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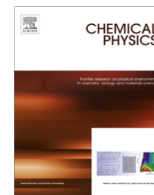

Structures of quasi-freestanding ultra-thin silicon films deposited on chemically inert surfaces

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ABSTRACT

Silicon thin films were deposited on a sapphire and a highly oriented pyrolytic graphite (HOPG), which have atomically flat and chemically inert surfaces. The electronic and geometrical structures of the films were analyzed by X-ray photoelectron spectroscopy (XPS) and polarization-dependent X-ray absorption fine structure (XAFS). It was found that the silicon *K*-edge XAFS spectra for ultra-thin silicon films thinner than 0.2 monolayer exhibited two distinct resonance peaks which were not observed for bulk silicon. The peaks were assigned to the resonance excitations from the Si 1*s* into the valence unoccupied orbitals with π^* and σ^* characters. The average tilted angle of the π^* orbitals was determined by the polarization dependencies of the peak intensities. It was demonstrated that direction of a part of the π^* orbitals in silicon film is perpendicular to the surface. These results support the existence of quasi-freestanding single-layered silicon films with sp^2 configuration.

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1. Introduction

Graphene, one of the carbon allotropes, has recently attracted considerable attention because of its excellent optical and electrical properties. Graphene is atomically flat single-layered sheet exhibiting honeycomb structure containing sp^2 configuration. Silicon belongs to the same group as carbon in the periodic table, and generally takes tetra-valence states like carbon. However in contrast to carbon, silicon tends to form sp^3 configuration with the surrounding silicon atoms in solid phase. Even for a thin film, silicon atoms deposited on a solid surface generally agglomerate, and form three-dimensionally spread diamond-like structure with sp^3 bonds.

In spite of these generally accepted features, recent theoretical works have shown that there exists a stable phase of single-layered silicon with graphene-like structure either in a flat or in a slightly puckered configuration [1–10]. A single-layered silicon with graphene-like structure is recently called "silicene". If silicene structure surely exists, an outstanding characteristic is the presence of a Dirac cone in the band structure like graphene [3]. The existence of a Dirac cone results in the gapless excitations with a linear dispersion, which leads to the applications to optoelectronics and transistors in micro-electronics composed of only silicon atoms. Furthermore a graphene-like silicon may exhibit excellent electric properties such as tunable band-gap induced by quantum spin Hall effect and topological modification [11–21]. However, it should be noted that the graphene-like silicon dealt with in these theoretical works are assumed to be "freestanding", where the interaction between the substrate and silicon is not fully considered.

Up to now, many experimental works have been conducted as to the synthesis of silicene [22–36]. In these works, metallic single crystals such as Ag(111) were used as substrates. However, it should be noted that silicon atoms are highly reactive with many metals and tend to form stable silicide. Therefore the contribution of the hybridization between silicon and substrate cannot be excluded in these experimental works. Actually it was reported that band structure of silicene deposited on Ag(111) drastically modified by the hybridization between the silicon and silver atoms, and the silicene loses its Dirac fermion characteristics due to substrate-induced symmetry breaking [37]. The effect of the hybridization between silicene and metals was supported by the theoretical calculations [38,39].

As to the graphene-like silicon that is weakly bound on the substrate, Fleurence et al. have recently showed that graphene-like silicon is formed through surface segregation on zirconium diboride thin films grown on Si wafers [40]. The layer obtained in their work was buckled. They concluded that the electronic properties of single-layered silicon are modified by the buckling due to epitaxial

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strain. Neek-Amal et al. have calculated by density functional theory that singe-layered silicon intercalated between graphene layers is weakly bound though van der Waals force, and it is possibly stable well above the room temperature [41]. The stable silicon layer calculated by them was also buckled hexagonal arrangement. In spite of these works, a question still remains as to whether a "freestanding" sheet of mono-layered silicon with graphene-like structure surely exists or not.

As mentioned above, silicon atoms tend to interact with most of metals forming stable silicide, so the better way to synthesize "freestanding" graphene-like silicon is to deposit silicon on "atomically flat" and "chemically inert" surfaces. In the previous communication, we presented the results for the X-ray absorption fine structure (XAFS) analysis for ultra-thin silicon films deposited on a highly oriented pyrolytic graphite (HOPG) [42]. On the basis of qualitative speculation, we have shown that a part of the deposited layer lies flat on the surface [42].

In the present paper, we show the XAFS spectral data for ultra-thin films of silicon deposited on sapphire substrate as well as on HOPG. Both substrates are chemically inert and atomically flat, so it is appropriate surfaces for the deposition of freestanding silicon films. Transparent and insulating properties of sapphire are suited for future applications of silicene as optical and electric devices. On the basis of the quantitative analyses of the polarization dependencies in the Si *K*-edge XAFS spectra, the average tilted angle of the molecular orbitals relative to the surface was determined, and the existence of quasi-freestanding graphene-like silicon film is discussed.

2. Experimental

As substrates, a sapphire (C-plane (0001), 10 mm × 10 mm × 0.2 mm, Jiaozuo City Crystal Photoelectric Materials Co., Ltd.) and an HOPG (10 mm × 10 mm × 1 mm, Techno Chemics Inc.) were used. The surface of the sapphire was polished, and it was annealed at 900 °C for 60 min in air to prepare an atomically flat surface. The sapphire was then rinsed by supersonic waves in ethanol for 15 min, and was introduced into the vacuum chamber. A fresh surface of HOPG was obtained by cleaving in dry nitrogen atmosphere. Then the sample was transferred into the vacuum chamber without exposing to air.

For the evaporation of silicon, a high-purity silicon rod was used as a source material. The evaporator consisted of a tantalum crucible surrounded by the spiral tungsten filament. The crucible was floated at +1.5 kV. The filament was grounded, so the crucible was heated by the bombardment of 1.5 keV electrons. The distance between the crucible and the substrate was 20 mm. A shutter that is electrically isolated from the ground was set between the crucible and the substrate. A part of evaporated silicon atoms was ionized due to the surface ionization, thus a positive current was observed at the shutter during the evaporation. The thickness of the film was estimated by the product of the shutter current and the evaporation time using a calibration curve obtained in advance by the X-ray photoelectron spectra (XPS). The base pressure of evaporation chamber was 5×10^{-9} Pa, and the typical vacuum pressure during the deposition was 1.3×10^{-4} Pa. The substrate was kept at room temperature during the evaporation.

The XPS and XAFS measurements were performed at the soft X-ray beamline (BL-27A) of the Photon Factory in the High Energy Accelerator Research Organization (KEK-PF). In this beamline, photons were emitted from the bending magnet, and they were linearly polarized at the horizontal direction. The photon energy was tuned by an InSb(111) double crystal monochromator. The typical photon flux was $\sim 10^{10}$ photons cm^{-2} s^{-1}. The energy resolution of the monochromator was 0.85 eV at 1850 eV (around Si *K*-edge).

The experimental apparatus at the end of the beamline was composed of two vacuum chambers, *i.e.*, analysis chamber and preparation chamber. The analysis chamber consisted of a four-axis manipulator, an electron energy analyzer, and an electron flood gun for surface charge compensation. The base pressure of the analysis chamber was 1×10^{-8} Pa. The sample was vertically located, and it was 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 5×10^{-9} 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 35° from the surface, and the take-off direction of photoelectrons was surface normal. Typical photon energy used in XPS measurements was 3000 eV. Sapphire is a wide-gap insulator, so the surface charging induced by photoemission caused a serious problem in XPS measurements. Using electron flood gun, the charging effect was fairly reduced, and the kinetic energy of all photoelectrons were linearly shifted by a few eV to lower energy. So, the binding energy for sapphire substrate was calibrated by the O 1*s* photoelectrons from sapphire at 531.6 eV [43]. For HOPG, the binding energy was calibrated by the C 1*s* photoelectrons from HOPG at 284.3 eV [43].

The XAFS spectra were measured by plotting a sample drain current as a function of the photon energy (total electron yield, TEY). The sample current was normalized by the photon flux measured by the drain current of an aluminum mesh located in front of the sample. Before the silicon deposition, we measured the XAFS spectra for clean surfaces of sapphire and HOPG as background spectra. These background spectra were subtracted from the XAFS spectra after the silicon deposition.

3. Results and discussion

Fig. 1 shows the Si 1*s* XP spectra of silicon deposited on sapphire (left) and HOPG (right). The thickness of the silicon layer was estimated from the XPS peak intensity ratio of silicon (Si 1*s*) to substrate (Al 1*s* for sapphire and C 1*s* for HOPG). In these estimation, we assumed that the deposited layer is homogeneous. So the thickness and number of silicon layers shown in the figure are averaged values. The details of the thickness calculation were described elsewhere [42]. For sapphire (left figure), the energy of the Si 1*s* peak (marked A) for 5.5-layered sample is located at 1840.9 eV. This energy is almost the same as that for bulk silicon [44]. Also a plasmon loss peak (marked B) is clearly seen at 18 eV higher binding energy (lower kinetic energy). Thus, 5.5-layered sample exhibits bulk feature. On the other hand, the peak energy for the 0.09-layered film (marked C) is higher by 4.5 eV than that for the 5.5-layered film. The higher binding energy peak for a thin film than that for the bulk are not due to the formation of SiO_2 as following reasons. Firstly, evaporation was conducted under ultra-high vacuum condition without oxygen contamination. Secondly, if the deposited silicon is bonded to oxygen in sapphire, the silicon atom would be bonded to at most two oxygen atoms. Thus silicon atoms do not form SiO_4 network but partially oxidized. The present energy shift (4.5 eV) is larger than that for partially oxidized silicon such as divalent silicon [45]. Furthermore, the Si K-edge XAFS spectra for the thin films is different from that for SiO_2 (see Fig. 2, discussed later). This fact also confirms that the higher binding energy of the Si 1*s* for 0.09 layer is not due to the formation of SiO_2. Such energy difference between thick and ultra-thin films is also observed for HOPG substrate (right figure). The energy of Si 1*s* peak observed for 1.8 layer and 0.15 layer (marked F) is higher by 4.2 eV than that for bulk 38-layered sample (marked D). This energy shift

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