27A/2012G553

Polarization dependence observed in NEXAFS for ultra-thin silicon films

Yuji BABA*, Iwao SHIMOYAMA, Norie HIRAO, Tetsuhiro SEKIGUCHI
Japan Atomic Energy Agency, Tokai-mura, Naka-gun, Ibaraki 319-1195, Japan

Introduction

Theories have predicted that mono-layered silicon would be stable as a freestanding sheet either in a flat or in a slightly puckered configuration, exhibiting similar structure to graphene [1]. Experimentally, many attempts have been made as to the synthesis of graphene-like silicon [2], but a question still remains as to whether a flat freestanding sheet of mono-layered silicon with graphene-like structure surely exists or not. In the present study we applied X-ray photoelectron spectroscopy (XPS) and Si *K*-edge near-edge X-ray absorption fine structures (NEXAFS) using synchrotron radiation to elucidate the geometrical and electronic structures of ultra-thin silicon films deposited on a highly oriented pyrolytic graphite (HOPG).

Experimental

All the experiments were performed *in situ* at the BL-27A station. High-purity silicon rod was heated by electron bombardment, and evaporated on an HOPG surface. The thickness of the layer was calibrated by XPS peak intensities. 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

For Si 1*s* XPS spectra, the peak energy of the Si 1*s* for the ultra-thin film (0.041 nm) is higher by 4.2 eV than that for the bulk silicon. The higher-energy shift of core-level for thin film can be interpreted by the increase in the ionization potential due to the low dimensionality of the film.

Figure 1 shows the Si *K*-edge NEXAFS spectra for silicon film on HOPG. The thicknesses of the layer was 0.041 nm, which corresponds to 0.15 monolayer. Two distinct peaks (A and B) are observed, both of which were not seen in bulk silicon. Deduced from the C *K*-edge NEXAFS spectra for graphite [3], it is suggested that the peaks A and B are due to the resonance excitations from Si 1*s* into valence unoccupied states with π^* and σ^* characters, respectively. Such core-to-valence resonance peaks in low-dimensional silicon were firstly reported by Padova *et al.*, who have measured reflection electron energy loss spectra (REELS) for silicon nano-ribbons on Ag(110), and observed the loss peaks corresponding to the transitions Si $1s\rightarrow\pi^*$ and Si $1s\rightarrow\sigma^*$ [4]. In order to confirm the peak assignments and the energy of the resonance peaks, we calculated the electronic structures of mono-layered silicon with graphene-like structure using discrete variational (DV)-Xα method. It was elucidated that the valence unoccupied orbitals are composed of two distinct states. The lower energy state is attributed to out-of-plane molecular orbital that consists of mainly Si 3*p* orbitals, and the main components of the higher energy state are attributed to in-plane molecular orbitals [5]. So we assign that the peak A to the resonance from Si 1*s* into Si $3p_z^*$ that is perpendicular to the surface (out-of-plane), and the peak B is due to that from Si 1*s* into the orbitals that are parallel to the molecular plane (in-plane).

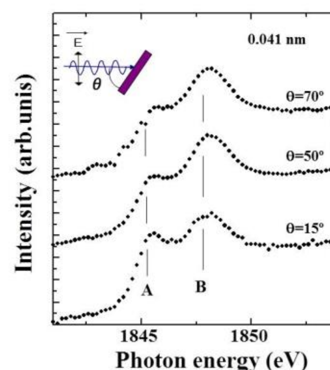

Fig. 1 Incident-angle dependence of Si *K*-edge NEXAFS spectra for Si films deposited on HOPG. Thickness of the layer is 0.041 nm. The top view of the sample is illustrated in the upper side. The incident angle of X-rays is shown in each spectrum.

A clear polarization-dependence is observed as to the intensities of two peaks. Judging from the C *K*-edge NEXAFS spectra for graphite [3], the observed angle dependence indicates that a part of the ultra-thin silicon film has anisotropic configuration, and the layer would form graphene-like structure that is parallel to the HOPG surface.

References

[1] For example, K.Takeda, K. Shiraishi, Phys. Rev. B **50**, 14916 (1994).
[2] For example, A. Fleurence *et al*. Phys. Rev. Lett. **108**, 245501 (2012).
[3] R.A. Rosenberg, P. Love, P. R. LaRoe, V. Rehn, C. C. Parks, Phys. Rev. B **31**, 2634 (1985).
[4] P. De Padova, C. Quaresima, B. Olivieri, P. Perfetti, G. Le Lay, Appl. Phys. Lett. **98**, 081909 (2011).
[5] I. Shimoyama, private communication.

* baba.yuji@jaea.go.jp