

Electronic structures of silicon monoxide film probed by XPS and NEXAFS

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Introduction

Non-stoichiometric silicon oxide (SiO_x ; $0 < x < 2$) have been widely studied due to their various applications such as electric and optical devices. However, the structures of SiO_x are not fully understood. Furthermore, a controversy remains as to the crystal and electronic structures of silicon monoxide (SiO), which is the simplest intermediate compound between Si (Si^0) and SiO_2 (Si^{4+}) [1]. In this report, we present the electronic structures of SiO thin films deposited on a solid surface by X-ray photoelectron spectroscopy (XPS) and NEXAFS. As a substrate, we used highly oriented pyrolytic graphite (HOPG), because its surface is flat and chemically inert, so we will possibly obtain pure electronic structures of SiO without hybridization with the substrate.

Experimental

All the experiments were performed *in situ* at the BL-27A station. High-purity silicon monoxide powder was evaporated on an HOPG surface. The thickness of the layer was precisely controlled. The surface chemical states were analyzed by XPS and Si *K*-edge NEXAFS. NEXAFS spectra were recorded by total electron yield mode.

Results and discussion

Fig.1 shows the Si 1s XPS spectra for SiO deposited on HOPG and reference materials. Thickness of the SiO film was about 0.060 nm, which corresponds to one-fifth of monolayer. For the SiO powder (spectrum (b)), two peaks (marked C and D) are seen, which correspond to the elemental Si (Si^0) and SiO_2 (Si^{4+}), respectively. The intermediate valence states are scarcely seen. On the other hand, a single peak (marked E) is observed for the SiO deposited on HOPG. The energy of this peak (1843.6 eV) is located just between those of the Si (Si^0) and SiO_2 (Si^{4+}), which suggests that the silicon atoms in deposited SiO remain divalent states.

Fig.2 shows the NEXAFS spectra for SiO on HOPG and reference materials. For Si(001) (Si^0) and SiO_2 (Si^{4+}), the most intense peaks (marked A and B) are due to the resonance excitations from the Si 1s to the valence unoccupied σ^* states mostly composed of $3p^*$ orbitals. For SiO powder, the resonance peaks corresponding to Si^0 and Si^{4+} are observed as main species. In addition, a shoulder (marked C) is seen just between two peaks, which suggests the existence of divalent states. For SiO on HOPG, a sharp peak (marked D) and a shoulder (marked E) are observed. The energy of these peaks is close to that of the peak C, suggesting that the valence states of silicon in deposited layer was mostly Si^{2+} . The double peak structures (D and E) would be attributed to

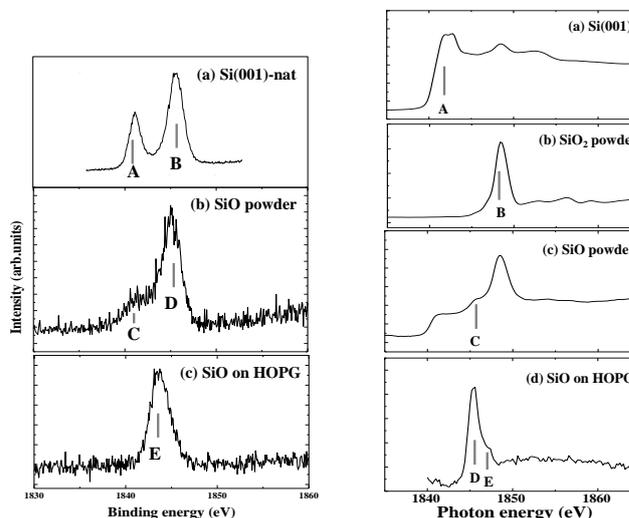


Fig.1 Si 1s XPS spectra for (a) naturally oxidized Si(001), (b) SiO powder, and (c) SiO deposited on HOPG. Photon energy was 3000 eV.

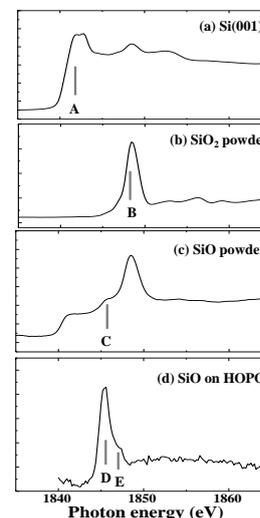


Fig. 2 Si *K*-edge NEXAFS spectra for (a) Si(001) , (b) SiO_2 powder, (c) SiO powder, and (d) SiO deposited on HOPG.

the resonance excitations from Si 1s to valence unoccupied orbitals with π^* and σ^* characters in the Si-O triple bond, respectively [2]. To confirm the assignments of these two peaks, we calculated the electronic structure of an SiO molecule using discrete variational (DV)-X α method [3]. As a result, it was elucidated that the lower-energy resonance (peak D) corresponds to the excitation from the Si 1s into $3e_1$ state with π^* character, while the high-energy one (peak E) is attributed to that into $8a_1$ state with σ^* character. It was also calculated that the energy separation of these two peaks are 3.8 eV [3], which is closed to the experimental values of the energy difference between peaks D and E.

On the basis of the results, it was elucidated that the SiO molecules deposited on HOPG surface remain their molecular forms, and the valence states of silicon in the deposited layer are surely divalent.

References

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