Development of techniques for the formation of a planar electric vacuum diode based on an array of CNTs synthesized at the edge of the Co-Nb-N-(O) film

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Abstract. This work shows the possibility of forming a planar diode structure based on carbon nanotubes formed on a catalytic alloy film Co-Nb-N-(O). The paper presents a technological route for the formation of a planar diode structure Si/SiO2/Si3N4/Co-Nb-N-(O)/SiO2 and studies the emission characteristics. The current-voltage characteristic of the obtained diode structure in the Fowler-Nordheim coordinates is close to linear in the range from 15 to 22 V, which confirms the phenomenon of electron emission.

1. Introduction
In the modern world, intelligent robotic systems are used in almost all sectors of the economy and rapidly developing. It is impossible to imagine modern mechanical engineering, medicine, automatic spacecraft, unmanned vehicles and aircraft, and more without using them [1-3]. All the work of intelligent robotic systems is possible due to the development of semiconductor integrated circuit (IC) technology. A known disadvantage of semiconductor electronics is the low radiation resistance of common integrated circuits. The operation of semiconductor ICs turns out to be sensitive to the action of high-energy particles, which manifests itself in the appearance of radiation defects and disruption of the operation of p-n junctions, and, as a consequence, leads to failure of the IC [4-6].

Integrated field emission microdevices is a promising area of microelectronics associated with the qualitatively new materials using that can be used as low-voltage and highly stable field-emission emitters for flat-panel displays and devices for vacuum microwave microelectronics. The attractiveness of these devices lies in the fact that high-energy particles and large temperature differences do not affect the performance of these devices. The relatively small diameter of carbon nanotubes (CNTs) compared to their length leads to a unique aspect ratio that plays an important role in emission electronics. The high aspect ratio, in combination with high mechanical strength and chemical stability, make the use of carbon nanotubes (CNTs) more attractive as emission cathodes for electric vacuum devices in comparison with other known materials, for example, molybdenum,
silicon, diamond, graphite. [7-11] However, today there are no technologies for the manufacture of these devices in micron and integral form, when a plurality of these elements is concentrated in a small volume.

In the traditionally used methods of growing carbon nanotubes, catalyst particles are forming on the surface of a solid by condensation of a small amount of the catalyst. This method is difficult to integrate into an integrated technology because of the layer of catalyst particles can be uncontrollably removed during the etching operation. In previous studies, our research group has already obtained structures with CNTs synthesized on a catalytic amorphous alloy. The possibility of local growth of carbon nanotubes at the edges of the Ni-Nb-N-(O) film was also demonstrated [12-15]. The attractiveness of the proposed approach is the using of multicomponent alloy films. It makes possible to carry out the etching operation and then, during heat treatment, locally form clusters on the surface of a thin alloy film.

In this work, the growth of carbon nanotubes was carried out on a Co-Nb-N-(O) catalytic film with a low content of the catalytic substance. A test design of a planar microelectro-vacuum diode was developed. The possibility of forming test elements, including an anode and a cathode with carbon nanotubes, has been demonstrated. The current-voltage characteristics of this structure were obtained, which made it possible to evaluate the emission characteristics of the formed device.

2. Experimental
To form a planar diode structure, 100 mm monocrystalline silicon substrates were used. The substrates have previously passed the standard chemical treatment in KARO and PAR solutions. A SiO$_2$ film with a thickness of about 300 nm was formed on the surface of the wafers by thermal oxidation of silicon. Next, a thin Si$_3$N$_4$ film with a thickness of 170 nm was formed by chemical vapor deposition using an HCVD-55 machine. A catalytic film of the Co-Nb-N-(O) alloy was deposited by magnetron sputtering in a vacuum. The thickness of the Co-Nb-N-(O) catalytic film was about 350 nm. Then, the obtained multilayer structure Si/SiO$_2$/Si$_3$N$_4$/Co-Nb-N-(O) was covered by a masking layer of SiO$_2$ with a thickness of about 800 nm, formed by CVD. Then the photolithography process was carried out to create a relief of the multilayer structure.

The resulting structure Si/SiO$_2$/Si$_3$N$_4$/Co-Nb-N-(O)/SiO$_2$. Etching process is an important stage which makes possible to form a relief and create open edges of the catalytic film. The main etching mechanism was ion bombardment, and the etching was monitored by using SIMS sensors. At the final stage, the synthesis of arrays of carbon nanotubes was carried out using plasma-stimulated chemical vapor deposition at PlasmaLab System 100 (Oxford Instruments). CNTs were formed by the CVD method at substrate temperature of 700°C in a flow of acetylene with added ammonia during 5 minutes. Experimental samples were studied using scanning electron microscopy at FEI Helios NanoLab 650i. The resulting planar diode structure is shown at figure 1. At this stage, in order to simplify the technological process, the same catalytic material was used as the anode material as for the cathode. In the future, the structure will be modified to obtain CNTs only at the cathode.

![Figure 1. Schematic diagram of a planar emission diode based on CNTs formed at the edge of a Co-Nb-N-(O) thin film.](image-url)
The emission characteristics study of the obtained planar diode structures was carried out on a special stand using a software-hardware complex. This complex includes the following equipment: Keithley 2410C picoammeter, Yokohawa 710120 oscilloscope, Agilent N9310A RF signal generator, Agilent N9320B spectrum analyzer. The stand for measuring the field emission characteristics of samples with CNTs makes it possible to perform electrophysical measurements at constant voltages under vacuum conditions.

3. Results and discussion
A technological route was developed for the formation of structures with carbon nanotubes at the edges of the Co-Nb-N-(O) catalytic film. All operations on the formation of the relief made it possible to create the final geometry of the diode planar structure. At the last stage, the formation of arrays of carbon nanotubes at the ends of the catalytic film was carried out. The created topology of test structures has a cathode and an anode (figure 2). The average diameter of a CNT is about 15 nm, the length is in the range from 0.8 to 5 µm.

![Figure 2. Test element of a planar diode structure with a cathode and anode.](image)
The results of measuring the emission properties of the resulting diode structure are shown at figures 3-4. Figure 3 shows the current-voltage characteristic of this structure. As you can see from the figure, the I–V characteristic has a nonlinear dependence. A sharp increase in current is observed at voltages above 15 V. To substantiate that the obtained form of the experimental I–V characteristic is due to the phenomenon of electron emission, it was analyzed on the basis of the Fowler-Nordheim theory [16].

Figure 3. Current-voltage characteristic of the obtained diode structure based on CNTs.

Figure 4. Current-voltage characteristic of the resulting structure in Fowler-Nordheim coordinates with approximation of the area from 0.045 to 0.065 by a linear dependence.
Figure 4 shows that in the Fowler-Nordheim coordinates, the current-voltage characteristic has a zigzag shape. As you can see, in the range of values 0.045 to 0.065, there is a section that can be approximated by a linear function. As can be seen from the figure, the characteristic for the obtained structure in the Fowler-Nordheim coordinates is indeed close to linear in the range from 15 to 22 V, which confirms the phenomenon of electron emission. Forbes test was performed to confirm the phenomenon of electron emission. Forbes test consists in calculating the range of \( f_1 \) and \( f_2 \), where \( f \) is the scaled barrier field on the emitter surface \( f \) at a certain voltage \( U \). The calculated values of \( f_1 \) and \( f_2 \) for the obtained experimental data were 0.11 and 0.14, which is close to the lower edge of the permissible range and indicates the correspondence of the registered I–V characteristic to the «orthodox» theory.

4. Conclusion

A technique for the formation of a planar emission diode with a cathode based on CNTs formed at the edge of a thin film of the Co-Nb-N-(O) alloy was demonstrated in this work. The attractiveness of the proposed approach of using multicomponent alloy films makes it possible to carry out the etching operation and then, during heat treatment, locally form clusters on the surface of a thin alloy film. The formed planar diode structure demonstrated an emission I-V characteristic with a fairly low emission threshold of ~15 V.

Acknowledgement

This work was supported by the Russian Foundation for Basic Research (project 19-38-90206) and by the State assignment 2020-2022 № FSMR-2020-0018.

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