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Fabrication and field emission characteristics of LaB_6 field-emitter arrays*

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Abstract: Lanthanum hexaboride field-emitter arrays (LaB_6 FEAs) with tip structures are fabricated by oxygen plasma oxidation-etching method. The field emission characteristics are studied in a conventional diode test cell in vacuum system. LaB_6-FEAs exhibit a much lower turn-on field of 7 V · μm^{-1} due to its lower work function of 2.6 eV. The Fower-Nordheim plot obtained from the current-voltage characteristic is found to be nearly linear in accordance with the quantum mechanical tunneling phenomenon. In addition, oxygen plasma oxidation-etching method is also compared with argon-oxygen plasma etching method and electro-chemical etching method, which indicates that oxygen plasma oxidation-etching method is a very promising fabrication technique for the preparation of LaB_6-FEAs.

Key words: Lanthanum hexaboride(LaB_6); field-emitter arrays; oxidation; etching method

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In contrast with the conventional thermionic cathode, the field emitter array (FEA) cathode has many advantages, including room-temperature operation, higher emission current density, lower power dissipation, excellent ON/OFF isolation characteristics and instant turn-on characteristics. It has the potential to be used as an electron source in a wide variety of applications, such as microwave power amplifiers, flat panel displays, electron microscopy, and electron beam lithography[1-4]. However, there are some important limitations of micro-fabricated FEAs in their reliability and efficiency[5]. As a result, the research today concentrates on the improvement of field emission current density and emission stability.

Highly efficient and highly reliable FEAs can be realized in two ways: improving the existing fabrication technology and selecting other favorable field emitter materials. Compared with the common field emitter materials (silicon and molybdenum), lanthanum hexaboride (LaB_6) has lower work function (2.3~2.8 eV), lower resistivity, lower sputtering yield, higher melting point and higher chemical stability. It has been widely used as thermionic emitters, offering high brightness and long life[6-8]. LaB_6 is also an excellent material for field emission cathodes due to its lower work function and excellent mechanical stability against ion bombardment[9]. A single tip LaB_6 field emission cathode has been fabricated and it has shown excellent performance[10].

The fabrication technology of LaB_6 tip field emission arrays has been reported by Nakomoto et al[11]. This paper will report another fabrication technology of LaB_6-FEA by oxygen plasma oxidation-etching method and the field emission characteristics will be investigated.

1 Experiments

Among various field emission array cathodes, Si-FEA is one of the most popular cold cathodes. The fabrication technique about Si-FEA has been developed for many years[12-13]. Thus similar fabrication technique was introduced for the preparation of LaB_6-FEA. Firstly, cylindrical specimen about 1.5 mm thick was cut from (100) single crystal LaB_6 and subsequently polished with diamond slurries. Before mask layer deposition,

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the sample was ultrasonically cleaned in acetone, alcohol and water and was dried in air at 200 ℃. Next SiO_2 insulating layer about 1 μm thick was deposited on the specimen by plasma-enhanced chemical vapor deposition (PECVD) method, and then patterned to obtain an array of 2 μm diameter SiO_2 disks by reactive ion etching (RIE) method. During the SiO_2 deposition process, the specimen temperature was kept constant at 230 ℃ in a vacuum of 60 Pa, and the chosen RF power was 15 W. Finally, using these SiO_2 disks as hard masks, the underlying LaB_6 was etched to form tip field emission arrays.

When the temperature of LaB_6 is higher than 600 ℃, LaB_6 could react with oxygen, and as the temperature varies, the corresponding resultants are different. When the temperature is from 800 to 1 000 ℃, the following oxidation reaction occurs

$$4LaB_6(s)+21O_2(g)=4LaBO_3(s)+10B_2O_3(s) \quad (1)$$

When the temperature is up to 1 100 ℃, the $LaBO_3$ will be converted into $La(BO_2)_3$ and the corresponding reaction is as follows

$$LaBO_3(s)+B_2O_3(s)=La(BO_2)_3(s) \quad (2)$$

According to the above LaB_6 oxidation mechanism, oxygen plasma oxidation-etching method was introduced in our experiment to etch LaB_6 specimen. Fig. 1 shows the oxidation device applied in our experiment. The LaB_6 specimen and the anode were set in a glass tube and the distance between the specimen and the anode was kept at about 3.5 cm. R_A was an external resistor of 5.1 kΩ to limit current burst under short circuit conditions and the specimen holder was graphite. Firstly, the oxidation chamber was evacuated to a base pressure of 3×10^{-3} Pa using diffuser casing pump and subsequently oxidation was carried out in an oxygen ambient pressure of 20 Pa. When the anode was exerted 500 V, oxygen atoms between the anode and the specimen were ionized, generating a mass of oxygen ions with enough energy and activity. Bright glow discharge was observed. The oxygen plasmas reacted with the uncovered LaB_6 and generated boron oxides and lanthanum oxides. During the whole oxidation process, the specimen was heated to 550 ℃ to accelerate the reaction and the oxidation period lasted 1 h. After that, the LaB_6 specimen was taken out from the vacuum chamber and immersed into hydrochloric acid (HCl) solution to remove the boron oxides and lanthanum oxides. Next, a second period consisting of oxidation and HCl etching began, until the SiO_2 mask layer broke itself. Usually the whole process consisted of tens of periods.

In addition, some other etching methods were used to investigate the fabrication techniques of LaB_6-FEA further, including argon-oxygen plasma etching method and electro-chemical etching method. With the argon-oxygen plasma etching method, the ratio of gas-flow rate of argon to that of oxygen was about 1∶3. The etching set was similar to the oxidation device shown in Fig. 1. With a certain positive voltage applied to the anode, argon and oxygen atoms were ionized. Oxygen plasmas reacted with the uncovered LaB_6 surface and argon plasmas etched the corresponding oxides with enough energy. During the whole oxidation and etching process, the specimen was heated to the temperature of 550 ℃ to accelerate the reactions. The oxygen plasma oxidation-etching method uses HCl solution to etch the resultant oxides, while the argon-oxygen plasma etching method uses argon plasmas instead.

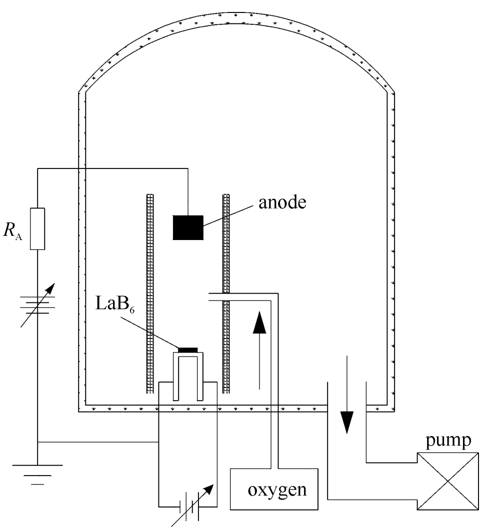
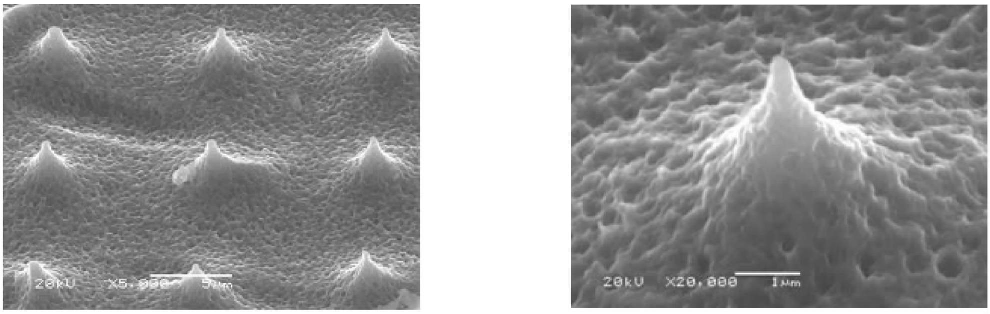


Fig. 1　Oxidation device applied in oxygen plasma oxidation-etching method

With the electro-chemical etching method, the etching apparatus was made to have a positive electrode with LaB_6 sample having patterned SiO_2 mask layer and a negative electrode with a graphite rod. Electrolytes in this process were ethanol (CH_3CH_2OH) containing 2%(volume ratio) hydrochloric acid and the electrolytic current was 0.6 mA. The experimental details have been described in ref. [14].

2 Results and discussions

The scanning electron microscopy (SEM) photographs of a LaB_6-FEA fabricated by oxygen plasma oxidation-etching method with 6 μm spacing between tips are presented in Fig. 2. The oxidation period is 1h and the fabrication process has 88 periods. The tip is approximately 2.0 μm in height and about 250 nm in radius. The substrate and tip surface of LaB_6 sample are somewhat roughened, while the apparent indents in Fig. 2 (a) are probably resulted from the flaw of LaB_6 material.



(a) SEM micrograph of LaB_6-tip field-emission array (b) SEM micrograph of individual LaB_6 tip

Fig. 2 Fabricated LaB_6-FEA using oxygen plasma oxidation-etching method

The SEM image of a LaB_6-FEA fabricated by argon-oxygen plasma etching method is shown in Fig. 3. The plasma etching process lasted totally 10 h. The SiO_2 mask layer broke during the etching process and the tip height is about 0.76 μm, which indicates that the SiO_2 mask layer is not strong enough for the energy of argon ions.

Fig. 4 shows the appearance under SEM of a LaB_6-FEA using electro-chemical etching method. The emitters are about 1.7 μm in height and exhibit excellent tip uniformity. The surfaces of the emitters and the substrate are smooth. However, serious anisotropy of the emitters is observed, which might be caused by the erosion selectivity for different crystalloid surface with this method[14].

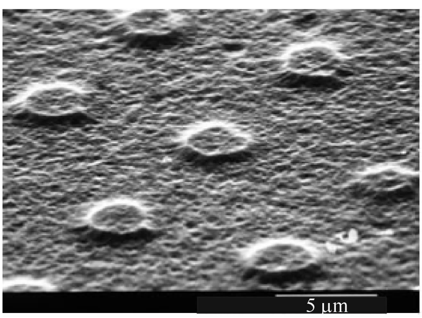


Fig. 3 SEM micrograph of fabricated LaB_6-FEA by argon-oxygen plasma etching method

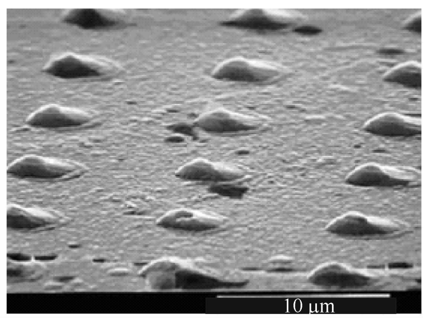


Fig. 4 SEM micrograph of fabricated LaB_6-FEA by electro-chemical etching method

Compared with the argon-oxygen plasma-etching method and the electro-chemical etching method, the oxygen plasma oxidation-etching method is a promising fabrication technique for preparing LaB_6-FEAs.

Field emission properties of the fabricated LaB_6-FEA by oxygen plasma oxidation-etching method were measured using diode geometry at a base pressure of 5×10^{-5} Pa. During the whole measurement, the anode plate with a positive voltage was placed 0.1 mm above the tips, and the emitter was grounded. Fig. 5(a) shows the current-voltage (I-V) characteristics of the LaB_6-FEA at 5×10^{-5} Pa in diode geometry. An emission current of 200 nA with the onset voltage of 700 V was observed reproducibly. With the increase of the applied voltage, the emission current increased rapidly and a current of 75 μA was drawn at the applied voltage of 1 500 V. The fabricated LaB_6-FEA with a large tip radius of 250 nm exhibited a low turn-on field of 7 V^{-1}, which is comparable to other material field emitters, including a Si nanotip array of 8.5 V^{-1} [15] and carbon nanotubes field emitters of 2～5 V^{-1} [16-18]. Furthermore, the Fowler-Nordheim(FN) plot, a graph of ln (I/V^2) versus $10^3/V$ derived from the I-V curve is shown in Fig. 5(b). The linear FN plot shows that the emission from the fabricated LaB_6-FEA follows a quantum mechanical tunneling process[19]. The observed FN plot is similar to that reported for the LaB_6 single tip emitter[10].

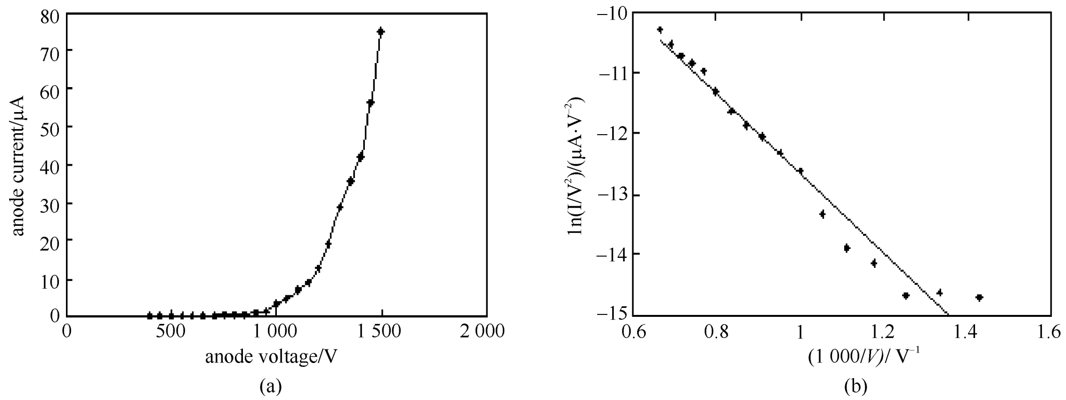


Fig. 5 Field emission current-voltage(I-V) characteristics of fabricated LaB_6-FEA by oxygen plasma oxidation-etching method (a) and the Fowler-Nordheim (FN) plot (b)

3 Conclusion

LaB_6-FEAs are obtained by oxygen plasma oxidation-etching method. The tip height is more than 2 μm and the tip radius is about 250 nm. Field emission measurement shows that the fabricated LaB_6-FEA can operate at low voltages and the turn-on field is as low as 7 V • μm^{-1} mainly due to the lower work function of 2.6 eV. In summary, oxygen plasma oxidation-etching method is a promising fabrication technique for the preparation of LaB_6-FEA, which will accelerate the practical application of LaB_6-FEA in various devices.

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六硼化镧场发射阴极阵列的制作及特性

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摘　要： 采用氧等离子体氧化刻蚀工艺,制备出尖锐的六硼化镧(LaB_6)微尖锥场发射阵列。在二极管结构中测试了 LaB_6-FEAs 的场发射性能,得到了真空度为 5×10^{-5} Pa 下的 *I-V* 曲线及相应的 Fowler-Nordheim 节点。结果表明,由于 LaB_6 材料较低的逸出功,使得阴极的开启电压较小,开启场仅为 7 V/μm。此外,将氧等离子体氧化刻蚀方法与氩氧等离子体刻蚀方法和电化学刻蚀方法进行了比较,表明氧等离子体氧化刻蚀方法是制备 LaB_6 场发射阴极阵列的一种理想工艺。

关键词： 六硼化镧(LaB_6)； 场发射阵列； 氧化； 刻蚀方法