Fabrication of vertically aligned single-crystalline lanthanum hexaboride nanowire arrays and investigation of their field emission

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High-quality, uniform, one-dimensional (1D) lanthanum hexaboride (LaB6) nanostructures with different morphologies (for example, sparse or dense nanoneedles, or nanorods and nanowire arrays) were fabricated through an effective, easily controlled, one-step, catalyst-free chemical vapor deposition process. The morphologies, structures and temperature-dependent field emission (FE) properties were systematically investigated. FE measurements at room temperature (RT) showed that LaB6 nanowire arrays possess the best FE characteristics among all 1D LaB6 nanostructures, with a low turn-on electric field ($E_{\text{to}}$, 1.82 V μm⁻¹), a low threshold electric field ($E_{\text{thr}}$, 2.48 V μm⁻¹), a high current (5.66 mA cm⁻² at 2.92 V μm⁻¹) and good stability (at a testing time of 1000 min, fluctuations were < 6.0%). Temperature-dependent FE showed that the turn-on and threshold electric fields decreased from 1.82 to 1.06 and 2.48 to 1.62 V μm⁻¹, respectively, whereas the emission current density increased significantly from 0.20 to 9.05 mA cm⁻² at 2.20 V μm⁻¹ when the temperature was increased from RT to 723 K. The emission current density and the dependence of the effective work function on temperature were also investigated. We attribute the significant reduction of the turn-on and threshold fields and the remarkable increase of emission current to a decrease in the effective work function with temperature.

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INTRODUCTION

Cathode-nanostructured materials are significant in the field of electronics, particularly in flat panel displays, electron microscopes and X-ray sources. Field emission (FE) is a quantum mechanical tunneling phenomenon in which electrons are emitted from the surface of the material to a vacuum under an applied external electric field. Numerous one-dimensional (1D) materials, including carbon nanotubes (CNTs1), oxides (ZnO2, WO3), carbides (SiC4), nitrides (AlN5, GaN6) and metals (W7), have been comprehensively studied as candidates for FE applications. Among these materials, CNTs and oxide nanowires have exhibited excellent FE performances characterized by relatively low turn-on fields, a high current density and a high enhancement factor. However, higher work functions (the work functions are all ~4.0 eV for the materials considered), uncontrolled structures (especially chiralities in CNTs), the lack of adequate long-term and/or high-temperature FE stabilities and unsatisfactory mechanical properties have hindered the development of these materials for practical applications. The Fowler-Nordheim (F-N) theory9 predicts that electron emitters made of materials with a low-work function and a high aspect ratio can greatly enhance an FE current and lower the needed turn-on voltage. Therefore in addition to improving the FE properties of the CNTs and oxide nanostructures, developing and searching for new materials (that is, the low-work function materials) have attracted a considerable interest from both fundamental and practical viewpoints.

Lanthanum hexaboride (LaB6) brings together a unique combination of all desired properties required for excellent cathode materials: low-work function (2.6 eV), low volatility at high temperatures, high brightness, high chemical resistance and high mechanical strength.10–15 Thus, 1D LaB6 nanostructures should be an ideal candidate for FE applications, especially if LaB6 nanostructures have...
an elongated geometry and sharp emitting tips. Zhang et al.\textsuperscript{10} have demonstrated room temperature (RT) FE of a single LaB\textsubscript{6} nanowire with a current density as high as $5 \times 10^4$ A cm\textsuperscript{-2} at a working voltage of 800 V, which is one order of magnitude higher compared with that of the state-of-the-art W/ZrO\textsubscript{2} thermal field emitters working at 1800°C with a 3-kV extraction voltage. An individual LaB\textsubscript{6} nanowire also shows an emission current density comparable to that of an individual C nanotube with a diameter 10-50 times smaller. However, the fabrication of 1D LaB\textsubscript{6} nanostructures is still challenging. For example, a large number of experiments indicate that the traditionally effective methods, such as solid-state reactions, boron reduction processes, thermal evaporation and hydrothermal reaction, are not suitable for the growth of high-aspect-ratio 1D LaB\textsubscript{6} nanostructures. Recently, Zhang et al.\textsuperscript{11–13} and Xu et al.\textsuperscript{14} synthesized LaB\textsubscript{6} nanowires using BCl\textsubscript{3} as a boron precursor; but in the application of this method, it was difficult to obtain large-area, high-quality LaB\textsubscript{6} nanostructures. This difficulty might be attributed to the inherent properties of the boron precursor (that is, BCl\textsubscript{3} is not an effective boron precursor,\textsuperscript{16} and strong corrosion of BCl\textsubscript{3} can damage the surface of the substrates and the nanowires produced at high temperatures). Brewer et al.\textsuperscript{15} reported an effective chemical vapor deposition (CVD) method to synthesize LaB\textsubscript{6} nanoobelisks by using LaCl\textsubscript{3} and B\textsubscript{10}H\textsubscript{14} as the starting materials and platinum (Pt) or gold (Au) as the catalysts. The problem with this method is that on the one hand, B\textsubscript{10}H\textsubscript{14} is a solid precursor and it is not easy to control its flow under CVD; control of its flow under CVD would require external heating devices and complex pipelines into the reactor. On the other hand, the utilization of Pt and Au catalysts would greatly limit the large-scale production of LaB\textsubscript{6} nanowires owing to the cost. Investigation of a simpler, more effective method to synthesize LaB\textsubscript{6} nanostructures is therefore of great interest. For FE applications, well-aligned vertical nanowires with a high density are especially desirable because such morphology can enhance the FE properties. To our knowledge, the controllable synthesis and tuning of FE properties of 1D LaB\textsubscript{6} nanowires have not yet to be demonstrated.

In addition to the work function and morphology of the cathode materials, the ambient temperature of the cathode is an important factor for FE performance, which has a strong influence on the material FE characteristics. For example, temperature-dependent field-electron emission\textsuperscript{17–20} can provide deep insight into the physical properties of a nanostructure, reveal the relationship between the electron emission characteristics and different temperature conditions, and allow the investigator to understand the direct thermal electric conversion. Recently, extensive efforts have been devoted to a study of temperature-dependent FE of CNTs,\textsuperscript{20,21} ZnO nanowires,\textsuperscript{17} AlN nanotips,\textsuperscript{5} graphene films\textsuperscript{19} and SiC nanostructures.\textsuperscript{18} All of the authors obtained similar results: both the turn-on and threshold electric fields decreased with increasing temperature. However, an elaborate research program on high-temperature FE for aligned LaB\textsubscript{6} nanowire arrays has not yet been initiated, making the investigation of temperature-dependent field-emitter LaB\textsubscript{6} arrays indispensable.

In this work, we have developed an effective, easily controlled, one-step, catalyst-free CVD method to synthesize high-quality, uniform LaB\textsubscript{6} 1D nanostructures with different morphologies such as sparse and nanoneedles, dense nanorods and well-aligned nanowire arrays. The morphology of LaB\textsubscript{6} nanostructures can be adjusted by changing the reaction temperature and the distance between the precursors and the substrate. Our results demonstrate that among the above-mentioned four nanostructures, the well-aligned nanowire arrays are the best field emitters, with a low turn-on field (1.82 V \textmu m\textsuperscript{-1}), a low threshold field (2.48 V \textmu m\textsuperscript{-1}) and good stability (testing time, 1000 min; fluctuation <6.0%). The temperature-dependent FE properties of the aligned LaB\textsubscript{6} nanowire arrays were also investigated to elucidate the FE mechanism of the arrays.

EXPERIMENTAL PROCEDURES

Synthesis of LaB\textsubscript{6} nanostructures was conducted in a horizontal tube furnace with an internally mounted 50-mm outside diameter quartz tube (as shown in Supplementary Figure S1). In brief, 0.2 g of lanthanum chloride heptahydrate (LaCl\textsubscript{3} \textperiodcentered 7H\textsubscript{2}O; mass purity, 99.99%) was loaded near the closed end of the quartz test tube and deposited in the uniform temperature region, while Si wafers were placed upstream to act as deposition substrates. The distance between the substrate and the source was \textsim 3 cm for sample a, \textsim 5 cm for sample c, and \textsim 8 cm for samples b and d. Before heating, each quartz tube was evacuated and washed with a mixed gas (30% H\textsubscript{2}/70% Ar; volume percent calculation). The quartz tube was then heated to 930°C (samples a and b) or 970°C (samples c and d) at a heating rate of \textsim 15°C min\textsuperscript{-1} under a base pressure of \textsim 5 Pa. Then, a steady mixed gas (5% volume B\textsubscript{2}H\textsubscript{6}/95% volume Ar) at \textsim 30 s.c.c.m. was flowed for 30 min under a reaction pressure of \textsim 15 Pa. After the reaction, the furnace was cooled to RT under vacuum. Four representative samples (a, b, c and d) were fabricated by varying experimental parameters; the detailed growth conditions are listed in Table 1.

The synthesized products were characterized by scanning electron microscopy (SEM; S-4800, Hitachi, Tokyo, Japan), Raman spectroscopy (Horiba Jobin-Yvon T6400 instrument, Tokyo, Japan), transmission electron microscopy (JEM-3000F instrument, JEOL, Tokyo, Japan) and X-ray energy dispersive spectroscopy (VG Scientific, UK) with 300 W Al K\textalpha\ radiat. The FE properties were analyzed on a home-built parallel-plate electrode high-vacuum FE system with a base pressure of \textsim 5.0 \times 10\textsuperscript{-7} Pa at different controlled temperatures. The distance between the substrate surfaces and the anode of the vacuum chamber was fixed at 500 μm.

RESULTS AND DISCUSSION

The morphology, structure and growth mechanism of LaB\textsubscript{6} nanostructures

Representative morphologies of LaB\textsubscript{6} nanostructures obtained were investigated by FE SEM, as shown in Figure 1. The low-magnification

Table 1 Growth conditions for one-dimensional LaB\textsubscript{6} nanostructures

| Sample | Si substrates | Distance between the source and the substrates (cm) | T (°C) | t (min) | Reaction pressure (Pa) | Wash gas: the ratio of H\textsubscript{2}/Ar and | Reaction gas: the ratio of H\textsubscript{2}/B\textsubscript{2}H\textsubscript{6} | Flow (s.c.c.m.) | Flow (s.c.c.m.) |
|--------|---------------|---------------------------------------------------|--------|--------|------------------------|---------------------------------|---------------------------------|----------------|----------------|
| a      | <100>         | No                                                | 3      | 930    | 30                     | ~15                             | 3.7; 100                      | 1.19; 30         |                |
| b      | <100>         | No                                                | 8      | 930    | 30                     | ~15                             | 3.7; 100                      | 1.19; 30         |                |
| c      | <100>         | No                                                | 5      | 970    | 30                     | ~15                             | 3.7; 100                      | 1.19; 30         |                |
| d      | <100>         | No                                                | 8      | 970    | 30                     | ~15                             | 3.7; 100                      | 1.19; 30         |                |
nanowire arrays. That the LaB₆ structures have a smooth and masonry tower-like view of the nanowire arrays, taken from the top (Figure 1d2), reveals substrates (Figure 1d1 and Supplementary Figure S2). A magnified needle-like nanorods, with diameters of lanthanum hexaboride (LaB₆) nanostructures: (a₁, a₂) sparse nanoneedles; (b₁, b₂) dense nanoneedles; (c₁, c₂) dense nanorods; and (d₁, d₂) nanowire arrays.

SEM images (Figures 1a₁, b₁, c₁ and d₁) show that the nanostructures cover the entire substrates uniformly. The high-magnification SEM images (Figures 1a₂, b₂, c₂ and d₂) illustrate that the morphologies are quite different when different distances between the precursors and the substrates are utilized. At a short distance (∼3 cm) and low temperature (930°C), sparse and thinner needle-like nanorods, with diameters of ∼30–50nm and lengths up to several micrometers, are formed (Figure 1a). With an increase in the distance, longer and thicker needle-like nanorods grow (Figure 1b). The diameters of the nanowires are ∼70–130 nm, and the lengths are ∼5–10 μm. The use of a higher-source temperature (970°C) and a short distance (∼5 cm) leads to the formation of dense nanorods. A dense cage of nanorods, with a typical length up to 3–8 μm, covers the substrate (Figure 1c). High-magnification SEM images (Figure 1c₂) show that the nanorods have a relatively uniform cross-section and a diameter of 100 nm. When the distance increases to ∼8 cm at a higher temperature (970°C), high-quantity, smooth, well-faced LaB₆ nanowire arrays grow nearly vertically on the substrates (Figure 1d₁ and Supplementary Figure S2). A magnified view of the nanowire arrays, taken from the top (Figure 1d₂), reveals that the LaB₆ structures have a smooth and masonry tower-like morphology, with a typical diameter of ∼80–120 nm and a length of ∼15–20 μm.

The detailed microstructures of the well-aligned LaB₆ nanowires arrays were further studied by TEM. Figure 2a shows a typical low-magnification TEM image of a nanowire portion with a diameter of ∼90 nm. Figure 2b gives a high-resolution TEM lattice image, demonstrating the single crystalline nature of the nanowires. Two groups of mutually perpendicular interference fringes can be seen clearly, and the two d-spacings, which are ∼0.41 nm each, correspond to the (100) and (010) crystal faces. Selected area electron diffraction was used on tens of nanowires to determine their structures. Figure 2c shows a typical selected area electron diffraction pattern taken along the (001) crystal zone axis. Selected area electron diffraction reveals that LaB₆ nanowires adopted a single crystal structure, and the calculated lattice constant is a = 0.41 nm, which is close to the lattice constant of cubic LaB₆, according to the JCPDS database (No. 73-1669, a = 0.416 nm). Figure 2f illuminates the corresponding structural model. The superb crystal quality excludes the possibility of any grain boundaries and/or other interfaces, which usually act as recombination sites in polycrystalline materials. This crystal quality should favor improved FE and electron transport properties. The La and B elemental maps from LaB₆ nanowire arrays are displayed in Figures 2d and e. Figure 2d reveals the uniform distribution of La in the nanowires. Compared with the La species, it is difficult to detect the B species accurately (Figure 2e) because of the small atom number. The results of the TEM, high-resolution TEM, electron diffraction analysis and elemental mapping confirm the presence of high-quality single-crystalline LaB₆ nanowires oriented along the [100] direction.

An X-ray diffraction pattern of the aligned LaB₆ nanowire arrays is presented in Figure 3a. Except for the peaks of Si from the substrate (JCPDS Card, No. 78–2500), the rest of the peaks can readily be indexed to cubic LaB₆ with a lattice parameter of a = 0.419 nm, matching the literature data (JCPDS Card, No. 73–1669) well. The sharp diffraction peaks indicate the good crystallinity of the product. The relative intensities of the peaks differ from the standard pattern of a bulk material because of the preferred orientation and distribution of LaB₆ nanowires. A pattern taken from the nanowires shows a strong (100) diffraction peak, possibly owing to the growth of cubic LaB₆ along the [100] direction, in accord with the high-resolution TEM results. Raman spectroscopy was employed to investigate the nanostructures further. Figure 3b depicts a room-temperature micro-Raman spectrum of LaB₆ nanowire arrays. The Pm-3m symmetry of the LaB₆ structure gives us the following normal lattice vibration modes: G = A1g + E₉ + T2g + 2T₁u + 2E₉, where the Raman-active phonons are A1g, E₉, and T₂u; two T₁u modes are infrared active; and T₁g and T₂g are optically inactive. The peaks at 761, 1121 and 1260 cm⁻¹ match the Raman-active modes T₂g, E₉ and A1g of LaB₆, respectively, and they completely satisfy the polarization selection rule in the cubic symmetry. An extra peak located at 213 cm⁻¹ can be regarded as the vibration of the rare earth ions in the cage and can be assigned as the ‘optical’ T₁u mode.²² The mode <200 cm⁻¹ and a broad peak at 1400 cm⁻¹, denoted by asterisks, are commonly observed for trivalent and intermediate-valent crystals.²⁰ The band around 1156 cm⁻¹, denoted by arrows, is characteristic of the LaB₆ sample, as reported in the literature.²¹ The relatively intense and sharp peaks suggest that the nanowires are highly crystalline, consistent with the X-ray diffraction pattern and the high-resolution TEM results.

Further evidence of the high quality of the crystal was obtained using X-ray photoelectron spectroscopy. Figure 4a shows the survey
spectrum of the aligned LaB$_6$ nanowire arrays, and no peaks of other elements except La, B, O and C are seen. The La and B signals come mainly from the synthesized sample, and the C and O peaks derive from atmospheric contamination owing to the exposure to air. The La 3d peaks at 838.9 (La 3d$_5$) eV and 853.0 (La 3d$_3$) eV, shown in Figure 4b, and the B 1s peak at 188.0 eV, shown in Figure 4c, agree relatively well with the data obtained in earlier reports and serve as additional confirmation of the LaB$_6$ phase.

In most cases, the mechanism of formation of nanostructures has been suggested to be vapor-liquid-solid growth and the vapor-solid mechanism. To give a conceptual description of LaB$_6$, which excludes the vapor-liquid-solid mechanism, and self-catalysis have condensed melts at the tip parts, as shown in Figures 1 and 2, confirmation of the LaB$_6$ phase.

To illustrate the proposed mechanism, the samples were studied to and the current density, $\beta$, is the field enhancement factor, $E$ is the applied electric field, $\phi$ is the work function of the emitting material (2.6 eV for LaB$_6$). The inset in Figure 5 shows the F-N plots (that is, $\ln(J/E) = \ln(A \beta^2 E^2/\phi) - \beta E$) produced by a given electric field ($E$) is described by the F-N equation:

$$J = A_E \beta^2 E^2 \frac{\exp(-B_E \phi^{3/2})}{\beta E}$$

or

$$\ln(J/E^2) = \ln(A_E \beta^2) - \frac{B_E \phi^{3/2}}{\beta E}$$

where $A_E = 1.54 \times 10^{-6}$ A eV V$^{-2}$, $B_E = 6.83 \times 10^3$ eV$^{-3/2}$ μm$^{-1}$, $J$ is the current density, $\beta$ is the field enhancement factor, $E$ is the applied field and $\phi$ is the work function of the emitting material (2.6 eV for LaB$_6$). The inset in Figure 5 shows the F-N plots (that is, $\ln(J/E^2)$ vs $1/E$; the F-N plots), and these plots have an approximately linear relationship within the measurement range, confirming that the electron emission from LaB$_6$ nanostructures follows the traditional
F-N behavior. The calculated field-enhancement factors are also summarized in Table 2. The dense nanoneedles have the highest $b$-value (1441) compared with the sparse nanoneedles (463), the dense nanorods (884) and the well-aligned LaB$_6$ nanowire arrays (1072). Although $b$-values are related to the emitter geometry (the aspect ratio), sample a (sparse nanoneedles) exhibited a lower field-enhancement factor, possibly owing to fewer emitters (compared with samples b, c and d). Furthermore, these $b$-values are comparable to the values summarized in Table 3 and are more than sufficient for device applications.

The stability of the field emitters is another technologically important parameter. Figure 6 shows the variation of the emission current density of sample d (the aligned LaB$_6$ nanowire arrays) over a period of 1000 min in a macroscopic electric field of 2.30 V $\mu$m$^{-1}$. A small current fluctuation (<6%) was observed, which is much more stable than previous reports, as summarized in Table 3. This fluctuation (<6%) may be attributed to incompletely removed surface contamination because recently, Zhang et al. reported that no current degradation occurs for LaB$_6$ emitters after careful elimination of surface contamination by the field evaporation treatment. If the surface of LaB$_6$ nanostructures is entirely clean and contamination free, then the stability of the nanowire arrays may be even better than the value reported here. For comparison, Table 3 summarizes the key performance parameters of some field emitters.
Nanowire fabrication and their FE investigation

J Xu et al

Field-emission (FE) properties of (a) sparse nanoneedles; (b) dense nanoneedles; (c) dense nanorods and (d) nanowire arrays. The insets are the corresponding Fowler-Nordheim (F-N) $\ln(JE^2) - (1/E)$ plots showing linear dependence.

Table 2 Turn-on fields, threshold fields and field-enhancement factors ($\beta$) for the produced LaB$_6$ nanostructures

| Sample  | Morphology        | Turn-on field $J_{on}$ ($\mu$m$^{-2}$) | Threshold field $J_{th}$ ($\mu$m$^{-2}$) | $\beta$ |
|---------|-------------------|----------------------------------------|------------------------------------------|---------|
| a       | Sparse nanoneedles| 4.12                                   | —                                        | 463     |
| b       | Dense nanoneedles | 2.16                                   | 3.48                                     | 1441    |
| c       | Dense nanorods    | 2.80                                   | 4.15                                     | 884     |
| d       | Aligned nanowire arrays | 1.82                         | 2.48                                     | 1072    |

reported in the literature. The aligned LaB$_6$ nanowire arrays are comparable to other nanostructured emitters. Such decent FE can be attributed to the specific characteristics (low work function, good electrical conductivity (metal), well-aligned vertical growth and high crystallinity) of our samples.

Temperature-dependent FE properties of well-aligned LaB$_6$ nanowire arrays

For temperature-dependent FE, the total current density $J$ is given by the simplified F-N equation and the Richardson equation as follows:

$$J = J_E + J_T = A_R \frac{B_E^2}{\phi} \exp\left(-\frac{B \phi^{1/2}}{\beta E}\right) \frac{\theta}{\sin(\theta)} + A_R T^2 e^{-\phi/kT}$$

$$\theta \approx \frac{2.2\pi (kT/q) \phi^{1/2}}{1.959E}$$

where $J_E$ is the field current density, $J_T$ is the thermionic current density, $A_R = 1.54 \times 10^{-6}$ A eV$^{-3}$, $B = 6.83 \times 10^{10}$ eV$^{-3}$ s$^{-1}$ cm$^{-1}$, $E$ is the applied field, $\beta$ is the field enhancement factor, $\phi$ is the work function of the emitting material, $A_R$ is the Richardson constant with a theoretical value of 120 A cm$^{-2}$ K$^{-2}$, $T$ is the emitter temperature, $k$ is the Boltzmann constant and $\theta$ is the temperature correction factor.

Specific to LaB$_6$ with a work function of 2.6 eV and a temperature $<1000$ K, the value of $\frac{1}{\sin(\theta)}$ is always 1.0 within the temperature range that we studied. Therefore, the contribution of thermionic emission to the current density is much smaller than that of FE. The temperature-dependent FE characteristics can be expressed by the traditional F-N equations (1) and (2).

Figure 7a depicts the $J$-$E$ plots of the well-aligned LaB$_6$ nanowire arrays at an anode-sample distance of 500 $\mu$m at different temperatures in the range of RT (303 K)–723 K. All curves show the same characteristics: when the applied electric field is beyond a certain value, the current density increases nearly exponentially with an increase in the applied electric field. The turn-on field and threshold field decrease from 1.82 to 1.06 and 2.48 to 1.62 V $\mu$m$^{-1}$, respectively, (for $E_{th}$ at 373 K, refer to Supplementary Figure S5), as shown in Figure 7b. The FE is strongly dependent on the temperature. For example, the emission current density increases significantly from 0.20 to 9.05 mA cm$^{-2}$ (at 2.20 V $\mu$m$^{-1}$, or 45 times increase) upon increasing the temperature from RT to 723 K, as also shown in Figure 7b. The decrease of the turn-on field and the increase of the emission current density with an increase of the temperature might be a result of the effective work function decrease for LaB$_6$ nanowire arrays.

As demonstrated above, the temperature-dependent FE characteristics have the same nature as the FE at RT. To test whether the electron emission with the temperature originates from electron tunneling, the F-N equation is commonly used to examine this quantum effect. Figure 8a shows the F-N plots, $\ln(J/E^2)$ versus $1/E$, under different temperatures. The approximately linear relationship of the F-N plots implies that the electron emission from LaB$_6$ nanostructures in the range from RT to 723 K follows the conventional FE mechanism in which the electrons are tunneling through the potential barrier. Generally, the $\beta$-value is related to the emitter geometry (such as aspect ratios), the crystal structure and the spatial distribution of emitters. $\beta$ may thus be a constant in the range of temperatures tested (RT–723 K). To estimate the effective work function ($\phi_e$) of the well-aligned LaB$_6$ nanowire arrays, we assumed
that the initial work function at RT for LaB₆ is 2.6 eV and that β does not change with temperature, and we calculated \( f_c \) through the relation 
\[
k = \frac{C_0}{\beta f_c^{3/2}}
\]
while making F-N plots, as shown in Figure 8(b). The effective work function \( f_c \) decreased with temperature, which explains the increase in emission current density within the measured temperature range.

To date, the temperature-dependent FE characteristics of nanostructures have not been completely understood. Kan et al.²⁰ reported the enhanced thermal FE phenomenon of CNTs and ascribed these phenomena to defect band effects in the CNTs, which can raise the Fermi level into the band gap, and thus reduce the energy barrier through which the electrons must tunnel. Ahmed et al.²¹ also investigated the temperature-dependent FE properties of multiwalled CNTs and attributed the behavior to increasing enhancement factors. Choueib et al.⁴¹ reported the saturation effects in the emitter currents with temperature while observing the FE of individual single crystal SiC nanowires. Li et al.¹⁹ reported the temperature dependence of the FE characteristics of graphene film and attributed the temperature dependence to elevation of the Fermi level with temperature. Wei et al.¹⁸ observed the FE properties of SiC nanoneedles and ascribed them to the same phenomenon. Most authors attribute the enhanced FE properties to the increase of the Fermi level with temperature. LaB₆ is a metal, and its Fermi level decreases slightly as temperature increases. The above model is therefore not suitable for LaB₆ nanostructures. We noticed that a

Table 3 Key field-emission performance parameters of some nanostructure field emitters reported in the literature and in this work

| Materials            | Turn-on field (V\(\mu\)m\(^{-1}\)) | Threshold field (V\(\mu\)m\(^{-1}\)) | Field enhancement factor (\%) | Stability: testing time and fluctuation | Reference |
|----------------------|------------------------------------|--------------------------------------|--------------------------------|-----------------------------------------|-----------|
| Carbon nanotube arrays | —                                  | 2.7–3.3                              | —                              | —                                       | 28        |
| ZnO nanowire arrays  | 5.6                                | 9.3                                  | 1397                           | —                                       | 29        |
| WO₃ nanostructures   | 6.2                                | 4.65                                 | 1480                           | —                                       | 30        |
| SnO₂ nanostructures  | 3.5                                | 4.65                                 | 1225                           | 40 h, –                                  | 31        |
| ZnS nanowires        | 5.5–11.67                          | —                                    | 1942–891                       | 8 h, –                                   | 32        |
| CdS nanowires        | 8.95                               | 10.39                                | 388                            | 1000 min, –                             | 33        |
| SiC nanotubular      | 5                                  | 10                                   | —                              | —                                       | 34        |
| GaN nanocolumns      | 2.5                                | 4.7                                  | —                              | —                                       | 35        |
| B nanowires          | 5.1                                | —                                    | 1904                           | 1 h, <7.4%                              | 36        |
| W nanowire arrays    | 4.0                                | —                                    | 405                            | 10 h, <10%                              | 37        |
| LaB₆ nanorods        | 4.62                               | —                                    | 1035–1165                      | 2.2 h, <10%                             | 38        |
| CeB₆ nanorods        | 9.5 at 0.1 \(\mu\)A cm\(^{-2}\)   | —                                    | 1072                           | 1000 min, <6.0%                         | This work |
| Aligned LaB₆ nanowire arrays | 1.82                             | 2.48                                 | —                              | —                                       | This work |
higher vacuum is important to obtain reliable FE properties and an intrinsic FE mechanism. Before FE application, high temperature flashing (~1773 K, that is, 1500 °C) is usually applied to eliminate surface contaminants to clean the LaB₆ surface. In fact, Zhang et al. have demonstrated that the FE of a single LaB₆ nanowire becomes stronger when the contaminant clusters on the nanowire tip are removed by the field evaporation treatment. On the basis of the above analysis, although the exact explanation of the observed temperature dependence of LaB₆ emission requires further research, the following effects may be considered. The removal of surface-absorbed gas molecular contamination may be responsible for the increase in FE current. The effective work function $\phi_\text{eff}$ drops rapidly from RT to 473 K and is almost constant from 473 to 723 K (from Figure 8b). This behavior can be explained by the fact that most of the absorbed gas molecules (mainly nitrogen and oxygen because of sample exposure to air) were released quickly at a low temperature (from RT to 473 K) and in high vacuum; the rest of the absorbed gas molecules were released slowly at a high temperature (from 473 to 723 K). These gas molecules may have a negative effect on the emission current, which has been confirmed in LaB₆ nanowires. The gas molecules release gradually, leading to a decrease in surface potential and the effective work function. Therefore, the effective work function of LaB₆ nanostructures decreases with an increasing temperature.

CONCLUSIONS

In summary, we have developed a simple, effective, one-step, catalyst-free CVD method for the synthesis of high-quality LaB₆ nanostructures with different morphologies, such as sparse and dense nanoneedles, dense nanorods and nanowire arrays. FE measurements at RT showed that among all previously studied 1D LaB₆ nanostructures, the present nanowire arrays exhibit superior FE characteristics, with a low turn-on field of 1.82 V/µm⁻¹, a low threshold field of 2.48 V/µm⁻¹ and good stability. Temperature-dependent FE on the nanowire arrays showed that the turn-on and threshold electric fields decreased from 1.82 to 1.06 and from 2.48 to 1.62 V/µm⁻¹, respectively, whereas the emission current density increased significantly with an increase from 0.20 to 9.05 mA cm⁻² at 2.20 V/µm⁻¹ at ambient temperatures from RT to 723 K. The emission current of the aligned LaB₆ nanowire arrays can be increased by ~45 times (to 9.05 mA cm⁻²) at 2.20 V/µm⁻¹ when the temperature increases from RT to 723 K. Such a good FE performance for the aligned LaB₆ nanowire arrays suggests that they have potential for thermionic emission, field-induced emission and thermal field-induced emission applications, which are valuable for TEM, SEM and flat panel displays, as well as direct thermal-to-electrical power converters and other electronic devices that require high-performance electron sources.

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