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Graphene On Au-Coated SiO_x Substrate: Its Core-Level Photoelectron Microspectroscopy Study

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The core-level electronic structures of exfoliated graphene sheets on a Au-coated SiO_x substrate have been studied using synchrotron radiation photoelectron spectroscopy (SR-PES) on a micron scale. The graphene's visibility on the Au-coated SiO_x substrate was first demonstrated by micro optical characterization, and then an SR-PES study was conducted. Because of the elimination of charging effect, a precise C 1s core-level characterization shows graphitic and contaminated carbon states of graphene. Different levels of Au-coating-induced p-type doping on single- and double-layer graphene sheets were also examined in the C 1s core-level shift. The Au-coated SiO_x substrate can be treated as a simple but high-throughput platform for *in situ* studying graphene under further hybridization by PES. © 2012 The Japan Society of Applied Physics

Graphene (a monolayer of graphite) is a unique low-dimensional system with fascinating electrical properties including linear electron energy dispersion and high room-temperature mobility,^{1,2)} which has been considered a prospective candidate for post silicon electronics. Recent progress in pristine graphene preparation has mainly been on exfoliated graphene, which is fabricated by micromechanical cleavage of graphite and then transferred to certain substrates that render it visible. A Si substrate capped with a 300 nm insulating SiO_x dielectric layer is frequently used for supporting graphene. In the gapless band structure of pristine graphene, the Fermi level coincides with its conical points, but graphene on a SiO_x substrate or metal surfaces would shift its band structure significantly.^{3,4)} In addition to concern on the influence of graphene bottom contacts, recent studies have attempted to functionalize the graphene top surface by absorbing or incorporating various materials to modify its electronic structure, e.g., control the band gap formation.⁵⁾ Therefore, through the band structure shift and core-level variation of graphene, how to consistently understand the coupling of graphene to its environment is crucial for fundamental studies and for graphene applications in future devices.

With extensive analysis based on high-resolution core-level C 1s spectra, photoelectron spectroscopy (PES) is considered a powerful tool for graphene characterization. By characterizing the valence band and core-level spectra of graphene, PES provides direct information on hybridization with the environment, and determines graphene metallicity, defect density, and contamination.^{6–8)} However, the presence of the normally used insulating SiO_x substrate complicates PES characterization. Although PES can measure graphene on a SiO_x substrate, previous results on local charging and screening effects remained unclear.^{9,10)} In this work, we demonstrate that a thin conducting Au film grown on SiO_x can serve as a graphene-supporting substrate. This substrate shows a similar optical microscope (OM) contrast as the pristine SiO_x substrate, and can be used to successfully perform micro-Raman investigations on the proposed system. The conducting Au thin film enables precise core-level PES

studies on exfoliated single-layer (SLG), bilayer (BLG), and multilayer-graphene (MLG) using local photoelectron image/spectroscopy on a micron scale. The graphitic sp² carbon and contaminated carbon states of graphene were characterized precisely in the core-level spectroscopy. Different levels of Au-coating-induced p-type doping of SLG and BLG were also examined on the basis of its core-level shifts.

The graphene samples were prepared by mechanical exfoliation on a Si(100) substrate covered with 300 nm SiO_x and a 9 nm Au layer. The sputtered thin Au film is suitable particularly for PES measurements because Au is a bottom electrode for preventing local photoelectron charging, and does not obscure the optical interference that makes graphene visible to instant optical inspection. The graphene sheets with different numbers of layers were identified using an optical microscope, and also confirmed by micro-Raman spectroscopy (μ -Raman) measurements before conducting localized PES studies. The localized synchrotron-radiation PES (SR-PES) studies were performed using the monochromatic (480 eV) soft X-ray at the scanning photoelectron microscopy (SPEM) end station of the National Synchrotron Radiation Research Center (NSRRC) in Hsinchu, Taiwan. The soft X-ray beam focused by the Fresnel zone plate and order-sorting aperture at the focal plane was about 100–200 nm in diameter. The emitted photoelectrons were collected at the same time using a multiple-channel hemispherical electron energy analyzer. While raster-scanning the sample, a two-dimensional (2D) distribution of the particular element can be mapped by setting the electron-collecting energy window of the analyzer to a characteristic core-level emission. Based on the SPEM images, the focused beam can be moved to specific locations to perform high-resolution microscopic-area PES (μ -PES).

Figure 1 show a summary of the optical image and spectroscopy results of the graphene sheets with different layer thicknesses on the Au-coated SiO_x substrate. The graphene thicknesses were identified using an optical microscope, and then confirmed by μ -Raman measurements. Generally, to enhance the interference effect between the graphene and SiO_x layer, a 300-nm-thick SiO_x layer is optimal for white light illumination.¹¹⁾ Because the Au layer was thin enough, the OM images displayed in Fig. 1(a) show that the optical

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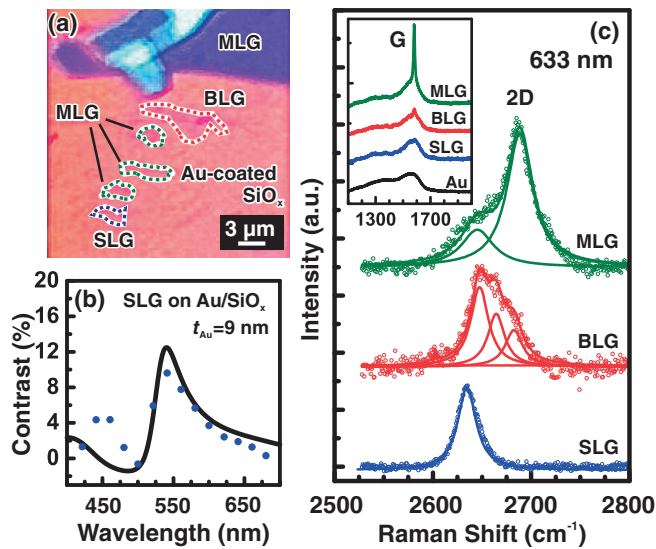


Fig. 1. (a) Optical microscopy image of SLG (blue-dashed line), BLG (red-dashed line) and MLG (green-dashed line) graphene sheets exfoliated on Au-coated SiO_x substrate used for μ -Raman and SPEM/S measurements. (b) Comparison of calculated (solid line) and measured (blue dots) contrast of graphene on thin Au ($t_{\text{Au}} = 9$ nm) coated SiO_x substrate ($t_{\text{SiO}_x} = 300$ nm). (c) μ -Raman 2D band spectra obtained at the areas of SLG, BLG, and MLG. The inset shows that the G band spectra are strongly influenced by the Au Raman signal.

contrast was sufficient for graphene identification where blue- and red-dashed lines enclose the SLG and BLG regions separately, and other three small MLG regions (enclosed by green-dashed lines) were performed to locate SLG and BLG regions easily for further μ -PES measurement. The OM image contrast of graphene on the Au/SiO_x substrate was quantitatively evaluated through the reflection spectrum (RS), as shown in Fig. 1(b). Using Fresnel's model for the graphene/Au/SiO_x trilayer system on the Si substrate, the 9 nm Au thin film on the SiO_x substrate shows best fitting in the RS with the highest visibility of SLG under 550 nm wavelength visible light, and the validity of exfoliated graphene characterization is given. The μ -Raman characterized the quality and number of the layers of exfoliated graphene sheets that were identified with the OM image. The strong Raman background signal from Au significantly influenced the graphene G band (SLG, BLG, and MLG) between 1100 to 1700 cm⁻¹; therefore, the 2D band was used to identify the number of graphene layers. In Fig. 1(c), the Raman spectra of SLG present a very sharp (~ 30 cm⁻¹ in width) and symmetric 2D band at around 2634 cm⁻¹. In contrast, the 2D bands of BLG and MLG are considerably broader (~ 59 and ~ 70 cm⁻¹ in width) and can be fitted by multiple peaks. According to the double resonance theory, the variation in the 2D band as thickness increases is attributed to the evolution of the electronic structure of the multilayered graphene.¹²⁾

After optically characterizing the graphene sheets on the Au/SiO_x substrate, Figs. 2(a) and 2(b) show the SPEM images, corresponding to the spatial distributions of Au 4f and C 1s photoelectron emissions, respectively. In the Au 4f image, the bright region corresponds to the Au-coated substrate, and the dark region shows the graphene-covered areas. This shows good agreement with the OM image in Fig. 1(a). However, C 1s chemical mapping did not clearly

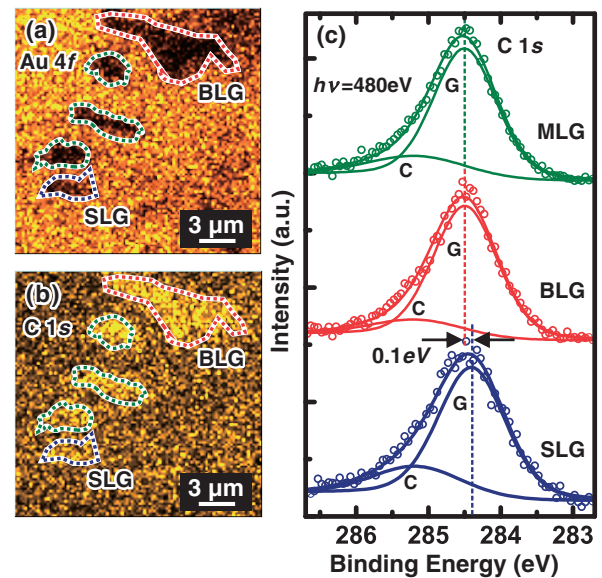


Fig. 2. SPEM/S measurements of the SLG and BLG sheets on Au-coated SiO_x substrate by using an incoming SR photon energy of 480 eV. (a, b) Chemical mapping images taken from selected energy channels show the Au 4f and C 1s distinctive chemical regions, respectively. The blue, red, and green dashed lines mark the boundaries of SLG, BLG, and MLG respectively, which are consistent with the optical microscopy image shown in Fig. 1(a). (c) μ -PES C 1s core-level spectra taken in the regions of SLG, BLG, and MLG.

indicate the SLG and BLG regions because of the carbon contamination covering the sample surface. By combining μ -Raman measurements, the SLG, BLG, and MLG regions can be located easily to perform μ -PES characterization.

Figure 2(c) shows the C 1s spectra taken on the regions of SLG, BLG, and MLG using 480 eV photon energy. All the spectra show pronounced asymmetry on the higher binding energy side, which implies that these graphene regions show conducting behaviors as opposed to nonconducting carbon materials, which exhibit a symmetric line shape.¹³⁾ The C 1s spectra (SLG, BLG, and MLG) were fitted by two components:^{9,10,14)} one represented the graphitic sp² (G) state mainly reproduces the asymmetric line shape following a Doniach–Sunjic function with a full width at half maximum (FWHM) of about 0.8 eV, which is strongly related to the low-energy electron rearrangement as the core hole creation,^{15,16)} and the other represented the contaminant (C) state (at +0.6 eV with respect to the G component) with a large FWHM value of about 1.2 eV. In addition, the line shape asymmetry, characterized by the asymmetry factor α , can be used as a probe of the core-hole screening that depends on the levels of graphene defects and imperfections. The SLG, BLG, and MLG G peaks all have similar low α values of 0.08, showing high structural perfection. Additionally, the contaminant C peak accounts for amorphous carbon sp³ bonds showing a symmetric line shape. The G peak of SLG (284.4 eV) has a binding energy of 0.1 eV lower than those of BLG (284.5 eV) and MLG (284.5 eV). This is because of the nonequal charge transfer to Au between SLG and BLG, which is dominated by different work functions between SLG (4.6 eV) and BLG (4.7 eV) to Au (5.54 eV).¹⁷⁾ Moreover, BLG and MLG show nearly identical C 1s spectra, implying that no charge transfer difference existed between them.

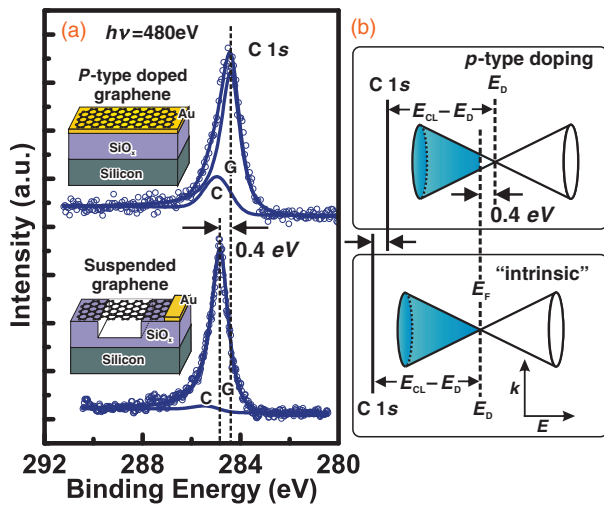


Fig. 3. (a) μ -PES C 1s core-level spectra of the suspended and Au-supported SLG sheets for determining the Au-induced doping level in graphene. Note that the core-level spectra are aligned to the corresponding core levels at the same sample contact Au. (b) Energy-band diagram of intrinsic and Au-induced p-type SLG sheets based on the measured values of their C 1s core-level energy difference in (a).

In the graphene-metal contact system, the work function difference leads to the electron transfer between graphene and metal, and naturally makes graphene have n- or p-type doping.^{4,18)} On the conducting Au-SiO_x substrate, the metal-contact-induced doping of graphene can be easily examined and characterized using a core-level PES technique. To have a reference for the graphene doping level, the suspended exfoliated SLG was treated as the intrinsic graphene for comparison. The suspended SLG was prepared by mechanical exfoliation on a partially etched SiO_x substrate (300 nm thick), which was made by conventional photolithography and dry etching to have a trench pattern (with 3 μ m width and 250 nm depth). A part of SLG was suspended over the trenches to exclude the influence of the SiO_x substrate, and thermal evaporation of Au through a shadow mask was used to have a microelectrode contact on suspended SLG. Using the focused synchrotron radiation beam, the photo-excited charge in the SiO_x trench would not affect the C 1s core-level signal taken on the SLG trench region, and therefore revealed the intrinsic state of graphene. Figure 3 shows the suspended SLG C 1s core-level photoemission spectrum with the same peak decomposition. The G peak of SLG on the Au-coated substrate has a binding energy (284.4 eV) lower than that of the suspended SLG (284.8 eV) by 0.4 eV. The measured energy difference between the C 1s core level and the Dirac point energy (E_D) of graphene is a material constant, that is, independent of environment and substrate-induced effects. Therefore, the core-level shift is related directly to the E_D shift. With the Fermi level (E_F) reference on the suspended SLG (which is at E_D), the E_F of SLG on the Au-SiO_x substrate was 0.4 eV lower than E_D as p-type doping, which is schematically shown in Fig. 3. This result is reasonable because the SLG has a work function (4.6 eV) lower than that of Au (5.54 eV), which makes electron transfer from graphene to Au result in p-type doping. The value of the E_F shift (0.4 eV) is in good agreement with the previous calculation result on graphene in contact with to Au with a separation of 5 Å .⁴⁾ In addition, based on the linear dispersion of the density

of states near the SLG E_D , the energy difference between E_F and E_D can be used to evaluate the hole concentration with

$$N_h = \frac{4\pi}{h^2 v_F^2} (|E_F - E_D|^2), \quad (1)$$

where N_h is the hole concentration and $v_F \approx 10^6$ m/s is the Fermi velocity of graphene.¹⁹⁾ The induced hole concentration of SLG was around $1.1 \times 10^{13} \text{ cm}^{-2}$ and showed a significant band structure shift, which can be successfully characterized by core-level PES.

In summary, a thin Au film was deposited on SiO_x, which is normally used as a graphene-supporting substrate. Because of the elimination of the charging effect, graphitic and contaminated carbon states of graphene can be characterized clearly in C 1s core-level spectra. Different levels of Au-coating-induced p-type doping on SLG and BLG sheets were also examined in the C 1s core-level shift. Combining a thin Au film and SiO_x substrate is a simple but high-throughput method of *in situ* studying of various hybridization states of graphene by PES or other excited-electron-detection techniques without complicated micro fabrication processes for metallic contact.

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