Low-temperature controllable preparation of vertically standing graphene sheets on indium tin oxide glass and their field emission properties

Fei Zou ^a, Haitao Zhou ^a, Ning Yu ^b, Zhaohui Yao ^b, Fei Liu ^c and Chengmin Shen ^{d*}

^a Chinese Aeronautical Establishment, Beijing, 100012, China

^b School of Aerospace Engineering, Tsinghua University, Beijing 100084, China,

^c State Key Laboratory of Optoelectronic Materials and Technologies, School of Physics and Engineering, Sun Yat-sen University, Guangzhou 510275, China

^d Institute of Physics, Chinese Academy of Sciences, Beijing Key Laboratory for Nanomaterials and Nanodevices, Beijing 100190, China

* Corresponding author

Telephone: 0086-82649817

E-mail: cmshen@iphy.ac.cn

Abstract

Vertically standing graphene sheets (VSGs) were successfully grown on indium tin oxide (ITO) glass through plasma enhanced chemical vapor deposition system. The lateral size of the graphene sheets was evidently affected by the growth temperature. The VSGs with smaller sheet size were obtained at 600 °C than at 500 °C. The dependence of the field-emission behavior of VSGs grown on ITO glass (VSGs/ITO) on the sheet size was investigated. The VSGs/ITO films with smaller sheet size possessed a higher field-enhancement factor and a lower turn-on field, which was proposed to be attributed to more field-emission sites and better electrical conductivity.

Keywords: CVD; scanning electron microscopy; glass; electrical properties; vertically standing graphene

1. Introduction

Two-dimensional materials have attracted much attention recently because of their unique microstructures and superior physical properties [1-5]. Preparations and applications of two-dimensional nanomaterials have been extensively explored, especially for those lying flat on the substrates. Recently, an alternative configuration of vertically standing two-dimensional nanomaterials on the substrates is also increasing attention because plenty of high exposed atomic edges, larger aspect ratio, excellent thermal conductivity and good mechanical properties make them promising applications in field emission, energy storage, and optoelectronics devices. [6-8]

Due to good optical transmittance, high electrical conductivity, and excellent physical and chemical stabilities, graphene has been considered to be one of the most promising electrical materials [9-14], which can be prepared on various substrates, such as glass and non-metal powders. [15-17] Chemical vapor deposition (CVD) has been considered the most promising method for the in-situ preparation of large-scale and high-quality graphene. [18, 19] As field emission cooling cathode materials, the vertical standing few-layer graphene were better emitters due to their atomic, sharp thickness and better uniformity. [20] On the other hand, the vertical standing few-layer graphene directly grown on glass substrate were suitable for integration of field emission devices. Nevertheless, the demands of high growth temperature and catalysts in the CVD method make it difficult to deposit graphene on glass substrate, which will melt at relative low temperature. [21] Plasma enhanced chemical vapor deposition (PECVD) method is a promising method which can deposit vertically standing graphene sheets (VSGs) on copper foils and the VSGs exhibited good performance as field emitters. [20] However, the non-transparent Cu foil is an obstacle for its direct use in field emission displays. Therefore, it is important to prepare VSGs directly on the

transparent substrates under lower temperature, such as indium tin oxide (ITO).

Here we reported the preparation of VSGs directly on ITO at low temperatures by using PECVD system. [20] The morphology and size of the VSGs grown at different temperature were compared. The photoelectric properties and hydrophobic behavior of the VSGs film were characterized. Compared with the graphene film flat lying on the substrate surface, the VSGs possesses enhanced field emission performance because a large amount of exposed graphene sheets could act as field emission sites. [20] Therefore, the field-emission behavior of the VSGs/ITO was also investigated and the influence of growth temperature on the field-enhancement factor and turn-on field was discussed.

2. Experimental Section

2.1 Preparations of VSGs

The VSGs films were grown on the ITO glass using a PECVD system. Firstly, the ITO glass was cleaned by ethanol and acetone and dried by argon. Then, the ITO glass was transferred into CVD chamber (quartz tube) with the conducting side facing up and vacuumized to 1×10^{-1} Pa. Subsequently, 100 sccm (standard cubic centimeter per minute) H_2 /Ar mixed gas (H_2 , 10 vol.%) was induced as the protective gas throughout the whole preparation process (the pressure changed to ~ 40 Pa), and the temperature was increased to 500 °C at the rate of 10 °C/min. The temperature was kept at 500 °C for 10 minutes, and 20 sccm methane was induced into the tube as the carbon source (the pressure slight increased to ~ 50 Pa). Simultaneously 120 watt radio frequency (RF) was generated to dissociate methane. After growth for 30 minutes, CH_4 source and the RF were shut off while the pump continued running until the sample was cooled down to room temperature naturally under the protection of 100sccm H_2 /Ar gas. Finally, the VSGs/ITO grown at 500 °C (VSGs/ITO-500) was obtained. A VSGs/ITO grown at 600 °C (VSGs/ITO-600) was prepared following the same procedures except that the temperature is changed to 600 °C.

2.2 Characterizations

The VSGs/ITO was characterized using field emission scanning electron microscope (FE-SEM, Hitachi S-4800). Raman spectroscopy was recorded with a laser wavelength of 532 nm and an incident power of ~ 1 mW. The transparency of VSGs/ITO-600 was obtained by a UV-vis spectrometer (Cary, UV-5000) with a pristine ITO glass sample as a reference. The sheet resistance of VSGs/ITO was measured by a four-wire sensing system (GUANGZHOU 4PROBES SCIENCE & TECHNOLOGY LTD., RST-9) and the contact angle (CA) was measured by a POWERREACH contact angle measuring instrument.

Field emission studies were performed in a diode-type geometry with a DC-bias inside a vacuum chamber (base pressure of 2.6×10^{-5} Pa). The anode consisted of an ITO-coated glass substrate with a phosphor layer and the VSGs/ITO was used as the cathode. The area of the sample was 0.81cm^2 and 0.76cm^2 for VSGs/ITO-500 and VSGs/ITO-600, respectively.

3. Results and discussion

Figure 1. (a)-(d) SEM images of VSGs/ITO-600 at different magnifications. (e) Cross-sectional SEM image of VSGs/ITO-600. (f) SEM images of VSGs/ITO-500.

The VSGs/ITO were synthesized under different growth temperature using PECVD method and were characterized through FE-SEM. Figure 1a-d showed the SEM images of VSGs/ITO-600 under different magnifications. From lower magnification SEM images (figure 1a-1b), it could be found that a large area and high density graphene sheets were grown uniformly on the ITO substrate with planar graphene. The SEM images from figure 1c and 1d indicated that each graphene sheet was vertical standing on the ITO substrate. The cross sectional SEM images (Figure 1e) demonstrated that the as-grown graphene sheets were perpendicular to the substrate with the sheet height varying from 198 nm to 329 nm. Figure 1c and Figure 1f showed the SEM images of VSGs/ITO grown at different temperatures of 500 °C and 600 °C under the same magnification, respectively. The lateral sheet size of VSGs/ITO-500 was about 600 nm, much larger than 300 nm of VSGs/ITO-600. According to previous reports, a two-step mode was proposed for the growth of the graphene: the layer growth of graphene islands flat lying on the substrate and a transition to vertical growth to form the VSGs. [20, 22] In a thermal CVD, graphene films with larger crystal grains and lower nucleation density will be obtained under high temperatures because of the decomposition energy of methane, especially for graphene growth on glass substrate which almost does not have any catalytic capability. [19] While for growing graphene on ITO glass with PECVD systems, the methane could be dissociated easily by the plasma under low temperature, and the graphene nucleation will not be restrained by the growth temperature. [23, 24] During the graphene nucleation process, there is a competition between the growth and etching of graphene that dominates the growth behavior of graphene islands. [25] Under higher growth temperature, the growth process is the dominant, and more graphene nucleation sites will grow fast enough to be left, giving rise to smaller size of graphene islands. The subsequent vertical growth on the graphene islands proceeds and finally VSGs with smaller graphene sheets are obtained, which were proved to some extent by the SEM results discussed above.

Figure 2. Raman spectroscopy characterizations of VSGs/ITO-500 and VSGs/ITO-600.

To further verify the quality of VSGs/ITO-500 and VSGs/ITO-600, Raman spectroscopy was conducted as shown in Figure 2, and a typical Raman peaks of graphene could be observed. G band located at 1582 cm^{-1} with a full width at half-maximum (FWHM) of 27 cm^{-1} was associated with the doubly degenerate phonon mode (E_{2g} symmetry) at the Brillouin zone center. [20, 26] The 2D band at 2680 cm^{-1} was associated with second-order zone-boundary phonon. For VSGs/ITO-500 and VSGs/ITO-600, the broadened 2D band (FWHM of 74 cm^{-1} and 54 cm^{-1} , respectively) was due to the relaxation of double resonance Raman selection rules related to the random orientation of the graphene layers. [20] The D band near 1350 cm^{-1} and the D' band near 1620 cm^{-1} are the disorder-induced features associated with the intervalley $K \rightarrow K'$ and intravalley K (or K') double resonance scattering processes, respectively. [26] As temperature increased from $500\text{ }^{\circ}\text{C}$ to $600\text{ }^{\circ}\text{C}$, the intensity of D band versus G band (I_D / I_G) increased from 1.9 to 2.5, indicating a decrease of the size of graphene sheets as can be seen in the SEM images by comparing Figure 1c and Figure 1f. [27] It could be proposed that randomly stacked few-layer graphene sheets with a large portion of edges on the top were grown on ITO glass. [26]

Figure 3. Sheet resistance and UV-vis transmittance spectra in the wavelength range of 350–800 nm of VSGs/ITO-600 with ITO glass as reference. The inset shows the surface wetting behaviors of VSGs/ITO-600 (right) and ITO glass, respectively.

To explore the optical and electrical properties of VSGs films, the transparency and the sheet resistance of

VSGs/ITO-600 were characterized as shown in Figure 3. At a wavelength of 550 nm, the transmittance of the VSGs/ITO-600 was $\sim 50\%$, along with an average sheet resistance of $3.2 \text{ k}\Omega \text{ sq}^{-1}$ (lower than $3.6 \text{ k}\Omega \text{ sq}^{-1}$ of VSGs/ITO-500). The surface wetting behaviors of the ITO glass substrate before and after growth of VSGs films at 600°C was shown in Figure. 3. A pristine ITO glass sample was used as a reference and displays a hydrophilic behavior with a CA of 85° . After growing graphene on the ITO glass, the CA of VSGs/ITO-600 reached $\sim 136^\circ$, indicating a hydrophobic behavior. [28] The growth temperature had little influence on the transmittance and the hydrophobic behavior of VSGs/ITO in our experiments.

Figure 4. (a) Electron-emission current density (J) versus applied electric field (E) for VSGs/ITO-500. (b) Corresponding F–N plots of VSGs/ITO-500. (c) Stability of emission current of VSGs/ITO-500. (d) Electron-emission current density (J) versus applied electric field (E) for VSGs/ITO-600. (e) Corresponding F–N plots of VSGs/ITO-600. (f) Stability of emission current of VSGs/ITO-600.

To extend the application of VSGs, the field-emission behavior of VSGs/ITO was investigated. Figure 4a displayed the current density (J) as a function of electric field (E) for VSGs/ITO-500. The fabricated field emitter exhibited a turn-on field ($J = 10 \mu\text{A cm}^{-2}$) around $7.6 \text{ V } \mu\text{m}^{-1}$. The Fowler-Nordheim (F-N) plots of $\ln(J/E^2)$ versus $1/E$ of VSGs/ITO-500 was shown in Figure 4b, which could be linearly fitted and was in good agreement with the F-N equation. F-N theory predicts that the field enhancement factors of an emitter are inversely proportional to the slope of the F-N plot ($\beta = -B\Phi^{1.5}/S$, where B is a constant, Φ is the work function, and S is the slope). [29] Taking the work function of graphite as 5 eV , [20] the field-enhancement factor was calculated to be about 1.75×10^3 . The stability of the field-emission current of VSGs/ITO-500 was evaluated by recording the current density of 0.15 mA cm^{-2} over 60 min . As shown in Figure 4c, no obvious degradation of emission performance was observed. This is probably due to homogenous surface morphology of VSGs/ITO-500 as shown in SEM images.

As can be seen in Figure 4d and e for VSGs/ITO-600, a turn-on field ($J = 10 \mu\text{A cm}^{-2}$) around $5.0 \text{ V } \mu\text{m}^{-1}$ was exhibited and the F-N plot were also in good agreement with the F-N equation. The field-enhancement factor was calculated to be 2.06×10^3 , which was higher than that of VSGs/ITO-500, and the current density kept at about 0.1 mA cm^{-2} did not show obvious degradation (as shown in Figure 4f). It is known that the larger enhancement factor allows a lower turn-on voltage for electrons tunneling. [20] There may be some reasons for better field-emission behavior of VSGs/ITO-600. On one hand, the VSGs/ITO-600 exhibited higher graphene density as seen in Figure 1, and this could lead to more field-emission sites for reducing the turn-on field; on the other hand, VSGs/ITO-600 exhibited lower sheet resistance than VSGs/ITO-500.

4. Conclusion

In conclusion, VSGs were successfully grown on ITO glass with PECVD system. The growth temperature had a significant influence on the sheet size of graphene. Graphene sheets with smaller size were obtained in higher temperature. The transmittance of the VSGs/ITO-600 was ~ 50%, along with an average sheet resistance of 3.2 k Ω sq⁻¹. The growth of graphene led to the change from hydrophilic to hydrophobic of the ITO glass, with the CA increasing from 85° to 136°. The field-emission behavior of VSGs/ITO was investigated. Due to more field-emission sites and better electrical conductivity, the VSGs/ITO grown at higher temperature had a larger field-enhancement factor and smaller turn-on field. This offers an opportunity to optimize the field-emission performance by adjusting the preparation parameters of VSGs in the future.

Acknowledgements

This work was supported by National Basic Research Program of China (Grant No. 2013CB933604) and National Science Foundation of China (Grant No. 51602300, 61390501, 51325204).

References

- [1] A.K. Geim, K.S. Novoselov, *Nat. Mater.* 2007 6(3) 183-191.
- [2] F. Xia, H. Wang, Y. Jia, *Nat. Commun.* 2014 5 289-305.
- [3] Q.H. Wang, K. Kalantar-Zadeh, A. Kis, J.N. Coleman, M.S. Strano, *Nat. Nanotechnol.* 2012 7(11) 699-712.
- [4] O. Minoru, S. Takayoshi, *Adv. Mater.* 2012 24(2) 210-228
- [5] C.R. Dean, A.F. Young, I. Meric, C. Lee, L. Wang, S. Sorgenfrei, K. Watanabe, T. Taniguchi, P. Kim, K.L. Shepard, J. Hone, *Nat. Nanotechnol.* 2010 5 722-726.
- [6] H. Li, H.Q. Wu, S.G. Yuan, H. Qian, *Sci. Rep.* 2016 6 21171.
- [7] K.J. Wang, G.D. Li, J.X. Li, Q. Wang, J.S. Chen, *Cryst. Growth Des.* 2007 7 (11) 2265-2267.
- [8] J.Y. Wang, T. Ito, *Diamond Relat. Mater.* 2007 16 589-593.
- [9] X.S. Li, Y.W. Zhu, W.W. Cai, M. Borysiak, B.Y. Han, D. Chen, R.D. Piner, L. Colombo, R.S. Ruoff, *Nano Lett.* 2009 9 (12) 4359-4363.
- [10] S. Bae, H.K. Kim, Y.B. Lee, X.F. Xu, J.S. Park, Y. Zheng, J. Balakrishnan, T. Lei, H.R. Kim, Y.I. Song, Y.J. Kim, K.S. Kim, B. Özyilmaz, J.H. Ahn, B.H. Hong, S. Iijima, *Nat. Nanotechnol.* 2010 5 574-578.
- [11] J.H. Du, S.F. Pei, L.P. Ma, H.M. Cheng, *Adv. Mater.* 2014 26 1958-1991.
- [12] G. Eda, G. Fanchini, M. Chhowalla, *Nat. Nanotechnol.* 2008 3 270-274.
- [13] J. Pu, L. Tang, C.W. Li, T.T. Li, L. Ling, K. Zhang, Q.W. Li, Y.G. Yao, *RSC Adv.* 2015 5 44142-44148.
- [14] M. Batmunkh, C.J. Shearer, M.J. Biggs, J.G. Shapter, *J. Mater. Chem. A* 2016 4 2605-2616.
- [15] J.Y. Sun, Y.F. Zhang, Z.F. Liu, *ChemNanoMat* 2016 2 (1) 9-18.
- [16] M.H. Rummeli, C. Kramberger, A. Grüneis, P. Ayala, T. Gemming, B. Büchner, T. Pichler, *Chem. Mater.* 2007 19 (17) 4105-4107.
- [17] A. Bachmatiuk, R.G. Mendes, C. Hirsch, C. Jähne, M.R. Lohe, J. Grothe, S. Kaskel, L. Fu, R. Klingeler, J. Eckert, P. Wick, M.H. Rummeli, *ACS Nano* 2013 7 (12) 10552-10562.
- [18] K.S. Kim, Y. Zhao, H. Jang, S.Y. Lee, J.M. Kim, K.S. Kim, J.H. Ahn, P. Kim, J.Y. Choi, B.H. Hong, *Nature* 2009 457 706-710.
- [19] R. Muñoz, C. G. Aleixandre, *Chem. Vap. Deposition* 2013 19 297-322.

- [20] L.L. Jiang, T.Z. Yang, F. Liu, J. Dong, Z.H. Yao, C.M. Shen, S.Z. Deng, N.S. Xu, Y.Q. Liu, H.J. Gao, *Adv. Mater.* 2013 25 250-255.
- [21] J.Y. Sun, Y.B. Chen, M.K. Priyadarshi, Z. Chen, A. Bachmatiuk, Z.Y. Zou, Z.L. Chen, X.J. Song, Y.F. Gao, M.H. Rummeli, Y.F. Zhang, Z.F. Liu, *Nano Lett.* 2015 15 5846-5854.
- [22] M.Y. Zhu, J.J. Wang, B.C. Holloway, R.A. Outlaw, X. Zhao, K. Hou, V. Shutthanandan, D.M. Manos, *Carbon* 2007 45 (11) 2229-2234.
- [23] D.C. Wei, Y.H. Lu, C. Han, T.C. Niu, W. Chen, A.T.S. Wee, *Angew. Chem. Int. Ed.* 2013 52 14121-14126.
- [24] K.J. Peng, C.L. Wu, Y.H. Lin, Y.J. Liu, D.P. Tsai, Y.H. Pai, G.R. Lin, *J. Mater. Chem. C* 2013 1 3862-3870.
- [25] L.C. Zhang, Z.W. Shi, D.H. Liu, R. Yang, D.X. Shi, G.Y. Zhang, *Nano Res.* 2012 5 (5) 258-264.
- [26] L.M. Malard, M.A. Pimenta, G. Dresselhaus, M.S. Dresselhaus, *Phys. Rep.* 2009 473 51-87.
- [27] S. Stankovich, D.A. Dikin, R.D. Piner, K.A. Kohlhaas, A. Kleinhammes, Y.Y. Jia, Y.Wu, S.T. Nguyen, R.S. Ruoff, *Carbon* 2007 45 (7) 1558-1565.
- [28] X.Q. Zhang, S.H. Wan, J.B. Pu, L.P. Wang, X.Q. Liu, *J. Mater. Chem.* 2011 21 12251-12258.
- [29] C.Y. Chen, K.Y. Cheng, Y.C. Chu, L.J. Chen, W.L. Fang, C.S. Chang, L.J. Chou, *J. Phys. Chem. C* 2012 116 12824-12828.