Available online at www.sciencedirect.com
ScienceDirect
JOURNAL OF RARE EARTHS
www.re-journal.com/en/
ELSEVIER
JOURNAL OF RARE EARTHS, Vol. 27, No. 6, Dec. 2009, p. 975

Enhancement of secondary emission property of molybdenum cathode co-doped with La_2O_3 and Y_2O_3

WANG Jinshu (王金淑), LIU Wei (刘 伟), REN Zhiyuan (任志远), YANG Fan (杨 帆), GAO Fei (高 非), ZHOU Meiling (周美玲)

(The Key Lab of Advanced Functional Materials, Ministry of Education China, School of Materials Science and Engineering, Beijing University of Technology, Beijing 100022, China)

Received 1 June 2009; revised 28 July 2009

Abstract: La_2O_3 and Y_2O_3 co-doped Mo secondary emitters were prepared by three kinds of doping method combined with high temperature plasma sintering. The secondary electron emission property and microstructure of the cathodes were studied. It showed that the cathode prepared by liquid-liquid doping method exhibited the best emission property among all the samples prepared by liquid-solid doping, solid-solid doping and liquid-liquid doping methods due to a uniform distribution of different substances. RE_2O_3 existed uniformly at the grain boundaries and diffused to the cathode surface during a cathode activation period. A surface layer of RE_2O_3 formed after activation played an important role in the emission. The secondary emission yield of La_2O_3 and Y_2O_3 co-doped Mo prepared by liquid-liquid doping method was 4.34.

Keywords: molybdenum; secondary emission; cathode; rare earths

Magnetrons have a wide application in the fields of broadcast, communication, industry and aviation etc.[1–3] As the heart of electron tube and magnetron, cathode plays an important role in the device. However, there are limited available emitters with sufficient high secondary electron emission yields (δ) and excellent anti-ion bombardment capability during the operation of devices to satisfy the continuously increasing requirements in the out-power and working frequency of magnetrons. At present, Ba-W cathodes[4], oxide cathodes and ThO_2-W cathodes, especially Ba-W cathodes, are commonly used in the high power magnetrons. However, Ba-W cathode is hard to make and sensitive to the atmosphere during the cathode preparation and treatment. The oxide cathode, as a thick film cathode, has higher secondary emission yield but with bad anti-ion bombardment property and short life. ThO_2-W cathode faces the problems of high working temperature and radioactivity of ThO_2. It was found in our previous work that La_2O_3-Y_2O_3-Mo prepared by solid-liquid doping method exhibited certain secondary emission property[5–8]. The secondary emission yield of about 3.0 was obtained after the cathode was activated at the temperature as high as 1600 ºC[9]. However, it is noticed that the high activation temperature of La_2O_3-Y_2O_3-Mo leads to some problems in the practical application due to the thermal damage to the anode surface and other parts of the magnetron, especially in the mm-wave magnetron in which the distance between anode and cathode is so small. In this study, we intend to improve the secondary emission yield and lower the activation temperature by improving rare earth oxide doping technique and cathode fabrication process.

1 Experimental

1.1 Sample preparation

La_2O_3-Y_2O_3 co-doped Mo powders were prepared by liquid-liquid doping using a sol-gel technique. Rare earth nitrate and ammonia molybdate were used as raw materials. The total content of rare earths is 30 wt.% and the mass ratio of La_2O_3:Y_2O_3 is 1:3. The doped molybdenum oxide powders were reduced into metallic molybdenum powders in dry hydrogen at 900 ºC. Then the powders were pressed into a pellet and sintered by spark plasma sintering (SPS) at 1500 ºC for 3 min to form RE_2O_3 doped Mo (RE_2O_3-Mo) bar.

Foundation item: Project supported by the 863 program of China (2006AA03Z524, 2008AA031001), National Nature Foundation (50801001), and Beijing New Century Hundred, Thousand and Ten Thousand Talent Project (Q1009001200802)

Corresponding author: WANG Jinshu (**E-mail:** wangjsh@bjut.edu.cn; **Tel.:** +86-10-67391101)

DOI: 10.1016/S1002-0721(08)60373-7

1.2 Measurement of emission properties

The sintered rare earth oxide (RE_2O_3-Mo) bar was machined into thin flakes (Φ10 mm×2 mm) and connected with molybdenum sleeves by laser welding. The cathode assembly was heat-treated under the flow of hydrogen. Emission properties of the cathodes activated at different temperatures were tested in a close-spaced diode configuration in an ultra high vacuum (UHV) system with a Mo-anode with a water-cooled copper anode. A computer-controlled automatic emission-testing instrument, which has been described in our previous paper[5], was applied for the measurements. During the testing, the collecting voltage was kept to be 250 V and the current of primary electron was held to be 40 μA. The secondary electron emission performance was carried out at about 600 ºC in order to avoid the influence of the thermionic emission.

1.3 Observation of microstructure and element analysis of the surface of sintered materials

The microstructure was observed with a Hitachi S-3500N scanning electron microscope, equipped with Oxford Inca EDAX equipment. "In situ" AES analyses were carried out with a VGM-ICROLAB MK-II system.

2 Results and discussion

2.1 Effect of rare earth doping method on the secondary emission property

Fig. 1 represents the secondary electron emission (SEE) curves for La_2O_3-Y_2O_3-Mo cathodes prepared by mechanically mixing of RE_2O_3 and Mo (called as solid-solid doping), liquid-solid doping (water soluble compound of rare earth nitrite and water insoluble compound of molybdenum oxide were used as raw materials) and liquid-liquid doping (two kinds of water soluble compounds of rare earth nitrite and ammonia molybdate were used as raw materials) methods followed by an activation at 1600 ºC in vacuum. As shown in Fig. 1, all the SEE curves have the parabola shape. At very low primary electron energy E_p, only a few secondary electrons are created due to the small primary energy. Since the number of the internal secondary electrons generated increases with E_p, secondary emission yield (δ) also increases with E_p. At very high E_p, progressively more secondary electrons are created, and are thus too far from the surface to escape, so δ decreases with E_p. It is also found from Fig. 1 that the cathode prepared by liquid-liquid doping method exhibits the highest secondary emission property whereas that prepared by mechanical mixing method exhibits the lowest emission secondary emission yield. The samples prepared by the doping methods, especially those prepared by liquid-liquid doping method, have uniform distribution of different substance since two compounds could be mixed more homogenously in the liquid state. The wide energy band gap in a semiconductor and insulator prevents internal secondary electrons from losing energy through collision with conduction electrons, resulting in a large penetration depth of primary electron and escape depth of the secondary electrons and a large SEE yield. Thus, it is evident that RE_2O_3 is the main generation source of secondary electrons, which implies that uniform emission from cathodes is correlated with the uniform distribution of RE_2O_3 in the Mo matrices.

2.2 Enhancement of secondary emission properties by activation

Fig. 2 shows surface micrographs of activated La_2O_3-Y_2O_3-Mo cathodes before and after pre-activation. Different from the surface microstructure of pre-activated samples, as shown in Fig. 2(c), where both RE_2O_3 and Mo are found on surface of annealed samples, there are a lot of pores and widespread white areas on the surface of un-treated samples. Such areas were verified to be composed of La_2O_3 and Y_2O_3 by energy disperse spectrum (EDS) results illustrated in Fig. 2(a) and (b). It was also found in our previous work that there are a lot of molybdenum oxides in the interior surface of secondary electron emission lifetest vacuum glass tubes of RE_2O_3-Mo emitters and that molybdenum almost disappeared from the cathode surface[6]. According to the above results, we assumed that pores might be caused by an elimination of molybdenum. Such disappearance of molybdenum should be due to the evaporation of molybdenum oxide, the chemical reaction product of molybdenum and oxygen released from the inside of the samples.

In order to investigate the possible sources of oxygen, TG analysis was performed to check the chemical behavior of

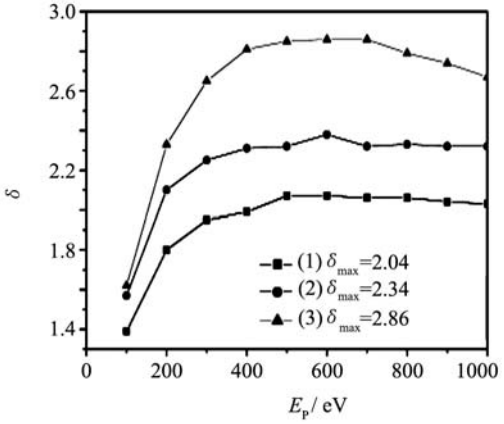

Fig. 1 δ~E_P curve of un-preactivated samples prepared by different doping methods after the activation at 1600 ºC in vacuum
(1) Solid-solid doping; (2) Liquid-solid doping; (3) Liquid-liquid doping