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Number of graphene layers as a modulator of the open-circuit voltage of graphene-based solar cell

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Impressive optical properties of graphene have been attracting the interest of researchers, and, recently, the photovoltaic effects of a heterojunction structure embedded with few layer graphene (FLG) have been demonstrated. Here, we show the direct dependence of open-circuit voltage (V_{oc}) on numbers of graphene layers. After unavoidably adsorbed contaminants were removed from the FLGs, by means of *in situ* annealing, prepared by layer-by-layer transfer of the chemically grown graphene layer, the work functions of FLGs showed a sequential increase as the graphene layers increase, despite of random interlayer-stacking, resulting in the modulation of photovoltaic behaviors of FLGs/Si interfaces. © 2010 American Institute of Physics. [doi:10.1063/1.3464319]

Graphene has shown remarkable photonic properties, such as high transparency and wide absorption spectral range, as well as outstanding electronic and mechanical properties, so extensive interest has developed toward applying it to optoelectronic devices.^{1–8} The success in growing a qualified wide-area few layer graphene (FLG), comparable to one exfoliated from graphite, using chemical vapor deposition method (CVD) enables researchers to readily apply it to optoelectronic devices and analyze physical properties of those.⁹ The graphene heterojunction system, which is composed of graphene on semiconductors or metal substrates, is the most commonly encountered structure in the study of graphene itself and in fabrication of graphene-based electronic devices. In these systems, graphene-substrate interactions induce significant effects on the observed results due to the atomic-order thinness of the graphene. One of these effects is the surface photovoltage which can be found in the low coverage metal/semiconductor (MS) junction.¹⁰ A similar effect was reported in the field effect transistor consisting of graphene on an insulating surface with metal pattern which showed a photoresponse driven by lateral band transition when the graphene crosses the different substrate surfaces, i.e., the edge effect.^{5,6,11,12} Recently, photovoltaic effect of the graphene/silicon structure with meaningful power conversion efficiency ($\sim 2.2\%$) was demonstrated.¹³

Photoresponses depend on the electronic structures of FLG with different numbers of layers in the graphene/semiconductor heterojunction system; the reasons for these responses are not well understood.¹⁴ In this study, we show that the work function of the FLG prepared by layer-by-layer transfer of the CVD-grown graphene increases as the number of layers increases, although random interlayer stacking of FLGs is observed by Raman spectroscopy. This is directly

connected to open-circuit voltage modulation of an FLG/Si photovoltaic cell.

The large-area graphene layers were synthesized by CVD of methane gas on Cu foils at 1000 °C.¹⁵ After the graphene film was spin-coated at 3,000 rpm with 5 wt % polymethylmethacrylate (PMMA) in chlorobenzene, the underlying Cu foil was etched by 0.5 M aqueous FeCl₃ solution. Subsequently, the PMMA-supported graphene layer was transferred onto Si substrates and dried on a hot plate at 80 °C. Finally, acetone was used to remove the PMMA layer. Annealing and spectroscopic measurement of the samples were carried out at the 4B1 PES II Beamline at the Pohang Light Source in the Pohang Accelerator Laboratory.

The Raman spectra showed that the transferred graphene film consists of >95% monolayers.¹⁵ As the graphene layers were transferred one after another,¹⁶ the intensities of G and 2D band peaks increased together but their ratios did not change significantly (Fig. 1). This is because the hexagonal lattices of upper and lower layers are randomly oriented,

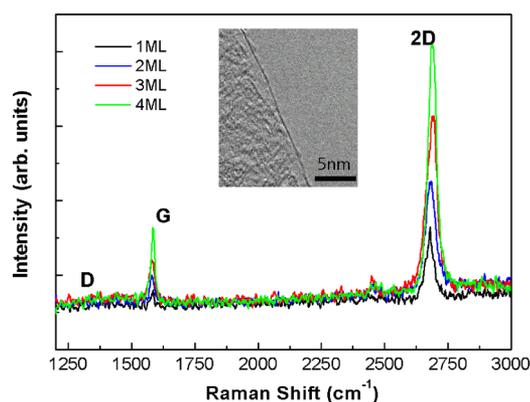


FIG. 1. (Color online) Raman spectra of graphene films transferred layer-by-layer onto a Si substrate. The 2D/G peak ratios don't change significantly as the number of layers increases from 1 to 4. The inset shows a TEM image of the monolayer graphene.

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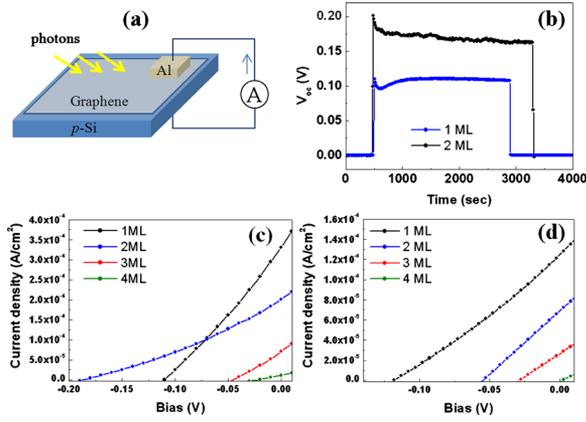


FIG. 2. (Color online) Photovoltaic responses of graphene/Si. (a) A schematic view of the sample. (b) Plot of open-circuit voltage, as a photovoltaic response to a photon source (100 mW cm^{-2}) vs time of 1 and 2 ML graphene/Si. Plot of J - V for 100 mW (AM 1.5G) illumination of as introduced samples with 1~4 ML graphene on Si, (c), and after annealing at 500°C for 12 h, (d).

unlike graphite, so that the original properties of each monolayer remain unchanged even after stacking into multilayers.^{17,18} This is clearly different from the case of multilayer graphene exfoliated from graphite crystals.¹⁹ The Raman spectra of the graphene layers transferred onto Si do not show D peaks near 1300 cm^{-1} , indicating the high quality of the graphene films. A schematic view of a prototype of the photovoltaic device is shown in Fig. 2(a). A graphene sheet (1 ML, $10 \times 10 \text{ mm}^2$) was repeatedly transferred onto a p -type Si (Density of N_a (Boron) = $2 \times 10^{15} \text{ cm}^{-2}$, $12 \times 12 \text{ mm}^2 \times 525 \mu\text{m}$) surface until the intended number of layers was reached. On the corner of the graphene, an Al contact ($2 \times 2 \text{ mm}^2$, 3000 \AA) to collect electrons was formed by e-beam evaporation through a shadow mask. Figure 2(b) shows the time evolution of the open circuit voltage (V_{oc}) of the devices with 1 and 2 ML graphene layers as a photovoltaic response to a photon source (100 mW cm^{-2}). Initial fluctuations of V_{oc} upon photon illumination rapidly disappeared and it stabilized at values of 0.10 V for 1 ML and 0.17 V for 2 ML devices. This is a transient effect as the devices approach a thermal equilibrium. The current density versus the bias voltage of as prepared devices is plotted in Fig. 2(c) for 100 mW illumination. The V_{oc} of devices with 1, 2, 3, and 4 graphene layers are -110 mV , -190 mV , -50 mV , and -3 mV , respectively. Power conversion efficiencies (η) for devices with 1 and 2 ML graphene are about 0.01% with a fill factor (FF) of about 0.23 for both with a short-current density (J_{sc}) of 0.22 and 0.42 mA cm^{-2} , respectively. However, the devices with 3 and 4 MLs had η below 0.001%.

As the work functions of the Si substrates in all devices are almost the same, V_{oc} is determined by the work function values of the FLGs. Except for 2 ML sample in Fig. 3(c), V_{oc} decreases as the number of graphene layers is increased. To remove unexpected effects induced by contaminants adsorbed on the FLGs during chemical preparation processes, the samples were annealed at 500°C for 12 h in the vacuum chamber (base pressure: 4×10^{-10} Torr) directly connected to the photoemission spectroscopy chamber. The J - V curves of the devices after annealing are shown in Fig. 2(d). V_{oc} decreased in sequence, -120 , -50 , -30 , and -5 mV , as the

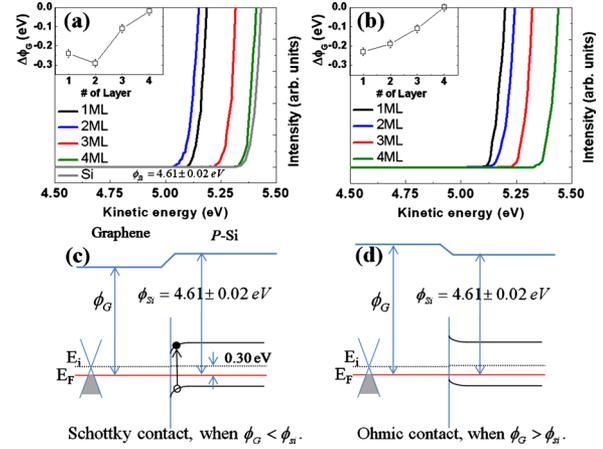


FIG. 3. (Color online) Work function modulation of FLG and electronic structure at interface of FLG and Si. (a) Onset of (SC) of ultraviolet photoemission spectroscopy spectra of as introduced FLG (1–4 ML graphene) and the pristine Si surface. The work function difference between FLG and the pristine Si surface is shown in the inset. (b) Onset of SC of the FLG after annealing at 500°C for 12 h, with work function differences in the inset. (c) Electronic structure when Schottky contact is established. The electron-hole pairs photogenerated within the depletion region of Si are separated by the built-in potential. (d) Electronic structure, with Ohmic contact.

number of graphene layers increased. This indicates that the work function difference of FLG from Si is decreased as the number of graphene layers increases. In J - V measurement electrons are collected by the aluminum contact through the devices, implying that the work function of FLG has to be lower than that of the Si substrate and that the work function of FLG is increased as the number of graphene layers increases. This result is consistent with the recent result of Yu *et al.*¹⁴ The onset of the secondary cut-off (SC), E_{SC} , of photoemission electron spectrum from as-introduced samples at a bias of -5.0 V was measured using an ultraviolet source (He I: $h\nu = 21.2 \text{ eV}$) [Fig. 3(a)]. The variation in SC value was directly dependent on the change in work function, as $\Delta\phi = \Delta\{h\nu - (E_f - E_{SC})\} = \Delta E_{SC}$, where, E_f , the Fermi level of a sample biased at -5.0 V , was 22.0 eV from the valence band spectrum. The inset of Fig. 3(a) shows the work function difference between as-introduced FLG, $\Delta\phi_G$, and the Si substrate ($\phi_{Si} = 4.61 \pm 0.02 \text{ eV}$). The work function of Si substrate beneath the FLG was estimated from the SC [gray line in Fig. 3(a)] of the exposed Si surface by Ar^+ ion sputtering until the signals of foreign atoms disappeared from the x-ray photoemission electron spectrum. The work function variation was similar with that of V_{oc} in Fig. 2(c), as the numbers of layers changed. Unexpectedly, 2 ML graphene had a higher work function and V_{oc} than the others. Figure 3(b) shows the SC of FLG after annealing at 500°C for 12 h in the vacuum chamber. Interestingly, the SC value is well behaved, i.e., it increased as the number of graphene layers increased without any exception. This implies a sequential decrease in contact potential energy, $\Delta\phi_G$, which agrees well with the behavior of V_{oc} in Fig. 2(d). Note that the work function difference (0.04 eV) between 1 and 2 ML graphene is smaller than that (0.12 eV) of exfoliated ones.¹⁴ This shows weak interlayer interactions of FLGs prepared by layer-by-layer transfer due to random interlayer stacking. The prominent dependence of V_{oc} on $\Delta\phi_G$ indicates that the photovoltaic effects in the FLG/Si structure can be described by the photovoltaic effect of a MS structure. The MS cell's

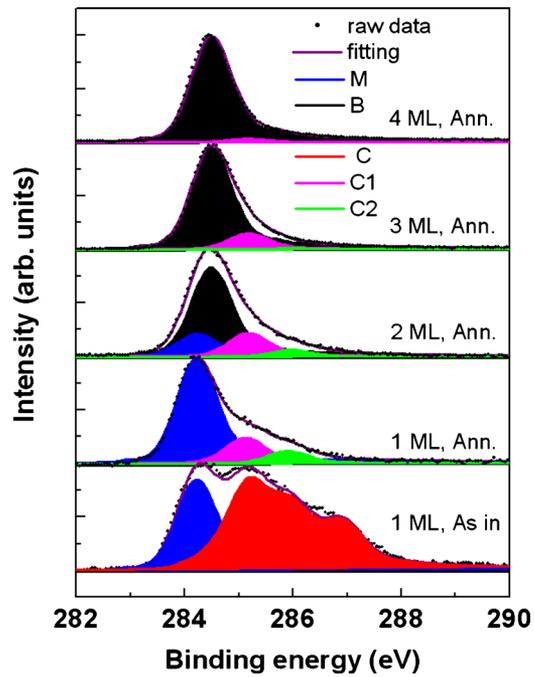


FIG. 4. (Color online) C 1s core level spectra taken at $h\nu=350$ eV. Peaks named by M and B are the main features of monolayer graphene and bulk graphene, respectively. Both have a Doniach–Sunjic line shape (Ref. 17). The C 1s spectrum of as-introduced 1 ML graphene, the bottom one, has one monolayer peak and four contaminant related peaks, which are integrated. C 1s spectra of 1–4 ML graphene after annealing at 500 °C are shown in the second to top figure. Two contaminant related peaks, named by C1 and C2, decreased as the number of layers increased, while the monolayer peak, M, is replaced by the bulk peak, B, at 4 ML graphene.

open-circuit voltage, $V_{oc}=n[\phi_B/q+(kT/q)\ln(I_s/A_cA^+T^2)]$, mainly depends on the contact barrier, $\phi_B=\phi_{Si}-\phi_G=\Delta\phi_G$, and diode quality factor, n , because kT at room temperature (~ 0.0259 eV) is far smaller than ϕ_B . A_c and A^+ are the contact area of the diode and the Richardson constant, respectively.^{20,21} The schematic view of electronic structure of FLG/Si structure is shown in Fig. 3(c) when $\phi_G < \phi_{Si}$ and Fig. 3(d) when $\phi_G > \phi_{Si}$.

Figure 4 shows the C 1s spectra at $h\nu=350$ eV from synchrotron radiation source. The parameters of decomposed peaks are characterized by two divided parts: The parameters of the peaks originating from FLG include a Doniach–Sunjic line shape, using a Lorentzian line width of 178 meV and an asymmetry factor of 0.07 following the previous result,²² while the parameters of peaks of contaminant carbon species with asymmetric character were excluded due to weak coupling of contaminants with the graphene layer. The C 1s spectrum of as-introduced 1 ML graphene was decomposed into one graphene peak and four peaks related with contaminants, which are integrated as the red area in the bottom spectra in Fig. 4. The considerable amount of uncontrollable contaminants explains the unexpected behavior appearing in the work function of as-introduced FLGs as a function of layers. Upon annealing the sample the C 1s spectra are well characterized by two peaks originating from FLG and another two peaks from contaminants. In the case of 1 ML graphene only one graphene related peak shown by blue area, named M, appears with two contaminant peaks named C1 and C2. In the 2 ML graphene, the monolayer peak, M, is decreased while a bulk graphene peak represented by black area is visible at 284.45 eV. In the 4 ML graphene, the mono-

layer peak is completely replaced by the bulk graphene peak B. This result is comparable to that of an exfoliated graphene sample whose work function depends on the number of layers.^{14,23}

In summary, we have shown the modulation of the work function of FLG by controlling the number of graphene layers prepared by layer-by-layer transfer of CVD-grown graphene. After unavoidably adsorbed contaminants were removed from the FLGs, by means of *in situ* annealing, the photovoltaic response is found to directly depend on the number of graphene layers in the FLG/Si structure, driven by the modulated electronic structures at interfaces. This evidently shows the established weak interlayer interactions via π orbital even in the randomly stacked FLGs.

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