Creating graphene and graphite coatings on metal field electron emitters to improve their characteristics

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Abstract. The growth of graphene and graphite structures during the catalytic dissociation of benzene molecules on the surface of iridium and rhenium field electron emitters was studied using field electron and desorption microscopy. The emission and operational characteristics of the manufactured emitters were studied. The carbon coating increases the resistance of emitters to adsorption of gas molecules and ion bombardment. The grown graphite crystal allows you to get a beam of electrons localized in a narrow angle when emitting from the angle of the crystal. Metal emitters with a carbon coating in relatively poor vacuum conditions have greater stability and longer lifetime compared to metal emitters.

1. Introduction
Point-shaped field electron emitters make it possible to obtain narrow electron beams with a high current density in the beam. Such emitters are very promising for use in various electron beam technologies and experimental techniques [1-3]. The main difficulty to the implementation of field electron emitters is considered to be insufficient stability in poor vacuum conditions.

Refractory metal field electron emitters are most commonly investigated and used [4]. They are resistant to temperature overloads and to mechanical effects of a strong electric field. In addition, metal tips are easily made by chemical or electrolytic etching of a wire or rod. The main obstacle to the introduction of field electronic emitters is considered to be insufficient stability in poor vacuum conditions. The causes of instability are changes in the electron work function during adsorption of residual gas molecules and changes in the local electric field when the surface relief is disturbed by ion bombardment.

Carbon emitters are relatively resistant to adsorption and ion bombardment [5,6]. The main difficulty in using carbon emitters is the difficulty (in comparison to metals) of manufacturing a tip from carbon materials. A possible way to overcome this difficulty may be to use combined emitters, in which the base is a metal tip made in the usual way, and the emission surface is created by applying a carbon coating to the tip. To solve this problem, it is necessary to study the growth features of carbon coatings on the surface of the tip made of potential emitter base materials.

The interaction of carbon and carbon-containing molecules with various metals in a vacuum is fairly well understood [7]. However, these studies were carried out using flat metal surfaces. A monatomic graphene film is formed on flat surfaces of catalytically active metals during decomposition of organic substances, including benzene vapors. The growth of a carbon coating on the surface of a crystal with a large curvature (tip) may have features that differ from the case of a flat surface.
2. Materials and methods

In this paper, we study the growth of the carbon coating on the tips of two metals (iridium, rhenium) by decomposing organic molecules (benzene) on their surface. We also studied the emission and operational properties of the emitters obtained. These metals are selected due to the properties of their interaction with carbon. Both of them do not form bulk carbides. At the same time, iridium practically does not dissolve carbon, and rhenium forms solid solutions with carbon.

The studies were carried out in a vacuum metal installation of a field emission microscope. We used methods of field electron microscopy, continuous field desorption microscopy [8] and measurements of the characteristics of field electron emission. The residual gas pressure did not exceed $10^{-9}$ Torr. Changes in the work function of the surface were calculated from the Fowler-Nordheim current-voltage characteristics. Emission images were recorded with a detector consisting of two microchannel plates with a diameter of 56 mm and a luminescent screen. The distribution of electron trajectories along the angle was determined from field emission images using the ImageJ computer program. A benzene vapor was introduced into the chamber through a needle leak.

The tip-shaped emitters were made of iridium and rhenium wires by electrochemical etching and were annealed in vacuum ($p < 10^{-9}$ Torr) at a temperature of $T = 2500$ K. During annealing, the tip was cleaned and its apex turned into a monocrystal with a hemispherical surface of radius about 500 nm. The cleaning processes and the formation of the tip were controlled by field electronic images. The carbon coating was deposited by exposure the tip heated to $T = 1700$ K in benzene vapor at a pressure of $5 \times 10^{-5}$ Torr [7]. As a result, graphene and graphite structures formed on the surface of the tip. Before and after exposure in benzene vapor, emission images were recorded and the work function of the surface was determined.

3. Results

3.1. Rhenium

Exposure of the rhenium tip in benzene vapor for less than 25 minutes did not change the work function. A similar regime of thermal decomposition of benzene on a flat rhenium surface initially led to the dissolution of carbon in volume [7]. The absence of changes in the rhenium tip at such exposures also seems to be due to the dissolution of carbon atoms in the rhenium volume.

Exposure for more than 25 minutes led to the work function decrease from 4.9 eV to 4.1 eV. The obtained work function (4.1 – 4.2 eV) usually observed for metal surface on which graphene covering was formed [5]. Analysis of field electronic images has shown that a monatomic graphene film was formed on close packed planes of the tip surface.

Heating the rhenium emitter covered with carbon to temperatures of the order of 3000 K did not lead to a change in the field electron image and emission characteristics, which indicates a high thermal stability of the obtained carbon coating.

3.2. Iridium

The surface of the apex of the iridium tip consists of flat faces corresponding to the close packed crystal planes (111) and (100), and the rounded areas surrounding them, consisting of monatomic steps with a decreasing width as they move away from the face. The formation of a carbon coating on the tip surface is different from what occurs on flat samples and occurred in several stages. At the first stage, a graphene film was formed on the crystalline planes (111) and (100). Separate carbon atoms and their clusters remained on the steps surrounding these faces.

At the next stage, after a greater exposure in benzene, the nucleation and growth of graphite layers on the steps began. Then, the graphite coating spread over the entire surface of the tip apex. At the top of the tip grows a graphite crystal. This process is significantly different for flat surfaces, where the formation of a carbon coating is limited to a monatomic graphene film.

When the operating voltage is applied to the emitter, only the angle of the formed graphite crystal emits electrons (see figure 1). A narrow electron beam is formed. Such beams are very promising for various electron-optical applications. Although the obtained emission currents and angular localization
are less than those obtained from metal emitters [9,10], the studied emitters showed greater stability when tested under poor vacuum conditions.

![Field emission image and angular distribution of trajectories](image1)

**Figure 1.** Field emission image (left) and angular distribution of trajectories of electrons emitted from the carbon coated iridium emitter (right)

3.3. *Emission and operational properties*

Measurement of emission characteristics showed good resistance to both adsorption of residual gases and ion bombardment. The characteristics practically did not change after exposure for dozens of days in the atmosphere of residual gases at a pressure of $10^{-3}$ Torr. The characteristics in Fowler-Nordheim coordinates are fairly well approximated by straight lines for both types of emitters under study (see, for example, figure 2).

![Fowler-Nordheim characteristics](image2)

**Figure 2.** Fowler-Nordheim characteristics of iridium and carbon-coated iridium emitters

The heating of the carbon covered rhenium and iridium emitters led to different results. After heating at any possible high temperature and then cooling to room temperature, the carbon coating on
the rhenium emitter remains. At the same time, all carbon could be thermally desorbed from the surface of the iridium tip. The difference can be explained by the possibility of dissolution of carbon atoms in the volume of rhenium [7,11]. When a carbon-coated rhenium emitter is heated, the carbon atoms move from the surface to the volume of the tip. At subsequent cooling carbon atoms return to the surface.

4. Discussion
To explain the observed processes, the following model can be proposed. Benzene molecules dissociate on the surface of the heated emitters. The released carbon atoms form a monoatomic graphene film on planar faces. There is no dissociation of benzene on the graphene film. The formation of a monatomic graphene film completes the process of decomposition of organic molecules on a flat metal surface.

The surface of the crystal tip apex contains stepped and rounded sections. In these areas, the graphene film is not formed. There are individual chemisorbed carbon atoms, their associations, and a clean metal surface. Dissociation continues on stepped surfaces and rounded sections of the surface. The carbon atoms released during dissociation can move along the surface. On the steps adjacent to the planes a graphite layer grows. This process results in the formation of a graphene crystal at the apex of the tip.

5. Conclusion
Metal tips with a carbon coating obtained by decomposition of carbon-containing molecules on their surface can show good characteristics as field electronic emitters. They are more resistant to adsorption of gas molecules and ion bombardment than metal emitters. The graphite crystal formed at the apex of the tip under certain exposure parameters in benzene vapor makes it possible to obtain a narrow electron beam during field emission. The ability of rhenium to dissolve carbon at high temperature contributes to the renewal of the carbon coating after its disappearance.

References
[1] Williams D B and Carter C B 2012 Transmission electron microscopy. A textbook for materials science (NY: Springer) pp 73-91
[2] Hagen W Appl. Phys. A 2014 117 1599–1605
[3] Alyamani A and Lemine O M 2012 Scanning electron microscopy. Ed. Kazmiruk V (Rijeka: Intech) pp 463-472
[4] Fursey G N 2005 Field emission in vacuum micro-electronics (NY: Springer) p 427
[5] Forbes R G 2001 Solid-State Electronics 45 779-808
[6] Sheshin E P 2001 Surface structure and field emission properties of carbon materials (Moscow: MFTI) p 288 (in Russian)
[7] Rut’kov E V and Gall N R 2011 Physics and applications of graphene — experiments. Ed. S Mikhailov (Rijeka: Intech) pp 209-292
[8] Bernatskii D P and Pavlov V G 2009 Bull. Russ. Acad. Sci.: Phys. 73 673
[9] Bernatski D P and Pavlov V G 2007 Techical Phisics 52 1592-1956
[10] Fursey G N Field electron emission 2012 (St. Petersburg: Lan’) pp 198-223 (in Russian)
[11] Bernatski D P and Pavlov V G 2017 Tech. Phis.Lett. 43 592-594