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Morphology-controllable fabrication and enhanced field emission of multilayer graphene–silicon nanowire composites

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ABSTRACT

Multilayer graphene–silicon nanowire (MLG–SiNW) composites were prepared by using microwave plasma enhanced chemical vapor deposition and their field emission (FE) characteristics were studied. The morphology of MLG–SiNW composites can be readily controlled by tuning the concentration of carbon source and the microwave power. The FE study indicates that MLG–SiNW composites have superior FE performance to that of SiNWs. MLG–SiNW composites with optimal morphology exhibit excellent FE properties. They have a low turn-on electric field of 2.42 V/μm and also have good FE stability. We consider that both the large aspect ratio of SiNWs and the unique structure of MLGs are responsible for the enhanced FE properties.

1. Introduction

Aligned graphenes have recently been considered as high-performance field emitters due to their excellent conductivity, atomic thin edges, and unique two-dimensional structure [1–3]. However, aligned graphenes often have high turn-on electric fields (E_{on}, applied field (E) at 10 μA/cm^2) as compared with carbon nanotubes (CNTs), which are a one-dimensional field emission (FE) material having ultralow E_{on} [4,5]. The composition of graphenes and other good field emitters thus exhibits promising prospects in applications. We have reported the fabrication and FE properties of graphene–CNT composites in our previous studies [6,7], and found that the composites had far superior FE properties to their respective components. Nonetheless, the chemical vapor deposition (CVD) prepared CNTs adhere badly on substrates, which is detrimental in applications. It is thus essential to find a substitute for the CNTs. This substitute should not only have large aspect ratio but also adhere firmly to substrates. In this regard, we choose silicon nanowires (SiNWs) to act as a new composite material. The SiNWs have large aspect ratio and they are prepared by direct chemical etching of Si [8], so they have no adhesion issue as the CNTs.

In the present study, multi-layer graphenes (MLGs) are fabricated on chemically prepared SiNWs by using microwave plasma enhanced chemical vapor deposition (PECVD), and the FE properties of MLG–SiNW composites are investigated.

2. Experimental

SiNWs were prepared on Si wafers in a HF–$AgNO_3$ solution and a HF–H_2O_2 solution with Ag as an etching catalyst [8]. The fabrication of MLGs on SiNWs was carried out by using microwave PECVD. The growth of MLGs was catalyst-free, and the morphology of MLGs was controlled by tuning the concentration of carbon source and the microwave power. All these experimental details are described in *Methods* of the Supplementary material (pages S1–S3, including Figs. S1 and S2).

The structures of MLG–SiNW composites were characterized by scanning electron microscope (SEM), transmission electron microscope (TEM), Raman spectroscopy (633 nm), and photoelectron spectrometer. The FE tests were performed by using a diode setup. All the details for the sample characterizations and FE tests are shown in *Methods* of the Supplementary material (pages S3–S5, including Fig. S3).

3. Results and discussion

The morphology of MLGs on SiNWs can be readily controlled by tuning experimental parameters. We first investigated the characteristics of MLG growth stages. The MLG growth is less obvious in the first hour (Fig. 1(a)), and the SiNWs have morphology

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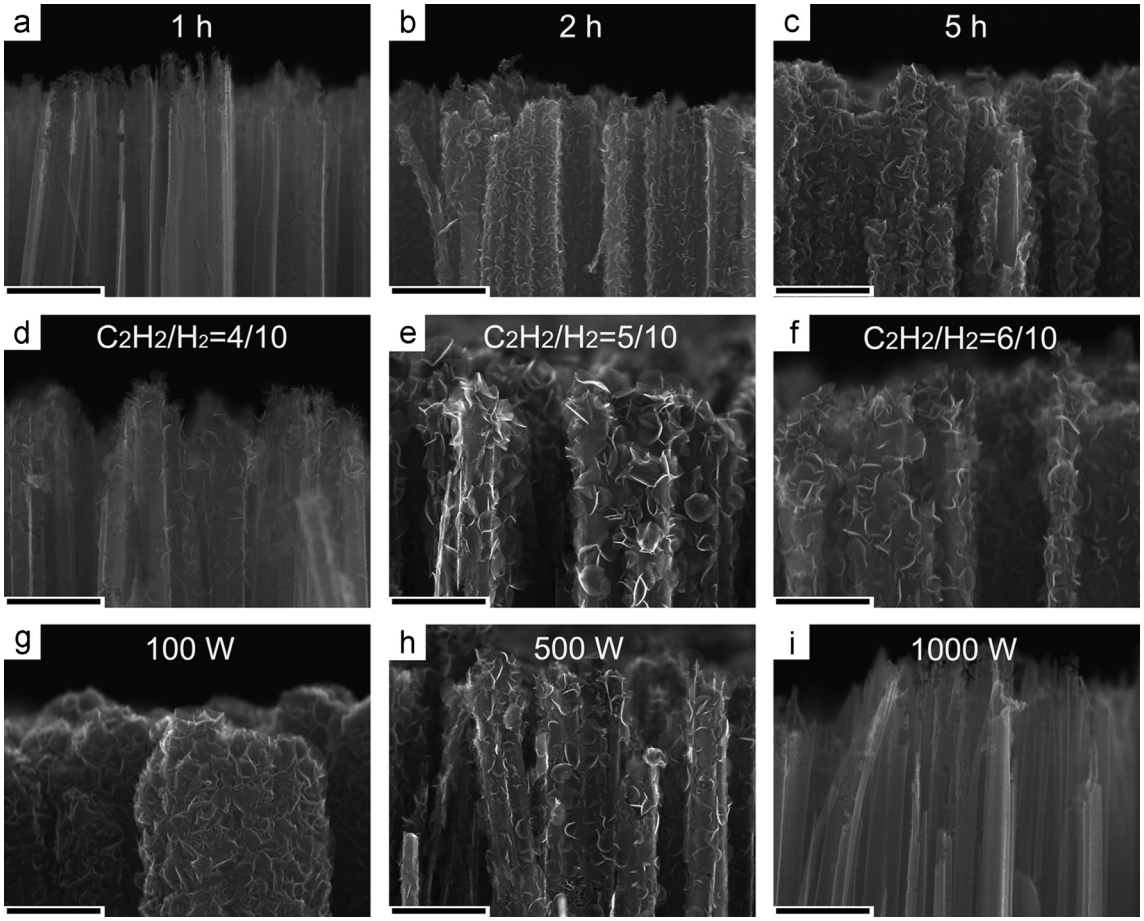

Fig. 1. SEM images of MLG–SiNW composites grown in (a) 1 h, (b) 2 h, and (c) 5 h. Other growth conditions are $C_2H_2/H_2=7/10$, 1 kPa, 400 W, and 800 °C. SEM images of MLG–SiNW composites grown in C_2H_2/H_2 ratios of (d) 4/10, (e) 5/10, and (f) 6/10. Other growth conditions are 1 kPa, 400 W, 800 °C, and 5 h. SEM images of MLG–SiNW composites grown at (g) 100 W, (h) 500 W, and (i) 1000 W. Other growth conditions are $C_2H_2/H_2=5/10$, 1 kPa, 800 °C, and 5 h. All the scale bars are 500 nm.

similar to the as-grown ones (see Fig. S1 of the Supplementary material). The density and size of MLGs increase dramatically with the growth time (Fig. 1(b) and (c)). In addition, the diameter of SiNWs increases concomitantly. We attribute this to the high concentration of carbon source induced quick deposition of amorphous carbon on SiNWs. The influence of the concentration of carbon source on MLG growth was also studied. The density and size of MLGs increase greatly when the C_2H_2/H_2 ratio is increased from 4/10 to 5/10 (Fig. 1(d) and (e)). However, with further increasing the C_2H_2/H_2 ratio to 6/10 (Fig. 1(f)), the MLG size decreases and the SiNWs thicken slightly, indicating that the quick deposition of amorphous carbon hinders the MLG growth. This increase of amorphous carbon can be evidenced by using Raman spectroscopy, as shown in Fig. S4 of the Supplementary material (page S5). The intensity ratio of the disordered carbon related D-peak to the graphite carbon related G-peak (I_D/I_G) for sample 5/10 is 1.61, smaller than 2.33 for the sample 6/10, indicating that the sample 6/10 has more defects [9]. In fact, this amorphous carbon layer can be reduced by changing microwave powers, as shown in Fig. 1(g)–(i). It can be seen that the amount of amorphous carbon on SiNWs decreases with the increase of microwave powers. This is ascribed to the hydrogen plasma etching on the loosely bounded amorphous carbon.

The fine structure of MLG–SiNW composites was observed by using TEM, which can help us understand the growth of MLGs. Sample 5/10 (see Fig. 1(e)) was chosen to perform the TEM observation. Fig. 2(a) shows a low-resolution TEM image of this sample. The MLGs are found to be well-separately distributed on the SiNWs. This morphology is believed to facilitate electron tunneling during FE [10]. The high-resolution TEM image (Fig. 2(b)) shows that a carbon buffer layer is deposited on the defected surface of SiNWs before the growth of MLGs. We ascribe this to the different compatibility in lattice between carbon and silicon. The MLGs need a carbon-based substrate to achieve homo-epitaxial growth, thus the deposition of this carbon buffer layer is essential. The growth mechanism of MLGs on carbon-based materials has been discussed in our previous study and need not be repeated here [6]. Fig. 2(c) shows a high-resolution TEM image of a MLG edge. It only has two layers. This thin nature of MLGs can also be characterized by Raman spectroscopy, as shown in Fig. 2 (d). The intensity ratio of the 2D peak (at $\sim$2646 cm^{-1}) and the G peak (at $\sim$1576 cm^{-1}) is often used to roughly evaluate the thickness of graphenes. For example, the 2D peak of a single-layer graphene is roughly 4 times more intense than the G peak [9]. The I_{2D}/I_G ratio of this sample is 1.09, indicating that the MLGs are ultrathin graphenes.

The FE properties of MLG–SiNW composites with typical morphology were measured. They are samples shown in Fig. 1 (d)–(g), and we name them here as sample 4/10, 5/10, 6/10, and 100 W for convenience. The FE *J–E* curves (emission current density *versus* applied field) are shown in Fig. 3(a) and the corresponding FE results are shown in Table 1. It can be seen that the MLG–SiNW composites have superior FE properties to those of the as-grown SiNWs. They have a lower E_{on} and a larger J_{max} (the largest emission current density). The sample 5/10 has the optimal FE properties. It has an ultralow E_{on} of 2.42 V/μm, far smaller than

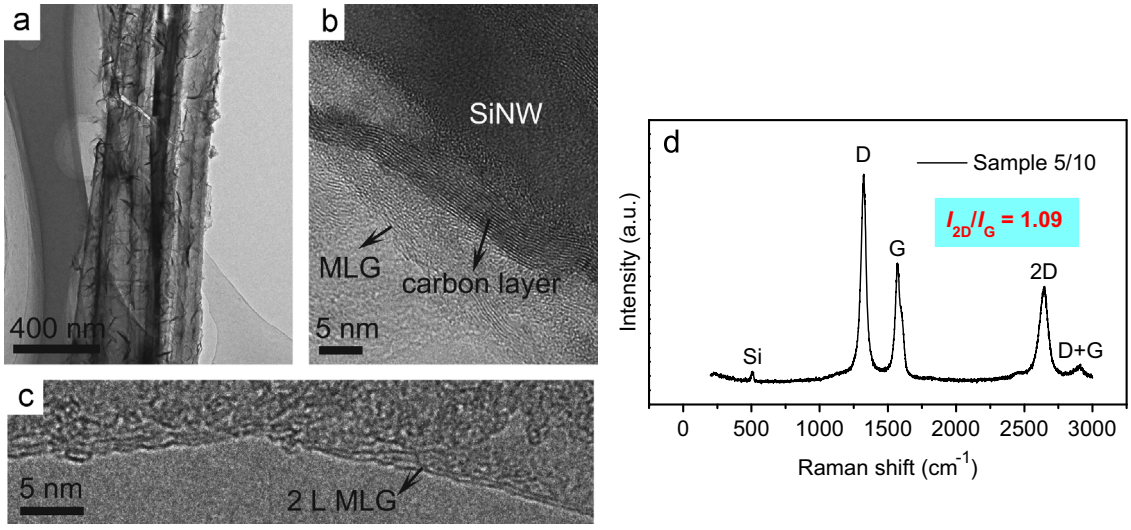

Fig. 2. (a) Low- and (b) high-resolution TEM images of MLG–SiNW composites. (c) High-resolution TEM image of the edge of a 2-layer (2L) MLG. (d) Raman spectrum of the MLG–SiNW composites.

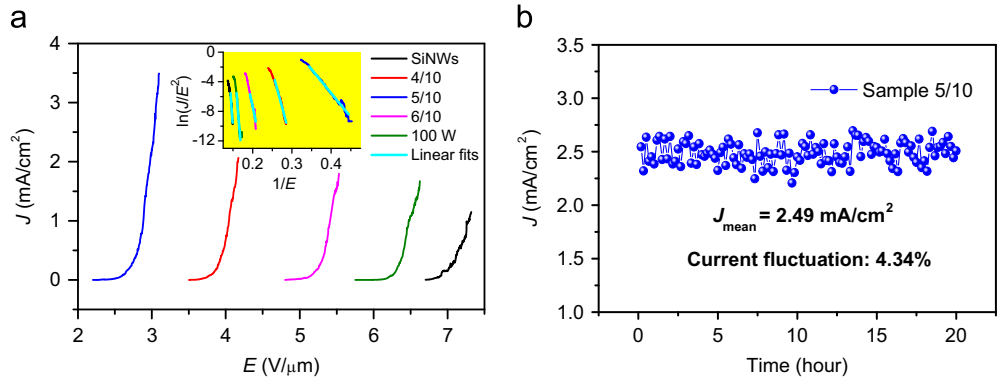

Fig. 3. (a) FE *J*–*E* curves of SiNW arrays and the chosen MLG–SiNW composites. (Inset) Corresponding *F*–*N* curves given in terms of $\ln(J/E^2)$ *versus* $1/E$. (b) FE stability of the sample 5/10. J_{mean} is the mean emission current density.

Table 1
FE testing results. E_{on} is the E at 10 μA/cm^2, J_{max} is the largest J, Φ is the work function, and β is the field enhancement factor.

Samples	E_{on} (V/μm)	J_{max} (mA/cm^2)	Φ (eV)	β
SiNWs	6.75	1.15	5.07	108
4/10	3.64	2.06	4.86	372
5/10	**2.42**	**3.49**	**4.67**	**1068**
6/10	4.93	1.80	4.74	281
100 W	6.12	1.67	4.72	109

that of the aligned graphenes and even approaches the low E_{on} of CNTs reported previously [6,11]. With the work function (Φ, measured by using photoelectron spectrometer) and the *F*–*N* curves ($\ln(J/E^2)$ *versus* $1/E$, inset of Fig. 3(a)), the field enhancement factor (β) of our samples can be obtained [12]. The sample 5/10 has the largest β, suggesting that its superior FE behavior mainly results from its morphology, specifically, from SiNWs with large aspect ratios and MLGs with sharp edges. Fig. 3(b) shows the FE stability (J-time) of the sample 5/10. The current stability at a mean J of 2.49 mA/cm^2 was tested over a period of 20 h and stable FE was observed with a current fluctuation of only 4.34%. We attribute this excellent FE stability to the unique two-dimensional structure of MLGs that allows faster heat dispersion and thus effectively weakens Joule heating induced decrease of effective emission sites [13,14].

4. Conclusions

We have demonstrated the fabrication of MLGs on chemically prepared SiNWs by using microwave PECVD. The morphology of MLGs can be readily controlled by adjusting the concentration of carbon source and the microwave power. High concentration of carbon source facilitates the growth of MLGs but it also thickens SiNWs by forming amorphous carbon, which is detrimental to FE. However, the amorphous carbon can be reduced by increasing the microwave powers. The FE performance of MLG–SiNW composites with different morphology was studied. The MLG–SiNW composites with optimal morphology exhibit excellent FE properties. They have a low E_{on} of 2.42 V/μm, a large J_{max} of 3.49 mA/cm^2, and excellent FE stability. We attribute this to the large aspect ratio of SiNWs, the sharp edges and unique two-dimensional structure of MLGs. Our results indicate that MLG–SiNW composites are an excellent FE material in potential applications for vacuum electron sources.

Acknowledgments

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.matlet.2014.09.124.

References

[1] Eda G, Unalan HE, Rupesinghe N, Amaratunga GAJ, Chhowalla M. Appl Phys Lett 2008;93:233502.
[2] Hojati-Talemi P, Simon GP. Carbon 2011;49:2875–7.
[3] Huang CK, Ou YX, Bie YQ, Zhao Q, Yu DP. Appl Phys Lett 2011;98:263104.
[4] Deng JH, Hou XG, Cheng L, Wang FJ, Yu B, Li GZ, et al. ACS Appl Mater Interfaces 2014;6:5137–43.
[5] Baughman RH, Zakhidov AA, de Heer WA. Science 2002;297:787–92.
[6] Deng JH, Zheng RT, Zhao Y, Cheng GA. ACS Nano 2012;6:3727–33.
[7] Deng JH, Wang FJ, Cheng L, Yu B, Li GZ, Hou XG, et al. Mater Lett 2014;124:15–7.
[8] Peng KQ, Wang X, Lee ST. Appl Phys Lett 2008;92:163103.
[9] Ferrari AC, Meyer JC, Scardaci V, Casiraghi C, Lazzeri M, Mauri F, et al. Phys Rev Lett 2006;97:187401.
[10] Wu ZS, Pei SF, Ren WC, Tang DM, Gao LB, Liu BL, et al. Adv Mater 2009;21:1756–60.
[11] Wang JJ, Zhu MY, Outlaw RA, Zhao X, Manos DM, Holloway BC, et al. Appl Phys Lett 2004;85:1265–7.
[12] Fowler RH, Nordheim L. Proc R Soc London, Ser A 1928;119:173–81.
[13] Dean KA, Burgin TP, Chalamala BR. Appl Phys Lett 2001;79:1873–5.
[14] Zhang Y, Du JL, Tang S, Liu P, Deng SZ, Chen J, et al. Nanotechnology 2012;23:015202.