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Improved electron field emission from morphologically disordered monolayer graphene

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Graphene was synthesized on copper foil by thermal chemical vapor deposition technique. To investigate the field electron emission property, planar graphene (PG) and morphologically disordered graphene (MDG) were fabricated on the doped silicon substrate by transfer of as-grown graphene. Incorporation of morphological disorder in graphene creates more emission sites due to the additional defects, edges, and atomic scale ripples. This resulted in (1) a dramatic increase in the maximum current density by a factor of 500, (2) considerable increase in the enhancement factor, and (3) decrease in the turn-on field of MDG compared to PG. © 2012 American Institute of Physics. [doi:10.1063/1.3679135]

The efficient and stable electron field emission from carbon based nanostructured materials has attracted considerable attention due to their unique structure and exceptional mechanical, chemical, and electrical properties.^{1–5} Field emission cathodes made of these materials have been proposed for applications such as flat panel displays, electron guns in electron microscopes, x-ray sources, and high power microwave amplifiers.⁶

The extraordinary mechanical, chemical, and electrical properties of two-dimensional graphene have attracted a great attention of scientific and industrial communities in recent years.⁷⁻¹⁰ Graphene is a promising material for field emission applications because of its low aspect ratio, chemical stability, and excellent electrical conductivity. Recently, few researchers have reported the electron field emission property of graphene film and few-layer graphene prepared by different techniques.^{11–15} Wu *et al.*¹¹ fabricated chemically exfoliated single-layer graphene by electrophoretic deposition technique, Qian et al.¹² prepared screen-printed graphene, and Qi et al.¹⁴ synthesized vertically oriented graphene by plasma enhanced chemical vapor deposition techniques to investigate its field emission properties. Palnitkar et al. used boron and nitrogen doping of graphene (produced by arc discharge method) to tailor the turn on field.¹⁵ Feasibility of graphene for technological applications has been verified after synthesis of high quality large area and large scale graphene.^{16–18}

In this letter, we explored the effect of morphological disorder on field emission property of graphene synthesized by thermal chemical vapor deposition technique (CVD). Incorporation of morphological disorder in graphene resulted in improved field emission performance. A factor of 500 increase in the maximum current density of morphologically disordered graphene (MDG) with respect to planar graphene (PG) was observed. Moreover, a considerable increase in

enhancement factor and decrease in turn-on field in MDG compared to PG was also observed.

Large area graphene was synthesized on copper foil by the thermal chemical vapor deposition technique. Copper foil of 70 cm× 35 cm× 70 μ m dimensions was inserted into a cylindrical CVD quartz reactor and evacuated by rotary pump. The temperature of the reactor was ramped to 950 °C in the presence of H₂ flow (80 sccm). After annealing of the copper foil for 1 h at this temperature, CH₄ (250 sccm) and H₂ (80 sccm) gases were introduced at same temperature and 1.5 Torr pressure for 20 min to synthesize the graphene.¹⁶

Graphene, thus obtained, was transferred on a p-doped silicon substrate for field emission study. The Cu foil was cut into $1 \text{ cm} \times 1 \text{ cm}$ pieces, spin-coated with poly methyl methacrylate (PMMA), and immersed into Cu etchant solution (FeCl₃) in order to etch away the Cu foil. After complete etching of copper, PMMA coated graphene sheets were rinsed in deionized water several times to remove etchant residues. PMMA coated graphene sheets were transferred on oxygen plasma treated and pristine p-doped Si (100) substrates and washed with acetone to remove PMMA and obtain PG and MDG samples, respectively. It was found that graphene adheres weakly to the pristine Si (100) surface and transfer process introduces morphological disorder in the form of agglomeration, discontinuity, additional edges, and ripples. On the other hand, oxygen plasma treatment of Si provides active sites that facilitate good adhesion to graphene, and the process resulted in a smooth and planar transfer of graphene (PG). Both samples (PG and MDG) were annealed at 300 °C in Ar flow for an hour to remove the residual particles trapped during transfer process and to improve the adhesion of graphene to the Si substrate. This resulted in p-doped silicon chips coated with graphene layer.

The PG and MDG samples were characterized by scanning electron microscopy (FESEM: JEOL JSM-7500F), atomic force microscopy (AFM: Veeco, Model: 840-012-711), and Raman spectroscopy (Renishaw, RM1000, 514.5 nm excitation

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FIG. 1. (Color online) SEM and AFM images. Figs. (a) and (b) are SEM images and (c) is the AFM image of PG sample. Figs. (d) and (e) are SEM images and (f) is AFM image of MDG sample.

wavelength). The electron field emission of graphene samples was measured in a high vacuum chamber with a parallel diodetype configuration at a base pressure of $\sim 10^{-7}$ Torr. The field emission current was measured at different voltages using an automatically controlled electrometer (Keithley 2001) and power supply (Fug Power HCN 700-3500).

SEM images of PG (graphene transferred onto oxygen plasma-treated Si substrate) are shown in Figs. 1(a) and 1(b) at different magnifications. Clearly, images confirm the planar and continuous nature of graphene. The dark wrinkled line in Fig. 1(b) may be associated with the graphene synthesis process. The difference in the thermal expansion coefficients of the copper foil and graphene has been found to introduce such wrinkles during the post-growth cooling.¹⁷ SEM images of MDG (graphene transferred onto pristine Si substrate) are shown in Figs. 1(d) and 1(e). A morphological disorder in the form of agglomeration, discontinuity, edges, and additional ripples of atomic dimensions can be observed in MDG samples. Figs. 1(c) and 1(f) show the topographic images of PG and MDG samples, respectively, obtained by AFM on a $5\mu m \times 5\mu m$ area. The AFM images are in agreement with SEM images and reveal the differences in heights of the topography as indicated by the inset bar.

Raman spectra of PG and MDG samples, recorded in the $1000-3200 \,\mathrm{cm}^{-1}$ range are shown in Fig. 2. Three dominant Raman bands (D, G, and G'-bands) which are fingerprint features of garphene are observable in the PG and MDG samples. In PG sample, the G-band which originates from the doubly degenerate phonon mode (E2g symmetry) is centered at 1584 cm^{-1} . The G'-band which originates from a secondorder process involving two phonons near the K point is observed at 2695 cm⁻¹. The D-band that originates from backscattering of phonon by disorder (edges and defects) in graphene is centered at 1348 cm⁻¹.^{17,19,20} All the Raman bands were analyzed by Lorentzian peak fitting. The intensity ratio of D to G-bands (I_D/I_G) and G to G'-bands (I_G/I_G) for PG sample are 0.10 and 0.27, respectively. In the case of MDG sample, no significant shift in Raman bands was observed. But the I_D/I_G ratio was found to be 0.16, which reflects that MDG has additional edges and defects. The increased $I_G/I_{G'}$ ratio (0.42) in MDG sample is associated with additional defects and edges present in it. The G' band is an overtone of the D band and originates from backscattering of a phonon by an electron instead of a defect. Thus, the presence of additional defects suppresses the backscattering of phonons by electrons and consequently increases the $I_G/I_{G'}$ ratio.

The field emission characteristics of PG and MDG samples are shown in Fig. 3. The emission current density as a function of applied electric field is shown in Fig. 3(a). The maximum emission current density of the PG sample was 0.007 mA/cm^2 at $4.26 \text{ V/}\mu\text{m}$ electric field intensity. The MDG sample, however, reached 3.52 mA/cm^2 current density at the same field intensity, a factor of 500 increase compared to PG. The turn-on electric field (defined at $10 \,\mu\text{A/cm}^2$ emission current density) for PG and MDG samples was found to be 4.31 and $2.26 \text{ V/}\mu\text{m}$, respectively. The field emission characteristics of the graphene samples were verified by Fowler-Nordheim (F-N) plot. According to F-N theory, the field emission current density *J* is related to the applied electric field E as

$$J = A(\beta^2 E^2/\phi) \exp(-B\phi^{3/2}/\beta E), \qquad (1)$$

where $A = 1.56 \times 10^{-6} \text{ A V}^{-2} \text{ eV}$, $B = 6.83 \times 10^{7} \text{ eV}^{-3/2}$ V cm⁻¹, β is the field enhancement factor, ϕ is the work



FIG. 2. (Color online) Raman spectra of PG and MDG samples.



FIG. 3. (Color online) (a) Field emission current density vs. electric field plot for PG and MDG samples and (b) the corresponding F-N plots.

function (eV), and E is the applied electric field in V/ μ m. The linear behavior in the F-N plots of the PG and MDG samples (Fig. 3(b)) confirms that the measured current is caused by the field emission phenomena. Moreover, the observed knee point in F-N plots of both samples (marked with * in Fig. 3(b)) implies that two subsequent phenomena in the applied electric field region take place within the validity of the F-N theory. The appearance of a knee point in F-N plots in this experiment is attributed to a combination of heating and double barrier formation effect. A similar knee point has been observed in carbon nanotubes (CNTs) field emitters and is explained in terms of heating of the CNT top surface as a rate limiting step in the high field region.²¹⁻²⁵ Similarly, the heating of the top surface of graphene in high electric field region decreases its work function²⁵ and leads to the emission current increase according to F-N theory. The weak interaction between Si and transferred graphene forms a double barrier for electron transport. According to the double barrier model,²⁴ the whole process of electron field emission would consist of two transport steps: (1) electron tunneling through the barrier between Si and graphene and then (2) electron tunneling from graphene to vacuum. The field emission in low electric field region is limited by Si-graphene barrier. However, the Si-graphene barrier in high electric field region becomes so narrow that electron emission would not depend on it. Thus, double barrier model also explains the appearance of a knee point in F-N plot. The field enhancement factors were calculated from the slope of the straight line in F-N plot assuming 4.5 eV work function of graphene.²⁶ The calculated enhancement factors in low electric field region are 1650 for PG and 1818 for MDG, whereas the values in high electric field region are 2382 for PG and 3414 for MDG samples.

The improved field emission of MDG sample is attributed to enhancement in geometrical factor due to additional defects and formation of edges. The increase of I_D/I_G ratio and SEM micrographs indicates the increase of defects sites and edges in MDG. These defects and edge formation in MDG samples provide new emission sites because the variation of electric potential is much larger at defects, edges, and ripples of atomic scales, which leads to larger local electric field over the MDG sample.²⁷ Similarly, defects and edges in disordered graphene act as a much sharper tip, with field enhancement factor (β) exceeding that of the planar graphene, which explains the low turn-on electric field and large emission current density observed in MDG. Additionally, the MDG sample contains discontinuous emission sites in the form of edges and ripples of atomic dimensions. Therefore, these atomically small emissions sites can emit electrons at relatively low electric field because of the resonance tunneling,²⁸ and consequently a very low turn on field can be achieved.¹⁵ Moreover, a significant shift in the Fermi level due to the presence of the topographical defects at the surface has been observed. However, the exact positions of these defect-induced energy levels could not be determined from the field emission measurements because of uncertainties in the local field enhancement and the emission area.²⁹ Further, the larger difference in the field enhancement factors observed in the high electric field region for the two types of graphene samples lends support to the double barrier model. Tunneling of electrons from Si to graphene occurs at low electric field, while F-N emission that occurs at higher electric field is from metal surface to vacuum level and thus highly influenced by morphological disorder present in graphene. That is why the enhancement factor in higher electric field region is larger than in the lower electric field.

In conclusion, field emission property of planar graphene (PG) and morphologically disordered graphene (MDG) grown by thermal CVD technique was investigated. The field emission property of graphene was found to be improved considerably in morphologically disordered state. Additional defects and edges in the case of MDG were confirmed by Raman spectroscopy, SEM and AFM. These additional defects and edges translate into the reduction in the turn-on field and the large enhancement in the maximum emission current density.

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