

On the nature of plastic deformation generated by hydrostatic pressure in silicon single crystals

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Macroscopic plastic deformation of silicon single crystals, caused by annealing at hydrostatic pressure and high temperature, was studied by X-ray topography and transmission electron microscopy. The analysis is given of elastic and thermal properties of material around surface cracks and scratches from which deformation process is propagated. The idea of elastic misfit between damaged self-strained material at cracks and scratches and defect-free silicon matrix, is introduced. On the basis of theoretical and experimental data it is concluded that the plastic deformation of silicon at high pressure consists of two processes. The first is a loss of coherency of cracks and scratches by the emission of dislocations at misfitting second phase precipitates present in silicon. The second is the macroscopic yielding from incoherent cracks and scratches at lower elastic strain energies.

The presented mechanism explains also the deformation behaviour of silicon crystals subjected to tensile stress at high temperatures; the generation and propagation of dislocations at oxide precipitates before the macroscopic yielding [3].

1. Introduction

Silicon single crystals can be plastically deformed at high temperatures only, above 600°C, as was shown by Sylwestrowicz [1] in his precursory paper. It is obviously known that plastic deformation resulting in dislocation propagation can occur due to shear stresses acting in a crystal. Shear stresses can be of the following origin:

- (i) Generated from external source (e.g. due to indentation or extension).
- (ii) Created due to elastic imperfections present in a crystal.
- (iii) Created due to temperature gradients in a crystal.
- (iv) Induced by condensation of point defects or by irradiation of a crystal.

The studies of deformation process in silicon single crystals subjected to external shear force at

high temperatures were carried out by Nishino *et al.* [2, 3] using *in situ* X-ray topography. It was observed that the deformation process begins from the propagation of plastic zones developed from the places of large strain (e.g. scratches) existing in the surface layer of the specimens. It was found also that dislocations are emitted from the oxide precipitates present in silicon before the macroscopic deformation propagated from the crystal surface. However the authors did not try to explain this behaviour.

On the other hand plastic deformation can appear during rapid cooling of a crystal. In these conditions two effects can be responsible for emission of dislocations. In the first case a non-uniform temperature gradient existing in the cooling material results in internal stresses: the surface of a crystal is at a lower temperature than

the crystal interior and therefore is subjected to larger contraction than the latter [4]. At high temperature the resulting stresses can be partly released by the formation of dislocations. In the second case rapid cooling (quenching) of a crystal results in large non-equilibrium concentration of point defects (i.e. supersaturation). The excess point defects condense within the crystal creating dislocation loops.

Hydrostatic pressure acting on defect-free, elastically isotropic single crystal cannot induce shear stresses in this material, according to the form of "stress-strain" elastic tensor. The generation of shear stresses by hydrostatic pressure is possible if the crystal contains regions of different elastic properties (e.g. second phase inclusions, structural defects, cracks or scratches).

Macroscopic plastic deformation of silicon, caused by hydrostatic pressure at high temperatures was observed by means of X-ray and electron microscopy techniques. We have tried to explain this behaviour using thermodynamic description of properties of crystals containing defects.

2. Theoretical conditions for plastic deformation

2.1. Description of the source of shear stress

As was shown earlier [5] hydrostatic pressure can induce shear stresses and dislocation formation in a crystal because of difference of bulk moduli (compressibilities) between ideal crystal lattice and crystal lattice containing defects. However for silicon crystals the plastic deformation is possible at high temperatures only [1]. Thus the difference between thermal expansion of perfect and imperfect crystal lattice which can result in emission of dislocations must be additionally taken into account. Silicon crystals may contain second phase inclusions and dislocations in the bulk and cracks and scratches on the surface. Generation of local stresses at precipitates and behaviour of dislocations under high pressure-high temperature conditions have been the subject of separate investigations [6, 7]. However, the nature of macroscopic plastic deformation which propagates in silicon from its surface under high pressure and high temperature has not been studied up to now. We suppose that damaged silicon layers at scratches and cracks on the silicon surface can be the sources of plastic deformation. A scratch and a crack can be schematically presented in the

simplest way in Fig. 1. A denotes an ideal crystal lattice and B the volume filled in with disordered material. We assumed for simplicity that volume B represents a self-strained medium which contains stress centres, i.e. defects of pure shear in nature. Such defects have elastic strain energy expressible in the form:

$$E = \alpha GV \quad (1)$$

where G is the shear modulus, V is the volume of the self-strained medium B and α is a constant independent of pressure p and temperature T . In fact, the strain fields associated with most defects are predominantly shear strains. Screw dislocations are composed entirely of shear strain. Edge dislocations and point defects, treated in a "sphere-in-hole" model [8], are predominantly shear. However, in our consideration we assume that disordered layer B contains shear stress centres which result from the damage of the material (e.g. microcracks or microvoids). When hydrostatic pressure and high temperature is applied to the crystal, the magnitude of the elastic strains introduced is determined by the misfit parameter defined as:

$$\epsilon_s^T = \frac{r_s - r_M}{r_{os}} \simeq \frac{1}{2} \frac{V_s - V_M^s}{V_{os}} \quad (2)$$

for the scratch (Fig. 1a), where r_s and r_M are the radii of the cylindrical layer of damaged self-strained material B and of cylindrical cavity in defect-free matrix material A (constructed by removing material B) measured at pressure p and temperature T , r_{os} is the radius of layer B for pressure $p = 1$ bar and temperature $T = 20^\circ \text{C}$ (for this condition $r_{os} = r_s = r_M$). V_s , V_M^s and V_{os} are the appropriate volumes of a semi-cylinder. For the crack (Fig. 1b) the misfit can be defined as for thin plate:

$$\epsilon_c^T = \frac{a_c - a_M}{a_{oc}} \simeq \frac{V_c - V_M^c}{V_{oc}} \quad (3)$$

for $b \gg a$ and $b \gg b_M - b_c$, where analogously to the description of the scratch, the figures a_c , a_M , b_c , b_M and V_c , V_M^c mark the bases, heights and the volumes of the wedge-shaped damaged material B and of wedge-shaped cavity in the material A at pressure p and temperature T . a_{oc} and V_{oc} concern atmospheric pressure and room temperature (for which $a_{oc} = a_c = a_M$). We assumed that the volumes of the grooves in both cases are small in comparison with the volume of self-strained medium B.

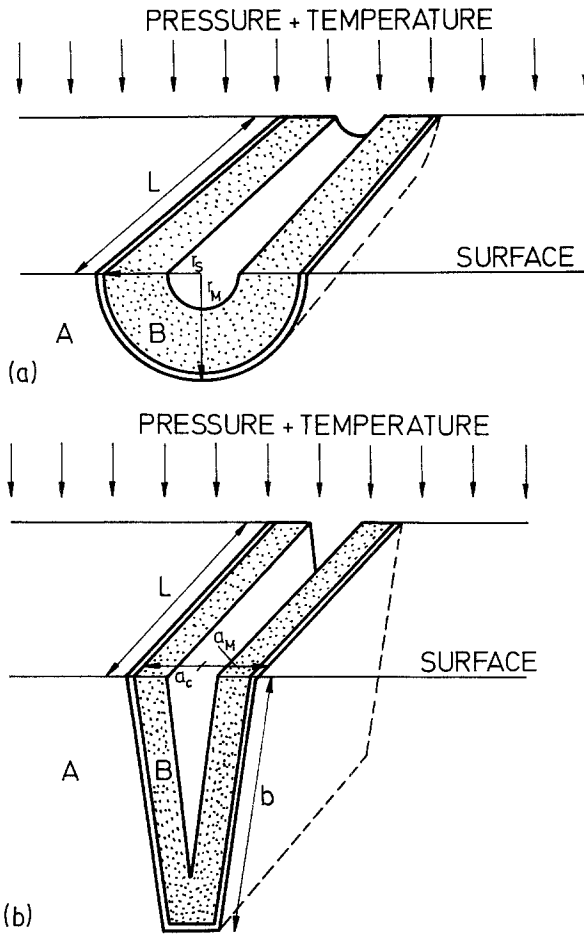


Figure 1 Schematic drawings of a scratch (a) and a crack (b) on a crystal surface under the influence of hydrostatic pressure and high temperature. A – defect-free crystal lattice, B – disordered material.

The relative change of volume can be replaced by the difference of compressibility and thermal expansion coefficients of perfect, defect-free material A and self-strained material B. Then the misfit ϵ_s^T is expressed by:

$$\epsilon_s^T = \frac{1}{2} \frac{V_s - V_M^s}{V_{os}} = \frac{1}{2} \left[p \left(\frac{1}{K_M} - \frac{1}{K_s} \right) + \Delta T (\beta_s - \beta_M) \right] \quad (4)$$

for the scratch and analogously for the crack. K_M , β_M and K_s , β_s denote bulk moduli and thermal expansion coefficients of defect-free and self-strained materials, respectively.

Under the assumption that the properties of the self-strained medium do not differ much in both cases, bulk modulus and thermal expansion coefficient of this material can be expressed as:

$$\begin{aligned} K_s &= K_c = K_M + \Delta K \\ \beta_s &= \beta_c = \beta_M + \Delta\beta \end{aligned} \quad (5)$$

where ΔK and $\Delta\beta$ are the modifications of coefficients for defect-free crystal resulting from the presence of stress centres.

Applying the results of Holder and Granato [8] derived from the principles of thermodynamics for isotropic self-strained silicon, K_s and β_s are equal to:

$$\begin{aligned} K_s &= K_M - K_M \left(\frac{1}{K_M} \frac{dK_M}{dp} - \frac{1}{G} \frac{dG}{dp} \right) \frac{nE}{V} \\ \beta_s &= \beta_M + \frac{1}{K_M} \left(\frac{1}{K_M} \frac{dK_M}{dT} - \frac{1}{G} \frac{dG}{dT} \right) \frac{nE}{V} \end{aligned} \quad (6)$$

where the energy of stress centre E is expressed by Equation 1, V is the volume of self-strained material and n is the number of stress centres in this material. According to arguments given in [8] the second order pressure and temperature derivatives of G were neglected.

Then the misfit can be written as:

$$\epsilon_s^T = \frac{1}{2} \epsilon_c^T = \frac{1}{2} \left[p \frac{\Delta K}{K_M(K_M + \Delta K)} + \Delta T \Delta\beta \right]$$

$$\begin{aligned}
&\simeq \frac{1}{2} \left[\frac{p}{K_M^2} \Delta K + \Delta T \Delta \beta \right] \\
&= \frac{1}{2} \left[\frac{p}{K_M} \left(\frac{1}{G} \frac{dG}{dp} - \frac{1}{K_M} \frac{dK_M}{dp} \right) \right. \\
&\quad \left. + \frac{\Delta T}{K_M} \left(\frac{1}{K_M} \frac{dK_M}{dT} - \frac{1}{G} \frac{dG}{dT} \right) \right] \frac{nE}{V}
\end{aligned} \tag{7}$$

where it was assumed that $K_M \gg \Delta K$. The figure $\xi = nE/V$ is the density of the elastic strain energy in self-strained medium B.

On the basis of [5] the real value of misfit is given by the equation:

$$\epsilon_s^c = \epsilon_s^T \left[\frac{3(K_M + \Delta K)}{3(K_M + \Delta K) + 4G} \right] \simeq \epsilon_s^T \left(\frac{3K_M}{3K_M + 4G} \right) \tag{8}$$

which expresses the fact that additional stresses are necessary to join together the interfaces of the defect-free and self-strained materials, separated due to Equations 2 and 3.

In the presented model we can treat the scratch and crack as the inclusion of material which has different elastic and thermal properties than defect-free silicon. When $\epsilon^T = 0$ the total elastic strain energy is equal to:

$$E_{e1}^0 = \xi V \tag{9}$$

But when the misfit ϵ^T is created by high pressure and high temperature the total strain energy is given by the expression:

$$\begin{aligned}
E_{e1} &= \xi V + 2G(\epsilon^T)^2 \frac{K_M + \Delta K}{3(K_M + \Delta K) + 4G} V \\
&\simeq \xi V + 2G(\epsilon^T)^2 \frac{(1 + \nu)}{9(1 - \nu)} V
\end{aligned} \tag{10}$$

where ν is the Poisson's ratio of defect-free matrix. The second term in the Equation 10 was taken from Eshelby's paper [9] and expresses misfit strain energy in the matrix and inclusion independently of the shape of the inclusion. Strain energy can be partly released by emission of dislocations.

2.2. Criteria for dislocation emission

As was pointed out by Ashby and Johnson [5] a misfitting inclusion embedded in the matrix can lose a part of its elastic energy by emission of dislocations but the value of the critical misfit ϵ_{cr} at which dislocations are formed depends on the

coherency of the inclusion. There are two criteria to the critical misfit, described by the lower and the upper limit resulting from the presence of the energy barrier for nucleation of dislocations. The lower limit for ϵ_{cr} was derived from the condition of the decrease of elastic energy when a single dislocation loop is placed round the inclusion. This limit is dependent on the size of the inclusion and applies to the incoherent precipitates. The upper limit occurs when the energy barrier vanishes and gives single value of ϵ_{cr} independently of the inclusion size. This criterion applies to the coherent precipitates.

In the case of scratches and cracks in silicon, the interface region between defect-free matrix and self-strained material of scratch and crack is wide and there are no well-marked boundaries separating these two materials. Thus we must treat the scratch and crack as the coherent inclusions in silicon. However the misfit and stresses needed for dislocation punching at cylinder- and plate-shaped coherent inclusions are expected to be very large ($\epsilon^T > 0.1$) as was estimated by Weatherly [10]. Such conditions are quite stringent and coherent inclusions must lose coherency by some other mechanism, e.g. the climb or glide of dislocations from an exterior source to the inclusion-matrix interfaces or the condensation of point defects from the matrix [10].

Silicon crystals may contain incoherent inclusions:

(a) amorphous SiO_2 precipitates which emit dislocation loops when under high pressure and high temperature the misfit exceeds the critical value [6, 7],

(b) copper silicide, Cu_3Si , precipitates which form and grow during heat treatment creating the colonies surrounded by pure edge dislocation loops [11, 12].

According to the above considerations, when silicon crystal is subjected to hydrostatic pressure and high temperature, dislocations nucleated at the incoherent precipitates (at low values of critical misfit), move under the internal stresses in the crystal. On the crystal surface, dislocations cause the loss of coherency of cracks and scratches. Then these incoherent centres can be the source of the repeated emission of dislocations in the crystal when the misfit at the centre exceeds the critical value ϵ_{cr} described by the lower limit. The misfit at the centres given by Equations 7 and 8 depends on the values of pressure p and temperature T .

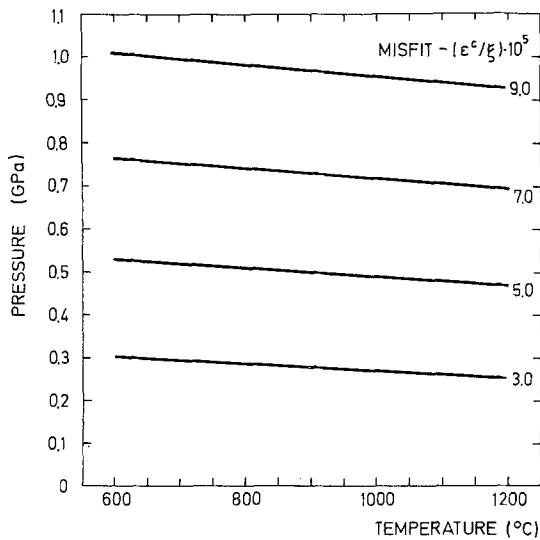


Figure 2 The lines of constant misfit described by Equations 7 and 8 for cracks and scratches on the silicon surface. The misfit is normalized to the density of elastic strain energy ξ in these centres. The values of ϵ_s^C/ξ are given per eV of defect energy. The lines for large values of misfit correspond to small dimensions of cracks or scratches and vice versa.

Then it is possible to plot the points on the pressure against temperature diagram, for which the misfit has the fixed value (Fig. 2). The misfit was normalized to $\xi = n^*E^*/V$ (Equation 7) where the number n^* of defects is taken to be the number of atomic volumes containing stress microcentres (in units of at %) and E^* is a defect energy in eV. The values of elastic constants and their pressure and temperature derivatives have been taken from [13, 14].

The calculated values of pressures and temperatures lying on the lines of constant misfit can be compared with the experimental values for which dislocation emission from cracks or scratches is observed.

3. Experimental evidence

In this section we compare the presented mechanism of dislocation generation at cracks and scratches in silicon with the experimental results observed in silicon under high pressure and high temperature. The results concerning generation of dislocations and stresses at second phase precipitates were taken from [6, 7].

3.1. Experimental procedure

Czochralski and floating zone silicon single crys-

tals, n-type and p-type, containing different concentrations of interstitial oxygen (from $2 \times 10^{17} \text{ cm}^{-3}$ to $8 \times 10^{17} \text{ cm}^{-3}$) were used in experiments. As a result of high pressure-high temperature investigations [6, 7], the crystals were classified among two groups for which the maximum values of radii of amorphous SiO_2 spherical inclusions present in the matrix were equal to: $r_{\text{max}} \approx 0.4 \mu\text{m}$ for crystals marked with C1 and $r_{\text{max}} \approx 0.25 \mu\text{m}$ for C2. The plates 300 to $1000 \mu\text{m}$ thick and perpendicular to the (1 1 1) axis were cut from silicon ingots, lapped and polished. The plates of dimensions $6 \times 12 \text{ mm}^2$ were annealed under hydrostatic pressure of argon or helium (99.999% purity) in high pressure chamber at temperatures up to 1200°C and pressures up to 1 GPa. To avoid temperature gradients and external shear stresses during annealing, the samples were wrapped in thin molybdenum or platinum foils and inserted on a flat alumina substrate. The samples were annealed at high pressure for 1 to 6 h. The cooling rates were changed from 0.3° to $20^\circ \text{C sec}^{-1}$. In one case, the specimens of C2 type were subjected, before high pressure annealing, to the heat treatment at atmospheric pressure of helium and at about 950°C for 150 h to stimulate the growing of SiO_2 inclusions. After annealing at high pressure the both surfaces of the samples were polished until the layer, $30 \mu\text{m}$ thick, was removed.

Before and after heat treatment at high pressure the samples were studied by means of X-ray transmission topography (XTT, Lang method, $\text{MoK}\alpha_1$ radiation) and transmission electron microscopy (TEM). No defects were observed in unannealed samples by TEM or XTT (the TEM method, 100 and 1000 kV, allows the detection of precipitates of diameters larger than some 10 nm and with defect densities larger than about 10^6 cm^{-3}). X-ray topographs were registered on Ilford G5 nuclear plates, $100 \mu\text{m}$ thick.

3.2. Experimental results

Using XTT method, the plastic deformation propagated from a silicon crystal surface was observed for samples simultaneously annealed at high pressure and high temperature (Figs. 3a, b and c). Two groups of samples marked with C1 and C2 differ in conditions of dislocation emission. In both cases the deformation process begins at the surface above the pressure 0.35 to 0.4 GPa, but above the temperature of 950°C for C1 and at temperatures above 1150°C for C2 crystals

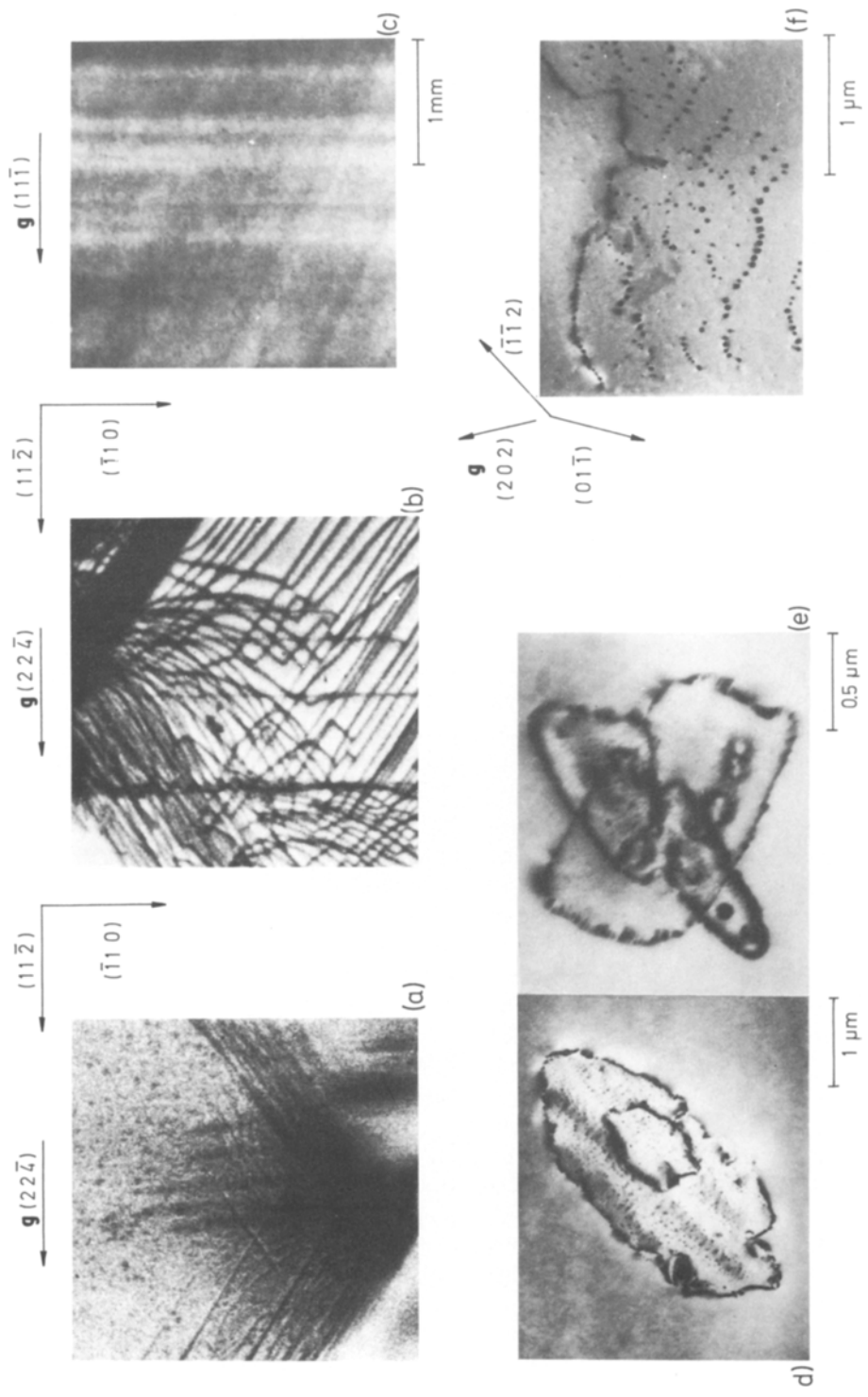


Figure 3 X-ray topographs (a, b, c) and TEM micrographs (d, e, f) of silicon crystals annealed at hydrostatic pressure: (a) 4 kbar (Ar), 1075° C, 1 h; (b) 5.3 kbar (He), 1200° C, 1 h; (c) 3.8 kbar (He), 1200° C, 6 h; (d) 7 kbar (Ar), 700° C, 6 h; (e) 6 kbar (Ar), 750° C, 6 h; (f) 3.8 kbar (He), 1200° C, 6 h.

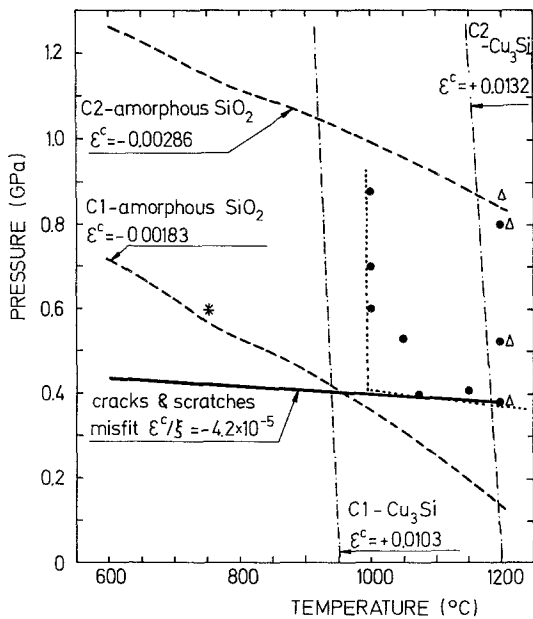


Figure 4 Pressures and temperatures of annealing, at which macroscopic plastic deformation of silicon crystals is observed (annealing time = 1 h): ●, ▲ – plastic deformation observed in C1 and C2 crystals, respectively (the region of plastic deformation of C1 crystals is marked with dotted line), * – plastic deformation observed in C2 crystal preannealed at 950° C and 1 bar for 150 h. The calculated lines of constant misfit for incoherent surface cracks and scratches and for Cu_3Si and amorphous SiO_2 precipitates are plotted.

(Fig. 4). These conditions are independent of the time of annealing and the cooling rate. The pre-annealing of crystals C2 at atmospheric pressure and at 950° C for 150 h in order to increase the diameter of SiO_2 inclusions (concentration of interstitial oxygen decreases) causes the decrease of the boundary temperature for deformation process during heat treatment at high pressure (Fig. 4). TEM examinations were carried out for C1 crystals and revealed the formation of the following defects during annealing at high pressure:

(i) Colonies of Cu_3Si precipitates surrounded by pure edge dislocation loops (Fig. 3d and e). Diameter of colony equals 1 to 2 μm and that of single precipitate some 10 nm. Colonies are characteristic for those annealed crystals in which dislocation generation from the surface was not observed by XTT.

(ii) Individual dislocations and slip bands decorated at regular distances with Cu_3Si precipitates (some 10 nm in diameter). The rows of Cu_3Si precipitates accompany dislocations

(Fig. 3f). These defects are characteristic for those annealed crystals in which dislocation generation from the surface was observed by XTT.

3.3. Discussion

In Section 2.2 it was concluded that macroscopic plastic deformation induced by annealing of silicon crystals at hydrostatic pressure consists of a two-step process:

(a) The first step is the loss of the coherency of the crystal surface cracks and scratches, which is caused by dislocations emitted from incoherent precipitates present in the bulk of silicon. Dislocations are formed and moved due to stress field created at precipitates by high pressure and high temperature because of the difference of elastic and thermal properties between an inclusion and the silicon matrix.

(b) The second step describes plastic deformation as a result of dislocation emission from incoherent cracks and scratches. The formation and movement of dislocations from the incoherent surface centres in silicon subjected to high pressure and high temperature, are possible at lower elastic strain energies than in the case of coherent centres. Dislocation emission begins when the misfit at the centres, which is given by Equations 7 and 8, exceeds the critical value independent of pressure and temperature (The lines plotted in Fig. 2 for different size of centres, give the calculated values of pressures and temperatures for which $\epsilon_s^c = \epsilon_{cr}$.)

Taking into account the mechanism presented above we have compared the experimental values of pressures and temperatures at which macroscopic deformation of silicon occurs, with the calculated values. The calculated data lie on the line of constant misfit created at incoherent surface cracks and scratches (Fig. 4). There is a good agreement between experimental boundary pressures (ranging from 0.35 to 0.4 GPa) and the calculated ones. The boundary temperatures (equal to 950° C for C1 and 1150° C for C2 crystals) at which plastic deformation is observed, can be explained by the coherency loss of the surface centres, caused by dislocations generated at misfitting precipitates. The lines of constant misfit for amorphous SiO_2 and Cu_3Si precipitates present in C1 and C2 silicon crystals are redrawn in Fig. 4 from [6, 7]. It is obvious that dislocations accompanying Cu_3Si particles are mainly responsible for coherency loss of surface cracks and scratches as

was confirmed by TEM observations (Fig. 3f). The difference of boundary temperatures between C1 and C2 crystals seems to be caused by smaller concentration of copper in C2 crystals. The decrease of boundary temperature for C2 silicon crystals annealed at high pressure can be obtained if additional sources of dislocations which can cause the loss of coherency of surface centres, become active. This was realized by the increase of size of SiO₂ precipitates during preliminary annealing at 950°C and atmospheric pressure for 150 h. The large elastic strain energy of misfitting growing precipitates gives the driving force for dislocation movement in a crystal.

4. Conclusions

Macroscopic plastic deformation of silicon crystals annealed at hydrostatic pressure can be explained by two processes:

(a) the loss of coherency of surface cracks and scratches due to glide of dislocations from misfitting precipitates to these centres and then

(b) the emission of dislocations from incoherent misfitting cracks and scratches.

However this argumentation can also be applied to the case of macroscopic plastic deformation of silicon (containing oxygen in concentration of $1.5 \times 10^{18} \text{ cm}^{-3}$) subjected to exterior tensile stress at high temperatures [3]. In this case the emission of dislocations from oxide precipitates (which were growing during preannealing) was observed prior to plastic deformation propagated from the crystal surface. It proves that the present model of coherent cracks and scratches which contain the layer of damaged, self-strained material of other

elastic and thermal properties than defect-free material, is correct. The tensile stress needed for macroscopic yielding increases when the concentration of misfitting precipitates or their dimensions decrease, as was found in [3]. On the basis of proposed mechanism, this behaviour can be explained by the smaller number of cracks and scratches which can lose their coherency. This is caused by the decrease of number of dislocations emitted from misfitting precipitates.

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