlier work that the magnitude of the unlocking stress of dislocations locked by oxygen in Cz-Si was dependent on the temperature of the unlocking process [26, 168]. It was therefore important that temperature of the three-point bending process was accurately controlled. In this present work, the temperature dependence of the unlocking stress of dislocations locked by nitrogen in FZ-Si was investigated. In order to do this the unlocking process was carried out at different temperatures in the 500 to 700°C temperature range.

It was important to perform the three-point bending process for long enough for the first set of unlocked dislocations to be clearly identified. Since the dislocation velocity is generally proportional to the resolved shear stress [166], the duration required for the three-point bend depends on the applied load. For low loads (< 20N) the three-point bend was left to run overnight. Furthermore, when large resolved shear stresses (> 150MPa) were being measured, a significant number of specimens broke on loading.

2.3.7 Determination of unlocking stress

After three-point bending the specimen was subjected to a preferential etch (see Section 2.4.2), which produced etch pits at points where the dislocations intersected the surface of the silicon bars. Differential interference contrast microscopy (see Section 2.5) was

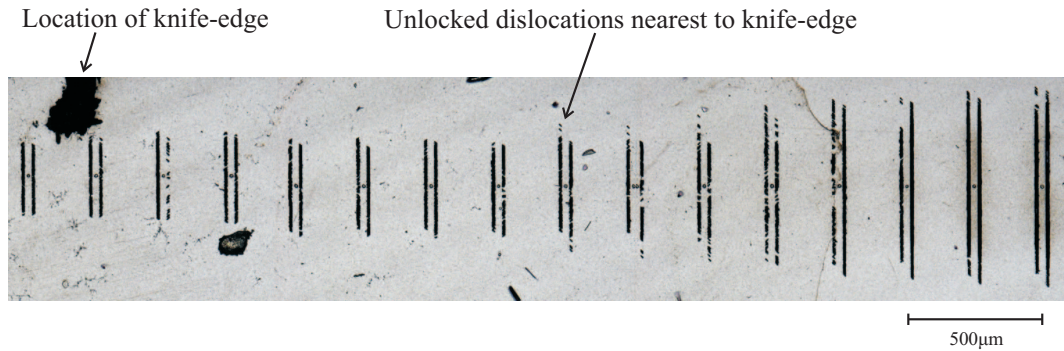


Figure 2.13: An optical micrograph showing part of a specimen containing locked and unlocked dislocations, which has been subjected to a preferential etch.

then used to determine the position of the first dislocation set arising from a particular indent that had moved during the three-point bending process.

An example of part of a specimen containing locked and unlocked dislocations that has been subjected to a preferential etch is shown in Figure 2.13. In the optical micrograph the set of unlocked dislocations nearest the outer knife-edge can be seen. The unlocking effect can be seen more clearly when each array of dislocations is observed at higher magnification.

The distance to the first unlocked set of dislocations from the knife-edge and the separation of the knife-edges were measured using the graticule of an optical microscope. A micrometer was used to measure the dimensions of the bar and the widths of the bar at each end were averaged. These measurements were made to $\pm 10\mu\text{m}$. By assuming the linear stress distribution of Equation 2.4, the position of the first unlocked dislocation was converted into an unlocking stress. Due to the symmetry about that central knife-edge, each specimen gave rise to two different unlocking stress values; the average of which was then found. Figure 2.14 illustrates how the unlocking stress is determined in an actual specimen.

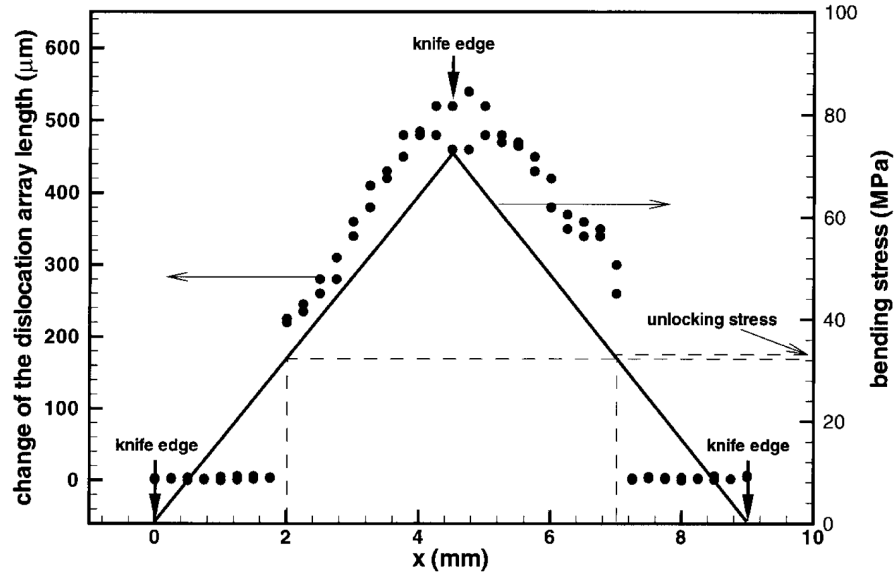


Figure 2.14: An example of how the unlocking stress is determined. The graph shows the change in dislocation diameter against position for a specimen which has been subjected to a three-point bend. The first set of dislocation half-loops which moves determines the unlocking stress (after Senkader *et al.* [16]).

2.3.8 Errors

The dislocation locking technique comprises many separate stages and potential sources of error exist at many of these. Errors which affect the measured value of dislocation unlocking stress can be introduced at the annealing stage (*e.g.* temperature, time), at the unlocking stage (*e.g.* temperature, load) and at the measurement stage (*e.g.* determination of first set of dislocations to move, dimensions). Two sources of error, that in the annealing temperature and that in the temperature at which the unlocking process takes place, are thought to be significantly larger than the others and represent the vast majority of the overall error in the dislocation unlocking stress measured.

The largest source of potential error is that in the annealing temperature, as the dislocation locking process is strongly thermally activated, with an activation energy of approximately 1.5eV for nitrogen [12] and for oxygen below approximately 650°C [24,167]. The magnitude of this essentially random error depends on the annealing set-up used, which in turn depends on the required annealing temperature (see Section 2.3.5). For annealing conditions chosen to lie on the initial rise in dislocation unlocking stress (regime 1), an error in the annealing temperature affects the measured dislocation un-

Error	Lower temperature	Maximum error	Upper temperature	Maximum error
$\pm 5^\circ\text{C}$	350°C	25%	750°C	9%
$\pm 10^\circ\text{C}$	800°C	16%	1000°C	11%
$\pm 20^\circ\text{C}$	1100°C	20%	1200°C	17%

Table 2.4: Error in the amount of impurity segregated to the dislocation core in the initial rise of dislocation unlocking stress (regime 1) due to an error in annealing temperature. It is assumed that the activation energy for dislocation locking process is 1.5eV.

locking stress. An estimate of the maximum error in the amount of impurity segregated to the dislocation can be made from the activation energy for the dislocation locking process. The maximum error in the unlocking stress can be calculated as the ratio of the dislocation locking stress at the highest temperature allowed by the estimated error to the dislocation unlocking stress at the intended temperature minus one. These errors are stated as a percentage at the extremes of the temperature range investigated with each different annealing set-up in Table 2.4. It can be seen that the maximum error in unlocking stress in the first regime due to an error in annealing temperature is approximately ± 9 to 25%.

Another large error is that in unlocking temperature. The unlocking temperature is known to $\pm 5^\circ\text{C}$. An estimate of the maximum possible error due to the error in unlocking temperature can be obtained from the work of Senkader *et al.*, who investigated the temperature dependence of the unlocking stress for given annealing conditions [26, 168]. This contribution to the overall error is approximately $\pm 5\%$.

Although the dislocation locking technique relies on a mechanical measurement, the effects of errors in the terms in Equation 2.4 used for the stress calculation are very small compared to the errors associated with temperature. The absolute value of the overall error in the unlocking stress depends on the annealing and unlocking conditions used. The absolute value of the error also depends on which regime the measured dislocation unlocking stress is in. For oxygen in Cz-Si, the error will generally be less in regime 2 than in regime 1, as the value of the unlocking stress in regime 2 is controlled by a lower activation energy (0.74 or 0.26eV depending on annealing temperature [26]). For nitrogen in FZ-Si, the error in regime 2 depends on the mechanism responsible for the formation of the second regime, which, as discussed in Chapter 4, is a matter of debate.

As a general rule however, it can be assumed that an unlocking stress measurement is accurate to better than approximately $\pm 25\%$.

A key feature of the dislocation locking technique used in this work is that it enables the transport of impurities to be measured, using the analysis presented in Chapter 3. Values of diffusion coefficients of impurities in silicon typically vary over many orders of magnitude over the temperature range over which silicon is processed. The precision of such measurements is limited and values are often stated to just one significant figure. Thus, the fact that there is an error of order 25% in the dislocation unlocking stress measured is not particularly significant from the point of view of transport measurements.

Another feature of the dislocation locking technique is that it can be used to identify the composition of the diffusing species. This relies on finding the ratio of effective diffusivity values in material with different impurity concentrations (see Section 3.4). Since it is only possible for nitrogen and oxygen concentrations to vary at most by approximately an order of magnitude, and because the expected ratio of effective diffusion coefficients may be expected to vary with the square root of the ratio of concentrations in some circumstances, an error of $\pm 25\%$ may be significant when analyzing the data in this way.

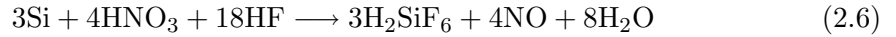
It should be noted that experimental data on a particular graph of unlocking stress versus annealing time may not show scatter of $\pm 25\%$. Since a large component of the experimental error arises from an error in annealing temperature, and because specimens were generally annealed in batches from which one specimen was periodically removed, it is may be the case that all specimens at a particular annealing temperature experienced the same error in annealing temperature. However, when comparing data taken in material with different impurity concentrations, which may have been taken by different investigators with slightly different annealing set-ups, it is important to take the full size of the potential error into account.

2.4 Etching

Two types of wet chemical etching were used in this work. A planar etch was used to remove uniform layers of material from the silicon bars; a process which was necessary after the annealing stage in the dislocation locking technique. A preferential (or defect-revealing) etch was used to reveal the intersection of the dislocations with the surface of the material as an etch pit, thus allowing dislocations to be observed by using optical microscopy. In this Section the etching processes used are described.

2.4.1 Planar etching

A planar etch, comprising 8% HF (40%), 75% HNO₃ (69%) and 17% CH₃COOH (glacial), was used to remove uniform layers of silicon. The nitric acid causes the formation of a silicon oxide layer on the surface of the silicon, which is stripped away by the hydrofluoric acid, according to:



The acetic acid dilutes the system so that the etching process is well controlled.

The planar etch used in this work is commonly used for removing layers of silicon, although previously published data for the rate of etching [194] were found to be unreliable, partly because the concentrations of the acids used were not always stated. It was therefore necessary determine the etch rate for the planar etch used.

The technique used to determine the rate of etching is illustrated in Figure 2.15. Two small drops of Lacomit varnish were applied to mirror polished pieces of high resistivity ($> 10,000\Omega\text{cm}$) nitrogen-doped FZ-Si. Lacomit varnish was chosen as it is not easily broken down by the acids. The pieces of silicon were placed with the Lacomit drops facing upwards in a beaker containing the planar etching solution. The etch was left for a controlled period of time at a known temperature and was not stirred. After the specimens were removed from the etching solution, the Lacomit drops were removed in acetone, leaving mesas unaffected by the etch. A Surfscan 3J Somicronic Profiler was used to measure the height of the mesa, which corresponds to the amount

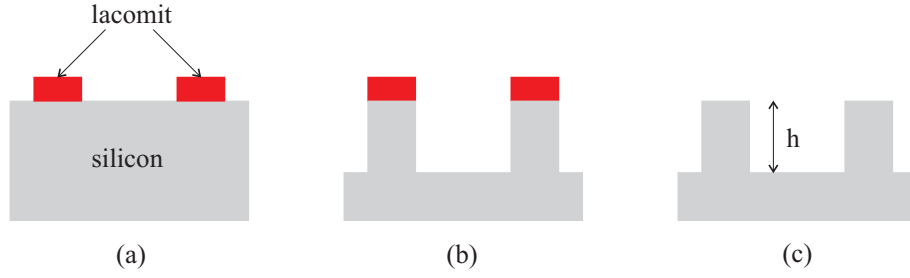


Figure 2.15: (a) Drops of Lacomit varnish are placed on the surface of some silicon and are allowed to dry. (b) The material is etched using a precisely made etching solution, which does not attack the Lacomit varnish. (c) The Lacomit varnish is removed in acetone and the height of the mesa, h , is determined by profilometry.

of material removed.

The amount of material removed as a function of time and temperature is shown in Figure 2.16. It can be seen that the planar etching solution removed silicon at the rate of approximately $0.78\mu\text{m}$ per minute at room temperature (21°C). The planar etching process was also found to be thermally activated, with an activation energy of approximately 0.28eV . The planar etching process was carried out at room temperature in this work.

2.4.2 Preferential etching

As well as removing uniform layers of silicon, chemical etching was used to reveal dislocations intersecting the surface of the silicon bars. The preferential etching process again relies on oxidation and dissolution. If the chemical reaction is such that dissolution is slow, then the etching process occurs more rapidly at sites where atomic bonds are weakened. The composition of the etch used depends on the electrical properties of the material being etched.

The etch pits enabled the position of the dislocations to be measured under optical microscopy, as shown by the example in Figure 2.13. The scanning electron micrograph in Figure 2.17 shows that the etch pits created are extremely deep.

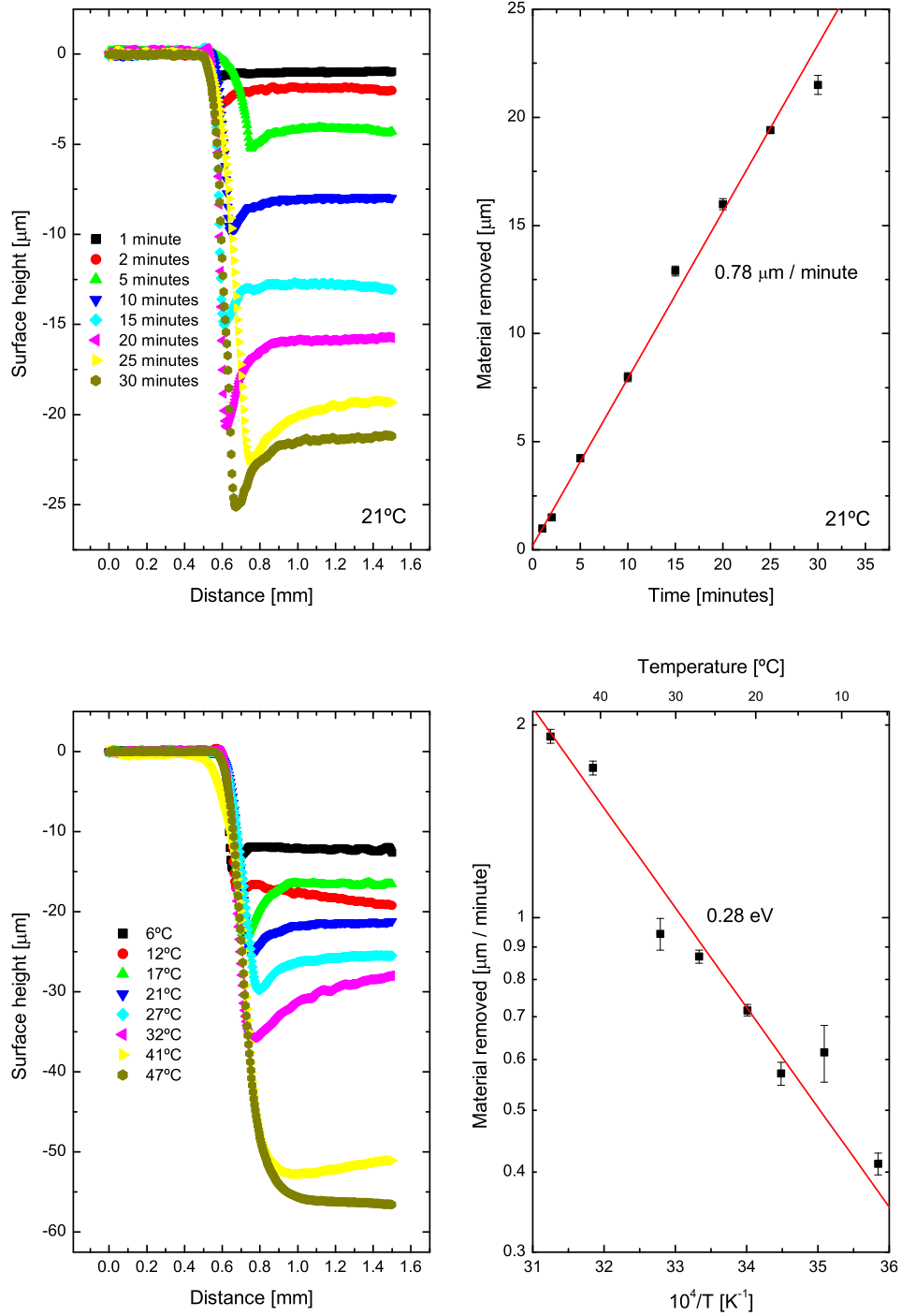


Figure 2.16: Planar etching as a function of time at 21°C (top) and temperature (bottom). The graphs on the left show profilometer data for the transition between the unetched and etched parts of the silicon bar, from which the graphs on the right are derived.

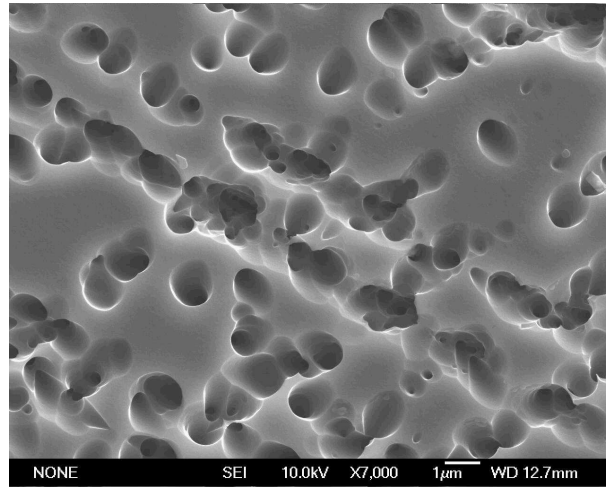


Figure 2.17: Etch pits created by preferential etching of dislocation-containing silicon with a standard electrical doping level, imaged using a JEOL 6500F scanning electron microscope (courtesy of D.J. Stowe and Dr A. Giannattasio).

Material with standard electrical doping level

An etch comprising 0.3M CrO_3 and HF (40%) mixed in the ratio 5:4 was used to reveal the presence of dislocations in silicon with standard electrical doping levels ($< 10^{17} \text{cm}^{-3}$). This is sometimes referred to as the Sirtl etch [195]. Dislocations could be seen after etching for a few minutes,. However, to make sure that all the etch pits were clearly visible, specimens were etched for approximately 10 minutes.

Material with high electrical doping level

In the course of work done previously in the Semiconductor Group, it was discovered that the preferential etch described above produced a mottled surface without dislocation-related etch pits in silicon with an electrical doping level of approximately 10^{18}cm^{-3} or higher [178]. Therefore, when etching material with a high electrical doping level, two different etching methods were used; one for n-type material and another for p-type material.

n-type material To reveal dislocation etch pits in highly-doped n-type material, the specimen was first subjected to a dip in HF (40%) for approximately 20s to remove any silicon oxide that may have formed on the surface. The specimen was then placed in a

preferential etch solution comprising HF (40%), HNO₃ (69%) and CH₃COOH (glacial) mixed in the ratio 1:3:10. It was found that the the rate at which defects are revealed by this etch is much slower than the rate at which defects are revealed when etching low-doped material. It was found that specimens needed to be etched for at least 30 minutes before etch pits could be seen clearly.

p-type material The same etching solution for highly-doped n-type material was used to etch highly-doped p-type material, except in this case it was necessary to perform the etching process in an ultrasonic bath under illumination from a microscope light source. It was found that it was necessary to etch the specimen in this way for approximately 10 minutes. The etch caused a dark stain to form on the surface of the specimens, so after etching it was necessary to clean the specimen in NH₄OH (10%) solution in an ultrasonic bath. This allowed the dislocations to become clearly visible under an optical microscope.

2.5 Differential interference contrast microscopy

Reflected light differential interference contrast (DIC) microscopy was used in this work to observe etch pits and slip lines associated with dislocations in silicon. Irregularities on the material's surface give rise to optical path differences upon reflection of light and these amplitude variations provide a topographic profile. In reflected light DIC microscopy, the image can often be considered to be a true three-dimensional representation of a surface geometry, provided that it is possible to make a clear distinction between raised and lowered regions of the specimen.

The key features of the reflected light DIC microscope are shown in Figure 2.18. The key component is a single Nomarski birefringent prism [196] which can be translated laterally along the optical axis. Light from an incandescent source is first passed through a polarizer. The beam is then passed through a prism that separates it into components which are separated by a very small distance. The beams then pass through the objective and then reflect off the specimen. The optical path taken by a light ray is also shown in Figure 2.18.

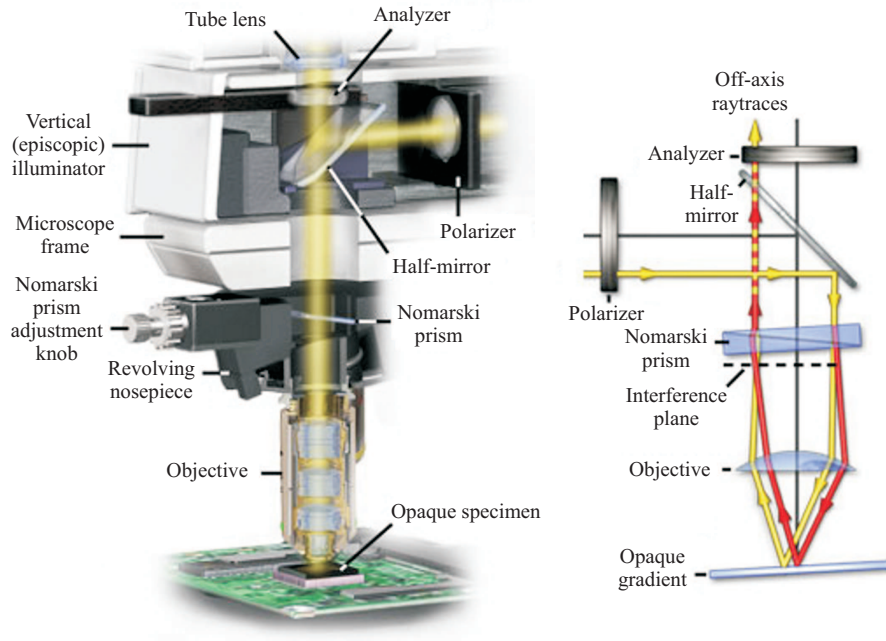


Figure 2.18: Reflected light DIC microscope (left) and the optical pathway for a single off-axis light ray (after Brandmaier *et al.* [197]).

A good optical microscope working in DIC mode can allow for features as small as 5nm in height to be detected. By first subjecting the specimen to a defect-revealing etch (see Section 2.4.2), much smaller crystal defects can be imaged. An example of an etched specimen imaged by a reflected light DIC microscope is shown in Figure 2.13.

2.6 DLTS

Deep-level transient spectroscopy (DLTS) is a capacitance transient thermal scanning technique which is a highly effective method of studying electrically active defects in semiconductors. DLTS probes the depletion (or space-charge) region of a Schottky barrier or p-n junction and is able to give the activation enthalpy of a trap, its concentration and its capture cross-section. In this work, the Schottky barrier method of operation is used to provide information on majority carrier traps due to nitrogen- and oxygen-related defects in silicon. An extension to DLTS, high-resolution (Laplace) DLTS (HR-DLTS), is also used in this work and is described in Section 2.7.

In this Section, a brief overview of the theory of emission by majority carrier traps

is presented, before the experimental set-up used is discussed. For more information on the theory behind DLTS, the reader is referred to the original work of Lang [77], and to review articles by Miller *et al.* [198], Palmer [199] and Mooney [200].

2.6.1 Schottky diodes

Schottky diodes are formed when a metal is brought into contact with a semiconductor. The physics of a Schottky diode is similar to that of a p-n junction insofar as a depletion region forms in the vicinity of the junction. From Gauss' theorem, it can be shown that the width of the depletion region, W , in the case that the number of shallow dopants, N_d , is much greater than the number of occupied trap states, is given by [201]:

$$W = \sqrt{\frac{2\epsilon_0\epsilon_s V_{\text{total}}}{eN_d}} \quad (2.7)$$

where ϵ_0 is the permittivity of free space, ϵ_s is the permittivity of the semiconductor (~ 11.695 for silicon [202]) and $V_{\text{total}} = V_{\text{bi}} - V_{\text{forward}}$ under forward bias or $V_{\text{total}} = V_{\text{bi}} + V_{\text{reverse}}$ under reverse bias. The fact that varying the applied bias varies the width of the depletion region is the basis of the DLTS technique. This is discussed later on in this Section.

For a given Schottky diode, the capacitance is determined by the width of the depletion region, W , and the Schottky barrier area, A , according to:

$$C = \frac{A\epsilon_0\epsilon_s}{W} \quad (2.8)$$

Since the width of the depletion region is given by Equation 2.7, the density of carriers can be deduced from a plot of $\frac{1}{C^2}$ against V_{applied} , which is positive in the case of a forward bias or negative in the case of a reverse bias. This so-called Mott-Schottky plot has the following form:

$$\frac{1}{C^2} = \frac{2(V_{\text{bi}} - V_{\text{applied}})}{A^2 q \epsilon_0 \epsilon_s N_d} \quad (2.9)$$

Alternatively N_d can be deduced directly from the experimental data, by using:

$$N_d = -\frac{2}{A^2 q \epsilon_0 \epsilon_s \frac{d}{dV_{\text{applied}}} \left(\frac{1}{C^2} \right)} \quad (2.10)$$

2.6.2 DLTS theory

The technique of DLTS involves measuring the capacitance change that occurs when a diode returns to equilibrium from a non-equilibrium condition. By repeating this measurement over a wide temperature range, it is possible to deduce information on the properties of the traps.

The technique is illustrated by the energy band diagrams in Figure 2.19, which show the same Schottky diode under different applied bias conditions. A deep-level due to an electrically active defect is included on the diagrams. In the initial state shown in (a), states in the deep-level with energies up to the quasi-Fermi level (or μ_{ref}) are filled with electrons. If the reverse bias is then increased so that the diode is in the state shown in (b), some filled states in the deep-level lie above the quasi-Fermi level. Electrons in these states then empty into the conduction band of the semiconductor. By Gauss' theorem, the width of the depletion region depends on the amount of charge enclosed. Additionally, by Equation 2.8, the capacitance of the Schottky diode depends on the width of the depletion region. Therefore, the charge that leaves the depletion region causes the variation in the width of the depletion region, which leads to the capacitance change measured in DLTS.

In Figure 2.19 the active depth sampled by DLTS is shown. This depth is a function of the initial applied bias (known as the *fill pulse*) and the applied reverse bias. It is often the case that near the surface of the material there are more defect states, which are not typical of the bulk of the material. Thus, by choosing a sufficiently large reverse bias fill pulse it is possible to avoid these defects.

The rate of emission from a trap is a thermally activated process. By the principle of detailed balance, the emission rate is given by [77]:

$$e = \frac{\sigma \langle v \rangle N}{g} \exp\left(-\frac{\Delta G}{kT}\right) = \frac{\sigma \langle v \rangle N}{g} \exp\left(-\frac{\Delta H}{kT}\right) \exp\left(\frac{\Delta S}{k}\right) \quad (2.11)$$

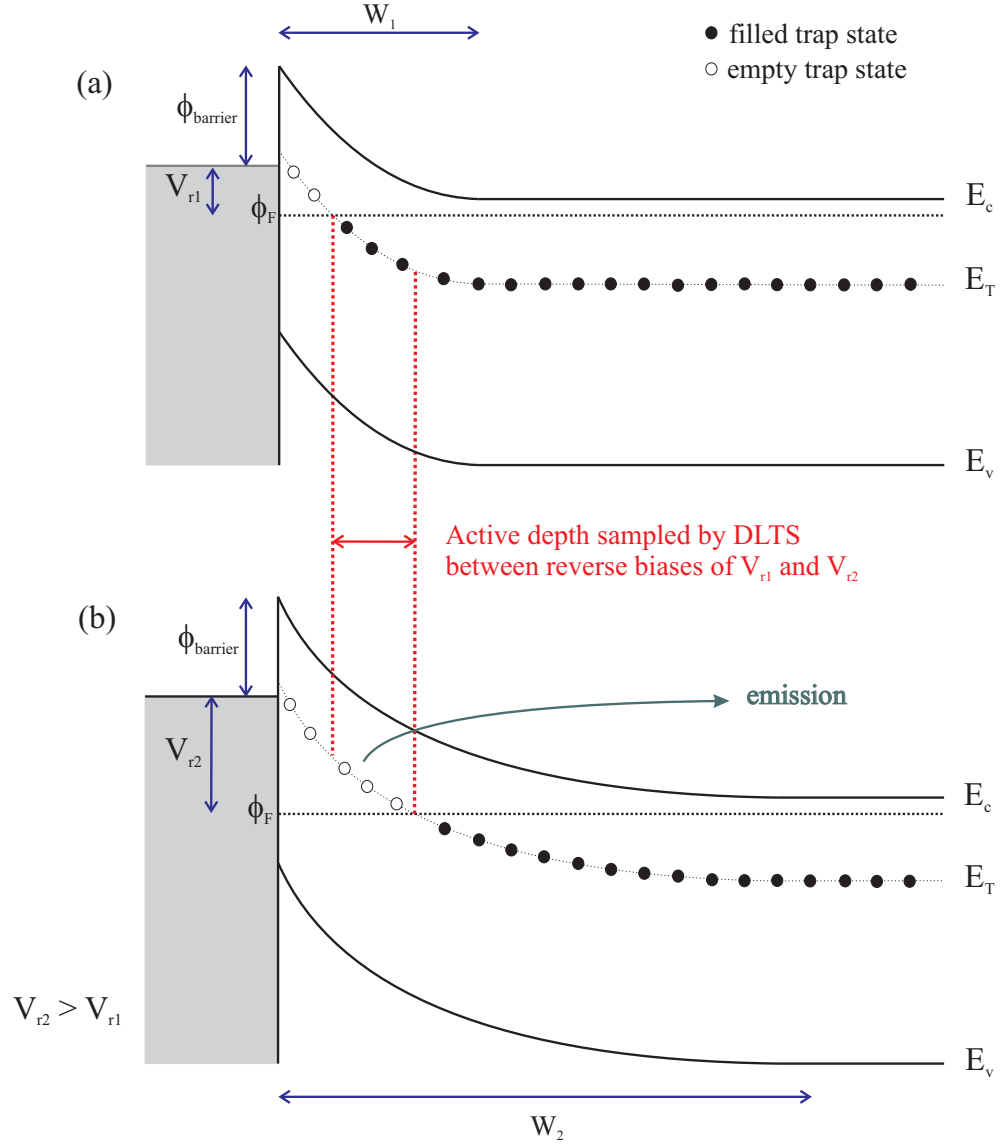


Figure 2.19: Energy band diagrams showing the energy band structure around a junction formed by a Schottky barrier and an n-type semiconductor to illustrate the principles of DLTS. Increasing the applied reverse bias from V_{r1} to V_{r2} means that some electrons which occupy trap states at $E_c - E_T$ then lie above the quasi-Fermi level, ϕ_F . These electrons are emitted into the conduction band and this causes a change in the width of the depletion region, W , which gives a capacitance change. (Shallow dopant levels are not shown).

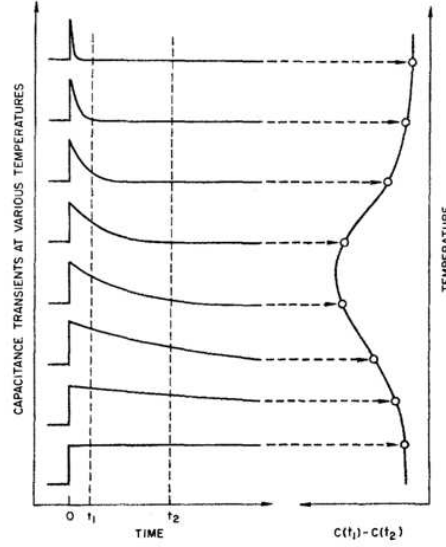


Figure 2.20: Illustration of how a double boxcar is used to define the rate window. The left-hand side shows capacitance transients at various temperatures, while the right-hand side shows the corresponding DLTS signal resulting from using the double boxcar to display the difference between the capacitance at time t_1 and the capacitance at time t_2 as a function of temperature (after Lang [77]).

where σ is the carrier capture cross-section, $\langle v \rangle$ is the mean thermal velocity of majority carriers, N is the effective density of states in the majority-carrier band, g is the degeneracy of the trap level, ΔG is the change in Gibbs free energy, ΔS is the entropy change and ΔH is the enthalpy change.

If the pre-factors in Equation 2.11 are independent of temperature, then a value of ΔH can be calculated from an Arrhenius plot of emission rate. To a good approximation in n-type silicon, this value is a measure of the energy difference between the trap state and the conduction band edge [203].

The key feature of the DLTS technique is the setting of a rate window, so that the apparatus only responds when it measures a capacitance transient within a specified window of emission rates. At a particular temperature, corresponding to a particular emission rate, the instrument will produce a peak in signal if the emission rate is within the chosen rate window. The technique makes use of a dual-gated signal averager (commonly known as a *double boxcar*), as shown in Figure 2.20.

Figure 2.21 illustrates a typical activation energy plot and shows how a measurement system which responds only to transients within a selected rate window can resolve the

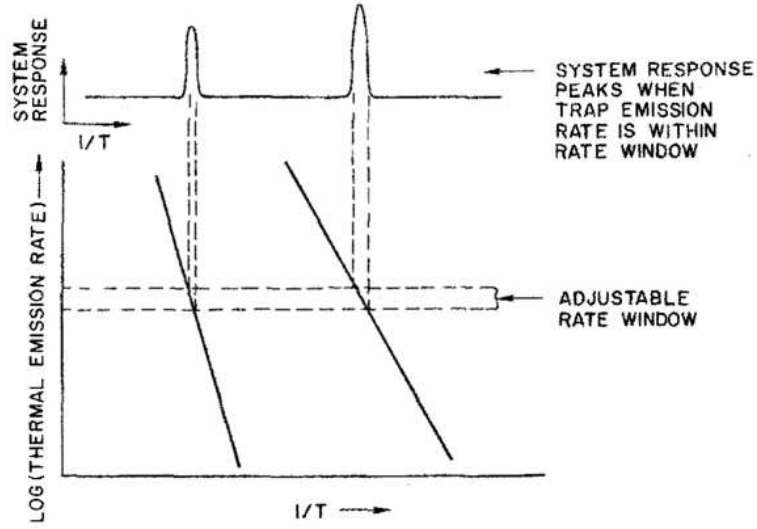


Figure 2.21: Schematic illustration of the basic DLTS method, namely the rate window concept. The lower part of the figure is a typical activation energy plot for the case of two traps. The upper part of the figure shows the resulting response of a capacitance transient measurement apparatus equipped with a rate window (after Lang [77]).

signals from different traps as a function of temperature. It is the strong temperature dependence of the emission rate given by Equation 2.11 which allows for the rate window thermal scan in Figure 2.20 to resolve signals.

With reference to Figure 2.20, the normalized DLTS signal, $S(T)$, is defined as:

$$S(T) = \frac{1}{\Delta C_0} [C(t_1) - C(t_2)] \quad (2.12)$$

where ΔC_0 is the capacitance change due to the pulse at $t = 0$. For exponential transients the emission rate which gives the maximum response can be shown to be given by [77]:

$$e_{\max} = \frac{\ln(t_2/t_1)}{t_2 - t_1} \quad (2.13)$$

Thus, it is clear that altering t_1 and t_2 fixes the emission rate and hence the temperature at which $e_{\max}$ occurs.

Trap concentration

The concentration of a trap, N_T is given by the height of the DLTS peak, according to:

$$N_T = \frac{2\Delta C N_d}{C_0} \quad (2.14)$$

where C_0 is the capacitance of the Schottky diode under the initial reverse bias conditions.

Capture cross-section

Another useful parameter of a trap is its capture cross-section, σ . It is possible to make a direct measurement of this by varying the fill pulse length at constant temperature using:

$$\ln\left(\frac{\Delta C_\infty - \Delta C_t}{\Delta C_\infty}\right) = \sigma \langle v \rangle N_d t_p \quad (2.15)$$

where t_p is the pulse length, N_d is the majority carrier concentration, $\langle v \rangle$ is the thermal velocity of the carriers, ΔC_∞ is the equilibrium capacitance value and ΔC_t is the capacitance at time t . It is also possible to obtain a value of the capture cross-section from an Arrhenius plot of emission rate using Equation 2.11. However, since the capture cross-section is temperature dependent [200], this is less accurate.

Sensitivity

The relative temporal capacitance change is given by:

$$\frac{\Delta C}{C_0} = -\frac{N_T}{2N_d} \exp(-et) \quad (2.16)$$

This shows that the sensitivity of the DLTS technique is dependent on the shallow dopant concentration. A good DLTS system can measure deep-levels which have a concentration of greater than approximately 1 in 10^4 of the shallow dopant concentration. Since it is difficult to make good Ohmic contacts to material with a doping level of 10^{13}cm^{-3} or lower, the lower limit for deep-level concentrations detectable by DLTS is around 10^9 to 10^{10}cm^{-3} .

2.6.3 Specimen fabrication

Cleaning

A rigorous cleaning procedure was carried out prior to diode fabrication. All the cleaning was done in a clean room at the School of Electrical and Electronic Engineering at the University of Manchester. Samples of approximately 1cm by 1cm were cleaved from wafers of silicon which had one polished side. They were cleaned with:

1. Organic solvents (trichloroethylene, acetone and methanol) for five minutes each in an ultrasonic bath.
2. Sulphuric acid and hydrogen peroxide mixed in the ratio 2:1 for 10 minutes.
3. Hydrofluoric acid (10%) for five minutes.
4. Ammonia, hydrogen peroxide and deionized water mixed in the ratio 1:1:5 for 10 minutes at 75 to 85°C (“RCA 1”).
5. Hydrochloric acid, hydrogen peroxide and deionized water mixed in the ratio 1:1:6 for 10 minutes at 75 to 85°C (“RCA 2”).
6. Hydrofluoric acid (48%) for ten seconds.

The specimens were rinsed in deionized water after each cleaning stage. Contacts were deposited as soon as possible after the cleaning process was completed, to avoid any unwanted oxidation of the silicon surface.

Fabrication of Schottky diodes

n-type silicon Schottky diodes were fabricated on n-type silicon by evaporation of gold. Gold was chosen as it is known to form a high Schottky barrier to n-type silicon ($\sim 0.80\text{eV}$ [204]). Several 1mm diameter circular contacts were deposited on each specimen.

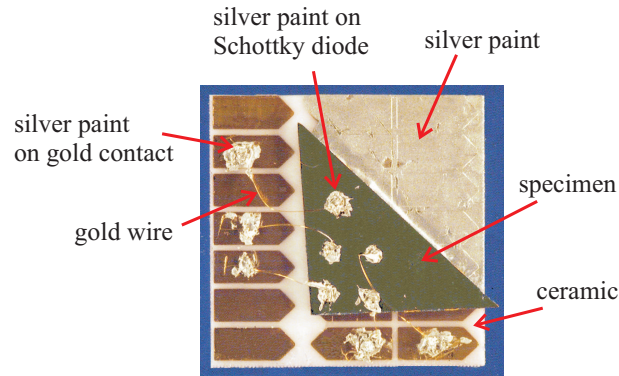


Figure 2.22: A wire-bonded DLTS specimen on a ceramic mount with dimensions 6mm by 6mm.

p-type silicon Schottky diodes were fabricated on p-type silicon by sputtering of titanium, which was chosen as it forms a high Schottky barrier to p-type silicon ($\sim 0.60\text{eV}$ [205]). To prevent oxidation of the titanium, a secondary layer of aluminium was sputtered on top of the titanium.

The sputtering was carried out in an Edwards E306A coating system using an 80W beam of argon ions. The thickness of the titanium barriers was controlled to be 75nm, on top of which 300nm of aluminium was deposited. Photolithographic methods were used to leave several 1mm diameter circular contacts free of photoresist, and after sputtering the photoresist was removed in acetone.

Fabrication of Ohmic contacts

Aluminium Ohmic contacts were deposited on both n- and p-type silicon by thermal evaporation. The aluminium was deposited on the entirety of the unpolished sides of the silicon specimens.

Wire-bonding and ceramic mounting

The back-side of each specimen was fixed to a specifically designed piece of ceramic using silver paint. The Schottky diodes were then wire-bonded with gold to the gold contacts on the ceramic, as shown in Figure 2.22.

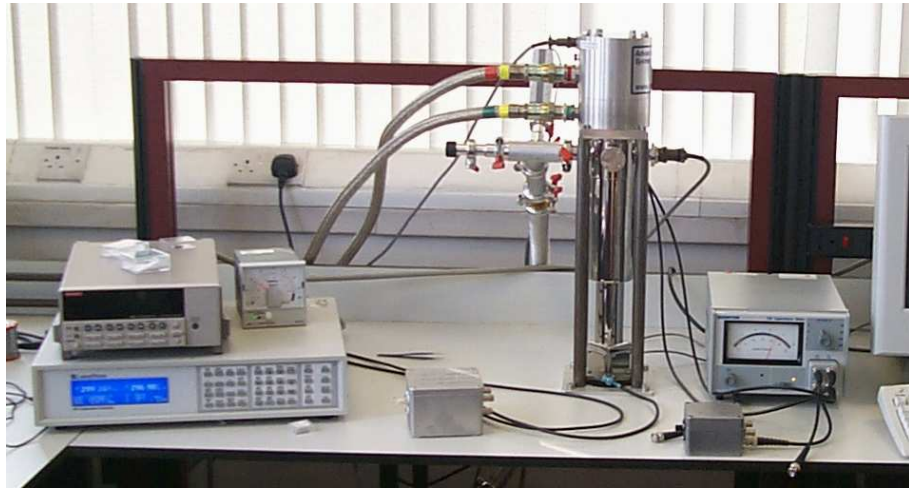


Figure 2.23: The system used for DLTS. From left to right; the temperature controller beneath the picoammeter and vacuum level gauge, the specimen chamber and the capacitance meter.

2.6.4 DLTS system

The DLTS system used in this work was located at the Materials and Engineering Research Institute at Sheffield Hallam University. The system consisted of a cold finger on to which the specimen was mounted, a variable temperature Advanced Research Systems cryostat controlled by a Lakeshore 370 temperature controller, a Boonton 72B capacitance meter and pulse generator, and a computer control system. The cryostat used was capable of keeping the specimen at stable temperature from 67 to 600K. A thermocouple was located close to the specimen for accurate temperature measurement. For the measurement of current-voltage (IV) characteristics a Keithley 6487 picoammeter and voltage source was used. The apparatus is shown in Figure 2.23.

The specimen was put into the specimen chamber at room temperature. Metal electrodes were used to make contact with the silver paint connected to the Ohmic contact and the gold contact on the ceramic connected to the Schottky diode, as shown in Figure 2.24. A vacuum pump evacuated the specimen chamber to a pressure of approximately 10^{-4} mbar or less.



Figure 2.24: A DLTS specimen in the specimen chamber.

2.6.5 DLTS measurements

DLTS data were taken using the TrapView software. The system was capable of taking data at two different rate windows simultaneously; 200 and 80s^{-1} , 50 and 20s^{-1} or 10 and 4s^{-1} . To get enough data for the activation energy to be found accurately, it was necessary to perform three separate temperature cycles.

All the data presented in this thesis were taken with the sample's temperature increasing. The temperature controller was programmed to ensure that the heating rate was approximately 0.05Ks^{-1} .

The full pulse bias was chosen so that the sampling region was sufficiently deep to avoid surface defects and the reverse bias was chosen to be as large as possible to maximize the signal produced. A typical fill pulse bias was -2V and a typical reverse bias was -7V .

2.7 High-resolution DLTS

One of the problems with DLTS is its lack of resolution, insofar as it is often difficult to resolve closely separated states. A technique, known as high-resolution (Laplace) DLTS (HR-DLTS), has been developed whereby many capacitance transients taken at constant temperature are averaged and analysed simultaneously [183, 184]. An advantage of HR-DLTS over conventional DLTS is shown by the example in Figure 2.25.

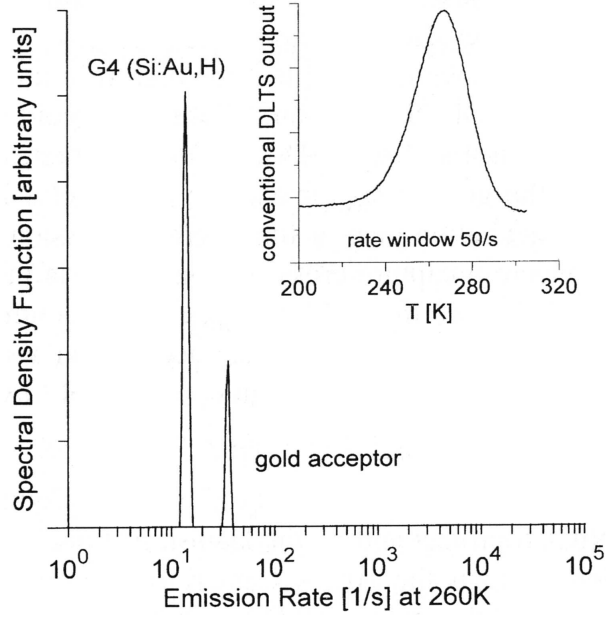


Figure 2.25: DLTS and HR-DLTS spectra of hydrogenated silicon containing gold. The broad DLTS peak at 260K is shown by HR-DLTS to be due to two separate states; the gold acceptor state and the G4(Si: Au, H) state (after Deixler *et al.* [206]).

The single broad peak given by conventional DLTS is shown to be due to two separate defects by HR-DLTS. In this Section a basic overview of HR-DLTS is given. For a more thorough analysis the reader is referred to review articles by Dobaczewski *et al.* [183, 184].

A common approach to the quantitative description of non-exponentiality observed in the capacitance transients is to assume that they are characterized by a spectrum of emission rates [183]:

$$f(t) = \int_0^\infty F(s) \exp(-st) ds \quad (2.17)$$

where $f(t)$ is the recorded transient and $F(s)$ is the spectral density function.

The problem of obtaining $F(s)$ from the measured capacitance transient, $f(t)$ is not an easy one in practice. It is necessary to take the inverse Laplace transform of $f(t)$. Because of this the technique is often known by the name of Laplace transform DLTS (LDLTS). For an analytical, multi-exponential function $f(t)$, Equation 2.17 has a unique solution, $F(s)$. However, for an experimentally obtained transient which has

noise and an unknown base line, the number of solutions can be infinite and these solutions can differ vastly.

HR-DLTS uses mathematical routines that are all based on the Tikhonov regularization method [207]. The one used in this thesis is known as FLOG [184]. Data were obtained by holding the specimen at constant temperature in the vicinity of a peak found by conventional DLTS and by using the same apparatus as before to produce many thousands of capacitance transients.

2.8 Summary

The experimental methods used to obtain the results presented in this thesis were described in this Chapter. The dislocation locking technique is applied to nitrogen in FZ-Si in Chapter 4, oxygen in Cz-Si in Chapter 5 and oxygen in Cz-Si with a high concentration of shallow dopants in Chapter 6. DLTS and HR-DLTS are applied to oxygen at dislocations in Cz-Si in Chapter 5 and to nitrogen-related defects in FZ-Si, Cz-Si and NTD FZ-Si in Chapter 7.

Chapter 3

Analysis of dislocation unlocking data in terms of impurity transport

3.1 Introduction

An experimental technique is used in this work which relies upon the ability of certain impurities to immobilize stationary dislocations. The stress required to move a pinned dislocation, the unlocking stress, is measured as a function of annealing time and temperature. The technique provides useful data on the mechanical effects of an impurity in silicon. A more important feature of the technique is that the data obtained can be interpreted to give quantitative information on impurity transport. This is useful since there are circumstances under which the dislocation locking technique can be used where conventional techniques for measuring impurity transport (*e.g.* SIMS) are unsuitable.

When the dislocation locking effect is due to impurity atoms, or clusters of a few impurity atoms, the dislocation unlocking data can be analyzed using the simple methods described in this Chapter. When the dislocation locking is due to impurity precipitates the analysis becomes more complicated. In this Chapter, it is shown how dislocation

unlocking data for dislocations locked by general impurity atoms can be analyzed to give information on the effective diffusivity of the impurity to a dislocation, the composition of the diffusing species, its binding energy to a dislocation and the density of the locking species at a dislocation core. This analysis is applied to nitrogen and oxygen in silicon in later Chapters.

3.2 Basic analysis

For all conditions investigated to date the unlocking stress has been found to rise approximately linearly with annealing time before reaching a constant value [12, 16, 24, 26]. This is shown schematically for Cz-Si in Figure 1.23 and with actual data for nitrogen-doped FZ-Si in Figure 1.26. Data in the two regimes can be analyzed separately to deduce transport and binding energy information.

3.2.1 Regime 1: activation energy for transport

In the first regime, the dislocation unlocking stress is found to rise approximately linearly with annealing time. The dislocation unlocking stress rises because the locking impurity diffuses to the dislocation core. In the case of locking by atomic impurities, the rate of increase in the dislocation unlocking stress with time, $\frac{d\tau_u}{dt}$, is directly proportional to impurity diffusion to the dislocation core, D , and to the background concentration of the locking impurity, C_0 . Therefore:

$$\frac{d\tau_u}{dt} \propto C_0 D \propto C_0 \exp\left(-\frac{E_A}{kT}\right) \quad (3.1)$$

where E_A is the activation energy for the dislocation locking process. From an Arrhenius plot of $\frac{1}{C_0} \frac{d\tau_u}{dt}$, a value of E_A can be deduced. An example of such a plot is shown in Figure 3.1.

The value of E_A is related to the activation energy for transport of the impurity species to the dislocation. If the species (*e.g.* monomer or dimer) responsible for transport to a dislocation is the impurity's majority species in silicon, then E_A is its activation energy for diffusion. If the dislocation locking occurs by the transport of

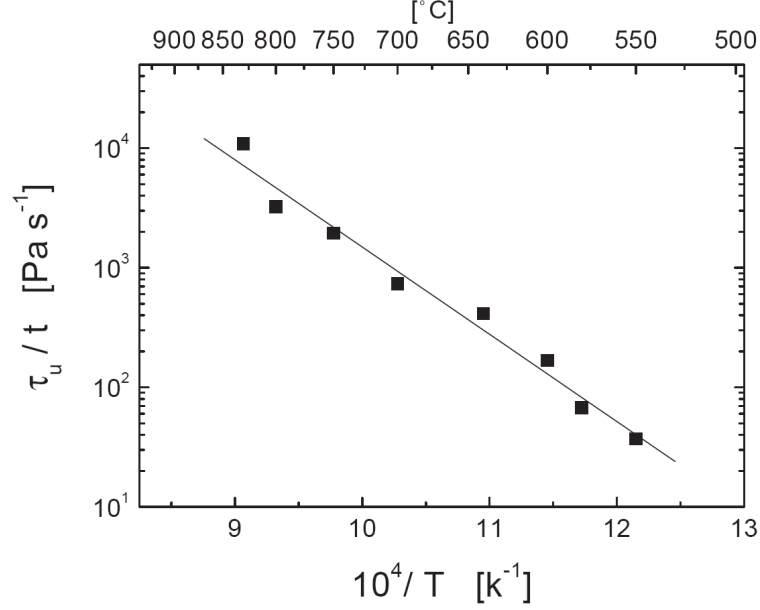


Figure 3.1: An Arrhenius plot used to deduce the activation energy for transport of nitrogen in FZ-Si as 1.45eV, on the assumption that atomic nitrogen is responsible for dislocation locking. The gradient of regime 1 is plotted as a function of reciprocal temperature (after Giannattasio *et al.* [12]).

some other species containing the impurity of interest, the E_A will be the sum of the formation energy for this other species and its activation energy for diffusion.

3.2.2 Regime 2: binding energy to a dislocation

In the second regime, the dislocation unlocking stress is found to take a constant value, $\tau_u^{\text{saturation}}$. To analyze the data it is first necessary to have information on the occupation of the sites at the dislocation core.

If the concentration of the locking species at the dislocation is small compared to the number of available sites at the dislocation core, then a local equilibrium between the locking impurities at the dislocation core and the impurities in the bulk of the material is established. The distribution of concentrations is given by a Maxwell-Boltzmann distribution:

$$\tau_u^{\text{saturation}} \propto C_{\text{core}} = C_0 \exp\left(\frac{\Delta G_{\text{binding}}}{kT}\right) \quad (3.2)$$

where C_{core} is the concentration of the impurity at the dislocation core, C_0 is

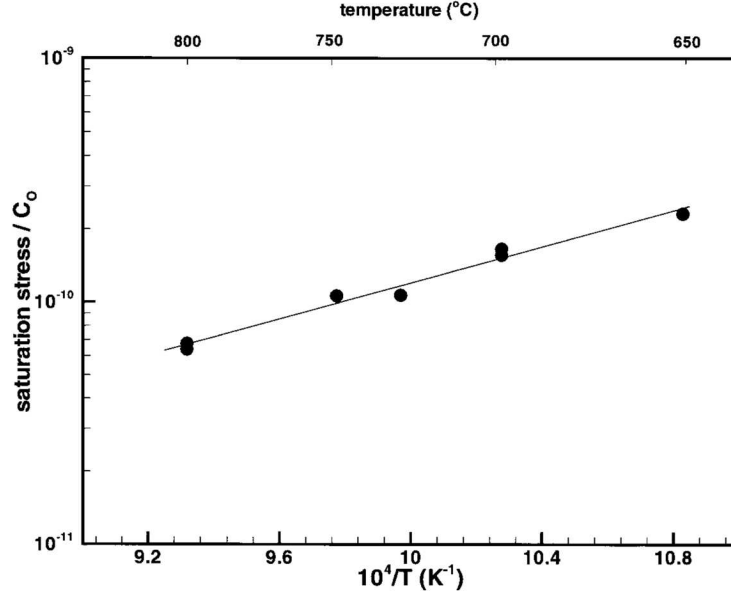


Figure 3.2: An Arrhenius plot used to deduce the binding enthalpy of oxygen to a dislocation in Cz-Si as 0.74eV. The average regime 2 unlocking stress normalized by oxygen concentration is plotted as a function of reciprocal temperature (after Senkader *et al.* [16]).

the bulk concentration of the impurity and $\Delta G_{\text{binding}}$ is the Gibbs free energy of the impurity-dislocation system, *i.e.* the binding energy between the impurity atom to the dislocation.

Given that $\Delta G_{\text{binding}} = \Delta H_{\text{binding}} - T\Delta S_{\text{binding}}$, an Arrhenius plot of $\frac{1}{C_o}\tau_u^{\text{saturation}}$ allows a value of the binding enthalpy of an impurity to the dislocation, $\Delta H_{\text{binding}}$, to be deduced. An example of such an Arrhenius plot in the case of oxygen in Cz-Si is shown in Figure 3.2.

If the concentration of the locking species at the dislocation is comparable to the number of available sites at the dislocation core, then this competition for states means that Fermi-Dirac statistics need to be used. The probability that a site at the dislocation is occupied is then:

$$p = [1 + \frac{1}{C} \exp(\frac{\Delta S_{\text{binding}}}{k}) \exp(-\frac{\Delta H_{\text{binding}}}{kT})]^{-1} \quad (3.3)$$

where $C = \frac{C_{\text{impurity}}}{C_{\text{silicon}}}$ is the relative concentration of the impurity and $\Delta H_{\text{binding}}$ is the binding enthalpy of the impurity to the dislocation core. This expression can be used

to put a lower limit on the binding enthalpy of the locking impurity to the dislocation, as shown in Section 4.3.

3.3 Modelling

In the case that the dislocation locking effect is due impurity atoms, the dislocation unlocking data can be used to give a value of the effective diffusivity of the impurity which diffuses to, and locks, the dislocation. The effective diffusivity is treated as a fitting parameter and a numerical solution to Fick's Equation (Equation 1.1) in the following form is found:

$$\frac{\partial C}{\partial t} = D_{\text{eff}} \nabla (\nabla C + \frac{C}{kT} \nabla (\Delta G_{\text{binding}})) \quad (3.4)$$

where C is the concentration of the impurity, D_{eff} is its effective diffusivity defined by Equation 3.12 and $\Delta G_{\text{binding}}$ is the binding energy of the impurity to the dislocation.

For a particular annealing temperature, Equation 3.4 is solved numerically in a cylindrical domain with the dislocation core at the centre, subject to two boundary conditions. The first boundary condition is:

$$C(R) = C_0 \quad (3.5)$$

where R is the minimum distance from the dislocation core at which there is no significant change in the impurity concentration, C , for all annealing times and temperatures considered, and C_0 is the background impurity concentration.

For the second boundary condition, capture and re-emission of impurity atoms at the dislocation core boundary (located at $r = r_0$) are considered. It is assumed that the capture rate is controlled by the impurity concentration next to the core, C_1 , the concentration of sites available at the core, C_a , and the concentration of occupied sites at the core, C_c , according to:

$$\text{capture} \propto C_1 \frac{C_a - C_c}{C_a} \quad (3.6)$$

Emission of impurity atoms from the core is assumed to be a function of the impurity concentration in the core and the escape probability of impurity atoms from the core, according to:

$$\text{emission} \propto C_c \exp\left(-\frac{\Delta G_{\text{binding}}}{kT}\right) \quad (3.7)$$

Thus, the flux of atoms crossing the cylindrical dislocation core boundary at r_0 is:

$$J = 2\pi r_0 D_0 \left[C_1 \frac{C_a - C_c}{C_a} - C_c \exp\left(\frac{\Delta S_{\text{binding}}}{k}\right) \exp\left(-\frac{\Delta H_{\text{binding}}}{kT}\right) \right] \quad (3.8)$$

$$\text{as } \Delta G_{\text{binding}} = \Delta H_{\text{binding}} - T \Delta S_{\text{binding}}.$$

The concentration of impurity atoms at the dislocation core is calculated from Equation 3.8 using a finite difference method. The calculation initially assumes a uniform concentration of impurity throughout the material, C_0 . A computer program is used to calculate the impurity distribution after successive small time steps. Thus, the concentration of impurity atoms at different annealing times at the chosen annealing temperature is calculated by running the program. The Fortran code used to perform the calculation is given in Appendix A.

The dislocation core is considered to be a cylinder with cross-sectional area πr_0^2 , such that the number of impurity atoms per unit length of dislocation core is $N_c = C_c \pi r_0^2$. The number of available sites per unit length of dislocation, n_a , is deduced by considering the number of impurity atoms at a perfect dislocation with interstitial sites separated by $3.8\text{\AA}$, the magnitude of the Burgers vector for a perfect dislocation in silicon. Thus, $n_a = (3.8 \times 10^{-8} \text{cm})^{-1} = 2.6 \times 10^7 \text{cm}^{-1}$. However, it should be noted that if there is little competition for states, *i.e.* if the dislocation is far from being fully occupied, then the values for diffusivity and binding energy are very insensitive to the value chosen for n_a .

The calculation gives the number of impurity atoms per unit length of dislocation core, N_c . Since the unlocking stress, τ_u , is proportional to the number of impurity atoms which segregate to the dislocation, the unlocking stress is therefore given by:

$$\tau_u = N_c \tau_0 \quad (3.9)$$

where τ_0 is the unlocking stress due to a single impurity atom pinning a unit length of dislocation core. To model the dislocation unlocking data it is therefore necessary to know τ_0 . This can be calculated by other means, as was the case for oxygen in Cz-Si where $\tau_0 = 7\text{Pacm}$ [16], or it can be estimated.

Since it is possible to make good estimates of r_0 and C_a , the dislocation unlocking data can effectively be modelled with just three fitting parameters. These are:

1. D_{eff} , the effective diffusivity of the locking impurity.
2. ΔS , the change in entropy.
3. τ_0 , the unlocking stress per single impurity atom per unit length of the dislocation core.

Given that the simulation has been found to be particularly insensitive to the value chosen for ΔS and that τ_0 is known or can be estimated, the critical fitting parameter is the impurity's effective diffusivity, D_{eff} . Therefore D_{eff} is chosen so that the results of the calculation fit the experimental data. A value of D_{eff} is deduced from dislocation unlocking data taken at a range of annealing temperatures. A best fit of these allows a full expression for the effective diffusivity of the species which diffuses to the dislocation to be stated.

3.4 Species responsible for transport

From investigating how the initial rise in dislocation unlocking stress varies with impurity concentration, it is possible to deduce information on the species responsible for transport. In this Section, it is shown that the scaling of the gradient in the initial rise in the unlocking stress (regime 1) when the impurity concentration is varied can enable the identification of the composition of the species which diffuses to the dislocations. The analysis presented in this Section again only applies when atomic impurities (as opposed to precipitates) are responsible for the dislocation locking effect.

It is usually one of two species that is responsible for transport of impurity X to a dislocation; a monomeric species (*e.g.* X, XY, XY₂ where Y is another impurity or defect) or a dimeric species (*e.g.* X₂, X₂Y, X₂Y₂). Consider a situation in which both dimeric and monomeric species are present in equilibrium with each other. In this situation, the total flux of atoms to the dislocation, J , can be written as:

$$J = -D_1 \frac{dC_1}{dx} - 2D_2 \frac{dC_2}{dx} \quad (3.10)$$

where D_1 , C_1 and D_2 , C_2 are the diffusivity and concentration of the monomeric and dimeric species respectively.

J can be approximated in terms of an effective diffusivity, D_{eff} , and the total impurity concentration, C , according to:

$$J \approx -D_{\text{eff}} \frac{dC}{dx} \quad (3.11)$$

where the effective diffusivity is defined as:

$$D_{\text{eff}} = \frac{C_1 D_1 + 2C_2 D_2}{C_1 + 2C_2} \quad (3.12)$$

It is usually the case that the majority species of an impurity in silicon is experimentally known. The majority species will usually be either a monomer or a dimer.

3.4.1 Majority of dimers

If the majority species is a dimer, as is the case for nitrogen in silicon [105], then $C_2 \gg C_1$, so Equation 3.12 becomes:

$$D_{\text{eff}} \approx \frac{C_1 D_1}{2C_2} + D_2 \quad (3.13)$$

If monomers, X_1 , are in equilibrium with dimers, X_2 , then:



The equilibrium concentration of dimers is therefore given by:

$$C_2 = C_1^2 \exp\left(\frac{|\Delta G_2|}{kT}\right) \quad (3.15)$$

where ΔG_2 is the binding energy of the dimer. Rearranging Equation 3.15 gives the monomer concentration as:

$$C_1 = \sqrt{C_2} \exp\left(-\frac{|\Delta G_2|}{2kT}\right) \quad (3.16)$$

Substitution of Equation 3.16 into Equation 3.13 gives:

$$D_{\text{eff}} \approx \frac{1}{2\sqrt{C_2}} \exp\left(-\frac{|\Delta G_2|}{2kT}\right) D_1 + D_2 \quad (3.17)$$

Therefore, in the case that the majority impurity species is the dimer, the effective diffusivity depends on impurity concentration if a monomeric species is responsible for dislocation locking or is independent of impurity concentration if a dimeric species is responsible for dislocation locking.

3.4.2 Majority of monomers

Alternatively, if the majority species is the monomer, as is the case for oxygen in silicon [70], then $C_1 \gg C_2$, so Equation 3.12 becomes:

$$D_{\text{eff}} \approx D_1 + 2\frac{C_2}{C_1} D_2 \quad (3.18)$$

Substituting Equation 3.15 into this gives:

$$D_{\text{eff}} \approx D_1 + 2C_1 \exp\left(\frac{|\Delta G_2|}{kT}\right) D_2 \quad (3.19)$$

Therefore, in the case that the majority impurity species is the monomer, then the effective diffusivity depends on impurity concentration if a dimeric species is responsible for transport to the dislocation and is independent of impurity concentration if a monomeric species is responsible for transport to the dislocation. Thus, by finding the

effective diffusivity of an impurity when present in different concentrations, it is possible to deduce information on the composition of the species responsible for transport to the dislocation.

3.5 Temperature dependence of the unlocking stress

The discussion in this Chapter up to this point has required the dislocation unlocking measurements to be made at the same temperature (usually 550°C). It is also possible to perform dislocation unlocking measurements at other temperatures. By measuring the variation in dislocation unlocking stress with unlocking temperature, it is possible to obtain further information on the locking impurity.

The data can be analyzed using the theory of thermally activated release of impurities from dislocations, which was developed for dislocations in silicon by Sumino and Imai [154]. According to their theory, the unlocking stress, τ_u , varies with temperature according to:

$$\tau_u = \frac{N}{b^2} [\Delta G^* - kT \ln(\frac{LN\nu}{\Gamma})] \quad (3.20)$$

where, L is the dislocation length, N is the number of impurities (locking points) along a unit length of dislocation, ΔG^* is the maximum interaction energy between an impurity and the dislocation, ν is the vibration frequency of the dislocation, Γ is the release rate of the locked dislocation and b is the magnitude of the dislocation's Burgers vector.

Several parameters in Equation 3.20 are unknown. One approach, adopted by Yonenaga is to estimate values for ν , L and Γ [14, 208], although this is unlikely to be particularly accurate. A better approach is to extrapolate measurements of the dislocation unlocking stress made as a function of temperature to absolute zero. For $T = 0\text{K}$, Equation 3.20 becomes:

$$\tau_{0K} = \frac{N\Delta G^*}{b^2} \quad (3.21)$$

Thus, given that the magnitude of the Burgers vector is known, it is possible to deduce the product of N and ΔG^* by measuring the temperature dependence of the dislocation unlocking process. This is useful because it may be possible to find either N or ΔG^* by the use of another method and so this analysis can allow an unknown quantity to be deduced.

3.6 Summary

In this Chapter it is shown how dislocation unlocking data can be interpreted in terms of transport of a general impurity to a dislocation, when the dislocation locking is due to segregation of atomic impurities at the dislocation. The methods presented in this Chapter are applied to nitrogen in FZ-Si (Chapter 4), oxygen in Cz-Si (Chapter 5) and oxygen in Cz-Si with a high concentration of shallow dopants (Chapter 6).

Chapter 4

Dislocation locking by nitrogen in FZ-Si

4.1 Introduction

Nitrogen in silicon is of significant interest to device manufacturers as it allows them flexibility in controlling oxygen precipitation [1–7], controls the concentration of voids [8–10] and improves mechanical strength [11–14]. The benefits of nitrogen in silicon are sufficient for manufacturers to add it to their wafers without fully understanding its properties. For instance, as was described in Section 1.4, the species (*e.g.* monomer or dimer) active in different temperature ranges, the diffusivity and the diffusion mechanism of nitrogen in silicon are a matter of debate [12, 115, 116, 119, 120, 122]. In this Chapter, quantitative data on the locking of dislocations by nitrogen in FZ-Si are presented. These data are interpreted in terms of the fundamental properties of nitrogen in silicon.

FZ-Si is an ideal system in which to investigate intentionally added impurities, as it is practically free of other impurities, including oxygen, so the effects pertaining to the added impurity can be easily isolated. As well as being a model system, there is a technological need to study the behaviour of nitrogen in FZ-Si. FZ-Si is found to be more susceptible to wafer warpage than Cz-Si at high temperatures, since FZ-Si does not contain an appreciable concentration of oxygen which improves mechanical

strength by immobilizing dislocations in Cz-Si [15, 16, 24]. Since nitrogen also immobilizes dislocations [11, 12, 14], its addition to FZ-Si can provide a significant improvement in mechanical strength.

The experimental results presented in this Chapter build on the work presented in a DPhil thesis by Giannattasio [177]. In this earlier study, dislocation locking by nitrogen impurities in FZ-Si with a high nitrogen concentration ($2.2 \times 10^{15} \text{cm}^{-3}$) was investigated in the 550 to 830°C temperature range. Some of the results from this previous work are shown in Figure 1.26. For all annealing temperatures investigated the unlocking stress measured at 550°C was found to exhibit two distinct regimes as a function of annealing time. In the first regime, the unlocking stress increases approximately linearly with annealing time, at a rate which is strongly dependent on temperature. In the second regime, the unlocking stress is found to take a constant value of approximately 50MPa for all annealing temperatures investigated. Giannattasio explained the temperature independence of the second regime by assuming that all the sites at the dislocation were filled by nitrogen impurities.

In his work, Giannattasio had a limited amount of material available, and was consequently only able to obtain dislocation unlocking data for annealing temperatures up to 830°C. It is therefore unknown whether there is a temperature below the melting point of silicon above which nitrogen “boils off” the dislocation, as oxygen does in Cz-Si above approximately 800°C [16]. If nitrogen remains at dislocations at higher temperatures, then in addition to improving the mechanical stability of FZ-Si, it is also likely to provide benefits if added to Cz-Si. However, a large binding energy of nitrogen to dislocations could also be problematic, as manufacturers of silicon-based electronic devices often perform annealing schedules at approximately 1100°C to anneal out dislocations created by ion implantation. The addition of nitrogen may therefore mean that these dislocations are more difficult to get rid of. Thus, whatever the effect, it is important to understand how nitrogen interacts with dislocations at high temperatures.

An investigation of dislocation locking in FZ-Si with a nitrogen concentration of $3 \times 10^{14} \text{cm}^{-3}$ is presented in this Chapter. The dislocation locking technique described in Chapter 2 is used over a wider range of annealing temperatures than in the previous

work (500 to 1200°C). Dislocation unlocking data obtained at high temperatures allow an estimate of the lower limit of the binding enthalpy of nitrogen to dislocations to be made. The dislocation unlocking data are analyzed in terms of nitrogen transport to dislocations. Further results presented in this Chapter show how the unlocking stress of a dislocation pinned by nitrogen varies with unlocking temperature in the 500 to 700°C temperature range. These results are important, as in a real device production schedule any dislocations that may exist in the material must be pinned by nitrogen at a range of temperatures.

4.2 Results

4.2.1 Dislocation unlocking as a function of annealing time and temperature

The dislocation locking technique described in Chapter 2 was used to investigate the behaviour of nitrogen in FZ-Si with a nitrogen concentration of $3 \times 10^{14} \text{cm}^{-3}$. Dislocation locking experiments were performed at various annealing temperatures (500 to 1200°C) and times (0 to 4,345 hours) and the data obtained are presented in Figures 4.1 and 4.2. Also shown in the Figure are data obtained by Giannattasio [177]. For control purposes, specimens made from nitrogen-free FZ-Si were also investigated. No appreciable locking was found to occur in these specimens. Full details of all the specimens used are given in Section 2.2.

Despite being present in such a low concentration, nitrogen was still able to provide a significant locking effect on dislocations. For the material investigated in this work, the dislocation unlocking stress at annealing temperatures of up to 900°C was found to exhibit the same two distinct regimes as were found in the material used by Giannattasio. At temperatures above 900°C only the second regime was observed, as with the experimental set-up used it was not possible to anneal specimens for short enough times to obtain data in the first regime. The first regime, in which the unlocking stress increases approximately linearly with annealing time, and the second regime, in which the unlocking stress takes a constant value, are analyzed separately in the following

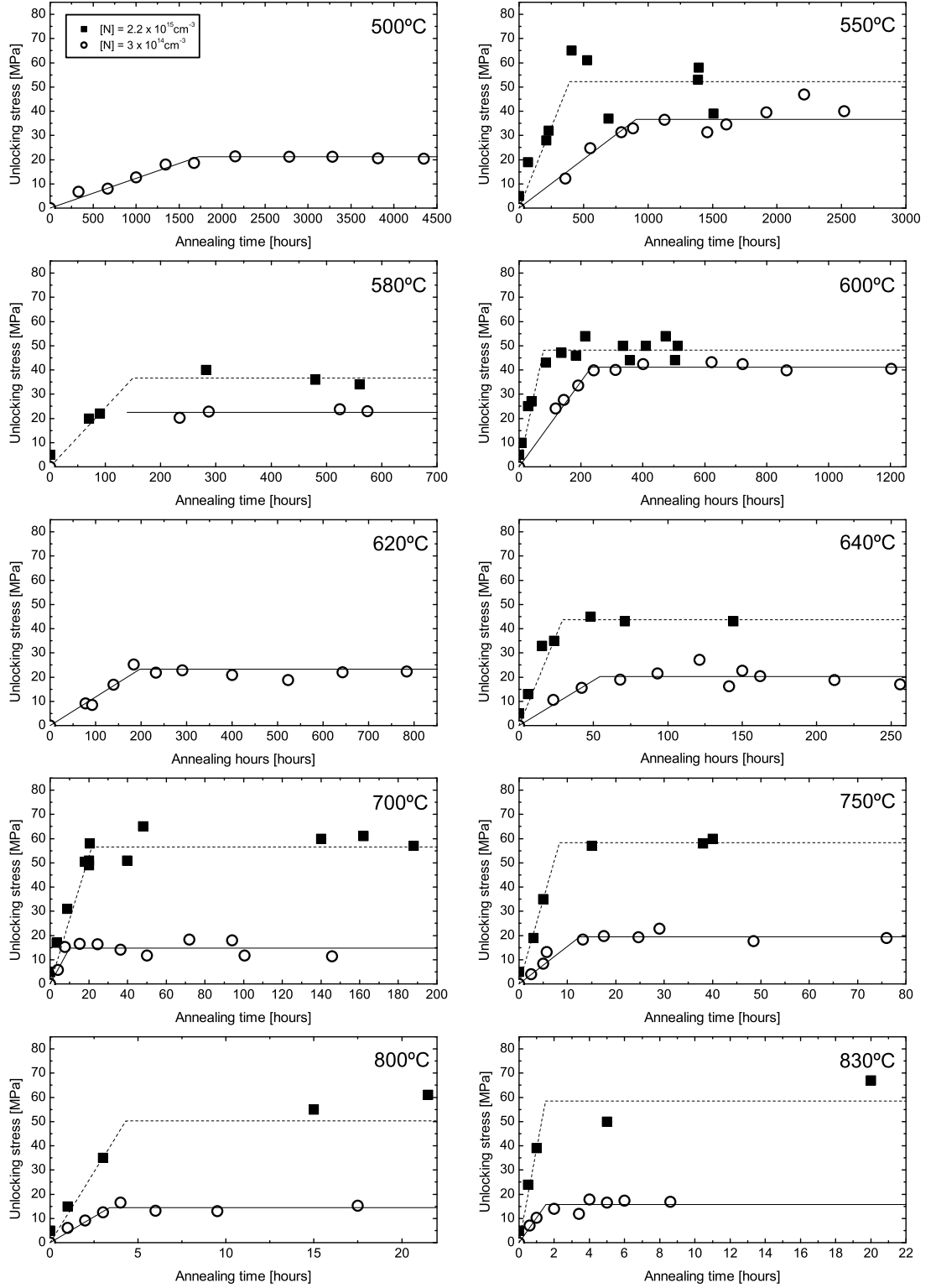


Figure 4.1: Dislocation unlocking stresses measured at 550°C as a function of annealing time at temperatures from 500 to 830°C for nitrogen-doped FZ-Si. Open circles are for the nitrogen concentration of $3 \times 10^{14} \text{ cm}^{-3}$ used in this work. Closed squares are for a nitrogen concentration of $2.2 \times 10^{15} \text{ cm}^{-3}$ obtained by Giannattasio [177]. The lines represent a best-fit of the experimental data in regime 1 and an average of the experimental data in regime 2.

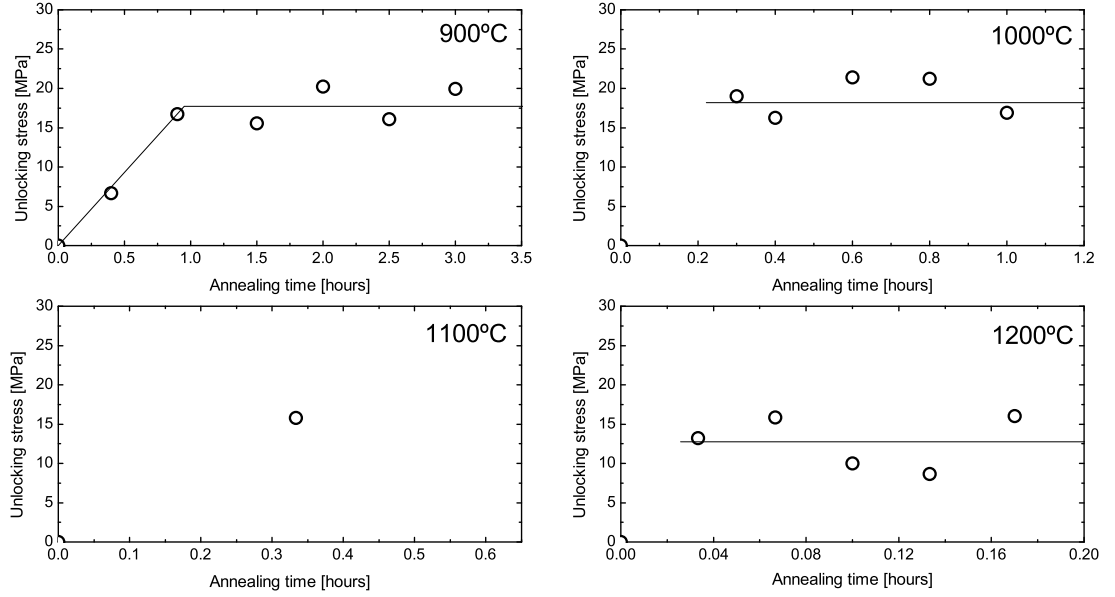


Figure 4.2: Dislocation unlocking stresses measured at 550°C as a function of annealing time at temperatures from 900 to 1200°C for nitrogen-doped FZ-Si with a nitrogen concentration of $3 \times 10^{14} \text{cm}^{-3}$. The lines represent a best-fit of the experimental data in regime 1 and an average of the experimental data in regime 2.

Sections.

In Cz-Si, where oxygen is responsible for dislocation locking, further regimes have been found (see Figure 1.23) which are believed to be associated with oxygen precipitation at the dislocation core [16,26]. Nitrogen-containing specimens annealed for very long times in this work showed no secondary increase in dislocation locking.

The scatter in the new data presented in this Chapter is less than in the previous work with nitrogen-doped FZ-Si [177] and is comparable to that for dislocation locking by oxygen in Cz-Si [16,24,26]. This may be explained by the fact that the specimens used in this present work were of better quality than in the original work. The wafers used in the present work were mirror polished and of (100) orientation, whereas in the previous work the (111) wafers were provided as-cut and were smoothed by polishing and chemical etching. The width and the thickness of the specimens in the previous work varied significantly along the length of the bar leading to possible errors in the unlocking stress calculated. Additionally, since in this present work specimens were cleaved from various parts of different FZ-Si wafers, the fact that there is very little scatter in the data at a particular annealing temperature indicates that the nitrogen

concentration in the wafers is fairly uniform.

Each data point in Figures 4.1 and 4.2 represents one iteration in the process illustrated in Figure 2.1. It should be noted that because very low dislocation unlocking stresses needed to be measured in this work, the three-point bend process was particularly time consuming. Specimens were usually left under load for 20 hours or more. Thus, the new data presented in Figures 4.1 and 4.2 represents a considerable proportion of the new experimental results presented in this thesis.

Regime 1: linear rise

For annealing temperatures of 500 to 900°C, the dislocation unlocking stress initially increases approximately linearly with annealing time. The rate of increase in dislocation locking, $\frac{d\tau_u}{dt}$, depends on annealing temperature, in accordance with:

$$\frac{d\tau_u}{dt} \propto \exp\left(-\frac{E_{\text{locking}}}{kT}\right) \quad (4.1)$$

where E_{locking} is the activation energy for the dislocation locking process. The rate of increase in the dislocation unlocking stress presented in Figures 4.1 and 4.2 is plotted in Figure 4.3 for annealing temperatures up to 900°C. The value of E_{locking} was determined from this Arrhenius plot to be $1.5 \pm 0.1\text{eV}$ for specimens with a low nitrogen concentration investigated in this work and for specimens with a high nitrogen concentration previously investigated by Giannattasio [177].

Regime 2: plateau

The data presented Figures 4.1 and 4.2 show that for all annealing temperatures investigated the dislocation unlocking stress eventually takes a constant value. The average value of the dislocation unlocking stress in regime 2 is plotted as a function of annealing temperature for both nitrogen concentrations in Figure 4.4. The constant value reached for specimens with a high nitrogen concentration is approximately 50MPa for all temperatures investigated. In the case of the specimens with a low nitrogen concentration, the constant value reached is generally about 18MPa.

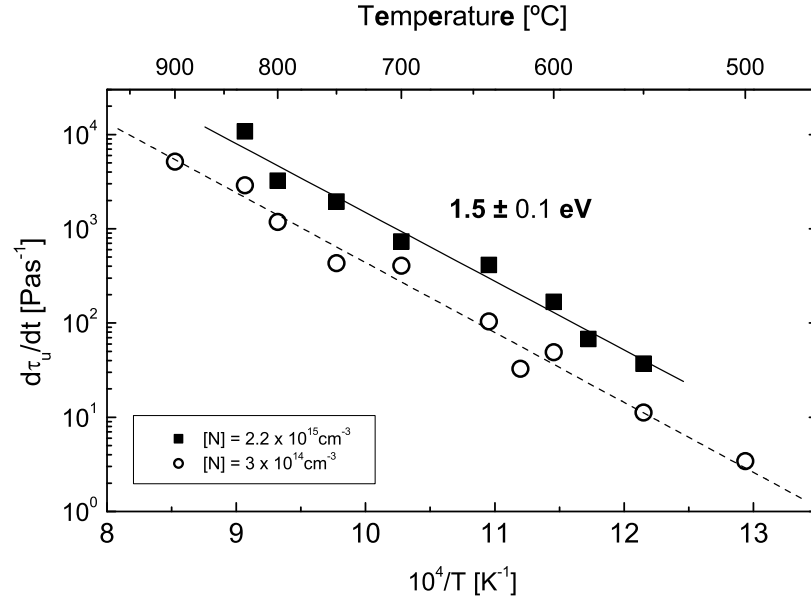


Figure 4.3: An Arrhenius plot of the gradient of the initial rise in dislocation unlocking stress, $\frac{d\tau_u}{dt}$, in the 500 to 900°C annealing temperature range. Open circles are for the nitrogen concentration of $3 \times 10^{14} \text{cm}^{-3}$ used in this work. Closed squares are for a nitrogen concentration of $2.2 \times 10^{15} \text{cm}^{-3}$ obtained by Giannattasio [177].

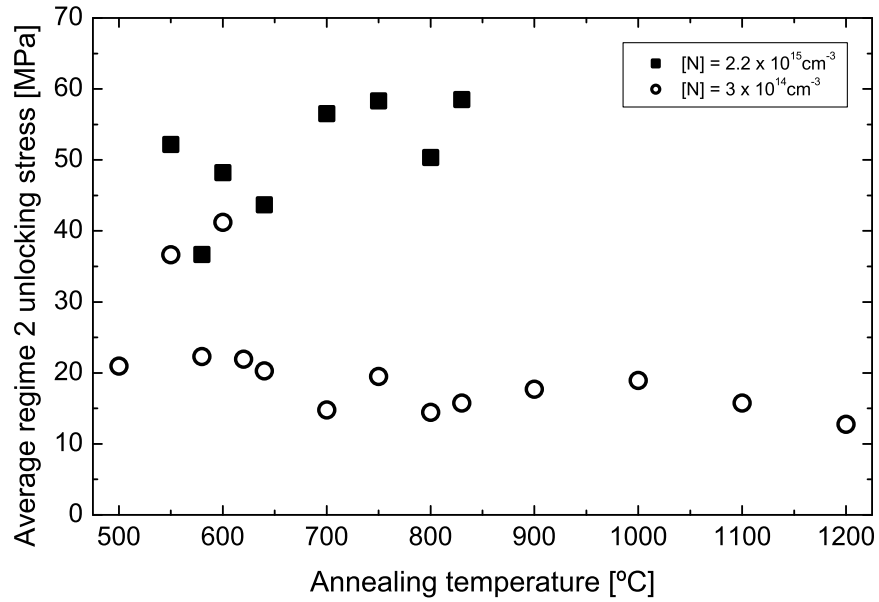


Figure 4.4: Average value of the dislocation unlocking stress measured at 550°C in regime 2 as a function of annealing temperature for the data presented in Figures 4.1 and 4.2. Open circles are for the nitrogen concentration of $3 \times 10^{14} \text{cm}^{-3}$ used in this work. Closed squares are for a nitrogen concentration of $2.2 \times 10^{15} \text{cm}^{-3}$ obtained by Giannattasio [177].

For the high nitrogen-containing specimens, the scatter in the saturation unlocking stress is consistent with the high degree of scatter in the individual data points. In the case of the low nitrogen-containing specimens, there are two temperatures (550 and 600°C) at which the saturation value in unlocking stress is significantly higher than at all other temperatures investigated. The scatter in the data taken with the low nitrogen-containing specimens is generally quite low and cannot explain the doubling in saturation unlocking stress at 550 and 600°C. However, data taken at an annealing temperature of 580°C, which is between these two apparently anomalous temperatures, is consistent with the data at other temperatures. The reason for the discrepancy at 550 and 600°C remains unclear. If the two anomalous sets of data at 550 and 600°C are ignored then the regime 2 value of dislocation unlocking stress is approximately independent of annealing temperature, but is dependent on the nitrogen concentration. The average regime 2 dislocation unlocking stress increases by a factor of 2.4 as the nitrogen concentrations varies by a factor of 7.3.

In the case of oxygen in Cz-Si, the value of the regime 2 unlocking stress depends strongly on the annealing temperature [16,26]. This allows the binding energy of the locking species to the dislocation to be calculated in accordance with Equation 3.2. In the case of nitrogen in FZ-Si, the average regime 2 unlocking stress is approximately independent of temperature. This implies that something more complicated than the establishment of a local equilibrium is causing the unlocking stress to reach a plateau. Possible explanations for this are discussed in Section 4.3.1.

4.2.2 Temperature dependence of the unlocking stress

The dislocation unlocking measurements presented in Figures 4.1 and 4.2 were all made at 550°C. This temperature was chosen so that the dislocations moved at a convenient rate and also so that data obtained could be compared to those obtained in earlier work [12,177]. In general, the stress at which a dislocation is unpinning from an impurity atom depends upon the temperature at which the unpinning takes place. This has previously been shown to be the case for oxygen in Cz-Si by using the dislocation locking technique [26] and in this Section results are presented for nitrogen in FZ-Si.

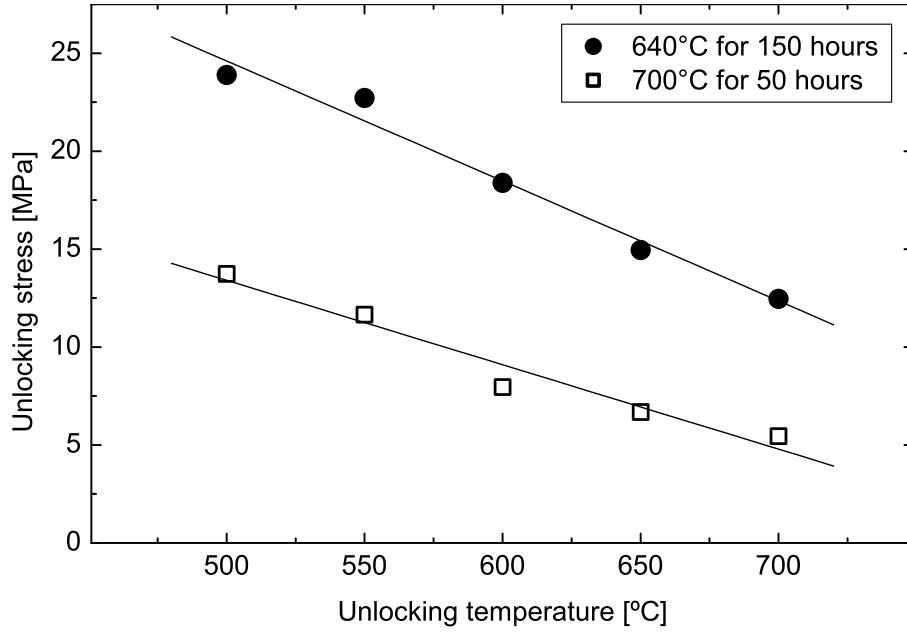


Figure 4.5: The dependence of the dislocation unlocking stress on unlocking temperature for nitrogen-doped FZ-Si with a nitrogen concentration of $3 \times 10^{14} \text{cm}^{-3}$. The filled circles represent dislocation unlocking stresses in specimens annealed at 640°C for 150 hours. The open squares represent unlocking stresses measured on dislocations locked by annealing at 700°C for 50 hours.

Two sets of several specimens were prepared from nitrogen-doped FZ-Si with a nitrogen concentration of $3 \times 10^{14} \text{cm}^{-3}$ and were annealed under two different sets of conditions. The annealing conditions investigated were 640°C for 150 hours and 700°C for 50 hours. The annealing conditions were chosen so that the expected unlocking stress was well into the second regime. The three-point bend process used to unpin the dislocations from the nitrogen impurities was then performed at different temperatures for the different specimens in each set. The lowest unlocking temperature was 500°C, for which the three-point bending process took several days. The highest temperature investigated was 700°C.

The variation of unlocking stress with unlocking temperature is shown for the two sets of specimens in Figure 4.5. The unlocking stress was found to decrease with increasing unlocking temperature for both sets of specimens.

It should be noted that given that both sets of data lie in the second regime and that the average values of the regime 2 unlocking stress are approximately the same

at 640 and 700°C, there is a discrepancy between the absolute values of the unlocking stress measured in the specimens. The reason for this discrepancy is not clear. A full understanding of the mechanism leading to the second regime of unlocking stress is likely to be able to offer an explanation (see Section 4.3.1).

4.3 Discussion

In this Chapter it has been shown that nitrogen is capable of providing a strong locking effect on dislocations, even though it is present in concentrations of just $3 \times 10^{14} \text{cm}^{-3}$ in some specimens. The dislocation unlocking stress measured at 550°C has been found to be significant for specimens annealed at temperatures of at least 1200°C. The highest annealing temperature at which nitrogen locking of dislocations has been reported previously is 830°C [12,177], so it is now known that nitrogen is capable of locking dislocations over the entire temperature range used for device processing.

The fact that nitrogen locks dislocations at 1200°C suggests that nitrogen binds strongly to the dislocation core. A lower limit on the binding enthalpy of nitrogen to dislocations can be found by assuming that a substantial fraction of states at the dislocation core are occupied by nitrogen. When such competition for states exists, the probability that a site at the dislocation core is occupied is given by Equation 3.3. Since the saturation value of unlocking stress is approximately uniform across the full range of annealing temperatures, if the locking strength of nitrogen is similar to that of oxygen, then it can be assumed that the occupation will be of order 10% [16] even at the highest annealing temperature investigated, 1200°C. The occupation probability given by Equation 3.3 as a function of temperature is plotted in Figure 4.6 for different binding enthalpies. It can be seen that a binding enthalpy of approximately 2.4eV or greater is required for the occupation to be essentially unchanged over the entire annealing temperature range investigated. This is in agreement with recent work by Yonenaga, who suggests that the interaction energy (ΔG^*) between atomic nitrogen and the dislocation is approximately 3.0eV [14].

In previous work, it was shown that dislocation locking by oxygen in Cz-Si is strongly

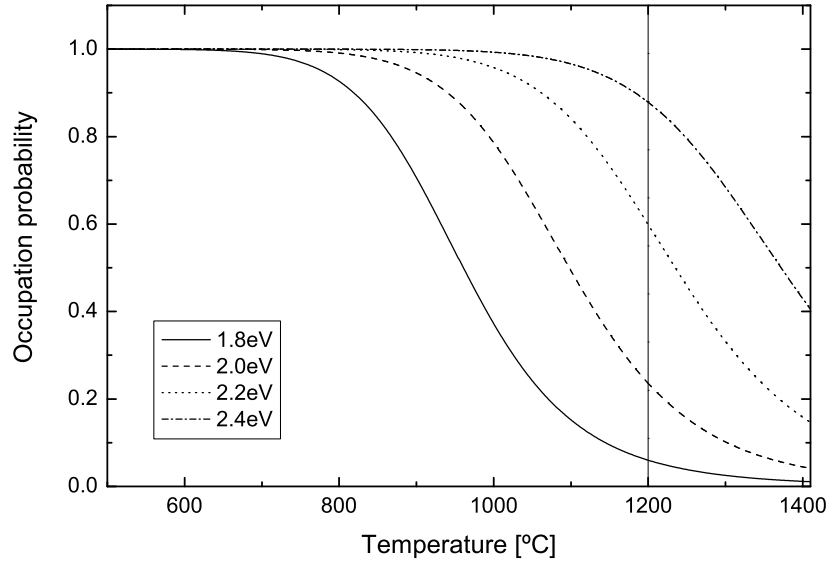


Figure 4.6: Probability of a dislocation core site being occupied by an impurity which binds to the dislocation with different enthalpies plotted as a function of temperature. The calculation assumes a Fermi-Dirac distribution function (Equation 3.3). The relative concentration of nitrogen atoms was taken to be $C = 4.4 \times 10^{-7}$ and the change in entropy to be $\Delta S = 8.6 \times 10^{-5} \text{eVK}^{-1}$.

reduced at temperatures greater than approximately 800°C, as above this temperature, oxygen, which has a binding energy to the dislocation core of 0.74eV, “boils off” the dislocation [16]. The present work shows that nitrogen impurities provide large amounts of dislocation locking in FZ-Si at temperatures at which oxygen impurities in Cz-Si do not. It is suggested that the addition of nitrogen to Cz-Si would be beneficial for the mechanical properties of these wafers, as nitrogen may be able to immobilize dislocations at temperatures at which the locking due to oxygen is practically non-existent.

The data presented in Figures 4.1 and 4.2 show that for all annealing temperatures investigated, the unlocking stress initially rises approximately linearly (regime 1), before it takes an approximately constant value (regime 2). Similar behaviour was found to occur for oxygen in Cz-Si. However, there is a major difference between the two sets of data. This is that the value of the unlocking stress in regime 2 was found to be approximately independent of annealing temperature in nitrogen-doped FZ-Si

(see Figure 4.4) and strongly dependent on annealing temperature in Cz-Si (see Figure 1.25). This difference in behaviour is highly significant and it has raised the question of whether the mechanism of dislocation locking is the same in both cases. One possibility is that nitrogen precipitates, rather than atoms, segregate at the dislocation cores in the FZ-Si. It is possible that the first and second regimes observed for nitrogen in FZ-Si actually correspond to the linear rise and plateau associated with precipitation observed in the case of oxygen in Cz-Si in regimes 3 and 4 (see Figure 1.23).

In the following Sections the experimental data are analyzed in terms of the locking of dislocations by atomic nitrogen, then by the locking of dislocations by nitrogen precipitates. In Section 4.3.3 the evidence for each proposed mechanism is discussed.

4.3.1 Dislocation locking by atomic nitrogen

Dislocation locking can occur by the segregation of impurity atoms, or clusters of a few impurity atoms, at the dislocation core. This is the case for oxygen in Cz-Si in regimes 1 and 2. If this is also the case for nitrogen in FZ-Si, then the methods described in Chapter 3 can be used to analyze the dislocation unlocking data, as follows.

Regime 1: linear rise

The unlocking stress initially increases approximately linearly for both nitrogen concentrations studied. In the case that dislocation locking occurs by atomic nitrogen, the activation energy for the locking process is the same as that for the transport process of the nitrogen to the dislocation, in accordance with Equation 3.1. Thus, in the case of atomic decoration, the activation energy for transport of the diffusing species is the $1.5 \pm 0.1\text{eV}$ found from the Arrhenius plot in Figure 4.3.

It should be noted that this value is the same as the activation energy for transport attributed to the oxygen dimer [24, 26]. It is not possible that the dislocation locking reported in this Chapter is due to oxygen, whose concentration in FZ-Si is thought to be of order 10^{15}cm^{-3} . By extrapolation of previous work [16, 24, 26], oxygen present in such a low concentration would not provide the amount of dislocation locking measured in nitrogen-doped FZ-Si. Additionally, in the case of oxygen in Cz-Si, the regime 2 un-

locking stress strongly depends on annealing temperature [26] and the results presented in Figure 4.4 show that this does not happen for nitrogen in FZ-Si. Furthermore, the activation energy for oxygen transport as measured by the dislocation locking technique has been found to take different values in different temperature ranges [16, 24, 26] and Figure 4.3 shows that the activation energy does not vary with temperature in the nitrogen-doped FZ-Si investigated.

The gradient of the initial increase in unlocking stress has been found to depend on the nitrogen concentration in the specimens. The relationship between nitrogen concentration and the gradient of the initial increase in dislocation unlocking stress can be used to determine the composition of the species responsible for transport to the dislocation. Since the majority nitrogen species in silicon is known to be the dimer [105], the analysis in Section 3.4.1 can be used to determine the number of nitrogen atoms in the species that diffuses to the dislocation. The analysis, which only applies in the case of atomic decoration, shows that the gradient of the initial increase in dislocation unlocking stress depends on the square root of nitrogen concentration in the case of transport by a species containing one nitrogen atom, or linearly with nitrogen concentration in the case of transport by a species containing two nitrogen atoms.

For the results presented in Figure 4.1, the average ratio of the gradient of the initial rise in unlocking stress for high to low nitrogen-containing specimens in the 500 to 900°C temperature range can be found from the data plotted in Figure 4.3. The average ratio at annealing temperatures at which data were taken for FZ-Si with both concentrations is approximately 3.4. The ratio of the high to low nitrogen concentrations is $\frac{2.2 \times 10^{15}}{3 \times 10^{14}} \approx 7.3$ and the square root of the ratio of the high to low nitrogen concentrations is $\sqrt{\frac{2.2 \times 10^{15}}{3 \times 10^{14}}} \approx 2.7$. Whether or not the data obtained can be used to identify the species responsible for locking depends on the experimental errors associated in the regime 1 dislocation unlocking stress measurements. The predicted ratio of initial rises is approximately 21% higher than expected if the diffusing species contains one nitrogen atom and is 115% lower than expected if the diffusing species contains two nitrogen atoms. As discussed in Section 2.3.8, the error in a typical regime 1 unlocking

stress measurement for nitrogen in FZ-Si is approximately $\pm 25\%$. Therefore, on the assumption that atomic nitrogen is responsible for the dislocation locking effect, the results presented in this Chapter are consistent with transport by a monomeric nitrogen species, but are inconsistent with transport by a dimeric nitrogen species. From the results presented in this work alone it is not possible to deduce the precise composition of such a monomeric species (*e.g.* N, NO, NV).

It should be noted that as the 1.5eV activation energy for transport has been shown not to be associated with the majority nitrogen species, the dimer, it therefore represents the sum of the formation energy of the species responsible for transport to dislocations and its activation energy for diffusion. Numerical simulations suggest that the activation energy for diffusion of the nitrogen monomer is approximately 0.4eV [117,118]. Thus, if the species responsible for nitrogen transport to dislocations is the nitrogen monomer, and not another monomeric nitrogen species, then the formation energy per monomer is approximately 1.1eV. If monomers form by simple dissociation of the dimer by Equation 1.6, then this puts the value of the binding energy of the nitrogen dimer at around 2.2eV. *Ab initio* calculations give the binding energy of the nitrogen dimer as 1.7eV to 4.3eV [108–110].

In summary, if nitrogen atoms are responsible for the dislocation locking effect, the results presented in this Chapter indicate that a monomeric nitrogen species, whose activation energy for transport is approximately 1.5eV, is responsible for transport of nitrogen to dislocations. This activation energy for nitrogen transport is significantly lower than the 2.8eV found for nitrogen in a SIMS out-diffusion study by Itoh and Abe [119]. Therefore, if the assumption that the dislocation locking occurs by segregation of atomic nitrogen at dislocations is correct, a different nitrogen species appears to be responsible for diffusion measured by dislocation locking than for out-diffusion.

Regime 2: plateau

In this work, the value of the unlocking stress in regime 2, was not generally found to vary significantly with annealing temperature for a given nitrogen concentration (see Figure 4.4). This is in contrast to previous work for dislocation locking by oxygen in

Cz-Si, which shows that the plateau in unlocking stress varies significantly as a function of annealing temperature as shown in Figure 1.25 [16, 26]. The assumption that a Maxwell-Boltzmann distribution existed between the oxygen at the dislocation core and in the bulk allowed a value of the binding enthalpy of the locking oxygen species to the dislocation to be calculated [26]. In the case of nitrogen in FZ-Si no such equilibrium appears to exist and it was therefore not possible to calculate the binding enthalpy in the same way as for oxygen in Cz-Si.

In previous work in which the dislocation locking technique is applied to FZ-Si with a higher nitrogen concentration, the value of the unlocking stress in regime 2 was found to be approximately 50MPa for all annealing temperatures investigated [12, 177]. The explanation given for this temperature independence was that the dislocation core was entirely filled by nitrogen atoms. The results presented in this Chapter for FZ-Si with a lower nitrogen concentration show that the unlocking stress generally levels off at approximately 18MPa for nearly all annealing temperatures investigated. Therefore, the previous suggestion of the dislocation core being entirely filled with nitrogen cannot be correct, as even in the case of the low nitrogen-containing specimens, there would always be enough nitrogen available in the bulk of the material to diffuse to the dislocations for the cores to become full.

To explain the second regime of dislocation unlocking, the following mechanisms are considered:

Out-diffusion Competition between nitrogen diffusion to the surface and nitrogen diffusion to dislocations can be considered as a possible mechanism for the second regime of dislocation locking. This mechanism does not explain the fact that regime 2 is independent of annealing temperature in the case of atomic locking. The activation energy for out-diffusion is known to be 2.8eV [119] and the activation energy for diffusion to a dislocation is 1.5eV in the case of dislocation locking by atomic nitrogen. Therefore, because both processes have different activation energies, the value of regime 2 unlocking stress would depend on annealing temperature if out-diffusion were responsible for the second regime.

Precipitation in bulk Competition between nitrogen diffusion to precipitates in the bulk and nitrogen diffusion to dislocations could also be considered as a possible mechanism for the second regime. The nucleation of precipitates is generally thought to be a strongly temperature dependent process, as shown for oxygen in Cz-Si in Figure 1.6. Thus, if this mechanism were responsible for regime 2 then it is likely that the unlocking stress in regime 2 would also significantly depend on temperature, which is not shown by the results. Furthermore, if homogeneous nucleation of precipitates were to occur in the bulk, then it is likely that heterogeneous nucleation at dislocations would also occur.

Thus, the mechanism responsible for the second regime of unlocking stress cannot presently be explained in terms of locking of dislocations by atomic nitrogen.

Diffusion coefficient of nitrogen

By solving the diffusion equation for nitrogen to a dislocation, the experimental data can be modelled by using the nitrogen diffusivity as a fit parameter. The full details of the model are described in Section 3.3. The model requires the locking strength per atom of the locking species at the dislocation core to be known. In the case of nitrogen this is not experimentally known, however it is likely to be similar in magnitude to that for oxygen, which has been found previously to be 7Pacm at 550°C [16], and cannot be less than that required if it is assumed that the dislocation core is saturated by nitrogen atoms. In this limit, with order of 1×10^7 nitrogen atoms per cm, the observed unlocking stress of ~ 50 MPa at 550°C is obtained with the locking due to each nitrogen atom of ~ 5 Pacm. The other parameters in the model were taken to be $\Delta S = 8.6 \times 10^{-5} \text{eVK}^{-1}$ and $\Delta H_{\text{binding}} = 1.7 \text{eV}$.

On the assumption that dislocation locking occurs by atomic nitrogen, the value of the effective diffusivity of nitrogen in silicon is given by:

$$D = D_0 \exp\left(-\frac{1.5\text{eV}}{kT}\right) \text{cm}^2 \text{s}^{-1} \quad (4.2)$$

where the diffusivity pre-factor, D_0 , is of order 10^{-5} or smaller. This value of the

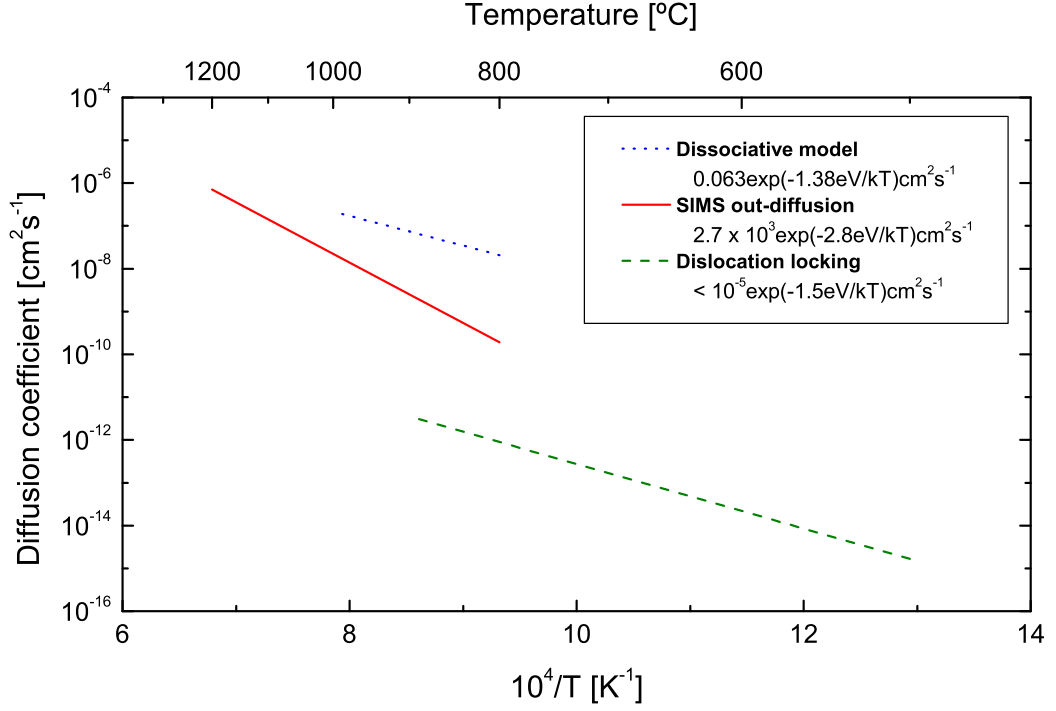


Figure 4.7: The diffusivity of nitrogen in silicon determined by different methods. Effective diffusivity is shown for a SIMS out-diffusion study by Itoh and Abe [119] and as deduced from dislocation locking experiments by assuming atomic locking. An absolute value of nitrogen diffusivity determined by the dissociative model of Voronkov and Falster [122] is also shown. The effective diffusivity deduced from the dislocation locking experiments is an upper limit.

diffusivity pre-factor is small compared to those usually found for impurities in silicon. Assuming the upper limit of D_0 , Equation 4.2 is plotted alongside the results of other studies in Figure 4.7.

Temperature dependence of the unlocking stress

As shown in Figure 4.5, the stress required to unpin a dislocation locked by a constant amount of nitrogen depends upon the temperature at which the unpinning takes place. For given annealing conditions, the unlocking stress decreases approximately linearly with the temperature at which the unlocking process takes place in the 500 to 700°C temperature range. Previous work using the same technique for oxygen in Cz-Si also shows an approximately linear dependence of dislocation unlocking stress on unlocking temperature [26].

The data in Figure 4.5 can be analyzed using the methods described in Section 3.5 to give a value for the product of the number of impurities (locking points) along a unit length of dislocation and the maximum interaction energy between an impurity and the dislocation, $N\Delta G^*$. Extrapolation of the data to absolute zero gives $\tau_{0K} = 72.0\text{MPa}$ for the specimens annealed at 640°C for 150 hours and $\tau_{0K} = 46.8\text{MPa}$ for the specimens annealed at 700°C for 50 hours. Taking the magnitude of the Burgers vector for a dislocation in silicon to be $3.8\text{\AA}$ and using Equation 3.21, gives values of $N\Delta G^*$ to be $6.5 \times 10^5\text{eVcm}^{-1}$ and $4.2 \times 10^5\text{eVcm}^{-1}$ for dislocations locked at 640°C for 150 hours and 700°C for 50 hours respectively. In a recent work, Yonenaga estimates the value of ΔG^* for atomic nitrogen to be 3.0eV by assuming values of ν to be the vibrational Debye frequency (10^{11}s^{-1}), L to be 10^{-4}m and Γ to be 1s^{-1} [14,208]. Taking this value gives an estimate of the density of locking nitrogen species of $2.2 \times 10^5\text{cm}^{-1}$ and $1.4 \times 10^5\text{cm}^{-1}$ for dislocations locked by atomic nitrogen at 640°C for 150 hours and 700°C for 50 hours respectively. Thus, each nitrogen atom at the dislocation core in FZ-Si is separated by the magnitude of approximately 150 Burgers vectors. For comparison, it is found that each oxygen atom at a dislocation in Cz-Si is separated by the magnitude of approximately 3 Burgers vectors [177].

Summary

The dislocation unlocking data have been analyzed in this Section by assuming that atomic nitrogen is responsible for locking the dislocations. Under this assumption, analysis of regime 1 implies that a monomeric nitrogen species diffuses to the dislocations with an activation energy for transport of approximately 1.5eV . From the temperature dependence of the unlocking stress measurements, the density of nitrogen at the dislocation core is estimated to be approximately $2 \times 10^5\text{cm}^{-1}$. The atomic locking assumption is unable to provide an explanation for the leveling off in unlocking stress observed (regime 2).

4.3.2 Dislocation locking by nitrogen precipitates

If the immobilization of dislocations is due to the formation of nitrogen precipitates at the dislocation core, then the analysis in the previous Section is not generally valid. In this Section the dislocation unlocking data are analyzed by assuming that the dislocation locking effect is due to nitrogen precipitates.

Mechanism of dislocation unpinning from a precipitate

If the dislocation locking effect is due to nitrogen precipitates, then it is necessary to understand the mechanism by which a dislocation unpins from a precipitate in order to analyze the dislocation unlocking data in terms of nitrogen transport properties.

The theory of precipitate-dislocation interactions has been studied by Cottrell [209], Kelly and Nicholson [210], Brown and Ham [211] and Kocks *et al.* [212]. For a complete understanding of the interaction of nitrogen precipitates with dislocations in silicon in terms of these models, it is necessary to know information on the physical properties of the precipitates. This includes:

- whether the precipitates are coherent or incoherent
- whether the precipitates are crystalline or amorphous
- the degree of misfit between the precipitates and the bulk
- the shape of the precipitates.

None of these properties are currently known for the nitrogen precipitates proposed in this Section. However, in spite of this, it is possible to use general considerations to derive how the stress required to unpin a dislocation from a spherical precipitate depends on the precipitate's radius, as follows.

Consider a dislocation pinned by precipitates with radius r , separated by distance l , as illustrated in Figure 4.8. In thermomechanical equilibrium, forces act on each precipitate due to a combination of physical phenomena. The forces due to different interactions are summarized in Table 4.1. Some of the forces act along the line of the

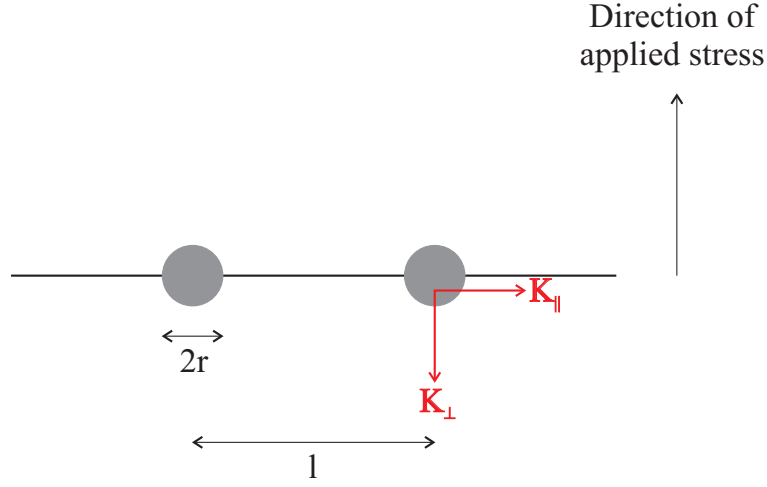


Figure 4.8: Spherical precipitates at a dislocation line. The forces which act on the precipitate in thermomechanical equilibrium are $K_{\perp}$ normal to the dislocation and $K_{\parallel}$ along the dislocation.

Mechanism	Resistance to edge dislocation	Resistance to screw dislocation
Friction stress	$K_{\perp} \sim \frac{\mu br}{100}$	$K_{\perp} \sim \frac{\mu br}{100}$
Disordering	$K_{\perp} \sim \frac{\mu br}{100}$	$K_{\perp} \sim \frac{\mu br}{100}$
Misfit stresses	$K_{\perp} \sim \frac{\mu br}{50}$	$K_{\perp} \sim 0$
Core energy difference	$K_{\parallel} \sim \frac{F_{\text{edge}}}{100}$	$K_{\parallel} \sim \frac{F_{\text{screw}}}{100}$
Modulus difference	$K_{\parallel} \sim \frac{\mu b^2}{100(1-\nu)}$	$K_{\parallel} \sim \frac{\mu b^2}{10}$
Interface step	$K_{\parallel} \sim \frac{\mu b^2}{100}$	$K_{\perp} \sim \frac{\mu b^2}{100}$

Table 4.1: The different mechanisms which give rise to forces on a precipitate at a dislocation at thermomechanical equilibrium. Their directions relative to the dislocation line are indicated, as are their approximate magnitudes in terms of μ , the shear modulus of the crystal, b , the magnitude of the dislocation's Burgers vector, r , the radius of the precipitate, F , the Helmholtz free energy of the edge or screw dislocation and ν , the Poisson's ratio (adapted from Kocks *et al.* [212]).

dislocation ($K_{\parallel}$) and others act normal to it ($K_{\perp}$). If it is assumed that the dislocation is unpinned from the precipitates by an applied stress normal to the dislocation line, then only the forces which have a component normal to the dislocation line determine the unlocking stress of the dislocation. These are considered below.

Friction stress If the precipitates are treated as discrete obstacles, it can be assumed that they exert no influence on the dislocation beyond their width. Therefore, any element of dislocation line between the precipitates experiences no frictional resistance to its motion. At each precipitate, an element of dislocation line with width $2r$ experiences

a force due to friction resisting its motion perpendicular to the dislocation. This force can be expressed as [212]:

$$K_{\perp}^{\text{glide}} = \tau_{\text{elem}} br \quad (4.3)$$

where τ_{elem} is the glide resistance of a dislocation element, b is the magnitude of the dislocation's Burgers vector and r is the radius of the precipitate. The value of τ_{elem} is of order $\frac{\mu}{100}$, where μ is the shear modulus of the crystal.

Disordering Another possible component in the precipitate-dislocation interaction is the force required to create an anti-phase-boundary. The magnitude of the force perpendicular to the dislocation can be written as [212]:

$$K_{\perp}^{\text{disordering}} = \chi_{\text{APB}} r \quad (4.4)$$

where χ_{APB} is the free energy per unit area of the anti-phase-boundary and r is the radius of the precipitate. The value of χ_{APB} is of order $\frac{\mu b}{100}$, where μ is the shear modulus of silicon and b is the magnitude of the dislocation's Burgers vector.

Misfit stresses Many precipitates are surrounded by misfit stresses, which are proportional to the strain induced by the precipitate [209,212]. By considering the volume misfit of spherical precipitates, it can be shown that the maximum average interaction force normal to the dislocation due to the misfit of a precipitate at an edge dislocation is [212]:

$$K_{\perp}^{\text{misfit}} = 2|\epsilon|\mu br \quad (4.5)$$

where $|\epsilon|$ is the unconstrained misfit strain, μ is the shear modulus of the crystal, b is the magnitude of the dislocation's Burgers vector and r is the radius of the precipitate. The magnitude of the misfit interaction for screw dislocations is considerably less than the value given by Equation 4.5 and can usually be considered negligible compared to the frictional and disordering forces [212].

Interface step The creation of a step at the interface between the precipitate and the dislocation also gives rise to a force on the precipitate at the dislocation core. For a screw dislocation, the magnitude of this force normal to the dislocation is independent of the precipitate radius and is given by [212]:

$$K_{\perp}^{\text{step}} = \chi_{\text{step}} b \quad (4.6)$$

where χ_{step} is the free energy per unit area of the step and b is magnitude of the dislocation's Burgers vector. The magnitude of χ_{step} is typically of order $\frac{\mu b}{100}$, where μ is the shear modulus of the crystal. For an edge dislocation, the force associated with the step creation acts along the line of the dislocation.

The total force required to unpin the dislocation from the precipitate is determined by combining the four forces described above. Since the dislocations considered in this work are usually screw or 60° in character, $K_{\perp}^{\text{misfit}}$ can be considered to be small compared to $K_{\perp}^{\text{glide}}$ and $K_{\perp}^{\text{disordering}}$. Furthermore, since it is generally the case that $r \gg b$, $K_{\perp}^{\text{step}}$ is negligible compared to the other terms. Thus, the force resisting dislocation motion perpendicular to the dislocation line is given by:

$$K_{\perp} \approx \tau_{\text{elem}} b r + \chi_{\text{APB}} r = (\tau_{\text{elem}} b + \chi_{\text{APB}}) r \propto r \quad (4.7)$$

Therefore, in the case that dislocation locking occurs by the formation of nitrogen precipitates at the dislocation core, the unlocking stress, τ_u , can be expected to vary approximately linearly with the radius of the precipitates, r . Furthermore, τ_u will be inversely proportional to the separation of the precipitates, l .

Regime 1: linear rise

By considering the mechanism by which a dislocation unpins from a precipitate, it has been shown that the the unlocking stress, τ_u , is approximately directly proportional to the radius of a precipitate, r . An analysis of diffusion to a precipitate in the bulk, which can be confirmed by dimensional analysis, shows that r varies with time, t , according

to [213]:

$$r \propto \sqrt{Dt} \quad (4.8)$$

where D is the coefficient of diffusion of the species responsible for precipitate growth. The unlocking stress would therefore be expected to be proportional to $\frac{\sqrt{Dt}}{l}$ if dislocation locking is due to spherical precipitates.

If heterogeneous nucleation at a dislocation were to occur, for instance, on features such as regularly spaced jogs, and if the density of these features were not to change with annealing time, then l will take a constant value. In this case:

$$\tau_u \propto \sqrt{Dt} \quad (4.9)$$

The data presented in Figures 4.1 and 4.2 indicate that τ_u is approximately proportional to t in the first regime. However, because of the magnitude of the errors in the experimental data (see Section 2.3.8), it is not possible to rule out the possibility that the unlocking stress initially shows the $\sqrt{t}$ behaviour predicted by Equation 4.9. If τ_u were to increase as $\sqrt{t}$, then analysis of the gradient in the experimentally-measured unlocking stress is more complicated than is the case for atomic locking, for which the unlocking stress increases linearly. This is because $\frac{d\tau_u}{dt}$ is now a function of time. The activation energy of the locking process, found to be $1.5 \pm 0.1\text{eV}$ from the Arrhenius plot in Figure 4.3, assumes that the unlocking stress rises linearly. It is interesting to note that taking this value and assuming that the unlocking stress varies as $\sqrt{D}$ gives an estimate of the activation energy for nitrogen transport of $3.0 \pm 0.2\text{eV}$. This value is consistent with the activation energy for transport of 2.8eV found in a SIMS out-diffusion study by Itoh and Abe [119].

In the above analysis, l was held constant, but in reality this may not be the case. It might be expected that the precipitate radius, r , would increase with annealing time and that new precipitates would form during annealing, hence reducing l . If this were to occur, then the value of τ_u measured would be sensitive to changes in both r and l . Quantitative analysis of this behaviour has not been attempted in this work. However,

it is noted that the Arrhenius plot in Figure 4.3 gives a straight line, which would be a surprising result if both l and r were to vary independently of one another.

Another mechanism which could be considered is precipitate growth by capture of nitrogen at the dislocation core, followed by pipe diffusion along the core. In this case, the variation of the unlocking stress with annealing time can be estimated as follows. If all the nitrogen in a cylinder of radius $x = \sqrt{Dt}$ is captured by the dislocation core, then the number of atoms in each precipitate is given by $\pi Dt C_0 l$, where C_0 is the bulk nitrogen concentration and the other variables are defined previously. Thus, the radius of the precipitate would vary in accordance with $r^3 \propto Dtl$ and the unlocking stress would be expected to vary as $\tau_u \propto \frac{(Dt)^{\frac{1}{3}}}{l^{\frac{2}{3}}}$. However, the experimental results are not consistent with this behaviour and consequently if precipitates are responsible for the locking of dislocations, it is inferred that the contribution of pipe diffusion to their growth is negligible.

Regime 2: plateau

An explanation for the mechanism responsible for the second regime in unlocking stress is that competition exists between nitrogen diffusion to the surface and to the dislocation. If the magnitude of the stress required to unlock a dislocation pinned by nitrogen precipitates depends linearly on the radius of a precipitate, then the activation energies for transport of nitrogen to the dislocation and to the surface are the same. This would therefore explain the finding that the regime 2 unlocking stress is approximately independent of annealing temperature. A problem with this explanation is that nucleation of precipitates is generally found to be strongly dependent on temperature, as shown for oxygen in Figure 1.6. It may be, however, that precipitates nucleated heterogeneously at dislocations are nucleated on certain defects which occur with an approximately uniform density, such as jogs, which seemed likely from the analysis of regime 1. This could mean that precipitation at a dislocation is not thermally activated and that the radius of a precipitate depends only on the diffusivity and concentration of nitrogen.

Another possible explanation is competition between nitrogen diffusion to the dislocation and the removal of nitrogen from the bulk by the formation of nitrogen-

containing precipitates in the bulk. However, this explanation is less likely to be correct, since nucleation of precipitates in the bulk (homogeneous nucleation) would need to be independent of temperature for the value of the unlocking stress in regime 2 not to depend on temperature. This is much harder to explain than temperature independent heterogeneous nucleation.

The value of unlocking stress in regime 2 remains constant for long periods of time. Since the unlocking stress is proportional to $\frac{\tau}{l}$, this indicates that $\frac{\tau}{l}$ does not change significantly during the time scale of the second regime. Unless $\frac{\tau}{l}$ is fixed for some reason, this indicates that no coalescing or dissolution of the precipitates occurs, which is perhaps surprising.

Temperature dependence of the unlocking stress

The temperature dependence of the dislocation unlocking stress data presented in Figure 4.5 can be analyzed in terms of Equation 3.20, which is:

$$\tau_u = \frac{N}{b^2} [\Delta G^* - kT \ln(\frac{LN\nu}{\Gamma})] \quad (4.10)$$

In the case of dislocation locking by precipitates, the interaction energy of nitrogen with the dislocation (ΔG^*) is likely to be significantly higher than the 3eV suggested by Yonenaga [14]. Therefore, it is expected that the first term in Equation 4.10 will dominate. Thus, in the case that locking is due to nitrogen precipitates the dislocation unlocking stress would not be expected to vary strongly with the unlocking temperature.

The data shown in Figure 4.5 show that the unlocking stress depends strongly on the temperature at which the unlocking process takes place. This is the expected behaviour for dislocation locking by atomic impurities and is difficult to explain if precipitates are responsible for dislocation locking.

Summary

The possibility that nitrogen at dislocations takes the form of precipitates has been considered in this Section. Given that the unlocking stress measured depends approx-

imately linearly on the radius of the precipitate, the activation energy for nitrogen transport deduced from dislocation unlocking measurements may be consistent with that found in a SIMS out-diffusion investigation by Itoh and Abe [119]. Nitrogen precipitation can explain the temperature independence of the second regime of unlocking stress, if heterogenous nucleation is not thermally activated. However, the problem with the analysis is that, at present, there are too many unknown variables and it is difficult to account for the apparent linear rise in unlocking stress in regime 1. It is thus particularly important to determine experimentally whether precipitates are present and, if this is the case, to understand how their radii and separation vary as a function of annealing time and temperature.

4.3.3 Atoms or precipitates?

In Sections 4.3.1 and 4.3.2 it is shown how the dislocation unlocking data can be analyzed in terms of the properties of nitrogen in silicon. The conclusions drawn differ vastly depending on whether atomic nitrogen or nitrogen precipitates pin the dislocations. As yet it is not known definitively whether nitrogen atoms or precipitates are responsible for dislocation locking effect and it is not possible to infer this from the experimental data presented in this Chapter.

A technique which may be able to determine whether atoms or precipitates are responsible for the dislocation locking effect is TEM. A study using this technique has been started in the Department of Materials, University of Oxford. An initial TEM investigation on dislocations in nitrogen-doped FZ-Si was performed by Dr A. Giannattasio and Dr S. Lozano-Perez. A dislocation-containing nitrogen-doped FZ-Si specimen was annealed at 750°C for sufficient time for the expected dislocation unlocking stress to lie in the second regime. It was then unlocked and made into a TEM specimen. Figure 4.9 shows a TEM micrograph of a line of precipitates in this specimen from which it is possible that a dislocation has moved away. The precipitates are separated by distances of approximately 350nm. Furthermore, an initial TEM investigation was performed, in conjunction with Dr K. Jurkschat, on annealed dislocation-free nitrogen-doped FZ-Si. A sample of as-grown nitrogen-doped FZ-Si was annealed at 900°C for



Figure 4.9: TEM micrograph of a line of precipitates in FZ-Si with a nitrogen concentration of $2.2 \times 10^{15} \text{cm}^{-3}$. The specimen was annealed at 750°C to be in regime 2 of dislocation locking and had been subjected to a three-point bend to unlock the dislocations from the pinning impurities (courtesy of Dr S. Lozano-Perez and Dr A. Giannattasio).

10 minutes and this was made into a TEM specimen. Many precipitates were observed in the specimen. A TEM micrograph of a typical precipitate is shown in Figure 4.10.

The TEM micrographs in Figures 4.9 and 4.10 represent only the beginning of an ongoing TEM study of nitrogen precipitation in silicon. It should be stressed that whilst precipitates have been found, there is as yet no direct evidence that the precipitates contain nitrogen. It is proposed that EELS may enable the elemental composition of the precipitates to be deduced. If these precipitates are indeed found to be due to nitrogen, then a systematic study of their radii and separation needs to be carried out in order for the unlocking stress measurements to be interpreted in terms of nitrogen transport. Further experiments are suggested in Section 8.3.1.

One additional piece of evidence for nitrogen precipitation in the bulk has been provided by the dislocation locking technique. A specimen was subjected to a pre-anneal for 5 minutes at 750°C by C.R. Alpass, before a controlled set of dislocation half-loops was introduced in the specimen and the specimen was subjected to a 48



Figure 4.10: TEM micrograph of a precipitate in the bulk of FZ-Si with a nitrogen concentration of $7 \times 10^{14} \text{cm}^{-3}$. The as-grown specimen was annealed in an argon atmosphere at 900°C for 10 minutes (courtesy of Dr K. Jurkschat).

hour anneal at 750°C . This specimen gave no dislocation locking whatsoever. Since it is unlikely that nitrogen could out-diffuse significant distances in this time [119], this result suggests that nitrogen somehow becomes immobilized. One possibility is that the immobilization occurs due to nitrogen becoming trapped in precipitates in the bulk. If nitrogen is able to precipitate readily in the bulk then this may be relevant to a complete understanding of regime 2 of dislocation locking.

At this stage it is not possible to say for certain whether atomic nitrogen or nitrogen precipitates are responsible for the dislocation locking effect. The evidence for and against each possibility was discussed in this Section and in Sections 4.3.1 and 4.3.2. This evidence is summarized in Table 4.2.

4.4 Summary

Dislocation locking by nitrogen in FZ-Si has been investigated in the 500 to 1200°C temperature range. It has been shown that nitrogen, despite being present at a concentration of just $3 \times 10^{14} \text{cm}^{-3}$ in some specimens, is effective at providing significant dislocation locking (measured at 550°C) across this wide temperature range. It is noted that, unlike oxygen in Cz-Si, dislocation locking by nitrogen in FZ-Si is effective at higher temperatures ($> 800^\circ\text{C}$) and it is suggested that the addition of nitrogen

	Atomic nitrogen	Nitrogen precipitates
For	1. Atomic locking is the most straightforward explanation. 2. Dislocation locking in regimes 1 and 2 in Cz-Si is by atomic oxygen [16, 24, 26]. 3. The dislocation unlocking stress rises approximately linearly with annealing time (Figures 4.1 and 4.2). 4. Strong dependence of unlocking stress on unlocking temperature (Figure 4.5).	1. The activation energy for transport ($3.0 \pm 0.2\text{eV}$) may be consistent with the value from a SIMS out-diffusion study (2.8eV) [119]. 2. TEM on a dislocation-containing sample shows a line of precipitates (Figure 4.9). 3. TEM on the bulk of annealed sample shows precipitates (Figure 4.10), which suggests heterogeneous nucleation is also likely. 4. No locking is found to occur in pre-annealed specimen [191] which suggests precipitation occurs in the bulk and that heterogeneous nucleation is also likely.
Against	1. Activation energy for transport ($1.5 \pm 0.1\text{eV}$) is inconsistent with value from SIMS out-diffusion study (2.8eV) [119]. 2. The dislocation unlocking stress in regime 2 is approximately independent of annealing temperature and this cannot presently be explained in terms of atomic locking.	1. Regime 1 appears to vary linearly with t, but if locking is due to precipitates then it is most likely that it should vary as $\sqrt{t}$. 2. Temperature independence of regime 2 is difficult to explain and would require temperature-independent heterogeneous nucleation. 3. Strong dependence of unlocking stress on unlocking temperature (Figure 4.5), which is indicative of atomic locking.

Table 4.2: Evidence for and against dislocation locking occurring due to atomic nitrogen or nitrogen precipitates.

to Cz-Si will improve its mechanical properties. The binding enthalpy of nitrogen to dislocation core is found to be greater than 2.4eV.

As a function of annealing time at a particular temperature, the dislocation unlocking stress is found to exhibit two distinct regimes. In the first regime, the unlocking stress increases approximately linearly at a rate which depends on annealing temperature and nitrogen concentration. In the second regime, the unlocking stress takes a constant value, which is found to be approximately independent of annealing temperature, but is dependent on nitrogen concentration. By analyzing the first regime, the activation energy of the dislocation locking process is deduced as 1.5eV. The release of a dislocation from the locking nitrogen has also been found to be a thermally activated process in the 500 to 700°C temperature range.

Analysis of the dislocation unlocking data in terms of transport properties requires further knowledge of the nature of the nitrogen species (*e.g.* atoms or precipitates) responsible for the dislocation locking effect.

Chapter 5

Interaction of oxygen impurities with dislocations in Cz-Si

5.1 Introduction

Oxygen is an unavoidable impurity in Cz-Si, as it becomes incorporated during growth from the dissolution of the silica (SiO_2) crucible that contains the melt. It is typically present in concentrations of approximately 10^{18}cm^{-3} . As described in Section 1.3, much research into oxygen in silicon has been carried out. A review article by Newman provides a summary of oxygen diffusion and precipitation [40] and a review article by Michel and Kimerling provides a summary of the electrical activity of oxygen in silicon [41].

In this Chapter, the dislocation locking technique is used to investigate the properties of oxygen in Cz-Si. Experimental results are presented which provide information on the equilibrium of oxygen monomers and dimers, and on the species responsible for oxygen transport in Cz-Si. The dislocation locking technique is also used to investigate impurity transport in nitrogen-doped Cz-Si to determine whether nitrogen affects oxygen transport in the 550 to 600°C temperature range. Additionally, DLTS and HR-DLTS are used to investigate the electrical properties of oxygen-decorated dislocations in Cz-Si.

5.2 Equilibrium of oxygen monomers and dimers

It is well established that thermal treatment of Cz-Si in the 300 to 500°C temperature range produced thermal donor defects [17, 214]. These defects, which are described in more detail in Section 1.3.4, are formed by the agglomeration of different oxygen species. Various models for thermal donor formation have been proposed [215–218]. Critical to each of these models is whether or not the species involved in the different stages of thermal donor formation are in thermodynamic equilibrium. Presented in this Section is the result of an experiment which tests if the first two species in the chain of thermal donor formation, the oxygen monomer and dimer, exist in equilibrium.

If it is assumed that oxygen monomers and dimers in Cz-Si exist in equilibrium:



then the oxygen dimer concentration as a function of temperature is given by [27]:

$$C_2 = \frac{C_1^2 g_2}{g_1 N_{\text{SO}}} \exp\left(\frac{\Delta G_2}{kT}\right) \quad (5.2)$$

where C_1 is the concentration of oxygen monomers, g_1 is the number of sites available in the unit cell for oxygen monomer, g_2 is the number of sites available in the unit cell for the oxygen dimer, N_{SO} is the number of sites available for oxygen atoms in the silicon lattice and ΔG_2 is the binding energy of the oxygen dimer. N_{SO} is 10^{23}cm^{-3} and it can be shown that there are 4 sites available in the unit cell for the oxygen monomer and 12 sites available in the unit cell for the oxygen dimer [27]. The binding energy of the oxygen dimer has been measured to be approximately 0.3eV by IR experiments conducted by Murin *et al.* [27]. The use of this value in Equation 5.2 allows the equilibrium oxygen dimer concentration to be calculated for a particular temperature. In equilibrium, the concentration of oxygen dimers increases with decreasing temperature.

Below a certain critical temperature, the diffusion of oxygen monomers will occur too slowly for oxygen dimers to be formed and the equilibrium breaks down. The concentration of dimers below this critical temperature is fixed and its value is less

than that given by Equation 5.2. It is said that the concentration of oxygen dimers is “quenched in” below this critical temperature. The critical temperature is dependent on the rate at which the Cz-Si is cooled.

An experiment has been devised which can determine this critical temperature. If Cz-Si is subjected to a long pre-anneal at a temperature below the critical temperature, it is expected that the pre-anneal would allow significant monomer diffusion to occur causing the creation of dimers. The concentration of oxygen dimers would therefore increase from the quenched-in value towards the equilibrium value at that temperature. By measuring and comparing the oxygen dimer concentration in Cz-Si which has and has not been pre-annealed, it is possible to deduce if the chosen pre-annealing temperature is below the critical temperature at which the oxygen dimer concentration is quenched in.

In this Section, the dislocation locking technique described in Chapter 2 is used as the means of measuring the oxygen dimer concentration. Cz-Si is subjected to a long pre-anneal at approximately 550°C, before the standard dislocation locking technique described in Chapter 2 is applied with an annealing temperature chosen to be in the temperature regime in which oxygen dimers are thought to be responsible for dislocation locking. If the oxygen dimer concentration is quenched in at temperatures above 550°C then the pre-anneal would increase the dimer concentration and for given annealing conditions, the dislocation unlocking stress measured in a pre-annealed sample would be higher than in a specimen which had not been subjected to the pre-anneal.

5.2.1 Results

A set of dislocation-free Cz-Si bars with an oxygen concentration of $6.3 \times 10^{17} \text{ cm}^{-3}$ (DIN 50438/I) were subjected to a pre-anneal at approximately 550°C for approximately 2,000 hours. Dislocation half-loops were then introduced in the usual way (see Chapter 2) and the specimens were subjected to an anneal at 500°C for 40 hours. 30 μm of material was then removed from the specimens by a planar etch before the stress required to bring about dislocation motion, the unlocking stress, was measured at 550°C. The annealing temperature of 500°C was chosen as it is thought from the work

Specimen	Pre-anneal	Pre-polish [μm]	Unlocking stress [MPa]
A	$\sim 2,000$ hours at 550°C	None	73.6 ± 7
B	$\sim 2,000$ hours at 550°C	~ 140	68.3 ± 10
C	None	None	65.2 ± 8

Table 5.1: Dislocation unlocking stresses measured at 550°C in Cz-Si with an oxygen concentration of $6.3 \times 10^{17}\text{cm}^{-3}$ in specimens subjected to different pre-treatments. After any pre-anneal and pre-polish, dislocations were created in the specimens and the specimens were annealed at 500°C for 40 hours.

of Senkader *et al.* that oxygen dimers are responsible for dislocation locking at this temperature [24, 26, 167].

The dislocation unlocking stresses measured in different specimens are given in Table 5.1. Specimen A was subjected to a pre-anneal at 550°C for approximately 2,000 hours. Specimen B underwent the same thermal treatment as specimen A and also had $140\mu\text{m}$ removed from its surface by means of a polish prior to dislocation creation, to negate the effects of any possible out-diffusion that may have occurred during the pre-anneal. Specimen C was a control specimen and was not subjected to either a pre-anneal or pre-polish.

It can be seen from Table 5.1 that, within experimental errors, the unlocking stress measured takes the same value of approximately 70MPa for the three specimens.

5.2.2 Discussion

Within experimental errors, the pre-anneal had no effect on the dislocation locking. Thus, the concentration of oxygen dimers in the material is not affected by the pre-annealing procedure, which implies that the concentration of oxygen dimers is not quenched in at the pre-anneal temperature (550°C). Therefore, at this temperature oxygen monomers and oxygen dimers are in thermodynamic equilibrium, with the concentration of dimers being given by Equation 5.2.

Senkader *et al.* deduced values of the effective diffusion coefficient of oxygen from dislocation locking experiments [24, 26, 167]. Given that the results presented in this Section show that oxygen monomers and dimers are in equilibrium at 550°C , it is likely that the equilibrium exists over the entire range of temperatures investigated by dislocation locking where enhanced transport is found to occur (350 to approximately

650°C). The reason for this is that the effective diffusivity values, plotted in Figure 1.24, lie on a straight line across this range of temperatures. If the rate of change of oxygen dimer concentration with temperature were to change abruptly, as would happen as the critical temperature is reached, then it is likely that the effective diffusivity, which shows a fairly consistent relationship with oxygen concentration over the temperature range, would also change abruptly.

The fact that oxygen monomers and dimers are in equilibrium means that an expression can be deduced for the diffusivity of the oxygen dimer from the values of effective oxygen diffusivity found by Senkader *et al.* [24,26,167]. In Section 3.4.2 it was shown for material in which the majority species is monomeric, such as is the case for oxygen in silicon, that the effective diffusivity is given by the following expression:

$$D_{\text{eff}} \approx D_1 + 2\frac{C_2}{C_1}D_2 \quad (5.3)$$

where D_1 and D_2 are the diffusivity of the oxygen monomer and dimer respectively, and C_1 and C_2 are the concentration of the oxygen monomer and dimer respectively. D_1 is well known over a wide range of temperatures [70], C_1 , which is approximately the bulk oxygen concentration can be measured experimentally (*e.g.* by IR or SIMS) and given that oxygen monomers and dimers exist in equilibrium, C_2 can be calculated from Equation 5.2.

It can be seen from Figure 1.24 that the monomeric component of oxygen transport is much less than the dimeric component of oxygen transport in the 350 to 600°C range. Thus, with the approximation $D_2 \gg D_1$, substituting Equation 5.2 into Equation 5.3 gives:

$$D_2 \approx \frac{g_1 N_{\text{SO}}}{2C_1 g_2} D_{\text{eff}} \exp\left(-\frac{\Delta G_2}{kT}\right) \quad (5.4)$$

Taking the effective diffusivities of Senkader *et al.* stated in Section 1.7.1 gives the following expression for the average absolute diffusivity of the oxygen dimer:

$$D_2 \approx 0.02 \exp\left(-\frac{1.8\text{eV}}{kT}\right) \text{cm}^2 \text{s}^{-1} \quad (5.5)$$

Thus, the activation energy for diffusion of the oxygen dimer is approximately 0.7eV lower than that of the oxygen monomer [70]. The pre-factor for oxygen dimer diffusion is approximately one order of magnitude lower than that for the monomer.

5.2.3 Conclusions

In this Section, it was shown that subjecting Cz-Si to a pre-anneal at 550°C for 2,000 hours prior to performing the standard dislocation locking technique makes no difference to the unlocking stress of the dislocations. It is concluded that the pre-anneal does not affect the concentration of oxygen dimers. Thus, the results presented are consistent with oxygen monomers and dimers existing in thermodynamic equilibrium at 550°C. Taking the value of the oxygen dimer binding energy measured experimentally by Murin *et al.* [27] allows an approximate value of the diffusivity of the oxygen dimer to be stated.

5.3 Dislocation locking in Cz-Si with a very low oxygen concentration

Dislocation locking by oxygen in Cz-Si with three different oxygen concentrations has been studied by Senkader *et al.* [16, 24, 167]. By modelling the dislocation unlocking stress in terms of oxygen diffusion to a dislocation they were able to deduce values for the effective diffusion coefficient of oxygen across the 350 to 850°C temperature range. These values, which are plotted in Figure 1.24, provided the first clear indication that different species are responsible for oxygen transport in different temperature ranges.

In the case of oxygen in silicon, where the majority oxygen species is the oxygen monomer, the analysis presented in Section 3.4.2 shows that the effective diffusivity is independent of oxygen concentration if the monomer is responsible for transport. In the case of transport by larger oxygen species, the effective diffusivity becomes dependent on the specimen's oxygen concentration. For instance, in the case of transport by the oxygen dimer, the effective diffusion coefficient is directly proportional to the oxygen concentration. If the analysis is continued for larger species, it can be shown that

if a single-species containing N oxygen atoms is responsible for transport then the effective diffusion coefficient will be proportional to the $(N - 1)$ th power of the oxygen concentration.

By analysing the effective diffusion coefficients deduced from the dislocation unlocking data in this way, Senkader *et al.* concluded that the oxygen monomer was principally responsible for oxygen transport at high temperatures (above approximately 650°C) and that the oxygen dimer was most likely to be principally responsible for oxygen transport at low temperatures (350 to approximately 650°C) [24, 26, 167]. In this Section, new experimental results are presented, which show dislocation locking in Cz-Si with a fourth oxygen concentration. It is thought that these new results will be able to provide further insight into the species responsible for oxygen transport at low temperatures.

5.3.1 Results

The dislocation locking technique described in Chapter 2 was applied to Cz-Si with an oxygen concentration of $7.8 \times 10^{16} \text{cm}^{-3}$. Full details of the material investigated are given in Section 2.2. Only a limited amount of material was available, from which approximately 25 specimens could be produced.

As can be seen in Figure 1.24, the magnitude of oxygen's effective diffusion coefficient in the temperature regime in which oxygen diffusion is enhanced depends on the concentration of oxygen in the material. Extrapolation of the data to account for the lower oxygen concentration in the new material implies that to investigate enhanced oxygen diffusion it is necessary to investigate annealing temperatures of 500°C or lower.

Anneals on dislocation-containing specimens have been started at 400, 450 and 500°C. Because of the low oxygen concentration in the specimens and the necessarily low annealing temperatures, the acquisition of a useful set of data will take several years at 400 and 450°C, and a few years at 500°C. Thus, whilst experiments have been started at these three annealing temperatures, in this thesis it is only possible to report preliminary results obtained at the highest temperature: 500°C.

The dislocation unlocking data for specimens annealed at 500°C are shown in Figure

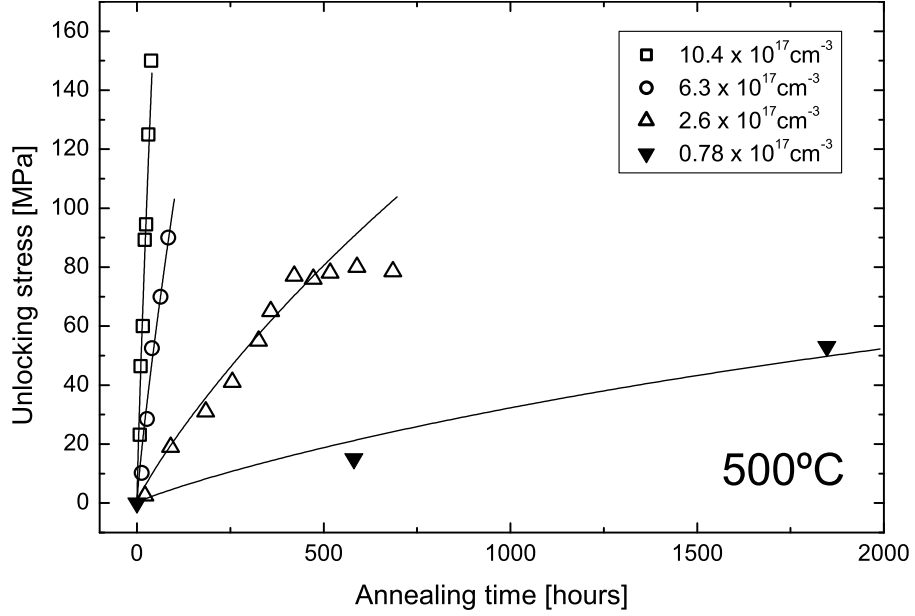


Figure 5.1: Dislocation unlocking stresses measured at 550°C for Cz-Si specimens with different oxygen concentrations annealed at 500°C. The open symbols are data from Senkader *et al.* [24,26,167]. The curves represent a best fit to the experimental data obtained from the numerical simulation described in Section 5.3.2. Oxygen concentrations are quoted to the DIN 50438/I standard.

5.1. Also shown are the data taken by Senkader *et al.* [24,26,167]. The rate of increase in dislocation unlocking stress with annealing time can be seen to be lower in this new material than in the sets of specimens with higher oxygen concentrations.

5.3.2 Modelling and discussion

The data presented in Figure 5.1 were modelled using the methods described in Section 3.3. With the exception of the bulk oxygen concentration, which was known for each set of specimens, the same set of fitting parameters was used for all the numerical simulations. The entropy was taken to be $S = 7.6 \times 10^{-5} \text{eVK}^{-1}$, the number of states at the dislocation core was taken to be $C_a = 5 \times 10^{22} \text{cm}^{-3}$, the binding enthalpy of the oxygen to the dislocation was taken to be $\Delta H_{\text{binding}} = 0.74 \text{eV}$ [16] and the radius of the dislocation core was taken to be $r_0 = 5 \text{\AA}$ [219]. The best fits to the dislocation unlocking data produced by the numerical simulation are plotted in Figure 5.1. The values of the effective diffusion coefficients which produce these fits are stated in Table 5.2.

Oxygen concentration [10^{17}cm^{-3}]	Effective diffusivity [$10^{-17}\text{cm}^2\text{s}^{-1}$]
10.4	5.2
6.3	2.5
2.6	1.1
0.78	0.80

Table 5.2: Effective diffusion coefficients at 500°C for oxygen in Cz-Si with different oxygen concentrations obtained by a numerical simulation of the dislocation unlocking data in Figure 5.1. Oxygen concentrations are quoted to the DIN 50438/I standard.

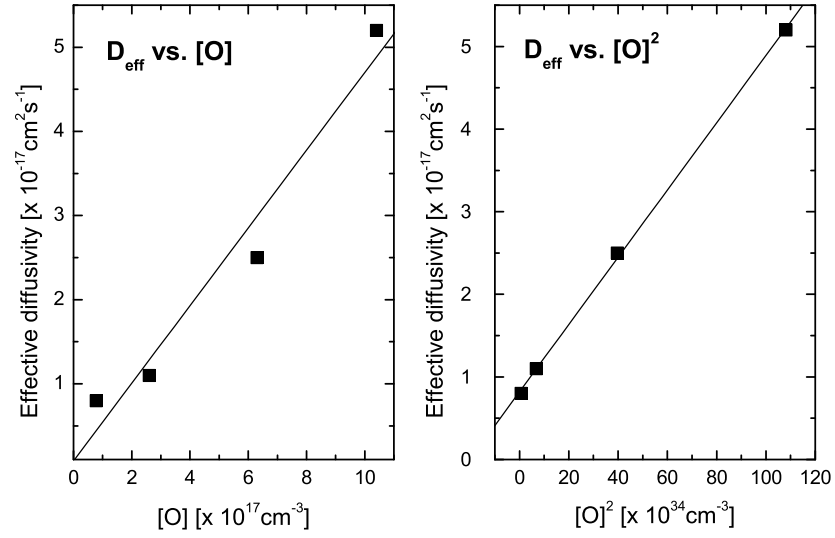


Figure 5.2: The effective diffusion coefficient for oxygen in Cz-Si at 500°C versus oxygen concentration (left) and the square of oxygen concentration. Oxygen concentrations are quoted to the DIN 50438/I standard.

The values of the effective diffusion coefficients in Table 5.2 are plotted against the oxygen concentration and the square of the oxygen concentration in Figure 5.2. It is clear that the effective diffusion coefficient depends on the oxygen concentration. This indicates that the oxygen monomer is not responsible for oxygen transport at 500°C. This fact was already known from the work of Senkader *et al.* [24, 26, 167].

Within the experimental errors of the technique, it is possible that the effective diffusion coefficient scales linearly with the oxygen concentration or with the square of the oxygen concentration. On the basis of dislocation unlocking data obtained in Cz-Si with just three oxygen concentrations, Senkader *et al.* concluded that the oxygen dimer was most likely to be responsible for the enhanced oxygen transport found at low temperatures [24, 26, 167]. However, whilst the new experimental results presented in this Section are consistent with transport by dimers after errors are taken into account, they are also consistent with oxygen transport by a species containing three oxygen atoms; the oxygen trimer. With the experimental results available being limited in number due to the speed of data acquisition, it is not possible to determine which of the two species is most likely to be responsible for enhanced transport. However, the results presented in this thesis certainly leave open the possibility that oxygen transport at low temperatures is dominated by species other than the monomer or dimer. It is clear that further experimental investigation is required.

5.3.3 Conclusions

The locking of dislocations in Cz-Si with an oxygen concentration of $7.8 \times 10^{16} \text{cm}^{-3}$ has been studied at 500°C and the effective diffusion coefficient of oxygen has been deduced from a numerical simulation of the experimental data. When compared to work by Senkader *et al.* with different oxygen concentrations [16, 24, 167], it is shown that the effective diffusion coefficient depends on oxygen concentration, indicating transport is by a species other than the oxygen monomer. At 500°C, the effective diffusion coefficients scale with oxygen concentration in a way which is consistent with transport to the dislocations occurring by diffusion of oxygen dimers or oxygen trimers.

5.4 Dislocation locking in nitrogen-doped Cz-Si at low temperatures

The addition of nitrogen to Cz-Si has become of interest since nitrogen provides wafer manufacturers with better control of oxygen precipitation processes [1–7]. Nitrogen also reduces the formation of voids [8–10] and is known to improve mechanical strength [11–14]. However, whether or not the presence of nitrogen affects the behaviour of oxygen in silicon has yet to be fully studied.

The dislocation locking technique, which is described in Chapter 2, has been used to study the independent behaviour of nitrogen (see Chapter 4) and oxygen [16,24,26,167] in silicon. The technique provides useful information on the mechanical benefits of nitrogen and oxygen impurities in silicon and the data obtained can be interpreted in terms of nitrogen and/or oxygen transport. In this Section, the technique is used for the first time on nitrogen-doped Cz-Si; silicon in which both nitrogen and oxygen impurities are present. By the use of this technique it will be possible to investigate the effect that nitrogen has on the mechanical properties of nitrogen-doped Cz-Si and to see if nitrogen affects the transport of oxygen.

The dislocation locking technique is used to investigate nitrogen-doped Cz-Si at low annealing temperatures (550 and 600°C) for times of up to 20 hours. If nitrogen and oxygen transport to dislocations are independent processes, then from work presented in Chapter 4 of this thesis and from work by Senkader *et al.* [24,26,167], a prediction of the dislocation locking behaviour can be made. For the annealing temperatures investigated oxygen is known to lock dislocations much more rapidly than nitrogen. Thus, given that the annealing times investigated are short compared to the time required for nitrogen to give significant locking, if the processes are independent then the dislocation locking in nitrogen-doped Cz-Si will be the same as that in nitrogen-free Cz-Si. However, it is possible that the presence of nitrogen could alter the behaviour of oxygen in some way. It is possible that nitrogen could change oxygen's mechanism of diffusion or that it could remove oxygen from the bulk by causing oxygen to precipitate or by the formation of nitrogen-oxygen complexes, which have been shown to exist [111–113].

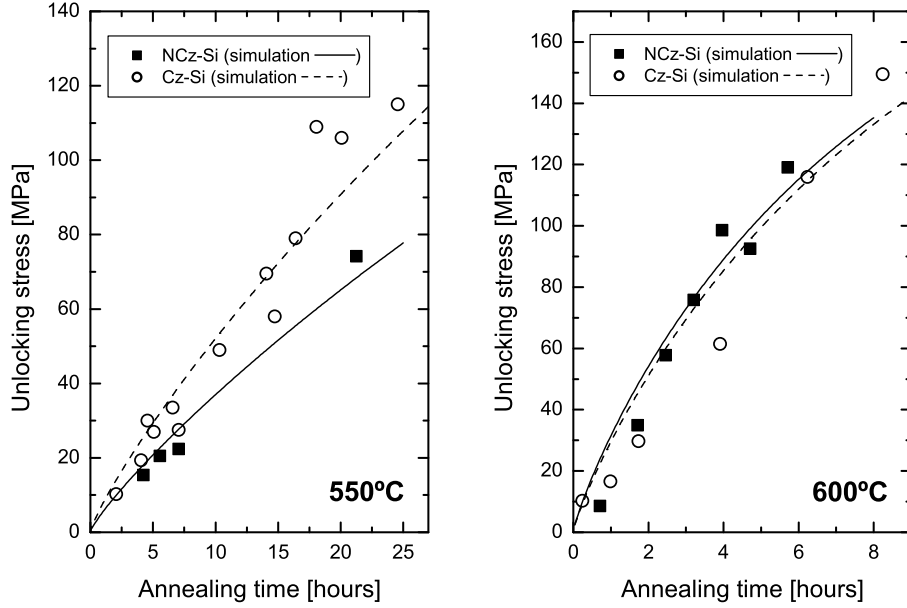


Figure 5.3: Dislocation unlocking stresses measured at 550°C in nitrogen-doped Cz-Si with a nitrogen concentration of $2.1 \times 10^{15} \text{ cm}^{-3}$ (closed squares) and nitrogen-free Cz-Si from Senkader *et al.* [24] (open circles). The oxygen concentrations in both specimens is approximately the same ($\sim 6 \times 10^{17} \text{ cm}^{-3}$). The curves represent the best-fit to the experimental data obtained from a numerical model described in Section 5.4.2.

5.4.1 Results

The dislocation locking technique was applied to nitrogen-doped Cz-Si with a nitrogen concentration of $2.1 \times 10^{15} \text{ cm}^{-3}$ and an oxygen concentration of $5.74 \times 10^{17} \text{ cm}^{-3}$. Full details of the material used are given in Section 2.2. The nitrogen-doped Cz-Si specimens used were chosen because the nitrogen concentration is approximately the same as that in the FZ-Si investigated by Giannattasio [177] and the oxygen concentration was approximately the same as that in the Cz-Si specimens with an oxygen concentration of $6.3 \times 10^{17} \text{ cm}^{-3}$ investigated by Senkader *et al.* [24, 167].

The dislocation unlocking stress measured at 550°C for nitrogen-doped Cz-Si specimens annealed at 550 and 600°C is plotted in Figure 5.3. Also shown in the Figure are the data obtained by Senkader *et al.* for nitrogen-free Cz-Si with an oxygen concentration of $6.3 \times 10^{17} \text{ cm}^{-3}$ [24, 167]. The dislocation unlocking stress is found to increase with increasing annealing time for all the experimental conditions investigated. The rate of increase in unlocking stress is approximately the same in both sets of specimens.

Temperature [°C]	[O] [$\times 10^{17} \text{cm}^{-3}$]	[N] [$\times 10^{15} \text{cm}^{-3}$]	D_{eff} [$\text{cm}^2 \text{s}^{-1}$]
550	5.74	2.1	8.5×10^{-17}
	6.3	< 0.1	9.5×10^{-17}
600	5.74	2.1	7.3×10^{-16}
	6.3	< 0.1	6.0×10^{-16}

Table 5.3: Effective diffusion coefficients of oxygen calculated from a numerical simulation of impurity transport to dislocations in nitrogen-doped Cz-Si and nitrogen-free Cz-Si at 550 and 600°C.

5.4.2 Modelling and discussion

The dislocation unlocking data presented in Figure 5.3 show that the rate of increase of the dislocation unlocking stress with annealing time is similar in the nitrogen-doped Cz-Si and the nitrogen-free Cz-Si. Given that the oxygen concentrations in the two sets of specimens is approximately the same ($\sim 6 \times 10^{17} \text{cm}^{-3}$), it concluded that dislocation locking in Cz-Si is not significantly affected by the presence of nitrogen for the experimental conditions investigated. Thus, for the conditions investigated nitrogen has no catalytic or inhibitive effect on oxygen transport and does not cause oxygen to be trapped either in complexes or precipitates. The dislocation locking is attributed solely to oxygen in both sets of specimens.

The dislocation unlocking data in Figure 5.3 can be used to deduce the effective diffusivity of the locking oxygen impurity by using the methods described in Section 3.3. The curves plotted in Figure 5.3 represent a fit to the experimental data made using this model. Other than the bulk impurity concentration, which was taken as the known oxygen concentration in the specimen, the same set of fitting parameters were used to model all the data presented in Figure 5.3. The entropy was taken to be $S = 7.6 \times 10^{-5} \text{eV K}^{-1}$, the number of states at the dislocation core was taken to be $C_a = 5 \times 10^{22} \text{cm}^{-3}$, the binding enthalpy of the oxygen to the dislocation was taken to be $\Delta H_{\text{binding}} = 0.74 \text{eV}$ [16] and the radius of the dislocation core was taken to be $r_0 = 5 \text{\AA}$ [219]. The effective diffusion coefficients that provide the best fits of the experimental data are given in Table 5.3.

It is known from previous work that at the annealing temperatures which the data in Figure 5.3 was taken, oxygen transport occurs by a species other than the oxygen

monomer, the majority oxygen species in silicon [24, 167]. Consequently, from the analysis presented in Section 3.4.2, the value of the effective diffusion coefficient deduced from a numerical simulation of diffusion to dislocations using the methods described in Section 3.3 should depend on the oxygen concentration in the specimen. Previous work indicates that the oxygen dimer is responsible for oxygen transport at the temperatures investigated in this Section [24, 26, 167]. In Section 3.4.2 it is shown that if the oxygen dimer is responsible for transport then the effective diffusivity will vary linearly with oxygen concentration.

The value of the effective diffusion coefficients in nitrogen-free Cz-Si and nitrogen-doped Cz-Si vary linearly with oxygen concentration at 550°C. The respective ratio of the oxygen concentrations is 0.91 and at this temperature the respective ratio of the effective diffusion coefficients is 0.89. The corresponding ratio at 600°C, 1.22, is not in such good agreement. However, there is a reason to think that the data taken by Senkader *et al.* at 600°C [24, 26, 167] was subject to a small temperature offset. A specimen annealed at 600°C gave an unlocking stress of 92MPa, compared to 62MPa in the work of Senkader *et al.*. The difference is accounted for if the annealing temperature intended to be 600°C in the work of Senkader *et al.* was in fact approximately 15°C lower.

5.4.3 Conclusions

Within the experimental errors of the dislocation locking technique, the data presented in this Section show that the presence of nitrogen makes no difference to the locking of dislocations in Cz-Si at 550 and 600°C for the annealing times investigated. It is therefore concluded that the presence of nitrogen makes no difference to oxygen transport at 550 and 600°C.

5.5 Electrical activity of oxygen at dislocations

DLTS has long been used to try to understand the properties of dislocation-related electronic states in silicon [220–224]. DLTS signals associated with the presence of dis-

locations are generally found in the 100 to 300K temperature range. However, attempts at detailed trap analysis are limited by the broad nature of the peaks found.

The presence of oxygen in Cz-Si is known to bring about many benefits, as were discussed in Section 1.3.2. A major benefit is that oxygen can improve the mechanical strength of the material by immobilizing dislocations [15, 16]. The electrical activity of oxygen in bulk silicon is well understood [41]. However, since the electrical activity of dislocations in silicon has also been found to be affected when the dislocations are decorated with other impurity atoms [225, 226] the influence of oxygen, commonly the most abundant impurity in Cz-Si, on dislocation-related electrical activity should also be studied.

Conventional DLTS measurements alone are often not sufficient to identify whether a point- or extended-defect is responsible for a deep-level. Other experiments, such as measuring the capture cross-section of a trap, need to be carried out in order to characterize the defect. The activation enthalpy of an isolated point-defect is independent of fill pulse duration. Extended defects are known to charge during a DLTS experiment. The change in the local bending which results from this charging leads to variations with fill pulse duration in both the activation enthalpy for the hole emission process and in the capture cross-section [227]. Electron capture into extended defects causes a Coulombic barrier to evolve with time, such that the DLTS signal has a logarithmic dependence on the fill pulse time, t_p [228]. The time-dependent trap occupancy, $n_T(t_p)$, is given by the following relationship:

$$n_T(t_p) = \sigma \langle v \rangle \tau N N_T \ln\left(\frac{t_p}{\tau}\right) \quad (5.6)$$

where σ is the capture cross-section of the trap, $\langle v \rangle$ is the mean thermal velocity of the carriers, τ is a measure of the time required for the trapped charge to affect the Coulomb barrier, N is the carrier concentration and N_T is the total trap concentration. Plotting the change in capacitance as a function of the logarithm of the fill pulse duration yields a straight line in the special case of emission from dislocation-related traps.

HR-DLTS has been previously used to investigate dislocated silicon [229]. Whilst it showed a complex series of emission rates which were difficult to interpret, it did also clearly show a variation in the emission rate as the fill pulse length was varied. This is consistent with previous findings that the apparent activation enthalpy of the deep-level in the vicinity of a dislocation, measured by conventional DLTS, varies as a function of fill pulse length [226].

In this Section, the techniques of DLTS and HR-DLTS were applied to Cz-Si containing dislocations with varying degrees of oxygen decoration. The techniques of DLTS and HR-DLTS are described in more detail in Sections 2.6 and 2.7 respectively. The experimental investigation in this Section was done in collaboration with Prof. J.H. Evans-Freeman, D. Emiroglu and Dr K.D. Vernon-Parry at the Materials and Engineering Research Institute at Sheffield Hallam University.

5.5.1 Specimen preparation

Specimens containing a controlled set of dislocation half-loops were prepared by indentation at $40\mu\text{m}$ intervals using a microhardness tester followed by four-point bending at 550°C . The specimens were cooled to below 400°C before the load was removed. The four-point bending conditions were chosen to give dislocation half-loops with a diameter of approximately $200\mu\text{m}$. The indentation and bending methods used are the same as those described in Section 2.3.

One of these specimens was not annealed and acted as a control. Two other specimens were annealed in argon atmosphere at 500°C for different times (15 and 35 hours). The annealing times were chosen to allow significantly different amounts of oxygen to segregate at the dislocation cores. The annealing conditions used allowed the unlocking stress and hence the concentration of oxygen at the dislocation to be found by comparison with earlier work by Senkader *et al.* [24]. The specimen that was not annealed can be considered to have dislocations that are almost totally free of oxygen, since by cooling the specimen under load to be below 400°C after the four-point bend stage, very little oxygen is able to segregate to the dislocation. The annealing conditions and the oxygen segregated to the dislocations in the specimens investigated are given in

Specimen	Annealing time at 500°C [h]	Dislocation unlocking stress [MPa]	Oxygen atoms at dislocation [cm ⁻¹]
A	35	150	2×10^7
B	15	75	1×10^7
C	0	< 10	$< 1 \times 10^6$

Table 5.4: Cz-Si specimens containing dislocation arrays with varying degrees of oxygen decoration. The bulk oxygen concentration in all the specimens was $1.05 \times 10^{18} \text{cm}^{-3}$ to the DIN 50438/I standard.

Table 5.4.

After the annealing stage the location of the dislocations was determined by differential interference contrast microscopy (see Section 2.5) and this information was used when deciding where to position the Schottky diodes for the DLTS experiments. Approximately $50 \mu\text{m}$ of material was removed from the surface of the specimens by mechanical and chemomechanical polishing, in order to remove damage associated with the indents and to negate the effects of any oxygen out-diffusion. The samples were not chemically etched at any stage, in order to avoid the introduction of hydrogen, which is thought to give rise to electrically active states [230].

Circular titanium Schottky diodes with a diameter of 1mm were sputtered onto the top surface. The Schottky diodes were positioned on top of the dislocation-containing areas. A typical dislocation separation is approximately $3 \mu\text{m}$. Using this and the indentation and bending conditions, gives an estimate of the number of dislocations under each diode to be approximately 3,000 to 4,000. Aluminium Ohmic contacts were evaporated onto the entirety of the rear surface. The Schottky diode and Ohmic contact production processes are described in more detail in Section 2.6.3.

5.5.2 Results

Conventional DLTS spectra for the three specimens are shown in Figure 5.4. The applied reverse biases were -4V , -1.5V and -2V for specimens A, B and C respectively. At these voltages, the respective values for the quiescent capacitance, C_0 , at 300K were 75pF, 50pF and 28pF. The fill pulse voltage was 0.1V for all measurements.

For temperatures below 100K, a sharp peak was found in specimens that had been

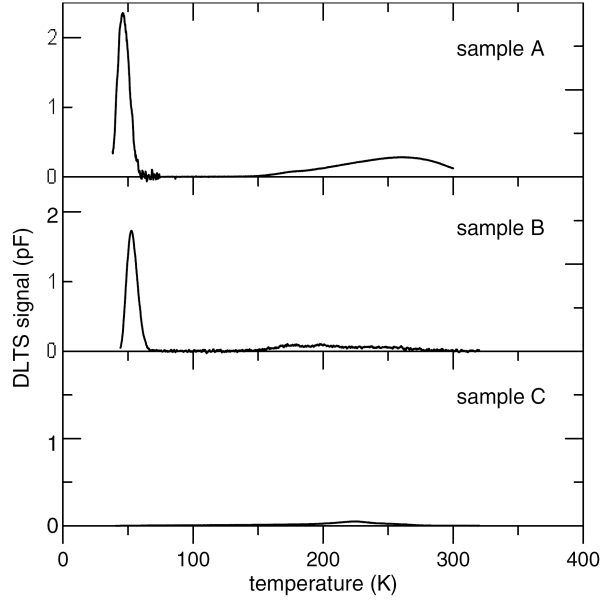


Figure 5.4: DLTS spectra for Cz-Si containing dislocations decorated with different amounts of oxygen. Specimen A has a high amount of oxygen at the dislocation core, specimen B has a medium amount of oxygen at the dislocation core and specimen C has no oxygen at the dislocation core. The rate window was 200s^{-1} and the fill pulse time was 1ms.

Specimen	Fill pulse duration [ms]	Activation enthalpy [meV]
A	1	250
	10	220
B	1	280
	10	260

Table 5.5: Activation enthalpies of the low temperature peak found in specimens A and B calculated from an Arrhenius plot at two fill pulse durations.

annealed (specimens A and B). The peak was found to occur at 40 to 50K for emission at 200s^{-1} . This peak was not observed in the specimen that had not been intentionally annealed (specimen C). The activation enthalpy of the low temperature peak found in specimens A and B was determined by performing conventional DLTS at different rate windows. The dependence of the activation enthalpy on the duration of the fill pulse was also investigated. The activation enthalpy results for this peak are presented in Table 5.5. The measured activation enthalpy was found to depend on the duration of the fill pulse used.

HR-DLTS was then carried out at temperatures close to the peak found by conventional DLTS. Figure 5.5 shows HR-DLTS spectra taken at 50K for sample B for

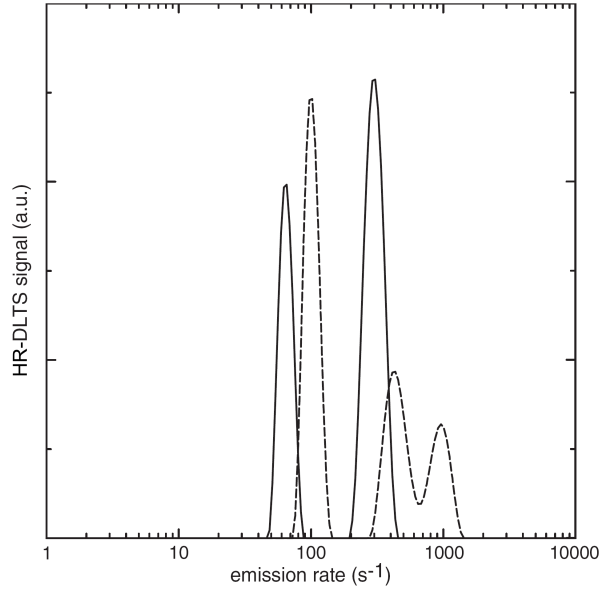


Figure 5.5: HR-DLTS spectra for Cz-Si containing dislocations decorated with $\sim 10^7 \text{cm}^{-1}$ of oxygen (specimen B). The spectra were both taken at 50K. The solid curves are taken with a fill pulse of 1ms and the dashed curve is taken with a fill pulse of 50ms.

two different fill pulse durations; 1ms and 50ms. From the Figure it can be seen that emission occurs at two rates with a 1ms fill pulse. As the fill pulse length is increased to 50ms, emission occurs at higher rates and an additional higher emission feature is observed.

The conventional DLTS spectra presented in Figure 5.4 also show a very broad peak at higher temperatures. This peak was also investigated by HR-DLTS. Specimens A and B exhibited a complex emission spectrum and the HR-DLTS spectrum for specimen B is shown in Figure 5.6. Emission has been found to occur at three different rates for fill pulses durations of both 10ms and 50ms. The location of the peak is independent of the fill pulse duration to within the errors of the HR-DLTS technique [183].

The high temperature peak found by conventional DLTS in specimen C is shown in more detail in Figure 5.7. It can be seen in the Figure that the peak consists of a narrow symmetrical peak centred at 225K for a 200s^{-1} emission rate, as well as higher and lower temperature shoulders, indicating that the sharp peak is superimposed on a broad background peak. An Arrhenius plot of the peak centred at 225K gives a constant value of activation enthalpy when the fill pulse duration is varied.

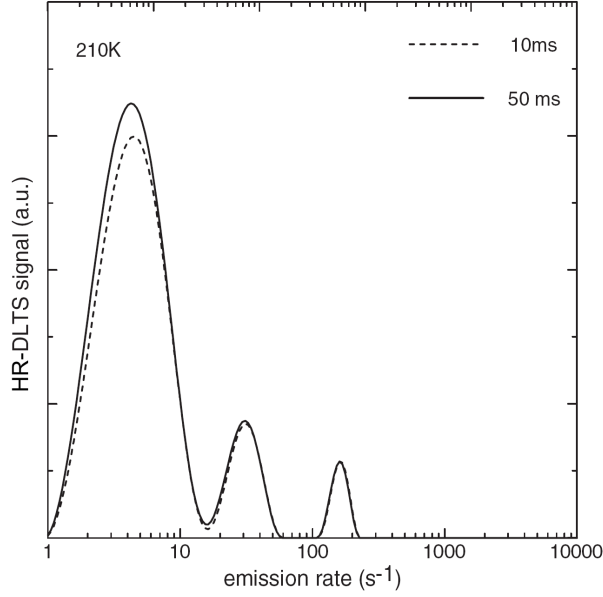


Figure 5.6: HR-DLTS spectra for the specimen containing dislocations decorated by oxygen with concentration of $\sim 10^7 \text{cm}^{-1}$ (specimen B) measured at 210K, with fill pulse durations of 10ms and 50ms.

The high temperature peak found in specimen C was investigated further by HR-DLTS. HR-DLTS spectra taken at 225K with two different fill pulse durations are shown in Figure 5.8. It is found that changing the duration of the fill pulse changes the emission rate for some of the peaks in Figure 5.8. Furthermore, an additional peak appears in the HR-DLTS spectrum as the fill pulse duration is increased from 1ms to 10ms.

The peaks with slower emission rates in Figure 5.8 were found to have an approximately constant emission rate with varying fill pulse. Figure 5.9 shows the low and high emission rates plotted separately on a linear axis, to confirm that the locations of the low emission rate peaks do not vary significantly with fill pulse duration. The very small variations observed for these peaks are well within HR-DLTS error bars [183].

5.5.3 Discussion

Low temperature peaks

The low temperature peak found at 40 to 50K in specimens A and B is sharp and narrow, as can be seen in Figure 5.4. This initially suggests that it is associated with

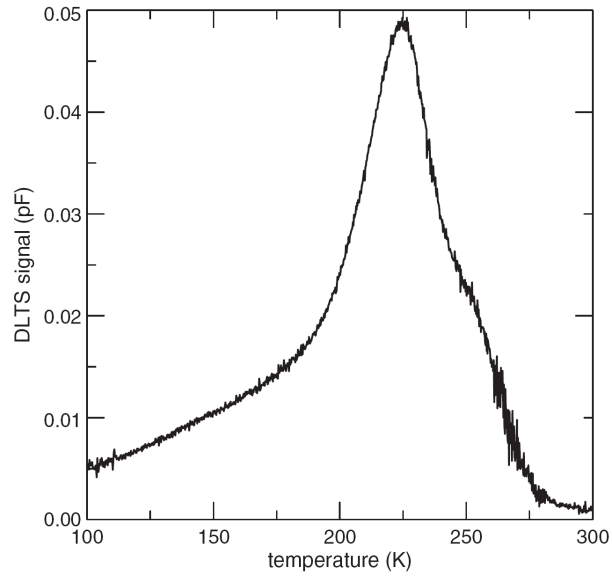


Figure 5.7: DLTS spectrum for the specimen containing dislocations which were not intentionally decorated by oxygen (specimen C) at a rate window of 200s^{-1} and a fill pulse duration of 1ms.

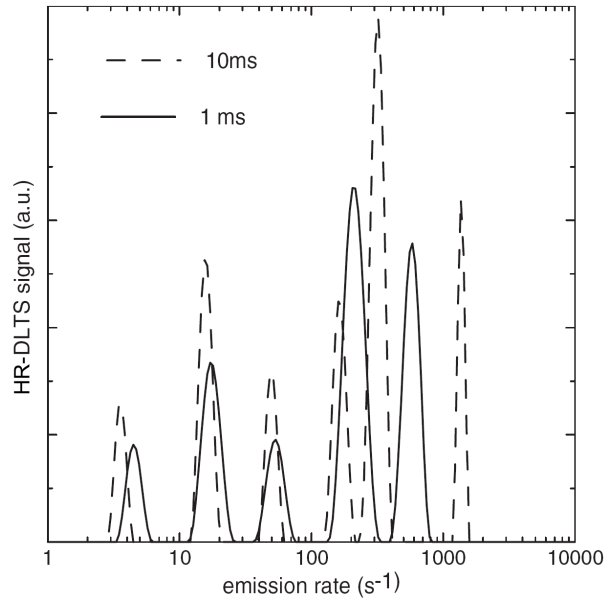


Figure 5.8: HR-DLTS spectra for the specimen containing dislocations which were not intentionally decorated by oxygen (specimen C) measured at 225K at two different fill pulse durations.

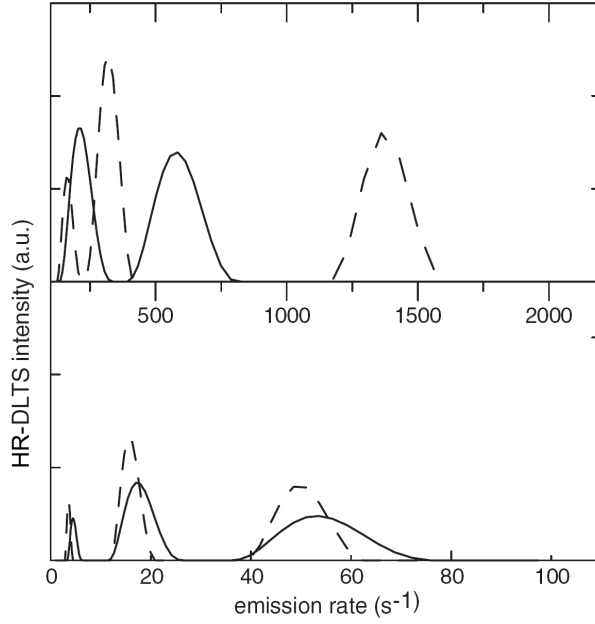


Figure 5.9: Linear plots of HR-DLTS spectra for the specimen containing dislocations which were not intentionally decorated by oxygen (specimen C) measured at 225K showing the change in emission rate of the deep states which emit at a rate of $> 100\text{s}^{-1}$.

an isolated point-defect state. However, several experimental results presented in this Section indicate that this is not the case and that the peak may be related to the presence of oxygen at the core of the dislocations.

The first piece of evidence that supports the hypothesis that the peak is due to oxygen at dislocations is that the peak is only found in the specimens which contain oxygen-locked dislocations (specimens A and B). No peak was found at this temperature in specimen C, in which the dislocations were not decorated with a significant amount of oxygen.

Secondly, the results presented in Table 5.5 show that the activation enthalpy of the state changes with fill pulse duration for both specimens. Since the activation enthalpy of a defect state is related to the state's position in the band gap, it is difficult to imagine how this could change with fill pulse duration for an isolated point-defect. A variation in the activation enthalpy with fill pulse duration is typical behaviour for states in the vicinity of extended defects [221, 226]. In this work, the activation enthalpy changes by 20 to 30meV when the fill pulse duration changed from 1 to 10ms. The magnitude of this change in enthalpy is comparable to that found by Qian *et*

al. in specimens containing oxidation-induced stacking faults decorated by metallic impurities [226]. In these specimens they found that changing the fill pulse between 0.5 to 5ms changed the activation enthalpy by 18 to 33meV. It is also the case that defects exhibiting DLTS peaks at such low temperatures usually have smaller activation enthalpies, usually corresponding to those of shallow dopants. The results presented in Table 5.5 show that the activation enthalpies of the defects found are much higher than those of shallow dopants. The unusually large activation enthalpies found at this temperature are attributed to the fact that the emitting centre(s) is (are) in the strain field of the dislocations [227, 231]. Both capture and emission at the traps are likely to be complicated processes in which the charging of the dislocation has a significant effect, which evolves with time.

Finally, the HR-DLTS spectra shown in Figure 5.5 show more than one peak, and as the fill pulse duration is increased an extra higher emission feature appears in the spectrum. This is not consistent with emission from an isolated point-defect state. This result can be explained by the existence of another state which requires a longer pulse to become filled and emit. The reason for the state becoming harder to fill may be due to the dislocation charging up during carrier capture. However, it may be that the peaks with high emission rates have no physical significance and are an artefact of the technique. The applicability of HR-DLTS to states whose emission characteristics are non-exponential may be limited to identifying whether a state is related to an extended defect or not. It is questionable whether any analysis beyond this is physically meaningful [184].

The sharp peak found at low temperatures was found to have an activation energy of 220 to 280meV. This has not been observed previously in studies on silicon containing dislocations [220–224]. Most of these studies are on n-type silicon [220, 221, 223, 224]. The study of Ayres *et al.* found a state at $E_v + 0.54\text{eV}$, which was not observed in this present work [222].

It is worth mentioning that whilst thermal donor defects could exist in silicon annealed at 500°C, it is thought that the concentrations formed would not be significant. As shown in Figure 1.8, the formation rate of thermal donors exhibits a sharp peak

at around 450°C and based on known formation rates [72] it is unlikely that a high concentration will be formed for the annealing conditions used to produce these DLTS specimens. Furthermore, the sharp peaks in Figure 5.4 are due to hole emission and the thermal donor peak known to exist in the temperature range of interest is due to electron emission [232]. Additionally, there is no evidence of type inversion in the behaviour of the Schottky diodes and the CV profile did not vary between specimens annealed for different times.

High temperature peaks

All the specimens, whether the dislocations were decorated with oxygen or not, were found to exhibit a broad emission spectrum between 100 and 300K. This emission is typical for silicon containing dislocations [220–224].

The conventional DLTS spectrum for the specimen which contained oxygen-free dislocations (specimen C) presented in Figure 5.7 shows two sets of features; a narrow symmetric peak centred at 225K and higher and lower temperature broad shoulders. An Arrhenius plot of the symmetric peak gives a value of activation enthalpy that does not vary with fill pulse duration. This is consistent with emission from an isolated point-defect. HR-DLTS was used to investigate the broad spectrum and revealed the complicated emission spectrum shown in Figure 5.8. In Figure 5.8 it is shown that increasing the fill pulse duration changes the emission rate for some, but not all, of the HR-DLTS peaks. This is consistent with some of the defect states being in the vicinity of a dislocation, since the shift in emission rate is due to the local band bending that occurs as the dislocation charges up during the experiment, and some of the defect states being due to isolated point-defect emission. Increasing the fill pulse duration also leads to the appearance of an extra peak in the HR-DLTS spectrum in Figure 5.8. This extra peak may be an artefact of the HR-DLTS technique, resulting from analyzing a non-exponential emission. Alternatively, a simple explanation of this extra peak is that it corresponds to a hole state possessing a low capture cross-section that only fills after a very long fill pulse. This is related to the concept of deep-levels near a dislocation becoming harder to fill as the dislocation charges up because of repulsive carrier band

bending effects [227, 228] and the effect was also observed at lower temperatures in specimen B, as shown by Figure 5.5. Another possible explanation would be that multiple states at the dislocation core fill at different rates depending on the occupancy of the other states [229]. Regardless of whether the extra peak has physical significance or not, it is clear that the high temperature electrical activity exhibited by specimen C occurs due to both emission from isolated point-defects and emission from states in the vicinity of a dislocation.

The high temperature HR-DLTS spectrum for specimen B presented in Figure 5.6 shows an emission spectrum comprising just three components. When the errors in HR-DLTS [183] are taken into account, the locations of the emission rate peaks do not vary with fill pulse duration. This is indicative of emission from point-defect states. Since specimen A exhibits the same behaviour it is concluded that specimens A and B only exhibit high temperature electrical activity associated with point-defects.

In summary, emission at higher temperatures from point-defects is observed for all specimens, regardless of the degree to which the dislocations were decorated with oxygen. Emission at high temperatures from deep-levels in the vicinity of dislocations was only found to occur when the dislocations were not decorated with oxygen.

Reproducibility

The results presented in this Section were obtained from a single set of specimens produced at the same time. As with any DLTS investigation on annealed material, there is a risk that transition metal impurities may have contaminated the samples. Therefore, to further investigate the electrical activity associated with the decoration of dislocations by oxygen and to check the original work, a second set of specimens was fabricated. For reasons that are still unclear, it was not possible to reproduce the original results, insofar as no low temperature peak was found in two annealed dislocation-containing specimens. The only significant difference in specimen preparation between the two sets of specimens was that the indentation for the second set of specimens was done with a nanoindenter rather than a microhardness tester.

5.5.4 Conclusions

DLTS and HR-DLTS have been applied to a set of p-type Cz-Si specimens containing a controlled set of dislocation half-loops decorated with different amounts of oxygen. Deep-levels associated with dislocations are found to be modified by the presence of oxygen at the dislocations.

All specimens containing dislocations, whether the dislocations are locked by oxygen or not, exhibit a typical broad DLTS emission between 100 and 300K. HR-DLTS has been used to establish that this broad emission feature only has components due to emission from deep states in the vicinity of a dislocation when the dislocations are not locked by oxygen.

A new peak at 40 to 50K was found in specimens which contained oxygen-locked dislocations. The activation enthalpy of this state was found to vary from 220 to 280meV as the fill pulse duration was varied between 1 and 10ms. It is suggested that this deep-level is due to oxygen at the core of the dislocations.

5.6 Summary

A dislocation locking technique, DLTS and HR-DLTS have been used in this Chapter to investigate the properties of oxygen in silicon.

Experimental results are presented which show that a 2,000 hour pre-anneal at 550°C makes no difference to the dislocation unlocking stress measured after an anneal at 500°C for 40 hours. This implies that the pre-anneal does not affect the concentration of oxygen dimers and it is concluded that oxygen monomers and dimers exist in thermodynamic equilibrium at 550°C.

The dislocation locking technique was used to extend the work of Senkader *et al.* [24, 26, 167] by performing experiments in Cz-Si with a fourth oxygen concentration at 500°C. The effective diffusivity obtained by numerical simulation of the dislocation unlocking data is found to vary with oxygen concentration, further confirming that oxygen transport at 500°C does not occur by the oxygen monomer. The effective diffusion coefficients found scale with oxygen concentration in a way consistent with

transport by the oxygen dimer or trimer.

The dislocation locking technique was also used to investigate nitrogen-doped Cz-Si at 550 and 600°C. Within the experimental errors of the technique, it is shown that the presence of nitrogen in a concentration of $2.1 \times 10^{15} \text{cm}^{-3}$ makes no difference to the dislocation unlocking stress measured. It is concluded that oxygen transport in Cz-Si is unaffected by the presence of nitrogen at the temperatures investigated.

DLTS and HR-DLTS were used to investigate the electrical activity of dislocations decorated by different amounts of oxygen in p-type Cz-Si. All specimens, regardless of the degree of oxygen decoration, were found to exhibit a broad DLTS emission between 100 and 300K. It is shown that the broad emission only has components due to deep-levels in the vicinity of a dislocation in the case when the dislocations are not locked by oxygen. Specimens containing oxygen-locked dislocations exhibited a DLTS peak at 40 to 50K, which was shown by HR-DLTS to be due to more than one energy state. The activation enthalpy of the peak was found to vary with fill pulse duration and it is suggested that the deep-level found is associated with oxygen at the core of the dislocations.

Chapter 6

Oxygen transport in highly-doped Cz-Si

6.1 Introduction

Cz-Si contains interstitial oxygen in a concentration of approximately 10^{17} to 10^{18}cm^{-3} , which is present as a consequence of the dissolution of the silica crucible which contains the melt. The presence of oxygen in Cz-Si is both beneficial and detrimental from the point of view of production of integrated circuits. Oxygen precipitates, which are formed by appropriate heat treatments, can act as gettering centres for unwanted metallic impurities [44]. Additionally, oxygen can improve the mechanical strength of wafers as it is known to immobilize dislocations that may be introduced during device processing [15,16,190]. However, excess precipitation can lead to dislocation generation, which adversely affects the wafer's mechanical stability (for a general discussion see reference [39]). For the benefits of oxygen to be exploited fully, and for the detrimental effects of oxygen to be minimized, a full understanding of the transport of oxygen in silicon is essential. The current understanding of oxygen transport in Cz-Si is reviewed in Section 1.3.

The transport of oxygen in Cz-Si containing a high concentration of shallow dopants is an area in which conflicting experimental results have been published and no clear picture has yet emerged. The effect of the electrical doping level on oxygen transport

in as-grown Cz-Si has been studied experimentally by SIMS [28–30]. The experimental results for the effect of high concentrations of antimony, boron and arsenic on oxygen transport in Cz-Si are summarized in Table 1.2. High concentrations of all three elements have been found to provide a retardation effect on oxygen transport at 800°C and below [29, 30], although the studies disagree on the temperatures at which the retardation takes place. In the study of Takeno *et al.*, a high boron doping level was found to slow oxygen transport at 600 and 700°C [30]. Since in the same work it was also found that oxygen transport is not affected by a high boron doping level at 500 and 800°C, the authors attributed the retardation to the formation of immobile oxygen complexes. None of the elements has previously been directly shown to provide an enhancement in oxygen transport in as-grown material. However, there is indirect evidence for the transport of oxygen being enhanced by a high boron concentration. One such piece of evidence is that oxygen precipitation, a process which is limited by oxygen transport, has been found to be enhanced in Cz-Si with a high concentration of boron [93]. Another is that oxygen transport, measured by SIMS, has been found to be enhanced in material into which boron had been diffused [94]. Density functional theory calculations by Adey *et al.* indicate that the activation energy for diffusion of an oxygen dimer should be lower in highly-doped p-type Cz-Si than in silicon with a low doping level [91]. The calculations predict an activation energy for oxygen diffusion in low doped Cz-Si to be 1.33eV and in highly-doped p-type Cz-Si to be 0.86eV.

In this Chapter, the dislocation locking technique described in Chapter 2 is used to investigate highly-doped Cz-Si. Cz-Si with a high concentration of boron and Cz-Si with a high concentration of antimony are investigated. Using the methods described in Chapter 3, the dislocation unlocking data are analyzed in terms of transport of oxygen to give the effective diffusion coefficients of oxygen in Cz-Si with high concentrations of boron and antimony.

Label	Dopant	Dopant concentration [cm^{-3}]	Oxygen concentration [cm^{-3}]
p	B	$\sim 1 \times 10^{15} \text{cm}^{-3}$	$6.3 \times 10^{17} \text{cm}^{-3}$
n ⁺	Sb	$0.56 \text{ to } 6.3 \times 10^{18} \text{cm}^{-3}$	$\sim 7.5 \times 10^{17} \text{cm}^{-3}$
p ⁺	B	$2.7 \text{ to } 8.0 \times 10^{18} \text{cm}^{-3}$	$\sim 10.6 \times 10^{17} \text{cm}^{-3}$

Table 6.1: The properties of the Cz-Si specimens for which dislocation unlocking results are presented in this Chapter. Oxygen concentrations are quoted to the DIN 50438/I standard.

6.2 Results

The dislocation locking technique was applied to Cz-Si with different electrical properties. The key properties of the specimens investigated are summarized in Table 6.1 and their properties are described in detail in Section 2.2. Specimens made from highly antimony doped and highly boron doped Cz-Si were annealed at temperatures in the 350 to 550°C temperature range for times up to approximately 250 hours. The results obtained were compared to results in Cz-Si with a low boron doping level taken by Senkader *et al.* [16, 24].

The dislocation unlocking stress as a function of annealing time at temperatures from 450 to 550°C for low boron doped p-type Cz-Si with an oxygen concentration of $6.3 \times 10^{17} \text{cm}^{-3}$ and highly antimony doped n-type Cz-Si with an oxygen concentration of $1.06 \times 10^{18} \text{cm}^{-3}$ is shown in Figure 6.1. For both sets of specimens, the dislocation unlocking stress increases approximately linearly with annealing time. The gradient of this initial linear rise is on average 3.0 times larger in the case of the highly antimony doped material. This higher gradient is attributed to the higher oxygen concentration in the highly antimony doped n-type Cz-Si and this is discussed in Section 6.4.

The dislocation unlocking stress as a function of annealing time at temperatures from 350 to 550°C for highly boron doped p-type Cz-Si with an oxygen concentration of $7.5 \times 10^{17} \text{cm}^{-3}$ and low boron doped p-type Cz-Si with an oxygen concentration of $6.3 \times 10^{17} \text{cm}^{-3}$ is shown in Figure 6.2. Again, the dislocation locking stress increases approximately linearly with annealing time. The dislocation locking by oxygen occurs at a much faster rate in the highly boron doped material. For instance, at 400°C, the rate of increase in dislocation locking occurs approximately 60 times faster in the highly boron doped Cz-Si compared to low boron doped Cz-Si. The magnitude of

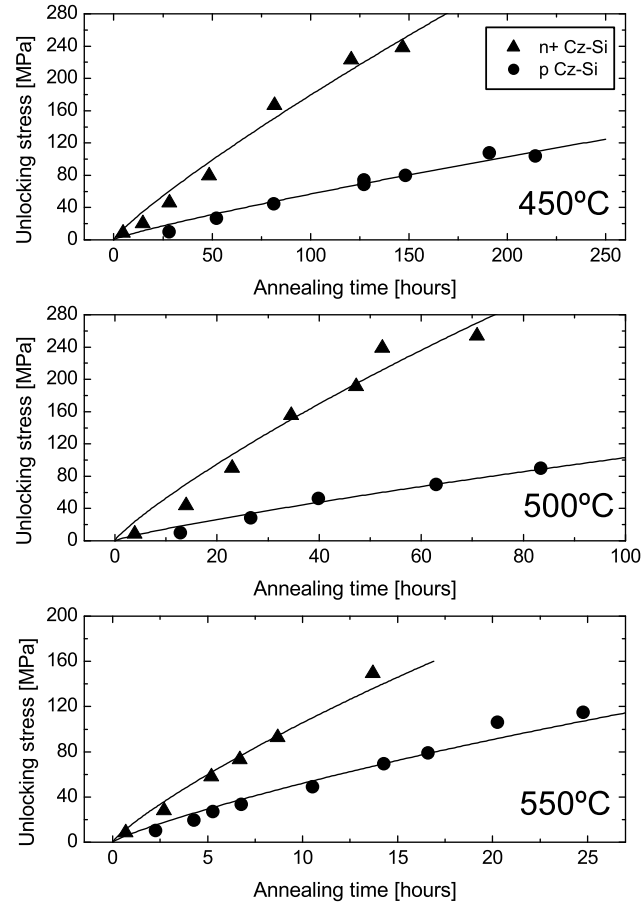


Figure 6.1: Dislocation unlocking stresses measured at 550°C for highly antimony doped n-type Cz-Si (triangles) and low boron doped p-type Cz-Si (circles) at different annealing temperatures. The curves represent a numerical simulation of oxygen diffusion to dislocations, as described in Section 6.3. The low boron doped data were taken by Senkader *et al.* [24].

the enhancement in the rate of dislocation locking cannot be explained by the slightly higher oxygen concentration and it is believed that high boron doping enhances oxygen diffusion. This is discussed in more detail in Section 6.4.

6.3 Modelling

The dislocation locking process occurs due to oxygen transport to the core of the dislocation. Thus, from analyzing the dislocation unlocking stress as a function of annealing time and temperature, it is possible to deduce information on oxygen transport.

The numerical simulation described in Section 3.3 is used to fit the experimental data presented in Figures 6.1 and 6.2. The following fitting parameters are used to simulate all the data obtained for all the different types of Cz-Si for which results are presented in this Chapter: the entropy was taken to be $S = 7.6 \times 10^{-5} \text{eVK}^{-1}$, the number of states at the dislocation core was taken to be $C_a = 5 \times 10^{22} \text{cm}^{-3}$, the binding enthalpy of the oxygen to the dislocation was taken to be $\Delta H_{\text{binding}} = 0.74 \text{eV}$ [16] and the core radius was taken to be $r_0 = 5 \text{\AA}$ [219]. This is a different approach to that taken in previous work using the same technique, where a small range of values were used for the entropy, number of states at the dislocation core and the binding energy to provide the best overall fit to a particular set of experimental data [16, 24, 26]. Therefore, the absolute values of the effective diffusivity for the Cz-Si with the low boron concentration presented in this work differ slightly from those presented in previous publications for which different fitting parameters were used. By fitting the simulation to the experimental data points, a value of D_{eff} is then determined at each temperature for each type of material. It is these values of D_{eff} which are taken as the measured value of effective oxygen diffusivity for the conditions studied. The value of the effective diffusion coefficients deduced from the dislocation unlocking data are given in Table 6.2.

The effective diffusivity of oxygen as deduced from dislocation unlocking experiments is plotted in Figure 6.3 for the Cz-Si with a high antimony doping level, Cz-Si with a low boron doping level and Cz-Si with a high boron doping level. Also shown

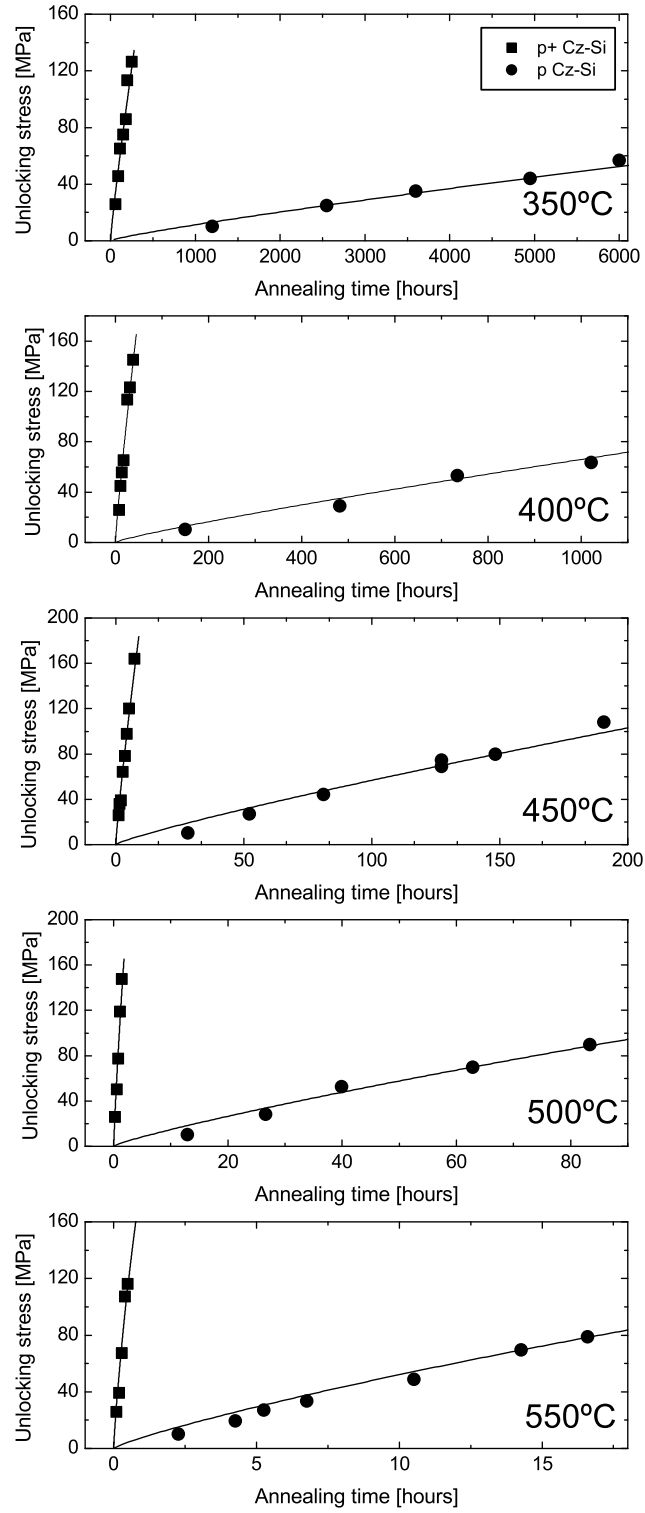


Figure 6.2: Dislocation unlocking stresses measured at 550°C for highly boron doped p-type Cz-Si (squares) and low boron doped p-type Cz-Si (circles) at different annealing temperatures. The curves represent a numerical simulation of oxygen diffusion to the dislocation, as described in Section 6.3. The low boron doped data were taken by Senkader *et al.* [24].

Temperature [°C]	D_p [cm ² s ⁻¹]	D_{n+} [cm ² s ⁻¹]	D_{p+} [cm ² s ⁻¹]
350	1.8×10^{-19}	-	9.3×10^{-18}
375	4.5×10^{-19}	-	-
400	1.4×10^{-18}	-	7.4×10^{-17}
450	1.2×10^{-17}	2.5×10^{-17}	4.3×10^{-16}
500	2.5×10^{-17}	6.1×10^{-17}	2.0×10^{-15}
550	1.15×10^{-16}	1.45×10^{-16}	5.0×10^{-15}
600	6.0×10^{-16}	-	-
650	4.0×10^{-15}	-	-
700	1.4×10^{-14}	-	-
730	1.0×10^{-14}	-	-

Table 6.2: Effective diffusion coefficients for oxygen in Cz-Si with different electrical properties. The effective diffusivity for the highly-doped Cz-Si was obtained from fitting a numerical solution to the diffusion equation to the data presented in Figures 6.1 and 6.2, as described in Section 6.3. The values of the effective diffusion coefficient in low boron doped material was fitted to the data of Senakder *et al.* [16,24].

in the Figure are data for oxygen diffusion in low doped Cz-Si obtained by a variety of other techniques [70]. A best fit of the effective diffusion coefficients plotted in Figure 6.3 gives the following expression for the effective diffusivity of oxygen in p-type Cz-Si with a low boron doping level:

$$D_p = 1.6 \times 10^{-7} \exp\left(-\frac{1.5\text{eV}}{kT}\right) \text{cm}^2\text{s}^{-1} \quad (6.1)$$

in the 350 to 600°C temperature range. The effective diffusivity of oxygen in p-type Cz-Si with the high boron doping level is given by the following expression:

$$D_{p+} = 2.7 \times 10^{-6} \exp\left(-\frac{1.4\text{eV}}{kT}\right) \text{cm}^2\text{s}^{-1} \quad (6.2)$$

in the 350 to 550°C temperature range.

6.4 Discussion

The data presented in Figure 6.1 show that, in the 450 to 550°C temperature range, oxygen is transported to dislocations approximately three times faster in the case of the highly antimony doped n-type Cz-Si with an oxygen concentration of $1.06 \times 10^{18} \text{cm}^{-3}$ than in the case of the low boron doped p-type Cz-Si with an oxygen concentration of

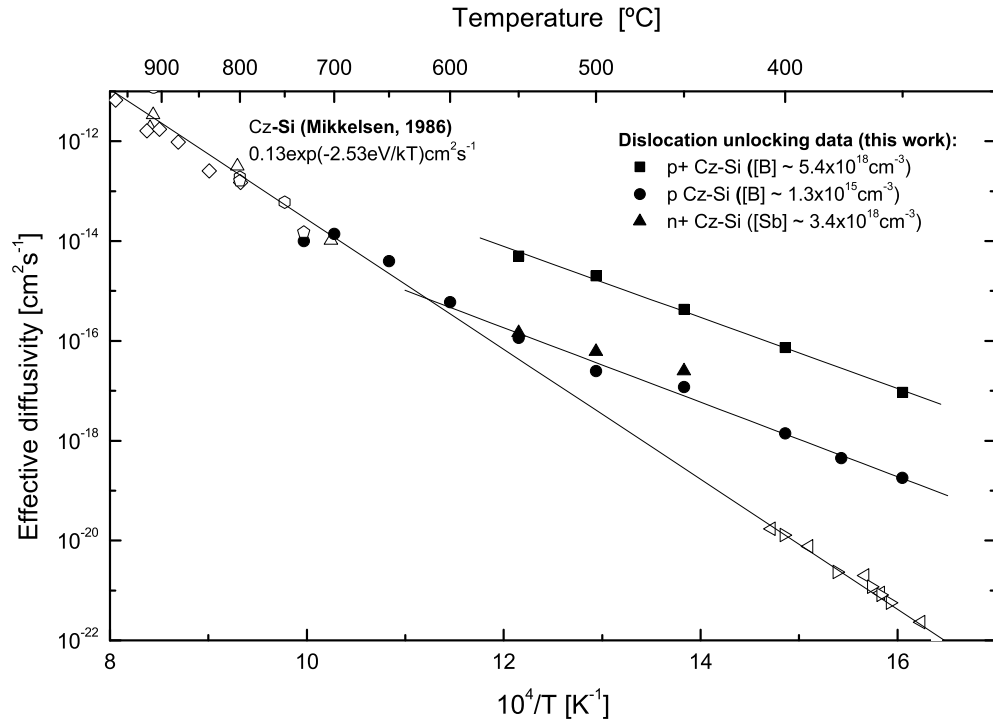


Figure 6.3: The effective diffusion coefficient for oxygen in silicon as a function of temperature. Data from the literature for Cz-Si with a low concentration of shallow dopants are denoted by open symbols [70]. Data from dislocation locking experiments are denoted by closed symbols [24, 26]. Closed circles are for low boron doped Cz-Si with an oxygen concentration of approximately $7.5 \times 10^{17} \text{ cm}^{-3}$, closed squares are for high boron doped Cz-Si with an oxygen concentration of approximately $6.3 \times 10^{17} \text{ cm}^{-3}$ and closed triangles are for high antimony doped Cz-Si with an oxygen concentration of $1.06 \times 10^{18} \text{ cm}^{-3}$.

$6.3 \times 10^{17} \text{cm}^{-3}$. If it is assumed that the oxygen dimer is responsible for dislocation locking at the temperatures investigated, which is suggested by previous work [24, 26], then it can be shown that the effective diffusivity of oxygen depends linearly on the oxygen concentration and hence the gradient of the initial rise in dislocation unlocking stress depends on the square of the oxygen concentration in the specimens [26]. The average ratio of the gradient of the initial rises in dislocation locking stress between high antimony doped material and low boron doped material is approximately 3.0, and the square of the ratio of the oxygen concentrations is $(\frac{10.6}{6.3})^2 \approx 2.8$. Within the experimental errors of the technique it is concluded that the difference in oxygen concentrations between the different materials accounts for the higher rate of dislocation locking in the highly antimony doped material and that a high concentration of antimony makes no detectable difference to the transport of oxygen. This effect can also be seen in the data plotted in Figure 6.3, which show that the effective diffusivity of oxygen in the n-type Cz-Si with the high antimony doping level is slightly higher than that in the p-type Cz-Si with the low boron doping level. As described above, this small variation is due to the dependence of the effective diffusivity on oxygen concentration.

The data presented in Figure 6.2 indicate that the oxygen transport to dislocations in the 350 to 550°C temperature range occurs much faster in the highly boron doped p-type Cz-Si with an oxygen concentration of $7.5 \times 10^{17} \text{cm}^{-3}$ than the low boron doped p-type Cz-Si with an oxygen concentration of $6.3 \times 10^{17} \text{cm}^{-3}$. This cannot be explained by a difference in oxygen concentration between the specimens. Assuming that the oxygen dimer is responsible for transport gives an expected enhancement due to the concentration difference of $(\frac{7.5}{6.3})^2 \approx 1.4$, whereas the rate of increase in dislocation locking is found to be enhanced by a factor of approximately 60 at 400°C. The effective oxygen diffusivity plotted in Figure 6.3 is significantly higher in p-type Cz-Si with the high boron doping level compared to p-type Cz-Si with the low boron doping level at all temperatures studied. It is concluded that high boron doping enhances oxygen transport in the 350 to 550°C temperature range. If the effective diffusivity for the low boron doped Cz-Si are scaled linearly to account for the difference in oxygen concentrations, then the enhancement in oxygen transport solely due to the high boron doping

is, on average, by a factor of approximately 44 in the temperature range investigated.

In this work it has been shown that oxygen transport in Cz-Si is not affected significantly by high antimony doping, but is strongly enhanced by high boron doping. The measured activation energies for transport for low boron doped p-type Cz-Si and highly boron doped p-type Cz-Si, given in Equations 6.1 and 6.2 respectively, are the same within experimental error. However, the experimentally measured effective diffusion coefficients vary significantly in their pre-factors.

Both crystal strain effects and electronic effects should be considered with regards to the mechanism of enhanced oxygen transport in highly boron doped Cz-Si. A high boron concentration is known to put the silicon lattice into compression [233] and this could affect the diffusion of oxygen. However, a high level of antimony doping would also introduce a lattice strain (in this case tensile) and the results presented in this work show that doping Cz-Si with a high concentration of antimony does not affect oxygen transport. Thus, it seems likely that lattice strain by itself is not responsible for the enhancement in oxygen diffusion observed in highly boron doped material. Whilst there is no direct evidence that electronic effects are responsible for the enhanced oxygen transport observed in highly boron doped Cz-Si, this remains a possible explanation, since for the doping concentrations used the material remains extrinsic over the entire temperature range studied.

The effect of Fermi level position on oxygen diffusion has been considered by Adey *et al.* [91]. They develop a theoretical model which suggests that the activation energy for oxygen dimer diffusion will be lower in highly-doped p-type material than in p-type Cz-Si with a low concentration of shallow dopants. They suggest that the oxygen dimer in highly-doped p-type Cz-Si exists in a double positive charge state, which diffuses by alternating between square and staggered forms with an activation energy of 0.86eV. However, in material with a low concentration of shallow dopants, the model suggests that the uncharged oxygen dimer is most stable and that it diffuses with an activation energy of 1.33eV. The values of activation energy found in this work given in Equations 6.1 and 6.2 represent those for oxygen transport and not diffusion. If the binding energy of the oxygen dimer is known then the activation energy for oxygen dimer diffusion is

the sum of the values found for transport and the binding energy, as is shown in Section 5.2.2. The binding energy of the oxygen dimer in low-doped Cz-Si has been measured to be approximately 0.3eV by Murin *et al.* [27], but has not been measured in highly-doped Cz-Si. Thus, using the value of Murin *et al.* for low-doped material and the activation energy in Equation 6.1 puts the oxygen dimer diffusion activation energy at approximately 1.8eV. Therefore, unless the binding energy in the highly-doped Cz-Si is smaller than approximately 0.1eV, which seems unlikely, the results presented in this work are not consistent with the 0.47eV reduction in the activation energy for diffusion between the highly-doped and low-doped p-type Cz-Si proposed by Adey *et al.*.

Sueoka *et al.* found that a high boron concentration led to enhanced oxygen precipitation in the 700 to 1000°C temperature range [93]. They suggest that this is due to enhanced oxygen transport, which has been found in this present work. However, other workers [29,30] have found that the effective diffusivity of oxygen is unchanged or actually reduced by high boron doping (see Table 1.2). In this work it has been found that a high antimony concentration in Cz-Si has little effect on oxygen transport in the 450 to 550°C temperature range. This contradicts the results of Takeno *et al.* who found that the activation energy for oxygen transport in such material is increased by 1.40eV in the 500 to 800°C temperature range [30].

6.5 Summary

The locking of dislocations by oxygen in Cz-Si with different concentrations of shallow dopants has been investigated experimentally. In the 450 to 550°C temperature range, the gradient of the rise in dislocation unlocking stress was found to be approximately a factor of three higher in highly antimony doped n-type Cz-Si with an oxygen concentration of $1.06 \times 10^{18} \text{cm}^{-3}$ than in low boron doped p-type Cz-Si with an oxygen concentration of $6.3 \times 10^{17} \text{cm}^{-3}$. This increase in the rate of dislocation locking is due to the higher oxygen concentration in the highly antimony doped Cz-Si. It is therefore concluded that doping Cz-Si with antimony in levels of approximately $3.4 \times 10^{18} \text{cm}^{-3}$ makes no difference to oxygen transport in the temperature range investigated.

In the 350 to 550°C temperature range, the gradient of the rise in the dislocation unlocking stress was found to be much higher in highly boron doped p-type Cz-Si with an oxygen concentration of $7.5 \times 10^{17} \text{cm}^{-3}$ compared to in low boron doped p-type Cz-Si with an oxygen concentration of $6.3 \times 10^{17} \text{cm}^{-3}$. The rate of increase in dislocation unlocking stress at 400°C was enhanced by a factor of approximately 60, which cannot be explained by the higher oxygen concentration in the highly doped Cz-Si. It is concluded that boron doping in levels of approximately $5.4 \times 10^{18} \text{cm}^{-3}$ strongly enhances the transport of oxygen in Cz-Si. From numerical solving the diffusion equation for oxygen transport to a dislocation, the effective diffusivity of oxygen in highly-doped Cz-Si is deduced to be $D_{p+} = 2.7 \times 10^{-6} \exp(-\frac{1.4\text{eV}}{kT}) \text{cm}^2 \text{s}^{-1}$. On average, the effective diffusivity of oxygen in highly boron doped p-type Cz-Si was found to be approximately 44 times higher than would be expected in low boron doped p-type Cz-Si with an identical concentration of oxygen.

Chapter 7

Electrical activity of nitrogen-related defects in silicon

7.1 Introduction

Nitrogen in silicon is known to bring about many benefits, including improving mechanical strength [11–14] and reducing the formation of voids [8–10]. In Cz-Si it also provides wafer manufacturers with flexibility in controlling oxygen precipitation necessary for gettering [1–7]. Because the benefits of nitrogen are so significant, it is already being added to commercial silicon, despite the fact that many of its basic properties, including its electrical activity, are not fully understood.

Authors of several studies have attributed electrically active defects in silicon to nitrogen [132–134, 137]. The results of these studies are summarized in Table 1.3. The results of the older studies [133, 134] should be treated with caution, as the silicon available at the time was of a significantly lower standard than it is today. More recent studies suggest that nitrogen results in levels at $E_c - 0.42\text{eV}$ [137], $E_c - 0.5\text{eV}$ [132] and $E_v + 0.55\text{eV}$ [132], with the level at $E_c - 0.5\text{eV}$ also being found in older work [134]. In this Chapter, DLTS and HR-DLTS are used to obtain new experimental results on the electrical activity of defects in nitrogen-doped silicon.

Neutron transmutation-doped (NTD) FZ-Si is used in applications where a low resistivity variation across the wafer is required, such as for high power devices. The

material is produced by bombarding conventionally-grown FZ-Si with neutrons, which induces a nuclear reaction in which some silicon atoms are converted to phosphorus atoms. As part of the standard production process for this type of material, wafers are subjected to an anneal at 800°C to remove lattice defects resulting from the neutron bombardment process [234]. This annealing procedure appears to work well in nitrogen-free NTD FZ-Si, but when the material is doped with nitrogen during growth there is evidence that electrically active defects remain in the material after the anneal. Results published by von Ammon and Dreier indicate that resistivity shifts of 5 to 10% can occur during subsequent annealing schedules of nitrogen-doped NTD FZ-Si [235], and it is thought that the nitrogen-related defect responsible for this will be observed in DLTS experiments. In this Chapter DLTS and HR-DLTS results are presented for as-grown nitrogen-doped NTD FZ-Si.

Nitrogen-oxygen complexes are known to form in Cz-Si [112]. It is possible that some of these complexes will exhibit electrical activity. In this Chapter, results are also presented for DLTS on p-type Cz-Si with a range of nitrogen concentrations.

The experimental results presented in this Chapter were obtained during a visit by the author to the group of Prof. J.H. Evans-Freeman at the Materials and Engineering Research Institute at Sheffield Hallam University. The details of the equipment and methods used for DLTS and HR-DLTS are described in Sections 2.6 and 2.7 respectively.

7.2 Electrically active defects in nitrogen-doped FZ-Si

The results of DLTS experiments on n-type nitrogen-doped FZ-Si and nitrogen-doped NTD FZ-Si are presented in this Section. The material chosen for use in this Section had a particularly high resistivity (~ 150 to $360\Omega\text{cm}$). Since the sensitivity of the technique depends upon the material's electrical doping level, the experiments done in this Section should allow the detection of electrically active defects in a concentration of below 10^{11}cm^{-3} .

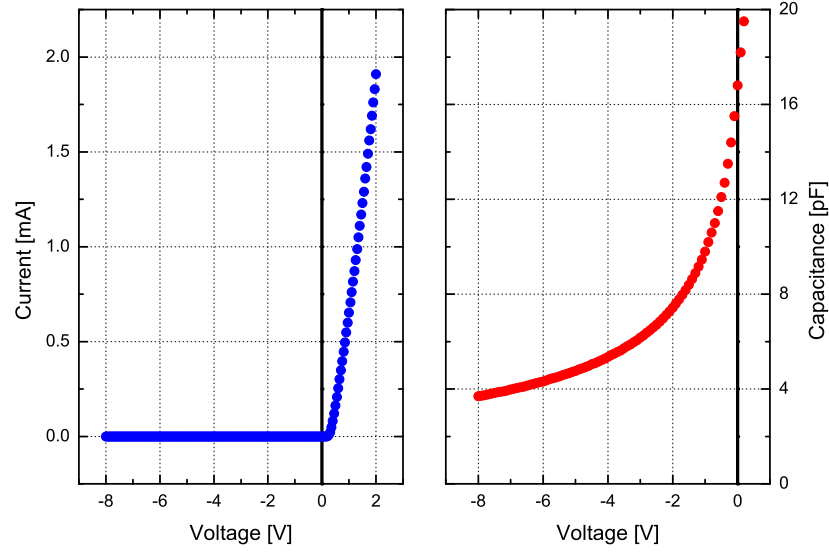


Figure 7.1: IV and CV plots at 300K for n-type nitrogen-doped FZ-Si with a nitrogen concentration of $7 \times 10^{14} \text{cm}^{-3}$ and a resistivity of approximately $300 \Omega \text{cm}$.

7.2.1 Nitrogen-doped FZ-Si results

The nitrogen-doped FZ-Si investigated in this Section was provided by Topsil Semiconductor Materials A/S. The material was n-type (phosphorus doped) with a resistivity of 240 to $360 \Omega \text{cm}$. The nitrogen concentration in the wafers was determined to be $7 \times 10^{14} \text{cm}^{-3}$ by SIMS carried out by Charles Evans and Associates [186]. Further details of the material used are given in Section 2.2. After a rigorous cleaning procedure, gold Schottky barriers and aluminium Ohmic contacts were deposited on the specimens. Full details of these processes are given in Section 2.6.3.

Prior to performing DLTS experiments, IV and CV plots were taken and these are shown in Figure 7.1. The IV plot shows that the diode fabricated could withstand applied reverse biases of at least -8V without breaking down. By applying Equation 2.10 to the CV data, the background carrier concentration in the material was deduced to be approximately $2 \times 10^{13} \text{cm}^{-3}$ and the carrier concentration was found to be approximately uniform for reverse biases larger than approximately -2V .

DLTS was performed on the nitrogen-doped FZ-Si specimen in the 67 to 340K temperature range. Data presented in this Chapter were taken with the specimen

warming up from the initial temperature. The reverse bias was chosen to be -7V and the filling pulse was chosen to be -2V with a length of 1ms . Data were taken at six different rate windows in the range 4 to 200s^{-1} and the DLTS spectra obtained are shown in Figure 7.2.

The data presented in Figure 7.2 show a peak at high temperatures. No other peaks were found in the temperature range investigated. The temperature at which the peak occurred was found to increase with increasing emission rate and was located at 283.0K for a 200s^{-1} emission rate. The amplitude of the peak was found to be approximately 0.03pF for all rate windows investigated. Given that the fill pulse length was chosen to be sufficiently long to completely fill the trap, the heights of the peaks in Figure 7.2 and the CV data in Figure 7.1 can be used in Equation 2.14 to calculate the trap concentration as $3 \times 10^{11}\text{cm}^{-3}$.

The variation in the peak temperature with rate window allows for the enthalpy of the trap to be deduced using Equation 2.11. From the Arrhenius plot in Figure 7.3, the enthalpy was found from the DLTS data to be $0.45(\pm 0.02)\text{eV}$.

HR-DLTS was then applied to the same specimen at different temperatures in the vicinity of the conventional DLTS peak found previously (250 to 270K). The reverse bias and fill pulse conditions were the same as for the conventional DLTS experiments. HR-DLTS was used with a sampling rate of $60,000\text{Hz}$. $7,000$ scans were made and $9,000$ samples were taken for each scan. With these parameters the sampling time was 21.3 minutes. HR-DLTS uses mathematical routines that are all based on the Tikhonov regularization method [207] and in this work the routine known as FLOG was used [184]. The use of this routine on the raw data produced the HR-DLTS spectra shown in Figure 7.4.

HR-DLTS gave rise to one peak for each temperature at which a set of scans was done. Thus, the spectra presented in Figure 7.4 show that the peak found by conventional DLTS (see Figure 7.2) is associated with a single defect state. The emission rate at which the peak occurred was found to increase as the temperature at which the scan was performed was increased.

The variation in the peak temperature with rate window allows for the enthalpy

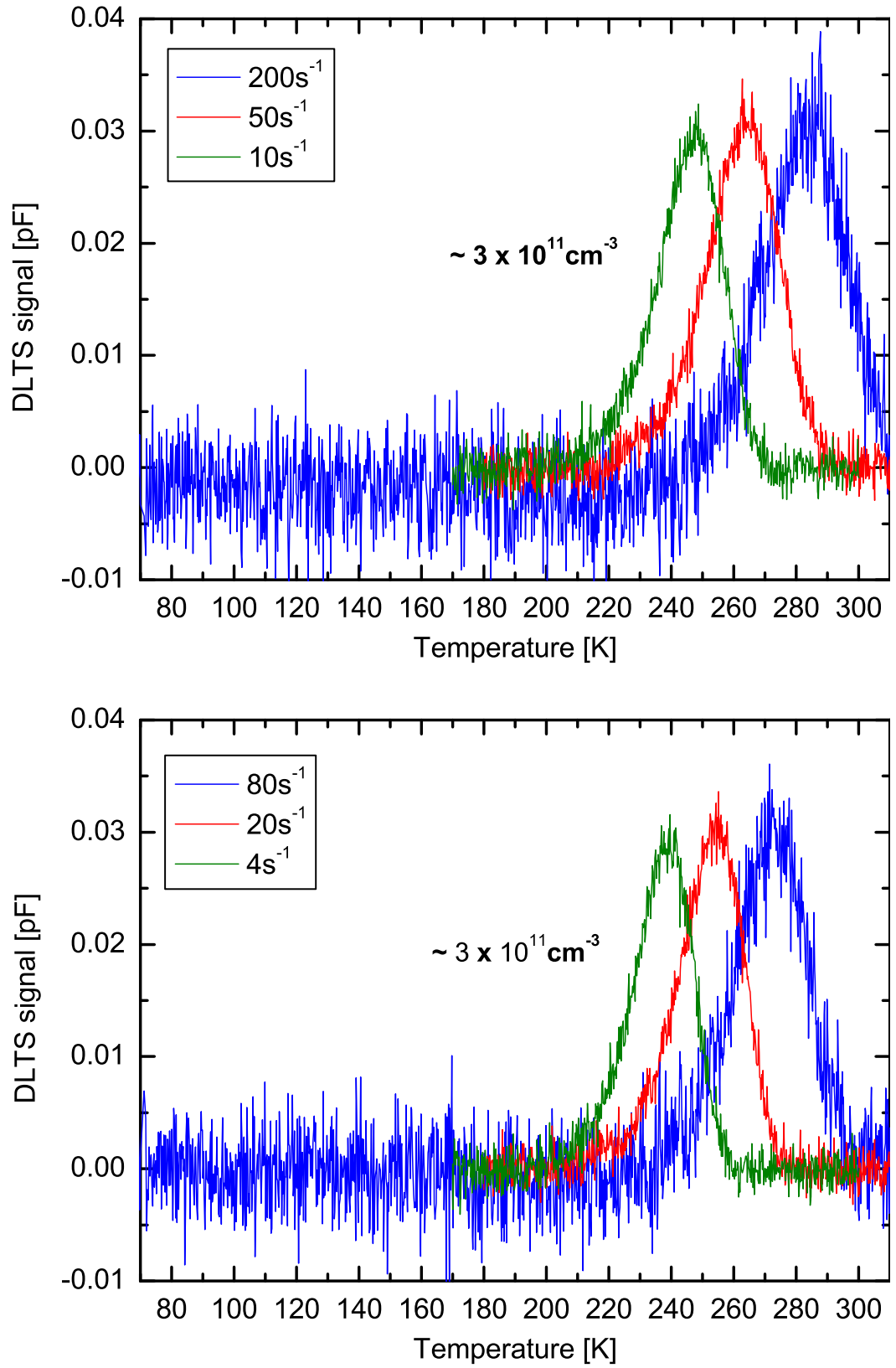


Figure 7.2: DLTS spectra taken with different rate windows for n-type nitrogen-doped FZ-Si with a nitrogen concentration of $7 \times 10^{14} \text{ cm}^{-3}$ and a resistivity of approximately $300 \Omega \text{ cm}$. The sample was subjected to a reverse bias of -7 V and a $1 \text{ ms } -2 \text{ V}$ filling pulse.

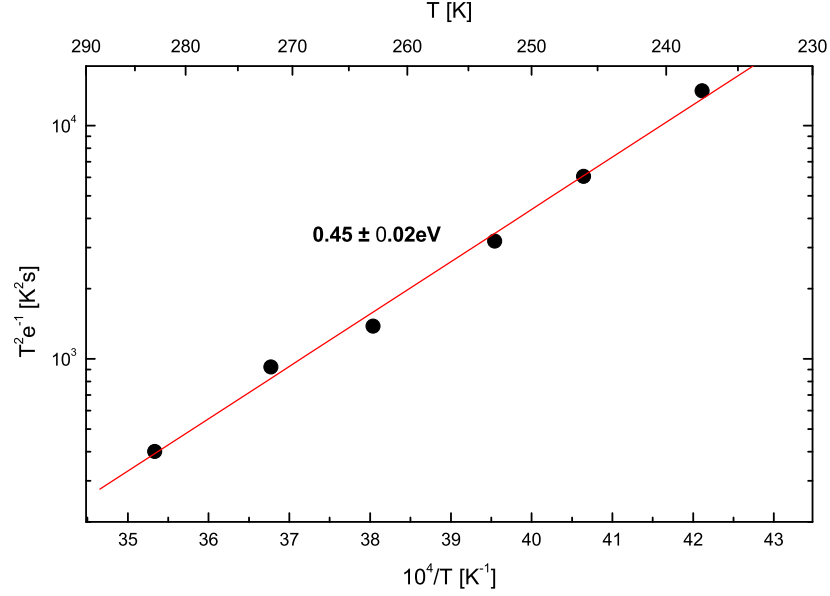


Figure 7.3: Arrhenius plot for n-type nitrogen-doped FZ-Si with a nitrogen concentration of $7 \times 10^{14} \text{cm}^{-3}$ and a resistivity of approximately $300 \Omega \text{cm}$ from the DLTS data presented in Figure 7.2.

of the trap to be deduced using Equation 2.11. From the Arrhenius plot in Figure 7.5 the enthalpy of the trap is found to be $0.50(\pm 0.01) \text{eV}$. It should be noted that whilst the enthalpy was of the trap also deduced from the conventional DLTS data using the Arrhenius plot in Figure 7.3, the fact that fewer transients were measured and that emission was observed at fewer rates means that obtaining the enthalpy from the conventional DLTS data gives a less accurate and less precise value than the one found from the Arrhenius plot in Figure 7.5.

A further parameter of a trap is its capture cross-section. This can be determined by monitoring the change in DLTS peak amplitude as the fill pulse duration is reduced. The shortest possible fill pulse duration with the equipment available was $10 \mu\text{s}$. No reduction in peak amplitude was observed when the fill pulse duration was reduced from the standard duration, 1ms , to this shortest possible duration. This can be used to put a lower limit on the capture cross-section. From Equation 2.15, the minimum capture cross-section is given by:

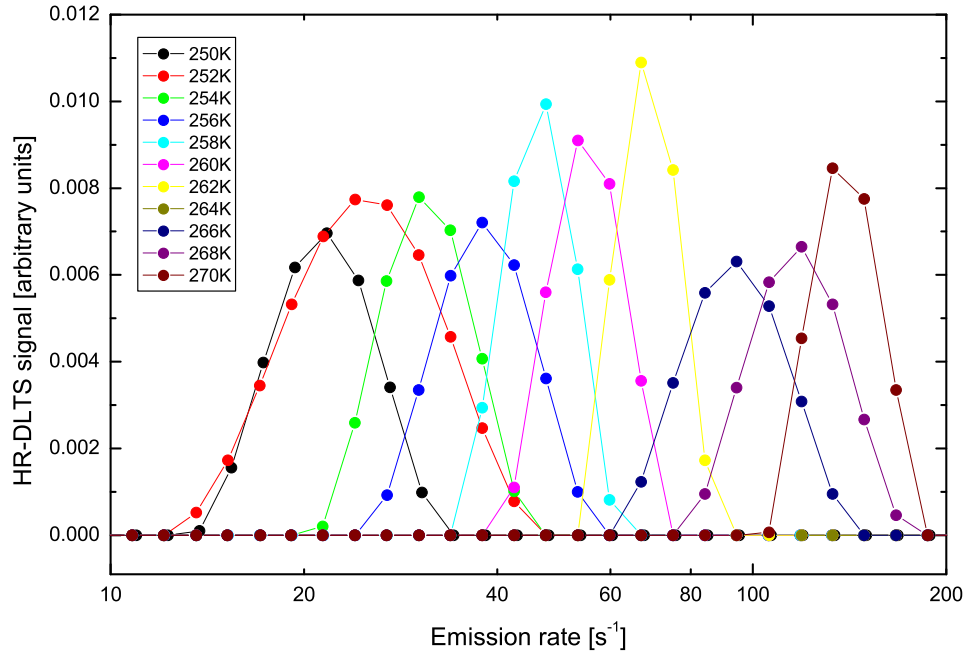


Figure 7.4: HR-DLTS spectra taken at different temperatures for n-type nitrogen-doped FZ-Si with a nitrogen concentration of $7 \times 10^{14} \text{cm}^{-3}$ and a resistivity of approximately $300 \Omega \text{cm}$. The sample was subjected to a reverse bias of -7V and a $1 \text{ms } -2 \text{V}$ filling pulse. The scanning frequency was $60,000 \text{Hz}$. 7,000 scans were made and 9,000 samples were taken in each scan.

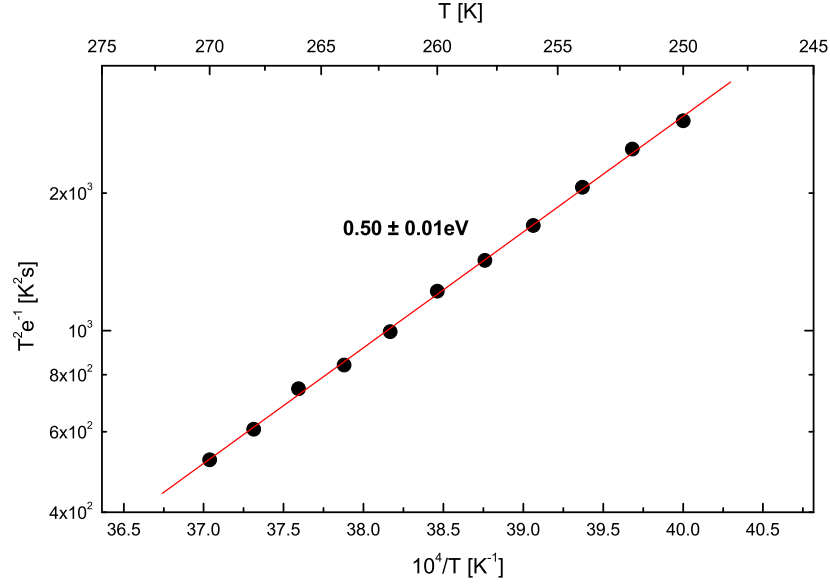


Figure 7.5: Arrhenius plot for n-type nitrogen-doped FZ-Si with a nitrogen concentration of $7 \times 10^{14} \text{cm}^{-3}$ and a resistivity of approximately $300 \Omega \text{cm}$ from the HR-DLTS data presented in Figure 7.4.

$$\sigma_{\text{minimum}} = \frac{1}{\langle v \rangle N_d t_p} \quad (7.1)$$

where the mean thermal velocity of the carriers, $\langle v \rangle$, is typically 10^7ms^{-1} for silicon and, for the material used, $N_d = 2 \times 10^{13} \text{cm}^{-3}$. Thus, given that no change in peak amplitude occurred when the fill pulse was reduced to its shortest duration, $10 \mu\text{s}$, this gives $\sigma > 5 \times 10^{-14} \text{cm}^2$. The magnitude of the capture cross-section of the trap found is indicative of either a neutral or donor state.

7.2.2 Nitrogen-doped NTD FZ-Si results

The nitrogen-doped NTD FZ-Si investigated in this Section was also provided by Topsil Semiconductor Materials A/S. The material was n-type (phosphorus doped by neutron bombardment) with a resistivity of approximately $150 \Omega \text{cm}$. The nitrogen concentration of these wafers was not measured directly, although it is likely to be around 10^{15}cm^{-3} . Further details of the material used are given in Section 2.2. Identical specimen prepa-

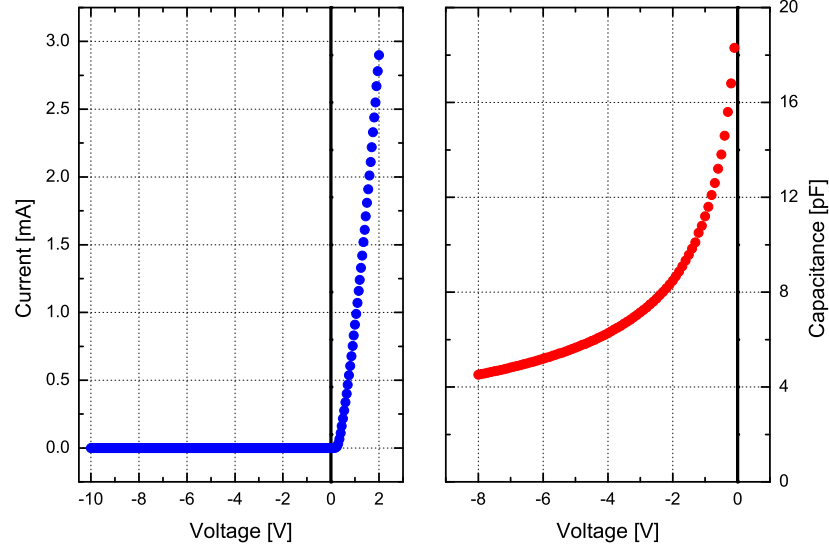


Figure 7.6: IV and CV plots taken at 300K for n-type NTD NFZ-Si with a nitrogen concentration of order 10^{15}cm^{-3} and a resistivity of approximately $150\Omega\text{cm}$.

ration was carried out as for the conventionally-doped nitrogen-doped FZ-Si in the previous Section.

IV and CV measurements for the nitrogen-doped NTD FZ-Si are presented in Figure 7.6. The IV plot shows that the diode fabricated does not break down under a reverse bias of -10V . From applying Equation 2.10 to the CV data, the background carrier concentration was found to be approximately $3.2 \times 10^{13}\text{cm}^{-3}$ and was found to be uniform for all reverse biases applied.

DLTS was performed on the nitrogen-doped NTD FZ-Si specimen in the 67 to 320K temperature range. The reverse bias was chosen to be -7V and the filling pulse was chosen to be -2V with a duration of 1ms. Data were taken at six different rate windows in the range 4 to 200s^{-1} and the DLTS spectra obtained are shown in Figure 7.7.

The data presented in Figure 7.7 show a small peak at high temperatures. No other peaks were found in the temperature range investigated. The temperature at which the peak occurred was found to increase with increasing emission rate and was located at 288.7K for a 200s^{-1} emission rate. The amplitude of the peak was found to be approximately 0.01pF for all rate windows investigated. Given that the fill pulse

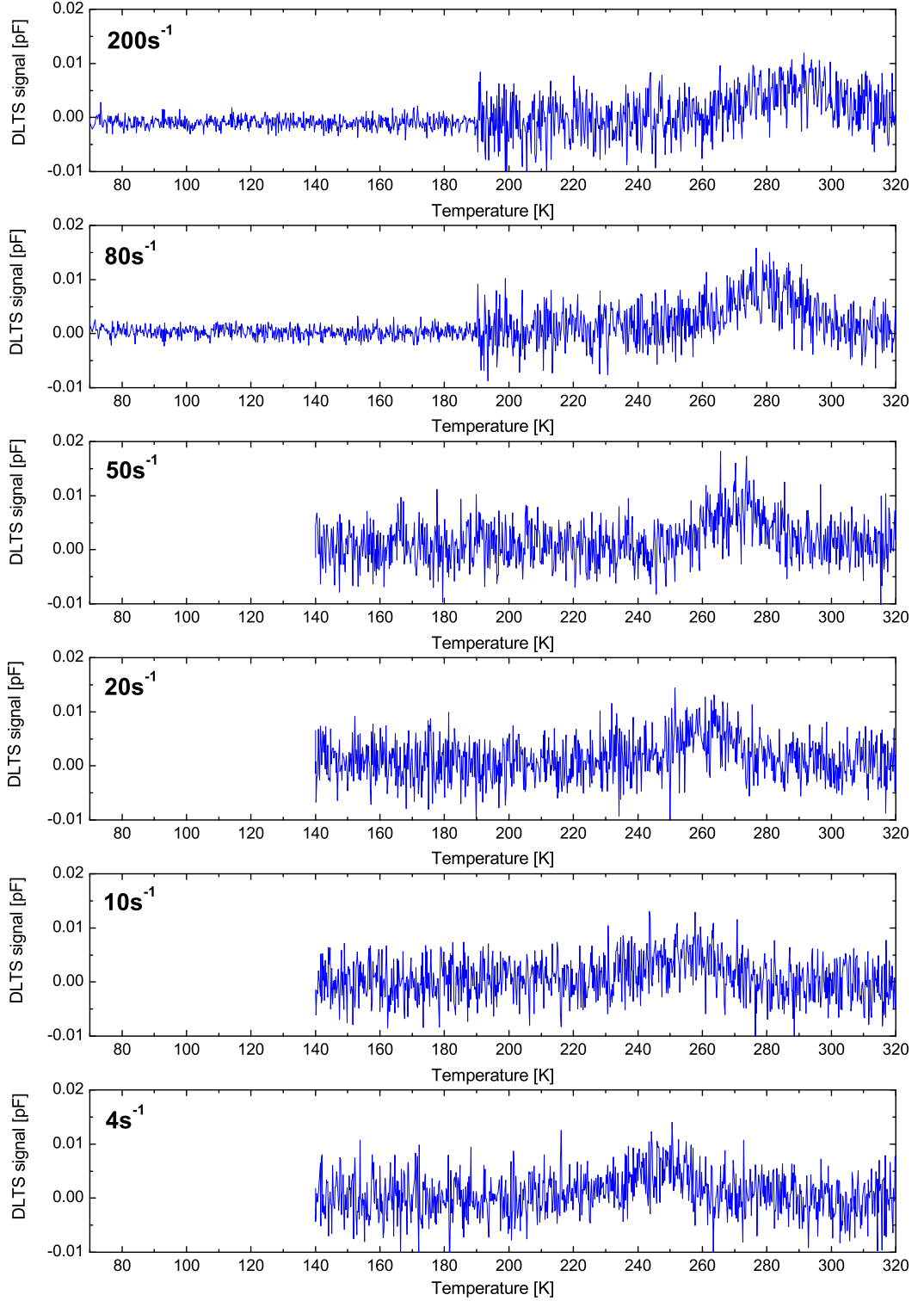


Figure 7.7: DLTS spectra taken with different rate windows for n-type NTD nitrogen-doped FZ-Si with a nitrogen concentration of order 10^{15}cm^{-3} and a resistivity of approximately $150\Omega\text{cm}$. The sample was subjected to a reverse bias of -7V and a 1ms -2V filling pulse.

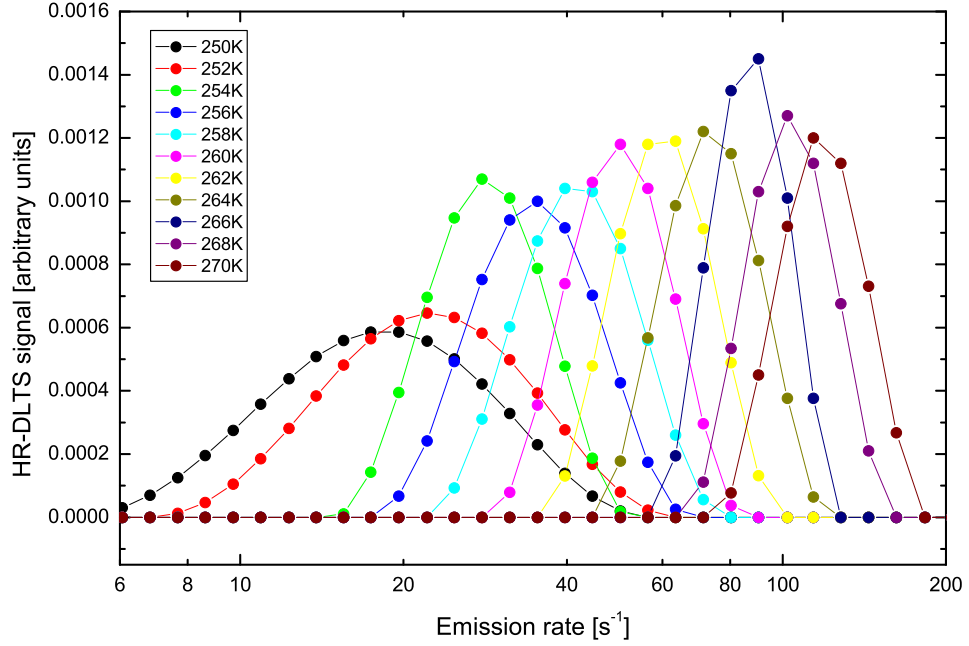


Figure 7.8: HR-DLTS spectra taken at different temperatures for n-type nitrogen-doped NTD FZ-Si, with a nitrogen concentration of order 10^{15}cm^{-3} and a resistivity of approximately $150\Omega\text{cm}$. The sample was subjected to a reverse bias of -7V and a $1\text{ms } -2\text{V}$ filling pulse. The scanning frequency was $60,000\text{Hz}$. 7,000 scans were made and 9,000 samples were taken in each scan.

duration was chosen to be sufficiently long to completely fill the trap, the height of the peaks in Figure 7.7 and the CV data in Figure 7.6 can be used to calculate the trap concentration using Equation 2.14 to be approximately $1 \times 10^{11}\text{cm}^{-3}$.

HR-DLTS was then applied to the same specimen at different temperatures in the vicinity of the DLTS peak found by conventional DLTS (250 to 270K). The reverse bias, fill pulse and sampling parameters were the same as in the case of the conventionally doped nitrogen-doped FZ-Si in Section 7.2.1. The FLOG routine was again used and the HR-DLTS spectra obtained by applying this routine to the raw data are shown in Figure 7.8.

HR-DLTS gave rise to one peak for each temperature at which a set of scans was done. Thus, the spectra presented in Figure 7.8 show that the peak found in Figure 7.7 is associated with a single defect state. The emission rate at which the peak

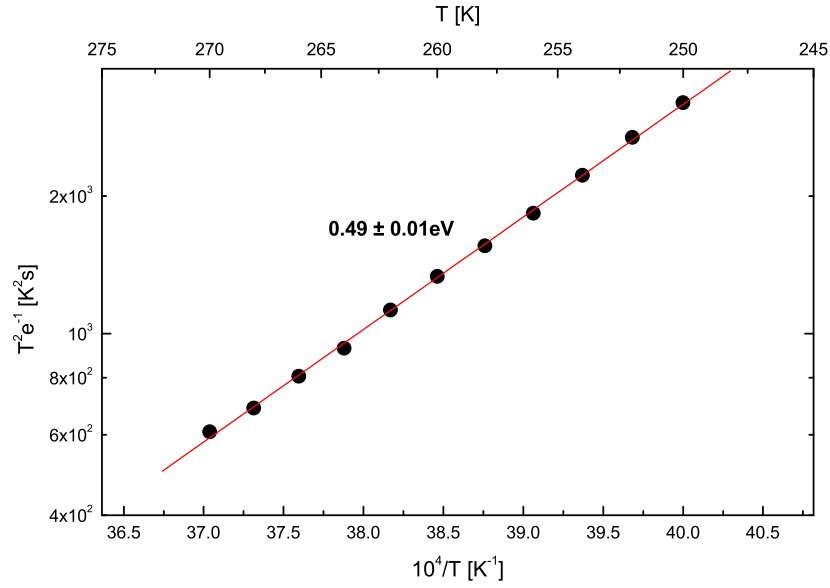


Figure 7.9: Arrhenius plot for n-type nitrogen-doped NTD FZ-Si with a nitrogen concentration of order 10^{15}cm^{-3} and a resistivity of approximately $150\Omega\text{cm}$ determined by the use of HR-DLTS.

occurred was found to increase as the temperature at which the scan was performed was increased.

The variation in the peak temperature with rate window again allows for the enthalpy of the trap to be deduced using Equation 2.11. The Arrhenius plot in Figure 7.9 uses the data obtained from HR-DLTS to give the enthalpy of the trap to be $0.49(\pm 0.01)\text{eV}$. It should be noted that it is also possible to deduce the enthalpy from the conventional DLTS data. However, since the signal-to-noise ratio for the conventional DLTS data presented in Figure 7.7 is low, precise determination of the peak location is difficult and so the value of enthalpy obtained would not be particularly accurate.

It was again not possible to obtain an exact value for the capture cross-section of the trap since the shortest fill pulse duration possible with the experimental equipment available was $10\mu\text{s}$. However, as in Section 7.2.1, a lower limit can be put on the capture cross-section by using Equation 7.1. In the case of the nitrogen-doped NTD FZ-Si, $\sigma > 8 \times 10^{-14}\text{cm}^2$. The magnitude of the capture cross-section again implies

that the trap found is either a neutral or donor state.

7.2.3 Discussion

A deep-level with a concentration of approximately $3 \times 10^{11} \text{cm}^{-3}$ with an enthalpy of $0.50(\pm 0.01) \text{eV}$ was found in nitrogen-doped FZ-Si with a nitrogen concentration of $7 \times 10^{14} \text{cm}^{-3}$. The trap was found to have a capture cross-section of greater than $5 \times 10^{-14} \text{cm}^2$.

To a good approximation the trap found in this work can be considered to be located at 0.50eV below the conduction band, *i.e.* at $E_c - 0.50 \text{eV}$. A trap at $E_c - 0.50 \text{eV}$ has previously been observed in DLTS experiments on FZ-Si doped with nitrogen during growth by Nauka *et al.* [134] and on silicon into which nitrogen had been in-diffused by Kakumoto and Takano [132]. In the work of Nauka *et al.*, the trap was not observed in as-grown nitrogen-doped FZ-Si, but was found to appear in a concentration of $4 \times 10^{11} \text{cm}^{-3}$ after annealing at 900°C for 3 hours [134]. In the work of Kakumoto and Takano, the trap concentration was found to depend on the in-diffused nitrogen concentration and was found to exist in concentrations of $7 \times 10^{13} \text{cm}^{-3}$ and lower [132]. Kakumoto and Takano measured the capture cross-section of the trap to be $7.6 \times 10^{-16} \text{cm}^2$. The results presented in this thesis are the first to show that the $E_c - 0.50 \text{eV}$ trap exists in untreated FZ-Si doped with nitrogen during growth. However, it is noted that the lower limit on the capture cross-section calculated in this present work is inconsistent with the value measured by Kakumoto and Takano [132].

No other deep-levels were observed in the present work. Other deep-levels have been observed in DLTS experiments on n-type nitrogen-doped silicon at $E_c - 0.19 \text{eV}$ [133, 134], $E_c - 0.28 \text{eV}$ [133, 134], $E_c - 0.42 \text{eV}$ [137] and $E_c - 0.58 \text{eV}$ [134]. The traps at $E_c - 0.19 \text{eV}$ and $E_c - 0.28 \text{eV}$ were observed in as-grown FZ-Si doped with nitrogen during growth. The studies in which these levels were found were conducted by Tokumaru *et al.* [133] and Nauka *et al.* [134] and they were published in 1982 and 1985 respectively. It is possible that the traps they observed were in fact nitrogen-related, but, with the vast improvements in silicon technology that have occurred in the past twenty years or so, that these defects no longer exist in detectable concentrations in as-grown

material. The deep-levels at $E_c - 0.42\text{eV}$ and $E_c - 0.58\text{eV}$ were only found to occur after annealing [134, 137]. Thus, it is likely that these traps do not exist in as-grown material, which is why they could not be observed in this work.

A deep-level with concentration of approximately $1 \times 10^{11}\text{cm}^{-3}$ and enthalpy of $0.49(\pm 0.01)\text{eV}$ was found in nitrogen-doped NTD FZ-Si with a nitrogen concentration of order 10^{15}cm^{-3} . The trap was found to have a capture cross-section of greater than $8 \times 10^{-14}\text{cm}^2$. Within experimental error, the enthalpy of this trap is the same as that of the trap observed in nitrogen-doped FZ-Si which had been shallow-doped by conventional means. The trap concentration is a factor of three less than that in the conventionally-doped material. However, it should be noted that the nitrogen concentration in the NTD material is only estimated from the growth conditions and it is possible that the nitrogen concentration could be significantly lower than 10^{15}cm^{-3} . This deep-level, which can be considered to be located at $E_c - 0.49(\pm 0.01)\text{eV}$, was the only deep-level found in nitrogen-doped NTD FZ-Si. It therefore appears that the neutron bombardment process itself creates no electrically active defects in a concentration detectable with the experimental configuration used with the specimens available. The noise of the DLTS spectra presented in Figure 7.7 is typically 0.005pF . Thus, by using Equation 2.14, an upper limit can be put on the concentration of electrically active defects related to neutron bombardment of approximately $6 \times 10^{10}\text{cm}^{-3}$.

The concentration of the deep-level found at approximately $E_c - 0.50\text{eV}$ in this work suggests that approximately 1 in every 2,300 nitrogen atoms form part of an electrically active defect. From the experimental results presented in this Chapter alone it is not possible to identify the precise structure of the deep-level observed. Kakumoto and Takano, who also found a defect with the same enthalpy, suggest that the defect is a N_2 -vacancy complex [132]. They deduced that dimeric nitrogen was part of the defect, as the diffusivity of nitrogen as deduced from their DLTS study was consistent with a SIMS out-diffusion study by Itoh and Abe [119], which concluded that nitrogen dimers were lost to the surface. Additionally, in their work, Kakumoto and Takano found that the concentration of the deep-level was decreased by injection of silicon interstitials from an oxide layer, so they deduced that vacancies were part of the defect.

Specimen	[N] [cm ⁻³]	[O] [cm ⁻³]	Carrier concentration [cm ⁻³]
High [N]	2.10×10^{15}	5.74×10^{17}	1×10^{15}
Low [N]	1.02×10^{15}	5.81×10^{17}	7×10^{14}
Control	$< 10^{14}$	6.59×10^{15}	1.5×10^{15}

Table 7.1: The properties of the Cz-Si investigated by DLTS. Oxygen concentrations are quoted to the DIN 50438/I standard.

The results of *ab initio* calculations may offer some insight into the structure of the defect found in this present work. The expected energy levels of nitrogen-related defects in silicon from a study by Goss *et al.* [138] are summarized in Table 1.4. The calculations predict a level at $E_c - 0.5\text{eV}$ due to the N_sV defect. It is possible that N_sV is responsible for the deep-level observed in this work.

7.3 Electrically active defects in nitrogen-doped Cz-Si

The results of DLTS experiments on p-type nitrogen-doped Cz-Si are presented in this Section. The material investigated was of a standard resistivity ($\sim 1\Omega\text{cm}$) in which it is only possible to observe electrically active defects which exist in a concentration of approximately 10^{12}cm^{-3} or greater.

7.3.1 Results

The Cz-Si investigated was provided by MEMC Electronic Materials Inc.. The material was p-type (boron doped). The nitrogen and oxygen concentrations of the material investigated were determined by FTIR and are stated in Table 7.1. Further details of the specimens used are given in Section 2.2. Titanium Schottky barriers and aluminium Ohmic contacts were deposited on to the specimens, as described in Section 2.6.3.

IV and CV plots were first taken and these are shown in Figure 7.10. The diodes were found to operate without breakdown to reverse biases of at least -8V for all the specimens investigated. From applying Equation 2.10 to the CV data, the background carrier concentration was found for all the specimens investigated. These values are also stated in Table 7.1. The carrier concentration was found to be approximately uniform for reverse biases larger than approximately -2V for all three specimens.

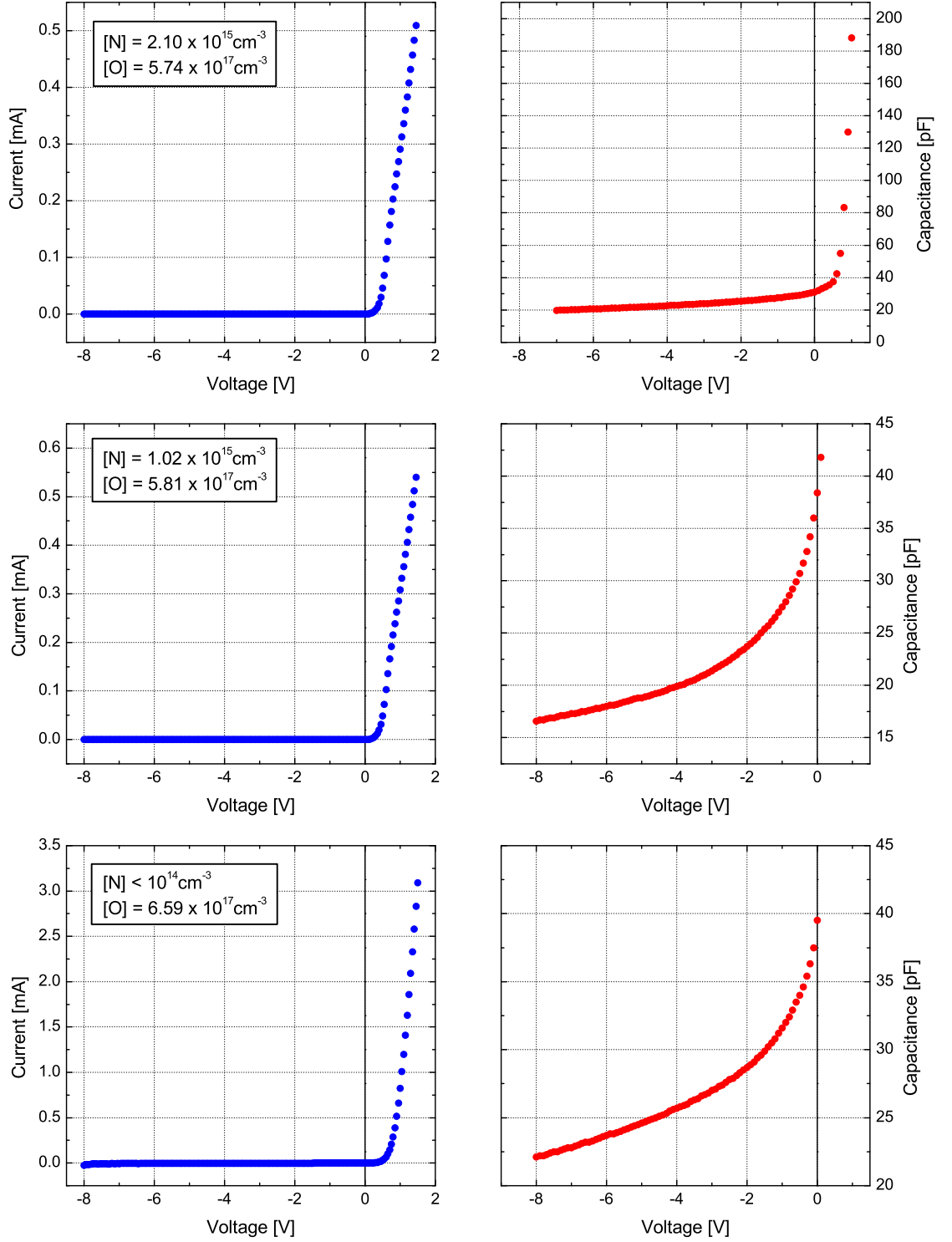


Figure 7.10: IV and CV plots taken at 300K for p-type Cz-Si with different concentrations of nitrogen.

DLTS spectra were taken with rate windows of 80 and 200s⁻¹ at temperatures from 67 to 320K. The same conditions were used for all Cz-Si specimens investigated. The reverse bias was chosen to be -7V and the fill pulse was -2V with a duration of 1ms. The DLTS spectra obtained are shown in Figure 7.11.

The spectra presented in Figure 7.11 show no clear peaks for any of the specimens investigated. In the DLTS spectra for the high nitrogen-containing Cz-Si there is a hint of a weak emission at high temperatures (approximately 270K at 200s⁻¹). This was investigated further by the use of HR-DLTS, but any possible signal was not strong enough for a trap to be detected.

7.3.2 Discussion

The DLTS results for p-type nitrogen-doped Cz-Si presented in Figure 7.11 show no clear deep-levels.

A previous study by Kakumoto and Takano found a deep-level at $E_v + 0.55\text{eV}$ in p-type Cz-Si into which nitrogen had been in-diffused [132]. This defect was not observed in this present work. A possible explanation for its absence is that the material used by Kakumoto and Takano had a resistivity which was a factor of 10 higher than in the material used here. Since, by Equation 2.14, the sensitivity of the DLTS technique depends linearly upon the free-carrier concentration, the factor of 10 increase would mean that experiments done in this present work are a factor of 10 less sensitive than those in the previous work.

An estimate of the upper limit of the defect concentration in nitrogen-doped Cz-Si material can be made from the data in Figure 7.11. The noise in the spectra for the higher nitrogen containing specimen is of order 0.01pF. Thus, from Equation 2.14, the smallest detectable electrically active defect concentration is approximately 10¹²cm⁻³. Thus, from this work it is concluded that no nitrogen-related defects exist in as-grown nitrogen-doped Cz-Si in a concentration of 10¹²cm⁻³ or greater.

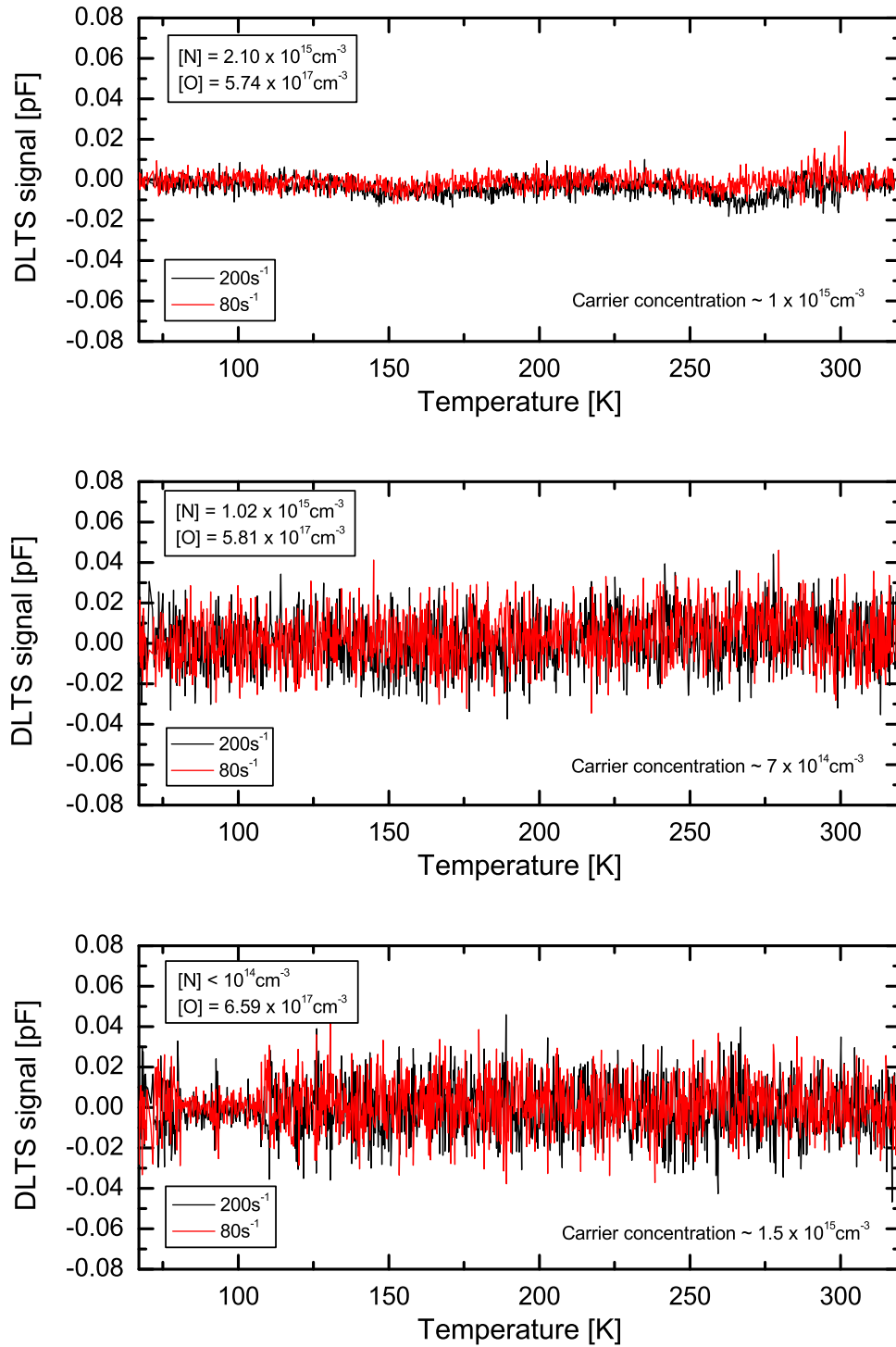


Figure 7.11: DLTS spectra for p-type Cz-Si with different concentrations of nitrogen, for a reverse bias of -7V and a $1\text{ms } -2\text{V}$ filling pulse.

7.4 Summary

DLTS was applied to nitrogen-doped silicon in this Chapter. A deep-level at approximately $E_c - 0.50\text{eV}$ was found to exist in nitrogen-doped FZ-Si shallow-doped by conventional means and by neutron-transmutation doping. The concentration of the deep-level was of order 10^{11}cm^{-3} and its capture cross-section was greater than $5 \times 10^{-14}\text{cm}^2$. No evidence was found for neutron-transmutation doping creating any extra defects in a concentration greater than approximately $6 \times 10^{10}\text{cm}^{-3}$. No deep-levels in a concentration of approximately 10^{12}cm^{-3} or greater were found in nitrogen-doped Cz-Si.

Chapter 8

Summary and further work

8.1 The properties of nitrogen in silicon

8.1.1 Mechanical properties

The results presented in Chapter 4 show that nitrogen in a concentration of just $3 \times 10^{14} \text{cm}^{-3}$ provides significant dislocation locking, as measured at 550°C , over the entire range of temperatures used for device processing (up to 1200°C). It is found that nitrogen binds strongly to dislocations, with a binding enthalpy of at least 2.4eV . Even though the nitrogen concentrations of the FZ-Si investigated in this work and in work by Giannattasio *et al.* [12, 177] are at least two orders of magnitude lower than the oxygen concentrations in the Cz-Si investigated previously [16, 24, 26], the magnitude of the dislocation unlocking stress measured at 550°C is similar for both impurities. For given annealing conditions, the stress required to unpin a dislocation immobilized by nitrogen impurities decreases approximately linearly as the temperature at which the unlocking process is performed increases.

For all annealing temperatures investigated, the dislocation unlocking stress is initially found to rise approximately linearly with annealing time (regime 1), before taking a constant value (regime 2). The rate of the initial rise depends strongly on the annealing temperature, with an activation energy of $1.5 \pm 0.1\text{eV}$. The rise in unlocking stress is attributed to the accumulation of nitrogen at the dislocation core. The value of the unlocking stress taken in regime 2 is found to be dependent on nitrogen concentra-

tion, but is found to be approximately independent of the annealing temperature. The mechanism responsible for the second regime for nitrogen in FZ-Si is different to that responsible for the second regime for oxygen in Cz-Si, for which a local equilibrium is formed between the oxygen at the dislocation and oxygen in the bulk [16,26]. The mechanism responsible for the second regime for nitrogen in FZ-Si is not understood.

It is suggested that adding nitrogen to Cz-Si will also be beneficial for the mechanical properties of these wafers at high temperatures. This is because oxygen, which is generally responsible for dislocation locking in Cz-Si, “boils off” dislocations at above 800°C [16] and the results presented in this thesis show that nitrogen is stable at dislocations to at least 1200°C.

8.1.2 Transport properties

The nature of the species responsible for the dislocation locking effect needs to be known before the 1.5eV activation energy measured for the dislocation locking process can be interpreted in terms of nitrogen transport to dislocations. The arguments for and against atomic nitrogen and nitrogen precipitates being responsible for the dislocation locking effect are summarized in Table 4.2.

If the dislocation locking effect is due to atomic decoration of dislocations, which is known to be the case for oxygen in Cz-Si [16, 24, 26], then the results obtained indicate that transport to dislocations is by a monomeric nitrogen species, which has an activation energy for transport of approximately 1.5eV. A SIMS study by Itoh and Abe gives the activation energy for nitrogen transport as 2.8eV and IR measurements made alongside the SIMS measurements show that nitrogen dimers are lost to the surface [119]. Therefore, if atomic nitrogen is responsible for dislocation locking, the dislocation unlocking data indicate that a different nitrogen species is responsible for diffusion to dislocations than for diffusion to the surface. By fitting numerical solutions of the diffusion equation to the dislocation unlocking data, the diffusivity of nitrogen to the dislocations is $D_N < 10^{-5} \exp(-\frac{1.5\text{eV}}{kT})\text{cm}^2\text{s}^{-1}$ if atomic nitrogen is responsible for the dislocation locking effect.

If nitrogen precipitates are responsible for the dislocation locking effect, then the

method by which the dislocation unpins from the precipitate needs to be understood for the dislocation unlocking data to be analyzed in terms of transport properties. However, if precipitates are responsible for the locking of dislocations, then the activation energy for transport of nitrogen to dislocations may be consistent with the activation energy found in the SIMS out-diffusion study [119].

Further work needs to be done to identify whether atomic nitrogen or nitrogen precipitates are responsible for locking of the dislocations. Possible experiments which may help identify the nature of the species at the dislocation are discussed in Section 8.3.1.

8.1.3 Electrical properties

The results presented in Chapter 7 show that a deep-level in a concentration of order 10^{11}cm^{-3} with an enthalpy of approximately 0.50eV exists in n-type nitrogen-doped FZ-Si and n-type nitrogen-doped NTD FZ-Si. The capture cross-section of the trap is greater than $5 \times 10^{-14}\text{cm}^2$. The state is attributed to a nitrogen-related defect, although from the results presented in this work alone it is not possible to identify which defect is responsible for the trap. A trap with the same activation enthalpy has previously been found in annealed nitrogen-doped FZ-Si [134] and silicon into which nitrogen had been diffused [132]. The results presented in this thesis are the first to show the trap in as-grown material however.

No evidence was found for neutron-transmutation doping creating any extra electrically-active defects in the FZ-Si studied, for which the detection limit was approximately $6 \times 10^{10}\text{cm}^{-3}$. No deep-levels were found in p-type nitrogen-doped Cz-Si, for which the detection limit was of order 10^{12}cm^{-3} .

8.2 The properties of oxygen in silicon

8.2.1 Transport properties

Cz-Si with low shallow dopant concentration

In Chapter 5 it is shown that applying the standard dislocation locking technique to specimens subjected to an anneal for approximately 2,000 hours at approximately 550°C gives the same value of unlocking stress that is measured in specimens which have not been subjected to the pre-anneal. This result is consistent with oxygen monomers and dimers existing in thermodynamic equilibrium at 550°C. Using this fact, and taking a value for the binding energy of the oxygen dimer from the IR study of Murin *et al.* [27], gives the absolute oxygen dimer diffusivity as deduced from dislocation locking experiments as $D_{O_2} \approx 0.02 \exp(-\frac{1.8\text{eV}}{kT})\text{cm}^2\text{s}^{-1}$.

The work of Senkader *et al.* [16, 24, 26] was extended by investigating the locking of dislocations in Cz-Si with an oxygen concentration of $7.8 \times 10^{16}\text{cm}^{-3}$. By fitting solutions of the diffusion equation to the dislocation unlocking data, the effective diffusivity of oxygen was deduced at 500°C for Cz-Si with four different oxygen concentrations. The effective diffusivity at 500°C is found to depend on oxygen concentration, which indicates that the majority oxygen species in silicon, the monomer, is not responsible for transport at that temperature. The effective diffusion coefficients deduced scale with oxygen concentration in a way which is consistent with transport to the dislocations at 500°C occurring by diffusion of oxygen dimers, although the limited amount of data available cannot rule out the possibility that oxygen trimers are responsible for transport. Further anneals have been started, which will take several years, and the results of these will add further information to the debate of which species are responsible for oxygen transport in Cz-Si at low temperatures (see Section 8.3.2).

The presence of nitrogen makes no significant difference to the locking of dislocations in Cz-Si at 550 and 600°C for the annealing times investigated. It is therefore concluded that the presence of nitrogen makes no significant difference to oxygen transport at 550 and 600°C.

Cz-Si with high shallow dopant concentration

The results presented in Chapter 6 show that oxygen transport is dependent on the concentration of certain shallow dopants. The effective diffusivity of oxygen, as deduced by fitting solutions of the diffusion equation to dislocation unlocking data, was found to be significantly higher in p-type Cz-Si with a boron concentration of approximately $5 \times 10^{18} \text{cm}^{-3}$ than in p-type Cz-Si with a boron concentration of approximately 10^{15}cm^{-3} in the 350 to 550°C temperature range. When the difference in oxygen concentrations is accounted for, the magnitude of the enhancement in effective diffusivity is, on average, by a factor of approximately 44 times. The expression for the effective diffusivity of oxygen in highly boron doped p-type Cz-Si was deduced to be $D_{p+} = 2.7 \times 10^{-6} \exp(-\frac{1.4\text{eV}}{kT}) \text{cm}^2 \text{s}^{-1}$ from a numerical simulation of oxygen diffusion to a dislocation. The effective diffusivity was also deduced from dislocation unlocking data for n-type Cz-Si with an antimony concentration of approximately $3 \times 10^{18} \text{cm}^{-3}$ and it was found that the effective diffusivity of oxygen in this material was approximately as expected for low boron doped p-type Cz-Si with the same oxygen concentration.

8.2.2 Electrical properties at dislocations

Results presented in Chapter 5 suggest that oxygen segregation to dislocations in Cz-Si modifies the electrical activity associated with the dislocations. The results presented show that dislocations give rise to a broad DLTS emission spectrum in the 100 to 300K temperature range. From the use of HR-DLTS, it is concluded that this broad emission feature only has components due to emission from deep-states in the vicinity of a dislocation when the dislocations are not oxygen-locked.

A new peak at 40 to 50K was found in specimens which contained oxygen-locked dislocations. However, because carrier emission from charged extended defects is non-exponential, the HR-DLTS analysis is unable to give true values for trap energies. It is suggested that the deep-level found is due to oxygen at the core of the dislocations, although the results need to be reproduced before this can be stated with greater

certainty.

8.3 Further work

8.3.1 Nitrogen in silicon

TEM study on annealed nitrogen-doped FZ-Si

To be able to interpret the dislocation unlocking data presented in Chapter 4 in terms of nitrogen transport, it is necessary to determine whether atomic nitrogen or nitrogen precipitates are responsible for the dislocation locking effect. In Section 4.3.3 preliminary results of a TEM study on annealed nitrogen-doped FZ-Si were presented. The preliminary results indicate that there is a possibility that nitrogen precipitates can form at dislocation cores and in the bulk.

It is important that a more extensive TEM investigation is performed on nitrogen-decorated dislocations. A technique such as EELS could be used in an attempt to deduce the elemental composition of the precipitates. Furthermore, if nitrogen precipitates are deemed to be responsible for dislocation locking, then by preparing specimens containing dislocations with varying amounts of nitrogen decoration, it should be possible to correlate the precipitate distribution with the unlocking stress of the dislocation. This could give information on the mechanism by which the dislocation unpins from nitrogen precipitates.

A more thorough TEM investigation should also be carried out to investigate nitrogen precipitation in the bulk. Understanding this phenomenon is important, as it may be that competition between nitrogen diffusion to precipitates in the bulk and nitrogen diffusion to the dislocation can help to explain the second regime in unlocking stress.

If nitrogen precipitation is found to occur readily in silicon then this would have important consequences for device processing. It may be that nitrogen precipitates could be used for gettering fast-diffusing metallic contaminants, in the same way that oxygen precipitates are used at present. It may also be necessary for device manufacturers to design their annealing schedules appropriately to avoid excessive nitrogen precipitation, which could lead to the generation of unwanted extended defects, and to

avoid the formation of nitrogen precipitates in near-surface regions where devices are fabricated.

Out-diffusion measurements using dislocation locking

By making a small modification to the dislocation locking technique it should be possible to make some sort of measurement of nitrogen out-diffusion. If it is assumed that nitrogen diffuses to the specimen's surface during the annealing process, then a nitrogen concentration profile will be produced. Therefore, upon annealing, the segments of the dislocations close to the specimen's surface experience a nitrogen concentration lower than those in the bulk and will consequently be less strongly locked. During the subsequent unlocking process, the dislocations will first unpin from the position at which they are locked least strongly, and it is this value of the unlocking stress that is measured. By removing different thicknesses of material after the annealing stage, the strength of the dislocation pinning at different depths beneath the surface can be measured and this is related to the nitrogen concentration at that depth.

A graph of unlocking stress against material removed will not be a simple out-diffusion profile, as given by out-diffusion studies using SIMS. This is because the dislocation locking and out-diffusion processes occur simultaneously, and the measured out-diffusion profile will be represent a superposition of the two processes. Given this limitation, it should be possible to use such profiles to give estimates of the distances over which diffusion is occurring. These distances can be compared to those expected from the results of the SIMS study [119]. These measurements will be useful in determining whether nitrogen transport to the dislocations is by the same species as nitrogen transport to the surface.

Nitrogen transport in Cz-Si at high temperatures

From the results presented in this thesis for nitrogen in FZ-Si, it is suggested that adding nitrogen to Cz-Si will provide a significant improvement to its mechanical properties at high temperatures (800 to 1200°C), at which oxygen has been shown to “boil off” dislocations [16]. If this is the case then it would be possible to make a signifi-

cant improvement to the material of choice for the fabrication of the vast majority of electronic devices by simply adding silicon nitride to the melt.

An important set of experiments is to use the dislocation locking technique to investigate dislocation locking in nitrogen-doped Cz-Si at high temperatures. It is necessary to perform these experiments as it may be that nitrogen-oxygen complexes or oxynitride precipitates form at these temperatures and these could have the effect of reducing the magnitude of the dislocation locking measured when only nitrogen is present.

Electrical activity of nitrogen-related defects

The effect of annealing on the electrical properties of nitrogen in FZ-Si should be investigated. Work done in 1985 by Nauka *et al.* showed that two levels were formed when nitrogen-doped FZ-Si was annealed at 900°C and higher [134]. The material investigated in their work is likely to be of a lower quality than the best material available today and consequently it is felt that the work should be repeated on state-of-the-art material. Additionally, deep-levels which are created during annealing may be responsible for the resistivity variation which occurs when nitrogen-doped NTD FZ-Si is thermally processed [235]. Furthermore, the results presented in this thesis are for n-type FZ-Si, and consequently it is suggested that DLTS should also be applied to p-type FZ-Si to investigate whether any deep-levels due to nitrogen exist in the lower part of the bandgap.

No deep-levels are found in the nitrogen-doped Cz-Si investigated in this work. The sensitivity of DLTS depends upon the carrier concentration and for the material investigated the detection limit was of order 10^{12}cm^{-3} . This limit is high and for a state to be detected approximately 1 in 2,000 of the nitrogen atoms in the material would need to exhibit electrical activity. By performing DLTS on nitrogen-doped Cz-Si with a higher resistivity the sensitivity of DLTS would be increased, and it is suggested that such experiments should be performed on both p-type and n-type material.

8.3.2 Oxygen in silicon

Oxygen transport in Cz-Si with a very low oxygen concentration at low temperatures

The dislocation locking technique has been applied to Cz-Si with four different oxygen concentrations at 500°C. Results presented in Chapter 5 leave open the possibility that oxygen transport at low temperatures could be due to a trimeric oxygen species. Further anneals have been started at 400 and 450°C and these will take several years. From the values of the effective diffusion coefficient obtained by modelling the dislocation unlocking data obtained from these specimens, it may be possible to determine which species is responsible for oxygen transport in the 400 to 500°C temperature range. These results are of interest because it is necessary to know which oxygen species are responsible for transport to fully explain the kinetics of thermal donor formation.

Effect of high concentrations of other shallow dopants on oxygen transport

In Chapter 6 results were presented which showed that oxygen transport was strongly enhanced by high boron doping. It was also shown that oxygen transport was unaffected by high antimony doping and consequently it was concluded that lattice strain effects were unlikely to be responsible for the enhancement in transport. Thus, it was proposed that the enhancement was due to an electronic effect. To verify this, oxygen transport should be investigated in Cz-Si with high concentrations of other shallow dopants. If an electronic effect is responsible for the enhancement then a high concentration of another group III element (*e.g.* gallium) should also provide an enhancement in oxygen transport, whereas the addition of high concentrations of other group V elements (*e.g.* phosphorus) should leave transport unaffected. A full understanding of oxygen transport in highly-doped Cz-Si is desirable, as device manufacturers are increasingly using highly-doped Cz-Si for device fabrication.

Thermal donor formation in highly boron doped Cz-Si

The enhancement in oxygen transport which occurs in Cz-Si doped with high concentrations of boron found in this work has implications for oxygen-agglomeration process in silicon. At high temperatures oxygen can form precipitates. Sueoka *et al.* have reported that the rate of oxygen precipitation is enhanced in highly boron doped Cz-Si at 700 to 1000°C [93]. At low temperatures the enhanced transport observed is likely to lead to an enhancement in the rate of thermal donor formation. Such an enhancement has not been reported, probably because conventional techniques for measuring thermal donor formation (*e.g.* DLTS, FTIR) suffer from a lack of sensitivity in highly-doped material. It is suggested that a recently introduced IR technique, which uses Brewster geometry to suppress interference effects [236], may have the sensitivity to measure the thermal donor concentrations in highly-doped Cz-Si. By subjecting highly boron doped Cz-Si and low boron doped Cz-Si to anneals of the same duration at around 450°C, the temperature at which the thermal donor formation rate is known to peak (see Figure 1.8), it should be possible to measure any increase in the concentration of thermal donors due to the enhancement in oxygen transport.

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Appendix A

Fortran code used to simulate impurity diffusion to dislocations

The following Fortran code was used to simulate the diffusion of an impurity to dislocations to deduce a value of the impurity's effective diffusion coefficient. It was originally written by Dr S. Senkader and was modified by Dr A. Giannattasio. The parameters shown are for oxygen in Cz-Si.

```
program oxygen

implicit double precision (a-h,o-z)
dimension flux(100),concentration(100),radi(100),deltaradi(100)
dimension area(100)

c *** LENGTH UNITS ARE IN CM ***
pi = 3.141592654
boltz = 8.61573E-5
cini = 1.06E18
rmax = 10E-4
rmin = 5E-8
cav = 5E22
pirmin = pi * rmin * rmin
av = pirmin*cav
entropy = 7.6E-5
atlock = 7
actenergy=0.74
enterprob = exp(entropy/boltz)
totf=cini*pirmin

c *** OPEN OUTPUT FILE ***
open(3,file='data.dat')
write(*,*)'Number of annuli? (MAX 100)'
read(*,*) n
write(*,*)
write(*,*)'What is the Temperature [C]?'
read(*,*) temperature
temperature=temperature+273.
write(*,*)
write(*,*)'How long does it take (in hours)?'
read(*,*) time
time=time*3600
```

```

        write(*,*)
        write(*,*)'Time STEP (milliseconds)?'
        read(*,*) step
        step=step*1.e-3

c *** SET THE NUMBER OF POINTS PER GRAPH (200)***
        ndata=200
        writestep=time/ndata

c *** DIFFUSIVITY AND ESCAPE PROBABILITY ***
        escapeprob = exp(-actenergy/(boltz*temperature))
        diffusivity = 1.45E-16
        pidiff = 2 * pi * diffusivity

c *** SET THE RADIUS OF ANNULI AND INITIAL CONCENTRATION ***
        i=1
        do while (i.le.n)
            radi(i)=dexp(dlog(rmin)+(i-1)*(dlog(rmax)-dlog(rmin))/n)
            concentration(i)=cini
            i = i + 1
        end do
        radi(n)=rmax

c *** SET THE DELTA-RADIUS AND DELTA-AREA ***
        i=1
        do while(i.le.n-1)
            deltaradi(i)=(radi(i+1)-radi(i))/2
            area(i)=pi*(radi(i+1)*radi(i+1)-radi(i)*radi(i))
            i=i+1
        end do

c *** START THE CALCULATION ***
        t=0.
        do while (t.lt.time)

c *** FLUX AT THE BOUNDARY (n=1) ***
            flux(1)=pidiff*radi(1)*(concentration(2)*(1-totf/av)--
                concentration(1)*escapeprob*enterprob)*step/deltaradi(1)
            totf=totf+flux(1)
            concentration(1)=totf/pirmin

c *** FLUX AT THE OTHER ANNULI (n=i) ***
            i=2
            do while (i.le.n-1)
                flux(i)=pidiff*radi(i)*((concentration(i+1)--concentration(i))/deltaradi(i))*step

c *** RECALCULATION OF THE CONCENTRATION AT THE ANNULUS i ***
                concentration(i)=concentration(i)+(flux(i)-flux(i-1))/area(i)
                i=i+1
            end do

c *** CONTROL IF ***
            if (totf.gt.av) then
                write(*,*)
                write(*,*) 'Please reduce the time step!'
            endif
            if (totf.gt.av) goto 1000
            t=t+step

```

```

c *** WRITE THE DATA EVERY T=TIMESTEP ***
  wstep=wstep+step
  if (wstep.gt.writestep) then
    write(3,*) t/3600, totf*atlock*1.e-6
    write(*,*) 'Percentage done ',100*t/time
    wstep=0.
  endif
  end do
  open(4,file='conc.dat')
  do i=1,n
    write(4,*) radi(i), concentration(i)
  end do
  close(4)
  write(*,*)
  write(*,*)'Data written on file every ',writestep,' sec'

1000 end

```