2.26 TWO-DIMENSIONAL GRAPHITE-LIKE Si,C OBSERVED BY POLARIZATION DEPENDENCE IN THE NEAR-EDGE X-RAY ABSORPTION FINE STRUCTURE

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Abstract
Solid carbon forms mainly two kinds of local structures, i.e., three-dimensionally spread diamond-like structure and two-dimensional graphite structure. In contrast, solid silicon and silicon carbide tend to prefer only diamond structure composed of sp\(^3\) bonds resulting in the formation of a three-dimensionally spread lattice. Recently, the theoretical calculation using an ab initio tight-binding-like method has revealed that two-dimensional graphite-like SiC layer possibly exists (M. Fuentes-Cabrera et al., Model. Simul. Mater. Sci. Eng. 7, 929 (1999)). In order to clarify whether or not such two-dimensional graphitic Si,C layer exists, we implanted Si\(^+\) ions in highly oriented pyrolitic graphite (HOPG), and the electronic structures localized at the silicon atoms were investigated in-situ by means of X-ray photoelectron spectroscopy (XPS) and near-edge X-ray absorption fine structure (NEXAFS) using linearly polarized synchrotron radiation. The resonance peak appeared at 1839 eV in the Si K-edge NEXAFS spectra for Si\(^+\)-implanted HOPG, and its energy is lower than the resonance peaks in any other Si-containing materials. The intensity of the resonance peak showed strong polarization dependence, which suggests that the final state orbitals around the Si atoms have \(\pi^*\)-like character. It is elucidated that the Si-C bonds produced by the Si\(^+\)-ion implantation are nearly parallel to the graphite plane, and Si,C phase forms two-dimensionally spread graphite-like layer with sp\(^2\) bonds.

Keywords: silicon carbide, graphite, two-dimensional layer, ion implantation, near-edge X-ray absorption fine structure, X-ray photoelectron spectroscopy, polarization dependence, synchrotron radiation

1. Introduction
Low-dimensional materials have been attracted much attention because of their unique properties, which are not observed in bulk materials [1]. Especially, recent rapid progress in semiconductor technology is accelerating the search for new two-dimensional (2D) semiconductor materials. Among numerous kinds of 2D materials investigated so far, graphite is considered to be ideal 2D layer. One sheet of graphite (graphene) is composed of six-membered aromatic rings with sp\(^2\) bonds, and its thickness is only in the order of one atom. Newly found carbon nanotube [2] which has similar structure to graphite is also classified into the graphite family, and it has been attracted much attention as a new electric material in nanotechnology. As to the electric property, graphite has semi-metallic conductivity. Besides graphite, hexagonal boron nitride (BN) which has a similar structure to graphite is a wide-gap insulator. Therefore, if some of the carbon atoms in graphite are substituted by the other atoms, we can possibly obtain ideal 2D thin films with various electric properties from metallic phase to insulator. Theoretical [3,4] and experimental [5,6] works have recently revealed that two-dimensional carbon nitrides of graphite-like structures surely exist. Also the synthesis of hybrid nanotubes composed of boron, carbon and nitrogen has been attempted recently for the purpose of controlling electric property [7,8].

On the other hand, silicon, belonging to the same group in the periodic table as carbon, tends to form three-dimensionally spread diamond structure with sp\(^3\) bond. If silicon atoms
are ordered in 2D layer, the interaction between the two 2D layers becomes stronger than the Van-der-Waals force resulting in the formation of puckered structure. Such three-dimensionally spreading character of silicon atoms makes it difficult to fabricate ultra thin layer of semiconducting Si and insulating SiO₂ in silicon technology. Although many of the organosilicon molecules having Si-Si double bonds are known, no stable solid phase composed of silicon and carbon has been synthesized so far. (Note that in the case of isolated graphite-like sheet would be placed. For sp³ bond, =120° which corresponds to the tetrahedral angle ≈ 109.47°.)

This situation also holds for the silicon carbide. There are some stable SiC phases such as α-SiC and β-SiC, all of which are composed of sp³ bonds. The local geometry of the typical β-SiC phase of zinc-blende structure is shown in fig.1 (a). However, the theoretical study on the possible graphite-like 2D layer for SiC has recently been conducted by Fuentes-Cabrera et al. using an ab initio tight-binding-like method. They calculated the stabilities of the aromatic phase of 2D monolayers of SiC. They concluded that the 2D SiC prefers to form the flat aromatic phase (fig.1(c), left) rather than puckered layer (fig.1(c), right), while Si prefers to puckered form and never forms flat aromatic phase. If the two-dimensional SiC phase does exist, we can possibly deposit ultra thin or just monolayer of semiconductor on solid surfaces. However, no experimental evidence has been reported so far as to whether or not the aromatic, flat SiC phase does exist.

In order to answer the above questions, we investigate the local electronic and geometric structures of silicon implanted in graphite. For this purpose, we chose highly oriented pyrolitic graphite (HOPG) as a starting material. We implanted low-energy Si⁺ ions in HOPG, and the electronic structures localized at the silicon atoms were investigated in-situ by means of the near-edge X-ray absorption fine structure (NEXAFS) spectroscopy. The local geometric structures were also clarified by the incident angle dependencies of the NEXAFS spectra using linearly polarized synchrotron beam. X-ray photoelectron spectroscopy (XPS) was used in elucidating the core-level binding energies and surface atomic compositions.

2. Experimental

The experiments were performed at the BL-27A station of the Photon Factory in the High Energy Accelerator Research Organization (KEK-PF) employing double crystals of InSb(111) as a monochromator. The energy resolution of the monochromator was 0.85 eV at 1.84 keV (Si K-edge). The synchrotron beam was generated in the bending magnet, and it was linearly polarized in the horizontal direction.

The ultrahigh vacuum system (base pressure 1 x 10⁻⁸ Pa) consisted of a manipulator
which can rotate around the vertical axis, a hemispherical electron-energy analyzer (VSW Co. Class-100) for XPS measurements, and a cold-cathode ion-gun (OMEGATRON Co. OMI-0045CK). An HOPG single crystal of 12 mm × 12 mm purchased from Advanced Ceramics Co. was used as a substrate. The orientation of HOPG was checked in the separate experiments at the BL-11A station of KEK-PF by means of the polarization-dependencies of the C K-edge NEXAFS spectra. For comparison, amorphous diamond-like carbon (DLC) mainly composed of sp³ bonds with no orientation was also used as a substrate.

Tetrafluorosilane (SiF₄) gas was used as ion source. Various atomic and molecular fragment ions such as F⁻, Si⁺, SiF⁻, and SiF₃⁺ were produced by the discharge of SiF₄ gas. Therefore the mass of the ions was separated by a Wien-filter-type mass separator using orthogonal electric and magnetic fields, and only atomic Si⁺ ions were bombarded on the sample. The accelerating voltage was 1 keV, and the ion flux was 1 × 10¹¹ atoms/cm² · sec. The NEXAFS spectra were taken by the total electron yields, which were obtained by the sample drain current. The total electron yields were normalized by the photon flux, which was always monitored by the current of aluminum foil located in front of the sample. In order to compare the spectral features, the NEXAFS and XPS spectra were also taken for the reference materials such as β-SiC (6H-SiC) and single crystal of Si(100).

3. Results and discussion

3.1 XPS

Figure 2 shows the XPS spectra around the Si 1s region excited by 2100-eV photons. The surface C/Si ratios of the Si⁺-ion bombarded HOPG and DLC were estimated to be 0.01 on the basis of the C 1s/Si 1s peak intensity ratios considering the photoionization cross sections [13] and inelastic electron mean free paths (IMFP) of photoelectrons [14]. The chemical shift between Si(100) and SiC is 1.6 eV, which means that carbon atoms are negatively charged compared with silicon atoms. The binding energy of the Si 1s for Si⁺-ion implanted DLC is almost the same as that for the SiC, which suggests that the amorphous SiₓC composed of sp³ bonds is formed. While the Si 1s peak for Si⁺-ion implanted HOPG shifts to higher binding energy by 1.3 eV than that for SiC. If the implanted silicon atoms form cluster resulting in the island structure, or if the implanted layer becomes amorphous SiₓC with only sp³ bonds, the binding energy of implanted silicon would be close to that of the bulk silicon. The observed higher binding energy suggests that the Si⁺-ion implanted HOPG forms new layer where carbon atoms are more negatively charged compared with normal SiC.

3.2 NEXAFS

Figure 3 shows the NEXAFS spectra at the Si K-edge. The spectrum for the Si⁺-ion implanted DLC represents a similar structure to that for 6H-SiC (see dotted bars). This
finding supports the XPS results, i.e., Si'-ion implanted DLC forms amorphous Si,C composed of sp\(^3\) bonds. On the other hand, the NEXAFS spectrum for Si'-ion implanted HOPG does not follow that for 6H-SiC, and new peaks marked A and B are observed. It is noteworthy that the energy of the peak A is around 1839 eV, and no peak is observed in such low-energy region for 6H-SiC. Also such low-energy peak has never been reported in Si K-edge NEXAFS spectra for any other silicon-containing compounds. In the case of carbon K-edge NEXAFS spectra, it has been established that the resonance peak corresponding to 1s\(\rightarrow\)\(\pi^*\) excitation is lower than that originating from 1s\(\rightarrow\)\(\sigma^*\) excitation. In fact, it was reported that the energy of the C 1s\(\rightarrow\)\(\pi^*\) resonance peak of graphite is lower by 10 eV than those of the C 1s\(\rightarrow\)\(\sigma^*\) peaks of graphite and diamond [15]. From the analogy to the carbon case, it is presumed that the peak A in fig.3 is attributed to the resonance excitation from the Si 1s to unoccupied orbitals which have \(\pi^*\)-like character.

3.2 Polarization dependences of NEXAFS spectra

Figure 4 displays the polarization dependence of the Si K-edge NEXAFS spectra for the Si'-ion implanted HOPG (a) and DLC (b) at a fluence of \(7 \times 10^{13}\) atoms/cm\(^2\). The top view of the sample location is displayed in the upper small inset of each figure. In the spectra for Si'-ion implanted HOPG, remarkable polarization dependence is observed for the peak A. The intensity of the peak A increases with the decrease in the incident angles of the synchrotron beam. On the other hand, no polarization dependence is observed in the spectra for Si'-ion implanted DLC. The peak intensity I of the NEXAFS spectra using the synchrotron beam of electric field E is expressed as follows [16],

Fig.3 NEXAFS spectra at the silicon K-edge taken by the total electron yield for (a) Si(100) single crystal, (b) 6H-SiC, (c) Si'-ion implanted HOPG, and (d) Si'-ion implanted DLC.

Fig.4 Polarization dependences of Si K-edge NEXAFS spectra for (a) Si'-ion implanted HOPG, and (b) Si'-ion implanted DLC. The fluence of the Si ions are \(7 \times 10^{13}\) atoms/cm\(^2\). The small inset shows the top view of the sample. E is the electric field vector of synchrotron beam and \(\theta\) is the incident angle defined by the angle between sample surface and synchrotron beam.
\[ I \propto |E \cdot O|^2 \propto \cos^2 \delta \]  

where \( O \) is the direction of the final state orbital and \( \delta \) is angle between \( E \) and \( O \). If this resonance peak is due to the dangling bond located at the silicon atoms, such polarization dependences will be never observed. Considering the polarization dependence in fig.4(a), we can suppose that the final state orbitals represented by the peak A are perpendicular to the basal plane of graphite sheet, i.e., parallel to the c-axis of graphite. In order to certify this speculation, we will next discuss the angle of the orbitals and chemical bonds more quantitatively.

In figure 5(a), the intensities of the peak A are plotted as a function of the incident angle \( \Theta \). (In the row spectra, the peaks A are overlapped with the higher-energy peaks. But the lower-energy sides of the peaks A show the Gaussian-like curves. Therefore we calculate the areas of the peaks A by the peak deconvolutions using Gaussian-curve fitting. The example of the curve fitting in the NEXAFS spectrum at \( \Theta = 30^\circ \) is shown in the small inset of fig.5(a)). The intensities of the peaks A were normalized by the total electron yields at 1860 eV for respective incident angles where no polarization dependence exists. It is seen that the intensity of the peak A monotonously decreases with the incident angle.

The resonance intensity in the NEXAFS spectrum is given as

\[ I(\Theta) = A [ P \cdot I_p + (1-P) \cdot I_V ] \]  

where \( I_p \) and \( I_V \) are the transition intensities associated with the angle-dependent matrix elements parallel and vertical, respectively, to the electric vector, \( \Theta \) is the incidence angle of the synchrotron beam, \( A \) is the normalization factor and \( P \) is the polarization factor [17]. The substrate used here is graphite, thus the substrate has a symmetry higher than threefold. In this case, the intensities are simply expressed as

\[ I_p = (1/3) \cdot [ 1 + (1/2) \cdot (3\cos^2 \Theta - 1) \cdot (3\cos^2 \alpha - 1) ] \]  

and

\[ I_V = (1/2) \cdot \sin^2 \alpha \]  

where \( \alpha \) is the polar angle of the final state orbitals [17]. The polarization factor of the synchrotron beam in the present experimental condition is estimated to be about 0.95 [18]. The theoretically calculated values of I for various \( \alpha \)-values are plotted as dotted lines in fig.5(b) as a function of \( 3\cos^2 \Theta - 1 \). The values are normalized such that the data at \( 3\cos^2 \Theta - 1 = 0 \) are 1/3. The normalized intensities of the peaks A are plotted as filled circles in fig.5(b). At first glance, the experimental data follow the line of \( \alpha = 0^\circ \). This means that
the final state orbitals point to the c-axis of the graphite. It is revealed that some of the carbon atoms in graphite are substituted by the implanted silicon atoms, and the Si-C σ-bond thus produced is nearly parallel to the basal plane of the graphite sheet. The top view of the obtained structure is displayed in the right side of fig.1 (b), and the side view is virtually represented in the left side of fig.1(c).

The present results clearly reveal that the two-dimensional Si,C layer surely exists at low Si concentration. Further research to clarify whether an aromatic SiC with stoichiometric composition shown in the left side of fig.1(b) exists or not is now in progress by synthesizing the samples at higher Si concentration and at higher temperature. The existence of two-dimensional Si,C layer will open up a possibility of future application of the formation of ultra thin or monolayered semiconductor phase.

4. Summary

We have investigated the local electronic and geometric structures of silicon atoms implanted in HOPG by means of NEXAFS and XPS using linearly polarized synchrotron beam. In the Si K-edge NEXAFS spectra, the resonance peaks were observed around 1839 eV, which is lower than the energies of the resonance peaks in any other silicon-containing compounds. The intensity of these resonance peaks showed strong polarization dependence. The quantitative analysis of the polarization dependence revealed that the final-state orbitals of the resonance peak point to the c-axis of the graphite plane. On the basis of the low-energy feature and the direction of the final-state orbitals, it is concluded that the observed low-energy resonance peaks originate from the excitation from Si 1s to π* orbitals which are perpendicular to the graphite plane. The present results show that the σ-type Si-C bonds produced by the Si'-ion implantation are nearly parallel to the graphite plane, and the Si,C phase forms two-dimensionally spread graphite-like layer with sp2 bonds.

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References