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Effects of interface roughness on the local valence electronic structure at the SiO_2/Si interface: Soft X-ray absorption and emission study

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Abstract. We investigated effects of interface roughness on the local valence electronic structures at SiO_2/Si interface in order to clarify the relation between interface structures and interface electronic properties, by using soft X-ray absorption and emission spectroscopy. For atomically smooth interface, the local valence structures depend on intermediate oxidation states at the interface. For atomically rough interface, on the other hand, the local valence structures at the interface show amorphous-like electronic states irrespective of the intermediated oxidation states.

1. INTRODUCTION

Study of SiO_2/Si interfaces has received much attention not only from an academic view point but also for the technological application of metal-oxide-silicon (MOS) devices, because the interfaces seriously affect the electronic characteristics of MOS devices [1]. Thus, an atomic level understanding of the properties at the SiO_2/Si interface should be important. It is reported that the roughness at SiO_2/Si interface influences the performance of MOS devices. Kobayashi's group and Hahn et al. reported that the interface state density (gap state density) strongly depended on the roughness [2,3]; the rougher interface exhibits larger gap state density. Yasuda et al. successfully produced the SiO_2/Si(111) interface with low interface state density by depositing SiO_2 layer on the atomically flat Si(111) surface [4]. Therefore, the effects of interface roughness on the interface properties should be clarified on atomic scale, which gives information on the improvement of electronic characteristics of MOS devices.

In the present study, we investigated the effects of interface roughness on the local valence electronic structure at SiO_2/Si interface in order to clarify the relation between the interface structures and the interface properties, by using soft X-ray absorption and emission spectroscopy [5].

2. EXPERIMENTAL

After cleaning wafers with an RCA method, atomically rough and smooth SiO_2/Si(111) interfaces were prepared by following methods: for the production of atomically rough interfaces, the wafers were simply immersed in a 1% hydrofluoric solution for 30 s and then 1.5 nm-thick oxide layer was prepared by thermal oxidation of the Si(111) substrate. For the preparation of atomically smooth interfaces, the wafers were immersed in a 1% hydrofluoric solution for 30 s followed by immersion in a 40% NH_4F solution for 15 min., and then a 1.8 nm-thick oxide layer was prepared by thermal oxidation of the Si(111) substrate. We confirmed the atomically rough and smooth SiO_2/Si(111) interfaces using atomic force microscopy; after the etch of the oxide layer away, mono-atomic steps were clearly observed for the atomically smooth interface but steps were not seen for the atomically rough interface. The synchrotron radiation experiments were performed using BL-27SU at SPring-8 with the approval of JASRI as Nanotechnology

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Support Project (Proposal No. 2003B0209-Nsa-np-Na and 2004A0345-Nsa-np-Na). The oxygen K-edge absorption spectra were measured by detecting O KVV Auger electrons at 510 eV and an instrumental energy resolution of 50 meV. Soft X-ray emission (SXE) spectroscopy was performed with 800 meV energy resolution.

3. RESULTS AND DISCUSSION

Figures 1 (a)-(c) show the oxygen K-edge absorption spectra of bulk SiO_2, SiO_2/Si(111) with atomically smooth interface, and SiO_2/Si(111) with atomically rough interface, respectively. As can be seen, the SiO_2/Si(111) spectra have a lower onset than that of bulk SiO_2. Muller et al. used electron energy loss spectroscopy in a scanning transmission microscope and reported that the oxygen K-edge was lowered by 3 eV at the interface compared to the bulk SiO_2 [6]. Thus, the lower onset in the spectra correlates with the unoccupied O 2p states at the interface, i.e., a reduced band gap at the interface. Note that the peak at 537.5 eV is due to the unoccupied O 2p states that are hybridized with Si 3s and 3p states of bulk SiO_2 [7].

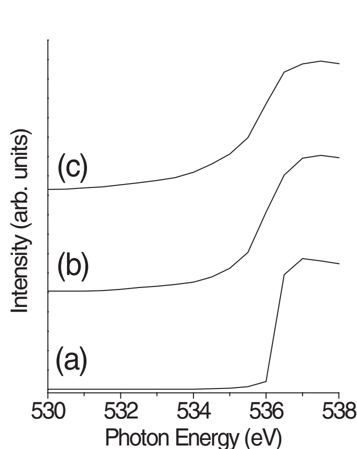

Figure 1. Oxygen K-edge absorption spectra of (a) bulk SiO_2, (b) SiO_2/Si(111) with atomically smooth interface, and (c) SiO_2/Si(111) with atomically rough interface. Incident photon angle was 36° from surface normal and p-polarized light was used. Note that absorption from O 1s orbital to O 2s orbital is forbidden due to the selection rule. Thus, these absorption spectra represent unoccupied O 2p states.

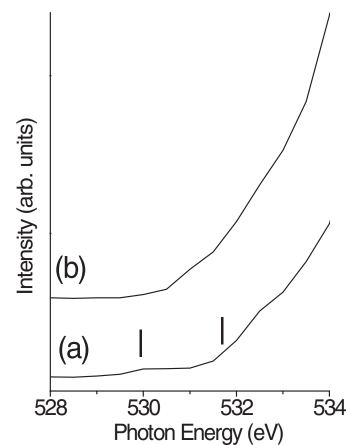

Figure 2. Oxygen K-edge absorption spectra for lower photon energy region of (a) SiO_2/Si(111) with atomically smooth interface and (b) SiO_2/Si(111) with atomically rough interface.

Figures 2 (a) and (b) show the lower absorption energy region for atomically smooth and rough SiO_2/Si(111) interfaces, respectively. The spectrum of the atomically smooth interface has a lower onset with edges structures at 530 and 531.5 eV. The spectrum of the atomically rough interface, on the other hand, has an onset at 531 eV and then exhibits gradual rise in intensity with increasing photon energy. According to our previous studies, absorption edges at 530 and 531.5 eV for the atomically smooth interface are assigned to an O atom bonding to Si^{1+} and Si^{3+} of sub-oxide species at the interface, respectively [8]. As for the atomically rough interface, Wallis et al. showed using theoretical calculations that the oxygen K-edge of the sub-oxide shifts to higher energy as the oxidation number of sub-oxide

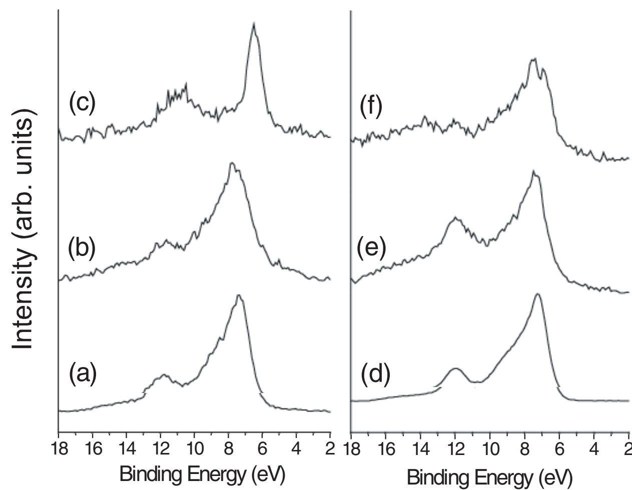

Figure 3. O K-edge SXE spectra for (a)-(c) SiO_2/Si(111) with atomically smooth interface and (d)-(e) SiO_2/Si(111) with atomically rough interface. For the SXE spectra, incident photon energies were 537.5 eV for (a) and (d), 533 eV for (b) and (e), 530 eV for (c) and 531 eV for (f). Incident angle was 60° from the surface normal and a p-polarized light was used. The binding energy was obtained as referred to the O 1s core-level energy.

increases [9]. Thus, the oxygen atoms bonding to Si atoms with higher oxidation number contribute to higher energy region of the absorption spectra. Therefore, we could obtain SXE spectra of specific oxygen atoms bonding to Si atoms with different oxidation number at the interface by choosing excitation energies.

Figure 3 shows the O K-edge SXE spectra for SiO_2/Si(111) with atomically smooth [(a)-(c)] and rough interfaces [(d)-(f)]. With a photon energy of 537.5 eV, the occupied O 2p states of amorphous SiO_2 predominantly contribute to the SXE spectra (Fig. 3(a) and 3 (d)). In these spectra, the peak at 7.25 eV and the shoulder at 8.65 eV are attributed to the O 2p non-bonding states, while the peaks at 11.75 and 14.33 eV are due to the bonding states between O 2p and Si sp^3 orbitals [10]. For the atomically smooth interface, the SXE spectrum shape depends on the incident photon energy. By exciting P1 (Fig 3 (c)), the peak at 6.50 eV, attributed to the non-bonding states of O 2p, is very sharp and has no shoulder. According to our previous sturdy, an ordered structure is formed at the interface [8].

For the atomically rough interface, on the other hand, the SXE spectrum shape is similar to that of amorphous SiO_2, irrespective of incident photon energy. This implies that the atomically rough interface has an amorphous-like state. According to a previous study, the gap state density at the interface for the smooth interface was always lower than that for the rougher interface [2]. Therefore amorphous-like electronic states at the interface play an important role in the formation of gap states at the interface. Moreover, our Si 2p spectra showed that the amount of Si^{2+} species in the interface region were reduced by forming the smooth interface although the amount of other suboxide species did not drastically change. Thus, Si^{2+} species should play an important role in formation of the amorphous-like electronic structure, which may result in formation of the gap states.

4. SUMMARY

We investigated the effects of interface roughness on local valence electronic structures at SiO_2/Si interface in order to clarify the relationship between the interface structure and the interface properties, by using soft X-ray absorption and emission spectroscopy. For atomically smooth interface, the local valence structure depends on intermediate oxidation states at the interface. For atomically rough interface, on the other hand, the local valence structure is always the amorphous-like electronic state. These results

indicate that the amorphous-like electronic state at the interface play an important role in the formation of gap states at the interface.

Acknowledgments

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