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# Effect of ionizing radiation on structural and conductive properties of copper nanotubes

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ABSTRACT

The use of electron radiation is an effective tool for stimulating a controlled modification of structural and conductive properties of nanomaterials in modern materials science. The paper presents the results of studies of the influence of various types of radiation on structural and conductive properties of copper nanotubes obtained by electrochemical synthesis in pores of templates based on polyethylene terephthalate. Such methods as SEM, X-ray diffraction and EDS show that irradiation with a stream of high-energy electrons with doses of 50–250 kGy makes it possible to modify the crystal structure of nanotubes, increasing their conductivity and decreasing the resistance of nanostructures without destroying the structure.



## 1. Introduction

Nowadays nanostructured materials and based products are of increasing interest for various research groups. This interest in nanostructures is recognized by some unusual properties that differ from large samples. Due to such properties, they find practical application in a number fields of physics, chemistry, electronics, and biomedicine [1–3]. Among all metallic nanomaterials, copper (Cu) is a unique, since copper nanostructures have high electrical conductivity and play an major role in the development of sensors for electronics [4], and are also used as catalysts [5]. Today there are several methods for the synthesis of Cu nanocrystals [6] with different morphologies, such as cubes [7], nanorods [8], cigar-shaped nanocrystals [9], triangular nanocrystals [10], nanodisks [11], nanowires [12]. The possibility of controlled regulation of physical and chemical properties of nanostructures contributes to the expansion of their use. At the same time, the stability of physical and structural properties of nanomaterials is at the basis of determining the reliability of devices based on them. Radiation modification is one of the ways to change the physical chemical properties of nanostructured materials. One of the actual problems of nanomaterials radiation modification is the controlled formation of defects in crystal structure and their recombination to improve the strength and conductive properties of nanostructures. At the same time, an important factor is the further migration of defects, which can significantly change the structure of materials. The simplest way to solve this problem is to simulate the processes of atomic collisions using Monte Carlo method [13,14], which allows one to calculate the distribution and concentration of primary defects without taking into account their further evolution: diffusion, recombination, the formation of defect complexes. Meanwhile, these processes determine violations in the crystal lattice during irradiation or ion implantation of nanomaterials. In this case, point radiation defects can annihilate or flow along the grain boundaries. The biggest problems during irradiation of nanostructures are associated with a decrease in plasticity, embrittlement, scaling, transmutation [15–17]. Radiation effects that appear in nanomaterials under the effect of ionizing radiation have several features that differ from similar effects in micro- and macro-dimensional objects [18–21]. At the same time, the presence of a large number of grain boundaries and joints, which serve as drains to remove radiation defects, contributes to the stability of nanomaterials in comparison with larger materials. The use of electronic and gamma radiation for modification is an effective tool for changing the physical chemical properties of

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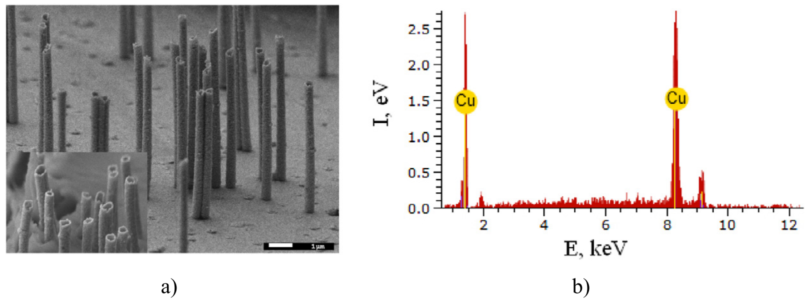


**Fig. 1.** a) SEM – images of nanotubes; b) EDS spectrum of nanotubes.

nanostructures. That is why it is interesting to study the effect of ionizing radiation, particularly, the flow of low-energy and high-energy electrons, as well as gamma quanta, on the structural and conductive properties of copper nanotubes.

The purpose of this paper is to study the dynamics of change in structural and conductive properties of Cu nanotubes under the influence of a high-energy electron beam.

## 2. Experimental part

### *2.1. Preparation of polymer templates*

Track membranes were made of polyethylene terephthalate of 'Hostaphan ®' brand manufactured by Mitsubishi Polyester Film (Germany). The films were irradiated on "DC-60" (Kazakhstan) accelerator of heavy ions by accelerated krypton ions with energy of 1.75 MeV/nucleon and a fluence of $4 \times 10^7$ ion/cm$^2$ [22]. The membranes were etched according to the standard double-sided etching technique in a solution of 2.2 M NaOH at a temperature of $85 \pm 1$ °C, the pore size according to gas porosimetry and SEM was about $380 \pm 10$ nm [23].

### *2.2. Electrochemical synthesis of copper in channels of nanoporous PET TM*

Electrochemical synthesis in the tracks of the template was carried out in potentiostat mode at a voltage of 1.0 V. The composition of electrolyte solution is the following: $CuSO_4 \cdot 5H_2O$ (238 g/l), $H_2SO_4$ (21 g/l). The yield of copper by current from sulfuric acid solutions of electrolytes is 100% [24]. The growth of nanostructures was monitored by chronoamperometry method with the 'Agilent 34410A' multimeter. When using magnetron sputtering in a vacuum, a gold layer no more than 10 nm thick was deposited on one side of PET matrix template, which subsequently was used as a working electrode (cathode) during electrochemical deposition.

### *2.3. Investigation of structure and properties of Cu-nanotubes*

Studying of structural characteristics and elemental composition of nanotubes obtained before and after irradiation was carried out using a 'Hitachi TM3030' scanning electron microscope with a 'Bruker XFlash MIN SVE' microanalysis system at an accelerating voltage of 15 kV. X-ray diffraction analysis was conducted on a D8 ADVANCE ECO diffractometer (Bruker, Germany) using CuK$\alpha$ radiation. To identify the phases and study the crystal structure, the software BrukerAXSDIFFRAC.EVAv.4.2 and the international ICDD PDF-2 database were used.

### *2.4. Modification of structural and conductive properties of Cu-nanotubes*

Modification of properties of synthesized Cu-nanotubes was conducted on the ELV-4 linear accelerator (Kurchatov, Kazakhstan)

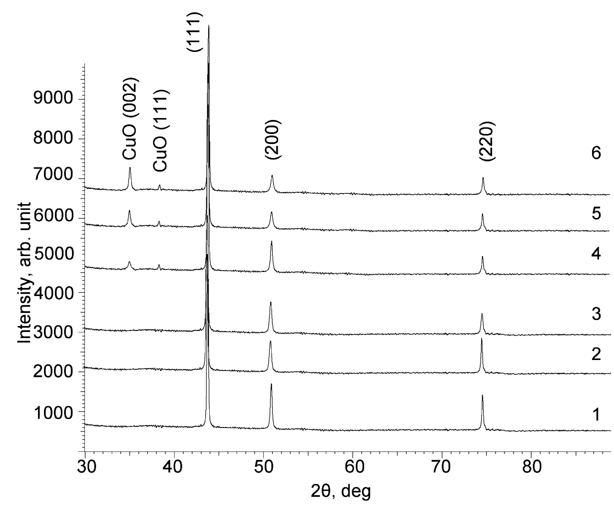


**Fig. 2.** X-ray diffraction patterns of Cu nanotubes irradiated with an electron beam at energy of 5 MeV: 1 – initial, 2 – 50 kGy, 3 – 100 kGy, 4 – 150 kGy, 5 – 200 kGy, 6 – 250 kGy.

by irradiating with an electron beam at energies of 5 MeV, with irradiation dose of 50–250 kGy in 50 kGy increments.

## 3. Results and discussion

The unique physical chemical properties of nanostructured materials are due to a crystalline structure that varies under the influence of external factors. In turn, irradiation with electrons and gamma quanta of metal nanostructures is a useful tool for stimulating controlled modification of structural and conductive properties of materials. Fig. 1 shows the SEM images and the EDS (energy dispersive spectroscopy) spectrum of obtained initial samples.

Analysis of electronic images of samples showed that the synthesized nanostructures are hollow nanotubes, whose height coincides with the thickness of 12 μm template matrix, the diameter of nanotubes correspond to pore diameters of $380 \pm 10$ nm. Determination of nanostructures internal diameters in PET templates was carried out by a manometric method for determining gas permeability, based on measuring the change in gas pressure in a closed chamber at a pressure in the range of 0.008–0.020 MPa in steps of 0.004 MPa. As a result of calculations, it was found that the internal diameters of nanotubes were $180 \pm 5$ nm, the wall thickness was about $100 \pm 5$ nm. According to the data of energy-dispersive spectroscopy, the nanotubes obtained as a result of electrochemical synthesis are 100% copper, and no peaks characteristic for oxygen were detected. Fig. 2 shows X-ray diffraction patterns of samples before and after irradiation. The type of diffraction patterns of the investigated samples is typical for polycrystalline nanoscale structures. Analysis of diffractogram of an initial sample made it possible to establish that the initial copper nanotubes possess a