LARGE-AREA GRAPHENE-BASED FLEXIBLE TRANSPARENT CONDUCTING FILMS

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A simple approach by direct synthesis of few-layer graphene sheets and transferring them onto flexible substrate is demonstrated. The hydrogen effect on the D band intensity of Raman spectra for few-layer graphene sheets synthesized by chemical vapor deposition (CVD) on Ni-evaporated silicon substrate is investigated by optimizing the mixing ratio of C_2H_2/H_2. While the Ni etchant is used to melt away the squeezed Ni layers between graphene sheet and silicon substrate, the graphene sheet is transferred onto polyethylene terephthalate film by a fishing method. It is found that the condition of graphene transfer strongly relies on the cooling rate of the film during CVD synthesis. The sheet resistance of the film decreases as the film thickness increases. A sheet resistance of 233 Ω/sq is obtained at a transmittance of 62%.

Keywords: Large area graphene; chemical vapor deposition; flexible transparent conducting film.

1. Introduction

Carbon material such as graphite and carbon nanotubes has been proven to be an excellent electrode material with high chemical stability, high transmittance, high specific surface area, and high conductivity.\(^1\)\(^-\)\(^4\) Recently, the graphene, two-dimensional form of graphite, has opened a possibility of variety applications, such as flexible thin film transistors and touch panel electrodes, due to its extraordinary electronic properties of nearly zero effective mass.\(^5\)\(^-\)\(^7\) Nevertheless, applications are still limited by the complicated sample preparation processes.\(^5\)\(^,\)\(^6\) For this reason, for transparent conducting film (TCF) applications, graphite oxide has been prepared to form thin film that was further reduced by chemical and thermal treatment.\(^8\)\(^,\)\(^9\) Although large-area reduced graphite oxide film was realized, the residual oxygen groups resulted in high sheet resistance of the film that failed to meet the requirement for practical applications.

There have been efforts to use chemical vapor deposition to synthesize large-area graphene layers directly on metal substrates or metal-deposited Si substrates.\(^10\)\(^-\)\(^12\) The presence of defects and control of the film thickness of the graphene layers have not been investigated, which are essential issues for many applications.\(^13\)\(^,\)\(^14\) An additional difficulty arises from the transfer of the graphene film onto a desired transparent film for applications, in particular, for TCFs. PMMA was used to transfer graphene in which PMMA was removed later.\(^12\) The problems often occurs during Ni etching. The etching of Ni layers by acid treatment and the simultaneous separation of the graphene film from the
underlying substrate have been of challenges, particularly in large-area graphene transfer.

In this report, large area graphene was synthesized in atmospheric pressure chemical vapor deposition (APCVD) chamber on Ni-film-deposited Si substrate. The hydrogen amount in the carbon-hydrogen gas mixture was optimized to reduce defect density and amorphous carbon quantity of graphene layers, and furthermore to obtain uniform thickness of graphene layers. We also found that the separation of graphene layers from Ni for transfer was strongly dependent on the cooling rate of the sample after growth. Hydrophobic graphene film, suspended on the hydrophilic etchant surface after the Ni-film was etched away, was successfully transferred onto another hydrophobic film of polyethylene terephthalate (PET) by a fishing method. The thickness of the film was controlled by the APCVD growth rate. The synthesized graphene size is only limited by the chamber and Si wafer size in the CVD approach.

2. Sample Preparation and Experimental Details

We synthesized graphene layers on Ni-deposited Si/SiO\(_2\) substrate by thermal APCVD. A Ni thickness of 400 nm was deposited on 4 inches of Si substrate by an e-beam evaporator. Since the chamber size limits our sample size up to 2 × 2 cm\(^2\), we cut Ni-deposited Si wafer into small pieces. The prepared substrate was placed in the APCVD chamber with a few degrees of tilt angle with respect to the incoming gas flow direction to obtain homogeneous gas contact to the Ni surface. The homogeneity of the graphene film thickness was degraded when the substrate was placed with no tilt angle. The chamber was heated to 900°C with H\(_2\) gas flow and kept for 10 min. The growth of graphene layers was then carried out at the same temperature with a flow of mixture of ethylene and hydrogen gases.

Unlike the epitaxial growth of semiconductor materials obtained from the typical CVD, carbon atoms deposited from the carbon source were precipitated into the Ni substrate during the gas flow. Graphene formation takes place via a segregation of C atoms out to the Ni surface during cooling after termination of the incoming gas. Growth has been carried out with different ratios of hydrogen and ethylene gases in order to optimize the conditions for high quality graphene with minimum defect density. The samples were cooled down to room temperature without any gas introduction to maintain smooth surface morphology. With a gas introduction, for instance argon gas, during cooling, we observed the negative effect on the surface morphology.

Raman spectroscopy (Renishaw RM10000-Invia) with laser excitation energy of 514 nm (2.41 eV) equipped with a notch filter of 50 cm\(^{-1}\) cutoff frequency was used to investigate defect density of graphene samples. Confocal Raman Microscope (Witech-CRM200) filtered by a Rayleigh rejection filter (<100 cm\(^{-1}\)) with an excitation energy of 2.33 eV and a focus spot size of 350 nm was used to measure the uniformity of graphene layers. Scanning tunneling microscopy (Seiko-SPA 400) with a DFM mode was used to study morphology of the transferred graphene. High resolution transmission electron microscopy (HRTEM: JEM 2100F, JEOL) was used to see the morphology of the synthesized and transferred graphene. Field emission scanning electron microscopy (FESEM: 6700F, JEOL) was used to study the number of layers and the morphology of graphene sheets. For the TEM sample preparation, the synthesized graphene on Ni substrate was submerged in diluted nitric acid. Etchant solution, where graphene layer is suspended, was diluted by deionized water after Ni sub-layer was etched away completely. The suspended graphene was then transferred onto the copper grid and dried at room temperature.

3. Results and Discussion

3.1. Quality and morphology of graphene sheets

Figure 1(a) shows Raman spectra of graphene layers synthesized with different gas mixing ratios. The data were averaged from 10 different locations of graphene layers for each plot. To obtain large grain size graphene layers and to investigate the defect density dependence on H\(_2\) mixing ratio, samples were kept for 10 min. Relatively thick layers up to 40 layers were formed. D/G peak intensities with different H\(_2\) ratios in Fig. 1(b) and the insets show that the C\(_6\)H\(_4\)/H\(_2\) ratio of 10/100 is the best ratio for graphene layers with lowest defect density and highest crystallinity. The C1s peak of XPS data in the inset obtained from our samples with 10/100 ratio is similar to that of highly oriented pyrolytic graphite (HOPG). This indicates that the quality of graphene layers obtained from our optimized conditions is close to that of HOPG.
Fig. 1. (a) Raman spectra, with an excitation energy of 2.41 eV, averaged over ten data points at different positions of the samples grown 10 min at 900°C. (b) Intensity ratio of D-band to G-band as a function of H$_2$ amount during growth. The left inset shows the Raman spectra of D and G bands at different H$_2$ amount. The right inset is XPS C1s peaks from CVD grown sample and HOPG. (c) Raman spectra averaged over ten data points taken on graphene after transfered onto SiO$_2$ and PET. (d) Confocal Raman spectra with an excitation energy of 2.33 eV taken on graphene after transfer onto SiO$_2$ showing G\textsuperscript{'} peak dependence on the number of layers.

To see the quality of thin graphene layers, the samples were prepared for a growth time of only 1 min and were transferred to another Si/SiO$_2$ substrate and the PET film (the transfer technique will be discussed later). Several features can be noted from Raman spectra in Fig. 1(c): (i) No noticeable D band is observed even for thin graphene layers, (ii) the intensity of G\textsuperscript{'} band near 2700 cm$^{-1}$ is comparable to that of G band due to the thin graphene layers, (iii) the peak positions of G and G\textsuperscript{'} bands are shifted due to the different interaction with substrate, and (iv) the intensity of G\textsuperscript{'} band is reduced significantly in the case of PET film. Our results indicate that the effect of substrate should be considered in the analysis of Raman spectra, for instance SiO$_2$ layer can act as a p-type dopant for graphene similar to carbon nanotubes, where the peak positions of G band is up-shifted with p-type doping.

The uniformity of the thin graphene layers was investigated by the confocal Raman spectroscopy. Figure 1(d) shows confocal Raman spectra with excitation energy of 2.33 eV at different positions. The peak positions and intensities of G\textsuperscript{'} band varies widely from 2690 to 2711 cm$^{-1}$ depending on the positions. This indicates inhomogeneous distribution of film thickness. One may extract information for the film thickness from the peak position. The peak position of G\textsuperscript{'} band decreases and the intensity ratio G\textsuperscript{'}/G increases as the film thickness decreases. Although the exact position of G\textsuperscript{'} band in correlation to the film thickness vary slightly with substrate,\textsuperscript{17} we can estimate the film thickness based on the previous results with Si substrate.\textsuperscript{16} These values are listed in the figure. Peaks near 2690, 2698, and 2705 cm$^{-1}$ are assigned to monolayer, double layer, and triple layer, respectively, while the peak near 2711 cm$^{-1}$ is assigned to 5–10 layers.
Figure 2 shows SEM and AFM images of the corresponding graphene layers. Several patches distinguished by colors indicate different layer thickness. These patches resemble the grains of Ni substrate layers in terms of their sizes and shapes. It is noted that the central dark area which is marked as SiO$_2$ is bare SiO$_2$ layer that the graphene layers in this area is completely burned out by laser beam irradiation during confocal Raman spectroscopy. Three-dimensional AFM image clearly shows the absence of graphene layers in the focused area. Some parts marked by the curved arrows indicate folding of graphene layers at the edge of opening. The thickness of the surrounding graphene grain was measured with respect to the bare SiO$_2$ layer. The number of layers is marked in each patch. The distribution of the number of layers obtained from AFM height measurement is similar to that obtained from confocal Raman spectra in Fig. 1(d). The pristine graphene layers on Ni substrate are also shown in SEM of Fig. 2. Nonuniform distribution of graphene layers is visible. After transfer to Si substrate, wrinkles are formed. The wrinkle formation is attributed to the stress release between Ni substrate and suspended graphene layers upon Ni etching and/or the surface stress accumulated between hydrophilic substrate and hydrophobic graphene layers. The inset shows the suspended graphene sheet floating onto the liquid surface after etching of Ni layer.

Figure 3 shows the TEM images taken after the graphene sheet was transferred onto the Cu TEM grid. Combination of grey and white parts of graphene layers in Fig. 3(a) is an evidence of the presence of different layer thickness. Some folding phenomenon observed in AFM images of Fig. 2(a) is again visible at the edge of the graphene flakes in Fig. 3(b). These folding at the edge enabled us to measure the graphene thickness, as shown in Fig. 3(c). One can clearly observe wide range of graphene thicknesses from monolayer up to eight layers. Electron diffraction patterns taken from double layer and seven layers are shown in Fig. 3(d). Clear hexagonal spots with alternating spot intensities are observed in the case of double layers. This indicates a formation of AB stacking order. However in the case of seven layers, a ring-like patterns are observed, which is an evidence of polycrystalline
phases. This indicates that the grain patches are stitched in different orientations.

3.2. Transfer process of graphene sheets

Since the graphene layers were synthesized on Ni-deposited Si substrate, it is necessary to transfer graphene layers to different substrate for a precise measurement of physical and chemical properties and many applications. In principle, Ni layer can be oxidized and etched away in acid solution. However, the accessibility of acid solution to Ni is limited to edges only, making it difficult for fast oxidation without damaging topmost graphene layers. We often observed that it took a long time to remove Ni layers which induced defects and damages to graphene layers. Therefore, we tried to create some crevices between Ni layer and Si substrate by using the concept of mismatch of thermal expansion coefficient. Once the CVD process was complete, the hydrocarbon and hydrogen gases were terminated. The chamber was then cooled down with different cooling rates.

Figure 4(a) shows the temperature changes as a function of time. As shown in the inset, when the cooling rate exceeds a critical value, the graphene layers were easily separated from the SiO$_2$ substrate. The thermal expansion coefficients of SiO$_2$ and Ni are $0.24 \times 10^{-6}$ and $13.4 \times 10^{-6} ^\circ$C$^{-1}$, respectively. This large thermal mismatch creates some crevices between two layers so that Ni etchant can penetrate into such crevices to accelerate the etching rate. The graphene layers were immediately separated from the substrate within a few seconds as shown in Fig. 4(b). The next step is to transfer the graphene film onto the PET film for TCF application. When the whole substrate was submerged in etchant solution, Ni and graphene layers were immediately suspended, as shown in Fig. 4(b) (see
Fig. 4. (a) Graphs showing different cooling rates of the Ni substrates. The shaded region in the inset is the region that the separation occurs. (b) Time evolution of images taken during the separation of Ni with graphene sheet from Si substrate and etching of Ni layer. After 5 min, Ni layer was completely etched away by diluted HNO$_3$.

The separated Si substrate was sunk and Ni layer was dissolved after 5 min. Because of the hydrophobic nature of graphene layers, the graphene layer was suspended on the etchant surface as shown in Fig. 4(b). The graphene layers was then fished by the underneath PET film. With this approach, the folding of graphene layer was minimized.

3.3. Flexible transparent conducting film

Figure 5(a) shows the sheet resistance and transmittance as a function of growth time. The sheet resistance and transmittance decrease as the growth time increases. During CVD process, carbon atoms are incorporated into the Ni layer and then outdiffused to form graphene layers at cooling step. At a short growth time, the number of carbon atoms incorporated into the Ni layer for a given growth time is small. Therefore, the thickness of graphene layers formed by outdiffusion of carbon atoms is expected to be thin. Average number of layers is estimated by taking account of the absorbance of incident light by each graphene layer that each graphene layer absorbs 2.3% of the incident light. The corresponding thickness of graphene layers at around 80% is nine layers. The sheet resistance
The optical micrographs exhibit the graphene film (1 × 1 cm²) on the PET film and demonstrate the macroscopic uniformity of the film. Control of the defects and uniformity of the film in large area are the key factors to improve the film performance. Another advantage of graphene film is the flexibility. Figure 5(b) shows the sheet resistance of the same films in Fig. 5(a) with bending angle. The changes in the sheet resistance becomes appreciable after 90 degrees. Nevertheless, the change is less than 15% up to 135 degrees. This implies that no appreciable cracks occur in the film during bending. This excellent flexibility is advantageous over the conventional indium tin oxide film.

4. Conclusions

We demonstrated a CVD synthesis method of large scale graphene for direct utilization to flexible transparent conducting film applications. An initial reduction of Ni surface by H₂ gas was necessary for uniform growth of the graphene layers. The control of relative content of H₂ gas with respect to hydrocarbon gas was also required to minimize the defects and remove unnecessary carbonaceous particles to decrease the sheet resistance of prepared few-layered graphene. Furthermore, a robust method of transferring graphene transparent conducting film on the desired substrate was demonstrated. Our approach of large area synthesis of graphene layers and their robust transfer to a desired substrate creates new possibilities for graphene film to be utilized for many electronic devices such as sophisticated high speed circuits and conducting films for touch panels, and common electrodes for flexible displays.

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References