Influence of the Structural Transition Layer on the Reliability of Thin Gate Oxides

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The injected charge-to-breakdown (Qbd) of thin thermal oxides under constant F-N tunneling current stress conditions is degraded by the structural transition layer of SiO₂ at the SiO₂/Si interface. The Qbd significantly decreases for oxides thinner than approximately 7 nm. Using a newly-developed X-ray diffraction technique, it is found that a "structural transition layer" with lower density than that of bulk oxide exists at the SiO₂/Si interface, and its thickness is approximately 7-8 nm. Based on these experimental results and theoretical analysis, a new model for the accelerated dielectric breakdown mechanism in thin thermal oxides is proposed.

1. INTRODUCTION

The performance of advanced MOS ULSI devices depends strongly on the reliability and integrity of the thin gate oxides within them. Since these oxide layers include an SiO₂/Si interface region, the ongoing reduction of device dimensions will result in a correspondingly thicker interface region. As a result, it is essential to ensure that the characteristics of the interface region can be adequately controlled. SiO₂/Si interface structures have been investigated using various analytical methods. The results of these investigations, however, have not yet reached the consistent interpretation for the interface structure. The influence of interface structure differences on the electrical reliability of thin oxides also has been scarcely discussed. Recent reports have shown that reducing the Si surface microroughness just before oxidation has a significant effect on electrical characteristics of thin oxides.

In this paper, the interface structure of thin thermal oxides is studied based on measurements made using a newly-developed X-ray diffraction technique, and the influence of this structure on electrical reliability under constant F-N tunneling current stress conditions is discussed. Supported on some theoretical analysis, the dielectric breakdown mechanism in thin oxides is also proposed.

2. EXPERIMENTAL

Silicon (100) wafers were chemically pre-treated by standard RCA cleaning and diluted HF treatment. 4-15 nm thick oxides were thermally formed at 750°C in pyrogenic steam or at 900°C in a dry O₂ atmosphere, using a conventional furnace. The overall concentration of heavy metal contamination elements measured during pre-treatment and thermal oxidation was less than 5x10⁷ atoms/cm². The Si surface roughness just before oxidation was very low, with the average surface roughness (Ra) of about 0.08 nm as estimated using atomic force microscopy analysis. The electrical characteristics of the thin oxides were investigated using simple MOS capacitors fabricated at lower temperatures (< 850°C) with poly-crystalline silicon gate electrodes and LOCOS isolation. The intrinsic reliability of the thin oxides was evaluated by constant F-N tunneling current TDDB measurements. The electrodes (0.001 cm²) were negatively biased to the substrates under 0.1 A/cm² and at 100°C stress conditions.

The oxide structure was analyzed using a grazing incidence X-ray diffraction technique in an extremely asymmetric scheme as shown in Fig. 1. The X-ray source (wavelength: 0.1400 nm) was synchrotron radiation on beam line 9C of the Photon Factory at the National Laboratory for High Energy Physics, Japan. The small incident angle (0.020°), which is almost equal to the total reflection angle of Si, leads to an increase in the X-ray path through the oxide. Consequently, it was possible to detect slight structural differences in the thin oxide, because the (311) reflection intensity is very sensitive to the absorption of the incident synchrotron radiation by the SiO₂ film.

3. RESULTS

The oxide thickness dependence of the injected charge-to-breakdown (Qbd) at 50% cumulative failure in shown in Fig. 2. It can clearly be seen that the Qbd rapidly decreases as the thickness is decreased below approximately 7 nm for both 750°C pyrogenic steam
Detector
Monocromater

Incident
monitor

X-rays

$\lambda = 0.1400 \text{nm}$

$[100]$

$[311]$

$\Delta l = \exp(-d/l(p))$

$0.20^\circ$

Si

SiO$_2$

can be fit to a single curve. This suggests that the CVD oxide film is composed only of a low-density layer. Its density is almost equal to that of the structural transition layer in thermal oxides. These analyzed interface structures are summarized in the schematic illustrations shown in Fig. 4.

Fig. 2. Qbd at 50% cumulative failure as a function of the oxide thickness for various thermal oxides.

oxides and 900°C dry O$_2$ oxides. Furthermore, above 7 nm thickness, the values of Qbd for the oxides formed at 750°C in pyrogenic steam are higher than those for the oxides formed at 900°C in a dry O$_2$ atmosphere.

Figure 3(a) shows the measured logarithmic X-ray intensity as a function of the oxide thickness for various thermal oxides. The diffracted X-ray intensities decrease with increasing oxide thickness because of absorption phenomena. It is found that the logarithmic intensity plots for each oxidation condition cannot be fit to a single curve, but require two curves. The oxide density can be calculated from these fitted curves. The result indicates that the thick oxides are composed of two layers with different densities; a low-density (2.37-2.40 g/cm$^3$) structural transition layer next to the Si substrate and an upper layer with the density of bulk SiO$_2$ (2.55-2.60 g/cm$^3$). Thinner films consist only of structural transition layer, the thickness of which is lower for 750°C pyrogenic steam oxides than for 900°C dry O$_2$ oxides (8 nm).

In order to investigate the origins of this transition layer in thermal oxides, chemical vapor deposition (high temperature oxidation) films were also analyzed using the same X-ray diffraction technique. The result is shown in Fig. 3(b), in which all the data

Fig. 3. Logarithmic X-ray intensity as a function of the oxide thickness for (a) various thermal oxides, (b) CVD (HTO) film. Plots labelled "Clean" are data for wafers with native oxide formed during RCA cleaning.
4. DISCUSSION
The Qbd behavior of thin thermal oxides shown in Figure 2 corresponds to the density and thickness variations of the structural transition layer. This shows that the reliability of thin thermal oxides degrades due to the existence of the structural transition layer. The difference between the structures of thermal oxides and the CVD oxide films also implies that the structural transition layer seems to be inevitably formed by volume expansion due to the thermal oxidation of silicon crystal at the SiO₂/Si interface. In the structural transition layer of the thermal oxides, stress and strain caused by the volume expansion result in severe distortion of the Si₄O₄ tetrahedron network at the SiO₂/Si interface.

The silicon atom of a Si₄O₄ tetrahedron can easily become hypervalent due to coordination with an oxygen atom. Ab-initio molecular orbital calculations lead to the Si-O bond elongation of Si₄O₄ tetrahedron under the hypervalent condition. Moreover, as a stretched Si-Si bond produced by the desorption of oxygen from coupled Si₄O₄ tetrahedrons captures an electron, the bond is more energetically stable. In other words, oxygen-vacancies form electron traps, known as negative U defects. These computational results suggest that an oxygen atom can easily desorb from a hypervalent Si-O-Si bond weakened by elongation, and that, after desorption of the oxygen, a stable Si-Si bond seems to be formed by trapping an electron.

Figure 5 shows the elemental process of dielectric breakdown accelerated by a hypervalent silicon atom and trapped electrons. The distorted Si₄O₄ tetrahedron network in the structural transition layer of thin thermal oxides enhances to produce a hypervalent silicon atom. A large number of Si-O-Si bonds can easily be changed to the Si-Si bonds by oxygen desorption and electron capture. This phenomenon is interpreted as the reverse process of thermal oxidation. The increase in Si-Si bonds leads to an increase in conductivity, and dielectric breakdown seems to occur after a sufficient number of Si-Si bonds have formed.

5. CONCLUSION
The 7-8 nm thick structural transition layer at the SiO₂/Si interface of thermal oxides has been experimentally observed for the first time by X-ray diffraction analysis using synchrotron radiation. The Qbd of thin thermal oxides less than approximately 7 nm thick rapidly degrades with decreasing film thickness due to the existence of this low-density structural transition layer.

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