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# Field emission properties of patterned boron nanocones

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**Abstract**
Large area patterned boron nanocones with low turn-on electric field of 2.8 V $\mu$m$^{-1}$ and low threshold electric field of 3.8 V $\mu$m$^{-1}$ were synthesized by a pre-manipulation to pattern the catalyst with a grid template as mask. The good field emission performance of patterned boron nanocones arise from the decreased screening effect and a favorable orientation of the nanocones. These results show that the patterned growth is a highly efficient way to enhance the field emission performance of boron nanocones, which have a great potential of application in flat panel displays and electron emission nanodevices.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

The cold cathodes based on the quasi-one-dimensional nanoscale materials have exhibited excellent field emission (FE) properties in contrast with the traditional materials [1]. The synthesis control of quasi-one-dimensional nanoscale materials, such as morphology, orientation, density, and interval, has become the key technology in integrative, higher efficient and size-reducing flat field emission displays [2–5]. Especially, the patterning of nanoscale cold cathodes can dramatically improve FE properties and increase FE enhancement factor by reducing screen effects between nanomaterials [6]. To date, much effort has been made to prepare patterned nanostructures, such as lithography, writing with a beam of photons or an electrical/magnetic field, and bottom-up approaches to form the pattern in nanoscale [7, 8]. Recently, boron one-dimensional (1D) nanostructures have considerably attracted much attention as promising candidates for cold cathode materials applied in FE display devices. Tian *et al* studied FE properties of the boron nanowires using patterns of assembled $Fe_3O_4$ nanoparticles [6]. Wang *et al* firstly reported preparation of large area crystalline boron nanocones and the excellent FE behavior [3]. However, the further increase of the FE property is limited due to the random growth of nanocones on the substrate and large distance between nanowires pattern unit. In order to obtain lower threshold electric field and higher enhancement factor, we employed a simple method to prepare large area patterned quasi-aligned boron nanocones, which exhibits much better FE properties of lower turn-on and threshold electric field.

In this paper, we used a facile and modified route to make a pre-manipulation pattern of catalyst on Si(111) substrate with a Mo grid template as a mask [9]. Thereafter, patterned boron nanocones were obtained on the Si surface by chemical vapor deposition (CVD). Compared to previous works [4, 6, 10], this patterned boron nanocones exhibits a lower threshold field and high stability of FE. The good field emission behavior indicates that patterned boron nanocones are promising candidates for applications in electron emission nanodevices.

## 2. Experimental details

As schematically illustrated in figure 1, an especial molybdenum grid of 8 mm inner diameter was used as the template to form catalysts pattern. Firstly, the Mo grid was tightly attached to a Si(111) substrate using a special clamp of our design, and then 2 ml mixed hexane solution with 60 mg $Fe_3O_4$ catalyst and 10 mg boron power was dropped into the interspaces of the Mo grid (figure 1(a)). Secondly, the Si substrate was dried at 100 °C under vacuum atmosphere and the Mo grid was removed to obtain Si substrate containing catalyst pattern (figure 1(b)). Lastly, the high density boron

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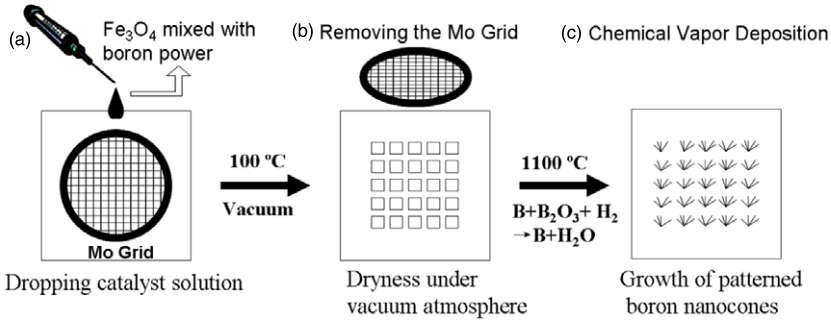


**Figure 1.** Schematic illustration of patterned growth process of boron nanocones prepared by a pre-manipulation to pattern the catalyst with a grid template as mask.

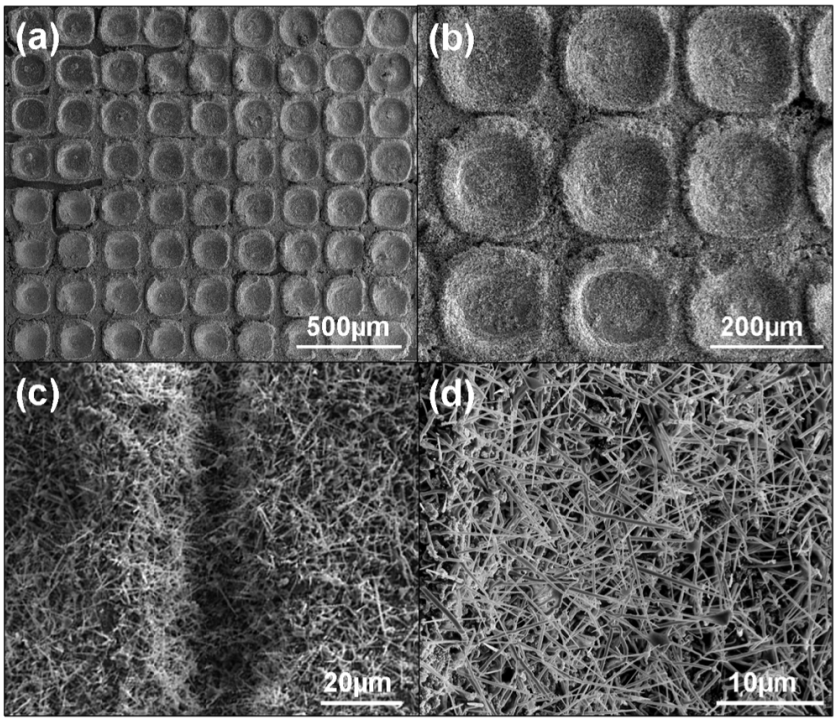


**Figure 2.** SEM images of (a) large-scale high density patterned boron nanocones. (b) Several blocks covered by boron nanocones. (c) A channel between two blocks. (d) Details of the dense boron nanocones on one block, revealing formation of uniform geometrical morphology and quasi-aligned boron nanocones.

nanocones pattern was prepared on the pre-manipulated Si substrate (figure 1(c)).

A horizontal tube furnace with an accurate controller of both the temperature and the gas flow rate was used for synthesis. Boron powder (99.9%) and boron oxide powder (99.99%) in a mass ratio of 1:1 were ground together as precursors. The prepared patterned substrate was placed above the precursors in an alumina boat. The boron nanocones grew in two steps of raising the temperature. At first, a carrier gas mixture of 90% Ar and 10% $H_2$ was introduced at a rate of 100 sccm (standard-state cubic centimeter per minute) after the system was pumped below 10 Pa. The temperature of the furnace was raised at 200 °C $h^{-1}$ to 400 °C and kept there for 30 min to eliminate oleic acid and oleylamine adsorbed on the surface of catalyst nanoparticles. Meanwhile, the system pressure was tuned to 2–3 $\times$ $10^3$ Pa. Then temperature of system is raised to 1100 °C at the same heating rate. At this temperature, the reaction was allowed to progress for 2 h. After the furnace was cooled down to room temperature, dark brown products were found on the surface of the substrate.

## 3. Results and discussion

Morphologies of boron nanocones were examined by a field emission scanning electron microscope (FE-SEM; Model XL-SFEG, FEI Corp., Hillsboro, OR). High resolution transmission electron microscopy (HRTEM; Tecnai $G^2$ 20 S-TWIN; FEI Co.) was used to investigate the microstructure of the boron nanocones. Field emission current was measured by a picoammeter (Keithley 6485).

Figure 2(a) is a typical SEM image of the large-scale patterned boron nanocones grown on the Si(111) substrate. It

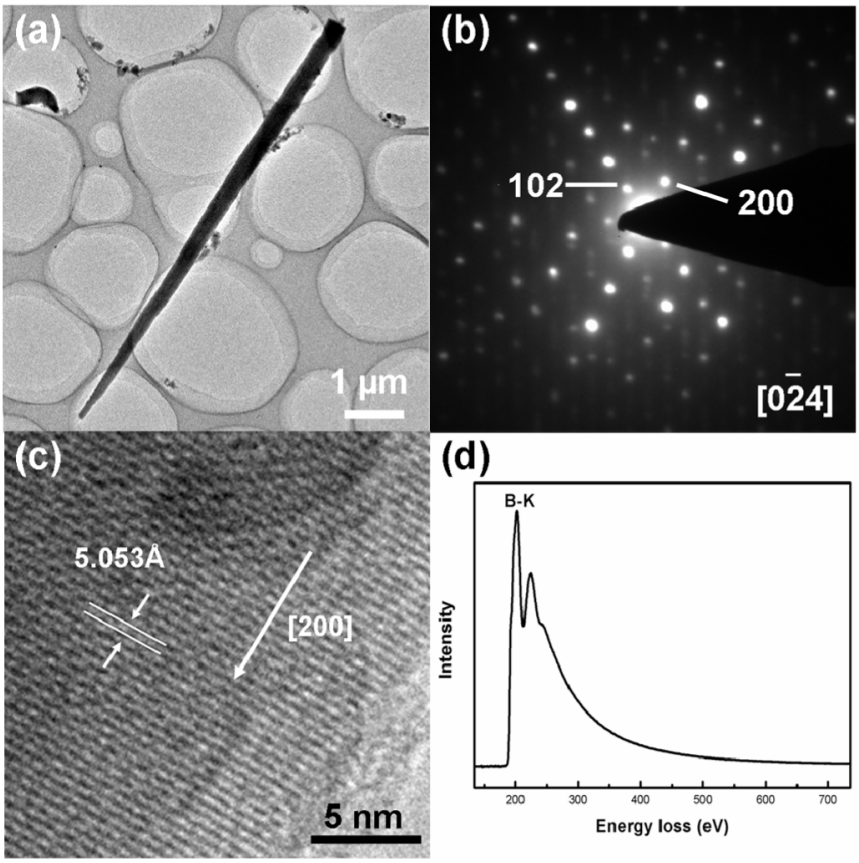


**Figure 3.** (a) TEM image of an individual boron nanocone. (b) SAED pattern and (c) HRTEM image, indicating single crystalline with a $\beta$-tetragonal structure and along the [001] growth direction. (d) EELS spectra from the individual boron nanocone shows characteristic boron K-edges at 188 eV.

is clear that a uniform pattern was formed on the substrate with each square deposited unit measuring 130 $\mu$m which fit closely within a square of the grid. In further analysis of figure 2(b), each unit of the pattern seems to be a bowl-like structure by reason of the soakage between the Mo grid and the catalyst solution. As shown in figure 2(c), the distance between two neighboring regions is about 20 $\mu$m. No boron nanocones could be observed in the bottom of channels between two patterned units. A higher magnification SEM image of boron nanocones is shown in figure 2(d). They have a uniform shape and narrow size distribution with the average length about 10 $\mu$m, and they are quasi-aligned. The cones become sharp gradually from the 200–300 nm diameter root to the 20–50 nm diameter tip.

Further structure characterization was performed by TEM and selected area electron diffraction (SAED). Figure 3(a) shows a low magnification TEM image of an individual boron nanocone, the diameter of this nanocone changes from 250 nm at root to 30 nm at tip, in accordance with SEM observations. The corresponding electron diffraction pattern shown in figure 3(b) can be indexed as a single crystalline structure along the [0$\bar{2}$4] zone axis. The HRTEM image (figure 3(c)) has clear crystal lattice fringes and the adjacent lattice distance is 5.053 Å. In addition, the side of the boron nanocone is covered by an amorphous sheath about 2 nm thick, which most likely originates from boron oxide. The growth of the boron nanocone is along the [001] direction, agreeing with the data of the Joint Committee for Powder Diffraction Standards (JCPDS) card No. 77-1275. Both the SAED pattern and HRTEM image show that the boron nanocones are perfectly single crystalline with a $\beta$-tetragonal structure. Figure 3(d) shows an electron energy loss spectroscopy (EELS) spectrum of the nanocone. The characteristic boron K-shell ionization edge at about 188 eV was observed. No oxygen, iron or other impurities could be detected, demonstrating that the as-prepared nanocone is boron.

Boron one-dimensional nanostructures have exhibited good FE behavior [3–6]. We further investigated the FE properties of the patterned boron nanocones. The FE measurements were carried out at room temperature inside a spherical vacuum chamber which was pumped down to $2.1 \times 10^{-6}$ Pa. A molybdenum probe (1 mm in diameter) controlled by a stepper was used as the anode. The Si substrate with the patterned boron nanocones acting as the cathode was stuck onto a stainless steel stage. During our experiments the anode–cathode distance was kept constant at 300 $\mu$m adjusted by a linear-motion step controller.

Figure 4(a) shows the relationship between current density $J$ and applied field $E$. Here we define the turn-on field ($E_{to}$) and the threshold field ($E_{thr}$) as the electric fields required to produce a current density of 10 $\mu$A cm$^{-2}$ and 1 mA cm$^{-2}$, respectively. The $E_{to}$ and $E_{thr}$ for this patterned boron

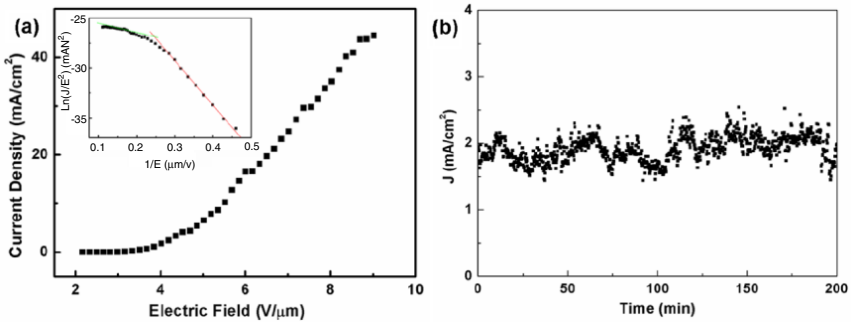


**Figure 4.** (a) Field emission characteristics of patterned boron nanocones at working distance 300 $\mu$m, inset is the FN plot of the $\ln(J/E^2)$ versus $1/E$. (b) Field emission current stability of patterned boron nanocones, exhibiting a stable field emission at current density of about 1.91 mA cm$^{-2}$ and a low fluctuation well below 10%.

nanocones are 2.8 and 3.8 V $\mu$m$^{-1}$. Both are lower than in the corresponding boron nanocones films, boron nanowires arrays films and patterned boron nanowires previously reported by our group [3–6]. It can be deduced that the enhanced FE of the patterned sample might be due to the decreased screening effect as a larger marginal area exists in the patterned samples. On the other hand, formation of quasi-aligned boron nanocones can also improve their FE properties. The $E_{\mathrm{to}}$ value is lower than that of periodic amorphous silicon array (4.5 V $\mu$m$^{-1}$) [11]. Although the $E_{\mathrm{thr}}$ value is still higher than that of aligned carbon nanotubes (1.6 V $\mu$m$^{-1}$) [12], it is lower than those of ZnO nanopins (5.9 V $\mu$m$^{-1}$) [13] and patterned AlN nanocones (4.8 V $\mu$m$^{-1}$) [9]. These results clearly indicate that patterned growth is a convenient and efficient method to enhance the FE of boron nanocones mainly due to the decreased screening effect.

The Fowler–Nordheim (FN) plot, $\ln(J/E^2)$ versus $1/E$, are shown in the inset of figure 4(a). According to FN theory, the field emission current originates from electron tunneling through the barriers as a result of the electric field. The slope of the FN plot is equal to $-6830\varphi^{3/2}/\beta$, where $\varphi$ is the work function and $\beta$ is the enhancement factor. If we assume that the work function $\varphi_{\mathrm{B}}$ is 4.5 eV, $\beta$ is estimated to be 1396 and 6852 at low and high electric fields, respectively, the two-sectional feature may be due to the space charge effect [14].

We investigated this material's emission stability at high emission current, which is critical for the practical application of cold cathode nanomaterials. Figure 4(b) shows a representative emission stability curve. The electrical field was fixed at about 4 V $\mu$m$^{-1}$ and the whole measurement lasted for 200 min, as the time-interval for acquiring the field emission current data was 12 s. It is evident that this material exhibits a stable field emission at current density of about 1.91 mA cm$^{-2}$ and the fluctuations are found to be well below 10% throughout the continuous emission operation. The low threshold field behavior of this patterned boron nanocone material along with its good stability under high current suggests that it is a good candidate as a field emitter.

In order to analyze how the patterned structure affect the FE property of boron nanocones, further electrostatic calculations of the electric field mapping were carried out [15–18], as shown in figure 5. According to the actual

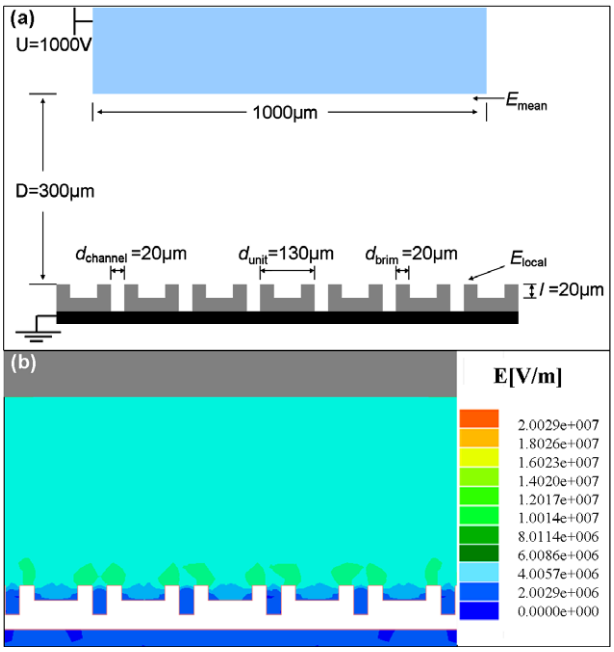


**Figure 5.** (a) Scheme of boundary condition in numeric simulation for electric field. (b) Calculated electric field mapping, demonstrating an electron field enhancement on the brim of the bowl-like unit.

experimental setup, the boundary condition was defined as in figure 5(a). The brim high $l$ and width $d_{\mathrm{brim}}$ of the bowl-like unit are both estimated to be 20 $\mu$m, close to $d_{\mathrm{channel}}$ (the distance of the channel between two patterned units). The electric potential at the molybdenum probe is set to 1000 V as anode and the substrate is set to 0 V as cathode. The potential far away from the two electrodes is also set to 0 V. The effective electric field $E_{\mathrm{eff}}$ is defined as the microcosmic electric field at the apex of the emitting tip. The mean electric field $E_{\mathrm{mean}}$ is defined as the electric field near to the anode. Here, $E_{\mathrm{mean}} = 3.33$ V $\mu$m$^{-1}$. Normally, the field enhancement factor $\beta = E_{\mathrm{eff}}/E_{\mathrm{mean}}$. Here we define $E_{\mathrm{local}}$ as the local electric field near the surface of boron nanocones. Figure 5(b) shows the distribution mapping of the local electric field, which indicates that $E_{\mathrm{local}}$ near the brim of the bowl-like unit is about 16 V $\mu$m$^{-1}$, five times the value of $E_{\mathrm{mean}}$. Thus, the field enhancement factor of the nanocones on the brim of the bowl-

like unit $\beta = E_{\text{eff}}/E_{\text{mean}} = 5 \times E_{\text{eff}}/E_{\text{local}} = 5\beta_0$. Here $\beta_0$ indicates the field enhancement factor of the no-patterned boron nanocones. $E_{\text{local}}$ near the center of the bowl-like unit is about 2.8 V $\mu$m$^{-1}$. Thus, the field enhancement factor of the nanocones in the center of the bowl-like unit is about $0.85\beta_0$. Considering the channel areas without nanocone growth cover about 25% of the Si substrate, the brim areas and center areas of bowl-like units cover about 40% and 36%, respectively, the calculated collective field enhancement factor of patterned boron nanocones is about $2.5\beta_0$. It is agreement with the experimental results. Moreover, the effect of $d_{\text{channel}}$ has been studied. The further theoretical calculations demonstrate that when the $d_{\text{channel}}$ compared to the relative height of the unit brim (20 $\mu$m), an optimum result will be got. If $d_{\text{channel}}$ is wider than 20 $\mu$m, the collective emitter quantity would decrease. If $d_{\text{channel}}$ is narrower than 20 $\mu$m, the limit of distance between the units would accumulate charge which can decrease the potential drop perpendicular into the film. This screen effect would reduce the field enhancement and thus the emitted current. These results indicate that this patterned structure plays a significant role for the enhancive field emission property.

## 4. Conclusion

In summary, a convenient and cheap method has been developed to obtain patterned $Fe_3O_4$ catalyst on Si substrate with Mo grid as a mask. The patterned Si wafer was subsequently used as substrate to grow patterned boron nanocones by chemical vapor deposition. TEM and SAED showed that the boron nanocone has a $\beta$-tetragonal structure with good crystallization. The good field emission properties show that the patterned growth is an efficient approach to enhance the FE properties of boron nanocones, because the increased marginal region decreases the screening effect. The results indicate that patterned growth method should be applicable to optimize the FE properties of other field emitter nanostructures.

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