JOURNAL OF MATERIALS SCIENCE **33** (1998) 4627–4632

Growth parameters on the defects formation in a grown silicon crystal

YOUNG K. KIM*, TAE S. HA, J. K. YOON
**Materials Engineering, University of Inchon, Inchon, 402-749, South Korea,*
Metallurgical Engineering, Seoul National University, Seoul, 152-742, South Korea
E-mail: YoungKim@lion.inchon.ac.kr

The growth of macroscopically dislocation-free Czochralski silicon crystals, various defects such as D defects and microdefects causing oxidation-induced stacking faults can form. The effects of growth parameters such as pulling speed or cooling rate of the crystal on the formation of these defects is examined. From an experiment on the continuous cooling of a silicon crystal from 1400 °C, it is found that there is an intermediate cooling rate range in which the nucleation of OISFs is enhanced. The impact of the presence of OISFs on the electrical properties of the silicon crystal is examined with a minority lifetime mapper, and the resistivity is measured with a four-point probe. A higher pulling speed of the crystal from the melt results in a higher density of particles on the polished silicon wafers. This implies that many of the particles present on the polished silicon wafers are related to solidification of the silicon crystal. Slower pulling from the melt followed by controlled cooling thereafter is suggested as a means of lowering these grown-in defects in Czochralski silicon crystals.
© *1998 Kluwer Academic Publishers*

1. Introduction

Stacking faults are frequently generated in silicon wafers during thermal oxidation processes in a temperature range typically between 900 and 1200 °C. Such stacking faults are called oxidation-induced stacking faults (OISFs) [1, 2]. Oxygen precipitation is one of the several sources generating OISFs. In particular, OISFs caused by oxygen precipitates are called "bulk" OISFs [3]. In this context, OISFs represent these "bulk" OISFs. These oxygen precipitates causing OISFs later during thermal oxidation are formed in a concentric ring in Czochralski silicon crystals [1–3]. A high density of OISFs present in this ring band after thermal oxidation can be seen in Fig. 1.

Porrini *et al.* [4] have shown that oxygen precipitates causing OISFs are formed in the specific temperature range of 950–1050 °C. Several other investigators have performed isothermal heat treatments to find temperature and time range at which the formation of oxygen precipitates causing OISFs is enhanced [5, 6]. All these studies have shown the effect of the thermal history during crystal growth on the formation of these oxygen precipitates causing OISFs. Since oxygen precipitation is the main cause of nucleation of these OISFs, it would be interesting to examine the effect of doping elements on the nucleation of OISFs as it is already known that dopant elements might suppress or enhance oxygen precipitation [7, 8].

In a recent study, crystal grown-in defects referred to as flow pattern defects (FPDs) or crystal-originated particles (COPs) have been investigated as these defects are known to degrade gate oxide quality in Czochralski silicon [9]. Like the D defects in floating-zone silicon, these defects are believed to be formed by clustering of point defects. If this is true, it would be interesting to study the dependence of their formation on the crystal pulling condition.

The aim of this work is to study the effects of crystal growth parameters such as the cooling rate and the type of dopant on the formation of oxygen precipitates causing OISFs and the effect of crystal pulling rate on the particle formation (so-called (COPs). From the results of the studies, suggestions are made to lower the density of microdefects causing COP and OISFs by suitable crystal-growing operations. The effect of OISFs on the electrical properties of silicon crystals are also be examined.

2. Experimental procedure

To study the effect of doping elements on the formation of oxygen precipitates causing the nucleation of OISFs, two silicon crystals of medium oxygen content were chosen. Sampling was done at regular intervals from the seed end to the tail end of the crystals. All the sampled wafers were cleaned in the usual way. For nucleation OISFs, the wafers were wet oxidized at 1100 °C. The oxide was stripped with HF, and the defects were delineated with Wright each [10]. The OISFs were counted with an optical microscope. To study the effect of OISFs on the electrical properties, the minority-carrier lifetime was measured with a lifetime mapper, and the resistivity was measured with a four-point probe.

In order to study the effect of thermal history on these defects, formation causing OISFs in the silicon

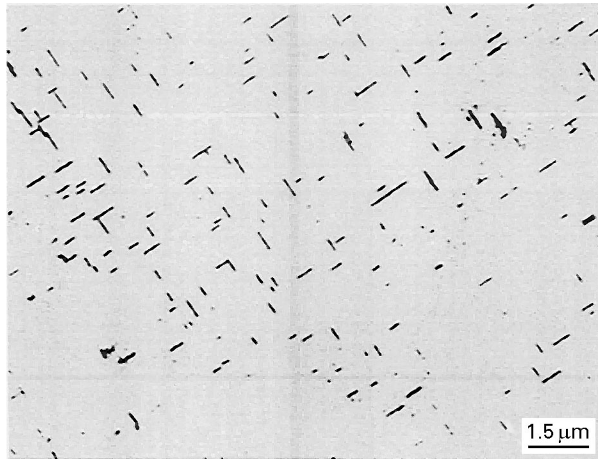


Figure 1 Optical micrograph of OISFs present in the ring band. Wright etched, ×150. (Wet oxidized at 1150 °C for 220 min).

crystals during their growth, the crystals were cooled from 1200 °C at various rates. Before cooling, annealing the crystal for 3 h at 1200 °C which is the highest temperature attainable in the normal silica tube is conducted to eliminate the previous thermal history of the crystal. It was found that the oxygen precipitates formed during thermal treatment can be redissolved and the oxygen atoms redistribute into interstitial sites after hours of annealing for 2 h at 1230 °C [11]. Also, it was proposed that conducting a homogenizing heat treatment at a high temperature (above 1200 °C) will minimize the variation in oxygen precipitation due to heterogeneous factors [12]. Furthermore, it was found that annealing at 1200 °C for 2 h can reduce the density of FPD, which are the well-known grown-in defects in Czochralski silicon crystals [13]. Not only the oxygen precipitates but also these grown-in defects are expected to provide heterogeneous nucleation centres for the formation of OISFs during the oxidation process. Although not perfect, annealing at 1200 °C for 3 h will reduce the heterogeneous nucleation centres significantly. Cooling rates between 2 and 20 k min^{-1} were tried because every part of the silicon crystal during pulling is believed to be cooled within this range of cooling rate. The silicon wafers were of 6 in diameter and about 600 μm thickness. This thickness is believed to be so thin that any point defect can leave the silicon through the surface. Therefore, for confirmation of this experiment, cooling of bulk specimen about 3 cm × 3 cm × 2 cm size after a homogenizing heat treatment at 1400 °C for 3 h under an argon atmosphere in the alumina tube is carried out. This annealing treatment is believed to be more effective in redissolution of the pre-existing microdefects which might induce heterogeneous nucleation during the cooling experiment.

To investigate the correlation between oxygen precipitation and the formation of OISFs. Fourier transform intervied studies were made on the silicon wafers which were subjected to oxidation and etching of OISFs. The oxygen contents and resistivities of the samples are shown in Table I.

To study the effect of pulling rate on the formation of micro defects causing COPs, crystals were pulled at

TABLE I Oxygen contents and resistivities of wafer specimen

Specimen	Dopant	Resistivity (Ω cm)	O_i (at ppm)
A	Boron	15.4–16.60	15.6–15.9
B	Boron	5.1– 5.14	16.8–16.9
C	Boron	19.0	12.0
D	Boron	15.2–15.8	11.6–12.2
E	Phosphorus	15.5–15.8	15.6
F	Phosphorus	18.2–15.8	18.7
G	Phosphorus	3.0– 3.1	15.4–15.5

two different pull rates, namely 0.7 and 0.5 mm min^{-1}. Samples of wafers were taken from crystals grown at these pull rates in the present study. Counting of particles on the silicon wafers was performed with particle counters used regularly for the inspection of polished wafers.

3. Results and discussion

Typical variation in the density of axial OISF nuclei for boron- and phosphorus-doped silicon crystals are shown in Fig. 2 and Fig. 3, respectively. Both crystals had oxygen concentrations in the medium range between 14 and 16 at ppm. The growth parameters for both crystals were identical. It can be seen from the figures that the density of OISF nuclei is higher near the tail for the phosphorus-doped crystal than for the

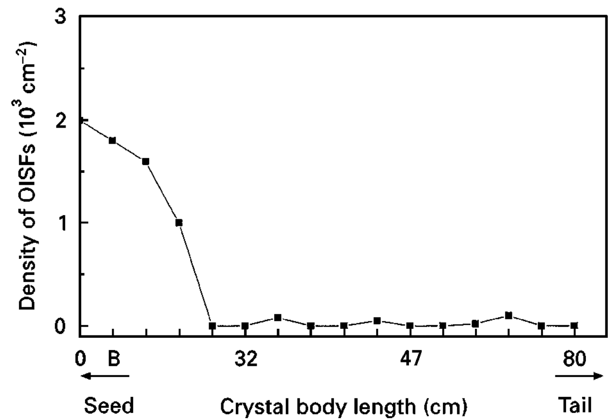


Figure 2 Axial variation in the density of OISFs in a boron-doped silicon crystal.

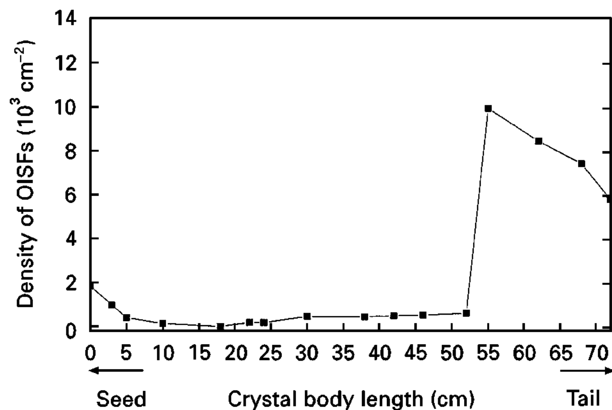
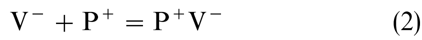


Figure 3 Axial variation in the density of OISFs in a phosphorus-doped silicon crystal.

boron-doped crystal. This indicates the possibility of Coulomb attraction between the charged point defects and the dopant atoms as described by de Kock *et al.* [7]. As growth proceeds, accumulation of dopants takes place near the tail of the crystal because segregation coefficients for both atoms are less than unity. As the concentration of boron increases, the concentration of silicon interstitials will be lowered by the reaction

$$I_{si}^{+} + B^{-} = I_{si}^{+}B^{-} \quad (1)$$



$$V^{-} + P^{+} = P^{+}V^{-} \quad (2)$$

$$I_{si}^{+} + V^{-} = Si_{sub} \quad (3)$$

Thus, the possibility of silicon interstitials clustered as planar defects which might act as nucleation sites for oxygen precipitates causing OISFs later will be reduced as growth proceeds in the boron-doped crystal. The situation is the opposite, if the dopant atom is phosphorus. As the crystal growth proceeds, the concentration of vacancies is reduced through the reaction $V^{-} + P^{+} = P^{+}V^{-}$. As the vacancy concentration is reduced, the number of interstitials disappearing according to te reaction $I_{si}^{+} + V^{-} = Si_{sub}$ will be reduced, enhancing the chance that they cluster and act as nucleation sites for the oxygen precipitates causing OISFs later. Thus the chance of nucleating OISFs is higher than in the boron-doped crystal as growth proceeds, if other growth conditions are same.

For both types of crystals, a higher density of OISF nuclei is frequently observed near the seed end than in the middle section of the crystals. There are two possible reasons for this phenomenon. Normally the seed end of the crystal has a higher concentration of oxygen. The seed end is also at higher temperatures for longer times than the tail is. A higher concentration of oxygen is itself sufficient to nucleate oxygen precipitates homogeneously if the oxygen concentration is higher than 16 at ppm. If the oxygen precipitation is high, it will be easier for OISFs to grow because, as the oxide grows during the oxidation heat treatment, silicon interstitials will be generated owing to volume expansion. Also, the longer time duration at high temperatures will enlarge the size of the oxygen precipitates which can grow into OISFs later.

The dependence of oxygen precipitation causing nucleation of OISFs on the cooling rate of silicon wafers is shown in Fig. 4 for boron-doped crystals and in Fig. 5 for phosphorus-doped crystals. For both types, the density of OISFs is the highest at a cooling rate of 20 K min^{-1} if the oxygen content is higher than 16 at ppm. However for both types of crystal, the maximum density of OISFs occurs when the cooling rate is 10 k min^{-1} if the oxygen content is in the medium or low range. Before starting the cooling studies, the specimen were homogenized by keeping them at 1200 °C for 3 h. As mentioned earlier, this homogenization treatment is believed is believed to redissolve the pre-existing oxygen precipitates which can grow to generate the silicon interstitials for the formation of OISFs later. This will keep the possibility of heterogeneous nucleation of defects as low as possible. Like any other nucleation-and-growth process,

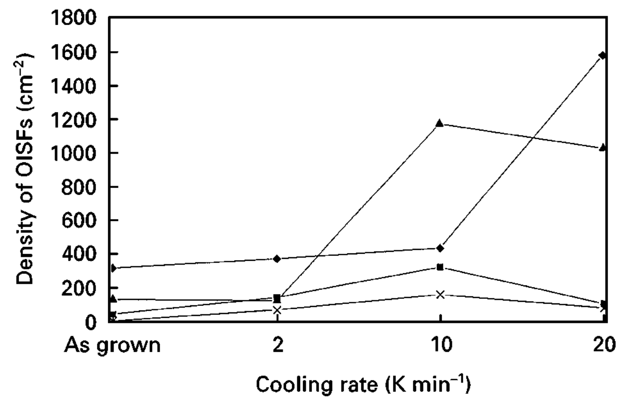


Figure 4 Density of OISFs in boron-doped silicon wafers cooled at various rate from 1200 °C. (▲) specimen A, (◆) specimen B, (×) specimen C, (■) specimen D.

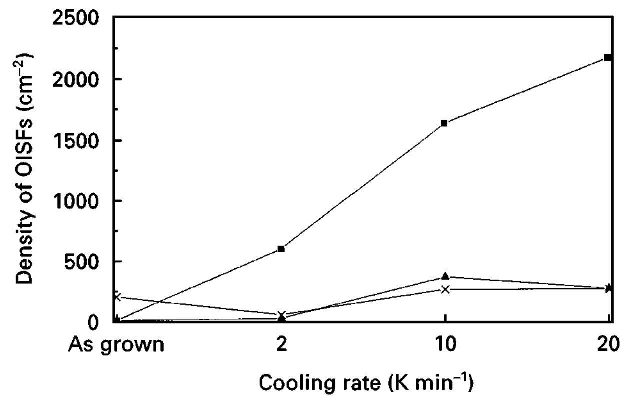


Figure 5 Density of OISFs in the phosphorus doped silicon wafers cooled with various rate from 1200 °C. (×) specimen E, (■) specimen F, (▲) specimen G.

the formation of oxygen precipitates causing OISFs is highest in intermediate cooling ranges. As the cooling rate is increased, the sizes of oxygen precipitates become smaller, so that the number of nuclei larger than some critical size for the growth of OISFs will decrease.

The dependence of oxygen precipitation causing nucleation of OISFs on phosphorus content in silicon crystals can be seen by comparing specimens E and G in Fig. 5. For both specimens, the oxygen contents are similar at 15.6 at ppm. Specimen G has a higher concentration of phosphorus and a higher density of OISF nuclei than specimen E does. This result appears to have a good correlation with the axial variation in nucleation of OISFs shown in Fig. 3. However, for boron-doped crystals, such correlation is not observed by comparing the results in Fig. 4 with Fig. 2. Specimen D has a higher concentration of boron than specimen C has but both have similar oxygen concentrations. However, as seen in Fig. 2, the density of OISF nuclei decreases as the crystal grows to the tail, in which the boron concentration is higher than in the seed side. This may be due to the different nucleation mechanisms in the two cases namely homogeneous in Fig. 4 and heterogeneous in Fig. 2. In heterogeneous nucleation which is observed in real crystal growth processes, dopant atoms will affect the

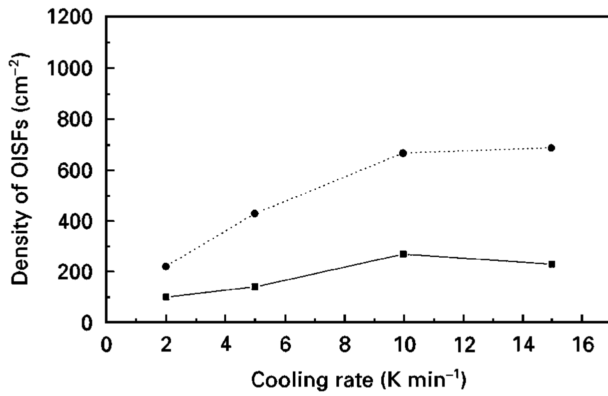


Figure 6 Density of OISFs in boron-doped silicon crystals cooled at various rate from 1400 °C (···●···) $[O_i] = 18.019$, (—■—) $[O_i] = 15.058$.

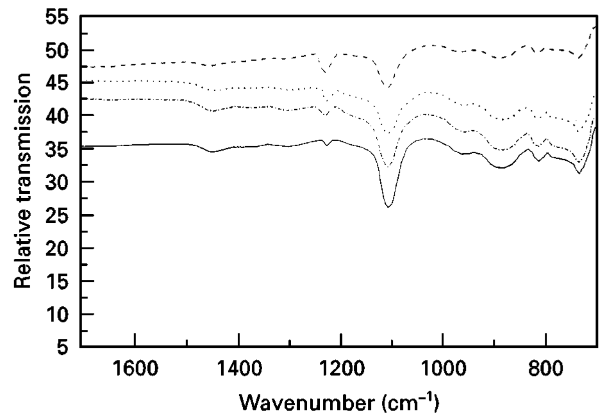


Figure 8 Fourier transform intrared obsorption spectra for boron doped Czochralski silicon crystals at different cooling rates from 1400 °C. (———) 2 K/min, (-·-·-·-) 5 K/min, (------) 10 K/min and (........) 15 K/min.

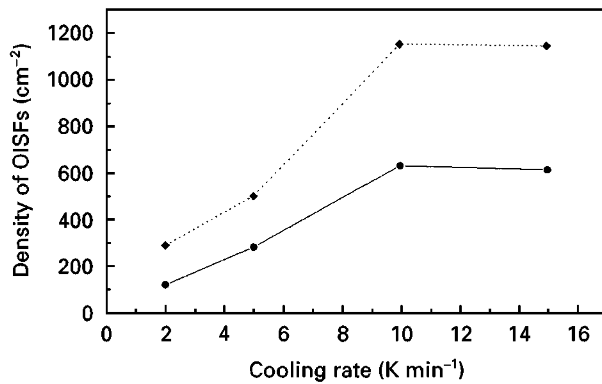


Figure 7 Density of OISFs in the phosphorus doped silicon crystals cooled with various rate from 1400 °C (—●—) $[O_i] = 16.025$, (···◆···) $[O_i] = 19.905$.

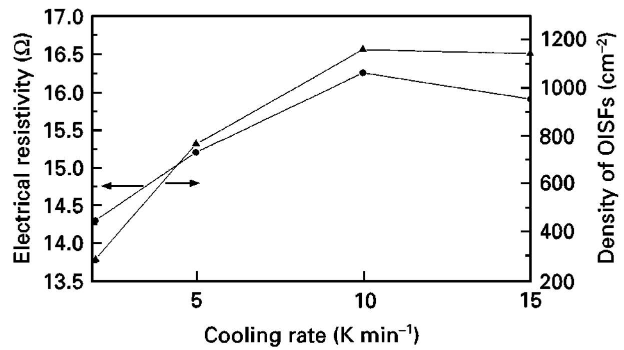


Figure 9 Variation in the resistivity of a silicon crystal cooled at various rate from 1400 °C. (—●—) Resistivity. The density of OISFs (—▲—) is also shown.

formation of point defects through reactions (1)–(3). The solidification process induces steeper thermal gradients in the crystal just solidified. Thus, the excess point defects will cluster and act as some heterogeneous nuclei for defects such as oxygen pricipitates. However, in the present cooling experiments, as in Fig. 4 and Fig. 5, the nucleation of oxygen precipitates causing OISFs is believed to be homogeneous because the thermal gradient induced by cooling from 1200 °C is not high enough for any point defects to cluster. In the homogeneous nucleation of oxygen precipitates causing OISFs, the role of dopant atoms is not so effective as in heterogeneous nucleations.

The results of cooling experiments employing 1400 °C annealing with bulk crystals are shown in Fig. 6 and Fig. 7 for boron and phosphorus-doped crystals, respectively. As in Fig. 4 and Fig. 5, here also, as the cooling rate is increased from 2 to 20 K min^{-1}, the formation of oxygen precipitates causing OISFs is enhanced. For silicon crystals with a medium oxygen concentration of 15–16 at ppm, there appears to be an intermediate cooling rate around 10 K min^{-1} at which the oxygen precipitation is highest. These precipitates act as OISF nucleation centres during the oxidation process. Since the results of these experiments are quite similar to the results for thin wafers and 1200 °C annealing, it can be concluded that the formation of point-defect clusters which can act as heterogeneous nucleation centres for the oxygen precipitates causing OISFs later must take place above 1400 °C, i.e., very close to the liquid–solid interface.

In Fig. 8, infrared absorption spectra for four silicon specimens are shown. The prominent peak at 1106 cm^{-1} is due to the oxygen interstitials and the peak at 1225 cm^{-1} is due to the silicon oxides. It can be seen that the peak height at 1106 cm^{-1} is inversely proportion to the density of OISFs in the specimens. The peak at 1225 cm^{-1} is maximum at a cooling rate of 10 K min^{-1}. These results show clearly the relationship between the oxygen content and the stacking faults in silicon crystals.

It would be easy to anticipate the effect of OISFs on the electrical properties of silicon crystals when they are located at p–n junctions or in the active region [12]. However, it would be interesting to study the effect of OISFs on electrical properties such as the minority-carrier lifetime and resistivity. As can be seen in Fig. 9, the resistivity of the silicon crystals is proportional to the density of OISFs in the silicon crystals. This indicates the possibility that OISFs obstruct the transport of free electrons by forming positive charge space as described by Matare [14]. The effect of the density of OISFs on the minority-carrier lifetime is shown in Fig. 10. This confirms that the OISFs

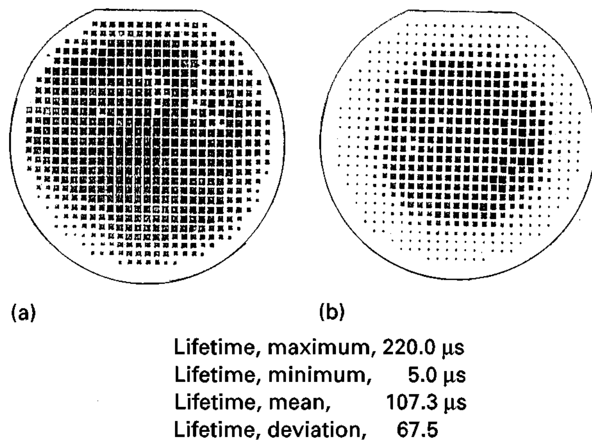


Figure 10 Lifetime mapping on the surface of the silicon wafers: (a) free OISFs; (b) ring of OISFs near the centre of the wafer.

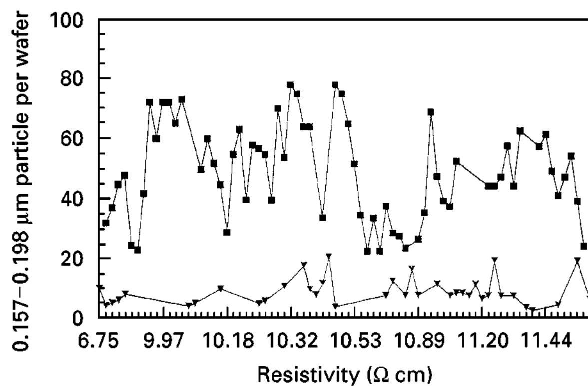


Figure 11 Number of particles on wafers of the crystal pulled at 0.5 mm/min^{-1} (▼) and 0.7 mm/min^{-1} (■).

lifetime of minority carriers as expected by forming traps or recombination centers.

In Fig. 11, the effect of the pulling rate of crystals on the particle formation is shown. The particles are counted with a particle counter on the polished silicon wafers. The higher pull rates result in a higher density of particles. This implies that most of the particles counted are not simple particles but defects related to the pulling conditions. This is in agreement with the expectation that higher pulling rates will give rise to a higher concentration of point defects and give them less chance to go back to the liquid–acid interface by uphill diffusion. Since the energy of formation and the activation energy for diffusion of vacancies are known to be smaller than those for interstitials in silicon crystals, most of these COPs, are believed to be formed as a result of the three-dimensional collapse of vacancies in the silicon crystals.

The experimental results and the above observations lead us to expect the formation of grown-in defects as follows. The concentration of point defects will exceed the equilibrium concentration as the crystals are pulled from the melt. Since the energy of formation of vacancies is smaller than that of self-interstitials, the concentration of vacancies would be much higher than self interstitials in silicon crystals. The excess vacancies will be consumed in three ways. Most of them will go back to the liquid–solid interface owing to the uphill diffusion. The remaining vacancies will collapse to form three-dimensional clusters which will act as centres for oxygen precipitates later. The concentration of interstitials will be higher than vacancies in the region near the surface of the crystal, because of the out-diffusion of vacancies. In this region, the excess interstitials will be clustered as planar-type stacking faults. These primary stacking faults will act as nucleation centres for oxygen precipitation during post-cooling of crystals. These oxygen precipitates will grow to generate silicon interstitials when the silicon crystals are subjected to an oxidative heat treatment. The excess self-interstitials are consumed to enlarge the primary stacking faults by climbing. Thus, it is expected that not only the cooling condition after pulling but also the pulling condition of the crystals from the melt will affect the nucleation of OISFs, considerably.

From these results, two ways of nuclear OISFs in silicon crystals can be proposed. One of them is to reduce the heterogeneous nucleation sites formed near the liquid–solid interface. This can be achieved in two ways. Chemically, the formation of point-defect clusters can be controlled by dopant atoms through reactions (1)–(3). Physically, controlling the pulling rate of the crystal from the melt might be another method of reducing the OISF nuclei in Czochralski crystal growth. Secondly, reducing the size of the oxygen precipitates smaller than some critical size will reduce the OISF density. Two methods can be suggested for this. Chemically, keeping the oxygen content as low as possible is one way to reduce the size of the oxygen precipitates. Physically, applying the optimum cooling rates which can induce the size of oxygen precipitates as small as possible is another way of reducing the nucleation of OISFs.

4. Conclusions

The present work confirms that an intermediate cooling rate between 5 and 20 K min^{-1} is very effective in nucleating oxygen precipitates causing OISFs for medium-oxygen content silicon crystals. Moreover, it is expected that the primary stacking faults which are believed to act as heterogeneous nucleation centres for oxygen precipitates causing OISF nucleation later are formed at temperatures higher than 1400 °C, i.e., just at the liquid–solid interface. The presence of OISFs affects the electrical properties of the silicon crystals by raising the resistivity and lowering the minority-carrier lifetime. Lowering the pull rates of crystals from the melt will result in a lower density of grown-in defects such as COPs or possibly primary stacking faults. Avoiding intermediate cooling rates after pulling the crystals from the melt would be right way to reduce the density of grown-in defects.

Acknowledgement

The authors are greatly indebted to Mr. Boyoung Lee of Siltron for his critical discussions on this paper.

References

1. M. HASEBE, Y. TAKEOKA, S. SHINOYAMA and S. NAITO, in "Defects control in semiconductors", edited by K. Sumino (Elsevier North-Holland, Amsterdam, 1990) p. 157.
2. S. MAHAJAN, G. A. ROZGONYI and D. BASEN, *Appl. Phys. Lett* **30** (1997) 73.
3. Y. K. KIM, H. S. CHO, H. W. LEE, D. BUCK, J. RIGOTTE, J. YEH, S. HAHN and W. A. TILLER, in "Electrochemical Society Spring Meeting, Washington, DC, May 5–10, Extended Abstract, Vol. **91–1**, 186, 1991.
4. M. PORRINI, G. BORIONETTI and G. FERRERO, in "Crystalline defects and contamination", 1993 edited by B. O. Kolbesen, P. Stallhofer, C. Claeys and F. Tardif, Proceedings of the Electrochemical Society, Vol. 93–15.
5. S. N. REA and H. M. GRIMES, in Electrochemical Society Spring Meeting, Philadelphia, PA, May 1987 (Electrochemical Society, 1987); Abstract 74, p. 98.
6. YAMASHITA and SHIMANUKI, in Electrochemical Society Spring Meeting, Philadelphia, PA, May 1989 (Electrochemical Society, 1989); Abstract 224.
7. A. J. R. de KOCK and W. M. van de WIJGERT, *J. Cryst. Growth* **49** (1980) 718.
8. H. TSUYA, Y. KONDO and M. KANAMORI, *Jpn. J. Appl. Phys.* **22** (1983) L16.
9. J. G. PARK, S. P. CHOI, G. S. LEE, Y.J. JEONG, Y. S. KWAK, C. K. SHIN, S. HAHN, W. SMITH and P. MASCHER, in "Physics and chemistry of SiO_2 and Si–SiO_2 interface 2", edited by C. R. Helms and B. E. Deal (Plenum, New York 1993) p. 289.
10. M. W. JENKINS, *J. Electrochem. Soc.*, **124** (1977) 757.
11. F. SHIMURA, *Appl. Phys. Lett.* **39** (1981) 987.
12. S. P. MURARKA, T. E. SEIDEL, J. V. DALTON, J. M. DISHMAN and M. H. READ, *J. Electrochem. Soc.* **127** (1980) 717.
13. R. RANTAMAKI, J. MOLARIUS, M. TILLI and T. TUOMI, *Physica Scripta* T **69** (1997) 264.
14. H. F. MATARE, in "Defect electronics in semiconductors" (Wiley–Interscience, New York, 1971) Chapters 8 and 10.

Received 19 May 1997
and accepted 2 April 1998