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The role of prismatic dislocation loops in the generation of glide dislocations in Cz-silicon

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Abstract

The aim of this work is to understand the mechanisms that lead to warpage of Czochralski silicon wafers. We propose that under sufficiently large stresses, the prismatic loops which are punched-out from oxide precipitates during precipitation can initially grow as long dipoles until they cross-slip. Subsequently, dislocation multiplication can occur at the sites where cross-slip takes place, by creation of Frank–Read sources. A model describing the movement of dipoles has been developed to calculate the time needed for the source to be operative. Calculated curves are found to be in agreement with experimental results. During high temperature treatments oxygen atoms can diffuse to the core of prismatic dislocation loops and consequently hinder the dislocation motion, or completely lock them. A model has been developed to predict the amount of oxygen at the dislocation core (and then the "unlocking" stress for a loop) by taking into account the background oxygen concentration, thermal history and position of prismatic loops. It has been shown that the model is capable of simulating the experiments.

Czochralski-grown silicon (Cz-Si) wafers can be easily deformed plastically when subjected to thermal treatments during device processing [1]. Thermal stresses must be taken into account and possibly be reduced during the fabrication of integrated circuits (IC) since the plastic deformation of wafers can lead to failure of devices [2]. For large diameter wafers (300 mm or more) gravitational stresses also become important and should be considered. Interstitial oxygen atoms can remarkably increase the strength of Cz-Si crystals under appropriate heat treatments [3]. At high temperatures, however, precipitation of oxygen resulting in the formation of oxide precipitates can lead to the nucleation of new sources of glide dislocations, which in turn, can cause macroscopic plastic deformation of crystals (precipitation "softening" [4]). Bulk defects like precipitates are undesirable in active regions of devices, but in inactive regions they are beneficial as gettering sites for metallic impurities ("internal" gettering). For this reason, the presence of oxide precipitates in silicon bulk is actually a requirement for modern IC technologies. Although oxide precipitates act like stress concentrators under applied stress, it

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is believed that they cannot directly generate glide dislocations since the magnitude of the stress concentration coefficient for an oxide precipitate is low (approximately 2) and not sufficient to nucleate glide loops [5]. However, the large misfit strain due to oxide precipitate growth induces the nucleation of prismatic dislocation loops [6]. These loops are punched-out from precipitates either during precipitate growth or on cooling the wafer in order to relieve the strain. It is arguable that under sufficiently large applied stress these prismatic loops can become sources of glide dislocations responsible for plastic deformation of crystals. Dislocation glide loops have been detected in all Cz-Si samples containing oxide precipitates after appropriate mechanical stress treatment even when the precipitate size was very small (<50 nm). The study of slip lines on the silicon surface has shown that the density of glide dislocation sources can be much smaller than the actual density of oxide precipitates (Fig. 1). This result indicates that an activation process is needed for the source to be operative and it is not every single precipitate which nucleates new dislocations. The activation process for the source depends on the duration and magnitude of the applied stress. It was possible to model the simple case of only one prismatic loop punched-out from the oxide precipitate and the prediction was found to be in good agreement with the experimental

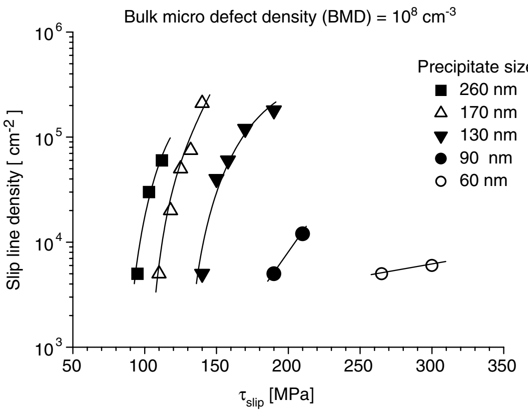

Fig. 1. Slip line density in Cz-silicon samples containing oxide precipitates of different sizes. Measured stresses were applied by using annular bending techniques [3].

results. More general experimental results involving large precipitates and associated tangles of dislocations have been published elsewhere [7].

1. Experimental procedure

Dislocation-free Cz-grown (0 0 1) silicon wafers (p-type, 10–20 Ω cm) were used for the experiments. The wafers had an initial oxygen concentration of about 6×10^{17} cm^{-3} (DIN 50438/I) and they were subjected to an annealing sequence in order to form oxide precipitates. A nucleation step at 650 °C for 16 h allowed the formation of silicon oxide nuclei in a density of about 10^9 cm^{-3} and a final precipitation step at 1000 °C for 1 h enabled the growth of oxide precipitates of less than 50 nm in size. Each wafer was mirror polished on one side and small bars with dimensions $0.65\times3\times30$ mm were cleaved along the [1 1 0] directions. Careful polishing of the sample sides was needed to remove any small scratches that may generate undesired dislocations when a stress is applied at high temperatures. The silicon bars were then annealed at 585 °C under three-point bending conditions (bending axis was $[1\,\bar{1}\,0]$) for different times (1–35 min) in pure argon atmosphere. Dislocation hexagonal loops created during three-point bending for the above geometry glide in the (1 1 1) and $(\bar{1}\,\bar{1}\,1)$ planes [8]. A preferential chemical etch was used to reveal the emergent parts of the loops as surface etch pits, visible under a differential interference contrast (DIC) optical microscope. The shear stress τ_c needed to detect one single dislocation glide loop was measured taking into account the applied stress distribution along the silicon bar and the position of the loop on the surface. τ_c was defined as the *critical resolved shear stress to generate a single dislocation glide loop*. For further details about the experimental procedure see Ref. [7].

TEM analysis of silicon samples showed that oxide precipitates are platelet shaped (Fig. 2) with a well defined habit plane (1 0 0) and side orientation [1 1 0]. The glide directions of punched-out dislocations are also geometrically defined along six possible orientations. Each of the four segments forming the prismatic loop lies on a different

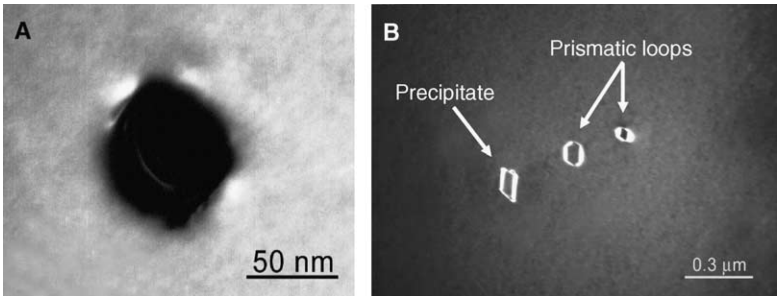

Fig. 2. (A) TEM image showing a platelet oxide precipitate in a sample annealed for 1 h at 1000 °C, (B) platelet precipitate and related punched-out dislocation loops produced in a sample after 3 h annealing at 950 °C.

(1 1 1) glide plane, but all of them move in the same direction with the same Burgers vector. It is known from earlier works that prismatic loops in silicon result to be edge in character [6]. The residual stress due to the misfit around a precipitate vanishes after a distance approximately equal to the precipitate size [9], which, in our case, is approximately 50 nm. Therefore it is assumed that after precipitation and strain relaxation the prismatic loop is at rest and positioned at 50 nm from the precipitate where the residual stress field is balanced by other stresses resisting dislocation motion (e.g., Peierls stress, unlocking stress). The application of a bending force along the [1 1 0] direction provides sufficient resolved shear stress to let two opposite parts of the prismatic loops move according with their Burgers vector and line orientation. This loop expansion results in the formation of a dipole which can glide along the prism [10] as shown in Fig. 3. We suppose that dipoles glide until one of the segments becomes screw in character and double cross-slips to another plane with the consequent nucleation of a Frank–Read source. The cross-slip mechanism is favorable because the shear stress in the new cross-slip plane is higher than in the original slip plane.

It is well known that dislocations in silicon containing oxygen impurities can be immobilized when the crystal is annealed at high temperature under no applied stress. The high resistance to warpage due to thermal stresses of Cz-Si wafers in comparison with floating-zone-grown silicon (FZ-Si) wafers is explained with the concept of dislocation locking by oxygen impurities in which interstitial oxygen atoms diffuse to the dislocation core at high temperatures and pin the dislocation [11]. Locking data have been collected using the technique previously described. Samples containing small precipitates were annealed for five hours at 600 °C and then were stressed under the same conditions as the other non-annealed samples from the same wafer.

2. Experimental results

Experimental results show that the critical resolved shear stress τ_c decreases with increasing

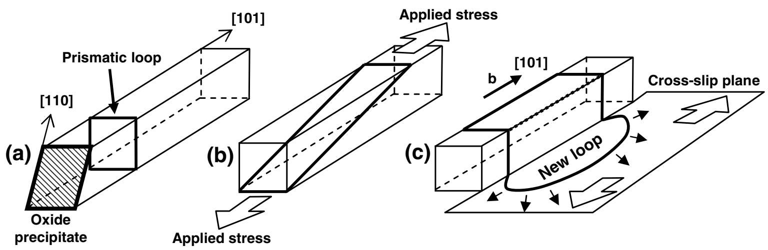

Fig. 3. Schematic representation of a prismatic loop (a), dipole formation under applied stress (b) and subsequent cross-slip (c).

duration of external stress application. This effect is less evident in samples with big precipitates where complicated tangles of dislocations were produced during precipitate growth. In this paper we did not investigate the role of dislocation tangles in the generation mechanism of glide loops; we considered single prismatic loops associated with small precipitates. Fig. 4 refers to samples containing oxide precipitates of size approximately 50 nm. The dependence of the critical stress τ_c on the duration of applied stress suggests that there is a time needed to activate the sources of glide dislocations. This time-dependence in the activation mechanism of the source is predicted by the model presented in Fig. 3.

Similar experiments have been carried out after the additional annealing of samples at 600 °C for five hours to investigate the possibility of increasing the resistance of silicon wafers against slip by segregation of interstitial oxygen atoms to the dislocation core. As shown in Fig. 4, after sufficient time the stress τ_c reaches a constant value equivalent to the "unlocking" stress, which is the minimum stress required to move a prismatic loop. The unlocking stress depends on the number of oxygen atoms at the dislocation core. Additional annealing allows extra oxygen atoms to diffuse to the core increasing the pinning force.

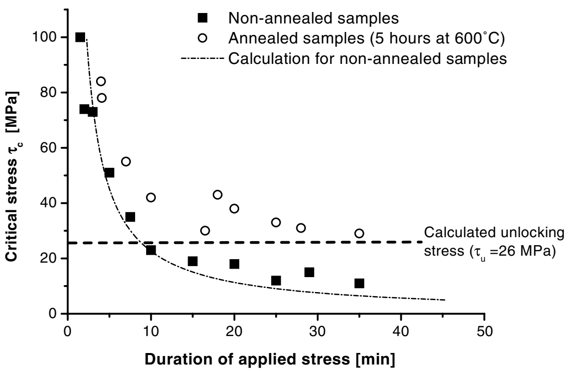

Fig. 4. Experimental data showing the time dependence of the critical stress for dislocations in samples with precipitates of less than 50 nm in size. The locking effect, as an increase in the critical stress after additional annealing, is also shown together with theoretical predictions.

3. Modelling and discussions

The results in Fig. 4 cannot be explained by just considering oxide precipitates as stress concentrators which nucleate new dislocations during three-point bending. However, the data can be explained using the above dipole model and calculating the amount of oxygen diffused to the core of the prismatic loops to give an estimate of their unlocking stress. A model has been used to calculate the number of oxygen atoms at the dislocation core by simulating the oxygen transport [11]. The migration of oxygen to dislocations is controlled by the diffusion process assisted by a drift flow resulting from the interactions of oxygen atoms with the dislocations. The oxygen transport equation can be written as

$$\frac{\partial C}{\partial t} = D_0 \nabla \left(\nabla C + \frac{C}{kT} \nabla(\Delta G) \right) \tag{1}$$

where C is the oxygen concentration, D_0 is the oxygen diffusivity, k is the Boltzmann's constant, T is the absolute temperature and ΔG is the Gibbs free energy of interaction between an oxygen atom and a dislocation given by

$$\Delta G = \Delta H - T\Delta S \tag{2}$$

where ΔH is the enthalpy change and ΔS is the entropy change. Boundary conditions for Eq. (1) are considered as follows: Assuming that the radius of the dislocation core r_0 is approximately 5 Å [12], the boundary conditions at a distance $R \gg r_0$ can be written as

$$C(R) = C_0 \tag{3}$$

where R is the distance from the dislocation core at which the oxygen concentration C does not change for the annealing times and temperatures concerned and it is equal to the initial oxygen concentration C_0. The flux at the boundary $r = r_0$ comprises two terms, one for the absorption and one for the emission of oxygen atoms. In the case of the absorption, incorporation of oxygen to the dislocation core is a function of the oxygen concentration adjacent to the core, C_1, and the fraction of available sites, i.e.,

$$\text{absorption} \propto C_1 \cdot \frac{C_a - C_c}{C_a} \tag{4}$$

where the concentration of the available and occupied sites in the core are C_a and C_c, respectively. On the other hand, emission of oxygen from the core depends on the oxygen concentration in the core C_c and the energy barrier to leave the core (the binding energy) ΔG

$$\text{emission} \propto C_c \cdot \exp\left(\frac{-\Delta G}{kT}\right) \tag{5}$$

Thus, the net flux J at the dislocation core is

$$\mathbf{J} \cdot \mathbf{n}|_{r=r_0} = \text{absorption} - \text{emission} = 2\pi r_0 D_0 \left[C_1 \frac{C_a - C_c}{C_a} - C_c \exp\left(-\frac{\Delta G}{kT}\right)\right] \tag{6}$$

where $\mathbf{n}$ is the unit vector normal to the core. The oxygen concentration surrounding a dislocation and the number of oxygen atoms at the dislocation core can be numerically calculated using the finite-differences method. In previous works [11] it was assumed that oxygen concentration is uniform everywhere and equal to the initial concentration C_0. That assumption is not valid in this work anymore because we are considering now samples in which precipitation has occurred and prismatic dislocation loops are at rest approximately 50 nm far from the precipitate. A residual oxygen concentration profile has to be taken into account when we consider the initial conditions for Eq. (1). The oxygen profile was calculated using Ham's theory of diffusion-limited growth of oblate spheroid precipitates [13]. Fig. 5 shows the oxygen concentration ($\sim 3.6 \times 10^{17}$ cm^{-3}) surrounding a loop at a distance of 50 nm from the precipitate. This background concentration has been considered in Eq. (6) for the calculation of the oxygen concentration at the dislocation core C_c. The unlocking stress τ_u is proportional to the number of oxygen atoms at the dislocation core, then

$$\tau_u = KC_c \tag{7}$$

where K is a constant [11]. Considering a background oxygen concentration at the dislocation site of 3.6×10^{17} cm^{-3}, the calculation of the

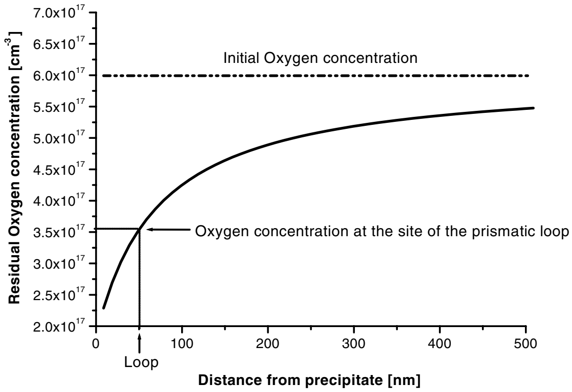

Fig. 5. Oxygen concentration function of distance from the oxide precipitate. The position of the punched-out prismatic loop before stress application is indicated.

unlocking stress for 5 h annealing of the samples at 600 °C gives the value $\tau_u = 13$ MPa. This is the stress needed to unlock a dislocation segment. Some other considerations are required in order to calculate the unlocking stress of a prismatic loop in the geometry of the experiment. When an external force is applied along the [1 1 0] direction on the silicon bar, a resolved shear stress τ_a acts on segments C and D of dislocation loop, as shown in Fig. 6. On the other hand, no resolved shear stress is present in the planes where segments A and B are. As a consequence, the work for unlocking segments A and B has to be done by the stress τ_a acting on C, which is also locked. The work dW necessary for moving the segment C of an infinitesimal distance dx is [14]

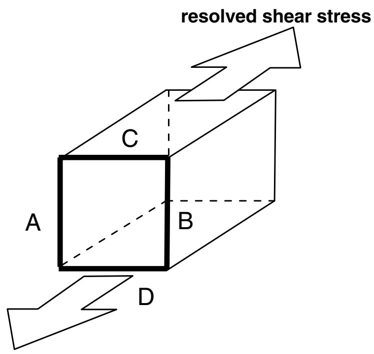

Fig. 6. Prismatic dislocation loop. Only segments C and D can be directly moved by applied stress in the [1 1 0] direction.

$$\mathrm{d}W = (\tau_a - \tau_u)bL\mathrm{d}x - 2\tau_u b\frac{L}{2}\mathrm{d}x \tag{8}$$

The work $\mathrm{d}W$ is positive when $\tau_a > 2\tau_u$, then the threshold value of the applied stress to be exceeded for unlocking the prismatic loop is

$$\tau_c = 2\tau_u \tag{9}$$

In our case, the calculated stress needed to unlock a single segment positioned at 50 nm far from the precipitate is $\tau_u = 13$ MPa. Therefore, according to Eq. (9), the value $\tau_c = 2\tau_u = 26$ MPa is necessary to start moving loops and subsequently generate new sources of glide dislocations by the cross-slip mechanism. The calculated value is compared with experimental results in Fig. 4 where data are shown to be in good agreement with predictions.

4. Conclusions

Mechanical properties of Cz-Si wafers containing small oxide precipitates (<50 nm) have been investigated using bending techniques. Experimental data suggest that it is not every single precipitate which nucleates new dislocation glide loops during the application of stress at high temperatures, but more likely it is the expansion of punched-out prismatic loops followed by the cross-slip of a segment into a new plane that accounts for wafer deformation and loss of device yield. Application of specific heat treatments can lead to the locking of prismatic dislocations associated with the precipitates in Cz-Si wafers. This in turn increases the mechanical strength of the wafers and their resistance to warpage. The effect of a particular thermal treatment on strengthening the wafers can be successfully predicted in the case of small precipitates considering the amount of oxygen atoms collected at the dislocation core during annealing. Accordingly it might be possible to develop a particular sequence of thermal treatments during device fabrication which allows the locking by oxygen atoms of all mobile dislocations and possible loop sources. In this way, the device yield would be improved remarkably.

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