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Thermionic and electrical properties of rhenium surface activated by yttria

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A laboratory technology for creating rhenium cathodes activated by yttria has been developed, both completely covered with an activated layer and with local activation, when only part of the surface is covered with a layer. The application of yttria leads to a significant decrease in the work function of rhenium cathodes from 5.15 eV for pure rhenium to 3.4 eV for an activated surface. The elemental composition of the activated surface is represented only by yttrium and oxygen atoms with a small proportion of rhenium. Such cathodes are thermally stable at least up to $T = 2500$ K, the calculated value of thermionic current at this temperature is ~ 100 A/cm^2.

Keywords: thermionic emission, emissivity, rhenium, yttrium, cathode, true temperature.

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Introduction

Efficient cathodes whose surface is activated by group III metal oxides or thorium have been known for more than 70 years. The most popular are iridium-yttrium cathodes, which have replaced tungsten-thorium cathodes since about the 70s of the last century and have gained wide popularity [1–5]. They are used in electrophysical devices for various purposes, high-vacuum sensors, electronic guns.

The main disadvantage of iridium-yttrium cathodes is their high cost and the need to use iridium, which is a bank metal and is under special control in many countries. In addition, iridium, even activated with yttrium, cannot be heated to very high temperatures, as it, like all metals, loses its mechanical strength as it approaches its melting point (2720 K). This limits the currents that can be received from such cathodes. In this regard, it seems promising to study the possibility of activation by yttrium oxide of higher-temperature metals, for example, rhenium. This is especially true for electrophysical devices that use electron impact heating, for example, in electronic spectrometers, double vacuum furnaces, etc.

The USSR had a technology for the production of activated cathodes, and they were mass-produced, but the „reforms“ of the last 30 years led to its loss and termination of production. Currently, such cathodes are manufactured only in the USA, are under export control and cannot be supplied to Russia due to sanctions. Rhenium cathodes activated with yttrium oxide are not mass-produced at all, there are only a few publications on this topic [6].

Previously, we proposed a laboratory technology for creating iridium-yttrium cathodes [7]. The purpose of this work is to study the possibility of activation of rhenium cathodes with yttrium oxide and to obtain data on their emission and electrophysical properties.

1. Experimental technique

When developing a rhenium cathode activated with yttrium oxide, the following tasks had to be solved. First, it was necessary to implement a method for applying yttrium oxide to the surface of a rhenium foil or wire and study the effect of the film on the surface's emissivity and thermal stability. Cathodes produced in the USA or in the USSR are usually coated with a 25–30 μm thick layer of Y_2O_3. Secondly, it is correct to measure the true temperature of the obtained film cathodes. Without accurate knowledge of the true temperatures, it is not possible to correctly determine termination the cathode work function. In the operating mode, most of the heat from the surface of the heated cathode is carried away by optical radiation [8], and without knowing the true temperature, it is impossible to choose the correct cathode heating mode, especially considering that the technical limit of temperature stability of rhenium emitters, both ribbon and wire, is about 2600 K. Thirdly, it seemed important to study the stability of activated cathodes in relation to high-temperature heating and vacuum conditions, in particular, to study the effect of heating on the elemental composition of the film and the possible micro- and nano heterogeneity of the cathodes.

The experiments were carried out in an ultrahigh vacuum chamber of a prism electron spectrometer, where it was also possible to measure the thermionic emission [8]. $40 \times 1 \times 0.02$ mm rhenium ribbons were used. Before applying yttrium oxide, the ribbon was cleaned by alternating heating in oxygen at $P \sim 10^{-5}$ Torr ($T = 1500$ K) and in ultrahigh vacuum at 10^{-9} Torr ($T = 2500$ K) by

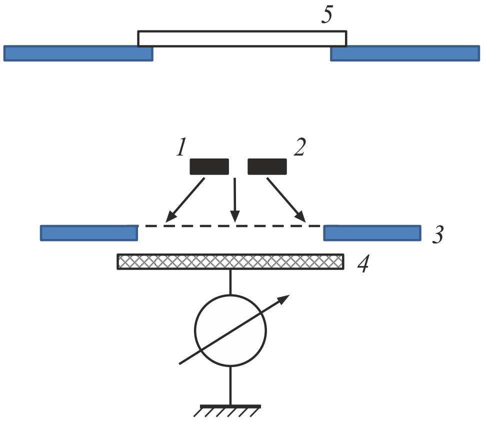

Figure 1. Simplified scheme of the experimental setup: *1* — pure rhenium ribbon; *2* — rhenium ribbon coated with yttrium oxide; *3* — anti-dinatron grid; *4* — collector; *5* — window for pyrometry.

direct heating by alternating current. All impurities were desorbed from the surface during this treatment, and only Auger peaks of rhenium. were recorded. The ribbon was textured at the same time as cleaning: the rolled texture was changed to a recrystallization one and the surface was expressed by a face (10−10), which had a work function of $e\varphi = 5.15\,\mathrm{eV}$ [3].

The degree of orientation of the face according to X-ray diffraction data was $\sim 99.5\,\%$; the surface was homogeneous in work function with an accuracy of $\pm 0.05\,\mathrm{eV}$. The temperature of the ribbon was determined with an optical micropyrometer with an accuracy of $\pm 5\,\mathrm{K}$, the entire central part of the sample was homogeneous in temperature.

Some of the experiments were carried out in a special high-vacuum chamber with an efficient thermoelectro collection unit and a sapphire glass pyrometry window. The diagram of the experimental setup is shown in Fig. 1. Two ribbon rhenium samples, purified as described above, were placed next to each other in the chamber. Both ribbons had the same geometric parameters, and they also had the same dependence of the brightness temperature and thermionic current on the heating current. Thermoelectrons were collected from the central parts of ribbons measuring 7 mm in length. The arrangement of the electrodes of the collector unit ensured a collection of thermoelectrons close to 100 %. Thus, both pyrometric and thermionic measurements can be carried out simultaneously for both atomically pure and yttrium-activated surfaces.

Studies of the surface topography on a scale from $10\,\mu\mathrm{m}$ to 10 nm, as well as the elemental composition of the samples were carried out in an hboxJSM-7001F scanning electron microscope (Jeol, Japan) equipped with an Inca X-sight X-ray microanalysis device (Oxford Instruments, England). The vacuum in the chamber was $\sim 10^{-6}$ Torr.

The pure rhenium surface turned out to be smooth, with microrelief in the form of long strips $2-3\,\mu\mathrm{m}$ wide along the rolling direction; on a smaller scale, point defects with a characteristic size $100-200\,\mathrm{nm}$, occupying an area fraction of the order of 5 %, were observed. The results of the elemental analysis confirmed the composition of the ribbon of 100 % rhenium with the presence of minor organic contamination on the surface.

2. Creation of a coating of yttrium oxide on the cathode

The yttrium oxide coating was mechanically applied to the rhenium surface in the form of yttrium trinitrate $\mathrm{Y(NO_3)_3}$. To do this, a sample of pure yttrium was dissolved in 5 % nitric acid, and the resulting solution was evaporated to a thick paste, and then it was applied to the surface of the rhenium ribbon at room temperature. Then the ribbon was dried, placed in a vacuum chamber and heated in a high vacuum. In this case, the $\mathrm{Y(NO_3)_3}$ molecules decomposed, nitrogen and oxygen were desorbed, and yttrium oxide remained on the surface, most likely of the composition $\mathrm{Y_2O_3}$. This method allowed either to cover the entire surface with a uniform layer, or to create yttrium oxide „spots" of different sizes in the range $(1-10)\,\mathrm{mm}^2$. The layer thickness was $20-40\,\mu\mathrm{m}$ according to our estimates, and it was visually homogeneous. The layer thickness was estimated as follows: ~ 5 mg of yttrium was dissolved in acid, and after evaporation of water, the resulting paste was completely applied to both sides of the tape. Knowing the area of the applied coating and the density of yttrium oxide, it is possible (approximately) to estimate the thickness of the resulting layer.

However, when observed with a micropyrometer, it was seen that when yttrium oxide was first applied, the surface was heterogeneous, and there were spots with a temperature difference of 30−40 K. The ribbons were then removed from the vacuum chamber and yttrium oxide was re-applied to them according to the procedure described above. At the same time, the situation changed: the surface turned out to be homogeneous in temperature over the entire pyrometry range with an accuracy of $\pm 5\,\mathrm{K}$. Further application of the oxide film did not lead to any qualitative changes.

3. Results

There is practically no data on the work function of rhenium-yttrium cathodes in the literature, although data on the existence of such cathodes are available [6]. This makes it difficult to use them in the design of installations, since it is not possible to correctly determine the thermal load on the assembly node and the values of the emission currents.

In this regard, we conducted direct measurements of the work function of rhenium-yttrium cathodes using the Richardson direct line method [9]. This method requires measuring the absolute temperatures of the emitting sample. In this experiment, only brightness temperature values were measured by pyrometry. To convert it to the true temperature, it is necessary to know the emissivity ε

of the studied sample. There are no reference data on this value in the literature, there are only data for the iridium-yttrium oxide film system, which we measured in Ref. [7], and data for bulk yttrium trioxide, which differ greatly in magnitude [10, 11]. Note that a thin dielectric film on a metal surface can differ greatly from a bulk material in emissivity due to the electric fields generated by the contact potential difference and penetrating deep into the bulk of the dielectric [12]. In this paper, we used the value $\varepsilon = 0.6$, which we previously determined for thin films of yttrium oxide on iridium [7].

3.1. Determination of the true temperature of a rhenium cathode with a yttrium oxide film

Coating the rhenium ribbon with yttrium oxide on both sides to a homogeneous layer resulted in a decrease in its brightness temperature by $\sim 100\,\mathrm{K}$ compared with the temperature of the pure sample (Fig. 2).

Let's use a well-known expression connecting the true T_t and the brightness T_b temperatures [13]:

$$1/T_b - 1/T_t = (\lambda/c)\ln(1/\varepsilon), \qquad (1)$$

where $\lambda = 6.65 \cdot 10^{-7}\,\mathrm{m}$ is the wavelength at which the brightness temperature was measured; $c = 1.438 \cdot 10^{-2}\,\mathrm{m{\cdot}K}$ is the Wien constant; ε is the emissivity of the sample. Let's take value of emissivity from our study [7], which defines the emissivity of a film made of yttrium oxide on iridium $\varepsilon = 0.6$. For example, for $T_b = 1523\,\mathrm{K}$ in the case of a yttrium oxide film based on rhenium and taking into account $\varepsilon = 0.6$, $T_t = 1580\,\mathrm{K}$ was obtained, although for the same pure rhenium tape, $T_t = 1740\,\mathrm{K}$ was obtained, i.e., the true temperature dropped by $\Delta T = 160\,\mathrm{K}$.

It should be noted that in the case of the yttrium oxide film on iridium, the true temperature decreased by $\sim 250\,\mathrm{K}$ [7], and it decreased by $\sim 160\,\mathrm{K}$ on rhenium; this is due to the fact that $\varepsilon_{\mathrm{Re}} > \varepsilon_{\mathrm{Ir}}$ [10]. We observed similar results earlier in the formation of graphite films on rhodium: a film with a thickness of only $\sim 30\,\mathrm{nm}$ reduced the true temperature of the ribbon sample by $400\,\mathrm{K}$ (!) due to a sharp increase in the emissivity by almost three times [14]. This is due to the fact that the central part of the heated ribbon lost power almost exclusively due to radiation.

3.2. Determination of the work function of rhenium cathodes coated with yttrium oxide

A film coating of yttrium oxide was created along its entire length on both sides on a rhenium ribbon purified as described above. The Richardson equation [9] was used to determine the work function:

$$I = (1 - R)A_0 \cdot s \cdot T^2 \exp(-e\varphi/kT), \qquad (2)$$

where I is the measured thermal emission current, R is the electron reflection coefficient from the surface, $A_0 = 120\,\mathrm{A \cdot cm^{-2} \cdot K^{-2}}$ is the universal constant (Richardson constant), k is the Boltzmann constant, s is the area of the emitting surface.

Fig. 3 shows the dependence of the thermionic current from a rhenium sample twice coated with yttrium oxide on the temperature of the ribbon (curve *1*). For comparison, a similar dependence is shown for pure rhenium (curve *2*). It can be seen that the coating with yttrium oxide increases the thermionic emission by more than four orders of magnitude. From the slope of the graph $\ln(I/T^2) = f(1/kT)$, we found the Richardson's work function $e\varphi = (3.4 \pm 0.1)\,\mathrm{eV}$. It should be noted that the same work function was obtained using the full current method, using the Richardson direct formula after substituting the true temperature, the measured thermionic emission current, taking into account $A_0 = 120\,\mathrm{A \cdot cm^{-2} \cdot K^{-2}}$, assuming that $R = 0$ and taking

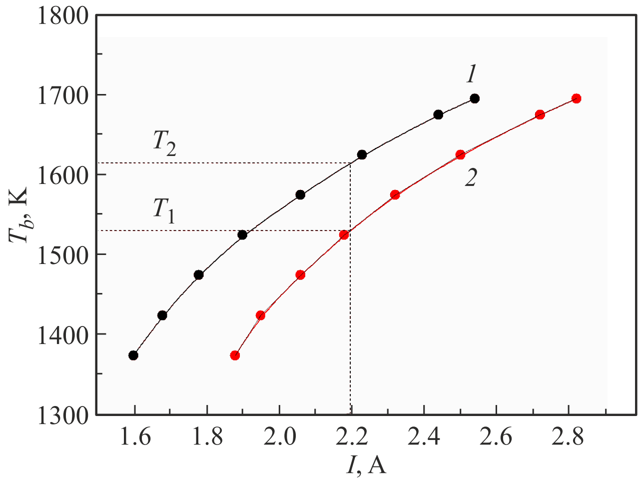

Figure 2. Dependence of the brightness temperature of pure rhenium (*1*) and a rhenium sample coated with yttrium oxide (*2*) on the ribbon heating current.

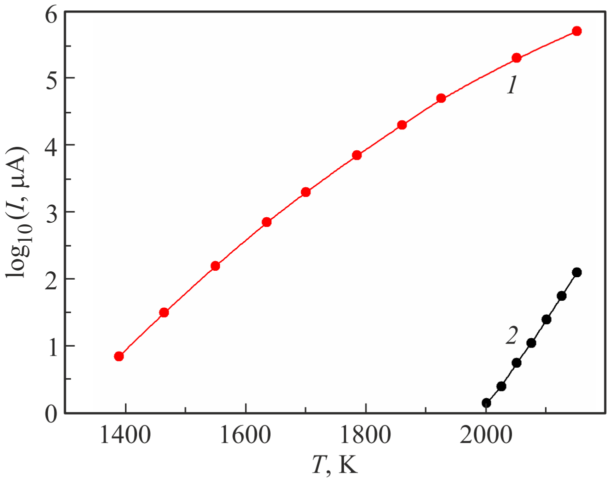

Figure 3. Dependence of the thermionic current of a rhenium sample coated with yttrium oxide (*1*) and pure rhenium (*2*) on temperature.

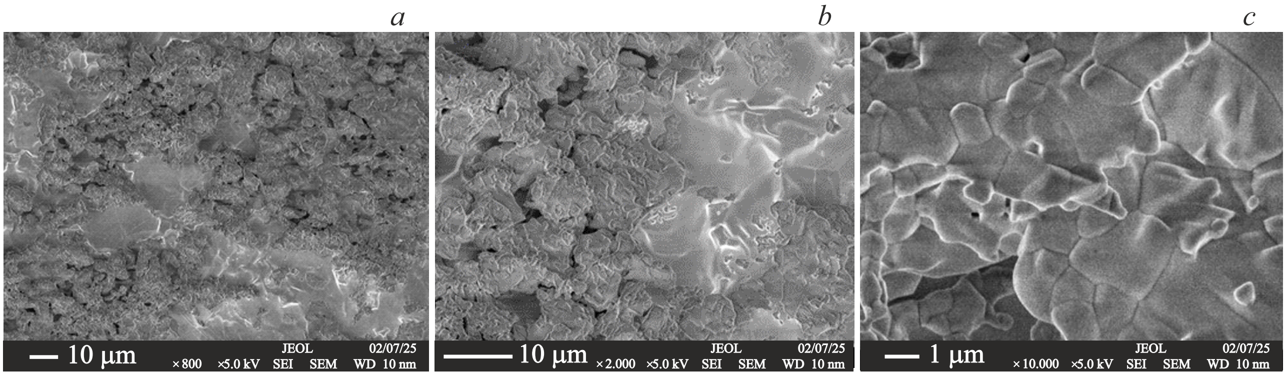

Figure 4. Electronic micrographs of the surface of a rhenium ribbon activated with yttrium oxide. The scale of the micrographs *a* and *c* differ by a factor of 10.

into account the fact that there was an electrode with a grid window in front of the collector $7 \times 20\,\mathrm{mm}$ — this allowed for almost complete collection of thermoelectrons from the ribbon over an emitting area of $7 \times 1\,\mathrm{mm} = 0.07\,\mathrm{cm}^2$.

In addition, using the formula (2), it is possible to find the difference in yield between pure rhenium and rhenium coated with yttrium oxide by measuring the thermal emission current from pure rhenium I_1 and from a sample with yttrium oxide I_2 at the same temperature. In this case $\ln(I_2/I_1) = \Delta e\varphi/kT$. For this case, $\Delta e\varphi = 1.8\,\mathrm{eV}$; knowing $e\varphi$ pure rhenium $(5.15\,\mathrm{eV})$, we obtain $e\varphi = 3.4\,\mathrm{eV}$ for rhenium with yttrium oxide.

3.3. Surface topography of rhenium cathodes coated with yttrium oxide

The surface topography was measured using an electron microscope in a wide range of scales from hundreds of microns to hundreds of nanometers. The measurement results are shown in Fig. 4.

It can be seen that at all scales the surface is significantly heterogeneous and very developed: it is covered with the similarity of „rosettes“, which have the character of fractals, reproducing in shape as the scale of the examination increases. According to microanalysis data, these „rosettes“ are formed by yttrium oxide, which forms on the surface during the thermal decomposition of trinitrate and the desorption of gases that make up its composition.

Such a complex topography raises the question of the nature of the measured Richardson's work function. Apparently, for such a developed surface, it is incorrect to consider it a thermodynamic constant, since the size of the emitting surface area included in the Richardson equation is unknown. It should be considered only an effective work function that describes the actual thermal emission properties, but should be used with caution in more nuanced studies of processes in the adsorption layer. In our case, a good coincidence of the yttrium oxide yield on rhenium, determined from the Richardson graph and the total current method, indicates that the actual emission area from the ribbon is close to the value $S = 0.07\,\mathrm{cm}^2$.

3.4. Elemental composition of the surface of film cathodes Re-YOx

The elemental composition of the film was determined by X-ray microanalysis. The depth of probing is determined by the depth of penetration of the primary beam of exciting electrons with an energy of 30 keV, which is on the order of 100−150 nm [15]. The measurement results are shown in the table.

As can be seen, oxygen and yttrium are mainly present on the surface, as well as rhenium in trace amounts. This means that the film has an almost continuous character and high-temperature heating up to 2500 K does not lead to the formation of mixed oxides or intermetallides, as one might expect.

It should be noted that the measured elemental composition cannot be attributed in any way to the traditionally described trioxide Y_2O_3, rather, this composition can be described by the formula YO_3, which is not observed in traditional chemistry. It should be noted that these measurements were not carried out in a high-vacuum chamber directly when the cathode was heated, but at room temperature after its transfer through the atmosphere. It is very likely that the measured oxide composition is oxygen-rich compared to what is actually available in working condition. So, earlier, when studying the iridium-yttrium cathode, a significant increase in its work function was

The elemental composition of the film, measured by X-ray microanalysis

Element	Concentration, at.%
O (K)	74.05
Y (L)	24.32
Re (M)	1.63

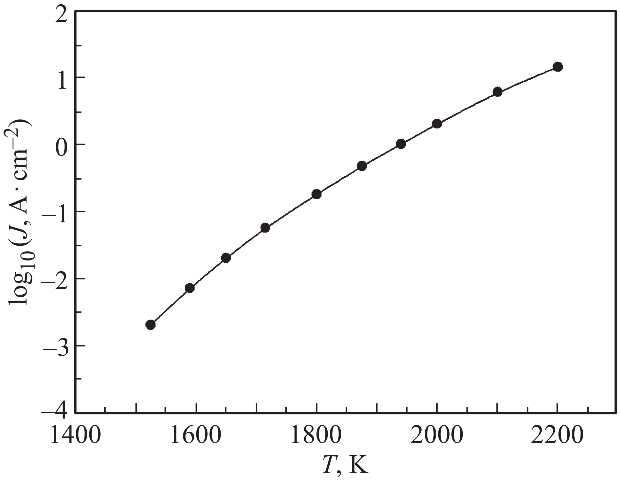

Figure 5. Temperature dependence of the current density J of a rhenium sample coated with yttrium oxide.

observed with a deterioration in the vacuum due to the influx of atmospheric gases, presumably due to the creation of oxygen excess in the surface composition of yttrium oxide.

3.5. Thermal stability of the film cathode and thermal emission current density

From a practical point of view, the main advantage of rhenium-yttrium cathodes over iridium-yttrium cathodes is the ability to operate at extremely high temperatures due to the high melting point of rhenium ($T \approx 3463\,\mathrm{K}$) [16]. Thus, iridium-yttrium cathodes, as a rule, burn out at $T = 2200{-}2300\,\mathrm{K}$, which corresponds well to the known technical limit of thermal stability of iridium wires and ribbons. For rhenium, this limit is 2500–2600 K, it is determined by the rate of rhenium sublimation from the surface, which makes it possible to obtain significantly high electron emission currents.

The ribbon was heated at $T = 2500\,\mathrm{K}$, and the thermionic emission current was measured at $T = 2000\,\mathrm{K}$, it was stable and did not change after high-temperature heating — this indirectly indicates the stability (non-destruction) of the film coating and the constancy of the work function, which allows calculating the value of the expected thermionic emission at $T = 2500\,\mathrm{K}$ using the Richardson formula. This thermal stability is primarily due to the high melting point of yttrium oxide ($T \approx 2688\,\mathrm{K}$) [16]. It should be noted that the calculated current density at $T = 2500\,\mathrm{K}$ is $J = 100\,\mathrm{A \cdot cm^{-2}}$, whereas in the experiment we recorded a current not exceeding 20 mA due to space charge limitations in accordance with the well-known Henry-Langmuir law [9].

The formation of a film of yttrium oxide on rhenium increases its thermal emissivity over the entire temperature range. The temperature dependence of the current density J of the cathode can be found from the data on the work function of the film cathodes and their true temperatures using the Richardson equation (Fig. 5).

3.6. Work of cathodes in medium vacuum conditions ($\sim 10^{-5}$ Torr)

A significant deterioration in the thermionic emission of iridium cathodes activated with yttrium oxide was detected when operating in medium vacuum $\sim 10^{-5}$, Torr [7], which is of great practical importance. Cathodes demonstrated very good reproducibility of thermionic parameters in ultra-high vacuum at $P \leq 10^{-8}$ Torr.

For the rhenium-yttrium cathode, such a decrease in the emission capacity also occurs. Thus, the deterioration of vacuum conditions to $5 \cdot 10^{-5}$ Torr due to the influx of atmospheric gases or pure oxygen at the cathode temperature $T \leq 1500\,\mathrm{K}$ leads to a decrease in the amount of thermionic emission by more than 100 times.

Pumping out gases does not lead to a complete restoration of emission at $T < 1500\,\mathrm{K}$, this requires a temperature rise to 1700–1800 K, which leads to an abrupt increase in the emission current by several orders of magnitude. Apparently, as in the case of iridium, the oxygen-deficient phase of yttrium oxide, which occurs during high-temperature heating in a vacuum, has high emission properties. It is known that oxygen adsorbed on the surface of metals significantly increases the work function, sharply reducing the thermal emission current [3,5]. Heating above 1700 K leads to the restoration of the emission capacity of the cathode, apparently due to the thermal desorption of excess oxygen. This means that under such conditions, the traditional cathode current stabilization system due to emission stabilization is relatively ineffective and can lead to rapid cathode burnout.

Conclusion

Thus, a laboratory technology for the manufacture of rhenium cathodes activated with yttrium oxide has been developed, and their effectiveness over a wide temperature range, including extremely high temperatures, has been shown. The work function of the surface $e\varphi = 3.4\,\mathrm{eV}$ has been determined. The high thermal stability of the cathodes and the potential for obtaining extremely high thermal emission current densities up to $100\,\mathrm{A \cdot cm^{-2}}$ and higher are shown. The temperature and pressure ranges at which the cathode is able to operate effectively in medium vacuum conditions have been identified.

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Conflict of interest

The authors declare no conflict of interest.

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