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Local atomic configuration of graphene, buffer layer, and precursor layer on SiC(0001) by photoelectron diffraction

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The layer-specific atomic structure of the 4H-SiC(0001) surface at each stage of single-layer graphene formation was studied using photoelectron diffraction. The 2π-sr C 1s photoelectron intensity angular distributions (PIADs) excited by circularly-polarized soft X-ray were measured. Taking the photoelectron inelastic mean free path into account, we have separated C 1s PIADs of the graphene overlayer together with the interface buffer layer beneath it and the precursor layer, $(6\sqrt{3} \times 6\sqrt{3})$-$R30°$, from that of the SiC substrate. Clear diffraction rings due to the intra-layer C – C bond scattering of graphene were observed. The forward focusing peaks indicating the directions of the neighboring atoms seen from the C atoms directly bonded to the SiC substrate were observed for the precursor and interface buffer layers. This result suggests that the structures of both layers have a common local atomic configuration.

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1. Introduction

Graphene is a single-layer carbon network arranged in a honeycomb lattice, and is expected to be a useful material for next-generation devices [1]. Epitaxial growth by the thermal decomposition of SiC substrate is a promising method for fabricating high-quality uniform graphene. To clarify the mechanism of graphene formation and determine the surface atomic arrangements at each stage, various kinds of surface analyses have been reported. Early studies revealed that the SiC(0001) surface at the graphitization precursor stage is terminated by a graphite-like structure covalently bonded to the SiC substrate with -$(6\sqrt{3} \times 6\sqrt{3})$-$R30°$ periodicity (hereinafter, called the precursor layer) [2–5]. Further elimination of Si leads to the formation of single-layer graphene (SLG) on a C-rich buffer layer [4–7]. Interaction of the buffer layer with graphene as well as with the substrate greatly affects the electronic properties of graphene [8]. Characterization of the buried buffer layer is a key to improving the performance of graphene devices. However, the atomic structure of the subsurface of SLG remains unclear.

A photoelectron from a localized core level is an excellent element-selective probe for surface structure analysis [8]. Forward focusing peaks (FFPs) appearing in the photoelectron intensity angular distribution (PIAD) indicate the directions of surrounding atoms as seen from the photoelectron emitter atom [9]. The distance between the emitter and scatterer atoms can be deduced from the circular dichroism shift of the FFP position [9–11] as well as from the opening angles of diffraction rings (DRs) appearing around the FFP [11,12]. Roth et al. used photoelectron diffraction (PED) to determine the structure of a deposition of a nearly free-standing graphene top layer and a corrugated boron nitride subsurface layer on a Cu(111) surface [13]. We have demonstrated that the stacking orientations of exfoliated bilayer graphene flakes can be determined by using PED [14].

Recently, de Lima et al. measured and separated C 1s PIADs of graphene and precursor layers on SiC(0001) by a chemical-specific PED approach [15]. They evaluated the ripple amplitude of long-range order in precursor layers and suggested just one type of hybridization for the local buckling structure. Furthermore, they proposed a rather flat structural model for the buffer layer. In fact, the buffer layer consists of various types of hybridizations, namely, sp^2, sp^3 and the intermediates [16–18]. However, their detection range did not include any FFP, which is the most sensitive signal for local structure.

Differentiating a series of PED data at the subsequent graphitization stages has been reported as an alternative approach for layer-resolved analysis. Matsui et al. successfully carried out an atomic-layer-resolved analysis of thin films of Ni by differentiating a series of PED data from wedged film [19]. Maejima et al. discussed the local subsurface structures of a thin SiON film grown on a SiC substrate [20]. In the current study, we have characterized each stage of the thermal graphitization of a 4H-SiC(0001) substrate by a similar approach. Site-specific PIADs

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were deduced by considering the dependence of escape depth on emission angle, and subtracting the substrate signal intensity. The local atomic arrangements of the SLG as well as buffer and precursor layers of the thermally graphitized substrate were investigated by layer-resolved photoelectron diffraction.

2. Experimental methods

Catalyst-referred etching (CARE) single-crystalline 4H-SiC(0001) wafer (N-doped, 0.02 Ω cm) with an on-axis oriented Si face ($0 \pm 0.5°$ off) was used as the substrate [21,22]. The wafer has an atomically flat and damage-free surface with a terrace width of 300–500 nm. Hattori et al. reported a procedure to obtain a large scale uniform graphene by annealing this CARE-SiC substrate in ultrahigh vacuum (UHV) without using the Si flux method during thermal epitaxial growth [23]. This specially treated sample is a solution for the graphene fabrication at much lower temperatures than can be applied in the conventional procedure without Si flux or Ar atmosphere. The ability to systematically test the effects of annealing was also achieved by eliminating the Si flux procedure parameter during the epitaxial growth. The number of graphene layers on CARE-SiC can be easily controlled as a function of annealing temperature and duration. Hattori et al. confirmed the change of the surface structure of the CARE-SiC(0001) substrate from the (1×1) to $(\sqrt{3} \times \sqrt{3})$-$R30°$ phase with increasing annealing temperature. The $(6\sqrt{3} \times 6\sqrt{3})$-$R30°$ precursor layer structure appeared when the annealing temperature exceeded 900 °C.

For the current study, we also prepared the samples step by step in the same manner as Hattori et al. All experiments were performed at the circularly-polarized soft-X-ray beamline BL25SU of SPring-8, Japan [24]. The sample preparation chamber was attached directly to two-dimensional display-type spherical mirror analyzer (DIANA) [25–27] and equipped with a reflection high-energy electron diffraction (RHEED) system. The sample was placed into a UHV chamber with a base pressure of less than 3×10^{-8} Pa, and then annealed by direct current injection. The surface structure was monitored by RHEED. Increasing the annealing temperature by 200 °C steps from room temperature up to 600 °C did not eliminate the (1×1) spots originating from the SiC surface. Annealing at 800 °C for 10 min yielded $6\sqrt{3}$ spots originating from the graphene precursor layer. Further annealing at 1000 °C for 10 min decreased the intensity of the $6\sqrt{3}$ spots, which is a strong indication of the formation of graphene on the SiC substrate [3,5,25]. These results are consistent with the previous reports [23].

PIAD from the sample at a specific kinetic energy is most efficiently measured using DIANA [25–28]. A two-dimensional angular distribution snapshot of electrons with a specific kinetic energy can be measured [9,29–33]. The acceptance angle of the analyzer is $\pm 60°$. Light was incident from the direction 45° inclined from the analyzer center. The dependence of PIAD on emission angle θ from 0 to 90° relative to the surface normal is measured simultaneously. A 2π-sr PIAD was obtained by scanning the sample azimuth for 360° [34, 35]. The helicity ($\sigma_{\pm}$) of monochromatized circularly-polarized soft X-ray was altered by switching the path of storage ring electrons in twin helical undulators at 0.1 Hz [36]. The photon energy resolution was better than 100 meV. The total acquisition time for a pair of 2π-sr PIADs excited by σ_+-helicity and σ_--helicity lights was 1 h. All data were measured at room temperature. Electric vector was in-plane; thus, core-level electrons were excited with completely *s*-polarized geometry. Diffraction rings and some interference patterns originating from in-plane structure become dominant. The energy window width of DIANA was set to 1 eV for spectroscopy measurements, while it was set to 40 eV for PIAD measurements, to achieve the best energy and angular resolution, respectively. All PIADs were obtained with a photoelectron kinetic energy of 800 eV, and displayed in stereo projection.

3. Results and discussion

The chemical composition at each stage of graphitization was characterized by constant-final-state-mode two-dimensional photoelectron spectroscopy. The photoelectron kinetic energy was fixed at 800 eV, while the photon energy was scanned from 800 eV to 1160 eV, so that we can detect the C 1s and Si 2p core-levels at the same kinetic energy. In this way, the probing depth of the photoelectron for each emission angle was kept constant for different binding energies.

Fig. 1 shows the signal intensity ratio of C 1s over Si 2p for different annealing temperatures and emission angles θ. The photoionization cross section was taken into account [37]. Normal- and grazing-angle emission spectra were sensitive to the bulk and surface of the substrate, respectively. The signal intensity ratio of C 1s to Si 2p did not change as the annealing temperature was increased to 600 °C. This result indicates that the surface composition of the substrate was maintained below this temperature. At 800 °C, the signal intensity ratio of C 1s over Si 2p at grazing- angle emission-angle emissions was larger than that of normal-angle emissions. This result implies that Si was eliminated from the SiC surface, and a C-rich surface was formed on the SiC substrate.

The thickness of the carbon overlayer on the SiC surface at 1000 °C annealing temperature was estimated by following Starke and Riedl's angular-resolved XPS analysis [38]. We analyzed six emission-angle-dependent-XPS spectra, at every 10° relative to the sample normal, and scrutinized the error of the C 1s/Si 2p intensity ratio. The calculation was calibrated against this ratio of the bulk SiC because the detection efficiency varies for different emission angles [39]. The carbon overlayer was determined to have a thickness of 0.34 ± 0.02 nm, which is close to the interlayer distance in graphite (0.335 nm), suggesting that a surface covered with SLG was obtained [40].

Fig. 2(a) and (b) respectively show the measured PIAD of and the corresponding local structural model of the hydrogen-terminated SiC surface. Two PIAD images using σ_+ and σ_- helicity lights are superimposed. When excited with σ_+ helicity light, the diffraction patterns rotated clockwise (red), while they rotated counterclockwise (blue) when excited with σ_- helicity light [9–11]. Red and blue arrows indicate the directions of the first-nearest neighbor Si_1 atoms and the second-nearest neighbor C_β atoms seen from the emitter C_α atom. FFP positions in the PIAD are indicated by open marks with corresponding colors in Fig. 2(a). The local structure is three-fold symmetric but the observed PIAD is six-fold symmetric. This difference is due to the two coexisting mirrored terraces at the surface, which in turn are due to the stacking faults of the 4H-SiC(0001) substrate. The FFP positions, diffraction patterns and their circular dichroism spectra are similar to

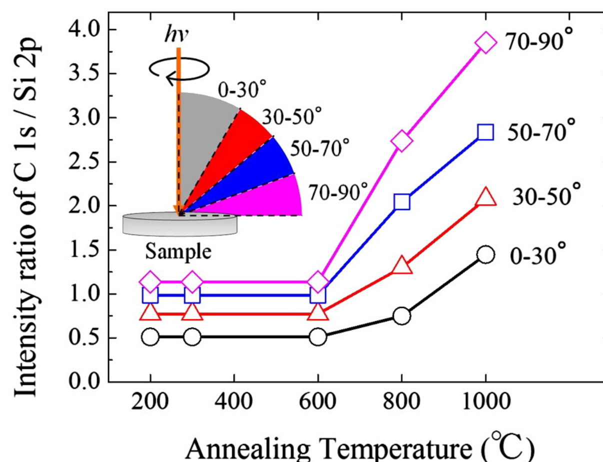

Fig. 1. The signal intensity ratio of C 1s over Si 2p deduced from constant-final-state-mode angle-resolved photoelectron spectra for different annealing temperatures.

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