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Function mechanism of carbide layer on surface of La_2O_3-Mo cathode①

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[Abstract] The ion implanting method has been taken for implanting lanthanum ions into the surface layer of molybdenum wires in order to study the function of carbide layer on the surface of La_2O_3-Mo cathode in the emission. The function mechanism has been discussed by using XPS and AES methods. The results show that the carbide layer mainly acts as a reduction reagent to produce metallic lanthanum. Moreover, it can store the activator substance and carry them to the surface. Based on the research results, the carbonization technique has been changed. By applying the new technique, the lifetime of the La_2O_3-Mo cathode has been improved from 14 h to more than 1 000 h —the minimum lifetime for practical uses.

[Key words] carbide layer; La_2O_3-Mo cathode; reduction; lifetime
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1 INTRODUCTION

Carbonization of cathode is a key process in the production of ThO_2-W (in brief Th-W) electron tubes. The process of carbonization is as follows: The filaments are heated to the temperature higher than the normal operating temperature of the tubes in the mixed gases of benzene vapor and hydrogen. Then they were held at that temperature for a period of time. In this period, benzene vapor will decompose into carbon and hydrogen when it touches the high temperature filaments and carbon will react with substrate tungsten to form W_2C. The operating temperature and emission property can be improved after the filament is carbonized. Because of the radioactivity of Th-W materials, people have been seeking for an alternative for thoriated tungsten materials. A new kind of rare earth doped molybdenum cathode material was invented by BBC Corporation of Switzerland at the end of 1970s[1~3]. The other researchers had also done much research in this field in the past two decades[4~6]. Although the emission current of this cathode is large enough, the emission current is not stable. As a result, this cathode can not be used commercially. Many methods, such as electron irradiation, have been taken for improving the emission stability, but it has not been improved a lot[7]. Because carbonization is an important procedure in the preparation of electron tubes, it is necessary to study the function mechanism of carbide layer. The former study shows that the activator substance LaO_x ($x < 1.5$) plays an important part in the emission, and the carbide layer just takes the function of storing the activator substance and carrying them to the surface[8]. However, this conclusion has not been proved by sufficient experimental results. In order to study the function mechanism, lanthanum ions have been implanted into the surface layer of molybdenum wires. At the same time, XPS and AES methods have been used in the analysis. The goal of this paper is to improve the emission stability of the cathode by changing the carbonization technique on the basis of mechanism study.

2 EXPERIMENTAL

2.1 Preparation of implanted lanthanum-molybdenum filament and La-Mo materials

Pure molybdenum wire diameter (d 0.26 mm × 15 mm), and pure molybdenum plate (8 mm × 8 mm × 1 mm) are put into an MEVVA-80 keV-10 mA ion implanting chamber. The pressure of the chamber is 10^{-2} Pa. The energy for ion implanting is 88 eV. The implanting dose of metallic lanthanum is 1×10^{17} cm^{-2}. A molybdenum plate was also placed in the chamber for further AES and XPS analysis. La_2O_3 (4%)-Mo (lanthanated molybdenum) materials was prepared by powder metallurgy.

2.2 Emission property and lifetime test of lanthanated molybdenum electron tubes

Some implanted lanthanum-molybdenum wires

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were carbonized in pure benzene vapor with hydrogen as carrier. The carbonized and non-carbonized implanted lanthanum-molybdenum wires were equipped in dipoles. Then thermionic emission of these tubes was measured in a specialized instrument.

In the lifetime test, each lanthanated molybdenum (La_2O_3-Mo) filament was 1.04 mm in diameter and 45.0 cm in length. It was welded on a molybdenum rod in the form of helices with nine turns. Four filaments were divided into two groups. Two filaments in a given group were carbonized at 1723 K, and the other two were carbonized at 2023 K. We took one carbonized lanthanated molybdenum filament from each group and equipped it into a 6T51 triode. The lifetime test was carried out on a specialized lifetime testing instrument.

2.3 XPS and AES analysis

The XPS and AES analyses for lanthanated molybdenum plate and implanted lanthanum-molybdenum plate were performed in VG-Lab5 malfunction spectrometer. The constituent on the surface of molybdenum rod to support the filament was investigated in a PHL-5300X Spectrometer after the carbonized filament was taken away.

3 RESULTS AND DISCUSSION

XPS spectra of the implanted lanthanum-molybdenum plate and lanthanated molybdenum plate are shown in Fig. 1. It can be seen that the implanted metallic lanthanum has been oxidized into lanthanum oxide. The ion corridors have been formed in the molybdenum plate because of ion implanting. Thus, the oxygen diffuse into the molybdenum matrix along these corridors when implanted lanthanum-molybdenum plate was taken from the implanting chamber and exposed to the atmosphere. The oxygen reacts with metallic lanthanum to form lanthanum oxide. Compared with La3d spectra of lanthanated molybdenum materials, the shape of La3d peaks of implanted lanthanum-molybdenum plate has changed because the amount of implanted lanthanum is too low.

In-situ Auger microbeam technology has been used to investigate the depth of implanted lanthanum in the molybdenum plate. The etching rate of Ar^+ ion is 1 Å/s. Depth analysis result is shown in Fig. 2. It is apparent that the depth is about 700 Å Intense oxygen peak has been found in the spectra because oxygen is easy to go into the molybdenum substrate along the corridors made by ion implanting and molybdenum has been oxidized severely. Fig. 2 also shows that molybdenum atomic concentration increases but lanthanum and oxygen atomic concentrations decrease with the etching time and depth. Some implanted lanthanum-molybdenum wires are equipped in diodes. The other wires are carbonized and equipped in diodes. The thermionic emission properties of these diodes are shown in Fig. 3. The $\lg I - \lg U$ curve (I —emission current, U —anode voltage) in Fig. 3 shows that there is an evident turning point in the $\lg I - \lg U$ curve.

The emission properties of La_2O_3-Mo cathode depend on the constituents of the surface. According to the polarized La_2O_3 molecule mechanism[4] and nanometer LaO_x ($x < 1.5$) particles (film)[7] mechanism, La_2O_3 molecules and LaO_x ($x < 1.5$) particles play an important role in the emission, and molybdenum carbide layer just stores activator substance and carry them to the surface. As shown in Fig. 1 and Fig. 2, the implanted lanthanum exists in the form of lanthanum oxide within 700 Åbelow the surface. Because La_2O_3 is in the surface layer of the cathode, the carbide layer will not take the function of carrying the activator substance to the surface. Thus, the emission current of implanted lanthanum-molybdenum wires and that of non-carbonized ones should be nearly the same. However, the experimental results (as shown in Fig. 3) show that the emission current of carbonized cathode wires is approximately one order of

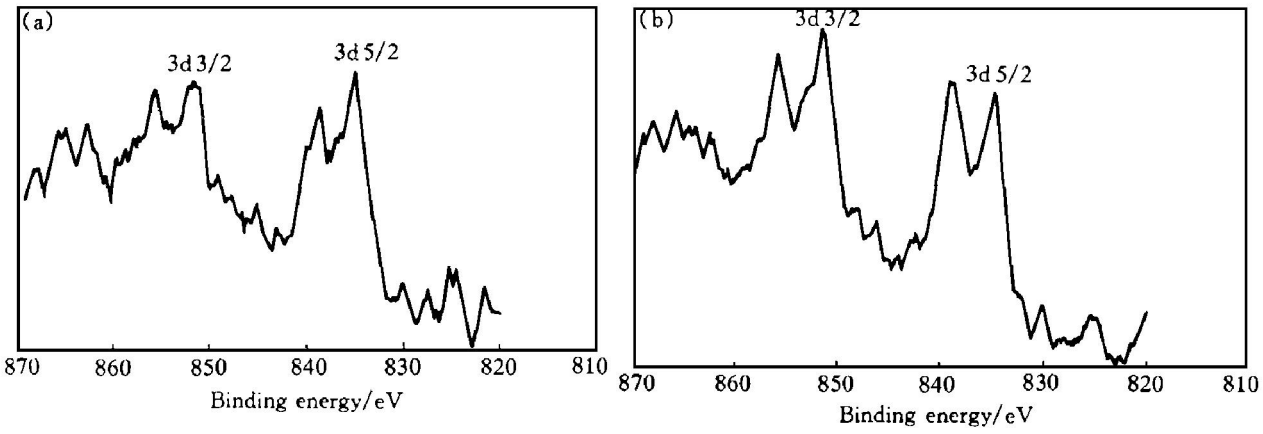

Fig. 1 X-ray photoelectron spectra for La3d in different materials
(a) —In implanted lanthanum-molybdenum plate; (b) —In lanthanated molybdenum plate

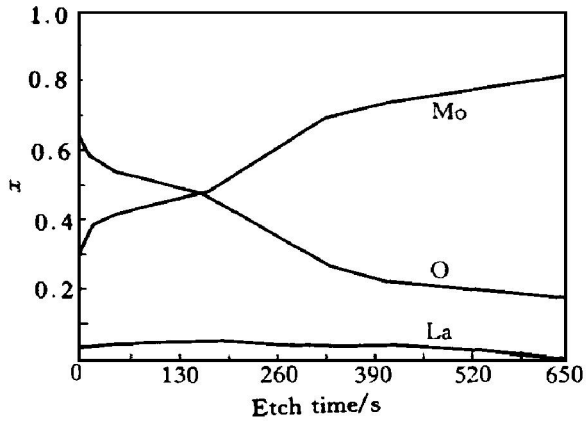

Fig. 2 Depth analysis of elements in implanted lanthanum-molybdenum plate

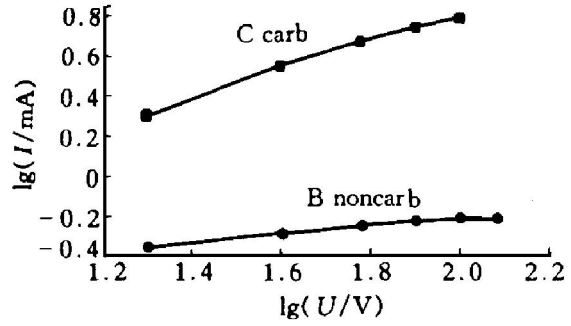

Fig. 3 Emission property curve for implanted lanthanum-molybdenum wires

magnitude higher than that of the non-carbonized ones. So, the role of carbide layer in the emission should be re-investigated. The studies show that La_2O_3 on the surface of the carbonized La_2O_3-Mo cathode is reduced to metallic lanthanum after heat treatment of the materials in vacuum[9]. Because lanthanum oxide has very good thermal stability, metallic lanthanum can not be produced by the thermal decomposition of lanthanum oxide[10]. The production of activator lanthanum requires the presence of reducing agent Mo_2C. At the operating temperature, La_2O_3 can be reduced by Mo_2C to metallic lanthanum. It is shown that it is the formation of a monoatomic film of metallic lanthanum on the surface of a filament which causes the high emissivity of the filament, so the carbide layer mainly acts as a reducing agent layer for the production of metallic lanthanum. As for La_2O_3-Mo cathode, La_2O_3 dispersing in the cathode diffuses towards the surface to keep continuous emission. There are many porous coarse grains in the carbide layer and these grain boundaries are perpendicular to the wire axis. This structure is favorable for the rare earth atoms to stay and diffuse towards the surface. So another function of carbonized layer is to store and transport the activator substance.

In carbonization procedure of the fabrication of large power electron tubes, the carbonizing temperature is about 2073 K. The studies show that La_2O_3 can be reduced to metallic lanthanum by Mo_2C at about 1523 K, so the chemical reaction between Mo_2C and La_2O_3 could take place at the carbonizing temperature. The vapor pressure of lanthanum at 1600 K is 1.76×10^{-3} Pa, higher than the vacuum in the electron tubes (10^{-4} Pa), so lanthanum evaporates on the surface of the cathode during the carbonization process. The higher the carbonizing temperature, the greater the evaporation amount of lanthanum. The experimental results show that the color of molybdenum rod for supporting the filament has changed from gray to blue-black after the filament is carbonized at 2023 K. XPS spectra of molybdenum rod show that there are La, C and O on the surface, and these elements exist in the form of La_2O_3 and graphite carbon, see Fig. 4. The presence of these elements can be explained as follows: during the carbonization process, metallic lanthanum produced by the reduction of La_2O_3 evaporates first and then deposits onto the molybdenum rod, together with carbon produced by the decomposition of benzene. When metallic lanthanum is exposed to atmosphere, it is oxidized to La_2O_3 rapidly. The molybdenum rod is covered with the mixture of carbon and La_2O_3, so the color of rod has been changed, Former studies show that the cathode can not be used anymore if there is no activator substance in the cathode[11], so the evaporation of activator lanthanum should be avoided. The lower the carbonizing temperature is, the smaller the evaporation rate of lanthanum is. However, the carbonizing temperature can not be too low because the reaction of molybdenum and carbon must take place at this temperature. The lifetime test of the filaments carbonized at 2023 K was performed on a specialized instrument. The result shows that the lifetime of this cathode is just 14 h. By contrast, the filament carbonized at 1723 K provides stable emission current and the lifetime of this cathode is 1436.5 h, higher than the minimum lifetime 1000 h for practical uses. At the same time, the color of the molybdenum rod has not changed after the filament is carbonized. So 1723 K is the optimum carbonizing temperature.

4 CONCLUSIONS

1) The carbide layer on the surface of the cathode serves as a reduction reagent to produce activator substance—metallic lanthanum, at the same time, it can store the substance and carry them to the surface.

2) La_2O_3-Mo cathode materials can not be carbonized by applying the traditional technique of Th-W cathode. The optimum carbonizing temperature is about 1723 K. The lifetime of this carbonized cathode

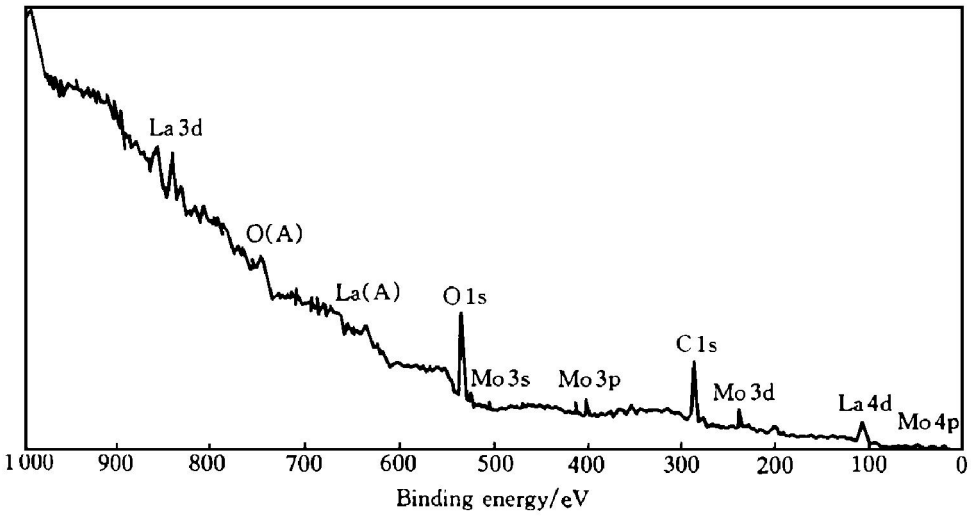

Fig. 4 X-ray photoelectron spectrum of surface of molybdenum rode

can meet the required lifetime for practical uses.

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