

Dependence of chemical structures of transition layer at SiO₂/Si(100) interface on oxidation temperature, annealing in forming gas, and oxidizing species

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Introduction

The chemical structures of 0.5-nm-thick compositional transition layer (CTL) formed at SiO₂/Si(100) interface [1] have been studied extensively [2,3] because of their significant influence on the performance of Si-based devices. However, the dependences of chemical structures of CTL stabilized by more than one monolayer of SiO₂ on oxidation temperature, annealing in forming gas, and oxidizing species were not clarified yet and is the subject of the present study using angle-resolved photoelectron spectroscopy (ARPES) at photon energy of 1050 eV.

Experimental Results and Discussion

Figure 1(a) shows the Si 2p_{3/2} spectra measured at photoelectron take-off angles at vacuum/oxide interface (TOAs) of 15° and 85° arising from the interface formed in dry O₂ at 900 °C. Figure 1(b), in which the spectra arising from Si-O₄ (Si⁴⁺), Si-Si-O₃ (Si³⁺), Si^{v+}, Si₂-Si-O₂ (Si²⁺), Si^{μ+}, Si₃-Si-O (Si¹⁺), Si substrate (Si⁰), α-Si, β-Si, and γ-Si are resolved, is obtained by taking difference between two spectra in Fig. 1(a), to eliminate the spectrum arising from the bulk Si after multiplying the spectrum measured at a TOA of 85° by an appropriate factor. Here, α-Si, β-Si were found to arise from Si substrate.[3] The α-Si are considered to be affected by its second nearest neighbor O atoms.[4] Because the binding energy (BE) of Si²⁺ > BE of Si^{μ+} > BE of Si¹⁺ can be explained by considering the influence of second nearest neighbor O atoms on Si¹⁺, Si^{μ+} is considered as Si¹⁺ in the analyses of the spectra. Also, because BE of Si³⁺ > BE of Si^{v+} > BE of Si²⁺ can be explained by considering the influence of second nearest neighbor O atoms on Si²⁺, Si^{v+} is considered as Si²⁺ in the analyses of the spectra.

Figures 2(a) and 2(b) show TOA dependences of I₀/I₁₊, I₁₊/I_{μ+}, I_{μ+}/I₂₊, I₂₊/I_{v+}, I_{v+}/I₃₊, I₀/I₄₊, I_α/I₁₊, I_β/I₁₊, and I_γ/I₁₊ measured for the interface formed in dry O₂ at 900 °C and those measured for the interface formed using oxygen radicals at 400 °C, respectively. Here, I₀, I₁₊, I_{μ+}, I₂₊, I_{v+}, I₃₊, I₄₊, I_α, I_β, and I_γ denote the integrated intensity of the Si 2p_{3/2} spectrum arising from Si⁰, Si¹⁺, Si^{μ+}, Si²⁺, Si^{v+}, Si³⁺, Si⁴⁺, α-Si, β-Si, and γ-Si, respectively. Because I_{μ+}/I₂₊ and I_{v+}/I₃₊ are almost independent on TOA in Fig. 2(a), Si¹⁺, Si^{μ+}, and Si²⁺ must be localized in the same layer, and form the first CTL (FCTL) with Si⁰, a part of which forms dimer bonds [5]. Also because I_{v+}/I₃₊ are almost independent on TOA in Fig. 2(a), Si^{v+} and Si³⁺ must be localized in the same layer and form the second CTL (SCTL) with Si⁴⁺. Here, TOA dependence of I₂₊/I_{v+}, which suggests the

spacing of 0.23 nm (> 0.136 nm) between the layer containing Si²⁺ and that containing Si^{v+}, is considered. The same compositions of FCTL and SCTL are also obtained for interfaces formed in dry O₂ at 1000 and 1050 °C, that formed in dry O₂ at 900 °C followed by annealing in forming gas at 400 °C (FGA). Thicknesses of SiO₂ layers denoted by d formed on SCTL in dry O₂ at 900, 1000, and 1050 °C, and that formed in dry O₂ at 900 °C followed by FGA are 0.58, 0.36, 0.44, and 0.61 nm, respectively.

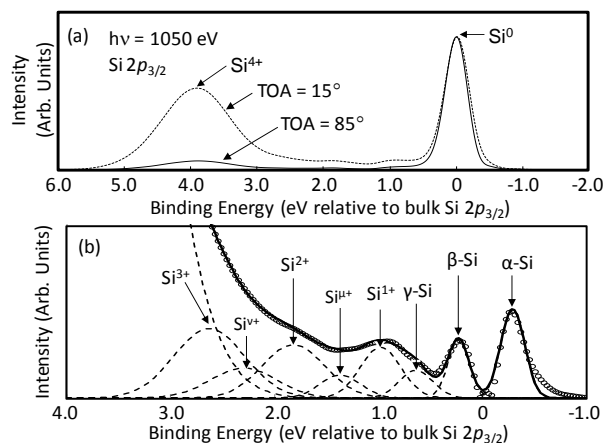


FIG. 1. (a) Si 2p_{3/2} spectra arising from interface formed in dry O₂ at 900 °C measured at photon energy of 1050 eV and photoelectron take-off angles (TOAs) of 15° and 85°, (b) spectrum obtained by taking difference between two spectra in (a) to eliminate the spectrum arising from bulk Si.

Figure 2 was analyzed by considering that one monolayer of Si⁴⁺, that of SCTL, that of FCTL, and that of Si⁰ are continuously connected with each other. For these analyses the volume of Siⁿ⁺ denoted by 1/c_{n+}, the thickness of hypothetical monolayer consisting of Siⁿ⁺ denoted by t_{mn+}, and the inelastic mean free path in hypothetical bulk Siⁿ⁺ denoted by λ_{n+} are defined as follows by considering that Siⁿ⁺ (n = 1, 2, 3) can be expressed as Si_{[1-(n/4)](SiO₂)_(n/4). Firstly, 1/c_{n+} is defined by eq. (1) as follows using c₀ (density of Si atoms in Si⁰) = 5×10²⁸ m⁻³ and c₄₊ (density of Si atoms in Si⁴⁺ in structural transition layer) = 2.38×10²⁸ m⁻³. Secondly, t_{mn+} is defined by D₁₀₀/c_{n+} using c_{n+}. Here, D₁₀₀ denotes areal density of Si atoms on Si(100) and takes a value of 6.8×10¹⁸ m⁻². Furthermore, if the oxidation-induced volume expansion occurs perpendicular to the interface by a factor of (1/c₄₊)/(1/c₀) = 2.10, t_{m4+} takes a value}

of t_{m0} ($=0.136 \text{ nm}$) $\times 2.10 = 0.286 \text{ nm}$. Thirdly, $1/\lambda_{n+}$ is defined by eq. (2) as follows using $\lambda_0 = 1.57 \text{ nm}$ and $\lambda_{4+} = 2.21 \text{ nm}$ by considering that $(1/\lambda_{n+})$ is proportional to the inelastic scattering cross section of Si^{n+} :

$$1/c_{n+} = \{[1 - (n/4)]/c_0\} + \{(n/4)/c_{4+}\}. \quad (1)$$

$$1/\lambda_{n+} = \{1 - (n/4)\}/\lambda_0 + (n/4)/\lambda_{4+}. \quad (2)$$

Contributions of Si^{1+} , $\text{Si}^{\mu+}$, and Si^{2+} to the FCTL and those of $\text{Si}^{\nu+}$ and Si^{3+} to the SCTL are determined as shown in Fig. 3 in such a way that TOA dependences of I_0/I_{1+} , $I_{1+}/I_{\mu+}$, $I_{\mu+}/I_{2+}$, $I_{2+}/I_{\nu+}$, $I_{\nu+}/I_{3+}$, and I_0/I_{4+} in Fig. 2(a) can be consistently explained. Contributions of α -Si, β -Si, and γ -Si to Si substrate spectrum were determined as shown in Fig. 4 in such a way that TOA dependences of I_{α}/I_{1+} , I_{β}/I_{1+} , and I_{γ}/I_{1+} in Fig. 2(a) can be explained. Furthermore, these contributions were found to depend on the oxidation temperature (OT) (900, 1000, and 1050 °C) and FGA as shown in Fig. 3.

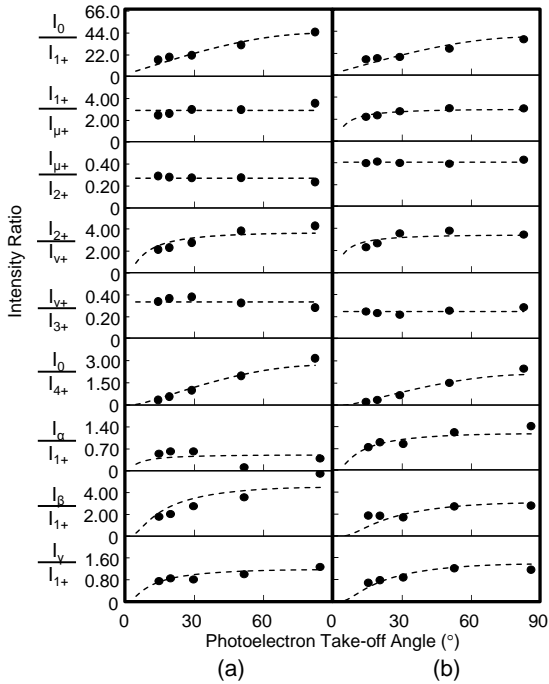


FIG. 2. (a) TOA dependences of spectral intensity ratios measured for interface formed in dry O_2 at 900 °C and (b) those measured for interface formed using oxygen radicals. Dashed lines show calculated curves.

Contributions of Si^{1+} , $\text{Si}^{\mu+}$, and Si^{2+} to the FCTL and those of $\text{Si}^{\nu+}$ and Si^{3+} to the SCTL for the interface formed using oxygen radicals are determined as shown in Fig. 3 in such a way that TOA dependences of I_0/I_{1+} , $I_{1+}/I_{\mu+}$, $I_{\mu+}/I_{2+}$, $I_{2+}/I_{\nu+}$, $I_{\nu+}/I_{3+}$, and I_0/I_{4+} in Fig. 2(b) can be consistently explained. TOA dependences of $I_{1+}/I_{\mu+}$, $I_{\mu+}/I_{2+}$, $I_{2+}/I_{\nu+}$, and $I_{\nu+}/I_{3+}$ suggest followings: 1) $\text{Si}^{\mu+}$ and Si^{2+} are localized in the same layer and are far from the interface only by 0.11 nm ($< 0.136 \text{ nm}$) with respect to the layer containing Si^{1+} . Then, Si^{1+} , $\text{Si}^{\mu+}$, and Si^{2+} are considered to constitute the FCTL with Si^0 as shown in Fig. 3, 2) $\text{Si}^{\nu+}$ and Si^{3+} are localized in the same layer and are considered to constitute SCTL with Si^{4+} as shown in Fig. 3. Contributions of α -Si, β -Si, and γ -Si to Si substrate spectrum are determined as shown in Fig. 4 in such a way that TOA dependences of I_{α}/I_{1+} , I_{β}/I_{1+} , and I_{γ}/I_{1+} shown in Fig. 2(b) can be explained.

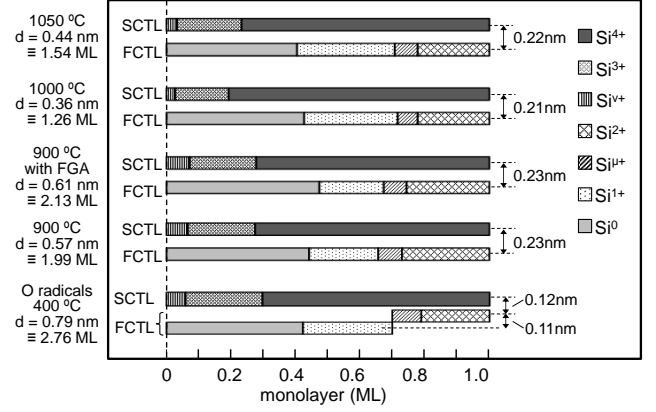


FIG. 3. Contributions of Si^0 , Si^{1+} , $\text{Si}^{\mu+}$, and Si^{2+} to the first compositional transition layer (CTL) and those of $\text{Si}^{\nu+}$, Si^{3+} , and Si^{4+} to the second CTL for five kinds of interfaces.

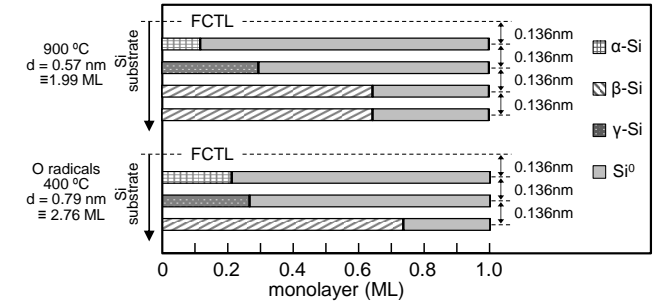


FIG. 4. Oxidation-induced chemical structural changes in amounts of α -Si, β -Si, and γ -Si in Si substrate for two kinds of interfaces.

Conclusion

The dependences of interfacial transition on the oxidation temperature (OT), annealing in forming gas (FGA), and oxidizing species suggest followings: 1) For five kinds of interfaces the first CTL consists of Si^{1+} , $\text{Si}^{\mu+}$, Si^{2+} , and Si^0 , while the second CTL consists of $\text{Si}^{\nu+}$, Si^{3+} , and Si^{4+} , 2) For the interfaces formed in dry O_2 increase in the amount of Si^{1+} with the increase in OT implies the increase in the area of (111) facet with the increase in OT, 3) FGA-induced decrease in the amount of Si^{1+} and Si^{2+} in the first CTL imply that Si-O bonds are broken to form Si-H bonds, 4) In contrast to the oxidation in dry O_2 , by the oxidation using oxygen radicals $\text{Si}^{\mu+}$ and Si^{2+} are formed far from the interface with respect to Si^{1+} , 5) Amount of β -Si formed using oxygen radicals is smaller than that formed by oxidation in dry O_2 .

Acknowledgements

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References

- [1] T. Aiba et al., Jpn. J. Appl. Phys. **34** (1995) 707.
- [2] T. Hattori, Crit. Rev. Solid State Mater. Sci. **20** (1995) 339.
- [3] J. H. Oh et al., Phys. Rev. B **63** (2001) 205310.
- [4] O. V. Yazyev et al., Phys. Rev. Lett. **96** (2006) 157601.
- [5] A. Bongiorno et al., Phys. Rev. Lett. **90** (2003) 186101.