

Microdefects in Si crystal

Koji Sumino

Institute for Materials Research, Tohoku University

2-1-1 Katahira, Aoba-ku, Sendai 980, Japan

An overview is given of recent topics on microdefects which are found in as-grown crystals of FZ- and CZ-Si. The origin and entity of such microdefects have not yet been well clarified. Structural defects in Si by themselves do not necessarily give rise to harmful effects on the electrical properties of Si. However, they become harmful when they react with impurities. The central problem in defect control in Si is, thus, understanding of reactions among structural defects and impurities.

1. INTRODUCTION

The performance of any semiconductor device suffers degradation when some kind of structural defects or impurities are present in the crystal. A term "microdefects" is commonly used in semiconductor device technology. It is not a scientific term but a word for convenience tacitly implying any structural defects or impurities in semiconductor crystals which give rise to negative effects on device function. Lattice defects defined in solid state physics are not always harmful to device function. Whether any given kind of defects are harmful or not depends on the type of device and the level of technology.

With an increase in the integration of circuits and with a corresponding decrease in the size of circuit pattern the demand for reducing microdefects in semiconductor crystals becomes increasingly severe.

Lattice defects are induced in a crystal for a variety of reasons. Such defects may react with each other and lead to the formation of complexes or clusters. Some characteristic feature inherent to a defect may be lost as a result of such reaction. Originally harmless or useful defects may become harmful and vice versa as a result of reaction with other defects or dopants. Most of the so-called microdefects in Si are reaction products of elementary lattice defects. Understanding of defect reaction gives the basis of the technology to control microdefects in semiconductors.

This paper gives an overview on current

problems concerning microdefects in Si mainly focusing on grown-in defects.

2. ORIGIN OF DEFECTS

Defects in a Si crystal are classified into four categories given below according to the cause by which they are introduced :

1. Defects induced in connection with solidification process of the melt.
2. Defects induced by energetic stimulation
3. Defects in thermal equilibrium or those frozen in from high temperature.
4. Defects introduced in connection with contamination.

During melt growth of a crystal the temperature at the solid-melt interface fluctuates due to the convection in the melt. This leads to the non-uniformity in the speed of solidification and results in the development of striation pattern, namely the spatial fluctuation of the dopant or impurity concentration in the crystal. Any impurity-related phenomenon which takes place during thermal processing proceeds in different ways among regions with different impurity concentrations and leads to the inhomogeneity of the crystal. Solidification and remelting may be repeated alternatively at the growth front of a crystal during the melt growth due to temperature fluctuation. Since the density of melt is considerably higher than that of a crystal in Si, local regions with excess atoms may remain within a grown crystal if remelting takes place heterogeneously [1]. Such excess atoms may condense into some kinds of ex-

tended defects which are regarded microdefects.

Thermal stress is induced within a crystal if the temperature distribution inside is not uniform. The magnitude of such thermal stress is usually not high enough to nucleate dislocations by itself but high enough to move slip dislocations and cause dislocation multiplication. Slip dislocations are nucleated at some local irregularities on the surface.

Recently, an important fact was found concerning irregularities on Si surface which act as a nucleation centers for dislocations [2,3]. Cross-sectional TEM observations have revealed that a microscopic region of amorphous Si is induced by scratching, abrasion or indentation under a very small load on a Si surface as shown in Fig. 1 even if no detectable groove or dent is formed on the surface. Such an amorphized region recrystallizes into a microregion containing dislocations when the crystal is kept at high temperature. Some of such dislocations come out of the such microregion and penetrate into the matrix crystal and undergo self-multiplication when the crystal is under stress [4]. Surface irregularities may be introduced in a Si crystal by energetic stimulation on various occasions during crystal growth as well as during preparation and processing of a wafer.

Intrinsic point defects such as vacancies and interstitial atoms exist in a crystal in thermal equilibrium. The formation enthalpies of these defects are now believed to be so high in Si that their equilibrium concentrations at room temperature are too low to give rise to any appreciable effects.

Important are point defects that are frozen in a crystal after the crystal is cooled from a high temperature. Usually, they develop so-called secondary defects such as small voids, tiny stacking faults, small loops of dislocations and so on. Excess point defects may be induced in a crystal also due to device fabrication processing. Oxidation or nitridation of silicon surface produces a high concentration of excess interstitial atoms or vacancies. Ion implantation also produces excess point defects.

Impurities are incorporated into a crystal due to contamination from a crucible during melt growth and also due to contamination from ambient gas during device production processing. Impurities incorporated at a high temperature become supersaturated when the crystal is brought at a low temperature. O impurity in CZ-Si precipitates in the matrix in the form of SiO_2 and most metallic impurities in the form of silicide. The volume is usually expanded at the place where precipitation takes place. Interstitial Si atoms are generated or dislocation loops are punched out around a precipitate depending on the temperature. The excess interstitial atoms are converted into stacking faults of extrinsic type or absorbed by dislocations and develop dislocation helices.

Defects contained in a crystal in the as-grown state are called grown-in defects. They may be introduced at the time of solidification of the crystal or introduced during post-solidification cooling of the crystal. It is reasonable to think that any grown-in defect has experienced evolution from its original form, depending on the thermal history of the crystal. The situation is complex in CZ-Si in comparison with FZ-Si since the former is supersaturated with O impurity throughout almost the whole temperature range until the crystal is brought to room temperature after solidification. We treat grown-in defects in CZ-Si and FZ-Si separately in the following.

3. GROWN-IN DEFECTS IN FZ-Si

So-called swirl defects were found in FZ-Si in 1965 when dislocations were successfully got rid of from crystals [5,6]. The defects are distributed along the striation of the crystal.

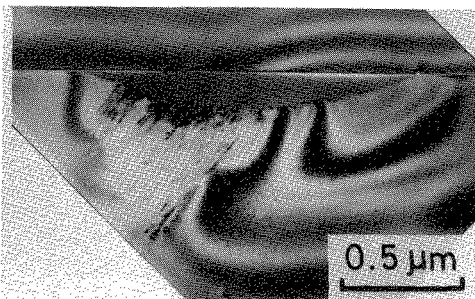


Fig. 1 Cross-sectional TEM micrograph of a amorphized region shown as a dark area underneath a scratch made on Si surface [3].

From TEM observations they are now believed to be interstitial-type dislocation loops [7,8] or small clusters of interstitial silicon atoms agglomerated on the {111} planes of the silicon lattice [9]. They are termed A-defects in the following.

Another type of grown-in defects, termed D-defects, were found in 1981 [10]. They are now commonly assumed to be of vacancy-type, though no direct identification has yet been accomplished. This type of grown-in defects were not observable by means of etch pit technique nor TEM but X-ray topography after Cu-decoration. They are distributed rather uniformly within the crystal without showing swirl pattern. In the case of a crystal with a rather small diameter, A-defects are developed under a relatively low growth rate of a crystal while D-defects under a high growth rate. An increase in the rate of crystal growth is equivalent to a decrease in the temperature gradient near the solid-melt interface.

On the basis of idea that grown-in defects are formed by agglomeration of excess point defects, two types of model have been put forward as to the origin of the excess interstitials or vacancies. One assumes that such point defects are incorporated into a crystal by non-equilibrium processes. Some parts of a crystal may remelt locally soon after solidification, forming droplets of the melt, due to temperature fluctuation and absorb Si atoms from surroundings. If the droplets crystallize quickly, excess atoms there go to the interstitial sites [1]. This type of model was applied to interpret the development of A-defects and was successful in explaining why A-defects are formed along the striation, developing the swirl pattern. The other type of model assumes that a high concentration of point defects which were in thermal equilibrium at a high temperature are frozen in the crystal during post-solidification cooling and become excess point defects. The latter model was elaborated to account for why A-defects are developed under a low growth rate while D-defects under a high growth rate. The equilibrium concentrations and the diffusion rates of interstitials and vacancies were chosen as control parameters [11,12].

It is questioned why A-defects develop the

swirl pattern and D-defects not. The swirl pattern of A-defects strongly suggests that A-defects themselves or their nucleation centers are formed in the close vicinity of the solid-melt interface just after the solidification of the crystal and quickly stabilized. In the first model interstitials emitted from droplets of the melt in the vicinity of the solid-melt interface may condense into small dislocation loops or tiny stacking faults of extrinsic type and form A-defects. On the other hand, in terms of the second model, the question may be answered with the idea that dopant or impurity atoms segregated in the striation pattern act as nucleation centers for agglomerations of frozen-in interstitials. A problem remains as to the latter idea to ascertain which kind of dopant or impurity interacts with interstitial Si atoms. A question remains also as to D-defects on why they do not grow into a size observable by direct observations by TEM if they are agglomeration of vacancies

An interesting fact was recently reported on the development of A- and D-defects in a crystal with a diameter as large as about 100 mm by Abe *et al.* [13]. The topograph in Fig. 2 shows the distribution of grown-in defects along the cross section of a crystal after Cu decoration. In the region near the side surface of the crystal A-defects dominate while in the central part D-defects dominate. These regions are termed A-region and D-region, respectively. The intermediate region is termed N-region.

The spatial segregation of A- and D-defects seen above may be caused if the concentration of frozen-in interstitial is higher than that of vacancies in the region near the surface while the situation is reversed in the interior region. The development of any types of microdefects depends on the distance to the sink for constituent defects. The outer surface of a crystal is a strong sink for any type of elementary defects not in thermal equilibrium. A depletion region for such defects develops near the surface. Actually, A-defects are observed to develop even in the region very near the surface, while D-defects are absent. This suggests that A-defects or, at least, nuclei of A-defects are much stronger sinks for interstitial atoms than the surface and stable even at temperature close to



Fig. 2 X-ray topograph showing the distribution of grown-in defects along the cross-section in a FZ-Si crystal with a diameter of 100 mm decorated with Cu. The edge of left hand side is the outer surface and that of right hand side the center of the crystal [13].

the melting point. The nuclei seem to be related to slow diffusers in Si. On the other hand, the surface seems to work as very effective sink for constituents of a D-defect which are now commonly believed to be vacancies.

On the basis of the above arguments we reach the following picture on A- and D-defects. They are developed independently during crystal growth and coexist in a FZ-Si crystal not interfering each other. A-defects are not visible by X-ray topography after Cu decoration when D-defects exist together since D-defects absorb Cu atoms more efficiently than A-defects. D-defects are observed to disappear at temperatures higher than 1140 °C in non-oxidizing ambient. A-defects are seen to develop in the region where D-defects disappear [10]. This gives an evidence for that A-defects and D-defects exist together in the same region. It also suggests that thermal stability of A-defects is higher than that of D-defects. Now, a central question is why constituents of A- and D-defects do not undergo pair-annihilation before developing their own agglomerates. The answer seems to be related to the structure of the defects.

4. GROWN-IN DEFECTS IN CZ-Si

Most Si crystals used in electronic devices are CZ-Si which is characterized by O impurity of a concentration of about 20 ppm which comes from quartz crucibles at the time of crystal growth. Oxygen atoms dissolved in a Si crystal immobilize dislocations very effectively and make CZ-Si wafers much more resistive against the occurrence of warpage caused by thermal stress than FZ-Si wafers. Thus, O impurity is indispensable in Si for fabrication of microelectronic devices. O impurity in CZ-Si becomes supersaturated at temperatures lower

than about 1300 °C. Hence, most defects observed in CZ-Si have some correlation with precipitation or clustering of O atoms. Precipitation of O impurity induces various kinds of defects such as punched-out dislocations and stacking faults of extrinsic type.

When the surface of a wafer of CZ-Si with a large diameter grown at a speed within a certain range is oxidized around 1100 °C, a well defined ring-shaped region with a high density of oxygen-induced stacking faults (OSF) is developed. Such a ring region is concentric with respect to the crystal axis as shown in Fig. 3 [14]. The density of OSF inside the ring-shaped region is higher than that outside by orders of magnitude and the periphery of the ring is extremely sharp.

The ring-shaped region is not developed in a crystal grown at a high speed and starts to appear at the side surface of the crystal when the growth rate is reduced to a certain value. Upon reducing the growth rate, the location of the ring-shaped region moves inward the crystal and finally disappears at a growth rate of 0.3 – 0.6 mm/min, depending on the structure of hot-zone of the CZ pulling furnace. Though precipitation of O impurity is much enhanced within the ring-shaped region in comparison with the outside region due to annealing at about 1100 °C, the situation is reversed when the wafer is subjected to a pre-heat-treatment at a lower temperature around 800 °C and, then, annealed at 1100 °C [15]. Some defects acting as precipitation centers at 1100 °C are supposed to be developed within the ring-shaped region during crystal growth. Such centers are less active as precipitation centers in comparison with the centers formed at 800 °C in the outside region. The reason why such centers are formed in the particular region of the ring is not understood at present.

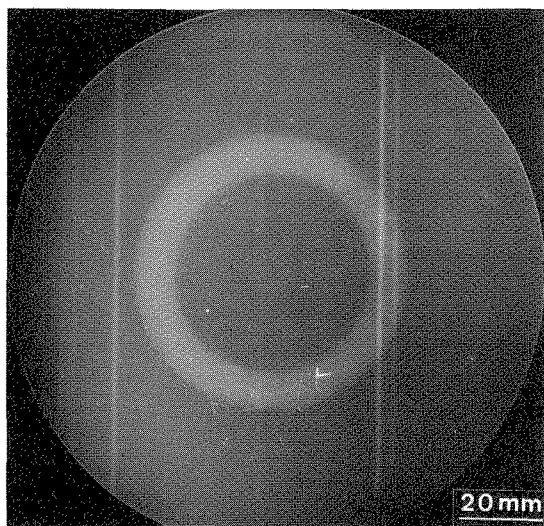


Fig. 3 Ring-shaped region in a CZ-wafer observed with X-ray topography [14].

When the integration of LSI was rather low, OSF were the main structural microdefects to be controlled. Metallic impurities precipitate along Frank-type partial dislocations bounding OSF and cause leakage current. The main task at that technological level was to suppress the generation of OSF in device-active regions, to minimize contamination during processing and to getter impurities from device-active regions.

Recently, defects in as-grown CZ crystals with large diameters call attention in connection with the integrity of gate oxide on a wafer as thin as the order of 10 nm in the thickness. They are revealed by (1) etch pits accompanying some surface pattern developed due to the Secco etching (FPDs) [16], (2) small pits formed by SC-1 cleaning process (COPs) [17], or (3) scattering centers of infrared light (IRSCs) [18]. It should be noted that defects revealed by FPDs or COPs are both probably not always of the same atomic structure, since FPDs or COPs show only that etching or dissolution of Si surface is enhanced there. FPDs and COPs are observed not only in CZ-Si but also in FZ-Si [19,20] and are absent in epitaxially grown Si. They are not developed in CZ- or FZ-Si which was held at a temperature around 1200°C for some duration during crystal growth [20,21]. From these observations we have a picture that FPDs and COPs are related

to the same nature of defects which are characteristic of melt-grown Si crystals and that their essential constituents are some point defects which are frozen and agglomerate most efficiently at temperatures around 1200 °C during cooling of the crystal from melting point. On the other hand, IRSCs are found only in CZ-Si and stable up to 1300°C, while FPDs and COPs in a grown CZ-Si crystal up to 800–1000 °C [20,22]. IRSCs are identified to be tiny precipitates of O impurity larger than a certain size which are developed during crystal growth [23]. TEM observation has revealed that a high density of O precipitates 10 nm in the size are involved in an as-grown CZ-Si [24].

The densities of FPDs, COPs and IRSCs all increase with an increase in the growth rate in CZ-Si [19,22,25]. It is interesting that in a crystal with a ring-shaped OSF-rich region the densities of all the kinds of defects in the outer region of the ring are much lower than those in the inner region, those in the outer region being lower than the detection limits [23]. Namely, the outer and inner regions are essentially different from each other in the defect state even if both show similar precipitation characteristics of O impurity. We are led to a picture that the outer surface of a crystal is an effective sink for constituents of defects giving rise to FPDs or COPs. Some theoretical treatments have been put forward to describe the spatial distribution of intrinsic point defects during cooling of a Si crystal from melting point [26,27,28]. IRSCs are thought to be microprecipitates of O impurity nucleated on FPDs or COPs. From similarity in the radial distribution of FPDs or COPs in CZ-Si and D-defects in FZ-Si, we may suppose that essential constituents of the defects related to FPDs or COPs in CZ-Si are the same as those of D-defects. However, the structure of the former is probably modulated by O atoms which are incorporated at relatively low temperatures. There is a big discrepancy among reports by different groups concerning the relation between defects related to FPDs, COPs or IRSCs and the gate oxide integrity. IRSCs, at least located near surface, have been shown to degrade the break-down voltage of the oxide [21,22]. On the other hand, the density of FPDs or COPs are reported not to

have a clear correlation with the integrity [22,25,29]. This seems to show that the contamination of this kind of defects with metallic impurities plays a decisive role in determining the break-down voltage when oxidized.

5. CONCLUSION

The origin and entity of so-called micro-defects in Si have not yet been well clarified. Technological problems related to these defects have mostly been overcome by means of trial and error without clarifying the physics. As a consequence, whenever some progress or innovation is achieved in the device production technology, some new aspects of microdefects appear as technological difficulties. Usually structural defects by themselves do not give rise to harmful effects on electrical property of Si. They are harmful when they react with certain kind of impurities. Thus, the reaction between structural defects and impurities is a central problem in controlling microdefects in Si.

REFERENCES

- J.Chikawa and S.Shirai, *Jpn. J. Appl. Phys.*, 18, Suppl. 18-1 (1979) 153.
- D.R.Clarke, M.C.Kroll, P.D.Kirchner, R.F. Cook and B.J.Hockey, *Phys. Rev. Lett.*, 60 (1988) 2156.
- K.Minowa and K.Sumino, *Phys. Rev. Lett.*, 69 (1992) 320.
- K.Sumino and H.Harada, *Phil. Mag. A*, 44 (1981) 1319.
- T.S.Plaskett, *Trans. Metall. Soc. AIME*, 233 (1965) 809.
- T.Abe, T.Samizo and S.Maruyama, *Jpn. J. Appl. Phys.*, 5 (1966) 458.
- A.J.R.de Kock, *Appl. Phys. Lett.*, 16 (1970) 100.
- H.Föll and B.O.Kolbesen, *Appl. Phys.*, 8 (1975) 319.
- T.Abe, *Oyo Buturi*, 59 (1990) 272.
- R.J.Roksnoer and M.M.B.Van den Boom, *J. Cryst. Growth*, 53 (1981) 563.
- V.V.Voronkov, *J. Cryst. Growth*, 59 (1982) 625.
- T.Y.Tan and U.Gösele, *Appl. Phys. A*, 37 (1985) 1.
- T.Abe and M.Kimura, *Semiconductor Silicon 1990*, H.R.Huff, K.Barrackough and J.Chikawa eds. (Electrochem. Soc., Pennington, 1990) p.105.
- M.Hasebe, Y.Takeoka, S.Shinoyama and S.Naito, *Defect Control in Semiconductors*, K.Sumino ed. (North-Holland, Amsterdam 1990) p.157.
- S.Shinoyama, M.Hasebe and T.Yamauchi, *Oyo Buturi*, 69 (1991) 766.
- H.Yamagishi, I.Fusegawa, N.Fujimaki and M.Katayama, *Semiconductor Science and Technology*, 7 (1992) 135.
- J.Ryuta, E.Morita, T.Tanaka and Y.Shimanuki, *Jpn. J. Appl. Phys.*, 29 (1990) L1947, 31 (1992) L293.
- P.Gall, J-P.Fillard, J.Bonnafe and T.Rakotomavo, *Defect Control in Semiconductors*, K.Sumino ed. (North-Holland, Amsterdam 1990) p.255.
- H.Takeno, S.Ushio and T.Takenaka, *Abstracts of 17th Meeting, Jpn. Soc. Cryst. Growth* (1993) 15.
- Y. Shimanuki, *Abstracts of 17th Meeting, Jpn. Soc. Cryst. Growth* (1993) 1.
- T.Shigematsu, M.Sano and S.Sumita, *Proc. 61st Meeting of 145 Committee, JSPS* (1992) 13.
- M.Kouno, H.Motoura, K.Uemura and M.Nishimura, *Abstracts of 17th Meeting, Jpn. Soc. Cryst. Growth* (1993) 5.
- S.Sadamitsu, S.Umeno, Y.Koike, M.Hourai, S.Sumita and T.Shigematsu, *Jpn. J. Appl. Phys.*, (1993) in press.
- K.Nakai, T.Nakashizu and H.Haga, *Proc. Oxford Conf. on Microscopy of Semiconductors (Conf.Ser.IOP, 1993)* in press.
- H.Suga, H.Abe, H.Koya, T.Yoshimi, I.Suzuki, H.Yoshioka, N.Kagawa and K.Akiyama, *Proc. 61st Meeting of 145 Committee, JSPS* (1992) 19.
- W.Wijaranakula, *J. Electrochem. Soc.*, 138 (1992) 604.
- R.Habu, I.Yunoki, T.Saito and A.Tomiura, *Jpn. J. Appl. Phys.*, 32 (1993) 1740.
- R.Habu, K.Kojima, H.Harada and A.Tomiura, *Jpn. J. Appl. Phys.*, 32 (1993) 1747, 1754.
- N.Fujimaki, I.Fusegawa, T.Abe and M.Katayama, *Proc. 61st Meeting of 145 Committee, JSPS* (1992) 44.