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# Deformation of silicon at low temperatures

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The dislocation arrangements produced around microhardness indentations made in silicon at room temperature have been studied by transmission electron microscopy. Loops consisting of 30°- and 60°-dislocations are produced and move on the {111} planes. It is suggested that, during indentation, the theoretical shear strength is exceeded locally and that the observed dislocations arise as a result of the accommodation of the displacements due to block slip. On annealing up to 1030°C the loops do not appear to be mobile, rather new loops consisting of edge and screw components are formed which can move large distances.

## 1. Introduction

The mechanism of surface damage at low temperatures in covalently bonded materials like silicon, and its subsequent annealing is not understood in detail. In semiconductor processing, all problems connected with surface damage are usually avoided by chemically removing the surface layers. However, in the processing of high power silicon devices such as thyristors, this is not the case, since diffusion is carried out through lapped surfaces.

Several studies [1, 2] have been made of the damage caused by grinding the surfaces of diamond structure semiconducting materials, but these were mostly aimed at determining the depth of damage. Many of these results for silicon have been summarized by Buck and Meek [3]. Only Stickler and Booker [1] have studied the nature of this damage at high magnification. A thorough study of the amount and type of damage due to many different abrasive particle sizes showed that, for fine diamond abrasives, individual dislocations could be produced near the specimen surfaces and for much coarser silicon carbide abrasives, the damage consisted of very strained dislocation networks and cracking.

Uniaxial stressing of silicon and germanium at room temperature has generally failed to produce evidence of substantial dislocation motion e.g. [4]. Specimens always break at relatively low stresses, presumably due to the effects of flaws. However, it has been shown for a number of brittle solids, that plastic flow occurs during indentation at low temperatures [5-7]. The reason for this is that the stress under the diamond indenter has a large hydrostatic component and very high shear stresses can be reached locally. Therefore, this technique is very suitable for studies of plastic flow at low temperatures in the brittle fracture region of strong solids.

In order to obtain details of plastic deformation processes during indentation, the high magnification of transmission electron microscopy (TEM) is necessary. Little work in this direction has yet been reported, probably due to difficulties of specimen preparation. TEM studies of indentations produced in silicon under light loads [5, 8] clearly showed that dislocations had been produced as a result of the indentation process at room temperature, but the arrangements were not analysed in detail. The dislocation arrangements seen around indentations made at higher temperatures confirmed those deduced from etch pit studies. Evidence was also found for twinning and a phase change in silicon which had been indented above 350°C. Gridneva *et al.* [9] have also proposed that a pressure-induced phase transformation occurs in silicon during indentation at room temperature.

The present paper describes experiments which were undertaken to study the deformation occurring in silicon when it is indented with a diamond at room temperature. TEM observations of the dislocations produced at room temperature and the changes which result from annealing up to 1000°C, are reported.

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## 2. Experimental

The silicon used in these experiments was 100 Ω cm N-type dislocation-free single crystal with either (1 1 1) or (1 1 0) surfaces. The surfaces were mechanically, then chemically polished to remove all possible surface damage and cut ultrasonically into 3 mm diameter discs, having a thickness of about 300 μm. Vickers hardness indentations were made using a Leitz Durimet Microhardness Tester with loads of 100 g applied for 20 sec. Samples were indented at room temperature and at 300° C. On each disc a square array of 25 indentations with a spacing of 50 μm was made.

The preparation of thin foils for the TEM was done in two stages. Firstly, the surface containing the indentations was protected and the disc was thinned electrochemically from the other side using a jet of very dilute hydrofluoric acid in water and an applied voltage of 300 V. The apparatus [10] was mounted on an optical bench so that it could be easily adjusted to produce the thin region at any desired point on the specimen surface. The thinning was stopped when the silicon was around 10 μm thick. The samples were then thinned from both sides by ion bombardment so that thin foils could be taken at any depth up to 10 μm below the indented surface.

The foils were examined in a Philips EM 300 electron microscope operating at 100 kV with a goniometer stage. Annealing experiments on these specimens were carried out in the microscope using a heating stage, and other samples indented at room temperature were vacuum annealed in the bulk prior to thinning for electron microscopy.

## 3. Results

### 3.1. Electron microscope observations of as-indented samples

The preparation technique allowed large areas surrounding indentations to be thinned sufficiently for the complete extent of the deformation to be examined. Dislocation loops were observed at distances up to 8 μm from the centres of indentations made on the (1 1 1) plane with a load of 100 g, at room temperature. These loops were grouped in four main lobes symmetrically placed around the indentation centre. The resulting large composite pictures cannot be reproduced satisfactorily here, therefore the dislocation arrangement is drawn schematically in Fig. 1, with a representative lobe in Fig. 2. The

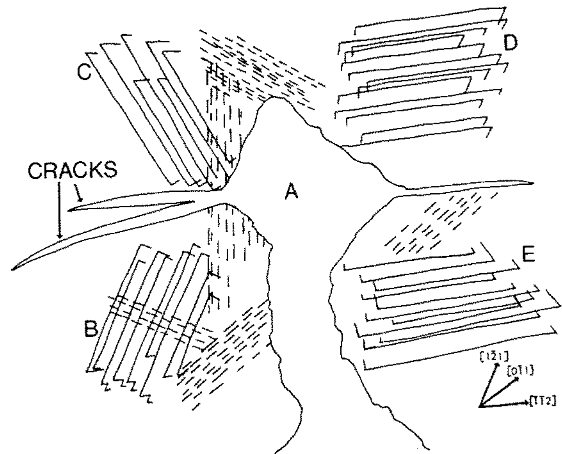


*Figure 1* Schematic drawing of the dislocation arrangements seen in the TEM surrounding a Vickers hardness indentation produced at room temperature. Plane of indentation and foil plane (1 1 1). Broken lines indicate dislocation loops lying in {1 1 1} planes inclined to (1 1 1).

foil lay about 2 μm below the original surface. Region A in Fig. 1 corresponds to the site of the impression. Nearby, the material was so highly strained that individual dislocations could not be resolved. Slip occurred on all four possible {1 1 1} planes and considerable cracking was also seen. The four large lobes, shown in Fig. 1 at B, C, D and E, consisted mainly of individual dislocation loops lying in the (1 1 1) foil plane.

All those loops examined had the same geometry. Lobe B, which is a typical example, is shown in Fig. 2. The loops consisted of one large straight section lying in a $\langle\bar{1}\bar{1}2\rangle$ direction bounded at one end by a shorter segment lying in a second $\langle\bar{1}\bar{1}2\rangle$ at 60° to the former and at the other by a second short segment lying in a $\langle 1\bar{1}0\rangle$ direction at 90° to the long section. Stereomicroscopy of loops lying in the (1 1 1) foil plane showed sets of concentric loops lying at different depths in the crystal. Burgers vectors were determined by realizing the $\mathbf{g}.\boldsymbol{b}. = 0$ criterion for at least two values of $\mathbf{g}$. This criterion was always satisfied by one $\langle 1 1\bar{1}\rangle$ and one $\langle\bar{3}1 1\rangle$ diffraction vector, e.g. lobe B was invisible using $\mathbf{g}$ $[\bar{1}1 1]$ and $\mathbf{g}$ $[3\bar{1}\bar{1}]$ giving $[0\bar{1}1]$ for the Burgers vector. These are then mixed dislocation loops which lie and expand in the (1 1 1) slip plane, i.e. they are shear loops [11]. In every case examined the Burgers vector was that $\langle 0 1\bar{1}\rangle$ direction which pointed radially out from the centre of the indentation and also lay between the two parts of the loop having

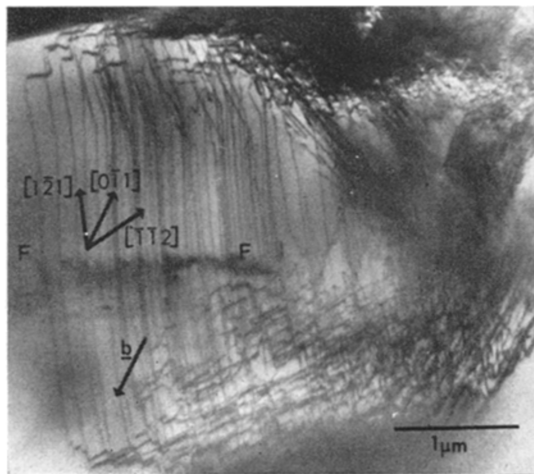


*Figure 2* Transmission electron micrograph showing the dislocations of lobe B of Fig. 1.

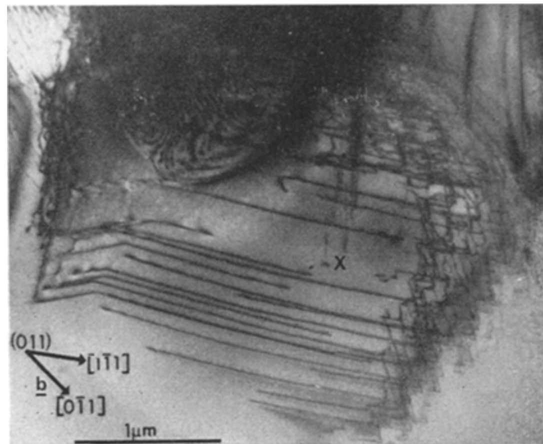


*Figure 3* Dislocations near an indentation in Si produced at room temperature. Plane of indentation and foil plane (011).

$\langle\bar{1}\bar{1}2\rangle$ line vectors. This means that the loop sections lying in $\langle\bar{1}\bar{1}2\rangle$ directions are 30° dislocations while the third loop section is a 60° dislocation. Approximately ten indentations were examined, in different samples, and it was found that the form and extent of lobes were almost identical and independent of the relative orientation of the indenter with respect to directions in the crystal surface.

Dislocations lying on the three {111} planes which are inclined to the surface of the foil, e.g. at F, were less clearly visible. Tilting experiments showed that these loops were again arranged in concentric clusters, on parallel planes. Burgers vectors were also found to be $\langle 0\bar{1}1\rangle$ types but a determination of the line vectors of the dislocation segments was not possible from {111} foils. However, the same loop geometry was found in samples indented on the (011) plane as seen in Fig. 3. For the dislocations lying on the $(\bar{1}11)$ plane the direction of the Burgers vector was determined as $[0\bar{1}1]$. There was no change of line direction for dislocations intersecting the foil surface, indicating no relaxation effects. Slip was also activated on the $(1\bar{1}1)$ plane normal to the (011) plane of indentation, e.g. at X.

### 3.2. Annealing of indented samples

Samples indented at room temperature, then thinned, were annealed in a heating stage in the electron microscope. The first effects of annealing could be distinguished after $\frac{1}{2}$ h at 550°C. These changes developed significantly following further annealing at 600°C. Two types of rearrangement were then observed, one in lobes B and E and the other in lobes C and D. Fig. 4a and b shows the structures in lobes B and D, respectively, after an anneal of 1 h at 600°C. The original loops produced at room temperature did not move without some form of rearrangement. In Fig. 4a, the original loops of lobe B are still visible, but they have begun to bow out and change their line direction so as to lie closer to edge orientation. In lobe D (Fig. 4b) the original lobe form has been modified by dislocation rearrangements which produce new loops. These loops originated in the highly strained region close to the indentation centre. They consist of bowed edge segments which move rapidly out trailing parallel pairs of screws. The velocity of the edge dislocations was estimated at $10^{-3}$ cm sec$^{-1}$ by direct observation. Far from the indent, the habit plane of the new loops is well defined as $(\bar{1}11)$, however, closer to the centre, screw components are clearly connected with the degenerating loops lying in the (111) plane. An analogous structure developed in lobe C, except that new loops lay on both the $(\bar{1}11)$ and the $(1\bar{1}1)$ planes. Further heating for 1 h at 750°C enhanced these effects with the screw dislocations moving towards the foil surfaces. More extensive rearrangement did not occur until the sample had been annealed at 1030°C for $\frac{1}{2}$ h as shown in Fig. 5. The long screw sections of lobes C and D migrated to the foil surfaces leaving the edge components behind as can be seen in Fig. 5a. These edge dislocations moved on the $(1\bar{1}1)$ and $(\bar{1}11)$ planes and were

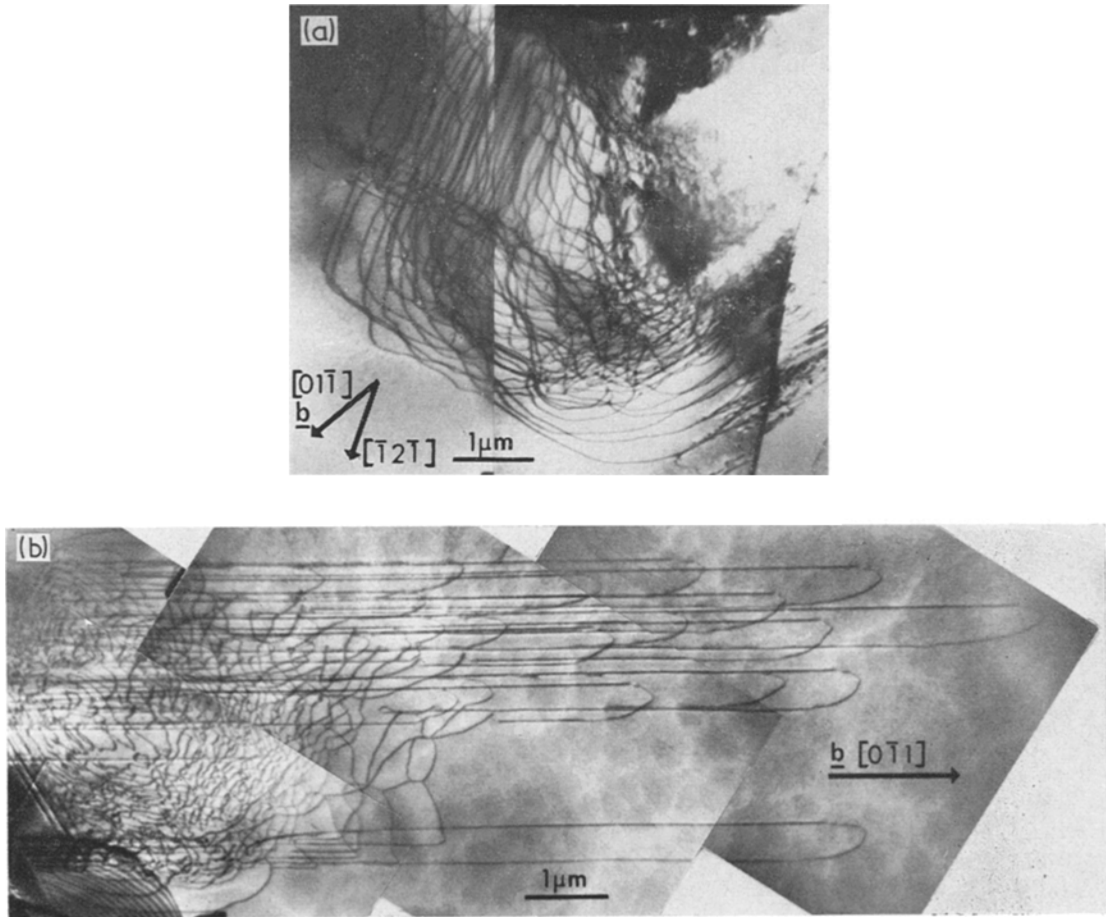


*Figure 4* Dislocation arrangements in (a) lobe B and (b) lobe D after annealing for 1 h at 600° C in the TEM.

observed at distances more than 20 μm from the indentation centre. At this point, T (Fig. 5a), the foil thickness was estimated as 11 000 Å from the projected lengths of the dislocations. In lobe D, additional new edge dislocations were produced and moved away in the (1 1 1) foil plane as can be seen in Fig. 5b. However, in lobes E and B, where no screw-edge loops were produced, the form of the original loops on (1 1 1) was little changed from that shown in Fig. 4a except that many dislocations had been annihilated.

The same general features shown in Fig. 5 were seen in (1 1 1) samples indented at room temperature, then annealed in the bulk at 750° C for $\frac{1}{4}$ h prior to thinning. Within the region up to 15 μm from such an indent in a direction parallel to the surface, a very high density of dislocations was visible. Among these were large numbers of the long screw-edge loops of the type seen in Fig. 4b. The area of high dislocation density ended in a well-defined front which appeared to act as a source emitting edge dislocations on the (1 1 1) plane. The appearance of this region was very similar to that in Fig. 5b. Such edge dislocations were observed at distances of more than 70 μm from the indentation centre. At this point the foil became too thick for further observation.

Specimens indented at 300° C contained similar dislocation configurations to those indented at room temperature. Fig. 6 shows one lobe near an indentation made at 300° C. The long 30° segments of the dislocation loops are not as straight as those produced at room temperature, and near to the centre of indentation the dislocations contain many bowed-out segments. This and the fact that dislocations

*Figure 5* Dislocation arrangements in (a) lobe C and (b) lobe D after further annealing for ½ h at 1030° C.

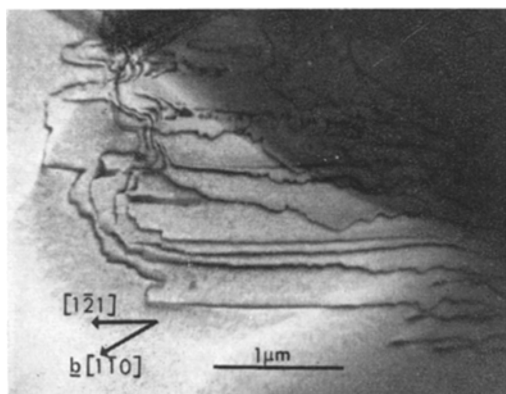


*Figure 6* Dislocations near an indentation in Si produced at 300° C. Plane of indentation and foil plane (1 1 1).

moved up to 10 µm from the indentation centre, compared to 8 µm at room temperature, suggest that there is some effect of thermal activation on dislocation motion even at 300° C.

## 4. Discussion

We have shown that silicon crystals indented with loads of 100 g at room temperature undergo extensive plastic deformation within a region up to 8 µm from the centre of the indentation. This confirms the observations of Nikitenko *et al.* [5, 8]. In their case the extent of dislocation motion was limited to a maximum depth of 6000 Å because of the low loads used, and it was suggested by them and subsequent authors [4] that the observed plastic flow might be related to possible differences in properties between the surface and the bulk of the crystal. However, in our experiments, we have detected dislocations at such depths below the surface,

that they are certainly within the bulk of the crystal.

Gridneva *et al.* [9] have reported that, during indentation at room temperature, the resistivity of silicon in the vicinity of the indenter drops considerably. On removal of the load the resistivity returns to the value for unstressed silicon. This observation was interpreted on the basis of a reversible stress-induced phase transformation in a thin layer adjacent to the indenter. Such phase transformations in the diamond structure are known to occur under high pressure conditions [12, 13]. It was further suggested that silicon only deforms plastically when it is in the metallic state. When the indenter has come to rest the equilibrium thickness of the metallic layer was calculated to be 0.05 μm, independent of loading up to 200 g. There is no evidence that the metallic phase ever extends to distances approaching the 8 μm in which dislocations have been observed. Comparing the present observations with those of Eremenko and Nikitenko [8], it is clear that the extent of dislocation motion at room temperature is strongly dependent on the applied load. Further the dislocation arrangements which we observe are completely consistent with what can be expected in the diamond structure [14]. In addition, shock wave compression experiments on germanium [13] show that plastic flow occurs at stress levels less than half that required for the phase transformation.

Although plastic flow certainly occurs when silicon is indented at room temperature, the types of dislocations and their arrangements differ considerably from those observed in silicon deformed at elevated temperatures [8, 15]. Indentation at room temperature produces shear loops composed of long 30° and short 60° sections. Arrays of dislocations of mainly 30° character have not previously been reported. They are apparently not important for deformation at elevated temperature where screw and 60° dislocations predominate. Further, the annealing experiments show that 30° dislocations do not move at high temperature under the residual stresses in indented samples, rather, screw and edge dislocations are formed. Above 400° C the hardness of silicon falls quite sharply with increasing temperature, whereas below 400° C the hardness is only slightly temperature dependent [16]. All these facts indicate that the mechanism which controls the motion of dislocations at room temperature differs from that which operates at elevated temperatures.

Bulk plastic flow under bending or uniaxial loading conditions first occurs above about 600° C, at relatively low stress levels, around 10 kg mm$^{-2}$. Under these conditions the flow is thermally activated and the dislocation velocity and stress are related by an expression of the form

$$V_d = B\tau^m \exp(-U/KT),$$

where $V_d$ is the dislocation velocity, $B$ is a constant, $\tau$ is the applied shear stress, $U$ is the activation energy for dislocation motion, equal to 2.2 eV in the case of silicon, and the exponent $m$ has a value around 2, depending upon the stress [17, 18]. At room temperature dislocation velocities become impossibly small for dislocation motion to be activated thermally even for values of stress equal to the theoretical shear strength of silicon.

A model for stress activated dislocation motion in strongly bonded solids at low temperatures has been proposed by Gilman [16]. In this case the breaking of highly stressed bonds is supposed to occur by the tunnelling of electrons through the potential barriers. The velocity of the dislocation, $V_d$, is given by the expression

$$V_d = V_k \exp^- \frac{\epsilon}{2V\tau},$$

where $V_k$ is a terminal kink velocity, approximately the shear wave velocity, $\epsilon$ is the potential energy barrier, $V$ the atomic volume and $\tau$ the applied shear stress. The exponential term represents the success probability for kink motion through tunnelling. One weakness of the model is that the nature of the potential energy barrier and its form when the crystal is highly stressed, is not known. Gilman has suggested that the barrier might be the band gap energy, which for silicon is 1.14 eV at room temperature, or the elastic energy of the dislocation which can be taken as $\frac{1}{2}Gb^3$ per atom [19], where $G$ is the shear modulus and $\boldsymbol{b}$ the Burgers vector. For silicon $\frac{1}{2}Gb^3$ is 10.1 eV. Thus widely different values for the dislocation velocity can be calculated depending upon the value assumed for $\epsilon$. A further difficulty of the model is that it does not describe slip in terms of the physical movement of atoms which is the essential feature of plastic flow.

In the case of hardness indentation, the observed deformation could have arisen if the theoretical shear strength of the material had been exceeded. An estimate of the compressive

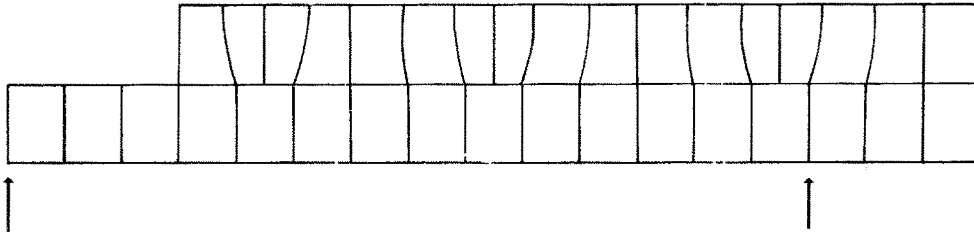

*Figure 7* Schematic diagram of the possible arrangement of atomic planes following block slip.

stress at which yielding occurred can be made using the method of Marsh [20]. In silicon, for a hardness value of 950 kg mm$^{-2}$, the equivalent value of the compressive yield stress is 450 kg mm$^{-2}$. Assuming that the shear stress, $\tau$, is half the compressive yield stress, then $\tau$ is 225 kg mm$^{-2}$ which corresponds to $G/\tau = 25.7$. This stress can be regarded as a mean or even a lower limit of the shear stress reached in the material if it were isotropic. However, the values of $\tau$ reached in certain crystal directions could be considerably higher, because of the effects of anisotropy. A value of $G/\tau$ of 25 indicates that $\tau$ is already in the region of the theoretical shear strength. Thus, a possible mechanism for the formation of a plastic impression in silicon is that the theoretical shear strength is exceeded locally, the lattice effectively collapses and block slip occurs. Dislocations would then be simultaneously generated at the edge of the slipped zone. This is shown schematically in Fig. 7. In this case block slip would have taken place over the section of crystal between the two vertical arrows. The expected high rate of release of energy during this process might cause a sufficient shock wave to move the dislocations further nto the crystal. This sort of model is difficult to quantify, but experiments are in progress to compare the deformation produced at hardness impressions with that induced by shock loading at room temperature.

## 5. Summary and conclusions

Microhardness indentation of silicon at room temperature and 300°C produces only shear dislocation loops which lie on $\{111\}$ planes and have $\langle 01\bar{1}\rangle$ Burgers vectors. The dislocation segments have line vectors $\langle\bar{1}\bar{1}2\rangle$ and $\langle 1\bar{1}0\rangle$, i.e. they are 30° and 60° dislocations. Dislocations produced at 300° C contain slightly bowed segments.

Dislocation rearrangement begins above 550°C in thin foils. The original loops are not mobile; rather they either tend to rotate into approximately edge orientation or complete rearrangement occurs to produce new screw-edge loops. Similar dislocation arrangements occur in indented samples annealed prior to thinning.

Plastic flow at room temperature cannot be described using the mechanism of thermally activated flow. It is suggested that the theoretical shear strength of the crystal could be exceeded locally and that the observed dislocations arise as a result of the accommodation of the displacements due to block slip.

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