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Surface Science

Electronic structures of silicon monoxide film probed by X-ray absorption spectroscopy

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ABSTRACT

Electronic structures of thin films of silicon monoxides (SiO) deposited on a solid surface have been *in-situ* investigated by X-ray photoelectron spectroscopy (XPS) and X-ray absorption fine structure (XAFS). As a substrate, a highly oriented pyrolytic graphite (HOPG) was used because the hybridization between molecules and substrate can be excluded due to the inertness of the surface. For thin films with less than monolayer, XPS spectrum showed that the binding energy of the Si $1s$ is located just between those of the elemental silicon (Si^0) and SiO_2 (Si^{4+}). The result indicates that the stable divalent silicon surely exists in the deposited SiO layer. For the Si K-edge XAFS spectrum of the SiO thin film, the energy of the core-to-valence resonance peak is also located between those of the elemental silicon (Si^0) and SiO_2 (Si^{4+}). The polarization dependence of the Si K-edge XAFS spectra for the SiO film revealed that the SiO molecules are well-ordered and almost perpendicularly oriented on HOPG surface. The XAFS results also support the existence of the silicon divalent states in the deposited SiO films. The obtained well-ordered SiO films with divalent silicon will become an excellent starting material for the synthesis of low-dimensional SiO_x films.

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1. Introduction

Non-stoichiometric silicon oxide (SiO_x with x < 2) has been widely studied due to their various applications. In early stage, thin films of SiO_x have been practically used as coating in metallic mirrors, antireflection coatings and low index layers for middle infrared rays [1–3]. During last decades, this material has become a target of interest as new electric and optical devices [4]. Recent rapid progress in nanotechnology is accelerating the interests in the nano-structures of SiO_x as well as silica. For example, nano-structured SiO_x has shown unique optical properties leading to promising applications in electronic and optical devices [5–7]. Also, SiO_x nanotubes have been extensively investigated due to its potential applications such as field effect transistors, gas sensors and bio-molecular delivery [8–14].

In spite of such rapid interests in SiO_x, the structures of SiO_x have not been fully understood. To begin with, surprisingly, the structures of stoichiometric silicon monoxide (SiO), the simplest intermediate compound between SiO_2 and Si, have not yet been fully elucidated. The structures of isolated molecular SiO have been rather well studied because of its stability in gas phase. The electronic structures of gaseous SiO have been clarified in terms of an equivalent electronic configuration with carbon monoxide. On the other hand, the crystal and electronic structures of solid SiO are still under controversy [15].

Concerning the electronic structures of solid SiO, Senemaud et al. have first measured the X-ray absorption spectra for SiO using X-ray

tube, and concluded that SiO is not a simple mixture of Si and SiO_2 but has several tetrahedral configurations [16]. This was supported by Kim et al., who have measured X-ray absorption fine structures (XAFS) for SiO, and clarified that silicon in SiO has intermediate oxidation states forming a random network of Si–Si and Si–O bonds [17]. Yubero et al. have measured the electronic structures of SiO deposited on oxygen-passivated Cu(100) surface by photoemission spectroscopy and XAFS, and identified the Si^{2+} species in polymeric form [18]. However, contradictory results have been reported. Friede et al. have measured the ^{29}Si nuclear magnetic resonance (NMR) and XAFS spectra and elucidated that SiO powder is simply the mixture of Si and SiO_2 [19]. These discrepancies may come from the instability of solid SiO phase. SiO easily converts to the mixture of Si and SiO_2 at an ambient condition through the disproportionation reaction; $2SiO \rightarrow Si + SiO_2$. Up to now, exact electronic structures of pure SiO without any Si and SiO_2 contribution have not been reported.

In the present paper, we report on the electronic structures of SiO thin films deposited on a solid surface. As a substrate, we chose highly oriented pyrolytic graphite (HOPG), because its surface is chemically inert, and perfectly flat, so we will possibly obtain pure electronic structures of SiO without hybridization with the substrate. The electronic structures were *in-situ* determined by X-ray photoelectron spectroscopy (XPS) and XAFS using soft X-rays from synchrotron light source.

2. Experimental

High-purity silicon monoxide (Furuuchi Chemical Co., Chunk) was used as a source material. The chunk was pulverized by mortar and

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put into the evaporation crucible. An HOPG (Techno Chemics Inc. 10 mm × 10 mm × 1 mmt) was used as a substrate. Fresh surface of the HOPG was obtained by cleaving in atmosphere, and it was immediately transferred into the preparation chamber. As reference materials, high-purity SiO_2 powder and Si(001) single crystal were also used.

Experiments were performed at the BL-27A station of the Photon Factory in the High Energy Accelerator Research Organization (KEK-PF). The X-rays were emitted from the bending magnet, and the photon energy was tuned by an InSb(111) double crystal monochromator. The X-rays were linearly polarized at the horizontal direction. The photon flux was ~10^{10} photons cm^{-2} s^{-1}. The energy resolution of the monochromator was 0.9 eV at 2000 eV.

The analysis chamber consisted of a manipulator, an electron energy analyzer, and a flood electron gun. The base pressure of the analysis chamber was 1×10^{-8} Pa. The sample was horizontally located, and it can be rotated around the vertical axis. The preparation chamber consisted of a vacuum evaporator and a sample transfer system. The base pressure of the preparation chamber was 1×10^{-6} Pa. The sample can be transferred between two chambers without exposing to air.

XPS spectra were measured with hemispherical electron energy analyzer (VSW Co. Class-100). The X-rays were irradiated at 55° from surface normal and the take-off direction of photoelectrons was surface normal. Typical photon energy used for XPS measurements was 3000 eV. The binding energy was normalized by the C 1s photoelectrons of HOPG at 284.3 eV.

The X-ray absorption fine structure (XAFS) spectra were measured by plotting a sample drain current as a function of the photon energy (total electron mode). The sample current was normalized by the photon flux measured by the drain current of an aluminum mesh located in front of the sample. Both XPS and XAFS measurements were carried out at room temperature.

The evaporator consisted of a tantalum crucible surrounded by the spiral type tungsten filament. The crucible was floated at + 1.5 kV while the filament was grounded. Thus the crucible was heated by the bombardment of 1.5 keV electrons. The distance between the crucible and the substrate was 30 mm. A shutter that is electrically isolated from the ground was equipped between the crucible and the substrate in order to control evaporation rate of the source material. Since some of the evaporated molecules are ionized due to the surface ionization, a positive current was observed at the shutter. The thickness of the film was precisely determined by the product of the shutter current and the evaporation time that was calibrated by XPS measurements. The typical vacuum pressure during the deposition was 1.3×10^{-4} Pa. The substrate was kept at room temperature during the evaporation.

3. Results and discussion

3.1. XPS spectra

Fig. 1 shows the wide-scan XPS spectrum for SiO film deposited on HOPG. The pressure during the deposition was 1.3×10^{-4} Pa, and the deposition time was 10 min. Under this condition, the shutter current was 3.0 nA. The narrow scans of Si 1s and C 1s regions are also shown as small insets. For Si 1s narrow scan, a single peak is seen, suggesting that the deposited SiO was not a mixture of different valence states (discussed later).

The saturated thickness depended on the evaporation rate. At extremely high evaporation rate (pressure > 1×10^{-3} Pa), multilayer SiO film was observed. But we consider that the formation of such multilayered film was due to the bumping of SiO chunk in the crucible. At normal evaporation rate (pressure < 5×10^{-4} Pa), the thickness of the film was saturated. In Fig. 2(a), the intensity ratio of the photoelectrons, $I_{\text{Si } 1s}/I_{\text{C } 1s}$, is plotted as a function of the deposition time. During the deposition, the pressure was constant to be 1.3×10^{-4} Pa. The
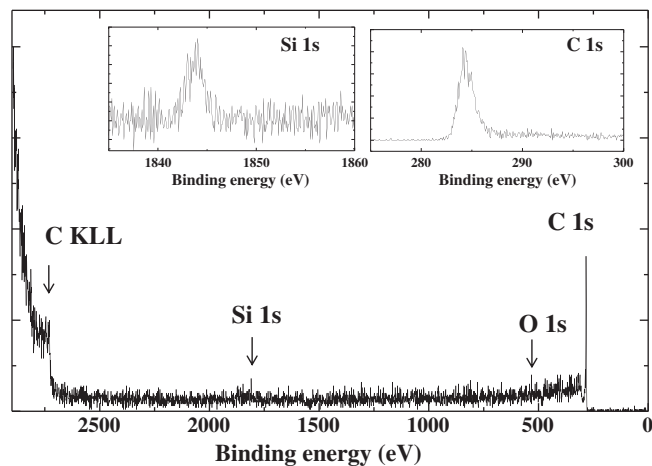

Fig. 1. Wide-scan XPS spectrum for SiO deposited on HOPG. The photon energy was 3000 eV. The pressure during the deposition was 1.3×10^{-4} Pa, and the deposition time was 10 min. Narrow scans in the Si 1s and C 1s regions are also shown in small insets as expanded scale.

$I_{\text{Si } 1s}/I_{\text{C } 1s}$ ratio for sample B (10 min deposition) is 0.14. The $I_{\text{Si } 1s}/I_{\text{C } 1s}$ did not increase even for longer deposition time (samples C and D). The result suggests that the multi-layered thick films were not produced under the present condition, which may come from the volatile property of silicon monoxide.

In order to know the saturated thickness of the SiO film, we estimate the thickness using the peak intensities of the C 1s (substrate) and Si 1s (adsorbate) in XPS. If we assume that the SiO layer is homogeneous, the intensity ratio of the photoelectrons, $I_{\text{Si } 1s}/I_{\text{C } 1s}$, is expressed as

$$\frac{I_{\text{Si } 1s}}{I_{\text{C } 1s}} = \sigma_{\text{Si } 1s} \cdot \lambda_{\text{Si } 1s \text{ in SiO}} \cdot n_{\text{Si in SiO}} \qquad (1)$$
$$\cdot \frac{1 - \exp(-d/\lambda_{\text{Si } 1s \text{ in SiO}})}{\sigma_{\text{C } 1s} \cdot \lambda_{\text{C } 1s \text{ in HOPG}} \cdot n_{\text{C in HOPG}} \cdot \exp(-d/\lambda_{\text{C } 1s \text{ in SiO}})}$$

where σ (barn) is the photoionization cross section [20] for the respective photoelectron indicated as a subscript, λ (nm) is the inelastic mean free path (IMFP) of the photoelectrons in the material indicated as a subscript [21], n is the atomic concentration of an element in the material shown as a subscript, and d is the thickness of the SiO layer in nm.

In Fig. 2(b), the $I_{\text{Si } 1s}/I_{\text{C } 1s}$ ratio calculated by Eq. (1) is plotted as a function of d (nm). As a result, the thickness of the samples B, C and D is about 0.060 nm. It is difficult to define the monolayer because the shape of SiO molecule is linear. If we assume that the shape of the SiO is sphere, the approximate thickness of a mono-layered SiO is about 0.32 nm, so the saturated thickness of the deposited layer is about one-fifth of monolayer. The reason of the thickness saturation would be that SiO molecules adsorb on the specific sites of the honeycomb structure of carbon atoms in HOPG surface. One of the plausible sites is the center of the hexagon of carbon atoms because of the strong interaction between Si and π^* orbitals, as described in Section 3.3.

Fig. 3 shows the Si 1s XPS spectra for the SiO film and reference materials. It is well known that the surface of silicon single crystal is covered with stoichiometric natural oxides whose composition is pure SiO_2 (Si^{4+}). Thus the peaks A at 1841.9 eV and B at 1846.0 eV for naturally oxidized Si(001) (spectrum (a)) are due to the elemental Si (Si^0) and SiO_2 (Si^{4+}), respectively. For the XPS spectrum of SiO powder (spectrum (b)), two peaks (C and D) are seen. The energies of the peaks C and D are in agreement with those of the peaks A and B, respectively. The intermediate valence states are scarcely seen between two peaks. This means that SiO molecules at the surface of the powder are disproportionate to Si (Si^0) and SiO_2 (Si^{4+}).