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Low-emission carbon coatings for control grids of high power vacuum devices

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Received April 21, 2022
Revised December 27, 2022
Accepted December 28, 2022

The influence of the dipole polarization of carbon film coatings on their secondary electron emission has been studied. It is shown that plasma fluorination of carbon coatings with low specific surface resistance obtained in microwave plasma of low-pressure ethanol vapor increases the electron work function by 0.6 eV and reduces the secondary electron emission by more than a factor of two. The results can be used to obtain collectors and anti-emission coatings on grid electrodes of high-power electrovacuum devices in the microwave and sub-terahertz ranges.

Keywords: microwave plasma, carbon film, plasma fluorination, work function, secondary electron emission.

DOI: 10.21883/TPL.2023.03.55680.19227

High-power microwave and subterahertz vacuum-tube devices (VTDs) are used widely in both ground and aerospace radioelectronic equipment that requires a constant improvement of operating characteristics. Specifically, more and more stringent reliability and durability requirements are imposed on equipment used in navigation and space communication systems.

Cathode-grid assemblies featuring a matrix-type cathode (MTC) with pores filled with a barium-containing impurity, which reduces the temperature coefficient of the electron work function, are used in microwave VTDs with low-voltage control. The emissive power is increased by raising the MTC operation temperature. The rate of thermal evaporation of active impurities in an MTC increases in this case alongside with the density of electron fluxes. The control grid enters an emissive state, which has a negative effect on the VTD parameters, as a result of deposition of impurities with a low work function onto it and interception of primary-beam electrons. This is one of the key factors limiting the power and operation lifetime of VTDs.

Carbon is presently regarded as the most promising material for antiemission coatings [1–4]. Low secondary electron-emission (SEE) coefficients are achieved with the use of carbon films with a developed surface relief. Nanocarbon coatings, which include various allotropic carbon modifications with high aspect ratios (graphene, carbon fibers, etc.) [2], are used for this purpose. However, such coatings have a high adsorption capacity due to rapid thermalization of impurity atoms evaporated from MTCs. This results in gradual „flattening“of the microrelief and growth of SEE coefficients in the course of operation of high-power generating tubes.

The aim of the present study is to fabricate and examine low-emissivity carbon coatings, which have a higher electron work function than traditional carbon coatings and a low rate of redeposition of active MTC impurities onto their surface, for passive structural elements of cathode-grid assemblies of high-power microwave VTDs.

Carbon film coatings were produced by plasma-chemical deposition in microwave ethanol vapor plasma in accordance with the procedure outlined in [5]. The power of microwave radiation and the magnetic field density were 250 W and 875 G. Carbon films formed on aluminum substrates at an ethanol vapor pressure of $(1-2)\cdot 10^{-2}$ Pa, a bias voltage of -300 V applied to the substrate holder in the process of plasma-chemical deposition, and a temperature of $300 \pm 10^{\circ}$C have a dominant peak with interplanar distance $d = 3.36$ Åin diffraction patterns, which corresponds to the reflection from planes (002) of the graphite phase. These carbon films were processed in microwave plasma with fluorine-containing gas CF_4 [5] being the plasma-forming one. The processing pressure and time were 0.1 Pa and 5 min, and the bias voltage at the substrate holder varied within the 100–300 V interval (Fig. 1).

The SEE characteristics of carbon coatings before and after processing in CF_4 plasma were determined by quantifying the change in brightness of images in a JEOL JSM-7600F scanning election microscope in accordance with the procedure outlined in [6]. These measurements were performed at a primary electron beam energy of 1 keV and a voltage of 50 V at the grid of the secondary-electron detector. Since antiemission grid coatings operate in high-temperature environments, similar dependences for carbon structures processed in CF_4 plasma were determined after their vacuum thermal annealing, which was performed under a pressure of 10^{-3} Pa at a temperature of 300°C for 30 min. It was found that the SEE values of carbon films decreased by a factor of more than 2 after processing in CF_4 plasma. Figure 2 presents the results of measurement of the secondary electron-emission coefficient of carbon films

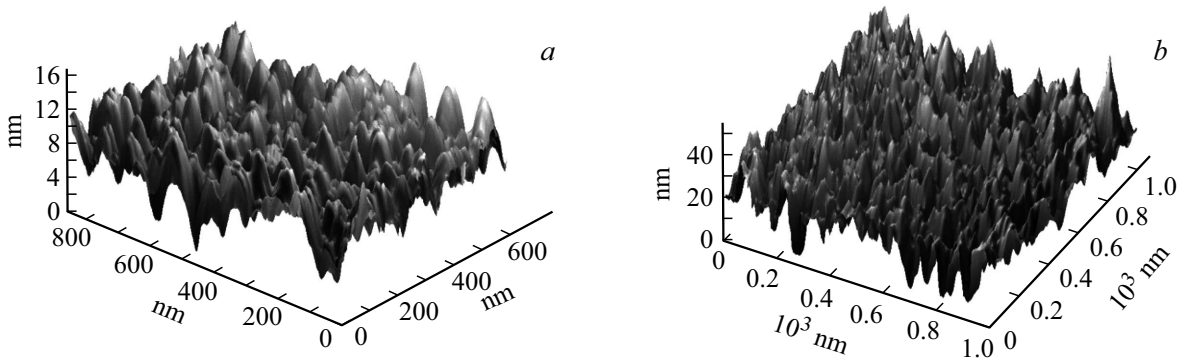

Figure 1. AFM images of carbon film structures with a sheet resistance of 90 kΩ/□ before (*a*) and after (*b*) plasma-chemical processing in CF_4.

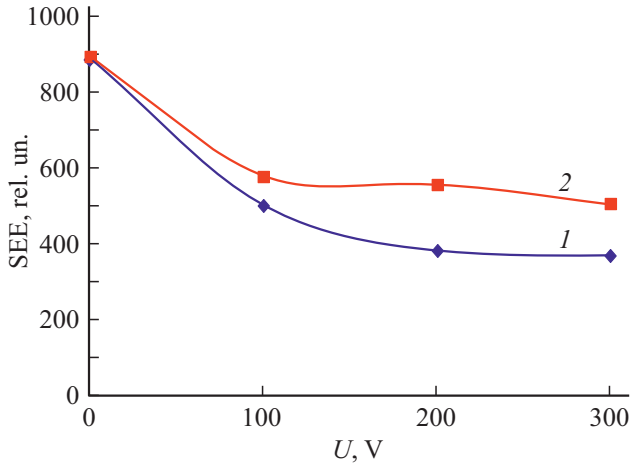

Figure 2. Dependences of SEE on the bias voltage applied to the substrate holder in processing of carbon films in CF_4 plasma before (*1*) and after (*2*) vacuum annealing.

processed in CF_4 plasma before (curve *1*) and after (curve *2*) vacuum annealing. The SEE intensified with increasing bias voltage at the substrate holder in the course of plasma processing and was suppressed after vacuum annealing of carbon films processed in CF_4 plasma.

The variation of electron work function for carbon structures in the process of plasma-chemical modification of their surfaces was calculated in accordance with the procedure detailed in [7]. Enhancement factors for the electric field at the cusps on carbon film surfaces were estimated based on the results of measurements with a P4-SPM-MDT atomic force microscope (AFM). Prior to processing in CF_4 plasma, cusps with a height of approximately 18 nm with tip curvature radii of 1–2 nm had the highest surface density. After plasma processing, the height of cusps with the maximum surface density increased to 23 nm due to etching of the carbon film. The surface density and the tip curvature radius of cusps decreased to $4 \cdot 10^{10}$ cm^{-2} and 0.5–1.0 nm, respectively, in the course of processing in CF_4 plasma.

Field enhancement factors K for these surface microgeometries are represented, as a first approximation, by ratios of the heights of cusps to their tip curvature radii and assumed the values of 10–20 prior to processing in CF_4 plasma and 25–50 after processing. These values of K were used to determine the electron work function based on field-emission current–voltage curves (CVCs) plotted in Fowler–Nordheim coordinates (Fig. 3).

The field-emission properties of carbon structures were examined using pulsed microsecond electric fields in high vacuum (10^{-6} Pa) and a diode arrangement with the capacity to adjust the interelectrode distance with an accuracy up to 1 μm. The distance between the cathode structure and the anode was 40 μm.

It was established that field-emission CVCs of carbon film structures prior to plasma modification in CF_4 and after such modification differ considerably, while the CVCs of structures after plasma processing and annealing are almost the same (Fig. 3). The equivalence of field-emission CVCs of annealed and non-annealed carbon structures processed in CF_4 plasma is in line with the dependences of SEE on the bias voltage at the substrate holder in the course of processing in CF_4 plasma (Fig. 2). Calculations of the electron work function of carbon structures with field enhancement factors $K_1 = 15$ (before processing in CF_4 plasma) and $K_2 = 30$ (after processing) revealed its growth from the initial level of 4.6 to 5.2 eV.

Ions CF_n^+, where $n = 0$–4; CF_n radicals; and neutral fluorine atoms are the chemically active particles involved in processing in highly ionized microwave plasma of a fluorine-containing gaseous medium (CF_4). They form $C{=}CF_m$ adcomplexes, where $m = 1$–3 [5], in the process of chemisorption on a carbon coating. These complexes passivate dangling bonds of surface atoms of the coating that emerged due to ion bombardment. Owing to a high electronegativity of fluorine atoms, passivation enhances the overall dipole moment of the carbon coating surface. The dipole moment induced by the adsorbate is directed from the coating surface to vacuum and contributes to an increase in the electron work function. The energy and the current density of CF_n^+ ions increase in plasma processing

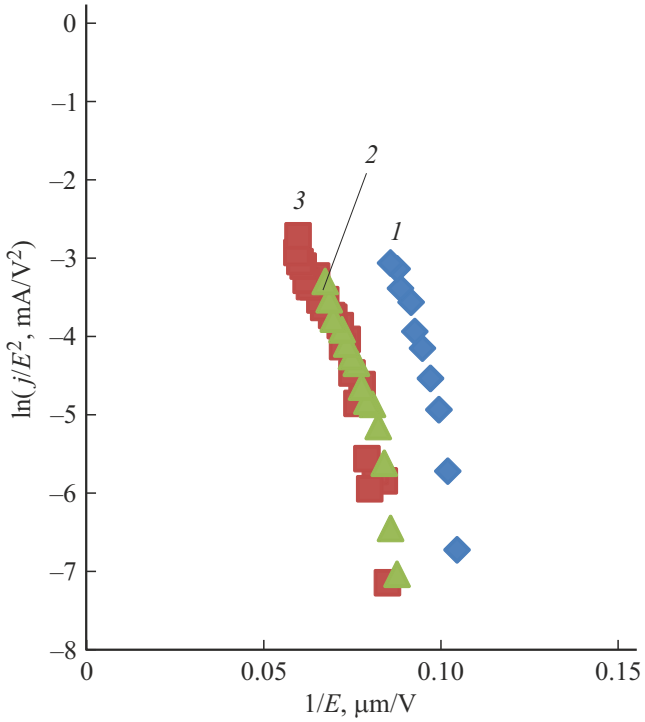

Figure 3. CVCs in Fowler–Nordheim coordinates for carbon film structures before processing in CF_4 (*1*), after processing in CF_4 (*2*), and after processing in CF_4 and vacuum annealing (*3*).

with increasing accelerating potential at the substrate [5]. The passivation efficiency and the overall dipole moment of the surface then also grow, resulting in an increase in the electron work function and, consequently, in SEE suppression at higher accelerating potentials (Fig. 2). Owing to this, the SEE coefficient decreases by a factor of more than 2 relative to the coefficient for the carbon coating that was not processed in fluorine-containing plasma.

Chemisorbed CF_m complexes have high chemical bond energies. The energy of C–F complexes (5.6 eV) is the highest: it exceeds the C–C bond breaking energy (2.74 eV) by a factor of more than 2. The bond strength in adcomplexes decreases with increasing m. In view of this, a fraction of adcomplexes with large m indices become detached from the carbon coating surface as a result of thermal desorption in the course of vacuum annealing. This exerts a negative influence on the overall dipole moment of the surface and the electron work function, and secondary emission in bombardment of coatings by the primary electron beam is enhanced as a result.

Coupled with an increase in the electron work function, plasma fluorination of carbon film structures reduces the probability of sticking of thermally evaporated atoms of MTC impurities, since CF_m complexes have a low electron polarizability that translates into a low surface energy of the coating and the dipole–dipole van der Waals interaction in adsorption. This reduces the lifetime of adatoms and the rate of nucleation of the new phase.

Conflict of interest

The authors declare that they have no conflict of interest.

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