13.4

The effect of magnetron sputtering conditions during deposition of $(BaSrCa)CO_3$ coatings on thermionic emission of film microcathodes

© G.A. Zhabin, O.V. Pelipets, N.A. Sharapov

JSC „RPC „Istok“ named after Shokin“ Fryazino, Moscow oblast, Russia
E-mail: zhabingennady@yandex.ru, gazhabin@istokmv.ru

Received December 6, 2023
Revised February 22, 2024
Accepted March 9, 2024

The effect of temperature and discharge power of ion-plasma deposition of molecular sputter-deposited oxide microcathodes (MSOC) on their emission activity has been experimentally investigated. The elemental composition of a thin coating of MSOC has been studied using Auge electron spectroscopy (AES) and X-ray fluorescence analysis (XRF). The effect of the atmosphere and residual gases on the operation of microcathodes is shown.

Keywords: molecular sputter-deposited oxide microcathode (MSOC), emission characteristics, durability, work function, electrovacuum device (EVD).

DOI: 10.61011/TPL.2024.06.58476.19827

Thermionic cathodes are used widely as electron sources in electrovacuum devices (EVDs), electronic microscopes, accelerators, and lithography equipment [1]. Although high current densities have been reported for Sc-containing thermionic cathodes at low temperatures, they are rarely used in commercial applications due to the nonuniformity of emission and a low durability [2]. Recently, there has been a significant amount of interest in thin-film cathodes. Thermionic cathodes with a barium strontium oxide (BaSr)O film with a thickness of approximately $1\,\mu$m were fabricated on tungsten substrates by magnetron sputtering at a temperature of 700°C. A minimum work function of 1.57 eV with a current density of $1.60\,A/cm^2$ was obtained at 1198 K and remained stable for 8 h [3]. Epitaxial $SrVO_3$ layers will probably find application in next-generation emitters. Both bulk and epitaxial $SrVO_3$ feature a work function of 1.9 eV, which agrees with the results of density functional theory (DFT) calculations and the characteristics of thermionic emission [4]. Magnetron deposition was used to fabricate and study thin-film dispenser microcathodes with a work function of 2.2 eV at a temperature up to 1200 K that are based on tungsten and multicomponent barium oxide. The above film cathodes have the following drawbacks: low current density, low durability, and weak weather resistance [5].

The aim of the present study is to examine the effect of an elevated power of ion-plasma target sputtering and vacuum conditions in EVDs on thermionic emission of microcathodes.

The „Bulat“ setup was used to deposit an emission coating $0.8\,\mu$m in thickness at normal and elevated target sputtering power levels onto molecular sputter-deposited oxide cathodes (MSOCs) with an emission area of $1.4 \cdot 10^{-4}\,cm^2$. The $Ar+CO_2$ gas mixture pressure was 0.13–0.11 Pa. Spray-deposited targets made of KTA-1-6 triple alkali-earth metal carbonates $(BaSrCa)CO_3$ were fabricated on a nickel substrate (base) and had a coating thickness of $127-130\,\mu$m [6]. The negative target potential in the standard process of sputtering of MSOCs with tungsten–rhenium bases and reference Si (111) samples was 800 V, and the discharge current was 200 mA. The temperature of a target heated by a tungsten heater was 780°C. The substrate with an MSOC was held at earth potential in the sputtering setup. The sputtering rate was 4–6 nm/min. Sputtered microcathodes were installed in diode models that were mounted in evacuation units for residual gases to be evacuated and to reach a vacuum level of 10^{-8} mm Hg. Thermal activation of MSOCs in vacuum was performed in the chemical process of decomposition of coating carbonates [7,8]:

$$BaCO_3 \rightarrow BaO + CO_2 \uparrow .$$

In the course of activation, CO_2 and oxygen were removed from the film MSOC coating and donor centers were formed in solid solution BaSrCaO [8].

Thermionic training and cathode current collection (with plotting of emission characteristics) were performed in sealed-off EVD models. The duration of activation by current collection at an anode potential of 22 V and a collector potential of 150 V was 25–30 min. Flash getters made of alloy NT-47 and a Penning pump were used to reach higher vacuum levels. The examination with an „AIST-NT“ atomic force microscope revealed that the average grain size of the MSOC coating after sputtering was 71 nm.

The following experiments were carried out to determine the resistance of MSOCs to the influence of residual gases. Microleakage was initiated in a copper tubulation of the first EVD model after evacuation. An emission characteristic (see Fig. 1, *a*) was plotted after 0.5 h of cathode operation. It follows from the shape of this curve that the cathode is a low-activity one. The MSOC emission weakened under

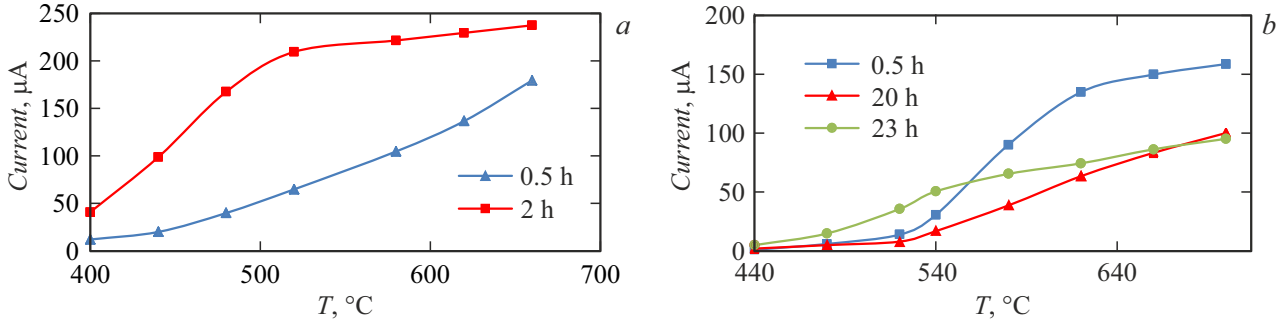

Figure 1. Effect of the duration of exposure to residual gases in an EVD with microleakage on thermionic emission of an MSOC. Panels *a* and *b* present the emission characteristics of MSOCs of two different devices (the first and second models, respectively).

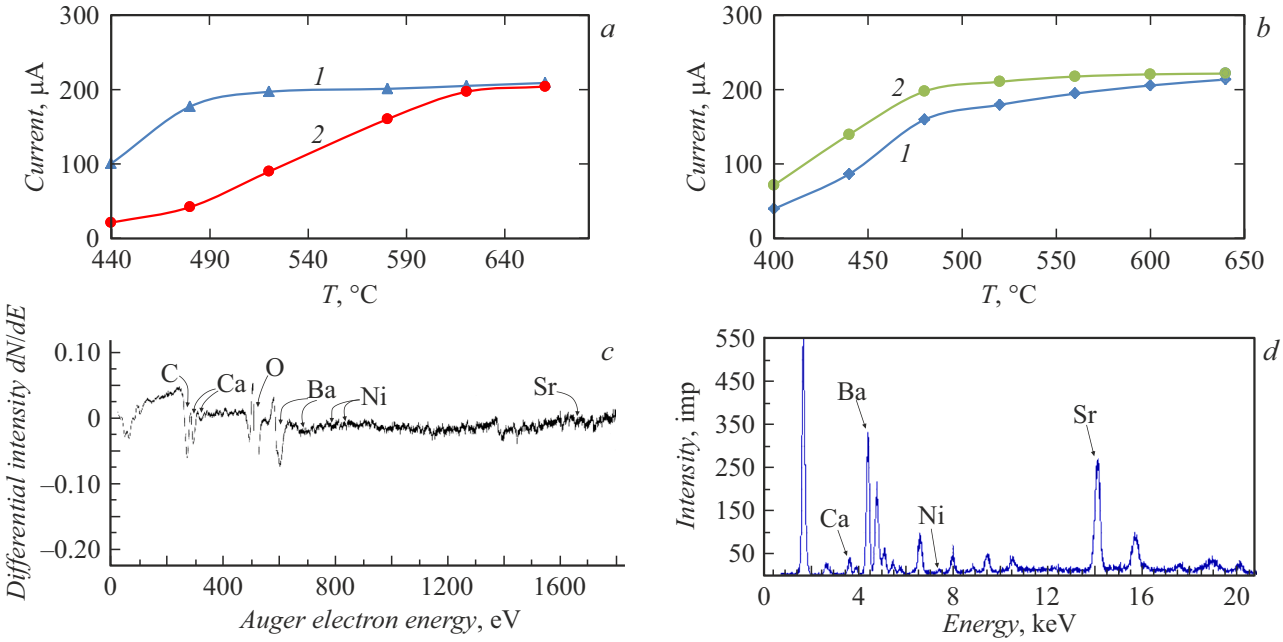

Figure 2. *a* — Emission characteristics of MSOCs in the third (*1*) and fourth (*2*) EVD models; *b* — emission characteristics at normal (*1*) and elevated (*2*) sputtering power levels; *c* — Auger spectra of sample No. 2; *d* — XRF spectra of sample No. 2.

the influence of adsorbed oxygen and other residual gases. The vacuum leak was localized precisely with the use of a helium leakage detector. The vacuum in the device dropped to $\sim 10^{-5}-10^{-6}$ mm Hg. When the leak was sealed and a better vacuum was achieved, the MSOC current increased considerably in just 2 h of operation. The durability of this microcathode exceeded 3000 h with an increased current. The cathode current of the second EVD model (Fig. 1, *b*) after evacuation was greater than 150 μA at a temperature of 660°C. An emission characteristic was plotted after 0.5 h of cathode operation. After 20 h of operation, the EVD case was found to be leaking, and an emission characteristic, which revealed a reduction in current, was plotted again. The vacuum level at this stage was $\sim 10^{-4}-10^{-5}$ mm Hg. When the EVD leak was sealed and a vacuum of 10^{-8} mm Hg was achieved, the initial cathode current value was not restored, since the cathode surface remained exposed to residual gases for a long time.

In order to examine the influence of atmosphere on emission, the third EVD model with an MSOC with a WRe base was devacuumized after 4000 h of operation without a reduction in emission. This cathode was then mounted into the fourth EVD model evacuated to 10^{-8} mm Hg. The emission characteristics of MSOCs in the third and fourth EVD models (after atmospheric exposure) are compared in Fig. 2, *a*. Atmospheric exposure led to an irreversible deterioration of MSOC emission.

Figure 2, *b* shows the emission characteristics of two batches of microcathodes with WRe/Ir bases at normal (curve *1*) and elevated (curve *2*) sputtering power levels. At an elevated power level (curve *2*), the MSOC coating was deposited at a target temperature of 780–800°C and a sputtering power of $\sim$ 180 W (voltage, 800 V; discharge

Table 1. Examination of the composition of samples at normal (sample No. 1) and elevated (sample No. 2) sputtering power levels by Auger electron spectroscopy

Sample number	Element concentration, mass%								
	O	C	Ca	Sr	Ba	Ni	Ar	Na	Cu
1	4.93	2.43	3.54	17.9	67.4	0.1	0.12	0.06	0.19
2	7.25	5.75	3.80	14.78	66.2	2.02	0.18	–	–

current, 220−225 mA). It follows from the analysis of test data for ten MSOCs in EVD models that an increase in discharge power and target temperature led to an increase in emission current.

The surfaces of coating samples prepared at normal and elevated (Figs. 2, *c*, *d*) sputtering power levels were examined by Auger electron spectroscopy with the use of an 09IOS-10-005 setup (Russia) and by X-ray fluorescence (XRF) analysis with a REAN analyzer (Russia).

The results of determination of the composition of samples are listed in Tables 1, 2. It follows from Table 1 that, according to Auger electron spectroscopy data, the concentration of Ni trace impurity on the surface of sample No. 1 on a Si substrate is 0.1 mass%, while the corresponding concentration for sample No. 2 is 2.02 mass%. The Ba/Sr ratio is 3.76 in sample No. 1 and 4.48 in sample No. 2. Table 2 lists the concentrations of elements in studied samples determined by XRF analysis. No nickel impurities were found in sample No. 1. The concentration of Ni in sample No. 2 is 0.74 mass%.

When the sputtering power grows in the transit mode of gas pressure, the sputtering yield of the target material and the velocity and energy of particles deposited onto cathodes also increase [9]. It is likely that an increase in target temperature and energy of bombarding particles induced an enhancement of intensity of the physical and chemical interaction of carbonated atoms of alkali-earth metals in the MSOC coating.

When the concentration of free Ba atoms in the base and the coating increases, barium dissolution in the lattice with the formation of donor centers, which contribute to an enhancement of the cathode emissivity, intensifies [10]. Atomic Ca, Sr, and Ni trace impurities in barium oxide facilitate the formation of donor-type surface states on the surface of BaO nanocrystallites. Nickel atoms in the crystal structure of BaO affect the parameters of electronic structure, altering the value and changing the sign of the surface charge of oxide, altering the direction of band bending at the surface, and reducing the work function [11,12].

A high vacuum in EVDs ($10^{-8}-10^{-9}$ mm Hg) is needed for efficient MSOC operation. Short-term (1-2 h) softening to $10^{-6}-10^{-7}$ mm Hg does not affect the subsequent MSOC operation performance. Long-term operation in vacuum worse than 10^{-6} mm Hg has an irreversible negative effect on the emission characteristics of an MSOC. The

Table 2. Examination of the composition of samples at normal (sample No. 1) and elevated (sample No. 2) sputtering power levels by XRF analysis

Sample number	Element concentration, mass%			
	Ca	Sr	Ba	Ni
1	3.94	18.46	77.6	–
2	4.03	17.79	77.44	0.74

well-known Richardson−Dushman equation [2,8] provided the following estimate of the work function for MSOCs at an elevated sputtering power level (curve *2* in Fig. 2, *b*): ~ 1.34 eV at $T = 600^{\circ}$C.

An increase in sputtering power led to an intensification of sublimation processes, and the ion-plasma impact on the target became more pronounced; the fraction of deposited Ni atoms in the surface coating of microcathodes also increased to 2.02 mass%. It is likely that doping with Ni atoms enhanced the conductivity of the emission layer, facilitating the formation of donor-type surface states and reducing the MSOC work function.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] D.M. Kirkwood, S.J. Gross, T.J. Balk, M.J. Beck, IEEE Trans. Electron Dev., **65** (6), 2061 (2018). DOI: 10.1109/TED.2018.2804484.
[2] M.N. Seif, Q. Zhou, X. Liu, T.J. Balk, M.J. Beck, IEEE Trans. Electron Dev., **69** (7), 3513 (2022). DOI: 10.1109/TED.2022.3172052
[3] Y. Liu, C.M. Day, S.A. Little, F. Jin, J. Vac. Sci. Technol. A, **24** (6), 2187 (2006). DOI: 10.1116/1.2363400
[4] L. Lin, R. Jacobs, S.D. Marks, P.G. Evans, D. Morgan, J. Booske, in *IEEE 21st Int. Conf. on vacuum electronics (IVEC)* (IEEE, 2020), p. 161–162. DOI: 10.1109/IVEC45766.2020.9520630
[5] K.R. Zavadil, D.B. King, J.A. Ruffner, AIP Conf. Proc., **552** (1), 1165 (2001). DOI: 10.1063/1.1358067
[6] G.A. Zhabin, A.V. Konnov, Prikl. Fiz., No. 2, 77 (2023) (in Russian). DOI: 10.51368/1996-0948-2023-2-77-83

[7] A.N.H. Al-Ajili, A.K. Ray, J.R. Travis, S.N.B. Hodgson, A.P. Baker, C.J. Goodhand, J. Mater. Sci.: Mater. Electron., **11** (6), 489 (2000). DOI: 10.1023/A:1008916501674
[8] A.B. Kiselev, *Metallooksidnye katody elektrovakuumnykh priborov* (Izd. Mosk. Fiz.-Tekh. Inst., M., 2001) (in Russian).
[9] D.M. Mitin, V.A. Aleksandrov, A.A. Skaptsov, S.B. Venig, A.A. Serdobintsev, J. Surf. Investig., **9** (3), 555 (2015). DOI: 10.1134/S1027451015030313.
[10] B.Ya. Moizhes, *Fizicheskie protsessy v oksidnom katode* (Nauka, M., 1968) (in Russian).
[11] V.I. Kapustin, I.P. Li, A.S. Serpichev, A.V. Shumanov, N.E. Kozhevnikova, Tech. Phys., **67** (3), 376 (2022). DOI: 10.21883/TP.2022.03.53270.211-21.
[12] V.I. Kapustin, I.P. Li, N.E. Kozhevnikova, E.F. Khudaigulova, Russ. Technol. J., **10** (6), 60 (2022). DOI: 10.32362/2500-316X-2022-10-6-60-69

Translated by D.Safin