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Multilayered Graphene Electrode using One-Step Dry Transfer for Optoelectronics

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In this study, multilayered graphene was easily transferred to the target substrate in one step using thermal release tape. The transmittance of the transferred graphene according to the number of layers was measured using a spectrophotometer. The sheet resistance was measured using a four-point probe system. Graphene formed using this transfer method showed almost the same electrical and optical properties as that formed using the conventional poly (methyl methacrylate) transfer method. This method is suitable for the mass production of graphene because of the short process time and easy large-area transfer. In addition, multilayered graphene can be transferred on various substrates without wetting problem using the one-step dry transfer method. In this work, this easy transfer method was used for dielectric substrates such as glass, paper and polyethylene terephthalate, and a sheet resistance of ~240 ohm/sq was obtained with three-layer graphene. By fabricating organic solar cells, we verified the feasibility of using this method for optoelectronic devices.

Keywords : Multilayer Graphene, One-Step Dry Transfer, Thermal Release Tape, Optoelectronic Devices
OCIS codes : (010.1320) Atmospheric transmittance; (160.4236) Nanomaterials; (160.4760) Optical properties; (230.4170) Multilayers; (250.2080) Polymer active devices

I. INTRODUCTION

Indium tin oxide (ITO) is widely used as a transparent electrode [1, 2] because of its excellent electrical and optical properties [3]. However, ITO electrodes are not flexible because of their brittleness, which is a critical disadvantage, and they are very expensive because of the scarcity of indium [4]. Many alternative materials to ITO have been developed for use as transparent electrodes [5-7]. Graphene, one of the most promising materials, has been used in various research fields as a next-generation transparent electrode. Graphene is not only flexible and elastic, but also has excellent electrical [8-10] and optical properties [11]. In order to exploit these properties of graphene for electrical and optical devices, a single layer or multilayered graphene transfer process is essential. However, it is difficult to transfer graphene, which is composed of a single layer of carbon atoms [12, 13]. Although graphene formed using the most widely used wet transfer method with poly (methyl methacrylate) (PMMA) [14] shows excellent properties, it is not suitable for commercialization because of its low productivity and its wetting problem. In this study, we demonstrate an easy multilayer graphene transfer method with a much higher productivity using thermal release tape while maintaining the same level of properties as those achieved with the wet transfer method. Using the proposed method, multilayered graphene can be transferred to the target substrate in one step without chemical contamination or wetting of the target substrate. To verify the feasibility of the multilayer graphene transfer method using the thermal release tape, a flexible conductive electrode and an organic photovoltaic (OPV) cell with a transparent electrode were fabricated and characterized.

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II. Method

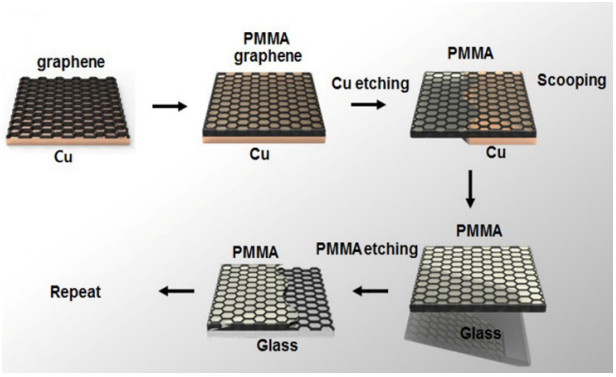
Graphene is a two-dimensional material consisting of only carbon atoms in a hexagonal structure [15]. Three of the four outer electrons of carbon form a strong covalent bond with the three neighboring carbon atoms in graphene. Four electrons form the sp^2 bond and have a hexagonal lattice structure as a whole.

Graphene has a charge mobility 150 times that of copper and a sheet resistance of less than 50 ohm/sq theoretically. In addition, its strength is 200 times that of steel, and its thermal conductivity is superior to that of diamond. Theoretically, monolayer graphene has an excellent transmittance of about 97.7% and a dense lattice structure that even He gas cannot penetrate.

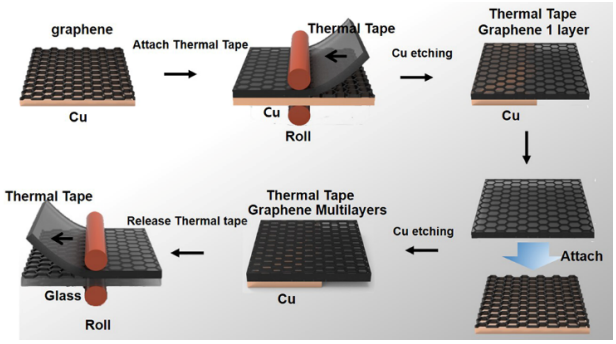
In this study, graphene was synthesized on a copper thin film, which acts as a catalyst layer, by chemical vapor deposition (CVD). Copper has very low carbon solubility at high temperature, in contrast to nickel. Therefore, precursor hydrocarbons are decomposed into carbon and hydrogen atoms, which react on the copper thin film surface. In this case, single-layer graphene can be synthesized by forming sp^2 bonds of carbon atoms that prevent contact with the hydrocarbons. Graphene was synthesized at 1,000°C for 30 min and methane gas was used as the carbon source for the graphene.

Figure 1(a) shows the wet transfer method for multilayer graphene using PMMA as a support layer. PMMA solution (9 wt%, Sigma Aldrich) was spin-coated on the surface of graphene at 600 rpm for 40 s. After removing copper with an etchant, the remaining PMMA/graphene thin film was washed in deionized water. After scooping the floated graphene with the target substrate, the thin film was dried using nitrogen gas and heat-treated to improve adhesion and prevent the formation of wrinkles. PMMA was removed by acetone for several minutes to finally afford the transferred monolayer graphene. Multilayered graphene was transferred to the target substrate by repeating the above steps.

Figure 1(b) shows an easy dry transfer method for multilayer graphene using thermal release tape as a support layer. In contrast to the general wet graphene transfer method, in this dry transfer method, several graphene layers are transferred not to the target substrate, but to the thermal release tape. At first, graphene synthesized on the copper film was attached to the thermal release tape using a roll laminator (EXCELAMI-3550, GMP). Once the copper was removed by the etchant and washed with deionized water, the single layer graphene was transferred to the thermal release tape. By repeating the above processes, multilayer graphene can be stacked on the thermal release tape. Then, the multilayered graphene can be transferred to the target substrate in one step using a heated roll laminator without any chemical contamination or wetting of the target substrate. The tape has to be released in one step by sufficient heat and pressure to transfer graphene with good properties.



(a)



(b)

FIG. 1. Process flow of (a) wet transfer method for multilayered graphene and (b) one-step dry transfer method for multilayered graphene.

III. RESULTS AND DISCUSSION

3.1. Characterization of Multilayered Graphene Formed by One-Step Dry Transfer

To characterize the structure and properties of multilayered graphene before and after transfer by the one-step dry transfer method, Raman spectra (Ramboss 500i, Dongwoo Optron Co.) were obtained as shown in Fig. 2. Figure 2(a) shows the Raman spectrum of the synthesized monolayer graphene. The number of graphene layers can be determined using the ratio between the G and 2D peaks. In monolayer graphene, the 2D peak has an intensity that is about twice that of the G peak. As the graphene layers are stacked, the intensity of the G peak relative to the 2D peak increases. Figure 2(b) shows the Raman spectrum of the multilayered graphene on the thermal release tape after transfer in one step. As shown in Fig. 2(b), the ratio between the G and 2D peaks is almost one because three layers of graphene were stacked. Due to the damage on the graphene surface during the transfer process, the D peak appeared in the Raman spectrum as shown in Fig. 2(b).

To examine the electrical properties of the transferred multilayered graphene, the sheet resistance was measured with a four-point probe system (CMT-SR2000N, AIT). Figure 3 shows the sheet resistance of the transferred graphene

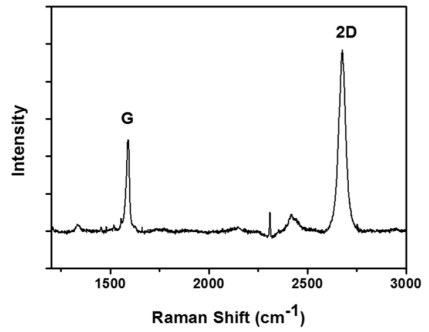


FIG. 2. Raman spectrum of (a) monolayer graphene, (b) multilayered graphene after one-step transfer.

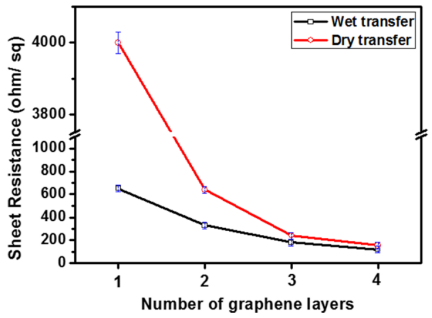


FIG. 3. Sheet resistance of transferred graphene according to the number of layers formed by wet and one-step dry transfer.

according to the number of layers formed by the wet and dry transfer methods. The sheet resistance of a single layer, two layers, and three layers of graphene formed by the wet transfer method was about 650 ohm/sq, 330 ohm/sq, and about 180 ohm/sq, respectively. On the other hand, the sheet resistance of a single layer graphene formed by the dry transfer method was very irregular and high, about 4000 ohm/sq. However, the sheet resistance of two layers was about 640 ohm/sq, and it decreased significantly for three layers, to about 240 ohm/sq. There is no significant difference in the sheet resistance between three layers and four layers formed by both transfer methods. The sheet resistance almost levels off at around 200 ohm/sq after three stacked layers.

The high sheet resistance of the transferred first layer of graphene is because the adhesion of the first layer of graphene to the substrate is not sufficient for complete separation of the graphene from the thermal release tape, leading to partial transfer to the target substrate or with cracked grains. Because of this mechanical damage, the sheet resistance of a single layer of graphene is very high. However, additional graphene layers transferred can cover the cracked areas and voids in the first transferred layer, leading to a similar resistance level of the transferred multilayer graphene as that of the wet transfer method.

To use the multilayered graphene as a transparent electrode, the optical transmittance for both the wet and dry transfer methods was measured using a spectrophotometer (EVO300, Thermo Fisher Scientific). Monolayer graphene has a theoretical transmittance of about 97.7% in the visible light region. Figure 4 shows the transmittance of graphene classified according to the wet and dry transfer methods. The transmittance of single layers of graphene transferred by the wet and dry transfer methods was measured as 97.6% and 96%, respectively. Because of residues or foreign materials, the transmittance of the transferred graphene was slightly lower than the theoretical value. The transmittance of the graphene transferred through the wet method decreased continually with an increase in the number of stacked layers as shown in Fig. 4(a), similar to the sheet resistance. In the case of graphene transferred layer-by-layer using the

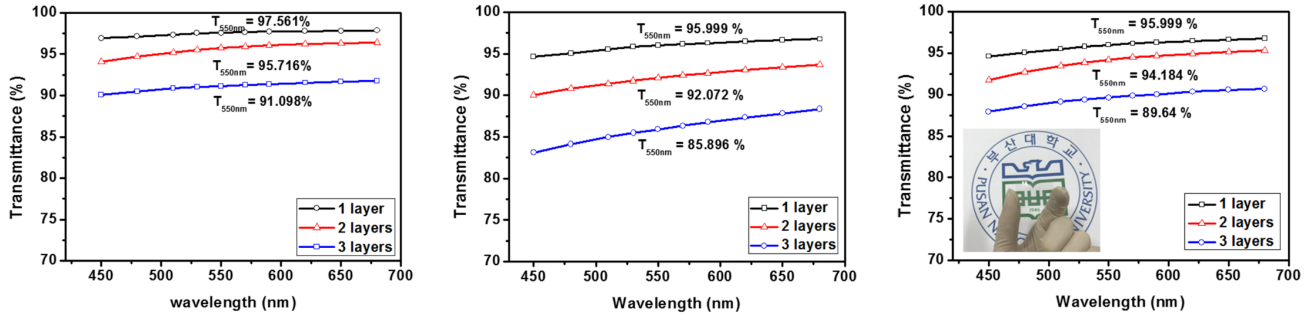


FIG. 4. Transmittance of multilayered graphene using (a) PMMA transfer, (b) thermal tape transfer by one layer after another, and (c) thermal tape transfer in one step.

dry transfer method, the higher the number of graphene layers transferred, the greater is the reduction in the transmittance because of accumulation of the residue of thermal release tape on the transferred graphene, as shown in Fig. 4(b). Figure 4(c) shows a transmittance result of multilayered graphene transferred by the one-step transfer method similar to that obtained by the wet transfer method. When multilayered graphene was transferred in one step, the reduction in the transmittance of graphene was not significantly different between the wet and dry transfer methods. This one-step method can minimize the residue of thermal tape on the transferred graphene because multilayered graphene is transferred in one step.

To verify the feasibility of using the multilayered graphene sheet as a flexible conductive electrode, the sheet resistance was measured after a bending test. Figure 5 shows the sheet resistance according to the number of bending cycles with a bending angle of 90°. The sheet resistance slightly increased with the increase in the number of bending cycles up to 4000. Because each graphene layer reaches an equilibrium state, after 4000 bending cycles the sheet resistance saturated at around 300 ohm/sq.

This method is simple and allows for the easy large-area transfer of graphene. In addition, the method is highly productive and involves dry transfer, where in the substrate does not need to be wet. Therefore, using this method, multilayer graphene can be transferred to various substrates such as paper. Figure 6 shows the multilayered graphene transferred to paper having ~800 ohm/sq by the one-step dry transfer method. The reason why the resistance on paper is higher than that on glass or PET is that the large roughness of paper prevents the adhesion between paper and multilayered graphene. If graphene is stacked more, the sheet resistance will be reduced. These conductive electrodes can be potentially used in optoelectronic devices in the future.

3.2. Organic Photovoltaics with Multilayered Graphene Electrode

In order to fabricate an OPV cell based on multilayer graphene, the interface between the graphene and PEDOT:PSS (AI4083) as a hole transfer layer is important. To deposit PEDOT:PSS on the multilayered graphene which has naturally a hydrophobic surface property, the graphene surface needs to be hydrophilic. The hydrophobic surface was transformed to hydrophilic by UV ozone treatment without damaging the graphene. Figure 7 shows the contact angle of PEDOT:PSS/graphene before and after surface treatment with UV ozone.

Despite the surface treatment, the efficiency of an OPV cell based on multilayer graphene was about 0.15%. Figure 8 shows the atomic force microscopy images of the transferred graphene surface. The surface roughness of a single layer of graphene was about several nanometers as shown in Fig. 8(a), but that of multilayered graphene was about tens of nanometers because of the presence of residues on the surface of graphene as shown in Fig. 8(b). Given that the typical thickness of PEDOT:PSS spin-coated on a graphene

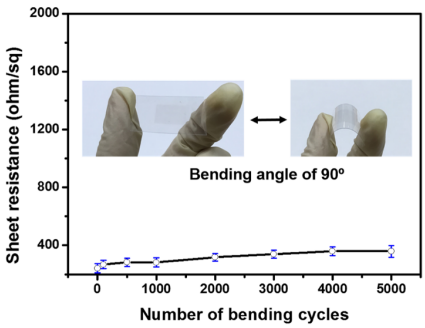
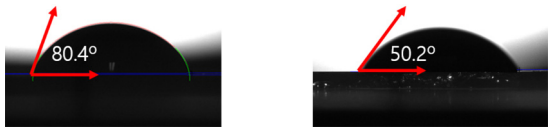


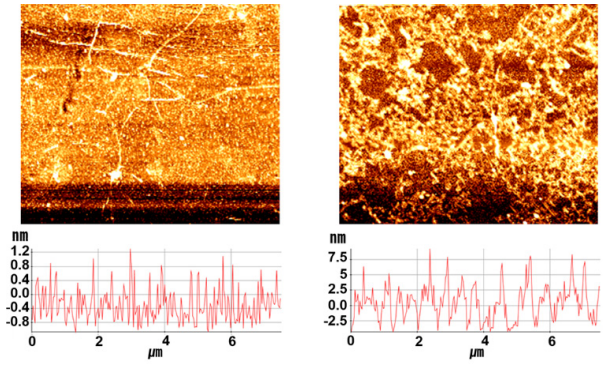
FIG. 5. Sheet resistance according to the number of bending cycles.

FIG. 6. Transferred multilayer graphene on paper (in red circle).



(a) (b)

FIG. 7. Contact angle before (a) and after (b) UV ozone surface treatment.



(a) (b)

FIG. 8. AFM images of transferred (a) single-layer graphene surface and (b) multilayered graphene surface.

surface is around 40 nm, the amount of this residue present is very critical in achieving high efficiency of OPV cells.

IV. CONCLUSION

The wet transfer method using PMMA, which is commonly used for graphene transfer, has been studied extensively because of the excellent electrical and optical properties of graphene. However, this method is considered unsuitable for the commercialization of graphene because it is a difficult process, has low productivity, and the target substrate needs to be wet. To overcome this limitation, a method of transferring multilayer graphene to various substrates in one step using a thermal release tape has been demonstrated here. The multilayer graphene transferred by the above method exhibited excellent electrical and optical properties similar to those of multilayer graphene transferred by the wet method. In addition, it has high productivity and enables large-area transfer, and can be used on various substrates such as paper or business cards since it is a dry method. The multilayered graphene transferred by the dry transfer method can be used as a flexible electrode. The sheet resistance of a multilayered graphene electrode was maintained over 4000 bending cycles. These results show that multilayered graphene is suitable for use as flexible electrodes. By applying to OPV cells, we verified that the multilayered graphene transferred by this method is suitable as a counter electrode. If the problem of residues can be overcome, the dry transfer method might be an excellent option for the mass production of optoelectronic devices.

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