Effective Work Function of an Oxide Cathode in Plasma

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Work function of an oxide cathode in a germicidal lamp was estimated from a photoelectric current measurement in microwave discharge conditions. A 25 mW He-Ne laser light at 1.9 eV photon energy had produced photoelectric current of the order of 1 nA, indicating the work function of a heated oxide cathode was lower than this photon energy. Thermionic electron emission from the cathode was measured in a vacuum condition by taking the cathode out of the lamp tube. The thermionic current showed a slow response against the change in temperature near the cathode activation temperature. The activation process of the oxide cathode had accompanied gas emission of C, O, CO and CO_2, which was attributed to decomposition of alkaline earth carbon oxides contained in the coatings of oxide cathodes. The thermionic work function of the cathode determined from the Richardson plot was 1.5 eV at the cathode operation temperature.

Keywords: oxide cathode, work function, fluorescent lamp, thermionic electron emission, photoelectric effect

1. Introduction

Low pressure Hg discharge lamps are operated with oxide cathodes to realize efficient photon production from near ultraviolet to visible light wavelength range. In these discharge lamps, tungsten electrodes are coated with so called emitters, consisting of mixtures of alkaline earth oxides like BaO, SrO and CaO. The coatings realize stable electron emission with low heating power because their work functions are lower than those of pure refractory metals by several eV [1]. Precise mechanisms of electron emission from oxide cathodes in fluorescent lamps are described in the text book of Waymouth [2], which discusses the importance of activation processes of cathodes to realize enough electron emission for maintaining a stable glow discharge.

Oxide cathodes are activated as they are heated up to a proper temperature by electrical powers. The actual work functions of oxide coated metal electrodes in plasmas should change in accordance with the operation condition of the electrode, or how they are activated in the discharge tube. However, little information is available on the work function of oxide electrodes in fluorescent lamps, as the widely separated two electrode structure of an actual lamp makes measurements of work function difficult.

The work functions of oxide electrodes in low pressure Hg discharge lamps were estimated by photoelectric method by turning off the plasma [3]. The measured photoelectric threshold of an as-received germicidal lamp was larger than 3.5 eV, and the threshold had become lower after a discharge operation of the lamp for 30 minutes. By continuously operating the lamp for 100 hours, the electrode work function exhibited a reduction of photoelectric threshold down to 2.2 eV. This result indicates that a work function of an electrode in a fluorescent lamp can change during the lamp operation.

In these experiments, the detection of photoelectric current had been only possible by a smooth diffusion of photoelectrons to the counter electrode of the discharge lamp. A method was developed to establish an enhanced flow of photoelectrons from the electrode surface to a microwave excited plasma for enlarging the photoelectric signal [4]. The method successfully produced a stable emission of photoelectric current from electrodes as long as the electron emission from the electrode was negligible compared with the ion saturation current flowing to the electrode from the plasma. The work functions estimated from the photoelectric current under a microwave discharge condition ranged from 2.2 to 2.4 eV.

In this report, results of further experiments using the set up that produces a microwave plasma in a germicidal lamp are described. The measured photoelectric threshold is compared with the thermionic work function of electrodes taken out from a germicidal lamp. Gas emissions from the electrodes are investigated to discuss the correlation between the photoelectric threshold and the thermionic work function.

2. Experimental Approach

Two experimental setups were employed to study electron emission from an oxide cathode in a low pressure discharge lamp. One is the device that excites a microwave plasma in a commercially available low pressure discharge lamp, which was explained in previous reports [4, 5]. A microwave power supply

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excited a plasma in a Model GL-20 lamp of Matsushita Electric Company to enhance electron emission from the electrodes due to lasers at 406, 532, and 633 nm wavelengths. The electrodes were contained in an UV transmitting clear glass envelope of the lamp.

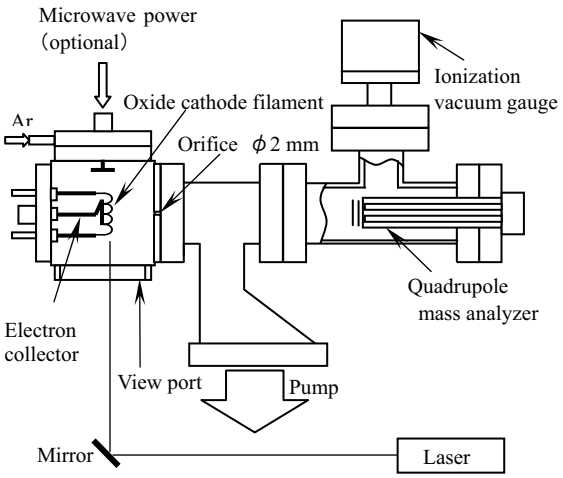

Fig. 1 Schematic diagram of the experimental setup.

Another setup shown in Fig. 1 was prepared to measure thermionic work function of an oxide cathode in vacuum environment. A small stainless steel chamber of 25 cm^3 volume served as a vacuum container for a BaO, SrO, and CaO mixed oxide cathode taken out from a Model GL-20 discharge lamp. An electron collector was mounted parallel to the filament with a 4 mm spacing. A 230 ℓ/s turbo-molecular pump evacuated the chamber through a 2 mm diameter orifice to realize pressure difference between the chamber and the downstream. The ultimate pressure downstream of the orifice was about $3X10^{-6}$ Pa. A quadrupole mass analyzer monitored the gas emission from the filament through the orifice. Introduction of Ar gas into the chamber realized a steady state glow discharge by electron emission from the oxide cathode.

The voltage and the current supplied to the cathode were constantly monitored to estimate the cathode temperature from electrical resistivity data of W [6]. When the cathode was heated up to more than 870 K, the temperature was measured by the YOKOGAWA model PM 174 optical thermometer detecting infrared radiation from the cathode through a sapphire window. The window also passed laser lights at 406, 525, and 633 nm wavelengths to let them irradiate the surface of the cathode for photoelectric current measurements. A lock-in amplifier detected photoelectric current through phase sensitive detection realized by amplitude modulation of a laser light with a rotating wheel light chopper.

3. Photoelectron Emission

In our previous experiment, the photoelectric current was measured without enough care to the cathode activation process [4]. When the cathode was properly activated either by heating it up to temperatures above some threshold, or by commencing a glow discharge after heating the electrode up to a proper temperature, both thermionic electron emission and photoelectron emission from a cathode irradiated by microwave excited plasma in a germicidal lamp had increased. As it was activated, the oxide cathode in a germicidal lamp had produced a detectable signal by irradiation of laser lights of all wavelengths. About 25 mW incident powers from lasers had excited the photoelectric current ranging from 0.1 to several nA. The photon energy of He-Ne laser light is 1.96 eV, and the cathode work function has to be smaller than this value at the lamp operating condition.

The oxide electrode was taken out of the germicidal lamp and mounted in the stainless steel chamber to test the performance as an oxide cathode. When the cathode was kept at room temperature only the laser light at 405 nm wavelength had produced photoelectric current of the order of 10 pA out of 25 mW laser power. No photoelectric current above 1 pA detection limit was observed for lasers of other wavelengths. This means the work function of the cathode in a room temperature condition is larger than 2.33 eV, which is the photon energy of 532 nm laser light.

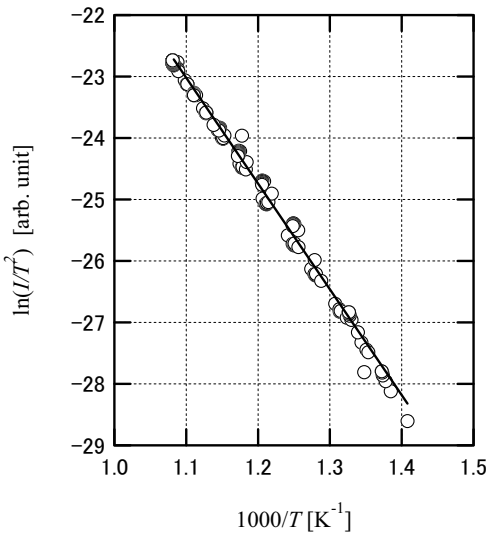

Fig. 2 A Richardson plot for an oxide cathode after activation. The solid line in the figure shows a least square fit to the data points.

4. Thermionic Work Function

The sample cathode was heated by running electric current in the stainless steel chamber to measure the thermionic electron emission. The Richardson plot of the tested cathode is shown in Fig. 2. The electric current corresponding to the thermionic electron emission exhibits a straight line with the work function about 1.5 eV. The electron current drifted after the electrode temperature was changed, and the entire measurement had to be finished within several minutes. When the measurement was made with a time duration much longer than several

minutes, a hysteresis was observed in the Richardson plot.

A hint of deactivation of the electrode can be seen in Fig. 2. The data points are plotted lower than the straight line drawn as an eye-guide in Fig. 2 above $1000/T = 1.3$, or the temperature below 770 K. The slope of the curve is also larger for these points. This corresponds to lower electron emission and higher work function at lower temperature. The recovery of thermionic electron current after electrode heating from a lower temperature condition took a time longer than the time for the cathode temperature to be stable, and this time to stabilize thermionic current was the order of a minute.

5. Gas Release during Activation

The observed slow change in thermionic electron emission was considered attributable to the change in surface conditions. To see if the change may have accompanied the adsorption of gases in a discharge tube, gas emissions from the cathode were monitored with a quadrupole mass analyzer. In Fig. 3(a), ion current signals of quadrupole mass analyzer are plotted as functions of time during heating of the cathode. Neither the signal of Ba nor that of Sr was observed. Signal due to Ca can appear at mass=40, but Ar atoms of the same mass adsorbed in the oxide cathode during the discharge operation of the cathode are released when the cathode is heated. Thus, the signal of mass=40 was assumed to be caused by Ar emission. Carbon at mass=12, carbon monoxide at mass=28, and carbon dioxide at mass=44 were found released by heating the cathode.

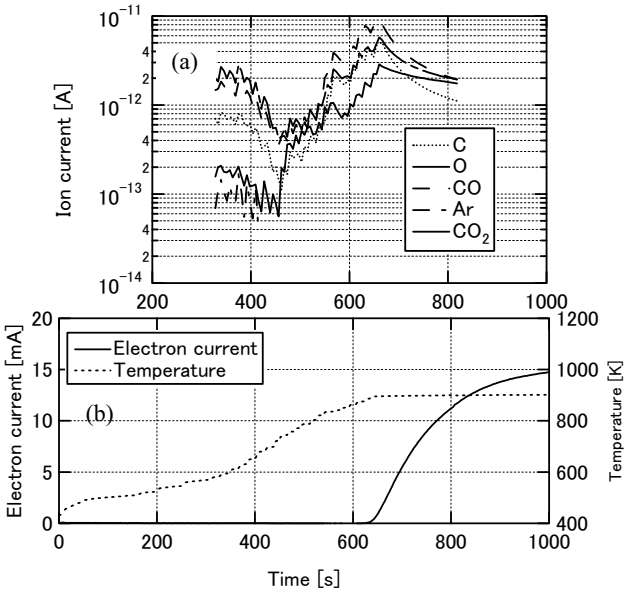

Fig.3 (a). Gas emission during the heating activation of an oxide cathode. (b). Cathode temperature and electron emission current during activation.

In Fig. 3(b) are plotted the cathode temperature estimated from the value of electrical resistivity, and the electric current from the oxide electrode due to thermionic electron emission during the cathode heating. As shown in the figure, keeping the cathode at constant temperature activates the cathode with the time constant of the order of several minutes. The mass spectrum during heating activation was recorded by the quadrupole mass analyzer. A typical mass spectrum during activation is shown in Fig. 4. It indicates that carbon oxides and oxygen atoms and molecules are the dominant species during activation.

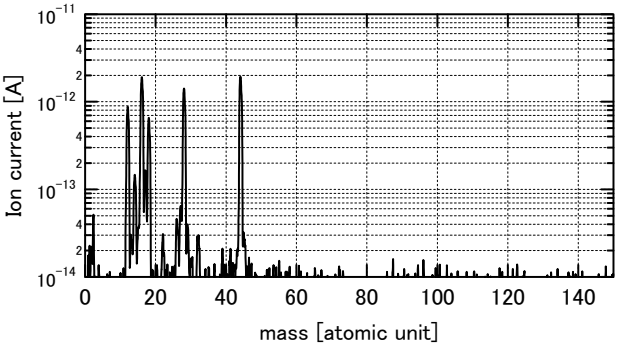

Fig. 4 A typical mass spectrum during heating activation of an oxide cathode.

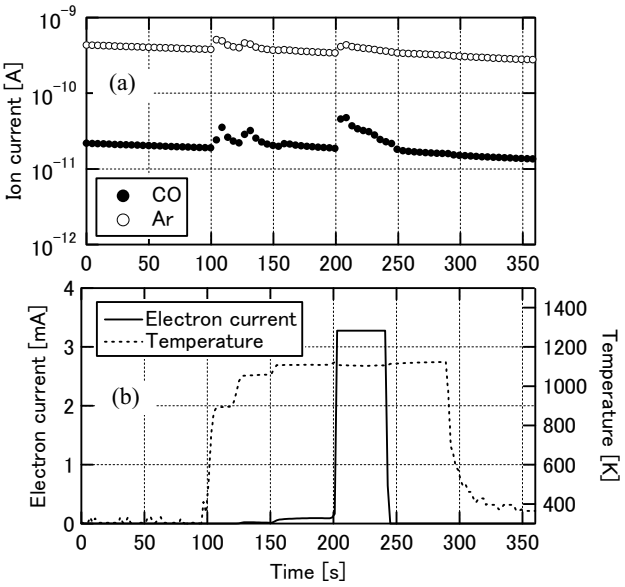

Fig. 5 (a). Quadrupole mass analyzer signals of CO and Ar during glow discharge excited by an oxide cathode. (b). Cathode temperature and cathode current during discharge.

6. Gas Release during Glow Discharge

The cathode was heated in 7 Pa Ar pressure to sustain a dc glow discharge. A -360 V discharge voltage was applied to the cathode with respect to the wall of the chamber serving as the anode for a discharge. Elevation of cathode temperature up to more than about 950 K started a stable discharge with the aid of current regulation by a power supply. In Fig. 5(a) are shown the gas release during rapid activation and that during discharge. As shown in Fig. 5(b), gas release of CO and that of Ar from the cathode were observed as the temperature of the cathode was raised stepwise. Larger amount of CO

emission was observed by the start of discharge, but it quickly decreased with time. The mass spectrum like the one shown in Fig. 4 was observed during the discharge. No detectable signal of Sr or Ba was found in the spectrum.

7. Discussion

The activation of oxide cathode had required some time depending upon the cathode temperature. When the temperature was kept constant near the activation threshold, as shown in Fig. 3, time of the order of several minutes was required for the electron current to be stable. Chemical reactions of the oxides with the speed determined from the cathode temperature seem responsible for causing the slow change in electron emission. Meanwhile, the abrupt jump of the current can be triggered by the activation of the cathode with several to several tens of seconds as it was seen in the case of glow discharge shown in Fig. 5.

The gas emissions during the heating phase of the cathode can be confirmed in both Figs. 3(a) and 5(a). These phenomena are always observed when a room temperature cathode is heated up to activation temperature. Large emissions of C, CO, O, and CO_2 suggest that these species are thermally desorbed from the oxides on the cathode. During the time the thermionic current from the electrode decreases at lower temperature, these species can be adsorbed by the oxides again. Existence of atomic Ba in oxide is believed to enhance electron emission from the cathode [7], while the Ba atoms can react with O, CO and CO_2 to form barium oxides and carbonates. After most of Ba atoms react with residual gas molecules, oxide layer is deactivated to reduce electron emission current. Thus, recycling of oxygen and carbon oxides at the surface of oxide cathode is considered present in a low pressure Hg discharge lamp.

The surface condition of the cathode was assumed homogeneous to determine the work function from the plot in Fig. 2. An oxide electrode usually has a double or triple coil structure, and the surface structure is not homogeneous but heterogeneous. The present work function is based upon the emission current averaged over the heterogeneous cathode surface, and may be different from the one for a homogeneous oxide cathode. There can be also a difference in temperature between the surface facing the inside, and that facing the outside of the coiled electrode structure. Myojo and Fukumasa had estimated temperature of an oxide cathode with the treatment similar to the present method [8], and reported that the cathode temperature during the operation was a little higher than our measurements. Assuming the present method underestimates the cathode temperature by 150 K due to observation of lower temperature part with the optical thermometer, the data points in Fig. 2 yield 1.8 eV as the value of the work function. Ends of the oxide cathode are attached to lead-in wires, and heat conduction takes place at the joints to make temperature distribution along the cathode. The work function may also vary along the oxide cathode surface due to the temperature distribution. Photoelectron emission from a cathode of a low pressure discharge lamp induced by a pulse laser light showed such spatial variation along the cathode [9].

Threshold energy for photoelectron emission in vacuum condition was determined for room temperature condition only, and was larger than 2.33 eV. This was far much greater than the thermionic work function determined from a Richardson plot at cathode operation temperature. The photoelectric effect for heated oxide cathode is now being investigated with the high vacuum system, but the thermionic electron emission from the oxide cathode itself causes a noise onto a small signal of photoelectric current to make the measurement difficult. Modification of the experimental system to diminish the noise of cathode current is indispensable to directly compare thermionic and photoelectric work functions in vacuum, and in plasma environments.

8. Conclusions

Activation of oxide cathode is indispensable to reduce work function and enhance thermionic electron emission from the cathode. As the cathode becomes cold by turning off the heating, it adsorbs the residual gas and is deactivated. The adsorbed gas is released again as the cathode is heated up to the operational temperature. An activated cathode has shown a straight line in the Richardson plot, indicating the thermionic work function to be about 1.5 eV at the operating temperature.

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