ANISOTROPY AND POLARITY OF HARDNESS IN III-V AND GROUP IV SEMICONDUCTORS

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ABSTRACT

'Hardness anisotropy' is the variation of measured hardness with orientation of a low-symmetry indenter on a particular crystallographic plane. 'Hardness polarity' is the difference in hardness, measured using a high-symmetry indenter, between (hkl) and $(\bar{h}\bar{k}\bar{l})$ planes in non- centrosymmetric crystals. Results are presented for Ge, GaAs and InSb, for the temperature range 20-400°C. Ge, GaAs and InSb all show hardness anisotropy on {001} faces, with indenter long-axis alignment along <100> giving the highest hardness value; in addition, InSb and GaAs show anisotropy between <110> and $\langle 1\bar{1}0 \rangle$ directions. Both InSb and GaAs exhibit hardness polarity on {111} faces.

A new model of flow patterns under and around contact zones in hard crystals has been developed, based on resolution of realistic elastic stress fields onto available slip systems. Slip systems fall generally into three categories: (a) those that converge beneath the indenter (high work- hardening rate); (b) those that diverge with increasing penetration into the crystal (low work-hardening rate); (c) those with slip direction parallel to the indenter surface ('rosette' slip). The orientation and work-hardening characteristics of these different sets of activated slip systems for different orientations of the indenter (and, in III-V compounds, the different mobilities of alpha and beta dislocations) accurately predict the observed slip and fracture patterns. The hardness polarity and anisotropy behaviour can then be explained in terms of the extent of slip on systems with a low work-hardening rate.

1) Introduction

Indentation tests allow rapid investigation of the plastic (and fracture) properties of materials. The relations between hardness pressures and dislocation mobilities are complicated. However, as will be shown here, study of dislocation arrangements and the modelling of stress fields in the vicinity of indentations can yield semi-quantitative information on the variation of dislocation mobility with doping, temperature and dislocation type. Further, indentation tests have a number of particular advantages over other techniques for the study of dislocation mobility, in particular:

1) Simplicity. Only a small area of flat polished surface is needed. This is particularly important if dislocation motion is to be studied in semiconduting materials not readily available as large single crystals (e.g. SiC, BN).
2) Information can be gained about plastic flow at low temperatures without catastrophic fracture, as the indenter imposes a large hydrostatic 'containing' pressure.
3) Flow and limited fracture often occur in the same test, and so their interactions can be studied.

There are, however, several difficulties in the quantitative interpretation of the results of indentation tests in terms of basic flow parameters. The work reported here forms part of a continuing study aimed at linking dislocation mobility parameters and (a) the geometry and extent of dislocation arrays around indentations and (b) ultimately, the hardness pressure itself.
It will be shown that, with correct interpretation, indentation testing can rapidly provide information about the variation of mobilities of dislocations with doping, temperature or dislocation type.

2) Hardness Polarity in III-V Semiconductors

It is generally found that the {111} (A) and $\{\bar{1}\bar{1}\bar{1}\}$ (B) faces of a compound semiconductor AB have different hardness values, within a certain temperature range. This effect is known as hardness polarity. Studies have been carried on GaAs (Hirsch, Pirouz, Roberts and Warren 1985) and InSb (Roberts 1986) over the temperature range 20-450°C. Results are summarised in Table I.
It can be seen that in all cases, where the A (III) face is harder than the B (V) face, B(g) (alpha) dislocations are more mobile than A(g) (beta) dislocations, and vice versa. In a previous paper (Hirsch et al. 1985), it was shown how this was a consequence of the patterns of slip around indentations, predicted by a model of the indenter stress field and confirmed by microscopy of cross-sectioned sub-indentation zones. Predicted and observed slip patterns fell into three classes: (a) those that converge beneath the indenter (high work- hardening rate); (b) those that diverge with increasing penetration into the crystal (low work-hardening rate); (c) those with slip direction parallel to the indenter surface ('rosette' slip). A low value of hardness is associated with the movement of fast dislocations on systems of class (b), and the relations between hard/soft faces and fast/slow dislocation types detailed above then necessarily follow from the point group symmetry (Hirsch et al. 1985)
So as to investigate further the relations between dislocation mobility, hardness and hardness polarity in GaAs, dislocation velocity measurement were carried out on the material used in the indentation

tests. Results are shown in fig. 1.; the derived activation energies for dislocation motion are given in Table II. These results are similar to those of Choi, Mihara and Ninomiya (1977). Comparison with the hardness polarity / temperature results for GaAs reveals a good correlation, in that:

1) The soft face for each doping type corresponds to the movement of the faster dislocation type on the 'free-running' type (b) systems.
2) The difference in hardness between the As and the Ga faces is greatest for n-type, the doping for which the difference between As(g) and Ga(g) dislocation velocities is greatest.
3) At high temperatures ($>\sim 200^{o}C$) the hardness number (mean of both faces) for each doping is related to the mobility of the dislocations - i.e. n-type is hardest, intrinsic softest, with p-type being slightly harder than intrinsic.

At low temperatures ($<\sim 100^{o}C$), it can be seen that p-type GaAs is slightly harder than n-type. This would not be expected from extrapolation of the dislocation velocity results to these temperatures. At such temperatures, however, the mechanism of yield beneath the indenter is possibly not predominantly the thermally-activated glide measured in the dislocation velocity experiments, performed at temperatures $>\sim 350^{o}C$. The work of Rabier, Garem, Demenet and Veyssière (1985) on compression testing of GaAs shows similarly anomalous behaviour at low temperatures. At $350^{o}C$, they find lower yield stresses to increase in the order p-type, intrinsic, n-type; at room temperature (compression with confining pressure) the order is reversed. The mechanisms of low temperature flow, and possibly the effect of hydrostatic pressure, obviously merit further investigation.

3) <u>Hardness Anisotropy</u>

Hardness anisotropy is the variation of hardness (typically as measured by the elongated 'Knoop' indenter) with orientation of indenter on a single crystal plane. For the {001} faces of a cubic semiconductor, typical Knoop hardness anisotropy (KHA) behaviour is shown in fig. 2. It can be seen that the <100> directions are harder than the the <110> directions (in this case for germanium). Modelling of the stress fields and cross-sectioning of the indentations, as for the case of Vickers indentations on {111} faces, has shown that this anisotropy is caused principally by the availability of non-workhardening diverging slip only in the <110> orientation of the indenter (of a type similar to class (b) in the hardness polarity analysis).

Consideration of the point group symmetry of III-V semiconductors (Warren, Pirouz and Roberts 1984, Warren, Roberts and Hirsch 1986) shows that the [110] and the $[1\bar{1}0]$ direction in the (001) surface are not equivalent. If A(g) dislocations operate on the non-workhardening planes for the [110] orientation, then B(g) dislocations will operate on the equivalent planes for the $[1\bar{1}0]$ orientation. If the mobilities of As(g) and B(g) dislocations are significantly different, there would then be expected to be an associated KHA asymmetry between [110] and $[1\bar{1}0]$. Fig. 3 shows this to be the case for GaAs. Sectioning on {111} faces whose traces on (001) are normal to the long axis of the indenter enables one to study the dislocation arrangements beneath the surface. Either an As or a Ga {111} face can be exposed; these can be distinguished by etching in nitric acid (Tuck 1975, Kyser and Millea 1964). Etching the Ga face with 1HF / $3H_2O$ / $6H_2O_2$ at $5^{o}C$ (Choi et al. 1977) and the As face with 1HF / $3HNO_3$ / $10H_2O$ + a few grains of $AgNO_3$

(Richards and Crocker 1960) reveals dislocation positions. In all cases, the arrangements of dislocations thus revealed correspond to those expected.

4) Comparison of Hardness Polarity and Hardness Anisotropy

It has been shown above that both hardness polarity and KHA are effective means of detecting the sense and magnitude of A(g) and B(g) dislocation mobility differences. However, the sensitivities of the two techniques at different temperatures are quite different, as can be seen for InSb in figs. 4 and 5 (Roberts 1986). For the case of hardness polarity, the detected asymmetry is within experimental error at room temperature, increases to a maximum at $\sim 250^{\circ}C$, and then decreases again with further increases in temperature. For {001} KHA, the <110>:<1$\bar{1}$0> asymmetry is largest at the lowest temperature and decreases with increasing temperature. The decreases in hardness polarity and <110>:<1$\bar{1}$0> KHA at high temperature are simply due to the decreasing difference in the mobilities of the In(g) and Sb(g) dislocations at these temperatures (Ninomiya 1979).
It was speculated (Roberts 1986) that the differences between the two testing methods at low temperatures might be due to differences in the stress fields (since the indenters are different shapes) driving the dislocations on the free-running slip systems. Further stress field analysis has shown this to be probable. Fig. 6 shows the variation of resolved shear stress on the free-running slip systems (diverging penetrating slip, class (b) above) for these two cases. In each case the stress fields is that for a flat rectangular punch (Love 1929) of aspect ratio appropriate to the different indenters (square for Vickers, 7.11:1 for Knoop). Each is oriented with an edge parallel to the trace of the relevant slip system on the indented surface. It can be seen that the stresses on the active slip system decay very rapidly for the case of the square indenter, and less rapidly for the 'Knoop' indenter. Thus one might expect a stronger interaction between a Knoop indenter and long-distance dislocation glide, even at low temperatures, where higher stresses are needed to activate glide. It is recognised of course that the stresses produced by these purely elastic solutions are only a first approximation to those acting in reality; a full elastic/plastic solution, taking into account dislocation interactions, is required. Such solutions, for simple geometries, are currently being investigated.

5) Summary and Conclusions

Hardness anisotropy and polarity experiments can be used to gain semi-quantitative information about the velocities of dislocations in semiconductors, particularly the relative velocities of A(g) and B(g) dislocations in III-V materials. At low temperatures, hardness anisotropy experiments are more sensitive, possibly because of the slower decay with distance of the stress field of the Knoop indenter.

Acknowledgements

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TABLE I

Hardness Polarity in III-V Semiconductors

Material	Doping	Temp. Range	Harder Face	Faster Disln.	Ref.
GaAs	n	20-400°C	Ga	As(g)	Hirsch et al. 1985
	int.	"	Ga	As(g)	
	p	"	As	Ga(g)	
InSb	n	40-460°C	In	Sb(g)	Roberts 1986
InSb	n	20-370°C	In	Sb(g)	Shimizu & Sumino 1970
GaP	n	20-500°C	Ga	P(g)	Maeda et al. 1977

TABLE II

Activation Energies for
Dislocation Motion in GaAs

Doping	Activation energy (eV) Ga(g)	As(g)
n (1.2×10^{18} Te cm^{-3})	1.10 ± 0.10	1.55 ± 0.21
int (5.0×10^{15} cm^{-3})	1.23 ± 0.04	1.35 ± 0.02
p (1.3×10^{19} Zn cm^{-3})	1.17 ± 0.07	1.04 ± 0.05

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Figure Captions

Fig. 1

Dislocation velocities in GaAs, at an applied resolved shear stress of 4kgmm^{-2} (40MPa): (a) n-type GaAs; (b) intrinsic GaAs; (c) p-type GaAs; (d) all data plotted together for comparison. Activation energies are given in Table I.

Fig. 2

Knoop hardness anisotropy on an {001} face of n-type Ge. The <100> direction is harder than the <110> directions.

Fig. 3

Knoop hardness anisotropy on an {001} face of n-type GaAs. The hardness values for the two <110> directions are not indentical, because of the different mobilities of the As(g) and Ga(g) dislocations.

Fig. 4

Hardness polarity on {111} faces of n-type InSb. The In-face is harder at all temperatures, though the difference is most significant at ~250°C.

Fig. 5

Knoop hardness anisotropy on an {001} face of n-type InSb; hardness is expressed as percentage variation from the harder <110> orientation. The degree of <110>:<1$\bar{1}$0> anisotropy falls steadily with increasing temperature.

Fig. 6

Resolved shear stresses on the non-workhardening slip systems appropriate to the cases of (a) hardness polarity (square indenter on {111}) and (b) hardness anisotropy (elongated indenter on {001}). The resolved shear stresses (from the elastic solution for a rectangular flat punch; Love, 1929) are shown as a function of distance from the indenter on the most favourably oriented slip system. The stresses from the 'Vickers' indenter decay rapidly compared to those from the 'Knoop' indenter.

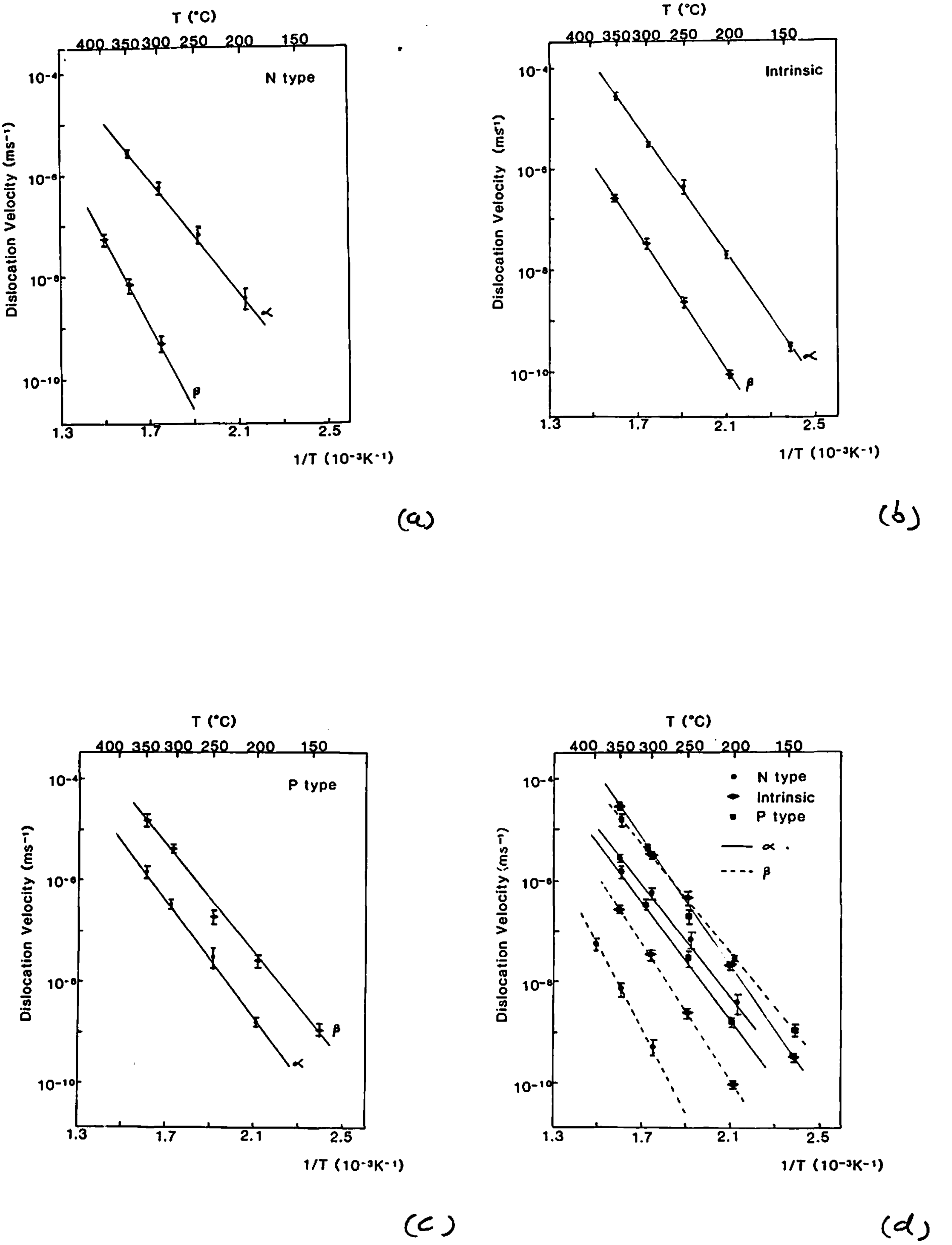

T (°C)
400 350 300 250 200 150
N type
Dislocation Velocity (ms⁻¹)
10⁻⁴
10⁻⁶
10⁻⁸
10⁻¹⁰
1.3 1.7 2.1 2.5
1/T (10⁻³K⁻¹)
α
β
(a)
T (°C)
400 350 300 250 200 150
Intrinsic
Dislocation Velocity (ms⁻¹)
10⁻⁴
10⁻⁶
10⁻⁸
10⁻¹⁰
1.3 1.7 2.1 2.5
1/T (10⁻³K⁻¹)
α
β
(b)
T (°C)
400 350 300 250 200 150
P type
Dislocation Velocity (ms⁻¹)
10⁻⁴
10⁻⁶
10⁻⁸
10⁻¹⁰
1.3 1.7 2.1 2.5
1/T (10⁻³K⁻¹)
β
α
(c)
T (°C)
400 350 300 250 200 150
N type
Intrinsic
P type
α
β
Dislocation Velocity (ms⁻¹)
10⁻⁴
10⁻⁶
10⁻⁸
10⁻¹⁰
1.3 1.7 2.1 2.5
1/T (10⁻³K⁻¹)
(d)

Fig. 1

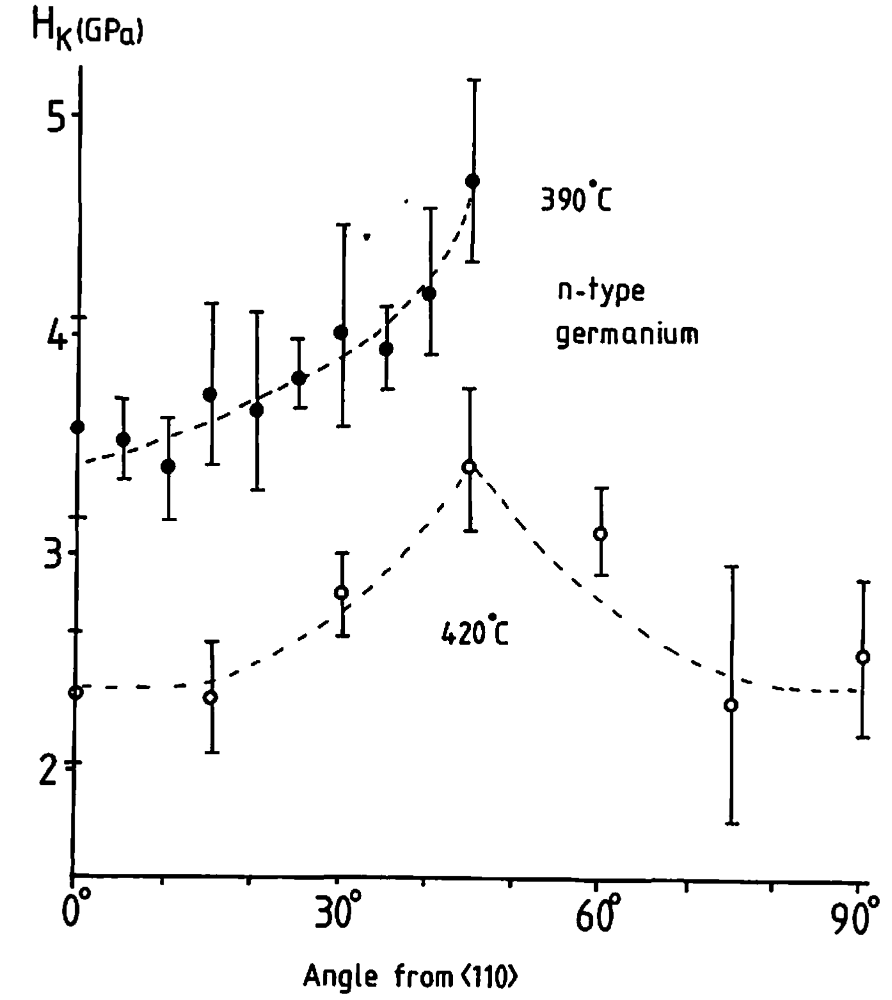

H_K (GPa)
5
4
3
2
390°C
n-type
germanium
420°C
0°
30°
60°
90°
Angle from ⟨110⟩

Fig. 2

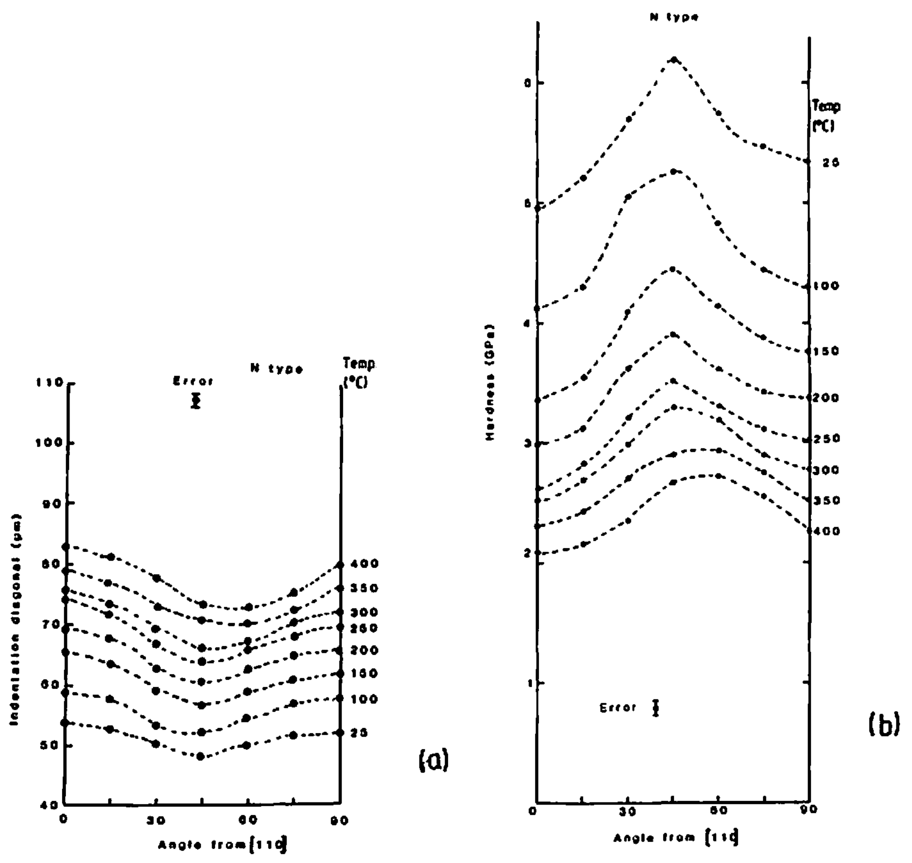
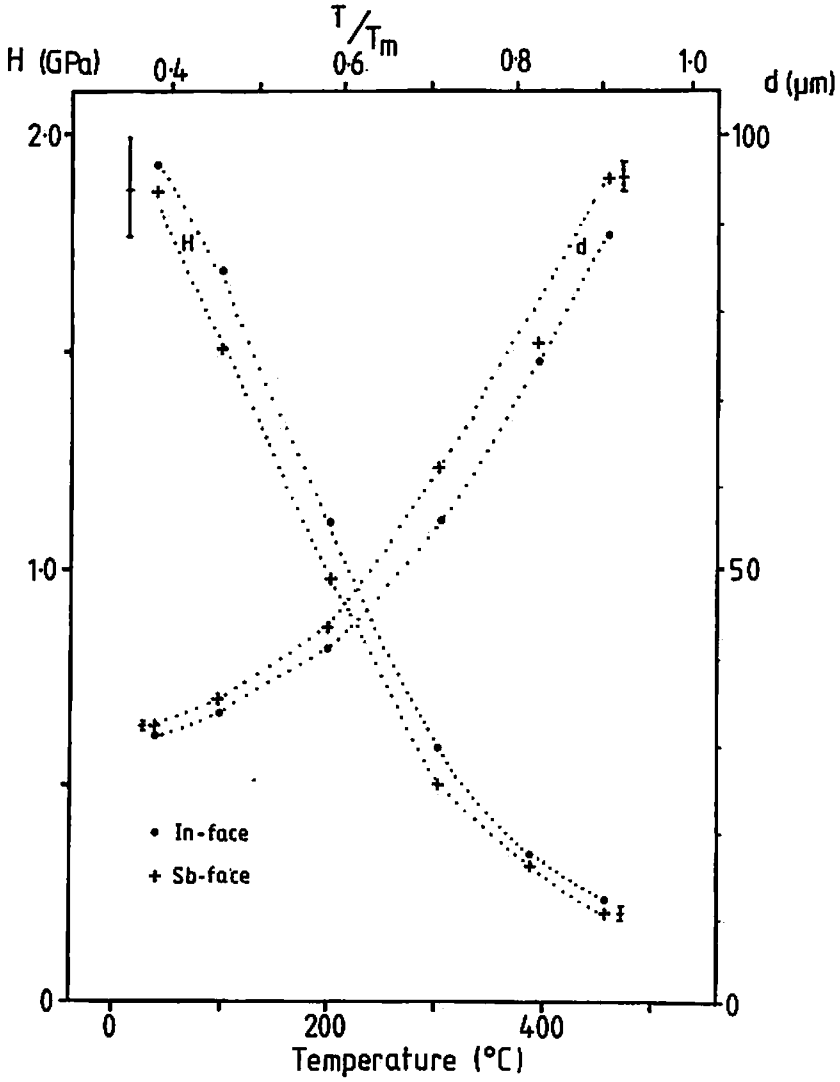

Error
N type
Temp (°C)
Indentation diagonal (μm)
110
100
90
80
70
60
50
40
400
350
300
250
200
150
100
25
0
30
60
90
Angle from [110]
(a)
N type
Hardness (GPa)
Temp (°C)
25
100
150
200
250
300
350
400
Error
0
30
60
90
Angle from [110]
(b)

Fig. 3



H (GPa)
T/Tm
0·4
0·6
0·8
1·0
d (μm)
2·0
1·0
0
100
50
0
H
d
In-face
Sb-face
0
200
400
Temperature (°C)

Fig. 4

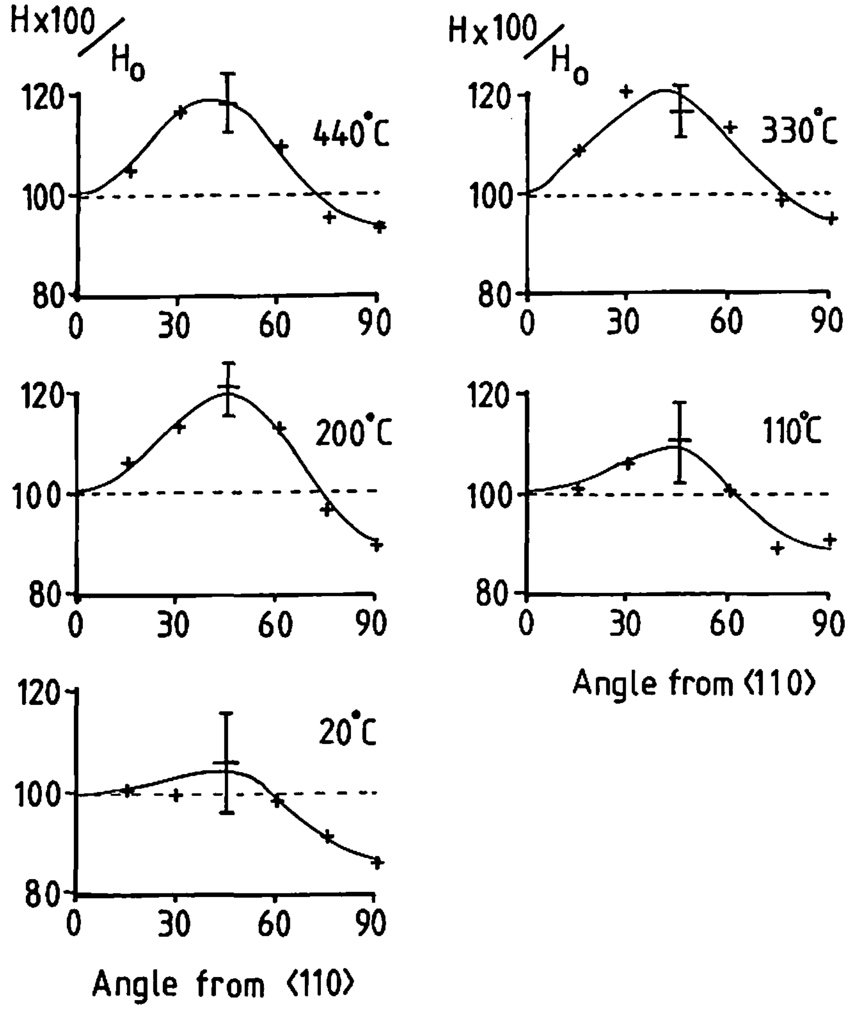
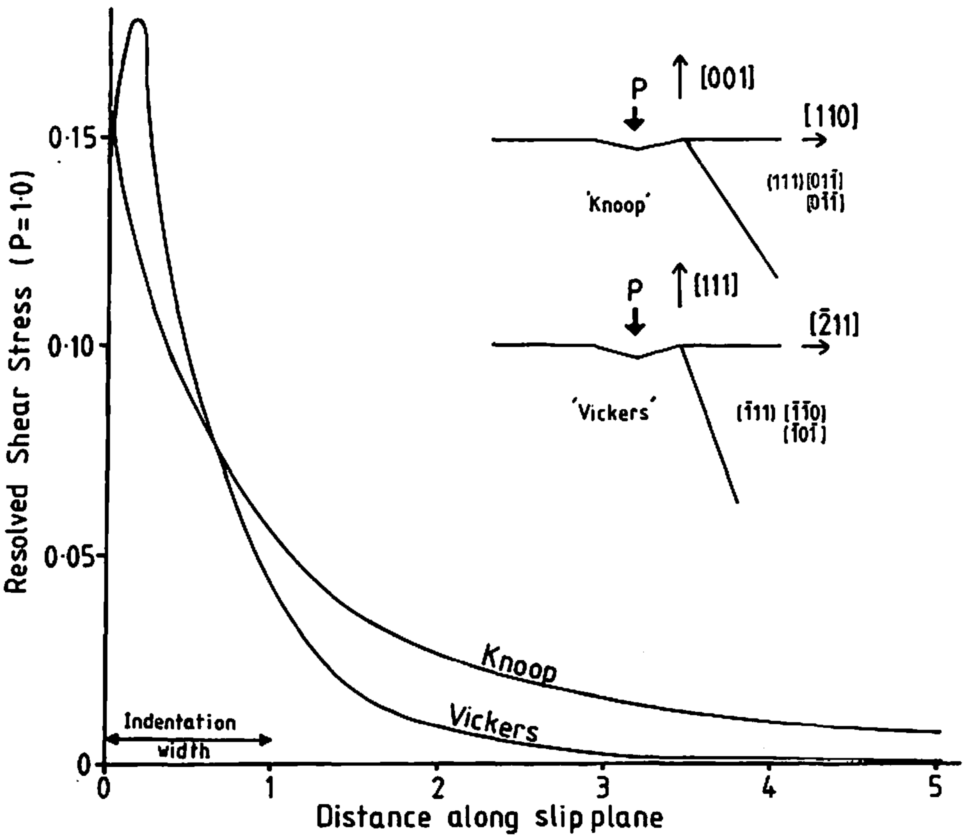

Hx100/Ho
120
100
80
0 30 60 90
440°C
330°C
200°C
110°C
20°C
Angle from ⟨110⟩

Fig. 5



Resolved Shear Stress (P=1·0)
0·15
0·10
0·05
0
0
1
2
3
4
5
Distance along slip plane
Indentation width
Knoop
Vickers
P
[001]
[110]
'Knoop'
(111) [01$\bar{1}$] [0$\bar{1}\bar{1}$]
P
[111]
[$\bar{2}$11]
'Vickers'
($\bar{1}$11) [$\bar{1}\bar{1}$0] [$\bar{1}$0$\bar{1}$]

Fig. 6