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Modification of the emission surface of a carbonized iridium field emitter during the adsorption of barium atoms

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Field electron microscopy was used to study the modification of the emission surface of a carbonized iridium field emitter when the concentration of barium atoms on the surface changes within the monolayer coating. When barium atoms are adsorbed at a temperature of $T = 300\,\text{K}$, no significant changes in the field electronic images of the emission surface are observed. The formation of barium islands on graphene in the region of the (100) iridium face at the annealing temperature $T = 1200\,\text{K}$ was detected. At the annealing temperature $T = 1500\,\text{K}$, the barium island is dissolved and graphene is intercalated by barium atoms. The emission surface increases and becomes uniform in emission.

Keywords: field electron emission, carbon, iridium, intercalation, field emitters.

The use of field emitters in various areas of science and technology is an important scientific and practical task [1-3]. Coating of metallic field electron emitters with carbon significantly improves their operation stability [3–5]. Value and stability of field electron emission current is heavily affected by operation of the work function of the emitter surface. It is well known that surface absorption of atoms of alkaline and alkaline-earth metals reduces the work function. In [6] it was shown that, during cesium atom adsorption onto the surface of a carbonized iridium field emitter at the temperature of $T = 300\,\text{K}$, cesium atoms can be located not only on the graphene surface, but also under the graphene layer as a result of intercalation. Both phases affect the work function. However, cesium, the same as other alkaline metals, is weakly bonded to the metal surface. Bond is chiefly provided by electrostatic forces: a valence electron passes into the metal and the forming ion is attracted to the metal by mirror reflection forces. Cesium atoms were easy to remove from the surface either by heating or by desorption by electric field.

Up to now, field electron emission of metallic emitters with a graphene film was studied only with adsorption of alkaline metals. During adsorption of divalent alkaline-earth metals, one valence electron passes into the metal, while the other electron remains in the atom and provides a stronger bond to the surface than in the case of alkaline metals. Moreover, as distinct from electrostatic repulsion of alkaline metal atoms, adsorbed on the metal or graphene surface, atoms of alkaline-earth metals attract to each other and can form two-dimensional islands [7,8]. The bond in the island additionally increases the desorption energy and coating stability. The study of impact of adsorption of electropositive atoms, more strongly bound to the surface, barium atoms in particular, onto the emission properties of a carbonized

iridium field emitter is of scientific and practical interest. The study was carried out using a field emission (electron and desorption) microscope [9], where a magnifying surface image ($\sim 10^5$ times) is obtained using a projection of the sample surface by emitted electrons on a luminescent screen. An assembly of two microchannel plates 56 mm in diameter is located in front of the luminescent screen to amplify weak currents from the field emitter surface. The following was performed in the electronic mode: measurement of the current of field electron emission and plotting of Fowler-Nordheim charts for determination the surface work function and field emitter parameters. Intensity of electric field, necessary for desorption, and desorption areas were determined in the desorption mode.

Field emitter samples in the form of a spike were made of iridium wire by electrochemical etching. Then the made samples were annealed in high vacuum (at pressure $p \sim 5 \cdot 10^{-9}\,\text{Torr}$) at the temperature of $T = 2300\,\text{K}$. During annealing, the emitter was cleaned and a single-crystal quasi-spherical top of the spike with a radius of about 500 nm was formed, with an exit to the surfaces of flat low-index faces. Formation of a single-crystal emitter top was monitored according to appearance of field electron images typical of iridium. Carbon coating was formed on the emitters in benzene vapors at pressure $\sim 10^{-5}\,\text{Torr}$ and sample temperature of 1700 K [10]. Carbon atoms on the iridium surface, forming due to benzene dissociation, form a single-layer graphene coating in the field of low-index flat faces. In the transient region from the flat face to a curvilinear surface there are a number of monoatomic iridium steps where several graphene layers may form and a field electronic image, typical of a ribbed crystal, can be obtained [11]. Graphene formation on the surface of the
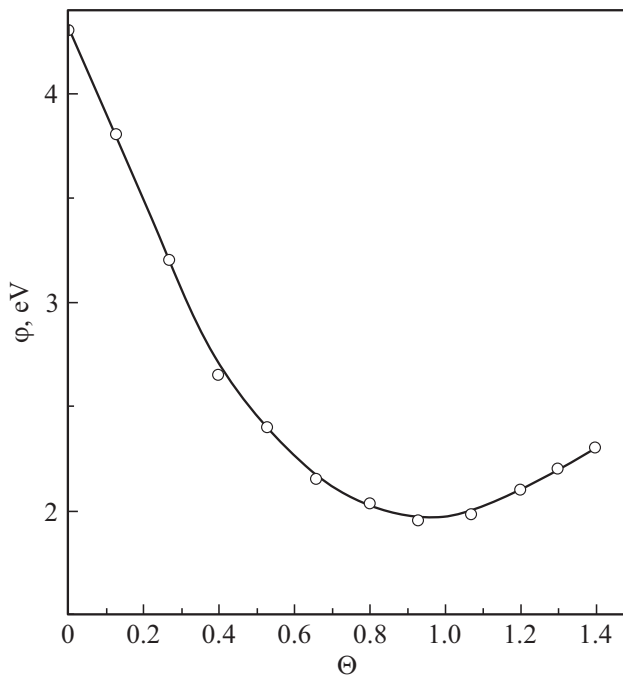
Figure 1. Dependence of the work function of carbonized iridium field emitter on degree of barium coating at $T = 300$ K.

iridium field emitter is accompanied with a decrease of the work function to $\varphi = 4.3$ eV.

During deposition of barium atoms onto the surface of the iridium field emitter with a graphene film at the emitter temperature of $T = 300$ K, video recording of the field electronic image was performed and the work function was calculated using the Fowler-Nordheim characteristics [12,13]. The surface work function φ upon increase of the degree of surface coating Θ with barium decreased from $\varphi = 4.3$ eV (carbonized emitter) to $\varphi = 2.3$ eV (multilayer barium coating), passing through the work function minimum $\varphi = 2.0$ eV at the optimal coating ($\Theta = 1$). Dependence on field emitter work function on degree of surface coating with barium is shown in Fig. 1.

Fig. 2 shows the field electronic images of the field emitter surface. The image at room temperature virtually did not depend on the degree of surface coating with barium (Fig. 2, a). Only the necessary voltage for assurance of field electron emission changed.

After application of multilayer barium coating on the emitter surface, the emitter was annealed with recording of field electronic images and calculation of the surface work function. Fig. 2, b shows the field electronic image of the field emitter surface in the region of the face (100) after annealing at temperature $T = 1200$ K for 20 s. At this temperature, barium atoms migrate along the surface and barium islands form in the central region of the face (100). Intercalation of graphene with barium was studied in papers [7,8] on flat iridium samples (texturized strips with chief exit of the face (111)) with graphene during barium adsorption, the formation of two-dimensional barium islands in the temperature region $1000 < T < 1500$ K was explained. It was assumed that an activation barrier exists on the island boundary for the migrating barium atoms. It has been shown that at the iridium temperature of $T > 900$ K the barium atoms migrate along the surface and graphene is intercalated with barium atoms, while at $T > 1600$ K the barium atoms are desorbed not only from the surface, but from the intercalated state as well. The work function of the iridium field emitter surface after annealing at $T = 1200$ K has increased from 2.3 eV to the value of 3.9 eV. Considering the difference in desorption energy of a single barium atom on graphene (1.9 eV) and energy of desorption from the bound state in the barium island on graphene (3.4 eV) [7], it should be assumed that at $T = 1200$ K and above there are virtually not single barium atoms, adsorbed on the surface, and the work function is determined by the barium islands.

Fig. 2, c shows the field electronic image of the field emitter surface in the region of the face (100) Ir after annealing of the emitter with a barium monolayer at the temperature of $T = 1500$ K. Barium islands on graphene do not form at this temperature, intercalation of graphene with barium atoms takes place and single barium atoms are desorbed from the graphene. The surface work function,
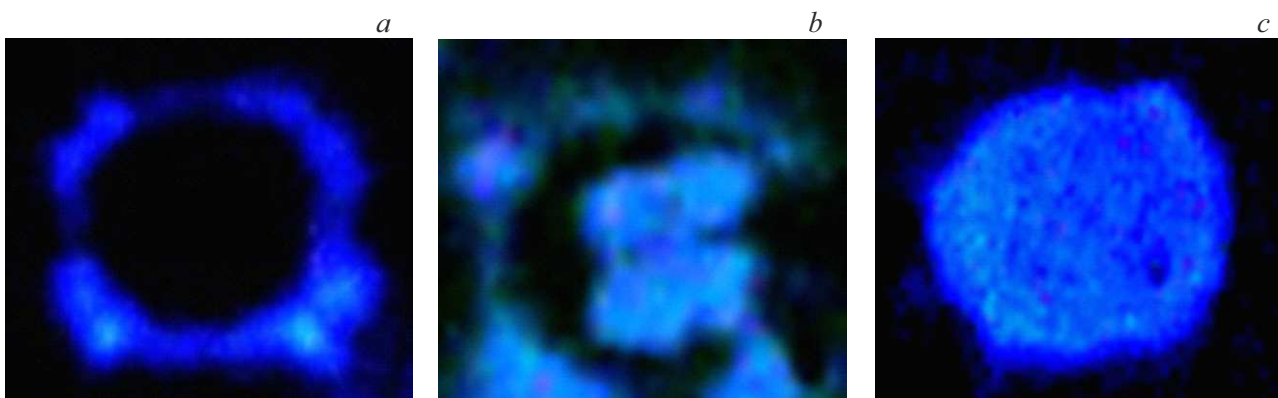

Figure 2. Field electronic images of the surface of the carbonized iridium field emitter. a — degree of barium coating $\Theta = 0$, $T = 300$ K; b — formation of a barium island, annealing at $T = 1200$ K; c — intercalation of graphene on the face (100) Ir by barium atoms after annealing at $T = 1500$ K.

as compared to the work function at $\Theta = 0$, decreases to $\varphi = 4.0$ eV. The emission surface becomes homogeneous and occupies the whole graphene surface on the face (100). The increased area of the emission surface and homogeneity of field electron emission are related to intercalation of graphene structures, forming on the field emitter surface after carbonization, with barium atoms.

Judging by the invariability of field images and emission characteristics, the graphene layer did not break down with desorption of the intercalated barium atoms up to the temperature of 2000 K. Field desorption of barium atoms, intercalated by graphene from the emitter surface, required a greater electric field intensity ($> 10^{10}$ V/m) than in the case of alkaline metals ($\sim 5 \cdot 10^9$ V/m).

Thus, the study results have shown the possibility of modification of the emission surface of the carbonized iridium field emitter during adsorption of barium atoms. Modification results in a decrease of the work function of the emitter surface, increase of the emission area and more homogeneous emission takes place during the formation of graphene structures on the emitter surface and meeting of conditions of their intercalation with barium atoms. The obtained coating that improves emission properties is more stable in relation to temperature and field loads as compared to coatings obtained with the use of alkaline metals.

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Conflict of interest

The authors declare that they have no conflict of interest.

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