Crystalline plate-like SiO_2 precipitates in silicon and their relation with new donors

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Czochralski grown silicon annealed at 750° C has been investigated with high-resolution electron microscopy, Hall effect and infrared measurement. Crystalline plate-like precipitates were observed and identified as β-cristobalite. The structure of the coherent interface of the new phase and its connection with the origin of the new donor are discussed.

1. Introduction

Oxygen in Czochralski (CZ) silicon is commonly supersaturated at temperatures involved in the process of large scale integration (LSI) device fabrication. Decomposition of this solid solution has long been a subject of investigation and the interest was greatly stimulated by the discovery [1–3] that oxygen precipitates and their induced lattice defects can be confined to the bulk of the wafer of semiconductor devices so as to act as intrinsic gettering sinks of undesirable impurities and surface defects, thereby improving the LSI device production yield.

In order to raise the rate of oxygen precipitation silicon wafers are often subjected to preannealing at temperatures near 750° C. From published reports [4–6] it is known that the dominant oxygen precipitates generated after long time annealing at such temperatures are plate-like amorphous SiO_2. However recently we have observed crystalline plate-like oxygen precipitates in CZ silicon annealed at 750° C with high-resolution electron microscopy (HREM) [7]. In this paper we shall present the investigation of the structure of these precipitates and their interface with the matrix. It will be shown that the interface structure of the new phase is related to the origin of new donor in CZ silicon the mechanism of which is not clear yet.

2. Experimental details

The material used was CZ silicon grown in the [1 0 0] direction with resistivity of 9.7 Ω cm by boron doping and 60 mm in diameter. The initial interstitial oxygen concentration was 1.5×10^{18} atoms cm^{-3} in accordance with ASTM-F121 and the carbon concentration was below the detection limit of 2×10^{16} atoms cm^{-3}. 0.5 mm thick slices were cut along the {1 1 0} plane for HREM study. In order to eliminate the influence of the crystal growth history and to promote the nucleation of oxygen precipitates the slices were preannealed at 1150° C for 1.5 h and 450° C for 24 h. The final heat treatment was carried out at 750° C for 0 to 100 h under nitrogen. The annealing tube furnace was double-walled and the protective gas was purified.

Transmission electron microscopy (TEM) specimens were prepared by mechanical grinding followed by argon ion milling. High resolution lattice images were taken in a JEOL 200CX microscope operating at 200 kV. With the electron beam parallel to the ⟨1 1 0⟩ direction of the silicon film thinned to about 10 nm thick at observed regions and the approaching Scherzer defocus of the objective lens a point resolution of 0.25 nm was attained.

Slices with thickness of 2 mm have been annealed along with the TEM specimens. They were used for the infrared transmission measurement to follow the decrease of dissolved oxygen and for the Hall coefficient measurement by van der Pauw method to obtain the concentration of new donor created during annealing.

3. Results and discussion

The dissolved interstitial oxygen decreased and extra donors (often called the new donors [8, 9]) were created in specimens during annealing at 750° C, as reflected by curves (a) and (b) respectively in Fig. 1

At the same time precipitates, which were absent in the original material, were observed. Specimens for TEM study were annealed 50 h. Low resolution observation (Fig. 2) indicates that besides a few rod-like defects which are identified as coesite [10], a polymorph of SiO_2, and dislocation dipoles, there are mainly small precipitates about 20 nm maximum in size and 10^{14} to 10^{15} cm^{-3} in density.

Small precipitates like those shown in Fig. 2 had been found in a wide annealing temperature range. They were shown as amorphous platelets in 750 to 870° C annealed silicon [4, 5, 10] and were postulated to have the same shape and structure after lower temperature annealing [10]. However, we have found crystalline plate-like oxygen precipitates by HREM, some of them are shown in Fig. 3 in which they are edge-on, running through the specimen and laying on {1 0 0} plane of silicon. Their cross-sections are very thin and are 10 to 20 nm in length.

Though the nature of the precipitates is difficult

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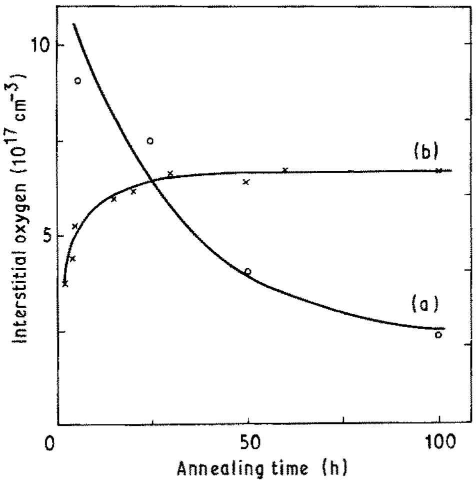

Figure 1 (a) Interstitial oxygen content and (b) new donor concentration plotted against annealing time at 750° C.

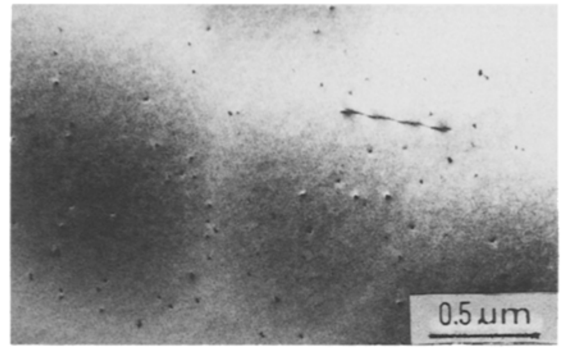

Figure 2 Bright-field micrograph of the small precipitates and a rodlike precipitate in CZ silicon annealed at 750° C for 50 h.

to judge from the image of thinner precipitates as in Fig. 3a, valuable information was acquired from Fig. 3b where a thicker precipitate of the second phase is evident. The projection of the atomic arrangement in the precipitate region of Fig. 3b is similar but not the same as coesite, the orientation relationship is different from what had been found before [5, 10], and the mismatch on the interface would be too large for coesite. From the rest of the known polymorphs of SiO_2 β-cristobalite [11] would be the most probable. β-cristobalite can be matched well with silicon, which had been used by Herman *et al.* [12] to simulate the connection between silicon crystal and non-crystalline SiO_2, and Ravi [13] had reported the observation of diffraction from coexisting α- and β-cristobalite precipitates in 1200° C annealed silicon. β-cristobalite has a diamond lattice with 0.716 nm in lattice parameter and an oxygen atom between every two silicon atoms. If the unit cell of β-cristobalite is expanded by 7% and rotated by 45° relative to the silicon unit cell about common [1 0 0] axis they can fit perfectly along the (1 0 0) plane as shown in Fig. 4a, where both the [0 1 0] direction of β-cristobalite and the [0 1 1] direction of silicon are perpendicular to the paper. It can be seen also from this diagram that when the interplanar spacing of {2 2 0} planes of β-cristobalite, 0.253 nm, is resolvable by the microscope and the nearest-neighbour atoms in silicon is unresolvable, then the periodicity of lattice viewed along the direction of projection is just like that observed in Fig. 3b.

In order to examine the proposed model, a computer simulation image of β-cristobalite viewed along its [1 0 0] direction was carried out by the multislice method [14] and the parameters remained constant. In Fig. 5 a computed image for a crystal thickness of 10 nm, spherical aberration coefficient $C_s = 1.2$ mm and defocus of the objective lens $\Delta = -65$ nm is inserted in an enlarged image of Fig. 3b, where the open dots corresponding to atomic tunnels. Taking into account that the precipitate is suffering some strain, the coincidence between the simulated and experimental images would be regarded as being quite good.

Images of non-edge-on case were seen more frequently. Typical examples are illustrated in Fig. 6. The lattice image inside the precipitate has the same regularity as the region outside, and their quantity relative to the edge-on precipitates indicates that they should arise from identical thin platelets on inclined {1 0 0} planes.

The structure of the interface between β-cristobalite and silicon is shown in Fig. 4b. Half of the silicon atoms are situated on coherent positions with mismatch of 7%, which leads to lower interfacial energy favouring the occurrence of the precipitates on {1 0 0} planes in the form of β-cristobalite platelets. The other half of the silicon atoms lacking nearest neighbours on the cristobalite side have two unpaired electrons each available as new donors [8, 9]. New donors arise in oxygen-rich silicon annealed at temperatures 550 to 800° C in contrast to the thermal donors [15, 16], which appear after 300 to 500° C annealing. It has been suggested that new donors are connected with

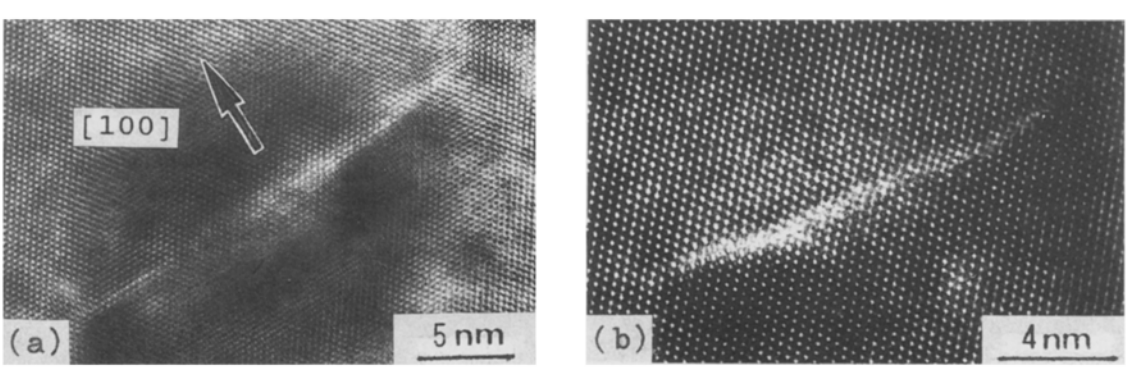

Figure 3 High-resolution lattice images of edge-on platelike precipitates on the {1 0 0} habit planes.

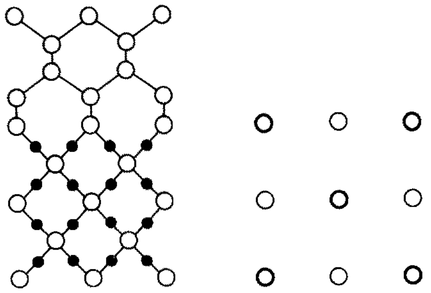

Figure 4 An atomic model of β-cristobalite and silicon joined along common (1 0 0) plane. (a) projection of (0 1 0) cristobalite and (0 1 1) silicon, (b) silicon atoms on interface. (β-cristobalite was expanded by 7%). (● oxygen, ○ silicon, **O** silicon on coherent site)

oxygen precipitates [17, 18], but the mechanism still need to be clarified. According to the present model, if the precipitates are square in shape with an edge length of 15 nm on average, then each β-cristobalite platelet can provide 3×10^3 donors. For specimens annealed at 750° C for 50 h the density of precipitates is 10^{14} to 10^{15} cm^{-3} and the measured concentration of new donors is about 2×10^{15} cm^{-3}, that means the ionization coefficient of the unpaired electrons is about 10^{-3}, which is close to the statistical result obtained by Zhong Lei *et al.* [18].

The nucleation and growth of β-cristobalite probably begin already at lower temperature, but their structure will remain undetected when they are small and thin as in the 650° C annealed specimens [5, 10]. On the other hand, the volume effect induced by β-cristobalite precipitation is very large: $V_{SiO_2}/V_{Si} = 2.3$, part of which is relaxed by emission of silicon interstitials, part is accommodated by elastic strain, but as the precipitates grow the accumulated incompatibility will eventually exceed the limit that could be borne by the new phase and gives rise to the appearance of an amorphous state. Along with the loss of coherency and coarsening of the precipitates the number of unbonded electrons on the interface hence the concentration of new donor decreases. This process would proceed quicker at higher temperature of annealing as has happened in practice [19]. Amorphous precipitates were not observed and the condition for the β-cristobalite platelets becoming amorphous may be different for particular crystal and heat-treatment and remains to be investigated. The main point of this work is, however, to present evidence of the existence of precursor phase of amorphous platelike oxide precipitates as anticipated by Fraundorf *et al.* [20] and Bergholz *et al.* [21] and to show that one of its forms is β-cristobalite.

4. Conclusion

Crystalline plate-like oxygen precipitates in CZ silicon annealed at 750° C for 50 h have been observed by HREM. It is suggested that they are β-cristobalite having {1 0 0} habit planes and (1 0 0) silicon ∥ (1 0 0) cristobalite, [0 1 1] silicon ∥ [0 1 0] cristobalite relationship with the matrix. On the {1 0 0} interface half of the silicon atoms are situated on coherent positions with a mismatch of 7%, the other half of the silicon atoms have two unpaired electrons each available for the origin of new donors.

Acknowledgement

The atomic images were taken at the Laboratory of Atom Images of Solids under the direction of Professor K. H. Kuo. His support is gratefully acknowledged.

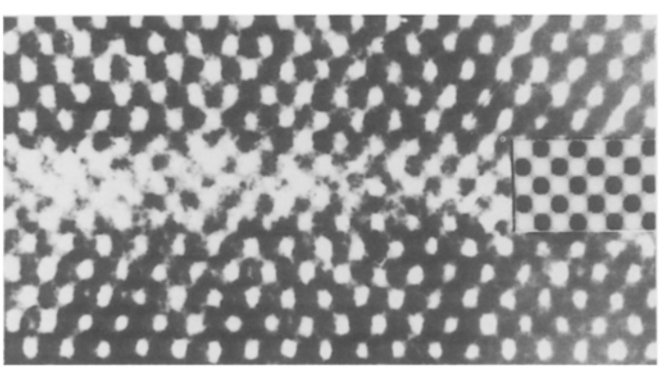

Figure 5 Enlarged image of precipitate shown in Fig. 3b. A simulated image of β-cristobalite is inserted for comparison, which was for a crystal thickness of 10 nm, spherical aberration $C_S = 1.2$ mm, defocus of objective lens $\Delta = -65$ nm.

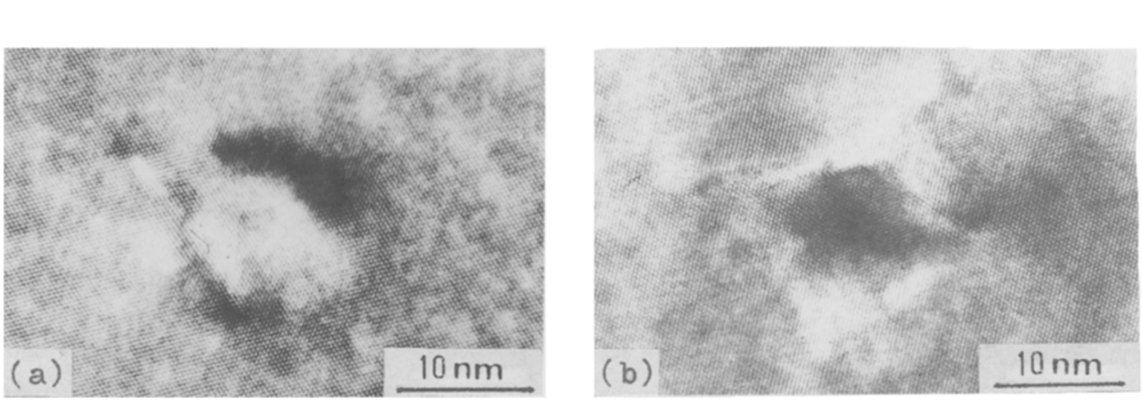

Figure 6 High-resolution lattice images of precipitates in non-edge-on cases.

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Received 26 July 1988
and accepted 5 January 1989