Tuning field emission properties of boron nanocones with catalyst concentration*

Li Chen(李 晨), Tian Yuan(田 园), Wang Deng-Ke(王登科), Shi Xue-Zhao(时雪钊), Hui Chao(惠 超), Shen Cheng-Min(申承民), and Gao Hong-Jun(高鸿钧)†

Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, *China*

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Single crystalline boron nanocones are prepared by using a simple spin spread method in which Fe_3O_4 nanoparticles are pre-manipulated on Si(111) to form catalyst patterns of different densities. The density of boron nanocones can be tuned by changing the concentration of catalyst nanoparticles. High-resolution transmission electron microscopy analysis shows that the boron nanocone has a β-tetragonal structure with good crystallization. The field emission behaviour is optimal when the spacing distance is close to the nanocone length, which indicates that this simple spin spread method has great potential applications in electron emission nanodevices.

Keywords: boron nanocone, spin spread method, optimize, field emission property

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1. Introduction

Boron is a very special element—the only electron-deficient nonmetal in the periodic table of elements. Boron bonds through a three-centre two-electron bond and its peculiar electronic structure make icosahedral B_{12} possible. So boron has unique chemical and physical properties, such as low density (2.364 g/cm^3), high melting point (2300 °C), small work function (4.5 eV), high hardness close to that of diamond, and good chemical and mechanical stability.[1−3] These features make boron one-dimensional (1D) nanostructures promising candidates for cold cathode materials applied in field emission (FE) display devices.[4−7] As a nanoscale cold material, the morphology such as orientation, density, and distance between nanostructures, can dramatically affect its FE behaviour.[8,9] Therefore, seeking for a simple method to improve the FE behaviour is thus highly desirable. Catalyst pre-treatment is an effectual method to control the morphology of one-dimensional nanoscale structure. In the past decades, much effort has been made to grow patterned one-dimensional nanomaterials through different routes. For example, Thompson Group[10] reported on the tuning of CNT diameter and areal density through catalyst pre-treatment; Liu Group[11] used the patterned-catalysts on a quartz surface, made by a one-step photolithography method, to grow orthogonal orientation control of CNTs. Sierra *et al.*[12] reported on the synthesis of high-density, vertically oriented Ge nanowires via biotemplating of Au nanoparticle catalysts. The well patterned carbon nanotube arrays were fabricated on Si substrate through a patterned SiO_2 mask with using Ni as catalysts. The FE properties of patterned NCT arrays exhibited that they have a low turn-on electric field (2 V/μm) and threshold field (3.26 V/μm).[13] In our group, patterned boron nanostuctures have been synthesized by self-assembled of magnetic catalysts nanoparticles and a pre-manipulation to pattern the catalyst with a grid template as mask. The results indicated that the FE property has been significantly improved.[4,14] In the present work, a simpler spin spread method is used to pre-manipulate the catalyst on substrate, and then tune the density of boron nanocones.

The Fe_3O_4 nanoparticles (NPs) catalyst are pre-manipulated on Si(111) by a simple spin spread method. Then boron nanocones of different densities are prepared by chemical vapour deposition (CVD) method. The morphology of the sample we made in this way is much more ordered than that of the sample

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†Corresponding author. E-mail: hjgao@aphy.iphy.ac.cn

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synthesized without using pre-manipulation. Moreover, the density of boron nanocones can be controlled by tuning the concentration of the catalyst. High resolution transmission electron microscopy (HRTEM) results show that the boron nanocone has a β-tetragonal single crystalline structure. Furthermore, field emission behaviours of boron nanocones in different densities have been compared. This simple spin spread method can conveniently tune the ratio between the separation of the boron nanocones and their length, hence optimizing the field emission behaviour, which indicates that this simple spin spread method is useful in synthesis for applications in electron emission nanodevices.

2. Experimental details

2.1. Pre-manipulation of Fe_3O_4 nanoparticles on Si (111) substrate

The mixed catalyst solutions were obtained as 12‘mg Fe_3O_4 NPs, 2 mg boron power, 1–3 mL 950000 molecular weight polymethyl methacrylate (PMMA), 4% in anisole were added into 0.4 mL hexane solution and sonicated for 10 min. A Si(111) wafer was tightly attached to a spin coater using a vacuum chuck, and then two drops of mixed catalyst solution were dropped on the surface of the Si substrate and was spun at 1000 revolution per minute (rpm). The concentration of catalyst can be tuned by changing the amount of PMMA. Then the Si substrate spread with mixed catalyst NPs was kept at 400 °C for 1 h under vacuum to eliminate the PMMA and oleic acid capped on the surface of Fe_3O_4 NPs.

2.2. Fabrication of boron nanocones

A single-stage furnace which can control both the temperature and the gas flow rate was used to synthesize the boron nanocones. Boron powder (99.9%) and boron oxide powder (99.99%) were mixed adequately as precursors with a mass ratio of 1:1. The precursors were put into an alumina boat, and then the as-prepared substrate was placed above the precursors. The substrate kept close to the precursors without gap. The boron nanocones grew by a simple CVD method. First, a carrier gas mixture of 90% Ar and 10% H_2 was introduced at a rate of 100 standard-state cubic centimeter per minute (SCCM) after the system had been pumped below 10 Pa. Second, half an hour later, the flow rate was reduced down to 50 SCCM, and the system pressure was tuned into $2\sim3\times10^3$ Pa. Then the temperature of the system was raised to 1100 °C at 200 °C/h. The reaction was kept at this peak temperature for 2 h. Finally the furnace was cooled down to room temperature naturally, and dark brown products were found on the surface of the substrate.

2.3. Characterization of boron nanocones

The morphology of the product was obtained by a field-emission scanning electron microscope (SEM; XL30 S-FEG). The detailed microstructure of the product was investigated by transmission electron microscopy (TEM; JEM-200CX) and high resolution transmission electron microscopy (HRTEM; JEM-2010) separately. Field emission current was measured by a picoammeter (Keithley 6485).

3. Results and discussion

Boron nanocones were successfully prepared using a simple CVD method. Figure 1(a) is a typical low magnification SEM image, showing that a large scale ordered boron nanocones are successfully fabricated on the Si(111) substrate. It is clear that the nanocones on Si substrate grow in a uniform height. The higher magnification SEM image (Fig. 1(b)) indicates that the typical nanocone structure has a sharp tip with an average length of about 10 μm. Further structure characterizations were carried out by TEM and HRTEM. Figure 1(c) is a low magnification TEM image of an individual boron nanocone, showing that the diameter of this nanocone varies from 200 nm at the root to 20 nm at the tip, in accord with SEM observations. Figure 1(d) is a representative HRTEM image, showing clear crystal lattice fringes and the adjacent lattice distance that is 5.087 Å (1 Å=0.1 nm) between the face (200). The growth is determined to be in the [100] direction. In addition, the side of the boron nanocone is covered by a 2 nm thick amorphous layer, which was most likely to form when the crystalline nanocone was exposed to air. The HRTEM image measurements accord with the data of the Joint Committee for Powder Diffraction Standards (JCPDS) card No. 77–1275, confirming that the boron nanocones each are perfectly single crystalline with a β-tetragonal structure.

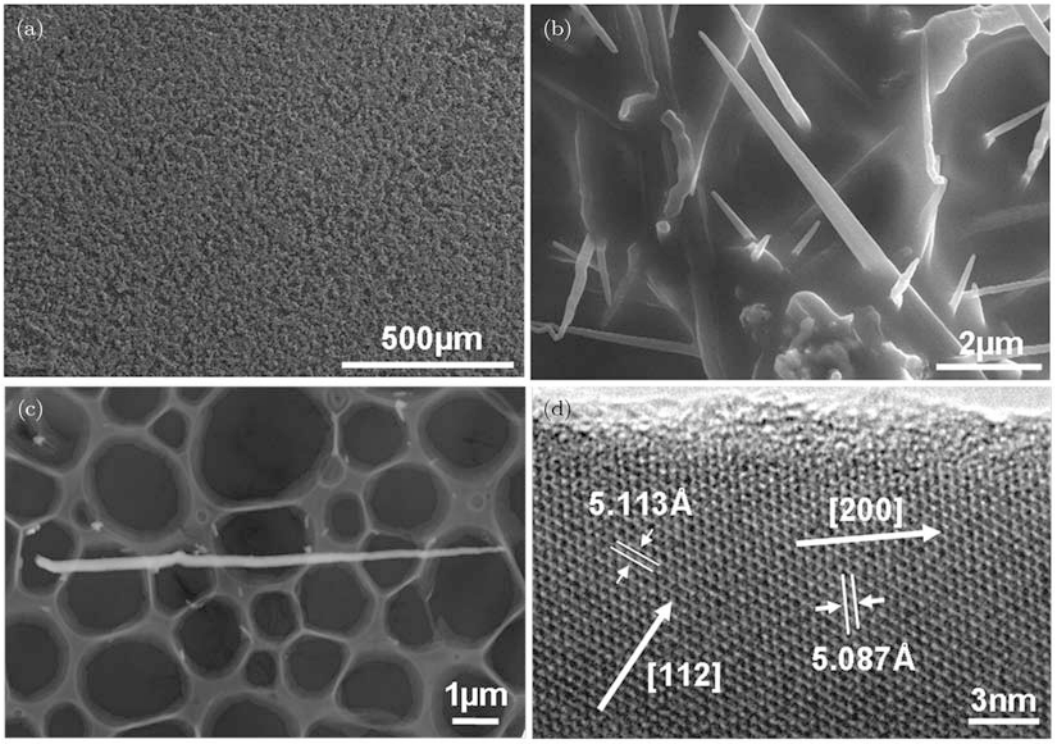


Fig. 1. Morphologies and structures of boron nanocones. Panel (a) shows a low-magnification SEM image of the large scale ordered boron nanocones. Panel (b) displays a high-magnification SEM image of boron nanocones. Panel (c) exhibits a TEM image of an individual boron nanocone. Panel (d) shows an HRTEM image, indicating single-crystal structure with a β-tetragonal structure and along the [100] growth direction.

Moreover, the density of boron nanocones on the substrate can be controlled by tuning the proportions of mixed catalyst solution. It was performed by changing the amount of PMMA in the mixed solution in the pre-manipulation process. Figures 2(a), 2(b) and 2(c) show the SEM images of boron nanocones with low, medium and high densities, which were obtained when the quantities of PMMA were 3, 2 and 1 mL in the mixed catalyst solution respectively. It is obvious that the proportion of mixed catalyst solution can affect the density of boron nanocones.

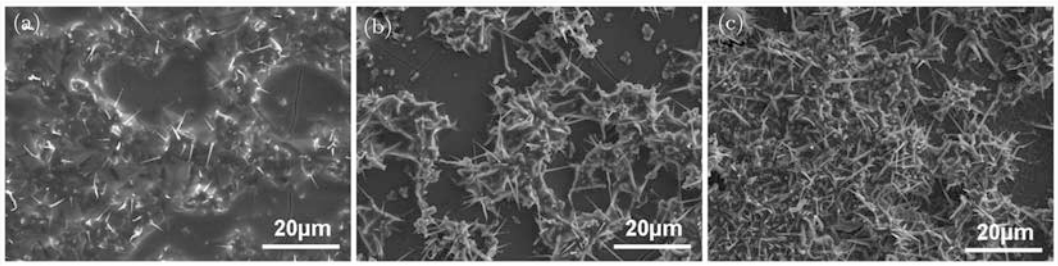


Fig. 2. SEM images of boron nanocones of (a) low density, (b) medium density, (c) high density.

Boron one-dimensional nanostructures have potential applications in the field-emission area. We have found that the field emission behaviour can be tuned by changing the density of the boron nanocones. The FE measurements were carried out in a vacuum chamber with a base pressure of about 2×10^{-6} Pa at room temperature. The sample was attracted to a stainless steel stage Si substrate as the cathode. A molybdenum probe with diameter 1 mm was used as the anode. During experiments the anode-cathode distance was fixed at 200 μm controlled by a linear-motion stepper. Emission current was measured by a picoammeter (Keithley 6485).

Figure 3(a) shows field emission behaviours of low, medium and high density boron nanocones shown in Fig. 2. We define the turn-on field ($E_{\rm to}$) and the threshold field ($E_{\rm thr}$) as the electric fields required to produce current densities of 10 μA/cm^2 and 1 mA/cm^2, respectively. From Fig. 3(a), we can see that the $E_{\rm to}$ and $E_{\rm thr}$ for low density boron nanocones are 7.6 V/μm and 11.5 V/μm. It is found the values of $E_{\rm to}$ and $E_{\rm thr}$ to decrease with the density of the boron nanocones on the Si substrate increasing. At medium density, the values of $E_{\rm to}$ and $E_{\rm thr}$ of nanocones were 4.7 V/μm and 7.6 V/μm respectively. The values of $E_{\rm to}$ and $E_{\rm thr}$ of the boron nanocones gradually increase when the density turns higher, reaching 5.5 V/μm and 8.9 V/μm respectively. It is clear that the field emission current can be influenced remarkably by the distance between the boron nanocones. According to our experiments, the optimum distance to achieve the strongest emission is about 10 μm, as shown in Fig. 2(b). Emission from low density boron nanocones (Fig. 2(a)) is poor because the emitters are few in number, whereas emission from dense boron nanocones decreases because screening effects reduce the field enhancement factor. The optimal spacing is close to the nanocone length, which is consistent with previous result of carbon nanotubes.[15] On the other hand, the formation of highly aligned boron nanocones can also improve their FE properties. These results clearly indicate that the spin spread pre-manipulation method is a convenient and efficient method to enhance the FE of boron nanocones, which can be used to synthesize other nanostructures.

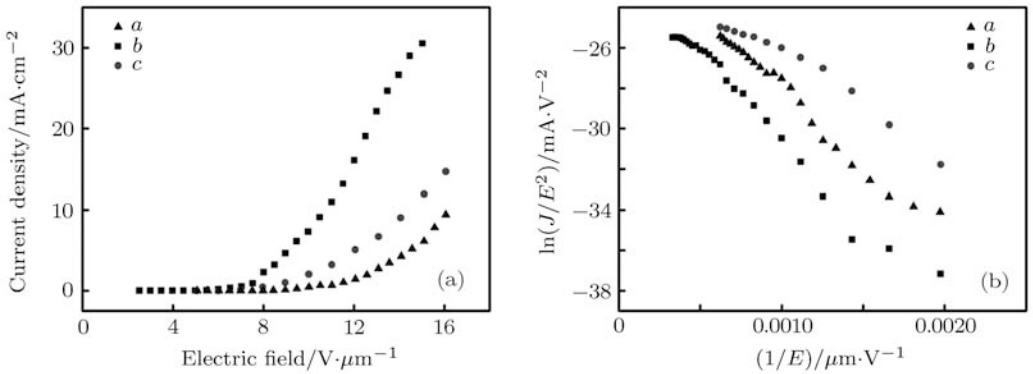


Fig. 3. (a) Field emission characteristics of boron nanocones of different densities at working distance 200 μm; (b) the corresponding F–N plots; *a*, *b*, *c* refer to boron nanocones with low, medium and high densities shown in Figs. 2(a)–2(c)).

The Fowler–Nordheim (F–N) plot, $\ln(J/E^2)$ vs. $1/E$, is shown in Fig. 3(b). The current originates from electron tunneling through the barriers as a consequence of the electric field. According to the F–N theory, the relationship between current density (J) and applied electric field (E) can be described as

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

where $A = 1.57 \times 10^{-10}$ A·V^{-2}· eV, and $B = 6.83 \times 10^9$ V·m^{-1}·eV$^{-3/2}$. The slope of the F–N plot is equal to $-6830\phi^{3/2}/\beta$, where ϕ is the work function and β is the enhancement factor. The linearity of the curve implies that the current originates from electron tunneling through the barriers as a consequence of the electric field.

4. Conclusions

A simple spin spread method is used to pre-manipulate Fe_3O_4 nanoparticles on Si(111) substrate. The ordered boron nanocones are synthesized on an as-prepared Si(111) substrate spread by catalyst nanoparticles. The density of boron nanocones can be controlled by tuning the concentration of catalyst mixed solution. HRTEM measurements show that the boron nanocone has a β-tetragonal structure with good crystallization. Furthermore, this simple spin spread method can tune the spacing distance of the boron nanocones close to the nanocone length easily, thus optimizing the field emission behaviour. These results indicate that this simple spin spread method is useful in synthesis for applications in electron emission nanodevices.

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