Efficient CVD Graphene Transfer Techniques by using Oxide Passivations

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1. Introduction

Graphene, a single layer of sp^2 -bonded carbon atoms, has attracted strong interest due to the unique electronic properties [1]. The charge carriers in graphene can have extremely high mobility owing to their massless nature in the linear band dispersion [2]. Thus, graphene-based field-effect transistors (FETs) are promising candidates for future high-speed devices. For fabrication of graphene FETs at low cost, chemical vapor deposition (CVD) is recognized as a powerful technique to produce large-area graphene. In particular, it has been reported that large-area graphene dominated by a single layer can be synthesized by CVD on polycrystalline Cu foils [3]. Graphene grown by CVD on metals must be transferred to insulating substrate, when applying it to a FET channel. In the typical graphene transfer process, graphene on metal is first coated with polymer, usually with photo- or electron-beam resist. The polymer layer works as a supporting layer while the metal is chemically etched. After that, such resist is repeatedly used in the lithography process to fabricate FETs. However, it has been reported that, after removing the resist, polymer residues robustly remain on point defects and grain boundaries of graphene [4]. In addition, such polymer residues induce the deterioration in transport characteristics as well as the extrinsic carrier doping into graphene. The surface contamination of graphene, arising from polymer residues, has long been a critical issue to be solved for achieving the high performance in graphene FETs.

In this work, we report on a newly developed CVD graphene transfer process with oxide thin films, which prevents polymer residues from being directly adsorbed on the graphene surface. Several oxide thin films have been adopted as a passivation layer for graphene. The efficacy of each oxide passivation has been examined by Raman and X-ray photoemission spectroscopies.

2. Experimental

Single layer graphene samples were grown by CVD on Cu films. The Cu films sputtered on the SiO₂(300 nm)/Si substrates were placed in a high-vacuum chamber. After Ar/H₂ annealing for 20 min, the graphene growth was carried out at 860 °C under a controlled pressure of 1 kPa for 60 min using CH₄ diluted by Ar and H₂ as the source gas. Oxide passivations for graphene were prepared by electron-beam evaporation. Each metal thin film (Al, Cr, Ti, and Ni: 1–3 nm) was deposited on graphene/Cu/SiO₂/Si under a base pressure of $<5 \times 10^{-5}$ Pa. They were then ex-

posed to air, and naturally oxidized to Al₂O₃, Cr₂O₃, TiO₂, and NiO. Oxide/graphene samples were transferred by a photoresist-assisted process in a Cu etchant (FeCl₃ and HCl solution) onto SiO₂(90 nm)/Si substrates. Raman spectroscopy was carried out using a Horiba Jobin Yvon LabRAM HR Raman microscope under ambient pressure at room temperature (RT). The wavelength and power of the excitation laser were 488 nm and below 0.5 mW, respectively. The spectral resolution was set to 4.5 cm⁻¹. X-ray photoemission spectroscopy (XPS) was performed with an ULVAC-PHI ESCA-1800 system under 5×10^{-7} Pa at RT. The x-ray source was the monochromatized Al *K* α line. The energy calibration was performed by the Au Fermi edge. The total energy resolution was set to 650 meV.

3. Results and Discussion

Figure 1(a) shows the Raman spectrum of graphene on the Cu film before transfer. The characteristic features from graphene are observed as the 2D- and G-peaks around 2700 and 1600 cm⁻¹, with the ever-increasing background from the Cu film. The intensity ratio between the 2D- and G-peaks (2D/G) after subtracting the background, is estimated to be $2D/G \sim 3.0$, which indicates clearly that the graphene is a single layer. The Raman spectra of graphene after transferring onto SiO₂/Si are presented in Fig. 1(b). After transfer without the oxide passivation the 2D/G is



Fig. 1. Raman spectra of (a) graphene on Cu/SiO₂/Si before transfer and (b) unpassivated and oxide passivated graphene on SiO₂/Si after transfer.



Fig. 2. Lorentzian fitting of (a) G- and (b) 2D-peaks in Raman spectra for unpassivated and oxide passivated graphene. The symbols and solid-lines indicate the experimental data and fitting curves. The light- and dark-shaded areas show the G^+ - and G^- -peaks. Each spectrum is normalized by the peak intensity.

significantly decreased to ~ 0.8 , which could arise from the polymer (resist) residues on the graphene surface. On the other hand, the estimated 2D/G is approximately 2 for all oxide passivated samples. It suggests that the graphene transfer using the oxide passivation can suppress the contaminations from the polymer residues.

For further discussing the quality of graphene under the oxide passivation layers, we have carried out Lorentzian fitting for each Raman spectrum. The fitting results for the G- and 2D-peaks are displayed in Figs. 2(a) and 2(b). The peaks can be fitted with a single Lorentzian except for the G-peaks of the TiO₂- and NiO-passivated graphene. It is noticed that the G- and 2D-peaks for the Al2O3- and Cr_2O_3 -passivated graphene shift by ~10 cm⁻¹ toward the lower wavenumber side compared to those for the unpassivated one. According to the G- and 2D-peak shifts with the gate doping [5], our results indicate that, in comparison to the Al₂O₃- and Cr₂O₃-passivated graphene, the unpassivated one is doped with holes because of the surface contamination from the polymer residues. Therefore, the Al₂O₃- and Cr₂O₃-passivations are effective to suppress the extrinsic carrier doping. Interestingly, the G-peak spitting is clearly observed in the TiO₂- and NiO-passivated graphene. The G-peak splitting is reproduced by assuming two Lorentzian components, known as the G^+ - and G^- -peaks centered at 1597 and 1588 cm⁻¹, as shown in Fig. 2(a). The G-peak spitting is attributed to the split of the doubly degenerate optical phonon of E_{2g} symmetry at the Γ point of the Brillouin zone. There are only a few reports on the G-peak splitting for graphene systems [6,7].

To reveal the origin of the observed *G*-peak splitting in the Raman spectra of the TiO₂- and NiO-passivated graphene, the electronic states have been investigated by XPS. The Ti (Ni) $2p_{3/2}$ core-level XPS spectra of TiO₂ (NiO)/graphene/Cu and TiO₂ (NiO)/Cu on the SiO₂/Si substrates are given in Fig. 3(a) [3(b)]. The shoulder structure



Fig. 3. Core-level $2p_{3/2}$ XPS spectra of (a) TiO₂/graphene/Cu and TiO₂/Cu as well as (b) NiO/graphene/Cu and NiO/Cu on SiO₂/Si substrates. Each spectrum is normalized by the peak intensity.

is clearly observed in the lower binding energy $(E_{\rm B})$ side of the Ti $2p_{3/2}$ peak for TiO₂/graphene/Cu [see the arrow in Fig. 3(a)] whereas the structure does not appear for TiO_2/Cu . As shown with the arrow in Fig. 3(b), the similar shoulder structure also exists in the lower $E_{\rm B}$ side of the Ni $2p_{3/2}$ peak for NiO/graphene/Cu. Such a shoulder structure is derived from the Ti- or Ni-C bonding states, i.e., the hybridized states between the Ti or Ni d and C $\pi(p_z)$ orbitals. In contrast, for the Al₂O₃- and Cr₂O₃-passivated graphene the distinct shoulder structure is not obtained in the lower $E_{\rm B}$ side of the Al or Cr $2p_{3/2}$ peak (data not shown). Hence, the observed G-peak splitting in the Raman spectra for the TiO2- and NiO-passivated graphene could arise from the band renormalization around the K point due to the d-p hybridization. The d-p hybridization affects the electronic structure of graphene, resulting in the reduction of the transport properties. Therefore, one concludes that TiO₂ and NiO are not suitable for a passivation layer for graphene.

4. Summary

The efficacy of the oxide passivations in graphene transfer has been examined by Raman spectroscopy and XPS. It has been found that the Al_2O_3 - and Cr_2O_3 -passivations are effective to suppress the contaminations from polymer residues on the graphene surface. Meanwhile, the TiO₂- and NiO-passivations are not effective since the interactions of Ti or Ni with C occur.

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