

Fabrication of Lanthanum Hexaboride Single Nanowire Field Emitter and Their Field Emission Properties

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Lanthanum hexaboride (LaB₆) single crystals have been used as thermionic source in high resolution electron microscopes for over 50 years. LaB₆ nanowires have great potential to be used as field emission electron point source, which offers larger brightness than thermionic source. We have developed a chemical vapor deposition process to synthesize LaB₆ nanowires on Si substrate with a yield rate of 0.5mg/cm². Epitaxial growth of vertically aligned LaB₆ nanowires has also been successfully realized on LaB₆ films. By using an electrostatic attaching method followed by focused ion beam welding, we successfully fabricated single LaB₆ nanowire field emitters. Field emission I-V curve measurement has been carried using a home-built 2010F HRTEM field emission *in-situ* holder. Extrapolated data shows that the nanowire field emitter has a low work function value of 2.3eV and it generates an emission current over 20uA and an emission current density in the order of 10⁸A/cm² at a low extraction voltage below 300V.

Key words: Lanthanum Hexaboride, Nanowires, Field Emission, TEM *in-situ* measurement, Epitaxial growth

1. INTRODUCTION

Lanthanum hexaboride single crystals have been widely used as superior thermionic electron source for the past 50 years. [1] It offers 10 times brighter electron beam compared to W filament in electron optical instruments such as TEM and SEM. The low work function, high melting point and good mechanical strength of LaB₆ also promise good opportunities of using this material as field emission source, which offers even brighter electron beam compared to thermionic source. However, the difficulty in making nano-scale sharp LaB₆ single crystalline needles has hindered this application. Our recent success in synthesizing single crystalline LaB₆ nanowires using a chemical vapor deposition (CVD) method has revitalized the research in using LaB₆ as field emission source material.[2,3]

However, the product yield in our previous work was not high enough for use of the material in large quantities. On the other hand, CVD synthesis of nanomaterials usually suffers from relatively severe impurity ratios due to the complexity of using different reactants. Purification procedures and subsequent assembly procedures to realize useful device structures often require large quantity of starting materials. Therefore, producing large quantity LaB₆ nanowires is in urgent need. For field emitter array (FEA) applications, it is much desired to have epitaxial growth of nanowires on single crystal substrate, which has a lattice plane matching that of the grown nanowires.[4] Such epitaxially grown nanowires stand vertically on the substrate surface and naturally bear the layout of FEA structures. However, epitaxial growth of LaB₆ nanowires has never been reported so far. In this article, we will present the first success in making LaB₆ nanowire arrays epitaxially grown on LaB₆ single crystal film.

To use nanotube/nanowires (NT/NW) as electron point source, the first step is to make a

single NT/NW field emitter structure, which usually consists of a free-standing NT/NW attached to the tip of an electrochemical etched tungsten needle. Current methods of fabricating single NT/NW emitters include direct growth,[5] electrophoresis[6], or simply putting supporting object in contact with NT/NW and stick it away by van der Waals force[7], acrylic based glue[8] or electron irradiation induced C contamination bonding[9]. These methods inevitably suffer from some of the following problems, such as reliability, controllability, severe contamination, poor thermal, and electrical contact. Therefore, they might not be suitable for making a practical electron emitter product. To avoid these problems and realize a practical emitter structure, we have developed a reliable single nanowire field emitter fabrication approach which involves using electrostatic force to pick up a single LaB₆ nanowire from growth substrate and subsequently 'weld' the nanowire with the supporting W needle using FIB deposition.

To test the field emission properties of the single nanowire field emitter made by this method, we mount it on a home-built 2010F HRTEM field emission *in-situ* holder and measured its emission I-V curve using a set of externally connected measuring circuit. The anode/cathode distance can be adjusted by a high resolution actuator and measured simultaneously using the imaging capability of the TEM. Detailed analysis of the emission property will be presented as well.

2. EXPERIMENTAL

The chemical deposition system used in this work consists of a tube furnace, in the center of which placed

a quartz boat used to hold LaCl_3 powders. A piece of Si substrate coated with Pt film is also placed inside the boat to collect deposited nanowires. The reaction is kept under an atmosphere of pure H_2 with a pressure of 10^4Pa . After the furnace temperature reaches 1200° , BCl_3 gas was allowed into the chamber to react with LaCl_3 vapor for 5 minutes. After the reaction, purple colored powders were found cover the entire substrate. The substrate was then examined with JEOL6500 SEM equipped with EDX spectrometer.

For fabricating single nanowire field emitters, a 0.1mm W wire was electrochemically etched in NaOH solution (1 Mol/l) to make needles with tip diameter around 200nm . The W needle tip was then approached to a single LaB_6 nanowire grown on the substrate under the control of a 3-D micro-stage. The selected nanowire was then attached and picked up the W needle after we applied a direct voltage of 30V between the substrate and the W needle. FIB was then used to deposit W film on the joint area between the nanowire and W needle. Both before and after the FIB welding, the W needle tip was imaged using SEM.

The detailed design of the home-built 2010F field emission *in-situ* holder will be introduced in another paper. Its head piece consists of a clamp used to hold W needle as cathode and a $100 \mu\text{m}$ thick copper foil connected as anode and placed with a $200 \mu\text{m}$ gap from the W needle tip. The gap can be further reduced using the 50nm increment actuator pushing the cathode needle. A high voltage power supply and a high sensitivity ammeter are connected in series with the field emission diode through vacuum feedthroughs. During emission measurement, the anode/cathode distance was kept at about $1 \mu\text{m}$. Extraction voltage increased from 0V to about 300V while emission current was recorded by the ammeter. All the measuring instruments are controlled by computer with home-programmed Labview software.

3. RESULTS AND DISCUSSIONS

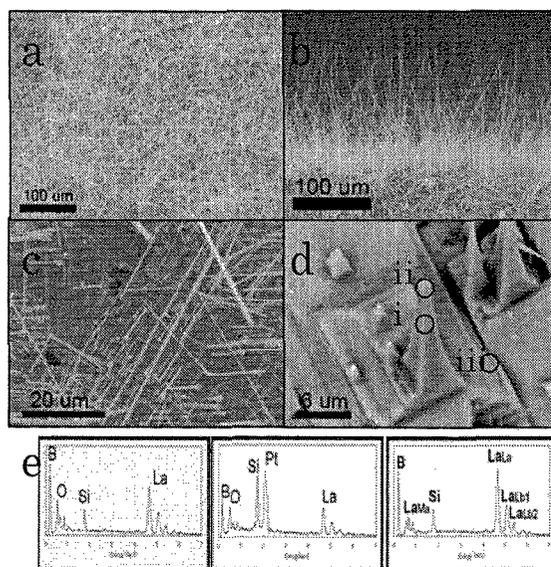


Fig.1. a. Top view of LaB_6 nanowires with the majority morphology grown on Pt coated Si substrate; b. Side view of the LaB_6 nanowires grown on the top edge of the substrate; c. Patches on the substrate where well

aligned LaB_6 nanowires epitaxially grown on LaB_6 films underneath; d. Magnified back-scattering image of the root area of the epitaxial LaB_6 nanowires. Brighter contrast spots indicate heavier element contained in the catalyst particles; e. EDX spectra taken from positions marked by black circles i, ii and iii in d.

After the reaction, we found the LaB_6 nanowires grown on the Si substrate have two major different morphologies. Type one, as presented in Fig.1a is usually observed nearer to the top edge of the Si substrate and further away from the LaCl_3 vapor source. These LaB_6 nanowires form very dense films. Through a rough estimation, we obtain a yield rate of about 0.5mg/cm^2 can be achieved during the 5 minutes of growth time. The distribution is even through the entire substrate area except some spots where the density is much looser due to epitaxial type of growth. A side view of nanowires grown from this region is shown in Fig.1b, where their length is clearly seen to be over $100 \mu\text{m}$. We can still see lots of shorter and thinner nanowires at the root area of those thick and long ones. We estimate the diameters of this type of nanowires range from 50nm to 500nm .

Some lighter purple colored patches usually appear in area closer to the LaCl_3 source on the substrate. Unlike the wool-looking appearance of the first type, this type looks smoother film-like when observed by naked eyes. A low magnification SEM image, as shown in Fig.1c revealed that they are loosely distributed LaB_6 nanowires grown on a film. The nanowires are well aligned with others grown at the near neighborhood. Nanowires from different regions usually form right angles between each other. Some of these nanowires are very thin, only a little bit over 10nm . Thick ones are about 200nm . Their lengths range from a few microns to about $50 \mu\text{m}$ and usually thicker ones also have longer length. Fig. d is a back-scattering SEM image magnified at the nanowires' root area. The nanowires in the image seem to be just formed. It is clearly revealed that each nanowire has an 'Eiffel tower' type of basis with square shaped cross-section. The cross-section gradually shrinks as the nanowire develops its vertical growth. The shrinking tendency stops after a certain diameter has been reached and nanowire with uniform diameter starts from a turning point. From the image, we also noticed many brighter contrast spots. Since the number of back-scattered electrons is sensitive to atomic weight of the presented elements, the brighter contrast spots are very likely to be the catalyst particles, which is Pt in our synthesis. To confirm this speculation, we acquired three EDX spectra at positions indicated by circles i, ii and iii in Fig. 1d. The spectra i, ii and iii are shown in Fig. 1e following a sequence of right to left. At position i, we detected B, O, Si and La signals. The presence of La and B confirmed the chemical composition of the nanowire to be LaB_6 . The Si signal is from the growth substrate and O is from the inevitable oxidation impurity during growth. Spectrum ii was acquired from the brighter contrast spot at the tip of the nanowire. With B, O and La signals about the same intensity ratio, we got a higher Si peak and an extra Pt peak in this spectrum. Therefore, we speculate the brighter contrast catalyst particle is composed of Si and Pt elements. To understand the

cause of the alignment of the LaB₆ nanowires, we also acquired a spectrum from the underlying film. It has the same chemical composition as the nanowire, which is LaB₆. We can also tell from the square shaped terrace structure on the LaB₆ film that the film is single crystalline with (100) lattice plane as terminating surface. Knowing that the LaB₆ nanowires grown from Pt catalyst is oriented along their <001> direction, [2, 3] we conclude that this type of growth is epitaxial. The reason that LaB₆ nanowires from neighboring regions form right angles could be that the LaB₆ film underneath are from different grains and have crystal orientations with 90° from each other.

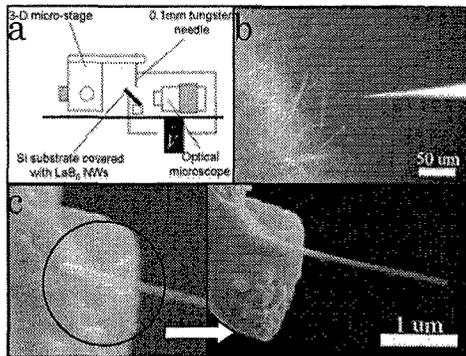


Fig.2. a. Schematic drawing showing the optical microscope assisted 3-D manipulation system designed to pick up individual nanowires by W needle; b. Optical microscope image showing the process of approaching a selected LaB₆ nanowire on substrate using a W needle; c. SEM images taken at a W needle tip where a single LaB₆ nanowire was loosely attached before and after the W metal layer deposition. The circle indicates the deposition site.

An optical microscope assisted 3-D micro-stage system has been designed to pick up a single LaB₆ nanowire using an electrochemically sharpened W needle. Fig.2a is a schematic drawing of the system. The Si substrate grown with LaB₆ nanowires is placed in the middle while the W needle gradually approaches a single LaB₆ from the bunch using the micro-stage, as shown in Fig.2b. Substrates with vertically aligned LaB₆ nanowires is more preferred for this operation. This is because the lower nanowire growth density makes it easier to approach the W needle to a single one nanowire. After the W needle gets close to the selected nanowire, a direct voltage about 30V is applied between the needle and Si substrate to generate electrostatic force to realize the attachment. After the LaB₆ nanowire is broken from the substrate by mechanic force, the needle is transferred into a FIB chamber for bonding layer deposition. Fig.2c is two SEM images of the W needle tip right before and after the FIB 'welding'. The circled area on the left image, where the LaB₆ nanowire was only loosely attached to the W needle top through van der Waals interaction was deposited with a layer of W metal, and the resulting structure is shown in the right image. A much stronger bonding has been formed and because of the metal layer, thermal and electrical conductance is likely to be greatly improved. The LaB₆ nanowire welded in this case is about 80nm in diameter and 2μm long.

To test the performance of the single LaB₆ nanowire field emitter, we mount the structure onto our home-built JEOL 2010F field emission *in-situ* holder. A low magnification TEM image of the cathode nanowire emitter and its counter anode is presented in Fig.3a. The externally connected measuring circuit is also illustrated on the drawing. The LaB₆ nanowire emitter in the image is about 80nm in diameter and about 100μm in length. The cathode/anode distance set in this image is about 5μm.

Fig.3b is a typical field emission I-V curve recorded using a control computer. The current goes above 1μA at 200V. When applied voltage reaches 260V, the emission current is almost 20μA without showing any sign of saturation. The current fluctuation is also very small. The room temperature field emission current density J is best described by the zero-temperature Fowler-Nordheim (F-N) equation [10]:

$$J = \frac{I}{A} = 1.5 \times 10^{-6} \frac{E^2}{\phi} \frac{10.4}{\phi^{1/2}} \exp\left(-\frac{6.44 \times 10^7 \phi^{3/2}}{E}\right) \text{ Amp/cm}^2 \quad (1)$$

where Φ is the work function of cathode material, I being the emission current, A being the emission area and E is the local electric field applied on the cathode tip, which can be expressed as

$$E = V / \beta \quad (2)$$

with V being the applied voltage and β being a field enhancement factor both related to the radius of the cathode tip and cathode/anode distance. F-N fitting of $\ln(I/V^2)$ versus $1/V$ was plotted with results shown in the inserted panel of Fig.3b. From the F-N formula, the slope of the plot

$$m = -\frac{6.8 \times 10^7 \phi^{1.5}}{\beta} \quad (3)$$

with Φ in the unit of eV and β in the unit of cm^{-1} ; The y intercept equals

$$b = \ln\left[\frac{A \cdot 6.2 \times 10^{-6} \cdot 1.45 \cdot \beta^2}{\sqrt{\phi}(2.12 + \phi)}\right] \quad (4)$$

with A in the unit of cm^2 . Therefore, if we know the value of Φ or β , all other emission parameters can be accordingly deduced. β , the field enhancement factor can be numerically calculated with the knowledge of the exact geometry information about the emitter. However, field emission is usually localized by very tiny surface extrusions or local spot with lower work function. Those emission sites are usually in the order of a few nanometers or even atomic. Therefore, knowing the exact emission spot is almost impossible. The deviation of β value from calculated can be off by orders of magnitude. On the other hand, for most metals, the work function Φ is usually in the range of 2-5eV. In the LaB₆

nanowire system, the possible contaminants, carbon or boron are all with work function around $5eV$ and LaB_6 with $2.3eV$ for its (100) plane. [2, 3] Emission area, A , value is very sensitive to that of work function. So it could be used as a good reference to tell which work function value should be used from a certain F-N plot. In this case, we use a value of $2.3eV$, which results in an emission area diameter of $6.6nm$. By putting contaminants work function value $5eV$, we got an emission area around 1\AA . Considering the much larger size of the emitter tip area, we believe this possibility should be excluded. The small emission area might be due to a local LaB_6 (100) surface extrusion just been formed after the burnt off of the contamination layer above it. This value corresponds to an emission current density in the order of $10^8 A/cm^2$. After that, the voltage was kept at $260V$ and stable current at $20\mu A$ was obtained with fluctuation less than 10%. The stability was much improved compared to our ex-situ measurement with glue attached or gold attached nanowire emitters. This is probably in account for the good attachment through the FIB method.

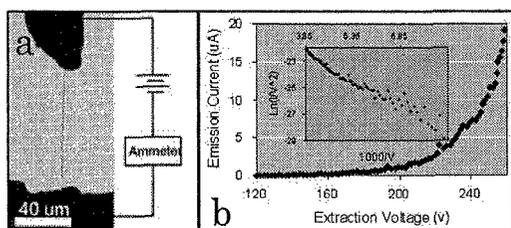


Fig.3. a. TEM image of a single LaB_6 nanowire field emitter connected as cathode inside a 2010F HRTEM. Its counter anode is a copper foil and placed $5\mu m$ in distance from the nanowire emitter; b. Field emission I-V curve and corresponding F-N plot recorded during the *in-situ* measurement.

4. CONCLUSIONS

In conclusion, a chemical vapor deposition synthesis procedure has been optimized to produce large quantity of LaB_6 nanowires on Pt coated Si substrate. Epitaxial growth of the nanowires took place on some pre-formed LaB_6 film with the assistance from Pt catalyst. A single LaB_6 nanowire was picked up using an electrochemically etched W needle and a single LaB_6 nanowire field emitter was subsequently fabricated after W deposition using FIB technique. The fabricated field emitter was mounted onto a home-built 2010F HRTEM field emission *in-situ* holder for field emission I-V curve recording. The data extrapolated from the curve indicates low work function, high emission current density and good stability of this new generation of electron point source.

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