Field emissions of graphene films deposited on different substrates by CVD system*

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Graphene films are deposited on copper (Cu) and aluminum (Al) substrates, respectively, by using a microwave plasma chemical vapour deposition technique. Furthermore, these graphene films are characterized by a field emission type scanning electron microscope (FE-SEM), Raman spectra, and field emission (FE) I–V measurements. It is found that the surface morphologies of the films deposited on Cu and Al substrates are different: the field emission property of graphene film deposited on the Cu substrate is better than that on the Al substrate, and the lowest turn-on field of 2.4 V/μm is obtained for graphene film deposited on the Cu substrate. The macroscopic areas of the graphene samples are all above 400 mm^2.

Keywords: graphene, chemical vapour deposition, field emission

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1. Introduction

Since Novoselov, Geim, Morozov *et al.*[1] prepared single layer free-standing graphene by mechanical cleavage of graphite with adhesive tape and measured its exotic electronic properties, the research on graphene has experienced explosive growth in recent years.[1−16] Graphene is the one single atom thick layer of graphite, and it has an unusual linear dispersion of the π-band at the Fermi level, a negative thermal expansion coefficient,[2] high tensile strength, and chemical resistance, which make graphene a most promising material for the future. Graphene is also an attractive candidate as a field emission source due to its high aspect ratio (the ratio of lateral size to thickness) and excellent electrical conductivity.[3] Such superlatives and unique properties of graphene have motivated much fundamental research into this material. However, graphene is difficult to produce in large scale and tends to exist in an aggregated state. Now there have been many methods to produce graphene films, such as ingenious exfoliation techniques,[1] Hummers technique,[4] solvothermal technique,[5] epitaxial growth,[6,7] chemical vapour deposition (CVD),[8−10] and so on.

In this paper, we compare the different substrates assisted depositing processes of graphene films via a chemical vapour deposition (CVD) system, and investigate the morphology characteristics and field emission performances of the two types of graphene films. The experimental result indicates that the field emission property of graphene film deposited on a copper (Cu) substrate is better than that on an aluminum (Al) substrate, and the lowest turn-on field of 2.4 V/μm is obtained for graphene film deposited on a Cu substrate. The macroscopic areas of the graphene samples are all above 400 mm^2.

2. Experimental procedure

Graphene films were deposited, respectively, on Cu substrates and Al substrates by a microwave plasma chemical vapour deposition (MPCVD) system. The substrates were first treated by abrasive paper for metallograph, and then they were cleaned in an ultrasonic cleaning machine for 30 min. Subsequently we placed these pretreated substrates into the quartz chamber and implemented the CVD process under the reaction conditions. The typical parameters used for the CVD process are listed in Table 1.

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Table 1. Parameters employed for the MPCVD process.

CVD process parameters	Values
Methane/hydrogen gas flows (sccm)	15/100
Substrate temperature/°C	600
Total gas pressure/kPa	4.5
Plasma processing time/min	10
Microwave power/W	450

The surface morphology and microstructure of the graphene films deposited on different substrates were characterized by Raman spectrum and field emission scanning electron microscopy (FE-SEM). The field emission properties of graphene films were tested by the parallel-plate diode structure in a vacuum system evacuated to a pressure of about 5×10^{-5} Pa with a Hyvac pump. Graphene film and phosphor-coated ZnO:Al/glass were used, respectively, as a cathode and an anode, which were parallel, separated by the mica spacer with a thickness of 100 μm. The current–voltage (I–V) characteristics were recorded by using a high voltage power supply. The current density-electric field (J–E) curves and the Fowler–Nordheim (FN) plots were obtained from the I–V data.

3. Results and discussion

Figures 1(a) and 1(b) show, respectively, the front and side of typical FE-SEM images taken from graphene films prepared on the Cu substrates. The films deposited on the Al substrates are also shown in Figs. 1(c) and 1(d), respectively. In Fig. 1(a), it is obvious that several layers of graphene twisted and stacked together, which accords with the microstructure of graphene. We can see from Fig. 1(b) that the film is of a layered structure and its thickness is about several tens of nanometers on the substrate, which shows that the thickness and structure of the graphene are relatively good. From Figs. 1(c) and 1(d) we can see that compared with the film on the Cu substrate, the film is in an aggregated state, but not in a layered state.

The structure, width, and location of Raman spectrum are related to the layered structure of graphene. For the graphite sample, the peak positions of the G band and 2D band are around 1580 cm^{-1} and 2720 cm^{-1}, respectively. The G band of graphene, different from that of graphite, has a wide peak and shifts to 1593 cm^{-1}. The strength of the G band is lower than that of the 2D band. In addition, different layers of graphene will make the peak position move slightly around 2720 cm^{-1}.[11,12]

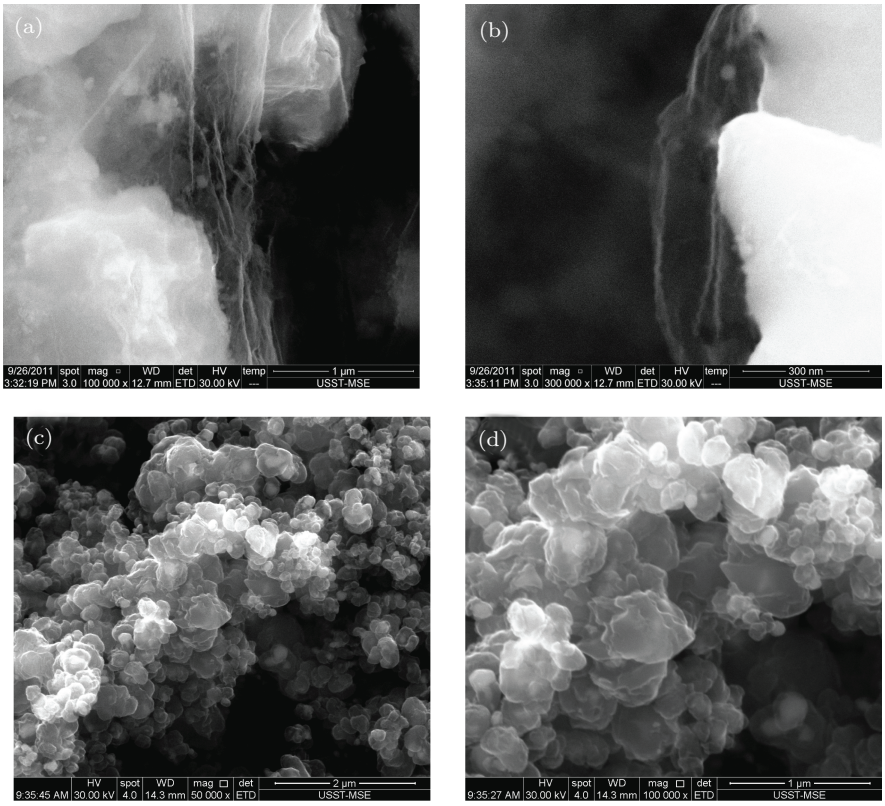


Fig. 1. FE-SEM images of the graphene films, showing the front (a) and the side (b) structures for the Cu substrate sample, and the front (c) and the side (d) structures for the Al substrate sample.

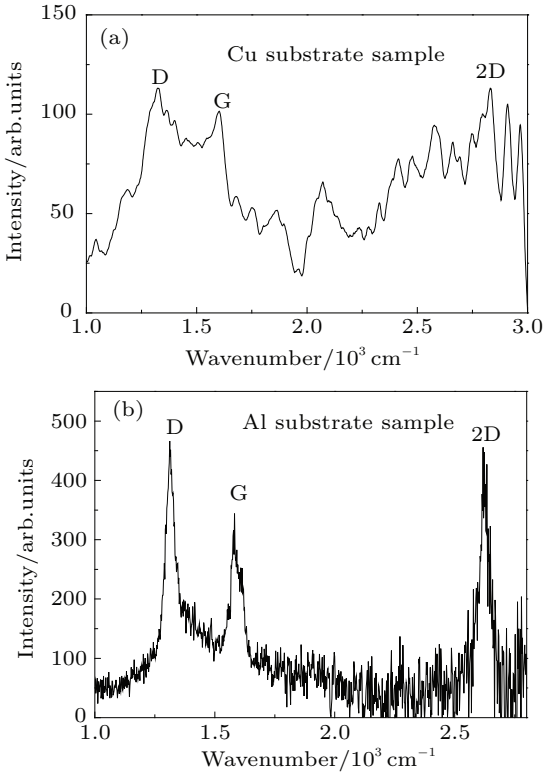


Fig. 2. Raman spectra of graphene films deposited on Cu (a) and Al (b) substrate.

The Raman spectra of the graphene films are shown in Fig. 2. For the sample of the Cu substrate (as shown in Fig. 2(a)), the peak positions of the G and 2D peak are around 1323 cm^{-1} and 2831 cm^{-1} respectively, and the 2D peak shifts from 2720 cm^{-1} to 2831 cm^{-1}. The reason may be that high temperature makes the structure and surface of the Cu substrate change in the deposition process, which makes the substrates unsuitable for the growth of the single layer structure of graphene. Moreover, the length of deposited time also has an effect on the layers of films, so the Raman spectrum of samples has a shift of the peak position. For the sample deposited on the Al substrate (as shown in Fig. 2(b)), the peak positions of the G and 2D peaks are around 1582 cm^{-1} and 2618 cm^{-1} respectively, which explains that the surface of the sample is mostly of the multilayer graphene.

According to Raman spectra and FE-SEM images, we believe that carbon film on the substrate has a structure of graphene, which explains the feasibility of preparing graphene films via the CVD system. However, the surface structure of graphene on the aluminum substrate is not so good as on the copper substrate. The possible reason is the low melting point of aluminum (only 660 °C) and the easy deformation of surface structure.

Figures 3(a) and 3(b) show, respectively, the J–E curves and FN plots of graphene films deposited on the Cu substrate and Al substrate. Different from the traditional FN curve, the FN plots of both graphene films do not have a negative slope linear relationship in low field, which neither shows the traditional cold cathode emission nor corresponds to the classical electron tunneling mechanism. In high field ($E > 1.3$ V/μm) the FN plot is a negative slope straight line corresponding to the classical electron tunneling mechanism.

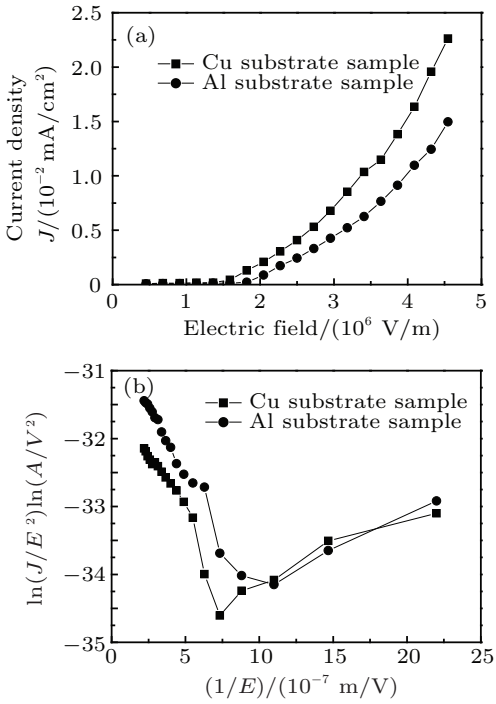


Fig. 3. (a) J–E curves and (b) FN plots of the graphene deposited on Cu and Al substrates.

The J–E data of the graphene sample does not follow the original FN relation in low field, which can be attributed to the surface adsorption of some foreign gases.

On the whole, the field emission property of graphene film is not comparable to that of the traditional carbon-based film, for instance, the device emitting area is too small, the light points are distributed unevenly, the phenomenon of field emission is unstable and the current density is too small (no one exceeds 0.1 mA/cm^2). So the preparation method and process of a graphene field emission device will be optimized further, meanwhile, the mechanism and property of field emission remain to be studied further.

4. Conclusion

Graphene films were prepared on Cu substrates and Al substrates by the MPCVD system. The structures and field emission performances of those graphene films were found to be different by comparison. The experiment results reveal that the structure of graphene deposited on a Cu substrate is relatively good.

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