

[Article ID] 1003- 6326(2001) 05- 0681- 03

Chemical stability of La_2O_3 in La_2O_3 -Mo cathode materials^①

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[Abstract] Chemical stability of La_2O_3 in carbonized and uncarbonized La_2O_3 -Mo cathodes was studied by in-situ XPS analysis. Experimental results show that chemical stability of La_2O_3 is not good enough. In vacuum and at high temperature, oxygen can be dissociated from the lattice of La_2O_3 in the uncarbonized La_2O_3 -Mo cathode. Binding energy shifts of $\text{La}3d_{5/2}$ and $\text{La}3d_{3/2}$ core peaks, and obvious decrease of satellite peak intensity in $\text{La}3d$ doublet with increasing temperature show that metallic La appears at carbonized La_2O_3 -Mo cathode surface at high temperature.

[Key words] lanthanum; chemical state; La_2O_3 -Mo; cathode; XPS

[CLC number] TG 146. 4; O 614. 33

[Document code] A

1 INTRODUCTION

ThO_2 -W thermionic cathodes are still widely used in high-power vacuum tubes for industrial heating. It is well known that the radioactivity of ThO_2 leads problems to its manufacture and application. La_2O_3 -Mo, one of the attractive alternatives, was invented in the midst of 1970s^[1~3]. Although this cathode has good emissivity, it has not been used commercially because of poor emission stability. The emission of La_2O_3 -Mo cathode is initially explained by imitating the traditional monoatomic film model of Th-W cathode, that is, the monoatomic film of metallic lanthanum at the surface of the cathode can be created after reduction of La_2O_3 by MO_2C during the activating and operating period of the cathode^[4]. However, this mechanism has not been proved by experiments at high temperature in vacuum. Minanov^[5] claimed that rare earth oxides including La_2O_3 have very good chemical stability because of their high formation heat except for Eu_2O_3 , Sm_2O_3 , Yb_2O_3 , which will decompose into MO_x ($x < 1.5$, $M = \text{Eu}, \text{Sm}, \text{Yb}$) when heated to extremely high temperature in ultra-high vacuum or will be reduced to MO_x by reduction reagent. According to Minanov's viewpoint, lanthanum oxide can not be reduced by molybdenum carbide to metallic lanthanum, which was proved by thermodynamic calculation^[6].

In this article, in-situ temperature analysis is carried on to study the chemical stability of La_2O_3 during the operation of La -Mo cathode (more than 1473 K under vacuum).

2 EXPERIMENTAL

The experimental samples were two Mo-4% La_2O_3 (mass fraction) thin sheets (4 mm × 4 mm × 0.3 mm). After it was grind and purged, one of the sheets was put into carbon powder to form MO_2C at 1673 K for 2 h under the protection of argon. Then these two sheets were connected to molybdenum sleeves (d 3.3 mm × 7 mm) by point-welding respectively. A heater was inserted inside the molybdenum sleeve for high temperature X-ray photoelectron spectrum (XPS) analysis.

XPS experiments were performed on a VGESCALAB MK-II malfunction spectrometer using monochromatic Mg K_α radiation. In the sample treatment chamber, the sample was heated by hot tungsten, and the temperature was measured by biotix pyrometer. After the sample was cooled to room temperature, it was transferred to the analysis chamber with pressure of $1 \times 10^{-8} \sim 2 \times 10^{-8}$ Pa. The maximum pressure during heating at 1400 K was 10^{-6} Pa in the sample treatment chamber.

3 RESULTS AND DISCUSSION

3.1 In-situ XPS analysis of uncarbonized La_2O_3 -Mo materials

The former XPS study on lanthanum in La -Mo cathode wires^[7] showed that the binding energy of lanthanum shifted little with temperature, which indicated that the chemical state of lanthanum changed little. In this article, the binding energy of oxygen in the materials at different temperature was studied.

① **[Foundation item]** Project (G1998061316) supported by the National Key Fundamental Research Program; project (2992006) supported by Beijing Fundamental Research Foundation; project (954810700) supported by Beijing New Star Program

[Received date] 2001- 01- 02; **[Accepted date]** 2001- 04- 09

The O1s X-ray photoelectron spectra of La-Mo cathode are shown in Fig. 1. It is shown that there are two kinds of oxygen species in the materials. At different temperature, the position of oxygen peak with lower binding energy ($E_b = 530.00$ eV) remains the same, but the strength and position of oxygen peak ($E_b = 533.00 \sim 531.80$ eV) changes a lot. Oxygen peak with lower energy is the peak of the surface lattice ion O^{2-} [6] and the others with higher binding energy are that of the absorbed oxygen ions (O^{2-} , O_2^{2-} , O^- , etc) [8], which comes from the adsorption and reaction of oxygen on the La_2O_3 -Mo surface. At room temperature, a strong peak with lower binding energy ($E_b = 530.00$ eV) and a weak peak with higher binding energy ($E_b = 533.00$ eV) are detected. When the sample is held at 983 K for 20 min, oxygen species with higher binding energy ($E_b = 532.50$ eV) almost disappear. This results show that only lattice oxygen species with lower binding energy exist on the surface of the cathode. When the sample is heated to 1583 K, a weak peak of oxygen appears on the high energy side ($E_b = 532.00$ eV). Further heated to 1823 K, the strength of oxygen with higher binding energy ($E_b = 531.80$ eV) increases, which shows that some of lattice oxygen dissociate from the La_2O_3 lattice and reabsorb on the cathode surface. The higher the temperature, the greater the amount of oxygen dissociated from the La_2O_3 lattice. When temperature is above 1823 K, the amount of absorbed oxygen species increases greatly. So much absorbed oxygen species at this temperature show that they

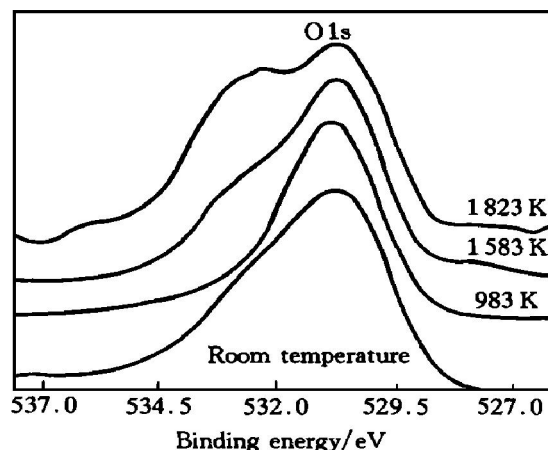


Fig. 1 XPS of La3d in uncarburized La-Mo material at different temperature

only come from La_2O_3 .

The in-situ XPS study show that the thermal stability is not good enough. At high temperature in vacuum, La_2O_3 is partially reduced to LaO_x ($x < 1.5$) with oxygen dissociating from La_2O_3 lattice.

3.2 In-situ XPS analysis of carburized La_2O_3 -Mo cathode materials

The carburized La_2O_3 -Mo sample was heated at 1123 K, 1303 K, 1523 K respectively, then cooled to room temperature for XPS analysis. The XPS of carburized La_2O_3 -Mo sample is shown in Fig. 2. The binding energies of La3d peaks at different temperature are listed in Table 1.

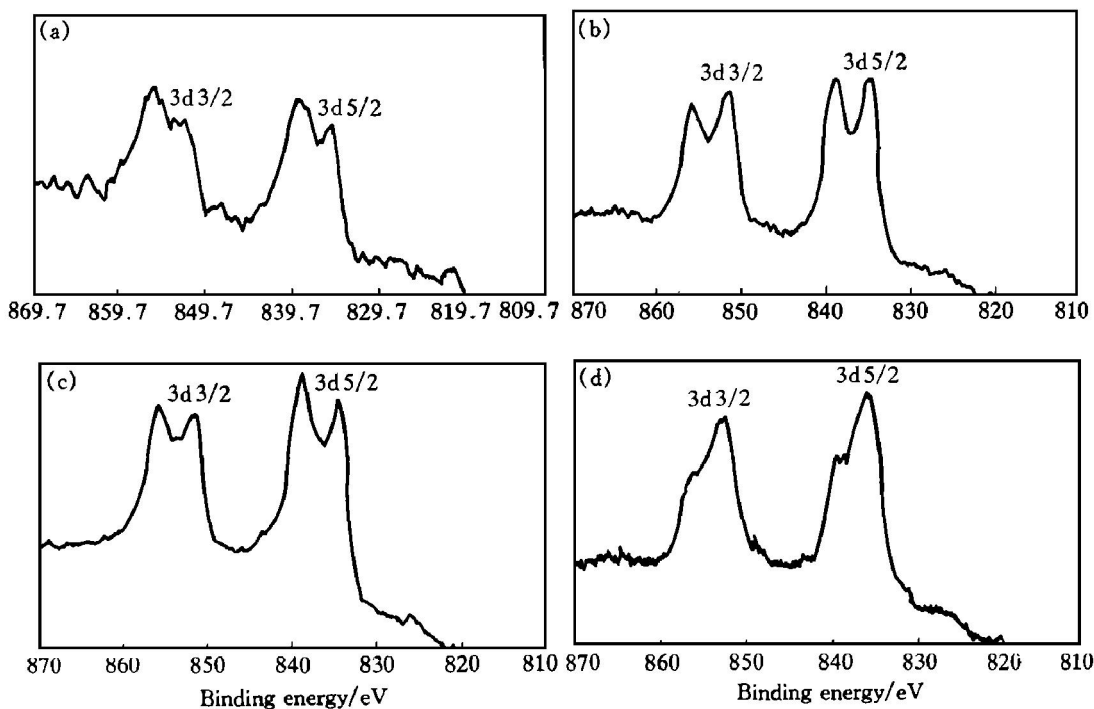


Fig. 2 XPS of La3d in carburized La-Mo material at different temperature (a) —Room temperature; (b) —1123 K, 10 min; (c) —1303 K, 5 min; (d) —1523 K, 10 min

Table 1 Binding energy for La 3d peaks by XPS analysis (eV)

Peak	Position	T/K			
		Room temperature	1 123	1 303	1 523
La 3d 5/2	Core	835.06	834.76	834.76	835.96
	Satellite	838.98	838.67	838.67	839.58
La 3d 3/2	Core	851.93	851.33	851.33	852.23
	Satellite	855.54	855.54	855.54	856.14

The La 3d spectra consist of two doublets. The energy-loss peaks appearing on the high energy side of the 3d5/2 and 3d3/2 peaks in Fig. 2 are called satellite peaks. These peaks are believed to result from composite core-hole screening by nearly degenerate ligand 2p and empty La 4f orbit^[9,10]. The general explanation for satellite peaks of rare earth oxide is that there is a charge transfer between metal atom and oxygen atom, so the extra electrons exist in the 3d or 4f orbits compared with the initial state. As shown in Fig. 2 and Table 1, the La 3d5/2, La 3d3/2 binding energy of the samples shifted 0.6 eV and 0.4 eV to lower binding energy side when temperature is raised from room temperature to 1 123 K. La 3d spectra taken at room temperature are irregular, and this irregularity may result from desorption of other kinds of compounds of lanthanum, such as the dehydration of hydrate of lanthanum. At 1 123~1 308 K, the positions of La 3d5/2 and La 3d3/2 peaks remain the same, but the satellite-split increases. When temperature is raised to 1 523 K, the La 3d5/2 and La 3d3/2 core peak levels are shifted to 835.96 eV and 852.23 eV, and the satellite peaks almost vanish. These binding energy shifts (1.2 eV for La 3d5/2 peak and 0.9 eV for La 3d3/2 peak) are interpreted as the change in chemical states of lanthanum in carbonized La₂O₃-Mo materials^[11,12]. According to Ref. [12], a negative chemical shift from La metal to La oxide occurs as the fraction of well screened 3d holes increases from almost zero to more than the half. The position of the La 3d5/2 peak at 835.96 eV is quite in agreement with the binding energy reported for metallic lanthanum of 835.9 eV^[12]. When temperature is raised to 1 573 K, the position of La 3d5/2 peak does not shift. The disappearance of satellite peak in the La 3d spectrum confirms the change in the chemical state of lanthanum. Because there is no charge transfer among metallic lanthanum atoms (lanthanum is the reaction product of La₂O₃ and Mo₂C at high temperature), the satellite peaks disappear from the spectrum of La 3d.

Because metallic lanthanum exists at the surface of La₂O₃-Mo cathode materials, the emission of Mo-La₂O₃ cathode can be explained by the monoatomic layer mechanism. Lanthanum oxide can be reduced to

metallic lanthanum by molybdenum carbide during activating period and operation of the cathode. The lanthanum atoms cover the surface of molybdenum with a monoatomic layer which has a lower work function than clean molybdenum.

4 CONCLUSIONS

1) The chemical stability of La₂O₃ is not good enough. At high temperature in vacuum, La₂O₃ decompose to LaO_x ($x < 1.5$) with some oxygen dissociating from La₂O₃ lattice.

2) La₂O₃ can be reduced to metallic lanthanum by reduction reagent (Mo₂C) at the operating temperature. The emission of La₂O₃-Mo cathode can be explained by monoatomic layer model.

3) The binding energy of metallic lanthanum is higher than that of La₂O₃. The binding energies of La 3d5/2 and of La 3d3/2 metallic lanthanum are 835.96 eV and 852.23 eV respectively.

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(Edited by YANG Bing)