Preparation of few-layer graphene-capped boron nanowires and their field emission properties*

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Large-area boron nanowire (BNW) films were fabricated on the Si(111) substrate by chemical vapor deposition (CVD). The average diameter of the BNWs is about 20 nm, with lengths of 5–10 μm. Then, graphene-capped boron nanowires (GC-BNWs) were obtained by microwave plasma chemical vapor deposition (MPCVD). Characterization by scanning electron microscopy indicates that few-layer graphene covers the surface of the boron nanowires. Field emission measurements of the BNWs and GC-BNW films show that the GC-BNW films have a lower turn-on electric field than the BNW films.

Keywords: boron nanowires, graphene-capped boron nanowires, field emission properties

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1. Introduction

Because boron has a unique crystal structure and stable physicochemical properties, it is a promising cold-cathode material for the flat field emission devices.[1–4] In the last few decades, different morphology boron one-dimension nanostructures, such as nanowires,[5–7] nanotubes,[8,9] nanocones,[10,11] and nanobelts,[12,13] have been prepared by chemical vapor deposition (CVD) and their field emission (FE) properties have been characterized. However, the surfaces of the boron one-dimensional nanostructure materials tend to form 2–3 nm thick oxide layers, decreasing the conductivity and emission of electrons.[14] Therefore, it is important to cover the surfaces of the boron one-dimension nanostructure materials with conductive materials. It improves the electrical properties, reduces the work function, and improves the field emission performance. Graphene, a single atomic layer of sp^2-hybridized carbon atoms having a honeycomb structure, has attracted considerable attention due to its unique electrical and thermal scattering properties.[15–17] Graphene has a high electrical conductivity and a thin edge of atomic layers, so it is considered as a promising material to cover the boron one-dimension nanostructures used in FE devices.[18–20] Graphene capped on the surfaces of the boron one-dimensional nanostructures increases the emission current for field emission displays.

Here, we report the preparation and field emission of graphene covered boron nanowires (BNWs). Large-area BNWs were first synthesized using boron powder and B_2O_3 powder as the precursors by chemical vapor deposition. Then graphene was deposited on the surface of the BNWs using microwave plasma CVD (MPCVD) in a methane and hydrogen atmosphere. The FE properties of the BNWs and the graphene-capped BNWs (GC-BNWs) were measured. The results of FE indicate that the GC-BNW films have a lower turn-on electric field.

2. Experimental details

2.1. Materials

Boron powder (99.99%), B_2O_3 (99.99%), and carbon powder (99.9%) were purchased from the Beijing Sinopharm Chemical Reagent Co. Argon (99.9%) and H_2/Ar (H_2, 10 vol.%) were purchased from the Beijing Praxair Application Gas Co., Ltd. Boron powder, B_2O_3, and carbon powder with the mass ratio of 4:2:1 were mixed together as the precursors.

2.2. Preparation of boron nanowires

The BNWs were fabricated by the CVD method used in our previous work.[17] 100 μL 8 nm Fe_3O_4 hexane solution[21] as the catalyst (20 mg/mL) was dropped on the surface of a Si(111) wafer; then the Si substrate was heated at 100 °C for 60 min to remove the hexane reagent; finally, Fe_3O_4 nanoparticles were obtained on the surface of the Si substrate. The Si substrate with an Fe_3O_4 nanoparticle catalyst was placed

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in an alumina boat, lying in front of the precursors. Then the alumina boat was transferred into a quartz tube in a horizontal tube furnace. After the system was pumped below 10 Pa, 50 sccm 10% H_2/Ar mixed gas (volume ratio) was introduced and the system pressure was changed to 1×10^2 Pa. Then the furnace was heated to 1150 °C at a rate of 8 °C/min and the system pressure was maintained at 1×10^4 Pa. The reaction was allowed to continue for 2 h at this temperature. The furnace was cooled down to room temperature at a rate of 8 °C/min. Brown-black products were found on the Si substrate.

2.3. Preparation of graphene-capped boron nanowires

The BNWs grown on the Si substrate were transferred into the chamber of a microwave plasma deposition system. The Si substrate with BNWs was placed on the quartz holder of the chamber; then the reaction chamber was pumped down and the system pressure was tuned to 600 Pa, mixed gas of 15 sccm H_2 and 30 sccm CH_4 was introduced into the reaction chamber while the microwave was injected (microwave power: 80 W) and maintained for 1 min; finally, the microwave and gas were shut down and the sample was cooled down to room temperature. The graphene-capped BNW sample was obtained. The whole preparation process of GC-BNWs is shown in Fig. 1.

2.4. Characterization of BNWs

The morphology of the BNWs was characterized by field emission scanning electron microscopy (FE-SEM: SFEG, FEI Corp). Measurements of the field emission (FE) properties of the patterned BNWs were performed on a high vacuum FE analysis system (4×10^{-5} Pa).

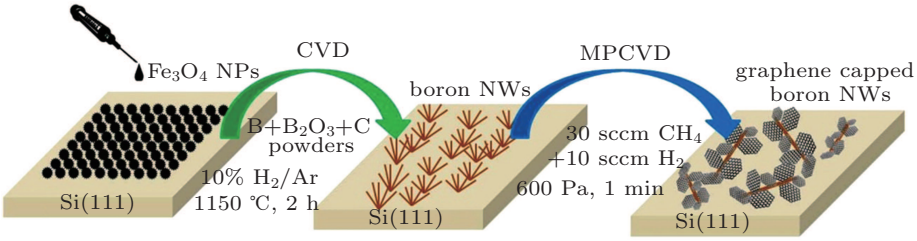

Fig. 1. Schematic diagram of graphene-capped BNW preparation.

3. Results and discussion

Large-area, high-density boron nanowires were fabricated by chemical vapor deposition. Figure 2(a) shows a typical SEM image of the boron nanowires. It is found that the BNWs fully cover the surface of the Si(111) substrate and have a uniform size distribution. We used transmission electron microscopy to characterize the morphology of the boron nanowires, as shown in the inset of Fig. 2(a). From the TEM image, it can be seen that the surface of the boron nanowires is smooth and they have a diameter of 20 nm. The graphene was coated on the surface of the boron nanowires by MPCVD. Figure 2(b) shows an SEM image of a modified sample. The surface of the boron nanowires has been covered by few-layer graphene. Compared to the large-area boron nanowires grown on the Si(111) substrate, the coverage of the graphene-capped boron nanowires is substantially decreased on the substrate, where the boron nanowires have been etched away by H_2 during the MPCVD process. It led to the formation of few-layer graphene-capped boron nanowires on the Si(111) substrate. In Fig. 2(b), we observe only graphene-capped boron nanowires, and no boron nanowires appear. It is clearly shown that few-layer graphene fully cap the boron nanowires. EDX analysis of the graphene-capped boron nanowires indicates that the concentration of carbon in the sample is 6.7 times larger than that in the boron nanowires (Tables 1 and 2). These results confirm that graphene coated the BNWs.

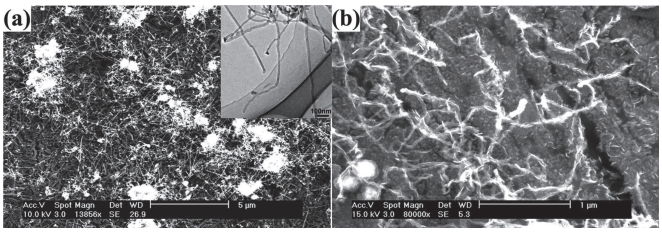

Fig. 2. SEM images of (a) BNWs and (b) GC-BNWs. The inset is TEM image of BNWs.

Table 1. EDX results of BNWs.

Elem.	Wt.%	At.%
B K	75.95	87.78
C K	1.81	1.89
O K	1.51	1.21
Si K	20.33	9.04
Fe K	0.36	0.08

Table 2. EDX results of GC-BNWs.

Elem.	Wt.%	At.%
B K	62.48	74.65
C K	11.83	12.72
O K	2.73	2.21
Si K	22.39	10.03
Fe K	0.58	0.13

In order to confirm that graphene was capped on the boron nanowires, a GC-BNW sample was characterized using Ra-

man spectroscopy, as shown in Fig. 3. In the Raman spectrum of the GC-BNWs, it is found that there are five typical peaks of graphene, located at 1346 cm^{-1}, 1580 cm^{-1}, 2688 cm^{-1}, 2940 cm^{-1}, and 3236 cm^{-1}, respectively, corresponding to the D, G, 2D, D+G, and 2D′ bands of graphene.[22] This result demonstrates that graphene has been coated on the surface of the BNWs. The relatively high D band peak indicates that some defects exist in the sample. The G and 2D bands of graphene in the Raman spectrum are a means to evaluate the number of graphene layers. The red shifts of the G and 2D bands indicate that the graphene capped on the BNWs is few-layer graphene.[23]

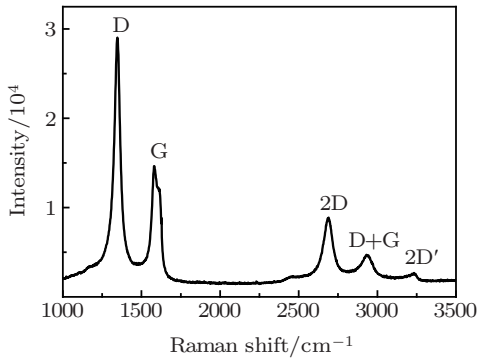

Fig. 3. Raman spectrum of graphene-capped boron nanowires.

In order to compare the field emission properties, we measured the turn-on electronic fields of the GC-BNWs and BNW films. The FE measurements were carried out at room temperature in a vacuum with the chamber pressure maintained at 4×10^{-5} Pa. The NW samples served as the cathodes, and a molybdenum probe (1 mm in diameter) was employed as the anode. The distance between the anode and the cathode was 300 μm.

The field emission properties of the GC-BNWs and BNW films are shown in Fig. 4. From the typical *J*–*E* curves (Fig. 4(a)), it is found that the turn-on fields of the GC-BNWs and BNW films are 6.4 V/μm and 7.5 V/μm (at 10 μA/cm^2 emission current density), respectively. The turn-on electronic field of the GC-BNWs is lower than that of the ZnO nanorods with AlN coating,[24] ZnO nanorods,[25] and Si-doped and Mg-doped AlN nanocones.[26] The field emission performance is improved when graphene covers the surface of the BNWs. This can be attributed to the better electronic conductivity and thermal transmission of graphene. Also, the thinner edge of the graphene sheets capped on the BNWs also helps to increase electron tunneling from the surface of the BNWs. The density of the GC-BNWs on the Si substrate decreases due to H_2 gas etching in the MPCVD process, but the turn-on electronic field of the GC-BNWs does not significantly decrease.

In addition, the GC-BNWs' FN plots are almost linear, as shown in Fig. 4(b), implying that the emission process conforms to the classical FN theory.[27] Compared to GC-BNWs' FN plots, BNWs' FN plots exhibit a nonlinear behavior and can be divided into three regions, which obey the FN theory of semiconductors.[10,28] This phenomenon also proves that conductivity is improved when graphene covers the BNWs.

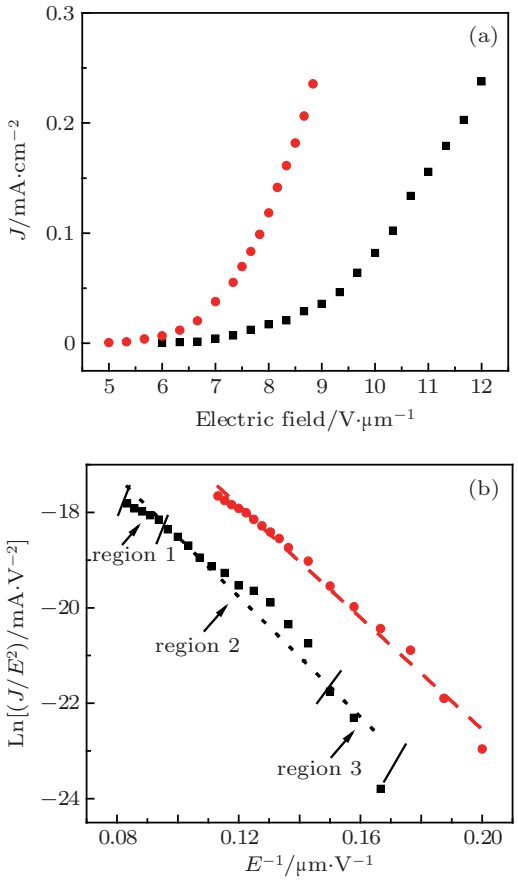

Fig. 4. (a) Field emission *J*–*E* curves of GC-BNWs (red) and BNW (black) films. (b) Fn plots of GC-BNWs (red) and BNW (black) films.

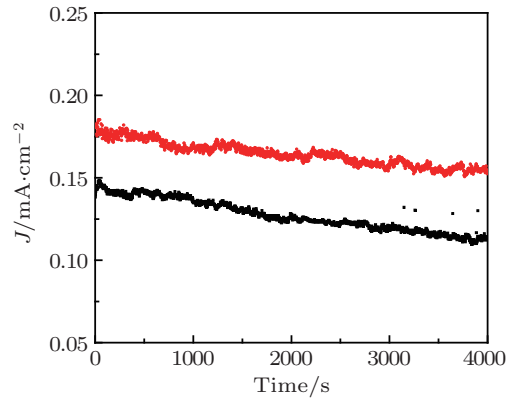

Fig. 5. Field emission current stability of GC-BNWs (red) and BNW (black) films. The GC-BNWs films exhibit stable field emission at the current density of about 0.165 mA/cm^2.

The emission current stability is a parameter to evaluate the FE properties of cathode materials. Figure 5 shows representative emission stability curves of the GC-BNWs and BNW films, respectively. The applied field was fixed at about 8.5 V/μm in the whole measurement process. It is found that this GC-BNW sample shows a stable field emission at the

current density of 0.16 mA/cm^2 and the current fluctuation is about 7.9%, while the current fluctuation of the BNWs is 14.2% and the emission current stability curve of the BNWs exhibits a gradual decrease with increasing measurement time. This indicates that the GC-BNWs sample has more stable emission than the BNWs, which suggests that the GC-BNWs are really good for FE applications.

4. Conclusion

Large-area boron nanowire films were first prepared on the Si(111) substrate using boron, boron oxide, and carbon powders as the precursors by chemical vapor deposition. Then graphene-capped boron nanowires were obtained by microwave plasma chemical vapor deposition in CH_4 and H_2 atmosphere. Characterization by scanning electron microscopy indicates that few-layer graphene covered the boron nanowires. Field emission measurements show that the turn-on electric fields of the BNWs and GC-BNW films were 6.4 V/μm and 7.5 V/μm, respectively.

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