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INTERACTION BETWEEN DISLOCATIONS AND IMPURITIES IN SILICON

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Résumé - En se basant sur les travaux de l'équipe dont l'auteur fait partie, certains aspects de l'interaction entre les dislocations et les impuretés dans des cristaux de silicium, sont étudiés ici. Les sujets étudiés sont : les conséquences de la présence d'impuretés sur la dynamique de la dislocation, le blocage des dislocations par les impuretés, la cinétique de l'agrégation d'atomes d'oxygène sur le coeur, et la structure et l'activité électrique des agrégats d'oxygène qui se développent au coeur des dislocations.

Abstract - Some aspects on the interaction between dislocations and impurities in silicon crystals are reviewed on the basis of the works of author's group. Topics taken up are effects of impurities on the dynamic behaviour of dislocations, locking of dislocations by impurities, kinetics of the aggregation of oxygen atoms on dislocation core, and the structure and electrical activity of oxygen aggregates developed at dislocation core.

1. Introduction

Interaction between dislocations and impurities in semiconductors is attracting a great amount of attention from both the fundamental and practical view points. The dislocation core or, at least, some irregularities on a dislocation line such as jogs and kinks are now known to be electrically active. Such segments naturally interact with electrically active impurities in the crystal. The electrostatic interaction is expected to play much more important role in the dislocation-impurity interaction in a semiconductor crystal than the elastic interaction due to the size misfit between an impurity atom and a host atom : the interaction energy of the former at an interatomic distance is much larger than that of the latter. Further, it should also be noted that the atomic arrangement characteristic in the dislocation core is never realized in a bulk crystal region. The impurity atoms located in the core region of dislocation is, thus, under a very special circumstance. The electronic structure of the impurity atoms may be altered from that in the normal bulk state and, also, some chemical reactions of the type which does not take place in the bulk crystal may proceed in this special region. In this paper, some aspects of the dislocation-impurity interactions in silicon will be presented briefly on the basis of the investigations conducted by author's group.

The dislocation-impurity interaction is now widely utilized in device production technology to suppress the occurrence of slip and warping of silicon wafers due to thermal stress at high temperature processings and also to remove harmful impurities from electro-active regions of device elements.

2. Experimental Background

The in situ X-ray topographic technique developed by our group /1/ has

facilitated the study of dynamic behaviour of dislocations in impure silicon crystals to a great extent. In the intermittent technique commonly adopted in previous works, dislocations are displaced at elevated temperatures and the resulting effects are observed at room temperature. Dislocations are kept at rest during the heating and cooling of the specimen. It is unavoidable with such intermittent technique to have the occurrence of dislocation locking due to the development of impurity atmosphere while the specimen is kept under zero effective stress at elevated temperatures. This brings about a serious difficulty to investigate the dislocation behaviour in impure crystals. Usually, the dislocation velocities in impure crystals have been deduced from the distance travelled by the leading dislocation of a row of dislocations generated from a scratch made on the specimen surface /2-4/. Such a technique naturally involves many origins for error.

In our in situ X-ray topographic technique, isolated fresh dislocations are successfully introduced into the impure specimen without the occurrence of locking : introduced dislocations are always kept in motion by the application of stress so that the impurity atmosphere can not be developed, and the motion of the dislocations is followed continuously on a T.V. monitor. This in situ technique has been applied to the investigation of dynamic behaviour of dislocations in both pure and impure silicon crystals /5,6/.

The developments of new techniques for impurity controlling have also made it possible to study the details of the dislocation-impurity interaction in silicon. The technique for the controlling of oxygen concentration in silicon in the range of 2 - 20 at.ppm has been established by growing crystals by the Czochralski method in a magnetic field /7/. The technique of doping of nitrogen in floating-zone silicon has also been established /8/. These developments in the technique of crystal growth have facilitated especially the quantitative investigations on the interaction between dislocations and light element impurities in silicon crystals.

3. Effect of Impurities on Dislocation Velocity

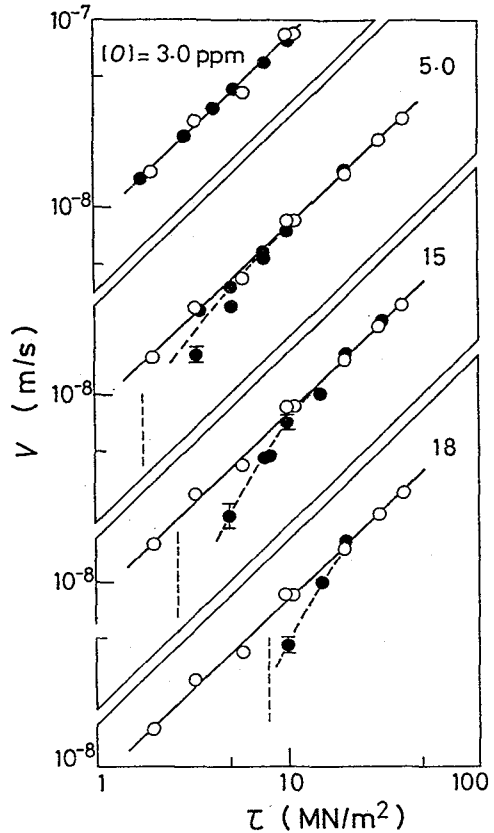
The dislocation velocity v in high purity silicon crystals measured by the in situ X-ray topographic technique is expressed as a function of the stress τ and the temperature T by the following simple equation /5/ ;

$$v = v_0 \tau \exp(-E / k_B T) \quad (1)$$

in the temperature range 600 - 800°C and the stress range 1.2 - 40.0 MN/m². Here, the magnitudes of v_0 are 1.0×10^4 and 3.5×10^4 m²/MN·s and those of E are 2.20 and 2.35 eV for 60° and screw dislocations, respectively, and k_B is the Boltzmann constant. In contrast to a previously published work done with the intermittent technique /4/, v is linear against τ down to a stress as low as 1.2 MN/m² which is the minimum stress that can be applied with the high temperature stage used. The above type of velocity equation can never be described with any existing theories which assume the double kink nucleation to play an important role in determining the dislocation velocity /9-14/. Equation (1) should be regarded as the appropriate one in the limiting case of low applied stress relative to the Peierls stress. Probably, the model based on the linear-response theory will give the correct description for the velocity relation under low stresses. The Hirth-Lothe theory /15/ based on such a model gives the dependences of v on τ and T given by Eq. (1). However, the magnitude of v_0 predicted by their theory turns out to be three to four orders of magnitude lower than the experimental one. This large discrepancy can be removed if the activation energy for the dislocation motion has a linear temperature dependence with a temperature-coefficient of $-6 \sim 8 \times 10^{-4}$ eV/K (Ishioaka, S. : private communication).

Light element impurities show some peculiar influence on the velocity vs. stress relation /5/. Carbon atoms up to a concentration of 2 at.ppm have no appreciable influence on the dislocation mobility. Oxygen atoms even of high concentrations also have no influence on the dislocation velocity in the high stress range. This is true down to a very low applied stress for oxygen atoms

Fig. 1 The relation between velocity v and stress τ for 60° dislocations at 647°C in silicon crystals doped with various concentrations of oxygen shown in the figure. Open marks are for a high purity floating-zone crystal /5/.



at a concentration of 3 at.ppm. However, in crystals doped with high concentrations of oxygen, the dislocation velocity becomes lower than that in the high purity crystal with the decrease in the stress, thus, bringing about the deviation from the linear $v - \tau$ relation as shown in Fig. 1. The deviation becomes more remarkable with the increase of oxygen concentration and with the decreases in the stress and the temperature. Further reduction of the applied stress results in the cessation of dislocation motion. The vertical broken line in Fig. 1 shows the critical stress below which dislocations originally moving under high stresses become immobile. This critical stress for the cessation of dislocation motion increases with the increase in the oxygen concentration. Nitrogen atoms at a concentration of 0.11 at.ppm show no appreciable influence on the dislocation velocity for the stress higher than about 4 MN/m^2 . However, dislocations which have been moving under high stresses are found to cease to move and to become immobile when they are brought under stresses lower than about 4 MN/m^2 . The magnitudes of the mean critical stress for the cessation of dislocation motion are shown in Table I for crystals doped with various types of impurity.

The dislocation mobility is increased by the doping of donor impurities /5/. The increase in the dislocation velocity is controlled by the concentration and not by the species of the dopants. The high dislocation mobility is related to the reduction in the magnitude of E in Eq. (1). These results are in agreement with previous works /2-4,16,17/. The dislocation velocity in the crystals doped with acceptor impurities is measured to be only slightly lower than in the high purity crystal throughout the whole temperature range,

Table I The magnitudes of the critical stress τ_c for the cessation of dislocation motion in various types of silicon /5/.

Materials	Impurity (at.ppm)	τ_c (MN/m^2)
FZ Si	B : 0.00004	<1.2
	C : 2.0	<1.2
	N : 0.11	4.2
	P : 240	8.5
MCZ Si	O : 3.0	<1.2
	O : 5.0	1.8
CZ Si	O : 15	3.0
	O : 18	8.0
	P : 120 (O : ~ 12)	4.5
	P : 300 (O : ~ 12)	11.5
	B : 280 (O : ~ 14)	5.0

and the magnitude of the activation energy also to be only slightly smaller than in the high purity crystal. These results are in serious disagreement with previously published data. The $v - \tau$ relations in the crystals doped with donor or acceptor impurities are both linear in the high stress range, being given by the equations of the type of Eq. (1). However, the deviation from the linearity as observed in the oxygen-doped crystals is observed in the low stress range. The critical stress for the cessation of dislocation motion exists also in these types of crystal. The above disagreements on p-type crystals between our data and the previous ones may be attributed to the errors involved in the previous measurements associated with the dislocation locking by impurities.

4. Effect of Impurities on the Morphology of Moving Dislocations

The shape of dislocations in motion in high purity silicon crystals observed by the in situ X-ray topography is a regular hexagon or a half-hexagon the segments of which are straight along $\langle 110 \rangle$ over the whole range of the applied stress 1.2 - 40.0 MN/m². This is found to be also the case in the crystals doped with light element impurities such as carbon, oxygen and nitrogen when dislocations move at the same velocities as in the high purity crystals, and to be the case in the crystals doped with electrically active impurities such as phosphorus when dislocations move at the velocities proportional to the applied stress, both in the high stress range /5/.

Whenever dislocations move at the velocities deviated from those obeying the linear $v - \tau$ relationship, the segments of a moving loop or a moving half-loop are observed to be perturbed from $\langle 110 \rangle$ straight lines : originally straight segments in motion under a high stress become to be perturbed from $\langle 110 \rangle$ straight lines during motion when the applied stress is reduced /5/. Such perturbation in the shape of dislocations in motion is reversible. If moving segments perturbed in the shape are brought under a high stress, the segments restore the straightness.

As mentioned in 3 the cessation of dislocation motion takes place in the lower stress region. Once originally moving dislocations cease to move in impure crystals, the stress necessary to restart the dislocations increases with increases in the duration and temperature where the dislocations have been kept at rest, depending on the species and concentration of the impurities involved.

All the above effects are observed commonly for both 60° and screw segments /5/.

The perturbation in the shape of moving dislocations and the cessation of dislocation motion are characteristic of the impure crystals. Thus, these phenomena are attributed to the interaction between dislocations and impurity atoms. Probably, the shape perturbation is related to the local locking of dislocations by impurity atoms and the cessation of the motion to the close locking along the dislocation line. The maximum of the dislocation velocities at which the perturbation in the shape of moving dislocations is observed is one or two orders of magnitude higher than the theoretical velocity at which the atmosphere starts to develop /18,19/. This discrepancy may be attributed to the fact that impurity atoms are actually distributed discretely in the lattice while the theory treats them as to be distributed on each lattice site at the equal probability.

5. Locking of Dislocations by Impurities

The in situ X-ray topography has been applied to study the relationship between the locking of dislocations and the development of impurity atmosphere /6/. Originally fresh dislocations in silicon crystals have been aged at elevated temperatures under no applied stress and the stress necessary to start such aged dislocations has been measured as functions of the duration and temperatures of aging, and of the species and concentration of impurities involved. This starting stress is defined as the locking stress, being known to be sensitive to the temperature at which the dislocations are released and

to be insensitive to the releasing rate of the dislocations.

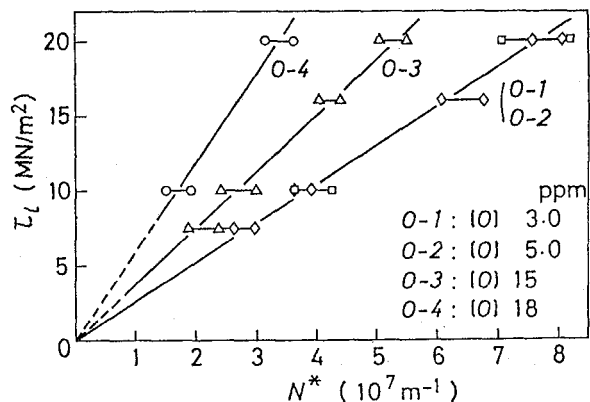
The locking stress at a certain temperature is measured to increase with the increase in the duration of ageing for the crystals doped with oxygen, nitrogen or phosphorus. No appreciable locking of dislocations is detected to occur in the high purity crystals and the crystals doped with carbon up to a concentration of 2 at.ppm.

In oxygen-doped crystals, the increase in the locking stress against the ageing duration is found to be faster for the crystals with higher concentrations of oxygen atoms. The mean diffusion distance of individual oxygen atoms during the ageing which results in a certain magnitude of locking stress is almost independent of the ageing temperature provided that the concentrations of oxygen atoms in the crystals are identical. This seems to show that the locking stress is determined by the number of the impurity atoms accumulated in a unit length of dislocations during ageing if the species and concentration of impurity atoms in the crystal are specified.

The number of impurity atoms accumulated in a unit length of dislocations during ageing can be evaluated by using the diffusion equation for impurities in the stress field of a dislocation and also by assuming that the core region of the dislocation acts as a sink for the impurity atoms arrived there. The calculation has been done in a numerical way with a computer. The concentration of the impurity atoms at the dislocation core has been obtained with this technique as a function of the ageing duration, the diffusion coefficient and the interaction energy of the impurity atom with the dislocation. Thus, the experimentally measured locking stress is related to the concentration of the impurity atoms along the dislocation line. Figure 2 shows such relations obtained for crystals doped with various concentrations of oxygen atoms. The locking stress in all the crystals is seen to increase linearly with the oxygen concentration along the dislocation core. Almost identical relations are obtained for the crystals doped with rather low concentrations of oxygen atoms. In the crystal with a high concentration of oxygen, however, a high value of the locking stress is achieved with the same oxygen concentration along the dislocation core compared with the crystal with a low oxygen concentration. This phenomenon is thought to be related to the inhomogeneous distribution of oxygen atoms inherent to a highly concentrated crystal.

Some interesting information on the dislocation-oxygen interaction in silicon is deduced if the data in Fig. 2 are analysed with the theory on thermally activated release of a dislocation from its impurity atmosphere. Let N^* be the concentration of the oxygen atoms accumulated on the dislocation core. Clusters of oxygen atoms, each consisting of n oxygen atoms, are assumed to be distributed at an equal interval of n/N^* along the dislocation line. The energy of interaction between such a cluster and the dislocation is taken to be E_n . If n is put to be one, the clusters turn to individual oxygen atoms. It is conceivable that the oxygen atoms accumulated on the

Fig. 2 The relation between locking stress τ_L at 647°C and the number N^* of oxygen atoms accumulated in a unit length of dislocations for silicon crystals doped with various concentrations of oxygen of which magnitudes are shown in the figure /6/.



dislocation line diffuse rapidly along the dislocation core to form small clusters.

The locking stress τ_l is given by

$$\tau_l = N^* [E_1 - k_B T \ln(LN^*v/n\Gamma)] / nb^2, \quad (2)$$

where L is the length of the dislocation, v the frequency of dislocation vibration, Γ the releasing rate of the dislocation from its atmosphere, and b the magnitude of the Burgers vector of the dislocation. Since the term $\ln(LN^*v/n\Gamma)$ depends weakly on N^* , τ_l may be regarded to be linear to N^* in accordance to the result in Fig. 2.

Equation (2) is fitted to the experimental τ_l - N^* relation for the crystals with low oxygen concentrations by substituting suitable values to L , v , Γ and b . Taking $n=1$, we obtain the magnitude of E_1 to be 3.0 eV which is about six times as large as that of the elastic interaction due to the size misfit between an oxygen atom and an interstitial site. It is not known whether there is any possibility for the occurrence of the change in the state of individual oxygen atoms when they are located at the dislocation core.

Small clusters of oxygen atoms or some small complexes including oxygen atoms are known to act as donors in silicon. They are often observed to develop during ageing of Czochralski silicon at relatively low temperatures. In the case where each cluster on the dislocation line is assumed to include four oxygen atoms ($n=4$), the fitting leads to E_1 of 3.5 eV in the magnitude. If such a cluster acts as a donor, it may interact with an acceptor site on the dislocation electrostatically. On the assumption that the donor and the acceptor are both singly charged, the energy of electrostatic interaction amounts to about 2 eV at one interatomic distance. The remaining part of the interaction energy, 1.5 eV in the magnitude, may be ascribed to the elastic interaction of the cluster with the dislocation, which seems to be of a reasonable magnitude. Further works seem to be necessary to clarify the details of the state of oxygen located at the dislocation core.

The relative strength of an impurity atom of various types in the interaction with a dislocation can be evaluated by comparing the mean diffusion distances of various impurity atoms during the ageings which result in the same magnitude of the locking stress. It is known that the interactions of individual atoms of phosphorus and nitrogen with a dislocation are much stronger than that of individual oxygen atoms. However, usually oxygen atoms manifest their interaction with dislocations most remarkably in silicon because of their high diffusion rate and their rather high solubility. The strong interaction of a phosphorus atom with a dislocation may be attributed to its high electrical activity as a donor and also to its high chemical reactivity with other kind of atoms. Individual phosphorus atoms interact with acceptor sites on dislocations electrostatically and phosphorus atoms trapped at the dislocation core will capture fast diffusing impurities in the crystal, leading to the formation of the complexes that have a high interaction energy. Little is known about the nature of nitrogen in silicon. Most nitrogen dissolved in a silicon crystal are electrically inactive in spite of the fact that they belong to the group V elements. They are believed to occupy the interstitial sites. The very small solubility of nitrogen in silicon seems to mean the energy of a nitrogen atom dissolved in silicon to be high. The very strong interaction of nitrogen atoms with dislocations in silicon may be understood well if some reaction which leads to a very stable state of nitrogen atoms proceeds at the dislocation core.

6. Kinetics of Aggregation of Impurities on Deformation-Induced Defects

During the deformation of a Czochralski silicon crystal at a temperature lower than about 1100°C, the concentration of dissolved oxygen in a supersaturated state decreases very rapidly /20/. Usually, the decreasing rate shows the maximum at a shear strain of 10~20 % and then diminishes with the increase in the strain due to the exhaustion of oxygen atoms in the matrix. The decrease in the concentration of dissolved oxygen atoms is so rapid that

almost all the supersaturated oxygen atoms are removed within 1 hr during the deformation at 900°C and a shear strain rate of 10^{-4} s^{-1} . In a dislocation-free crystal of usual Czochralski silicon, about 100 hr of annealing at 900°C is needed to accomplish the precipitation of the most of supersaturated oxygen atoms.

Deformation induces various types of defect into a crystal. It is interesting to know how these defects play their roles in the removal of supersaturated impurities in the crystal. This has been investigated by Yonenaga and Sumino /to be published/ with silicon crystals doped with various concentrations of oxygen.

On annealing a deformed crystal at the temperature same as one at which the deformation has been done, the decreasing in the concentration of supersaturated oxygen is found to proceed much more rapidly than in a dislocation-free crystal, provided that the deformation prior to the annealing is not so large as to allow the removal of all the supersaturated oxygen atoms. The decreasing rate is the highest at the beginning of the annealing and diminishes monotonically with the annealing duration. This seems to show that the defects introduced by deformation act as effective nucleation centers for oxygen aggregates. The duration of the annealing to complete the removal of supersaturated oxygen is shorter in the crystals with larger amounts of deformation prior to the annealing. The concentration of supersaturated oxygen in the crystal seems not to have any large influence on the kinetics of oxygen removal.

Dissolved oxygen atoms removed from the matrix of a crystal by deformation at around 900°C are restored upon annealing the deformed crystal at temperatures higher than 1100°C. The concentration of dissolved oxygen recovers to that prior to deformation by annealing at temperatures higher than 1150°C for short durations. The deformed crystals which are subsequently subjected to a stepwise annealing at 1100, 1150 and 1200°C, each for 15 min, are hereafter called the dissolution-treated crystals. By such dissolution-treatment, the concentration of dissolved oxygen prior to the deformation is completely recovered and the dislocation density as determined by etch pit counting is decreased by about 70%. Dislocation etch pits observed on the surface of the dissolution-treated crystal are distributed uniformly without forming polygon boundaries. The shape of dislocations survived after the dissolution-treatment is observed to be much more smooth than that prior to the dissolution-treatment by transmission electron microscopy. Furthermore, the so-called debris characteristic in the deformed state are removed completely by the dissolution-treatment. Thus, the role of

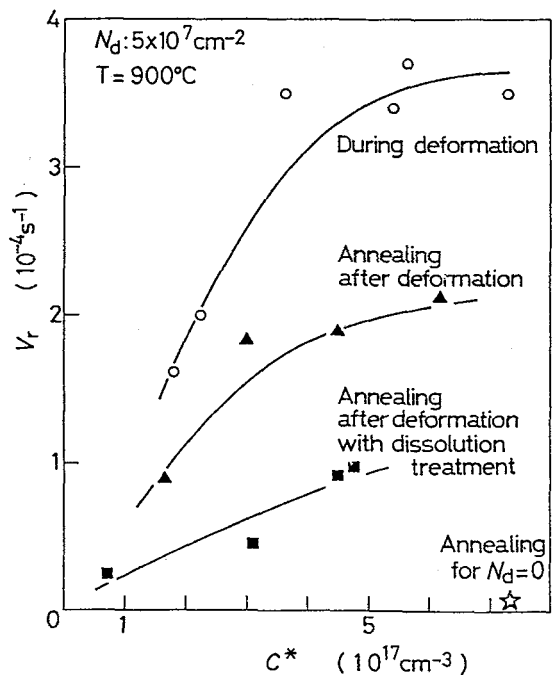


Fig. 3 The decreasing rate V_r of dissolved oxygen atoms at 900°C in the crystals with the same dislocation density $5 \times 10^7 \text{ cm}^{-2}$ at deformation, at annealing after deformation, and at annealing after the dissolution-treatment plotted against the concentration c^* of dissolved oxygen atoms (Yonenaga and Sumino /to be published/).

only dislocations in the aggregation behaviour of supersaturated oxygen can be investigated with the use of the dissolution-treated crystals.

It is found that the removal of the supersaturated oxygen proceeds much more slowly in the dissolution-treated crystal due to annealing in the temperature range 600 - 900°C compared with the deformed crystal which is not dissolution-treated and has the dislocation density same as that of the former crystal. Figure 3 compares the decreasing rates of dissolved oxygen in the crystals with the same densities of dislocations of $5 \times 10^7 \text{ cm}^{-2}$ for the deformation at 900°C, the 900°C annealing of deformed crystals, and the 900°C annealing of dissolution-treated crystals for various concentrations of dissolved oxygen. The ordinate shows the decreasing rate of dissolved oxygen atoms divided by the total concentration of the oxygen atoms that can be precipitated at 900°C and the abscissa shows the concentration of dissolved oxygen atoms in the crystal at the time of the measurement of the decreasing rate. The decreasing rates for deformed crystals and for dissolution-treated crystals are for the beginning of annealing at which the decreasing rates are the highest. Comparing the decreasing rate during deformation with that at annealing of deformed crystals, one may imagine that some processes facilitating the aggregation of oxygen atoms are operating during deformation. The diffusion of oxygen might be enhanced during deformation to a great extent. The difference of the decreasing behaviours in the deformed crystals and the dissolution-treated crystals clearly shows that debris and/or some irregularities on dislocations such as jogs play important roles in the aggregation of supersaturated oxygen. Possibly, they can act as effective nucleation centers for the aggregates. The decreasing rates measured for the dissolution-treated crystals agree approximately with those calculated with the diffusion equation for oxygen atoms in the stress field of a dislocation. These rates are much higher than those in dislocation-free crystals.

7. Infrared Absorption and Electrical Effect Associated with Dislocation-Impurity Interaction

Interstitally dissolved oxygen atoms in a silicon crystal give rise to an optical absorption peak centered at 1106 cm^{-1} which is associated with a local phonon mode of lattice vibration. The concentration of dissolved oxygen atoms in silicon is usually determined from the height of this absorption peak. During deformation of a Czochralski silicon crystal at 900°C, the height of this absorption peak decreases and, at the same time, absorption at smaller wave numbers becomes remarkable with the increase in the strain. A broad peak develops in the wave number range $980 - 1080 \text{ cm}^{-1}$ for larger strains /20/. On annealing a deformed Czochralski silicon crystal at 900°C, this broad peak becomes distinct more and more as the annealing duration increases if the supersaturated oxygen atoms still remain before annealing. Yonenaga and Sumino /to be published/ have found that the dissolution-treatment of a deformed Czochralski silicon crystal leads to the complete disappearance of the broad peak in the range $980 - 1080 \text{ cm}^{-1}$ and also to the recovery of the peak height at 1106 cm^{-1} to that before deformation. On annealing the dissolution-treated Czochralski crystal at 900°C, the height of the 1106 cm^{-1} peak decreases with the increase in the annealing duration without accompanying the development of any appreciable peaks in the wave number range $900 - 1300 \text{ cm}^{-1}$. Annealing of a dislocation-free crystal of Czochralski silicon at 900°C leads to the development of a distinct absorption peak centered at 1225 cm^{-1} at the expense of the height of the 1106 cm^{-1} peak. This peak at 1225 cm^{-1} is known to be due to precipitates of cristobalite SiO_2 which is the stable precipitate phase at 900°C. No distinct shoulder nor peak develops in the wave number range $980 - 1080 \text{ cm}^{-1}$.

From the above observations, it may be known that clusters or complexes of oxygen atoms with some special atomic arrangements of which frequencies of vibration are lower than that of interstitial oxygen atoms develop mainly on debris introduced by deformation. It has been confirmed that these atomic arrangements are very stable and do not transform to that of cristobalite even by a prolonged annealing at 900°C /20/. A considerable fraction of oxygen

atoms removed from the matrix crystal during deformation or by annealing after deformation, both at 900°C, seen in the previous section are thought to be in this state. It is known that clusters or complexes which develop upon annealing dislocation-free crystals of Czochralski silicon at 650 °C show the above type of absorption peak /20/. Thus, they may be similar in the atomic arrangement to those developed around the debris. Anyway, these clusters or complexes are not observable with usual transmission electron microscopy possibly because of the smallness in the size.

It is quite interesting to note that oxygen aggregates developed on dislocations at 900°C are different in the structure from those developed on debris. They show no characteristic absorption peak, at least, in the wave number range 900 - 1300 cm⁻¹. Thus, at present, no clue is available to suppose the characteristics in the atomic bonding within these aggregates. Again, they are not observable with transmission electron microscopy.

It is known that deep acceptors are introduced into silicon crystals by deformation; of which energy level is in the range 0.3 - 0.4 eV above the top of the valence band /21,22/. These acceptors are ascribed to debris or some irregularities on dislocation lines such as jogs and/or kinks since their density is found to be 1 - 2 orders of magnitude lower than the density of dangling bonds geometrically possible at the dislocation core. The relation between the carrier concentration and the temperature measured for a deformed n-type specimen of floating-zone silicon is fitted to a theoretical curve satisfactorily by simply adding deformation-induced deep acceptors to the

Table II The values of the parameters for the donors and acceptors in n-type specimens of floating-zone silicon (FZ-Si) and Czochralski silicon (CZ-Si) induced by deformation at 900°C /20/.

Crystal	Strain (%)	N _{DEP} (cm ⁻²)	N _{DD} (cm ⁻³)	E _{DD} (meV)	N _{DA} (cm ⁻³)
FZ-Si	0	0	0	-	0
	20	2.1 × 10 ⁸	0	-	6.0 × 10 ¹⁴
CZ-Si	0	0	0	-	0
	4.5	5.1 × 10 ⁷	7.7 × 10 ¹⁴	56	7.2 × 10 ¹⁴
	20	1.8 × 10 ⁸	3.7 × 10 ¹⁴	95	8.1 × 10 ¹⁴
			5.2 × 10 ¹⁴	200	
40	2.4 × 10 ⁸	4.0 × 10 ¹⁴	250	8.5 × 10 ¹⁴	
		4.0 × 10 ¹⁴	400		

N_{DEP} : Density of dislocation etch pits.

N_{DD} : Concentration of deformation-induced donors.

E_{DD} : Energy level of deformation-induced donors measured from the bottom of conduction band.

N_{DA} : Concentration of deformation-induced deep acceptors.

chemical donors and acceptors present in the control specimen. However, in the case of Czochralski silicon with supersaturated oxygen, it is impossible to describe the data on deformed n-type specimens on the assumption that only deep acceptors are introduced by deformation; the fitting needs the introduction of relatively shallow donors in addition to the deformation-induced deep acceptors. These donors are thought to be associated with oxygen atoms removed from the matrix during deformation. Table II shows the values of fitting parameters for deformation-induced acceptors and donors for n-type specimens of both floating-zone and Czochralski silicon. The fitting of the data on the Czochralski specimen after a small amount of deformation needs only one kind of deformation-induced donors, while those on the Czochralski specimens after large deformation need two kinds. The energy level of these donors becomes deeper as the strain increases. It is to be noted that the donors are introduced by deformation at a temperature of 900 °C where the generation of oxygen donors only by annealing is scarce in dislocation-free crystals of Czochralski silicon.

Yonenaga and Sumino /to be published/ have found that donors are also developed in the dissolution-treated specimens by the annealing at 900°C. The density of such donors coincides approximately with that developed during deformation if the dislocation density in the dissolution-treated specimen is approximately equal to that in the specimen during deformation. It may thus be concluded that oxygen atoms aggregated on dislocations at 900 °C are electrically active as donors.

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References

- /1/ SUMINO, K. and HARADA, H., *Phil. Mag.* A44 (1981) 1319.
- /2/ KULKARNI, S.B. and WILLIAMS, W.S., *J. Appl. Phys.* 47, (1976) 4318.
- /3/ PATEL, J.R., TESTARDI, L.R. and FREELAND, P.E., *Phys. Rev. B* 13 (1976) 3548.
- /4/ GEORGE, A. and CHAMPIER, G., *Phys. Status Solidi (a)* 53, (1979) 529.
- /5/ IMAI, M. and SUMINO, K., *Phil. Mag.* A47 (1983) in the press.
- /6/ SUMINO, K. and IMAI, M., *Phil. Mag.* A47 (1983) in the press.
- /7/ SUZUKI, T., ISAWA, N., OKUBO, Y. and HOSHI, K., *Semiconductor Silicon 1981*, HUFF, H.R. et al. eds. (1981) pp. 90.
- /8/ ABE, T., KIKUCHI, K., SHIRAI, S. and MURAOKA, S., *Semiconductor Silicon 1981*, HUFF, H.R., et al. eds. (1981) pp. 54.
- /9/ DORN, J.E. and RAJNAK, S., *Trans. Metall. Soc. AIME* 230 (1964) 1052.
- /10/ GUYOT, P. and DORN, J.E., *Canad. J. Phys.* 45 (1967) 983.
- /11/ NINOMIYA, T., THOMSON, R. and GARCIA-MOLINER, F., *J. Appl. Phys.* 35 (1964) 3607.

- /12/ CELLI, V., KABLER, M., NINOMIYA, T. and THOMSON, R., Phys. Rev. 131 (1963) 58.
- /13/ RYBIN, V.V. and ORLOV, A.N., Sov. Phys. - Solid State 11 (1970) 2635.
- /14/ MÖLLER, H.J., Acta Metall. 26 (1978) 963.
- /15/ HIRTH, J.P. and LOTHE, J., Theory of Dislocations (New York : McGraw-Hill) (1968) pp. 484.
- /16/ EROFEEV, V.N., NIKITENKO, V.I. and OSVENSKII, V.B., Phys. Status Solidi 35 (1969) 79.
- /17/ EROFEEV, V.N. and NIKITENKO, V.I., Sov. Phys. - Solid State 13 (1971) 116.
- /18/ COTTRELL, A.H. and JASWON, M.A., Proc. Roy. Soc. A 199 (1949) 104.
- /19/ YOSHINAGA, H. and MOROZUMI, S., Phil. Mag. 23 (1971) 1351.
- /20/ KOGUCHI, M., YONENAGA, I. and SUMINO, K., Jap. J. Appl. Phys. 21 (1982) L411.
- /21/ ONO, H. and SUMINO, K., J. Appl. Phys. 19 (1980) L529.
- /22/ ONO, H. and SUMINO, K., J. Appl. Phys. 54 (1983) in the press.