Morphology of Oxide Precipitates in Silicon Crystals[†]

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Morphology of thermally induced oxide precipitates (SiO_x , $x \approx 2$) in Czochralski-grown Si crystals are investigated using transmission electron microscopy.

In the case of annealing at 800 or 900°C, the morphology of oxide precipitates is of a square-plate having the {100} habit plane with the $\langle 110 \rangle$ sides and a column-like structure inside. When the annealing temperature is 1000°C and the oxide precipitation rate is fast, the direction of dendritic growth is $\langle 100 \rangle$ in the Si matrix and its top of the branch has a $\langle 110 \rangle$ facet. A slow oxide precipitation rate results in the $\langle 110 \rangle$ direction of the dendritic growth.

These precipitates are amorphous SiO_2 . Their morphology is determined by either the Si matrix which determines the shape of the precipitates (Si matrix negative crystal formation), or the interstitial oxygen which precipitates plate-like on the dislocations.

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I. Introduction

Czochralski-grown (CZ) silicon single crystal wafers contain oxygen atoms with concentration of about 10^{24} m^{-3} introduced from the quartz crucible during crystal growth. These atoms are supersaturated, and they precipitate during subsequent heat treatment to form SiO_x ($x \approx 2$) in the silicon lattice. The growth of these oxide⁽¹⁾⁻⁽¹⁴⁾ precipitates leads to secondary defects such as dislocation loops and stacking faults⁽¹⁾⁻⁽⁶⁾.

These precipitates and secondary defects thus formed cause device failure when they are located in the active region of a device. However, if they are outside the active region, they act a beneficial role as a sink for metallic impurities. Accordingly, the control of the defects induced by thermal treatment is important in fabricating devices with high reliability and high yield.

This paper describes results of TEM investigations on the formation mechanism and the morphology of the oxide precipitates under various annealing conditions.

II. Experimental Procedure

The samples used in this experiment were Czochralski-grown p-type Si wafers with a (001) surface, a diameter of 150 mm, a resistivity of $0.1 \Omega \cdot \text{m}$, and an interstitial oxygen concentration of about $10^{24} \text{ atoms/m}^3$. The pulling rate of the crystal was 1–1.5 mm/min. Under these conditions, ring-distributed defects⁽¹⁵⁾ are produced after heat treatment⁽¹⁶⁾⁽¹⁷⁾. The samples were annealed at temperatures ranging from 800 to 1100°C for 58 h in dry O_2 ambient.

The ring-distributed defects were located by using a

scanning photon microscope⁽¹⁷⁾ (SPM), and a chemical etch pit method (Secco etching). TEM (transmission electron microscopy) was used to observe {100}, {110} and {111} foils prepared by chemical etching and Ar ion milling, using a Hitachi H700-H at 200 kV with a bright-field image.

III. Results

1. Square-plate oxide precipitates with columnar structure

Figure 1 shows a TEM image of one of the ring-distributed defects generated by heat treatment at 800°C for 58 h in dry O_2 ambient. The incident angle of the electron beam is perpendicular to the $\langle 100 \rangle$ surface. The defect shown in Fig. 1 is an oxide precipitate of a square-

Fig. 1 TEM image of the square-plate oxide precipitate with columnar growth. Annealed at 800°C for 58 h in dry O_2 ambient.

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Fig. 2 Growth process of the square-plate oxide precipitates with a columnar growth. Annealed at 900°C for 58 h in dry O₂ ambient.

plate having the {100} habit plane with the $\langle 110 \rangle$ sides about 0.3 μm long. The defect contains column-like structures that perpendicularly extend from each side of the square toward the diagonal lines. The oxide which forms the defect is amorphous, because no extra spot or electron diffraction spot other than that from the Si crystal was observed.

Figure 2 shows three typical TEM images generated by heat-treatment at 900°C. The time and ambient of the annealing were the same as in Fig. 1. The defects are again oxide precipitates in the ring-shaped defect region. The defects in Fig. 2 seem to correspond to different growth stages of the square-plate oxide precipitate with columnar structures in Fig. 1.

In more detail, Fig. 2(a) shows an early stage of the oxide precipitation. The defect is of an irregular form. It is composed of a few dislocations that accompany small spherical oxides of high density. Figure 2(b) shows the next stage. The defect contains one dislocation that has a square shape. It has no definite structure inside. Figure 2(c) shows the final growth stage of the defect shown in Fig. 1. Each side of the square oxide is about 0.9 μm long, and is three times longer than in Fig. 1.

2. Dendritic oxide precipitates

Figure 3 shows typical TEM images of oxide precipitates generated by annealing at 1000°C. The time and ambient were again the same as in Fig. 1. The oxide precipitate shown in Fig. 3(a) is of a dendritic plate, and it is similar to the one reported by Tan and Tice⁽⁶⁾. The whole image of the defect is described by a circumscribing square with sides about 2.4 μm long. A microstructure of well-developed dendritic oxide with a nucleus of microprecipitate at the center is clearly seen. Morphology of the dendritic oxide is cross-shaped with main branches extending in the $\langle 100 \rangle$ directions. These main branches have the $\langle 110 \rangle$ facets at the front. Side branches grow from the main branches with the $\langle 110 \rangle$ facets at the front in a similar way to the main branches. The side branches are symmetrically formed along the main branches. The dendritic oxide has neither dislocation nor microtexture inside. Again, no electron diffraction extra spot was observed from the oxide precipitate. Therefore,

Fig. 3 TEM images of dendritic amorphous oxide precipitates. (a) Dendritic precipitate with a nucleus of microprecipitate at center. (b) Dendritically grown square-plate precipitates with growth stripes. Elongated directions of dendritically grown branches are the $\langle 100 \rangle$. Annealed at 1000°C for 58 h in dry O₂ ambient. The scale bars are 0.5 μm long.

this oxide is also considered to be amorphous.

The defect shown in Fig. 3(b) is accompanied by different precipitate of a square plate with the $\langle 110 \rangle$ directed sides, besides the dendritic oxide similar to the one shown in Fig. 3(a). Among the dendritic branches some stripe patterns are seen parallel to the $\langle 110 \rangle$ direction. These fringes seem not to be dislocations, but growth stripes of the oxide precipitates, for the following reasons. First, the fringe contrast is weaker than the diffraction contrast of dislocations. Secondly, no stripe extends from the surface to the back side of the sample in contrast to the dislocations. Thirdly, neither reaction nor crossing among the fringes was observed. These striped oxides also seem amorphous. Care must be taken not to misunderstand the contrast around dendritic oxide. At first sight, the striped oxides are seen crystalline, because their contrast changes with the electron diffraction condition. However this change can be attributed to the elastic strains produced by the dendritic oxides, considering that the volume of Si incorporated into SiO_2 is doubled by the oxygen precipitation, and that this volume expansion causes very large strains in the Si matrix.

Figure 4 shows the TEM micrographs of different defect generated under the same conditions as in Fig. 3. As shown in Fig. 4(a), this defect is also a dendritic oxide. In contrast to the one in Fig. 3, it is not only surrounded by the $\langle 110 \rangle$ -directed dislocations, but also contains dislocations between the branches. These dislocations exist in the Si matrix, but not in the oxide. Similarly to Fig. 3, most of main branches extend in the $\langle 100 \rangle$ direction, but some to the $\langle 110 \rangle$ direction. The dendritic oxide was accompanied by black contrasts around it, this result suggests the existence of strong elastic strains in the Si matrix. Figure 4 (b) shows a TEM micrograph of the same defect as in Fig. 4(a). The micrograph was observed under the condition where neither dislocation nor elastic strain is observed. In this figure, the dendritic oxide is not a single cluster, but composed of some separate dendritic oxides.

Figure 4(c) shows a cross-sectional TEM image of different dendritic oxide. The oxide is about 50 nm thick, and is surrounded by many dislocations.

Fig. 4 TEM images of segregated dendritic oxide precipitates. Micrograph (a) and (b) show different electron diffraction conditions in the same region, and (c) shows a section image of the precipitate. Annealed at 1000°C for 58 h.

Fig. 5 TEM images of dendritically grown square-plate oxide precipitates with $\langle 110 \rangle$ branches. (a) Plan-view micrograph of precipitate. (b) Plan-view of precipitate and interference fringes distribution. (c) Section of precipitate and interference fringe distribution. Heat treatments are two-step annealing. The scale bars are 0.5- μm long.

3. Dendritic oxide precipitates generated by two-step annealing

By single-step annealing the Si wafers at temperatures from 800 to 1000°C for 58 h, defects were generated only in a limited ring-like region where interstitial oxygen precipitated faster than in other regions. In the case of two-step annealing such as IG (Intrinsic Gettering) oxygen precipitates in the whole wafer. The oxides in the ring region have the same morphology as in Figs. 3 and 4.

Figure 5 shows some of the precipitates generated outside the ring region by two-step annealing (first: 650°C, 15 h, in N₂; second: 1000°C, 16 h, in O₂). Figure 5(a) is a TEM image of the precipitate observed from the $\langle 100 \rangle$ direction. A dendritic oxide is also observed. The main branches extend in the $\langle 110 \rangle$ direction that is tilted 45° from the one in Figs. 3 and 4. The branches have no facet at the front. Growth stripes between the dendritic branches are circular and concentric. These two features contrast with the features of the oxides in Figs. 3 and 4. The side of the square oxide is about 0.9 μm .

Figure 5(b) and (c) show the TEM bright field images of other oxides where the electron beam is again incident from the $\langle 100 \rangle$ direction of the Si matrix. Concentric circular interference fringes which reflect the strain⁽¹⁸⁾ in the Si matrix are clearly seen around the oxide, in Fig. 5 (b). Figure 5 (c) shows a sectional TEM image of different plate-like oxide, which has eight-shaped interference fringes.

4. Dendritic oxide precipitates generated by three-step annealing

In the fabrication of LSIs (large scale integrated circuits), IG is usually carried out by three-step annealing in order to form a surface region free from defects. Under this annealing, as well as two-step annealing, defects are generated in a deeper region even in high quality Si wafers that have no ring-distributed defect region. The defects thus generated are investigated here. The annealing condition is as follows. The first was carried out at 1100°C for 3 h in N₂, the second at 650 °C for 16 h in O₂, and the third at 1000°C for 16 h in O₂. Only the defects outside the ring-distributed defect region were examined. The TEM images of one of the oxides are shown in Fig. 6. Figure 6(a) is a $\langle 100 \rangle$ view of the Si matrix, which shows a dendritic square-plate oxide with a starfish-shaped oxide inside that extends in the $\langle 110 \rangle$ direction. Growth stripes of concentric circles are observed among the dendritic branches. The sides of the square-plate oxide are about 0.5 μm long.

Figure 6(b) is TEM image of different oxide observed from the $\langle 110 \rangle$ direction. The outline of the oxide seems to be rhomboid, although it is actually square. This is due to the electron beam direction which is not perpendicular to the oxide plane. Morphology similar to that of Fig. 5(a) is clearly seen in Fig. 6 (b). The difference in the direction of branch growth might be due to the different tendency for oxide precipitation. That is, when the precipitation takes place with difficulty such as in high

Fig. 6 TEM images of dendritically grown square-plate oxide precipitates with $\langle 110 \rangle$ branches. (a) $\langle 100 \rangle$ view of Si matrix. (b) $\langle 110 \rangle$ view. Heat treatments are three-step annealing. Observed in high quality Si wafers without ring-like distributed defects. The scale bars are 0.1- μm long.

quality wafers and in a region outside the ring region, the dendritic branches extend in the $\langle 110 \rangle$ direction, and when the precipitate is easily formed, the dendritic branches extend in the $\langle 100 \rangle$ direction.

5. Rectangular or circular oxide precipitates

Defects other than dendritic are examined in the following. Figure 7 shows a TEM image of rectangular oxides precipitated on dislocation lines. Figure 7(a) was observed with weak contrast, and Fig. 7(b) with strong contrast. In this defect, the oxides are precipitated on the $\langle 110 \rangle$ and $\langle 100 \rangle$ dislocation lines, and thus are composed of two kinds of rectangles.

Figure 8 shows a TEM image of oxide precipitates on

Fig. 7 Rectangular oxide precipitates on the tangled dislocations. Micrograph (a) and (b) were obtained with different electron diffraction conditions in the same region. Annealed at 1000°C for 58 h.

tangled dislocations. They are small with circular or rectangular precipitates.

6. Octahedral precipitates

Figure 9 shows the TEM images of octahedral precipitates generated by annealing in dry O_2 ambient at 1100°C for 58 h. The side of the octahedron is about 0.6 μm . Figure 9(a) is a $\langle 100 \rangle$ view of the Si matrix. Each

Fig. 8 Circular and irregular oxide precipitates on the tangled dislocations. Annealed at 1000°C for 58 h.

side of the square is directed to the $\langle 110 \rangle$. The edges of the regular octahedron are observed as diagonal lines. This oxide is amorphous because oxides have neither dislocation nor texture inside and because no electron diffraction spot is observed from the precipitate. Figure 9(b) shows a $\langle 111 \rangle$ view and Fig. 9(c) does a $\langle 111 \rangle$ view of a tetradecehedral precipitate which has the shape of a octahedron truncated by the $\{100\}$ planes.

IV. Discussion

1. Oxide precipitates and Si negative crystal

In addition to the generally accepted result that regular octahedral precipitates are amorphous⁽⁸⁾⁽⁹⁾, it was found by the present study that dendritic oxides are also amorphous. These results are consistent with the fact that the oxide film formed on Si crystal by thermal oxidation is amorphous. At first sight, it seems strange that the amorphous oxides are octahedral, or that they grow

Fig. 9 TEM images of the amorphous octahedral precipitate. (a) $\langle 100 \rangle$ view of Si matrix, (b) $\langle 111 \rangle$ view, and (c) $\langle 111 \rangle$ view of the truncated octahedral precipitate (tetradecehedral). Annealed at 1100°C for 58 h in dry O_2 ambient.

anisotropically, for example, in the $\langle 100 \rangle$ direction in crystals. This does not imply that the oxide precipitates have a tendency of an anisotropic growth, but that the oxide growth is regulated by the Si matrix. This phenomenon is called the Si matrix negative crystal⁽¹⁹⁾.

2. Morphology of oxide precipitates and vacancy density

Figure 10 shows the morphologies of oxide precipitates, such as square-plate, dendrite, regular octahedron and truncated octahedron (tetradecahedron) in relation to annealing temperature. This morphology changes strongly depending on the growth temperature of the oxide and the supersaturated oxygen. It is called a crystal habit change and a change of truncation degree of a cube (Wulff's polyhedron)⁽²⁰⁾⁽²¹⁾. In crystal growth from a solution, it has been known empirically that a dendritic crystal is formed when it grows rapidly under high supersaturation conditions, whereas a polyhedral crystal is formed when it grows slowly under low supersaturation condition⁽²⁰⁾⁽²¹⁾. The precipitation of oxides occurs in a similar way. Namely, in the case of high supersaturation of oxygen (low temperature annealing), the oxide precipitates are plate-like, or dendritic. In the case of low supersaturation (high temperature annealing), the morphology of the oxides is regular octahedron, or truncated octahedron (tetradecahedron).

Square-plate oxides with columnar structure are combinations of rectangles, and dendritic oxides are of plate-like squares. These are shown in the upper halves of Fig. 10(a) and (b). The difference in the growth direction of dendritic oxides suggests that the vacancy density around the oxides is also different between Figs. 4 and 5.

3. Formation mechanisms of dendritic and square-plate oxide precipitates

Dendritic oxide may be produced by the following three steps.

(1) It is believed that the oxygen precipitation is initiated at some nuclei such as carbon atoms, interstitial Si, vacancy, and impurity atoms⁽²⁾. This is because the strain existing around the nuclei attracts supersaturated interstitial oxygen atoms. Oxygen atoms thus aggregated react with the Si matrix, forming SiO_2 . The growth of SiO_2 leads to volume expansion. According to Mishima⁽²²⁾, G. P. (Guinier-Preston) zones are mostly formed on the $\{100\}$ plane under the condition of the difference greater than 10% in the atomic radius between the metal matrix and solvent atoms. Although SiO_2 is not monoatomic, it is possible to assume some virtual atoms instead of SiO_2 . Considering that the original volume occupied by Si reacted with interstitial oxygen is approximately doubled, the radius of the virtual atom is $\sqrt[3]{2}$ times larger than that of Si. This result shows that Mishima's proposed condition is satisfied in the oxide precipitation. Therefore, it is natural that oxide is precipitated in the $\{100\}$ plane as shown in Fig. 3. On the other hand, stacking faults produced by aggregated interstitial Si atoms exist in the $\{111\}$ plane. In the early stage of oxygen precipitation, it is assumed that the Si matrix and SiO_2 are matched, and that SiO_2 exhibits a phase similar to coesite⁽¹⁰⁾⁻⁽¹²⁾ (high-pressure crystalline SiO_2 phase).

(2) Oxide precipitate changes from crystalline to amorphous with the aggregation of supersaturated interstitial oxygen on the G. P. Zone. This becomes dendritic due to the mechanism of Si negative crystal.

Fig. 10 Various morphology of oxide precipitates. The regular octahedron and tetradecahedron in (c) show solid projections along $\langle 100 \rangle$, $\langle 110 \rangle$ and $\langle 111 \rangle$. Miller's indices in the figure are plane for Si matrix.

(3) The $\langle 110 \rangle$ dislocation lines⁽²³⁾ are formed in the Si matrix with the growth of the dendritic oxide. Then interstitial oxygen aggregates on these dislocations and these precipitations are accompanied by the large strain and form a dendritic square-plate oxide.

V. Conclusion

Morphology of thermally induced oxide precipitates (SiO_x , $x \approx 2$) in Czochralski-grown Si crystals were investigated using transmission electron microscopy. The results are summarized as follows.

(1) Amorphous oxides are precipitated in the $\{100\}$ Si matrix by annealing at temperatures ranging from 800 to 900°C. They are surrounded by a square with the $\langle 110 \rangle$ sides. They have columnar internal structure inside.

(2) In the region where oxygen is precipitated quickly, two kinds of dendritic oxide are formed by annealing at 1000°C. One is single dendritic oxide with main branches extending to the $\langle 110 \rangle$ of the Si matrix. The branches have the $\langle 110 \rangle$ facets at the front. The other is a square-plate oxide composed of the above-mentioned dendritic oxide with rectangular growth stripes between them. These oxides are amorphous, but their morphology is anisotropic due to the mechanism of Si matrix negative crystal.

(3) In the region where oxygen precipitation is slow, a plate-like oxide is formed. This has a starfish-like dendritic oxide extending in the $\langle 110 \rangle$ direction, and concentric circular growth stripes between the dendritic branches.

(4) Growth stripes observed between branches in the dendritic square plate-like oxide are formed in the following way. The dendritic oxides produce strain around them due to the volume expansion resulting from the precipitation. This strain generates rectangular dislocations between dendritic branches. Interstitial oxygen is then aggregated on the dislocations.

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