Octahedral-Structured Gigantic Precipitates as the Origin of Gate-Oxide Defects in MOSLSIs

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Gate-oxide defects (Fig. 1) originating in Czochralski silicon (CZ-Si) substrates were discovered by a Cu decoration method about fifteen years ago (1). Since then, sacrifice-oxidation (1), nitrogen annealing (2), and hydrogen annealing (3) methods have been developed to eliminate these defects. These three methods have been successfully introduced into actual fabrication lines for DRAMs and flash memories. However, many studies are still being made (4-6) on oxide defects coming from CZ-Si.

Recently, octahedral structures were found in the surface layer of standard CZ-Si just under the oxide defects, using Cu decoration and TEM (7). An attempt was made to characterize these structures by analysis with TEM-EDS. Experimental findings indicate that the structure is full of voids. This contradicts previously reported results that the octahedral structures found in Si bulk are filled with amorphous SiO₂ [8]. To explain this, a model for the formation of octahedral structures with voids is proposed.

Thermal SiO₂ (30 nm) was grown in dry O₂ on 6-inch-diameter [100]-oriented standard CZ-Si. Oxygen concentration in the Si was 8.8-9.2 x 10¹⁷ atoms/cm³. Cu decoration was then used to locate the oxide defects (Fig. 2). Energy-dispersive X-ray Spectroscopy (EDS, Kevex Level-5) was used to analyze the content of the structure. The diameter of the analysis beam was about 10 nm.

A typical TEM observation or plan view of the origin of the oxide defect, is shown in Fig. 3. It is square in shape and its side is oriented along the [110] axis. Size is typically 150-200 nm. Another typical TEM result is shown in Fig. 4, which is a cross-sectional view of the origin of the oxide defect. The angle between the face and the Si surface is 55 degrees, which indicates the face has a [111] orientation. Figures. 2 and 3 indicate a polyhedral structure, which is shown schematically in Fig. 5. Another typical TEM result is shown in Fig. 6, which is a cross-sectional view of the origin of the oxide defect. In this case, the bottom of the structure was observed. Tungsten deposited on the sample made the surface silhouette clearer. All ten samples indicate an octahedral structure.

Several points of the octahedral structure shown in Fig. 4 were examined by EDS. The results of analysis are shown in Fig. 7. The intensity of the oxygen is much smaller than it should be, if the structure were full of SiO2, even considering that the sensitivity of EDS is low around the signal of oxygen. These data imply that most of the structure is full of voids. Another sample examined showed the same result.

From another point of view, if the structure were full of SiO2, Cu would not be able to enter the structure and would not be able to be detected there. The detection of Cu (Fig. 7) also suggests that the structure is almost completely full of voids.

Another example is shown in Fig. 6. The silhouette of deposited tungsten indicates that most of the structure is empty or void before tungsten deposition.

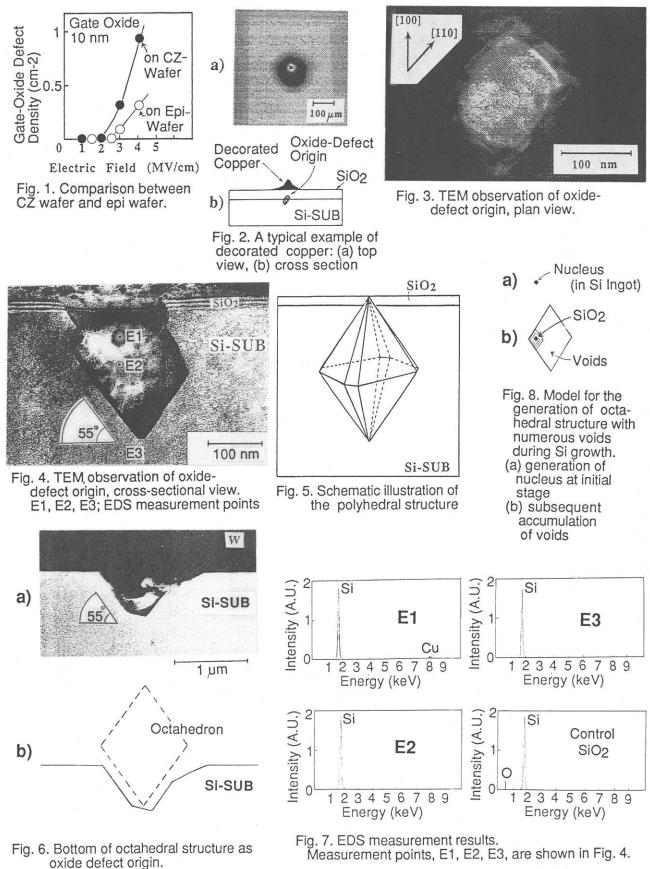
TEM results shown in Figs. 3 and 4 suggest that the octahedral structure is almost completely empty or void, because, generally, a smaller mass (or thickness) results in brighter contrast than that in the surrounding region.

Here, two models for the generation mechanism of the octahedral structure have been considered. In the first model, a nucleus induced in the Si ingot acquires vacancies rather than oxygen during Si crystal growth, as illustrated in Fig. 8. The accumulation of vacancies rather than oxygen suggests that the diffusion constant for vacancies may be much larger than that for oxygen in the Si ingot.

The second model is that the octahedral structure acquires oxygen and forms SiO₂ during Si crystal growth, and then, during the wafer cleaning process, much of the SiO2 is removed. If this is true, the etching rate for the SiO2 is estimated to be too large to be accepted. From this point of view, this model can effectively be discarded.

In conclusion, the octahedral structure that causes oxide defects contains a vast

number of voids. This property is explained by a model of vacancy diffusion (or gettering) to the structure during Si crystal growth. 1) M. Itsumi et al., APL 40 (6), 496 (1982). 2) F. Kiyosumi et al., SSD 83-66, 1 (1983). 3) Y. Matsushita et al., SSDM, 529 (1986). 4) H. Yamagishi et al., Semicond. Sci. Technol., 7, A135 (1992). 5) S. Sadamitsu et al., JJAP 32, 3675(1993). 6) J-G. Park et al., ECS Meeting, 94-1, 696(1994). 7) M. Itsumi et al., JAP 78(3), 1 (1995).



(a) TEM result, (b) schematic illustration