

Orientation of silicon monoxide adsorbed on highly oriented pyrolytic graphite

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Introduction

Silicon monoxide (SiO) is the simplest intermediate compounds between elemental silicon (Si⁰) and silicon dioxide (Si⁴⁺). SiO molecule is stable in gas phase due to its triple bond, so the electronic structures of SiO molecule have been well investigated in terms of an equivalent electronic configuration with carbon monoxide. On the other hand, a controversy remains concerning the structure of SiO in solid phase. As to the SiO deposited on highly oriented pyrolytic graphite (HOPG), we have found that the silicon atoms in deposited SiO film keep divalent states (Si²⁺) [1]. In this report, we present the structures of SiO deposited on HOPG by the measurements on the polarization-dependent Si *K*-edge NEXAFS spectra.

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 0.060 nm, which corresponds to one-fifth of monolayer. NEXAFS spectra were recorded by total electron yield mode. The sample was vertically located, and it was rotated around the vertical axis.

Results and discussion

Fig.1 shows the incident angle dependence of Si *K*-edge NEXAFS spectra for SiO on HOPG. The double peak structures (marked A and B) are attributed to the resonance excitations from Si 1s to valence unoccupied orbitals with π^* and σ^* characters in the Si-O triple bond [2]. The top view of the sample is illustrated in the figure. The X-rays from the synchrotron light source were linearly polarized at horizontal direction, and the sample was rotated around the vertical axis.

A remarkable polarization-dependence is observed as to the intensities of two peaks. The intensity of the peak A increases with the increase in the incident angles of X-rays. In contrast, the intensity of the peak B decreases with the increase in the incident angles. If a silicon atom in SiO molecule is hybridized with the adjacent atoms, such clear polarization dependence would not be observed, because silicon atoms prefer to form sp³ configuration with poor symmetry.

Peak intensity *I* of the NEXAFS spectra using the synchrotron beam of electric field vector *E* is expressed as,

$$I \propto |\mathbf{E} \cdot \mathbf{O}|^2 \propto \cos^2 \delta \quad (1)$$

where *O* is the vector of the final state orbital and δ is the angle between *E* and *O* [3]. Thus, the polarization dependences in Fig.1 indicate that the direction of the

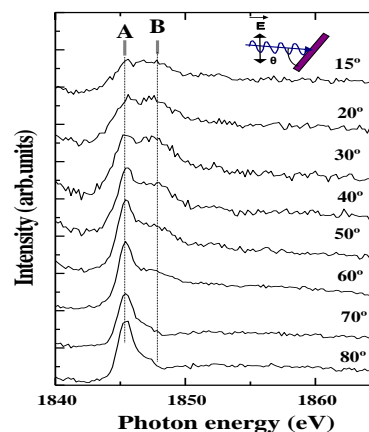


Fig.1 Incident-angle dependence of Si *K*-edge NEXAFS spectra for SiO deposited on HOPG surface.

final-state orbitals represented by the peak A is parallel to the HOPG surface, while that represented by the peak B is perpendicular to the surface. Thus the observed polarization dependence shows that SiO molecules are standing-up at the surface. The detailed angle of SiO axis was determined by the angle dependence of the intensities of the two peaks by deconvoluting the peaks [4]. As a result, it was elucidated that the angle between Si-O axis and the surface was nearly 90 degree. The observed standing-up orientation is similar to that reported for CO molecules adsorbed on a metal surface [5]. We consider the reason for the standing-up configuration is as follows.

Although HOPG surface is chemically inert and flat, the relatively strong interaction between CH bonds and π orbitals of aromatic compounds has been reported [6]. In that case, electrons are donated from π orbitals to CH bonds. In the present case, the π orbitals of HOPG surface attract terminal Si atoms in SiO, because silicon atoms in SiO molecules are positively charged. As a result, SiO molecules stand up on HOPG with Si atoms at lower side.

References

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