

Dependence of Electronic Properties of Epitaxial Few-Layer Graphene on Number of Layers Investigated by Photoemission Electron Microscopy

Few-layer graphene (FLG) is attracting considerable attention as a future electronics material owing to its superior electronic transport properties and compatibility with standard lithographic techniques. FLG whose transport properties have been studied has been mainly produced by exfoliating graphene flakes from bulk graphite and depositing them on SiO₂/Si substrates [1]. In general, however, its size is very small and its productivity is very low for practical applications. For a large-scale production of FLG, therefore, the epitaxial growth of FLG on SiC by thermal decomposition is being investigated actively.

During annealing SiC substrates, Si atoms preferentially desorb from the surface and C atoms left behind to form graphene layers, as schematically shown in Fig. 1. We hope that single-crystal FLG wafers produced by simple annealing methods will become a basis of the large-scale integration of graphene devices.

However, because the epitaxial FLG we have obtained so far still exhibits a thickness distribution, we should establish a reproducible method of growing wide, uniform FLG with the desired thickness. Toward this target, we have already demonstrated that the number of graphene layers N_G can be digitally counted from the quantized oscillation in the energy dependence of electron reflectivity using low-energy electron microscopy (LEEM) [2]. Another important aspect that should be clarified before device applications of epitaxial FLG is how the SiC substrate affects the electronic properties of FLG. The N_G dependence of the electronic properties provides important clues for understanding the effects of the substrate. Because it is still difficult to grow uniform epitaxial FLG, it is desirable to investigate the electronic properties using techniques that can

resolve N_G microscopically. In this work, we use a spectroscopic photoemission and low-energy electron microscopy (SPELEEM) instrument at beamline BL17SU to observe the same area using LEEM and photoelectron emission microscopy (PEEM), which enables us to investigate the electronic properties of epitaxial FLG for each N_G microscopically [3].

Figures 2(a)-2(c) show secondary-electron (SE) PEEM images of epitaxial FLG grown on 6H-SiC(0001) obtained at various electron energies. Numbers in Fig. 2(c) correspond to N_G values determined by LEEM. Areas with different N_G values can be discriminated in the SE PEEM images, but their relative intensities depend on the SE energy. Figure 2(d) shows the SE emission spectra obtained from the sequential PEEM images. The SE emission spectra depend on N_G in two aspects, namely, the threshold start voltage of the SE emission and the spectrum shape. The threshold voltage corresponds to the vacuum level. Therefore, Fig. 2(d) shows that the work function increases with N_G , and the measured work functions are plotted in Fig. 2(e).

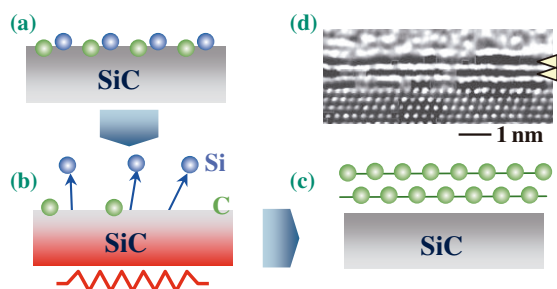


Fig. 1. (a)-(c) Schematic illustrations of SiC surface structures (a) before, (b) during, and (c) after annealing. (d) Cross-sectional transmission electron microscopy image of epitaxial FLG grown on 6H-SiC(0001).

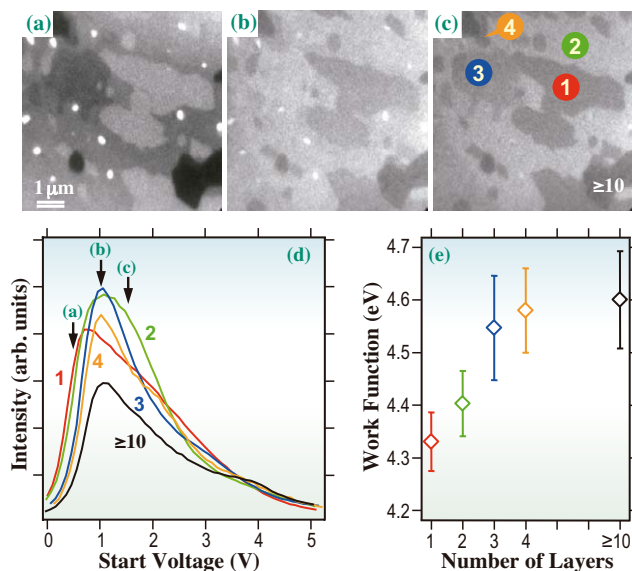


Fig. 2. (a)-(b) SE PEEM images of epitaxial FLG grown on 6H-SiC(0001) obtained under irradiation by monochromatized synchrotron radiation at energy of 400 eV. Here, we use the start voltage as a measure of the electron energy, and the start voltage multiplied by the electron unit charge is nearly equal to the electron energy. The start voltages used to obtain (a)-(c) were 0.5, 1.0, and 1.5 V, respectively. (d) SE emission spectra obtained from sequential SE PEEM images. Numbers in (c) and (d) indicate the N_G values. (e) N_G dependence of work function. We assumed that the work function of the thick graphene is equal to the reported value for bulk graphite (4.6 eV).

From the monolayer graphene to the thick graphene, the vacuum level gradually increases by about 0.3 eV. The SE emission spectra also include information about the unoccupied electronic structures [4]. The electronic structure of FLG changes with N_G , which leads to the spectrum shape change.

Figure 3(a) shows a PEEM image of epitaxial FLG obtained using C1s photoelectrons. Areas with different numbers of graphene layers can be discriminated in the C1s PEEM image. The C1s core-level photoelectron spectra in Fig. 3(b) show that the peak energy of the C1s photoelectron intensity depends on N_G , indicating that the C1s binding energy of the monolayer graphene is

about 0.4 eV larger than that of the thick graphene (Fig. 3(c)).

It is known that the Dirac point falls below the Fermi level owing to the charge transfer from the substrate to FLG and that the shift from the Fermi level decreases with the number of graphene layers [5]. The Dirac point, C1s core level, and vacuum level of FLG move with N_G rather similarly. In the first approximation, all the electronic structures of FLG rigidly shift due to the charge transfer. More strictly, however, the shift in the work function seems smaller than those in the Dirac point and C1s binding energies. To determine the reason for this, we need further experimental and theoretical studies.

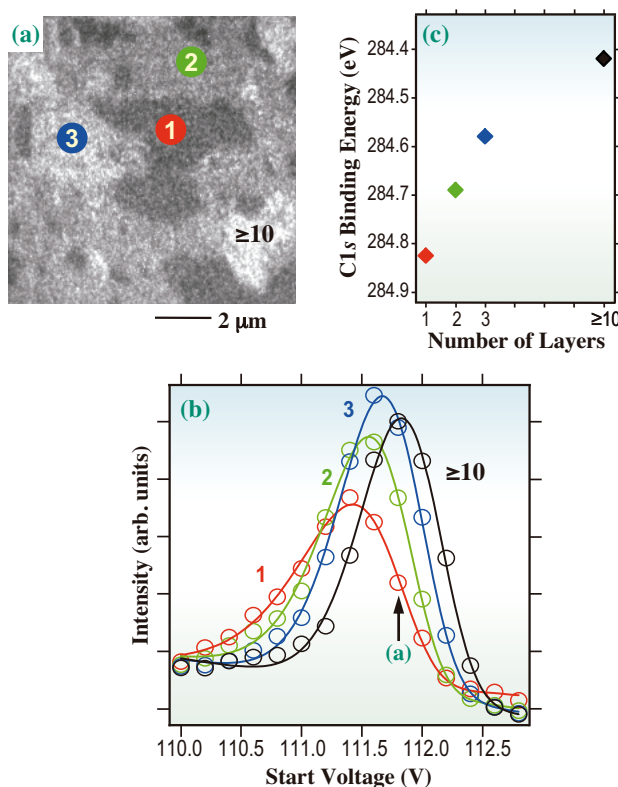


Fig. 3. (a) C1s PEEM images at start voltage of 111.8 V. The photon energy was 400 eV and the exposure time was 600 s. The areas whose N_G values are indicated are the same as those in Fig. 2(c). (b) C1s core-level photoelectron spectra obtained from sequential C1s PEEM images. Open circles denote the experimental data, and solid lines the results of fitting the data to an asymmetric Gaussian function with a linear background. (c) N_G dependence of C1s binding energy. The peak start voltage was converted to the binding energy by assuming that the binding energy of the thick graphene is the same as that of bulk graphite (284.42 eV).

Hiroki Hibino^{a,*} and Yoshio Watanabe^b

^a NTT Basic Research Laboratories

^b SPring-8 / JASRI

*E-mail: hibino@will.brl.ntt.co.jp

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