Exfoliated Bi-layer Graphene as an Alternative to Transparent and Conductive Film

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Abstract—*High quality, bi-layer graphene is fabricated using mechanical exfoliation of highly ordered pyrolytic graphite. The bi-layer graphene on the glass substrate is characterized using scanning electron microscopy, optical microscopy, micro-Raman spectroscopy and UV-vis spectrophotometer. The effects of substrate cleaning on the quality of graphene are investigated. From the structural and optical characterizations, it is confirmed that, the exfoliated bi-layer graphene can be useful for transparent and conductive film application in thin film solar cells.*

Keywords: *bi-layer graphene, HOPG, mechanical exfoliation, transparent conductive film*

INTRODUCTION

Graphene is a novel two-dimensional carbon materials arranged periodically in a honeycomb lattice. This is the building block for most of the allotropes of carbon except diamond and amorphous structures. This can be explained by the fact that when graphene is rolled, it forms 1-D carbon nanotube, when wrapped forms 0-D fullerene, and forms 3-D graphite when layers of graphene are stacked on each other [1]. Graphene has shown highly desirable properties [2] such as high transparency, extremely high charge carrier mobility, thermodynamic stability and mechanical hardness. Graphene in its primary stage of development has exhibited ideal properties for applications such as transistors [2], transparent electrodes [3], liquid crystal devices [4], ultra-capacitors [5], and ultra-tough paper [6].

Graphene can be fabricated mainly by two techniques such as, (i) physical technique-which involves (a) micromechanical exfoliation of highly ordered pyrolytic graphite (HOPG) [7] and (b) sublimation of silicon from SiC at high temperatures [8], (ii) chemical technique-which involves (c) reduction of graphene oxide [9] and (d) chemical vapor deposition (CVD) on transition metal catalysts [10]. Micromechanical exfoliation technique is the first experimental development for the fabrication of graphene by A. K. Geim and K. S. Novoselov at the University of Manchester, UK in 2004. This method promises to be the best for fabrication of high-quality graphene having field effect mobility of 3000-10000 $cm^2/V.sec$ [1].

Thin film solar cells (TFSC) are being pursued as viable alternatives to silicon solar cells. A critical aspect of these solar cells is the current conduction across the illuminated side of the device in the transparent conductor (TC), namely, the illuminated side (electrode) should be transparent with good conductance [11]. The conventional transparent conductive film (TCF) materials are ITO, FTO, ZnO, CNT random meshes, thin metal films, metal gratings, Ag nanowire networks. The desired TCF properties [12] such as (a) sheet resistance (R_s) = 10 Ω/sq, (b) Transmission (T) = 93-94 % in the wavelength range 400-1100 nm, (c) carrier concentrations (n) = Low, as increased free carrier absorption leads to a reduction of IR transmission, are indicated and a comparison of graphene with the best TCF used recently, i.e. ITO is shown with reference to the desired TCF properties in Tab. 1. The high transparency accompanied with large conductivity favors graphene as a very suitable material for TCF in thin film solar cells. It is evident that graphene has outperformed ITO in various categories owing to its excellent properties.

TABLE 1: A COMPARISON OF GRAPHENE WITH ITO WITH REFERENCE TO DESIRED TC PROPERTIES

Properties / TCF	Sheet Resistance (Ω/sq.)	Optical Transmittance (%)	Wavelength Range (nm)	Carrier Conc.	Carrier Mobility ($cm^2V^{-1}s^{-1}$)	Thickness (nm)
Desired	10	High	400-1100	Low	High	Low
ITO	< 100	90	450-750	10^{20} cm^{-3}	43	170
Graphene	< 125	97.7	450-750	10^{12} cm^{-2}	15,000	0.34

Herein, we report the fabrication of high quality bi-layer graphene (BLG) by micro-mechanical exfoliation technique and its structural and optical characterizations, which give an idea of exploring BLG as TCF material in thin film solar cells.

EXPERIMENTAL

The fabrication of graphene is done using the micromechanical cleavage of HOPG (ZYH Ceramics) of 12x12x3 mm^3 size. Glass of roughness (≈3 nm) was used as the substrate for graphene deposition.

Usually glass substrates contain impurities on it, which needs to be removed before graphene transfer. The glass pre-treatment is done using two step processes: (a) successive ultrasonication of glass in trichloroethylene, acetone and de-ionized water for 5 minutes each at 35 °C and (b) etching the glass substrate by dipping into hydrofluoric acid (HF) for 30 sec. Finally the substrates were rinsed in de-ionized water and dried using air blower.

Using commercial scotch-tape, graphene is mechanically exfoliated from HOPG and transferred to pre-treated glass substrates. The samples are characterized by optical microscope, scanning electron microscope (Hitachi-3400N, Tokyo, Japan), UV-vis spectrophotometer (UV-2450, Shimadzu, Japan) and Raman spectroscopy (Invia Reflex/514, Incoterm, UK). The laser light of wavelength 514 nm is used for Raman characterization.

RESULTS AND DISCUSSION

The optical microscopic image of the as transferred graphene on glass is shown in Figure 1. (a). Scattered deposits of graphitic patches on the etched glass surface are clearly observed. The presence of graphitic flakes is also observed by scanning electron microscopy (SEM) shown in Figure 1. (b). The flakes of around 10 µm in side length can be seen.

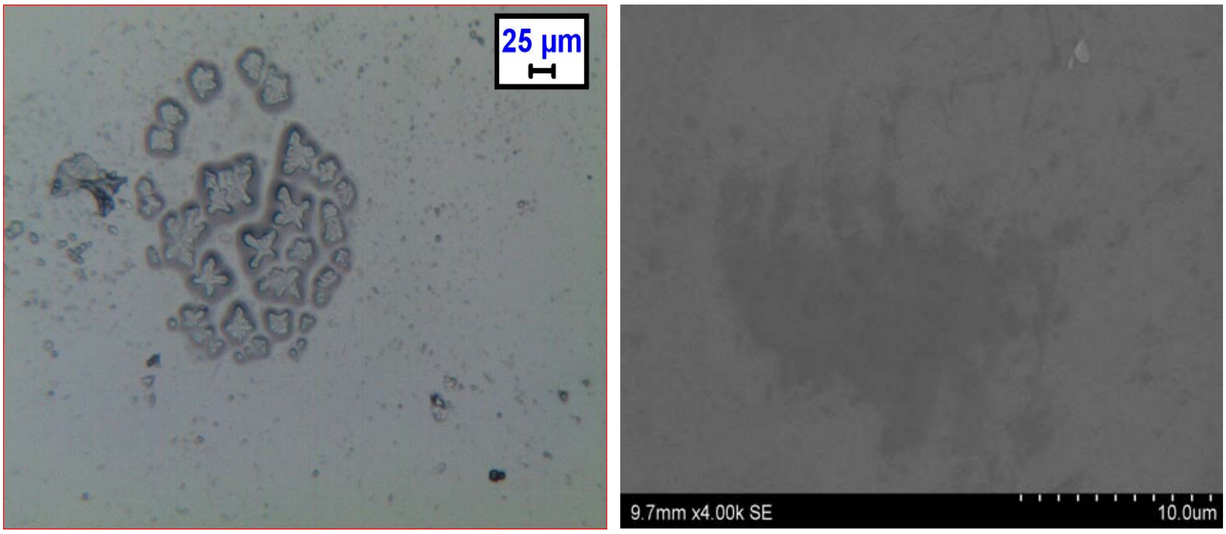

FIG. 1: (A) OPTICAL MICROSCOPY AND (B) SEM IMAGE OF GRAPHENE ON GLASS

The Raman spectrum of graphene on glass is presented in Figure 2. It contain four peaks: a weak D-band at 1350 cm^{-1}, a strong G-band at 1560 cm^{-1}, a strong 2D-band at 2700 cm^{-1} with FWHM of ≈ 40 cm^{-1}, and a week band at 2450 cm^{-1} is due to HOPG [13]. The very low intensity ratio of D band to G band indicates low imperfections in graphene [14] and high intensity ratio (≈ 1.67) of 2D band to G band with a narrow 2D-band full-width at half maximum of 40 cm^{-1} indicates the presence of bi-layer graphene [14].

The optical properties of as-transferred graphene films on glass is measured and shown in Fig. 3. Transmittance of > 85% is observed from the wavelength range of 350 nm to 750 nm. The strong absorption of light at 300 nm may be attributed to the band gap absorption corresponding to ~4.2 eV due to the π-π* transition of aromatic C-C bonds. A weak and broad absorption band centered at 650 nm may be attributed to the impurity based optical absorption which is mainly due to grapheme oxide [15].

It is also noted that the transfer of graphene onto untreated glass is not successful, because of the presence of grease on glass surfaces. The presence of grease impurities on glass surface restricts the vanderwalls force of attraction between glass and graphene. After the pre-treatment of glass substrate by trichloroethylene, acetone, de-ionized water and HF acid as described in the experimental section, the substrates become grease free and graphene can easily make a strong vanderwalls force of attraction with the glass surface.

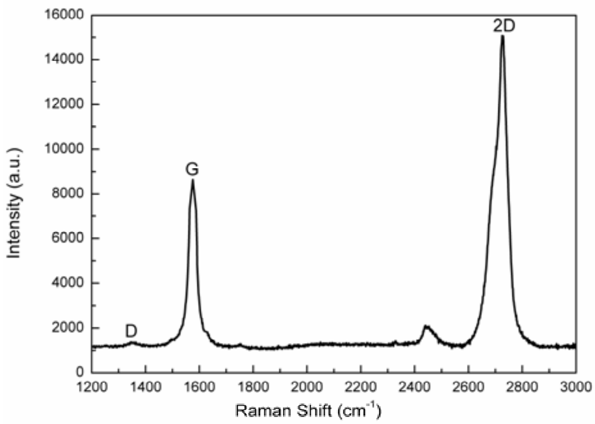

FIG. 2: RAMAN SPECTRUM OF GRAPHENE ON GLASS

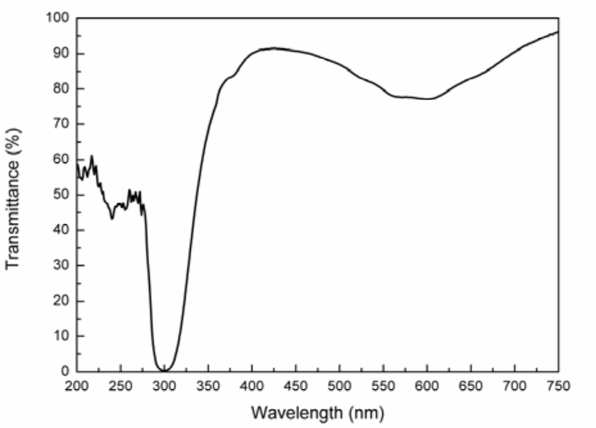

FIG. 3: TRANSMITTANCE VS. WAVELENGTH PLOT OF GRAPHENE ON GLASS

CONCLUSION

Bi-layer graphene is successfully fabricated and transferred onto pre-treated glass by micromechanical cleavage of highly ordered pyrolytic graphite using scotch tape. Raman spectra show that the graphene sheets is of high quality and UV-vis measurement shows that the bi-layer graphene has high transmittance of 85-95% in the range 350 nm-750 nm. From this, it can be said that BLG can be suitable use for TCF applications in thin film solar cells.

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REFERENCES

[1] A.K. Geim, and K. S. Novoselov, “The rise of Graphene”, Nat. Mater., 2007, pp. 183-191.
[2] M. Burghard, H. Klauk, and K. Kern, “A high performance top-gate field-effect transistor based frequency doubler”. Adv. Mater., 2009, pp. 2586-2600.
[3] X. Li, Y. Zhu, W. Cai, M. Boryslak, B. Han, D. Chen, R. D. Piner, L. Colombo, and R. S. Ruoff, “Transfer of Large-Area Graphene Films for High-Performance Transparent Electrodes”, Nano Lett., 2009, pp. 4359-4363.
[4] H.G. Craighead, J. Cheng, and S. Hackwood, “New display based on electrically induced index-matching in an inhomogeneous medium”, Appl. Phys. Lett., 1982, pp. 22-24.
[5] S.R.C. Vivekchand, C. S. Rout, K. S. Subrahmanyam, A. Govindaraj, and C. N. R. Rao, “Graphene-based electrochemical supercapacitor”, J. Chem. Sci., 2008, pp. 9-13.
[6] D.A. Dikin, S. Stankovich, E. J. Zimney, R. D. Piner, G. H. B. Dommett, G. Evmenenko, S. T. Nguyen, and R. S. Ruoff, “Preparation and characterization of graphene oxide paper”, Nature, 2007, pp. 457-460.
[7] K.S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigirieva, and A. A. Firsov, “Electric field effect in atomically thin carbon films”, Science, 2004, pp. 666-669.
[8] H. Huang, W. Chen, S. Chen, and A. Thye Shen Wee, “Bottom-up Growth of Epitaxial Graphene on 6H-SiC”, ACS Nano, 2008, pp. 2513-2518.
[9] V.C. Tung, M. J. Allen, Y. Yang, and R. B. Kaner, “High-throughput solution processing of large-scale graphene”, Nat. Nano., 2009, pp. 25-29.
[10] A. Reina, X. Jia, J. Ho, D. Nezich, H. Son, V. Bulovic, M. S. Dresselhaus, and J. Kong, “Large area, few-Layer graphene films on arbitrary substrates by chemical vapor deposition”, Nano Lett., 2009, pp. 30-35.
[11] Hu, Yun Hang, Wang, Hui, and Hu, Bo, Thinnest Two-Dimensional Nano-material-Graphene for Solar Energy, ChemSusChem, 2010, pp. 782-796.
[12] Rowell, Michael W., and McGhee, Michael D., Transparent electrode requirements for thin film solar cell modules, Energy Environ. Sci., 2011, pp. 131-34.
[13] Y. Wang, D. C. Alsmeyer, and R. L. McCreery, “Raman Spectroscopy of Carbon Materials: Structural Basis of Observed Spectra”, Chem. Mater., 1990, pp. 557-563.
[14] D. Yoon, H. Moon, Y. W. Son, J. S. Choi, B. H. Park, Y. H. Cha, Y. D. Kim, and H. Cheong, “Interference effect on Raman spectrum of graphene on SiO2/Si”, Phys. Rev. B, 2009, pp. 125422.
[15] Y. Hernandez, V. Nicolosi, M. Lotya, F. M. Blighe, Z. Sun, S. De, et al. “High-yield production of graphene by liquid-phase exfoliation of graphite”, Nat. Nano., 2008, pp. 563-568.