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Determination of non-uniform graphene thickness on SiC (0 0 0 1) by X-ray diffraction

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ABSTRACT

Epitaxial graphene thickness distribution grown on Si-terminated SiC (0 0 0 1) surface was analyzed by using an X-ray diffraction (XRD) pattern and a simple equation. These results were confirmed by low accelerating voltage scanning electron microscopy and angle resolved photoemission spectroscopy. Despite its simplicity, proposed XRD analysis provides fairly accurate information on layer spacing and thickness distribution of graphene layers. It is expected that this method is useful for quick evaluation of graphene layer numbers on large scale substrate.

1. Introduction

Graphene is an allotrope of carbon created by arrangement of carbon atoms in a two-dimensional honeycomb lattice. The unit cell of graphene, in which two carbon atoms are contained, is formed by two lattice vectors, $|a_G| = |b_G| = 2.4589$ Å [1,2]. In the electronic band structure, graphene has two important bonding types which are π bond (perpendicular to the planar sheet) and σ bond (in-plane sheet). Graphene also has many exotic properties such as high mobility and linear dispersion (Dirac cone) at the *K*-point in the Brillouin zone where the valence and conduction band touch each other [3–5]. These unique properties of graphene make it a promising candidate for the future electronic [6,7] and photonic devices [8].

Graphene can be formed by many ways such as mechanical exfoliation of graphite, chemical vapor deposition (CVD) of carbon-bearing gases on the surface of copper films [9], and cutting open nanotubes [10]. The growth of graphene by annealing SiC substrate is also one of the efficient approaches for a large scale production of graphene. The estimation of the graphene film thickness on SiC substrate is necessary since the properties of graphene depend on its thickness. In general, there are several techniques, such as scanning electron microscope (SEM) [11], Auger electron spectroscopy (AES) [12,13], X-ray photoelectron spectroscopy (XPS) [14], attenuation of substrate Raman intensity [14], angle-resolved photoemission spectroscopy (ARPES) [1] and surface X-ray diffraction (SXRD) [15,17] to determine the layer number of graphene grown on SiC. For the AES and XPS, the thickness determination relies on the Si/C intensity ratio and the model which assumes that graphene is grown uniformly on SiC substrate. Their accuracy could suffer from the unrealistic model and the inaccurate knowledge of the inelastic mean free path of electrons [12–14,18]. In the case of the estimation by attenuation of substrate Raman intensity, the accuracy depends on the Raman intensity of SiC which varies in position. In the case of ARPES, it can reveal the graphene band structure which implies only the combination of graphene layer but not respective coverages. The SXRD is a wonderful method which can estimate the film thickness. Nevertheless, this method is rather complicated and time consuming, that is the SXRD needs hundreds of truncation rod intensity measurements (which takes tens of hours) [16,17] and also needs many fitting parameters (such as 3-dimensional atomic positions of each atoms including interface and SiC layers and surface roughness) for structural analysis [15]. In particular, large number of parameters causes many candidates of best fit parameter sets as well as time consuming analysis. Low accelerating voltage SEM (LV-SEM) is a technique which can locally distinguish the relative graphene thickness regions by difference in contrast but it cannot exhibit the absolute graphene thickness unless contrast-thickness relation for each sample is obtained.

In this report, an X-ray diffraction (XRD) pattern around a graphene peak was used for layer number distribution determination of non-uniform graphene layers on SiC substrate. The XRD pattern was analyzed by using a simple equation and few numbers

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of parameters (such as layer spacing and layer coverage of graphene film). The XRD results were compared with LV-SEM and ARPES for confirmation.

2. Experimental

N-type Si-terminated 6H-SiC (0 0 0 1) substrates were employed for the graphene growth. The substrate was precleaned by ultrasonic in acetone. After acetone was evaporated, the substrate was immediately mounted on the sample holder and put in the main chamber with the base pressure of $\sim 10^{-8}$ Pa followed by silicon deposition (about 2 layers) on the substrate. After that the substrate was transferred to an argon chamber without exposure to air and then annealed in argon gas with a pressure of 0.05, 0.3 and 0.5 atm. The samples were named as the value of argon pressure where they were annealed in. The annealing temperature was in range from ~900 °C to graphitization temperature (1550 °C for the 0.05 atm sample, 1675 °C for the 0.3 atm sample and 1700 °C for the 0.5 atm.sample) with increasing temperature by ~100 °C. The annealing time was about 10–15 min for each temperature to produce a few layered graphene. The sample heating was carried out by direct current through the sample.

After annealing, an ex situ XRD measurement was carried out at the beam line 4C, Photon Factory, KEK (Tsukuba, Japan). Diffraction data were collected at X-ray energy of 10.2 keV and incident beam size of 1 mm at room temperature. An ARPES measurement was also conducted at room temperature at the beam line 5U of UVSOR-II in the Institute for Molecular Science, Okazaki, Japan. The excitation photon energy was set to 80 eV. An ultra-high vacuum (UHV)-SEM (Omicron Nano Technology) observation with incident beam of 1.7–2.2 keV was also carried out.

3. Results and discussion

Fig. 1 shows XRD profiles (blue dots) of graphene films grown on SiC under argon pressure of (a) 0.05 atm, (b) 0.3 atm, and (c) 0.5 atm. As indicated in the figure, diffraction peaks of graphene layers and SiC are observed at ~20° and 27.8°, respectively. The *d*-spacings of the SiC can be calculated from the peak position as about 2.51 Å, which corresponds to SiC bilayer spacing (2.52 Å) [1].

To estimate graphene thickness from XRD profiles, Laue diffraction function were used. At first, a simple model was assumed that the graphene was grown uniformly on SiC substrate. Under this assumption, the following simple equation was used for profile calculation.

$$|F|^2 \propto |f(\theta)|^2 \left| \sum_{j=0}^{N} e^{ika_j j} \right|^2 . \quad (1)$$

Here, F is a structure factor, N is the number of graphene layer, and $f(\theta)$ is an atomic scattering factor which can be taken from Ref. [19]. $ka_j = (4\pi d_j \sin\theta)/\lambda$ where d_j is a lattice spacing (between jth and $(j-1)$th layers) perpendicular to the surface, θ is an angle between the incident ray and the scattering planes, λ is a wavelength of X-ray. In order to avoid the effect of SiC substrate, the fitting was operated in the range of 2θ from 10 to ~22°. Green dotted line and red broken line in Fig. 1(a) are calculated curves from Eq. (1) with graphene layer number (N) of 1 and 2, respectively. The spacing d of 3.60 Å was employed. As shown in the figure, there are large discrepancy between the calculated curve and the experimental one, i.e. too broad for $N = 1$ or too narrow for $N = 2$. This suggests that the number of graphene layers on the SiC substrate is not uniform, but has a distribution.

In order to improve the fitting, another model which includes graphene thickness distribution was introduced as shown in Fig. 2. With this model and the Laue functions, XRD intensity can be calculated as

$$|F|^2 \propto |f(\theta)|^2 \left| \sum_{j=0}^{N} \beta_j e^{ika_j j} \right|^2 , \quad (2)$$

where β_j is a occupancy of jth graphene layer (its value is between 0 and 1). Solid lines in Fig. 1(a)–(c) show results of fitting by using Eq. (2). Parameters (d_j and β_j) used in those calculations are shown in Table 1. It is apparent that the curve obtained from the modified model exhibits better fitting than those of the uniform model. χ^2 ($=\sum(O-E)^2/E$; O is intensity from the calculation, E is that from experiment) dependence on β_j parameter change is shown in Fig. 1(d). It reveals steep valley which suggests the fitting resolution is good enough (less than 2%). For the interlayer spacings d_j,

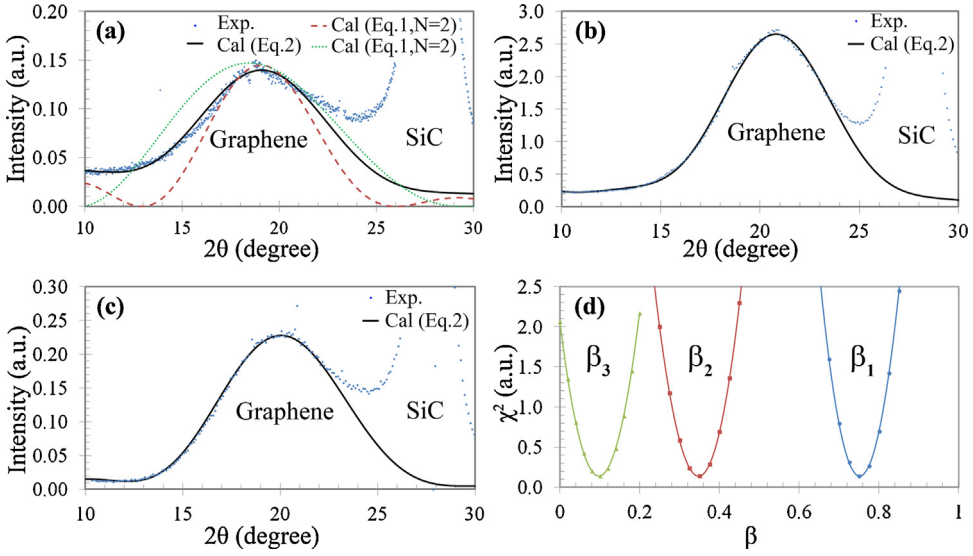

Fig. 1. Experimental XRD profiles (blue dots) of graphene films grown on SiC (0 0 0 1) surface, which was annealed under argon pressure of (a) 0.05, (b) 0.3 and (c) 0.5 atm. As written in the figures, peaks at ~20° and 27.8° correspond to graphene layers and SiC bilayers respectively. Green dotted line and red broken line in (a) are calculated results using fitting Eq. (1) with parameters $N = 1$ and $N = 2$, respectively. A solid line in each figure shows a calculated result using Eq. (2) and (d) the chi-squared (χ^2) dependence on β_j parameters for 0.3 atm sample. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)