

Carbon-coated electron field emitters

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The properties of field electron emitters made of iridium and rhenium, whose surface is coated with carbon by decomposition of benzene molecules on the surface, are studied. The stability of the emission characteristics and the stability of the obtained emitters to the adsorption of residual gas molecules and ion bombardment are shown. The coating is obtained either in the form of a monoatomic graphene film on the flat faces of the emitter, or in the form of graphite growths. The field electron emission is localized on the edges and corners of the faceted graphite outgrowth. After adsorption of alkaline and alkaline earth metals onto the carbon coating, an abnormally large increase in emissions from flat faces and localization of emissions on graphene-coated faces occurs. The emission amplification occurs in the presence of alkali metal atoms, both on the surface and only under the graphene film.

Keywords: electron emission, carbon, iridium, rhenium, alkali metals, barium, intercalation.

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Introduction

Field electron emitters have unique properties for obtaining and focusing electron beams with a high current density [1–3]. The use of field electron emitters creates good prospects for their use in electron microscopy, microanalysis and other types of electron beam techniques and technologies. Electronic emitters in the form of a tip made of refractory metal, most often made of tungsten, have become the most widespread. Such emitters are quite simple to manufacture, they are easy to clean from bulk and surface contamination by high-temperature heating in vacuum. Metal point emitters make it possible to obtain narrow electron beams with a record high current density of [1,2] and have a number of other advantages.

The main disadvantage of metal field emitters is their unstable operation in insufficiently good vacuum conditions. The adsorption of residual gas molecules leads to a change in the work function of the emitter surface. Bombardment of the surface with ions formed during electron emission leads to a change in the surface relief and, accordingly, to a change in the local electric field strength. Considering the exponential dependence of the field electron emission current density on the field strength and work function, such changes cause significant deviations of the emission current and can lead to the death of the emitter.

Emitters made of various carbon materials [4–6] have greater resistance to the listed factors of instability of operation. Compared with metals, carbon materials are more resistant to factors affecting the stability of the emitter, such as gas adsorption, ion bombardment, shape change due to surface self-diffusion.

In contrast to metals, the production of a carbon tip (graphite, diamond) seems to be a difficult task. Therefore,

in many works, the field electron emission of emitters consisting of a conductive substrate and various carbon coatings deposited on it is studied. And specifically there are works in which carbon coatings are designed to protect the surface of the metal tip [6].

One of the ways to obtain a graphene coating is the thermal decomposition of benzene molecules on the surface of metals [7]. Thermal decomposition of benzene on the quasi-spherical monocrystalline surface of the field emitter also leads to the formation of graphene nanostructures. At the tip (field electron emitter), a monoatomic graphene film is formed on flat densely packed faces or graphene growths [8,9]. The work function of the field emitter surface, calculated from the Fowler–Nordheim characteristics, decreases to 4.4 eV on iridium and to 4.3 eV on rhenium.

The formation of graphene on the flat surfaces of iridium and rhenium emitters was confirmed by the appearance of two phases of field desorption of alkali metals. The first phase is associated with the desorption of alkali metals adsorbed on the surface of the emitter, and the second phase (at a higher field strength) appeared due to the release of intercalated atoms from-under graphene films. After removing alkali metal atoms only from the emitter surface by heating the emitter at a temperature below 1000 K, the work function returned to the work function of the graphene film before the alkali metal was applied and only one phase of field desorption was observed, coinciding in field strength with the second phase.

The emission characteristics of carbon-coated emitters in the Fowler–Nordheim coordinates were straight and showed good resistance to the adsorption of residual gases and to ion bombardment. The characteristics and emission images did not change after exposure of the emitter for several days in a vacuum chamber without pumping

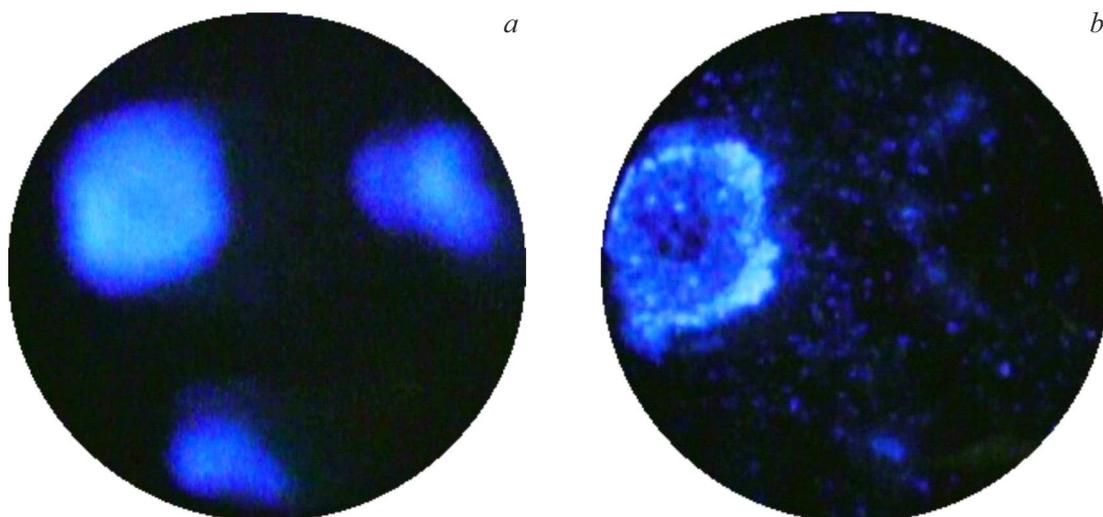


Figure 1. *a* — field electronic image of an iridium emitter with a sodium monolayer on a carbon coating (emitter voltage -3 kV); *b* — field desorption image (flash of sodium ions at emitter voltage $+15$ kV).

(pressure increased to 10^{-3} Torr). Experiments with the deposition of alkali metals were carried out on the same carbon-coated emitter for a month. Warming up the emitters to remove adsorbates returned the emission images and characteristics to their original state.

The adsorption of alkaline and alkaline earth metals significantly changed the emission properties of carbon-coated emitters. The influence was exerted by both atoms on the surface and atoms intercalated into carbon formations. The field strength required for emission decreased and the distribution of emissions over the emission surface changed. Localization of the emission was observed on certain areas of the surface.

The purpose of this work is to further study the properties of field electronic emitters, the emission surface of which is obtained by decomposition of benzene molecules on metal and the effect of adsorption of alkaline (sodium) and alkaline earth (barium) atoms on the emission properties of the obtained emitters.

1. Experimental procedure

The studies were carried out in a field emission microscope using the techniques of field electron microscopy, measurement of the characteristics of field electron emission and continuous field desorption microscopy. Using these methods, it is possible to study the structure and composition of the surface of the sample and adsorbate, to study the emission and operational characteristics of emitters. Changes in the surface work function were calculated from the Fowler–Nordheim characteristics for field electron emission currents. The electrons and ions emitted by the sample and the emission images formed by them were recorded by a detector consisting of two microchannel plates with a diameter of 56 mm and a fluorescent screen.

Iridium and rhenium were used as emitter materials. These metals do not form chemical compounds with carbon. Iridium practically does not dissolve carbon in volume, rhenium forms solid solutions with carbon. Samples of iridium and rhenium in the form of a tip with a vertex radius of about 500 nm were made of wire by electrochemical etching. The resulting points were annealed in vacuum at $T = 2500$ K, as a result of which a single crystal of equilibrium shape with a radius of curvature of the order of 500–1000 nm was formed at the tip of the tip.

Carbon coatings were obtained by holding a heated tip ($T = 1200$ – 1900 K) in benzene vapors (at pressure 10^{-8} – 10^{-5} Torr) [7]. Depending on the exposure modes, a monatomic graphene film on flat densely packed faces or graphene growths are formed in benzene vapor at the tip of the tip.

2. Experimental results

The surface of a pure metal tip heated at a high temperature consists of flat crystal faces and surrounding concentric steps of monoatomic height. Field electron emission comes mainly from the transition regions between the faces and is practically absent from the flat faces, which is due to a weaker electric field on a flat surface and higher work function of densely packed planes.

During the adsorption of sodium and barium atoms, a homogeneous emission was detected from flat densely packed faces, in particular the face (100), of an iridium emitter with a graphene coating. In the case of sodium, the homogeneity of emission was observed in the presence of alkali metal atoms on the surface and in the intercalated state (Fig. 1, *a*). After removing sodium from the surface with a slight warming up, the homogeneity of the emission disappeared. The work function returned almost to the

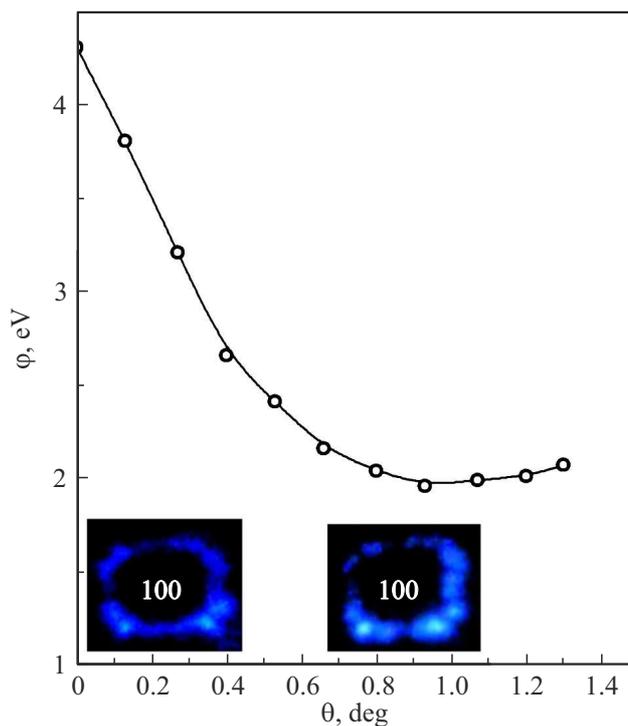


Figure 2. Dependence of the work function of the face of (100) iridium emitter with graphene film on the degree of barium coating. The inserts have electronic field images corresponding to $\theta = 0$ and 0.6 .

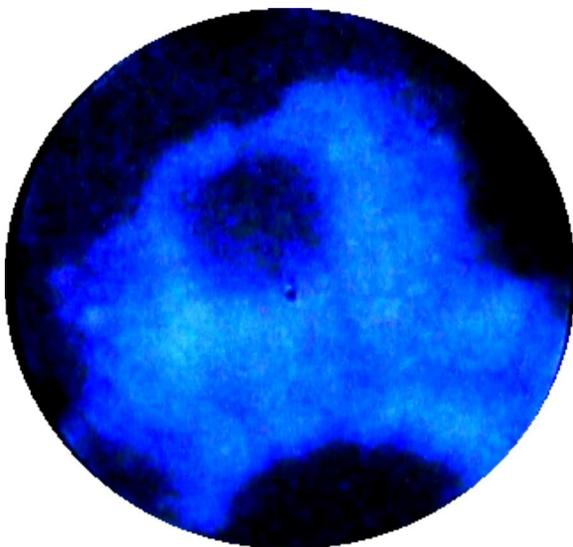


Figure 3. Field electronic image of an iridium emitter with a barium monolayer on a carbon coating.

original value of $\varphi = 4.3$ eV, but was slightly less by 0.1 eV. However, the sodium atoms intercalated under graphene remained under graphene. This was confirmed by field desorption of sodium atoms in the mode of field desorption microscopy (Fig. 1, *b*).

Figs. 2 and 3 illustrate the process of formation of the emission surface of an iridium tip with graphene and barium on the surface. Fig. 2 shows the change in the work function of the iridium yield with a graphene film with an increase in the surface concentration of barium atoms. Barium adsorption and measurement of the work function were carried out at room temperature. The inserts show field electronic images of the emitter at concentrations of barium atoms less than the corresponding minimum of the work function. Emission images are practically independent of the amount of barium. Emits only the area (ring) around the face (100). At a higher concentration of barium (close to the monolayer), the emission region expands significantly (Fig. 3).

Fig. 4 shows the changes in the distribution of electron emission along the face of (100) iridium in a horizontal section with a carbon film (Fig. 4, *a*) and adsorbed barium after annealing at $T = 900$ K (Fig. 4, *b*) and 1200 K (Fig. 4, *c*). Prior to annealing, as follows from Fig. 2, the electron emission is localized at the edges of the (100) iridium face region, which corresponds to the distribution shown in Fig. 4, *a*. The annealing of the emitter significantly changes the distribution of the electron emission. Initially, there is an expansion of the emission region inside the face (Fig. 4, *b*), up to the filling of the entire face (Fig. 4, *c*). The work

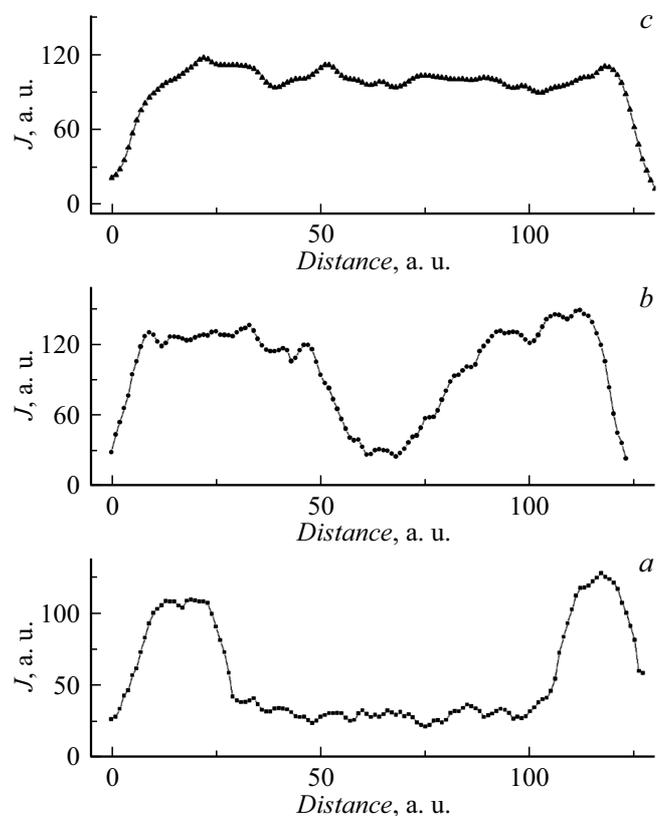


Figure 4. Distribution of electrons emitted from the face of a (100) graphene-coated iridium emitter with intercalated barium: *a* — before annealing, *b* — after annealing at $T = 900$ K, *c* — after annealing at $T = 1200$ K.

function decreases to a value of 3.9–4.0 eV. Further heating ($T = 1600$ K) led to the disappearance of the emission from the central region of the face, the contraction of the emitting region to the edges of the face (100) and an increase in the work function to a value of 4.3 eV.

3. Discussion of the results

For practical applications, an emitter is of interest, the emission distribution of which is shown in Fig. 4, *c* since the emission from a site of about 10 nm in size, with a small spread of electrons along the departure angle characteristic of field electron emission, is promising for electron-optical applications.

The emitter work function corresponding to Fig. 4, *c* (4 eV) and the absence of barium field desorption at field strength up to 10^8 V/cm show that there are no adsorbed barium atoms on the surface. At temperatures of 900–1200 K part of barium is desorbed, the other part is intercalated by graphene film [10,11]. There is no thermal desorption from the intercalated state at these temperatures. At a temperature of 1600 K and above, intercalated barium leaves graphene and is desorbed, which causes an increase in the work function to the initial value of the iridium–graphene system. At temperatures above 2000 K the graphene film is destroyed.

A homogeneous emission from the face of (100) iridium with a graphene film and adsorbed sodium and barium atoms was obtained, despite an increase in the field strength from the center of the face to the edges. The change in the work function may be due to a change in the double electric layer on the surface from due to the redistribution of the electron density and from due to changes in the distance of the graphene film and intercalated atoms from the surface. One can assume that the change in the local field strength is compensated by changing the work function, i.e. the double electric layer, for example, by changing the distance of the graphene film from the iridium surface under the action of an electric field. The graphene film can move away from the iridium surface at distances up to 1 nm and bend without disturbing the structure of [12].

Conclusion

Thus, the properties of field electron emitters obtained by thermal decomposition of benzene molecules on the surface with subsequent adsorption of sodium and barium have been studied. The possibility of obtaining an emission localized and uniformly distributed on a densely packed plane, at the tip of the tip, during intercalation of barium with a graphene film is shown. Emitters with a carbon film show the stability of emission characteristics during operation and prolonged exposure to residual gases in the atmosphere.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

- [1] *Nenakalivaemiye Katody*, ed. by M.I. Elinson (Sovietskoye radio, M., 1974) (in Russian)
- [2] G.N. Fursey. *Avtoelektronnaya emissiya* (Lan', SPb, 2012) (in Russian)
- [3] *Nanofabrication Using Focused Ion and Electron. Principles and Applications*, ed. by I. Utke, S. Moshkalev, P. Russell (Univer. Press, Oxford, 2012)
- [4] N.S. Xu, S.E. Huq. *Mater. Sci. Engineer.: Reports*, **48** (2–5), 47 (2005).
- [5] E.P. Sheshin, *Struktura poverkhnosti i avtoemissionnye svoystva uglerodnykh materialov* (Izd-vo MFTI, M., 2001) (in Russian)
- [6] G.G. Sominskii, T.A. Tumareva, E.P. Taradaev, A.A. Rukavitsyna, M.E. Givargizov, A.N. Stepanova. *Tech. Phys.*, **64** (2), 270–273 (2019). DOI: 10.1134/S106378421902021X
- [7] N.R. Gall, E.V. Rutkov. *Fizika poverkhnosti tverdykh tel. Grafen i grafit na poverkhnosti tverdykh tel: ucheb. posobie (manual)* (Izd-vo Politekh. un-ta, SPb, 2013), p. 7. (in Russian).
- [8] D.P. Bernatskii, V.G. Pavlov. *Tech. Phys.*, **62** (11), 1731–1735 (2017).
- [9] D.P. Bernatsky, V.G. Pavlov. *Pis'ma v ZhTF*, **47** (18), 18 (2021) (in Russian)
DOI: 10.21883/PJTF.2021.18.51466.18854
- [10] E.V. Rut'kov, A.Ya. Tontegode. *FTT*, **32** (10), 2960 (1990) (in Russian).
- [11] E.V. Rut'kov, N.R. Gall. In: *Physics and Applications of Graphene — Experiments*, ed. by S. Mikhailov (Intech, Rijeca, 2011), p. 209.
- [12] I.V. Makarenko, A.N. Titkov, Z. Waqar, Ph. Dumas, E.V. Rut'kov, N.R. Gall. *FTT*, **49** (2), 357 (2007) (in Russian).