

Clear Difference between Chemical Structure of SiO₂/Si Interface Formed Using Oxygen Radicals and That Formed Using Oxygen Molecules

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1. Introduction

Advanced ultra-large-scale-integrated (ULSI) devices used in future electronics will require the control of the oxidation process on an atomic scale. To meet this requirement, the oxidation utilizing oxygen radicals (OR) produced in a microwave-excited high-density Kr/O₂ mixture plasma [1] has been extensively studied in recent years [2-8] and has been used to form high quality oxide films on Si surfaces with any crystallographic orientation [2]. On the other hand, by the conventional thermal oxidation utilizing dry oxygen molecules, the high quality oxide film can be formed only on a Si(100) surface. The detail analysis near the SiO₂/Si interface is required for realizing high carrier mobility and high integrity gate insulator. The purpose of this study is to clarify the difference between the chemical structures of the SiO₂/Si interfacial transition layer formed on a Si(100) utilizing OR and that formed on a Si(100) utilizing dry oxygen molecules (OM) by measuring angle-resolved photoelectron spectra (ARPES) arising from the Si 2*p* core levels.

2. Experimental Details

To detect photoemission arising from Si 2*p* core levels at and near the SiO₂/Si interface through nearly 1-nm-thick silicon oxide films, an inelastic mean free path [9] of more than 2 nm in silicon oxide is necessary. To meet this requirement, Si 2*p* spectra were measured using photon energy (PE) of 1050 eV at Super Photon Ring 8 GeV (SPring-8). The wafers used in this study were 10 Ωcm p-type Si(100) substrates whose surfaces are atomically flat on a wafer scale [7, 8]. The wet oxidation of these substrates was performed at 1100 °C to form 1-μm-thick silicon oxide films. After etching the oxide films in a HCl/HF mixture solution [10], the substrates were cleaned in five steps [11]. The surface microroughness (Ra) of the cleaned substrates measured by atomic force microscopy was less than 0.08 nm. An oxide film was formed on cleaned substrate at 400 °C utilizing OR produced in a microwave-excited high-density Kr/O₂ mixture plasma [1, 2] at a pressure of 1 Torr. Here, the microwave frequency and power were 2.45 GHz and 2.7 W/cm², respectively. Oxide films were also prepared on the cleaned substrates at 900 °C, 1000 °C and 1050 °C utilizing OM.

3. Experimental Results and Discussion

Figure 1 shows the spectra arising from the interfacial transition layer formed utilizing OR and that utilizing OM at 900 °C obtained by taking difference between two Si 2*p*_{3/2} spectra measured at photoelectron take-off angles (TOAs) of 15° and 85° to eliminate spectra arising from bulk Si [5]. As shown in this figure, the Si 2*p*_{3/2} spectrum can be decomposed into those arising from intermediate states (IMs) consisting of Si-Si-O₃(Si³⁺), Si₂-Si-O₂(Si²⁺), Si₃-Si-O(Si¹⁺), Si^α, Si^β, and Si^γ. Here, Si^α denotes a Si atom affected by its second nearest neighbor O atoms [12]. The chemical shifts in binding energy of Si 2*p*_{3/2} core levels in the IMs thus determined from this decomposition are used in the following analyses of ARPES.

Figure 2 shows the integrated intensity ratios expressed by I(Si³⁺)/I(Si⁴⁺), I(Si²⁺)/I(Si³⁺), I(Si¹⁺)/I(Si²⁺), I(Si^α)/I(Si²⁺), I(Si^β)/I(Si^β), and I(Si^γ)/I(Si^α) as a function of TOA for the SiO₂/Si interface formed utilizing OR and that formed utilizing OM at 900 °C. Here, I(Si⁴⁺), I(Si³⁺), I(Si²⁺), I(Si¹⁺), I(Si^α), I(Si^β), and I(Si^γ) denote the integrated spectral intensity of the Si 2*p*_{3/2} spectrum arising from the Si⁴⁺, Si³⁺, Si²⁺, Si¹⁺, Si^α, Si^β, and Si^γ, respectively. It can be seen from Fig. 2 that for SiO₂ films formed using OR, 1) Si³⁺ layer is formed beneath Si⁴⁺ layer, 2) Si²⁺ and Si³⁺ are located in the same layer, 3) Si¹⁺ is located beneath Si²⁺ or Si³⁺ layer, 4) Si^α and Si^β located in the same layer beneath Si²⁺, and Si^γ is located above Si^α and Si^β. On the other hand, for SiO₂ films formed using OM at 900 °C, 1) Si³⁺ layer is formed beneath Si⁴⁺ layer, 2) Si¹⁺ and Si²⁺ are located in the same layer, 3) Si¹⁺ and Si²⁺ are located beneath Si³⁺ layer, 4) Si^α, Si^β, and Si^γ are located in the same layer beneath Si²⁺. Therefore, the compositional and structural transition layers at the SiO₂/Si interface formed using OR is clearly different from that formed using OM. The approximate bonding configurations of compositional transition layers at these two SiO₂/Si interfaces indicating this clear difference are illustrated in Figs. 3(a) and 3(b) [13].

Figure 4 shows Si 2*p*_{3/2} spectrum arising from an oxide film formed utilizing (a) OR and Si 2*p*_{3/2} spectra arising from oxide films formed utilizing OM at (b) 900 °C, (c) 1000 °C, and (d) 1050 °C, where the spectral intensities of bulk Si are adjusted to be equal to each other in order to demonstrate the influence of oxidation temperature on the the amounts of IMs at the interface. Here, the Si 2*p*_{3/2} spectra were measured at TOAs of 52°. In three thermally

grown oxide films, the composition of suboxides consisting of Si^{3+} , Si^{2+} , and Si^{1+} is almost independent on the oxidation temperature, while the amount of Si^β increases with increase in the oxidation temperature. One of the possible origins of Si^β is the interfacial stress in the Si substrate near the interface.

4. Conclusion

The chemical structures of the compositional and structural transition layers at and near the $\text{SiO}_2/\text{Si}(100)$ interface formed utilizing OR and OM were investigated by measuring angle-resolved Si $2p$ photoelectron spectra. A clear difference between the chemical structure of the SiO_2/Si interface formed using OR and that formed using OM was found. Furthermore, the increase in the amount of Si^β was found to increase with the increase in oxidation temperature. One of the possible origins of Si^β is the interfacial stress in the Si substrate near the interface.

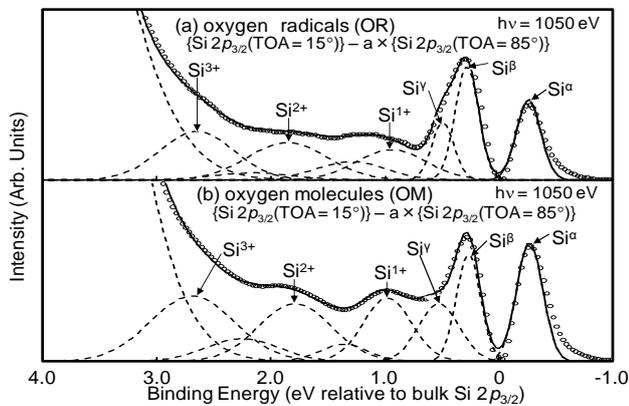


Fig. 1 Si $2p_{3/2}$ spectra obtained by taking difference between two spectra measured at TOAs of 15° and 85° to eliminate spectra arising from bulk Si are shown for SiO_2 film formed utilizing (a) oxygen radicals (OR) and that formed at 900°C utilizing (b) dry oxygen molecules (OM).

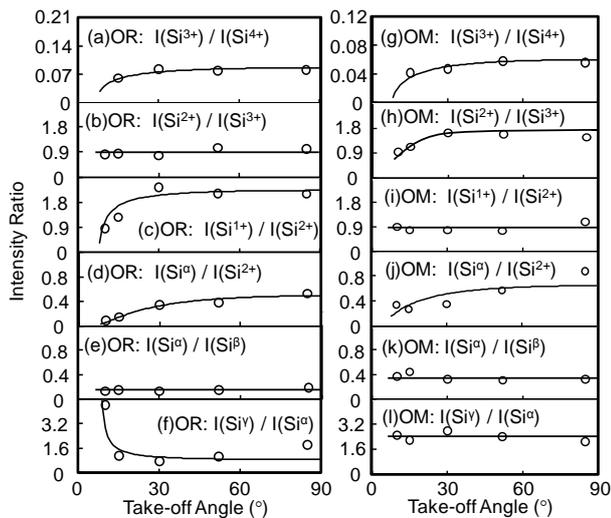


Fig. 2 Integrated intensity ratios expressed by $I(\text{Si}^{3+})/I(\text{Si}^{4+})$, $I(\text{Si}^{2+})/I(\text{Si}^{3+})$, $I(\text{Si}^{1+})/I(\text{Si}^{2+})$, $I(\text{Si}^\alpha)/I(\text{Si}^{2+})$, $I(\text{Si}^\alpha)/I(\text{Si}^\beta)$, and $I(\text{Si}^\gamma)/I(\text{Si}^\alpha)$ as a function of TOA are shown for the SiO_2/Si interface formed utilizing OR and that formed utilizing OM at 900°C .

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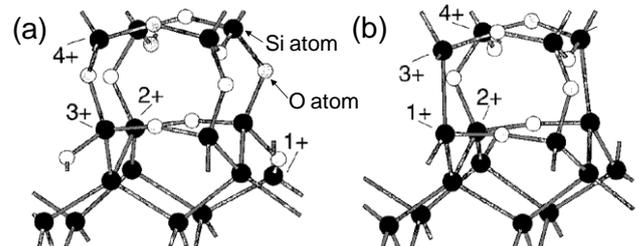


Fig. 3 (a) Approximate bonding configuration in the compositional transition layer at the SiO_2/Si interface formed utilizing OR and (b) that formed utilizing OM [13].

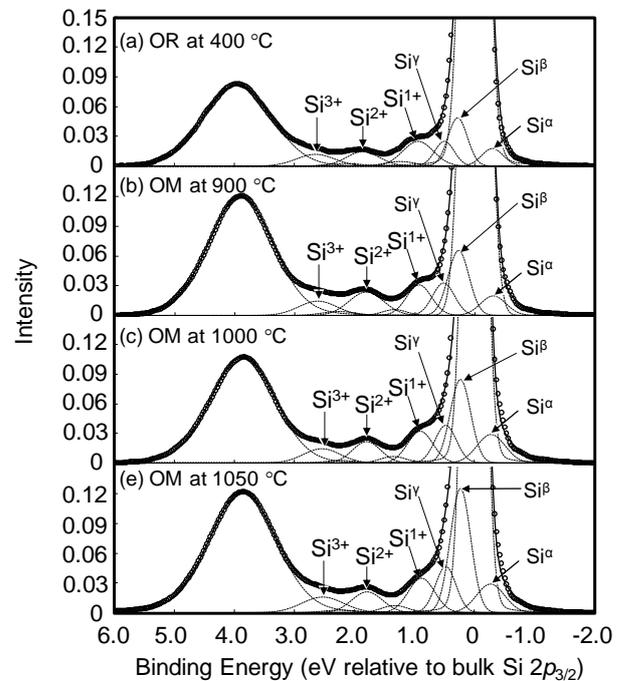


Fig. 4 Si $2p_{3/2}$ spectrum arising from (a) an oxide film formed utilizing OR and Si $2p_{3/2}$ spectra arising from oxide films formed utilizing OM at (b) 900°C , (c) 1000°C , and (d) 1050°C . Here, Si $2p_{3/2}$ spectra were measured at TOA of 52° .