POLY(ETHYLENE CO-VINYL ACETATE)-ASSISTED ONE-STEP TRANSFER OF ULTRA-LARGE GRAPHENE

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One-step roll-to-roll lamination transfer of graphene was achieved by poly(ethylene co-vinyl acetate) as a binding material which has thermoplastic property and wide rubbery-plateau region between $T_g - T_m$. The transferred graphene film has a transmittance of 96.7% at 550 nm and 1.96 kΩ/sq of sheet resistance measured by simple 4-probe method. Standard deviation was found to be 0.198 kΩ/sq.

**Keywords:** Graphene; transfer; supporting layer; EVA.

1. **Introduction**

Recently, two dimensional carbon layer of graphite, graphene, has attracted considerable interest due to its extraordinary electronic properties. Graphene has a high mobility of 15000 cm$^2$/Vs and room-temperature quantum Hall effect. Moreover, graphene has many potential applications such as thin film transistors, solar cells, touch panels, and LCDs. Nevertheless, applications are still limited by the complicated sample preparation processes.

In order to use graphene for such applications, a large-area sample preparation is required. The important issues are (i) growth of ultra-large size graphene uniformly over several tens centimeters, (ii) simple transfer of graphene to a desired substrate, and (iii) maintaining high quality of the transferred graphene so as to have uniform physical and electrical properties to improve the device performance. Recently, graphene has been synthesized on catalytic metal layers such as nickel and copper by chemical vapor deposition (CVD).

However, the growth of graphene has been limited to a size of few centimeters, which is not sufficient for practical device applications. For applications of graphene films as electrodes of various electronic devices, the film is required to be transferred to a desired substrate such as silicon and plastic film. Currently, graphene film, floated on etchant solution after etching, is transferred to substrate without or with an assistance of intermediate sacrificing layers of, for instance, poly(methyl methacrylate) (PMMA). However, these transfer methods produce defects such as cracks, holes, and wrinkles during the transfer process, degrading the quality of the graphene film and limiting its applications.

This technical issue becomes more serious when thinner and larger graphene layers are transferred.

In this work, a one-step transfer method of ultra-large graphene area to plastic substrate by a roll-to-roll lamination process without creating additional defects is proposed. Thermal CVD was used to synthesize monolayer or double layer graphene of 44 inches in diagonal size on Cu foil in a small chamber. The synthesized graphene with Cu foil was laminated with an assistance of adhesive layer, in our case, poly(ethylene co-vinyl acetate, EVA) with vinyl acetate (VA) as a supporting layer, to plastic film, followed by Cu etching. The transferred graphene revealed film uniformity with a resistance deviation of less than 10%. We found that EVA play a key role in acting as a binder between graphene and substrate and not as a sacrificing layer. EVA is activated at a specific temperature upon annealing to provide adhesive force to the graphene film and solidified upon cooling by retaining its morphology. This minimizes the formation of air traps and tearing, producing homogeneous electrical properties over the whole area of the resulting graphene film.

2. **Experimental**

Growth method of ultra-large area graphene on Cu foil: Cu foil (wacopa, purity 99.9%, thickness 75 µm) was rolled and inserted into the chamber to synthesize ultra-large graphene using 8 inches CVD chamber. The growth method was similar to the previous study. In brief, 80 sccm of hydrogen gas was fed into the chamber until around 800 mTorr. Temperature of the chamber was elevated up to 950°C for 2 h. Methane gas was injected for 30 min with a flow rate of 250 sccm for growth. Finally, temperature was cooled down to 180°C while maintaining methane and hydrogen gas for 3 h.

Characterizations of graphene film: The conformation of graphene after growth was carried out by contact angle of water (Kruess DSA15E, Germany). Number of graphene was analyzed by Raman spectroscopy (Renishaw RM1000-invia) with excitation energy of 2.41 eV (514 nm, Ar$^+$ ion laser). Transmittance of graphene film on plastic substrate was obtained using Varian Cary
5000 UV-Vis spectrometer. For TEM sample preparation, a size of $1 \times 1 \text{cm}^2$ graphene on Cu foil was floated on the etchant. After 30 min, Cu foil was fully etched away. Then, the etchant solution was diluted with deionized (DI) water to rinse the remaining etchant. Finally, the graphene sheet was simply picked up by carbon-coated copper grid. TEM observation of graphene sheet was done by JEM 2100F (JEOL).

Direct transfer method from Cu foil to plastic substrate: graphene on copper foil was laminated with laminating film (Ethylene-vinyl acetate (EVA)/Polyethylene terephthalate (PET) –50µm/50µm, GMP Co., LTD) at an elevated temperature of 115°C. Rolling speed in the rolling machine was kept at 1 cm/s. To remove the metal catalyst, the PET/graphene/Cu multi-layer film was dipped in etchant (Transene, type I etchant) for 30 min. The graphene transferred film was washed in DI water and dried by air.

3. Results and Discussion

Figure 1 shows a schematic of the synthesis and transfer process. Large-area graphene film was grown by thermal CVD method, where Cu foil was rolled and inserted into quartz tube chamber (a diameter of 8 inches) to facilitate large area, as shown in Fig. 2(a) (top). Uniform growth temperature and gas flow in a reaction zone were critical control parameters for the homogeneous graphene film formation on the entire Cu substrate. The graphene formation was hardly observable but was identified by hydrophobicity. Contact angle by water on graphene/Cu foil was 84.1° (bottom-middle), which is similar to that on HOPG (92.5°), as shown in Fig. 2(a) (bottom-right side). This was much larger than 55.6° (bottom-left side) of Cu foil.

The resulting samples have thin graphene layer of a mixture of monolayer and double layer in a large area of $75 \times 85 \text{cm}^2$ (44 inches in diagonal), as shown in Fig. 2(b).

This transferred graphene film has a transmittance of 96.7% at 550 nm (Fig. 3(a)). Since a single layer of graphene absorbs light by 2.3%, the transmittance of our sample indicates that our graphene layer is composed of a monolayer and a double layer. Number of graphene layers was also confirmed by Raman spectroscopy. G and G' band were observed at 1585 cm$^{-1}$ and 2699 cm$^{-1}$, respectively, as shown in Fig. 3(b). High intensity of G'-band with respect to G-band and red shift of G'-band indicates that our graphene layer is composed of a monolayer or a double layer, as reported previously. The plane view of transmission electron microscope (TEM) image in Fig. 3(c) shows no appreciable contrast in a given area, indicating the uniformity of monolayer and double layer, as shown in the edge of graphene in the inset. Formation of monolayer was dominant over a large area except thick spots, which was observed from optical microscopy. Diffraction pattern clearly shows a well defined
Fig. 2. (a) Top: Rolled Cu foil to insert for CVD. Two stainless steel rings in the inner and outer regions of Cu foil were connected to prevent collapse of Cu foil during high temperature CVD growth. Bottom: Graphene formation on Cu foil was confirmed by hydrophobicity. Cu foil: 55.6° (left side), graphene: 84.1° (middle), HOPG: 92.5° (right side). (b) Synthesized graphene film on Cu foil with a size of 44 inches in diagonal, 75 × 85 cm² (color online).

Fig. 3. (a) Transmittance of the film. It shows 96.7% at 550 nm. (b) Raman signal of graphene sheet was observed at 1585 cm⁻¹ and 2699 cm⁻¹ as a G-band and G' band, respectively. (c) Graphene sheet on TEM grid (Inset: cross-section image of graphene sheet, scale bar — 5 nm). (d) Diffraction pattern image of graphene.
hexagonal spots (Fig. 3(d)). This result indicates that our graphene layer is well ordered with high crystallinity. Formation of air traps, tearings, and wrinkles in transferred graphene can be detrimental to many electronic applications and therefore has been a serious drawback in typical transfer method let alone the complexity in the transfer process.\textsuperscript{10,12}

This problem becomes more serious when the size of graphene gets larger to industry level. Furthermore, the transfer method has to be simple for large area transfer. The roll-to-roll lamination process has been widely adopted in thin film industry because the process is easily adjusted to make multi-layer film structure. Because Cu foil is flexible in its nature, we can directly use a roll-to-roll based lamination process in order to make polyethylene terephthalate (PET)/graphene/copper multi-layer film. After eliminating Cu foil by acidic etching from the multi-layer film, a thin graphene layer on transparent PET film is obtained, as shown in Fig. 1.

The key ingredient in the lamination process is the formation of a supporting layer on the PET film to make the transfer process more effective. The supporting layer becomes active above glass temperature to cleave the graphene layer. This ensures minimal formation of air traps and tearings to make film transfer reliable and to have homogeneous electrical properties over a whole area of the resulting graphene film. In our experiment, we chose hot-melt adhesive material in thermoplastic polymer, poly (ethylene co-vinyl acetate, EVA) with vinyl acetate (VA) of 18\% (mp = 87°C, Melt index = 8 g/10 min) as a supporting layer. The content of VA determines crystallinity of copolymer and thus the melting temperature (Large amount of VA decrease the melting temperature. For instance, 25\% of VA decreases melting temperature to 75°C. (Melt index = 19 g/10 min))). Melting properties, wetting while in the melt, re-solidification, and the properties of the adhesive after re-solidification are all important for determining the adhesive force in hot-melt adhesive polymer. The dynamic mechanical spectrum of thermoplastic polymer is divided into a glassy region, rubbery plateau, and flow region. In the glass region, the material behaves as a glass, and is usually brittle. Semi-crystalline polymer has no dramatical drop of modulus at glass temperature ($T_g$) by maintaining a plateau. This region of semi-crystalline polymer exists in a wide range of temperature. The reason for this phenomenon is that the crystallite in the semi-crystalline polymer reinforces its rubbery region. At melting temperature ($T_m$), the modulus drops dramatically and polymer does not possess binding strength. Hence, it is important that a polymer has a semi-crystalline structure.

Another important factor to increase adhesive force is an increase of viscosity in the plateau region after $T_g$. That is, the existence of wide range of rubber plateau region in semi-crystalline polymer is crucial for providing stable adhesive force to graphene as shown in Fig. 4.

The incorporation of polar comonomer, VA, is unique for the formation of low density polyethylene, because VA generates highly linear structure. Therefore, the presence of VA decreases crystallinity and impart more flexibility to the final structure. In brief, increasing level of VA imparts better adhesion to other materials.\textsuperscript{17} Copolymerization of polyethylene with VA induces long chain branch of polyethylene back bone, leading to semi-crystalline polymer structure in Fig. 5. Since the amount of VA (18\%) is small, the...
melting temperature is high and furthermore the interaction is governed by hydrophobicity between polyethylene backbones and graphene layer. The copolymer increases viscosity after glass transition temperature and thus the contact area of polyethylene backbones increases by entropic disorder and thus adhesive force is enhanced in rubbery plateau region.

While graphene layer on Cu foil together with EVA-coated PET (EVA:PET = 50 µm:50 µm) was squeezed in by roll-to-roll process at a speed of 1 cm/s, the temperature was maintained at 115°C. The laminated film was immersed in etchant for 30 min to remove Cu foil. The transparent conducting film of ultra-large area graphene of 40 inches in diagonal was obtained, as shown in Fig. 6(a). The film was sometimes hazy due to the remaining EVA on the surface morphology of Cu foil. The haziness disappeared after annealing at 120°C for 10 min. Special care to remove wrinkles in Cu foil should be taken to eliminate this process. Furthermore, thickness of EVA and its content should be optimized to guarantee robust transfer and transmittance of the film in the future.

Figure 6(b) shows the film uniformity of sheet resistance in a size of 15 inches (21 × 33 cm²). Average sheet resistance was 1.96 kΩ/sq, which is similar to the reported data. The film have a standard deviation of 0.198 kΩ/sq, which is about 10% deviation. Relatively small deviation supports the robustness of our approach in eliminating defects such as cracks, air traps, tearings, and wrinkles, which affect the sheet resistance and uniformity over a whole area. In general, small air gaps exist between graphene layer and substrate surface, that is, the graphene layer is not fully attached to the substrate. The unattached regions tend to break easily and form cracks. Recently, this problem was resolved by carrying out extra coating of PMMA after fishing graphene from etchant. However, this method is unlikely to be used in industry applications due to the process complexity. Our method, one-step roll-to-roll lamination by a supporting layer resolves not only the formation of defects but also the complexity issue of the process.

4. Conclusions

Ultra-large area graphene was synthesized on Cu foil. We demonstrated an easy method of graphene transfer by introducing one-step roll-to-roll lamination process. This was achieved by introducing a supporting layer, EVA, on PET film. This method did not degrade electrical properties of transferred graphene film by eliminating defects such as cracks, tears, and wrinkles. Thickness of EVA and its content should be optimized to guarantee robust transfer and transmittance of the film in the future. The size of the demonstrated graphene film of 44 inches is already acceptable for practical industrial use. Furthermore, this process can be extended to establish roll-to-roll based continuous manufacturing process for large area flexible transparent electrodes.

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