IRSTI 29.35

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STUDY OF STRUCTURAL PROPERTIES OF COPPER NANOTUBES MODIFIED WITH IONIZING RADIATION

In modern materials science, irradiation with electron beams and a γ ray flux of metallic nanostructures is an effective tool for stimulating a controlled modification of structural and conductive properties of materials. The paper presents the results of the influence of various types of irradiation on structural and conductive properties of copper nanotubes obtained by electrochemical synthesis in pores of template matrices based on polyethylene terephthalate. The modification of properties of synthesized Cu-nanotubes was carried out at ELV-4 linear accelerator (Kurchatov, Kazakhstan) by irradiating with electrons flux of 5 MeV energies and γ quanta with of 1.35 MeV energy, doses of 50-250 kGy in 50 kGy increments. SEM, XRD and EDS methods established that irradiation with an electron beam and γ rays with doses of 50 and 100 kGy allows us modifying the crystal structure of nanotubes, increasing their conductivity and decreasing their resistance without destroying their structure. An increase in the irradiation dose leads either to an insignificant change in conductive properties for high-energy electrons and γ quanta, or to a deterioration of conductive properties due to the appearance of oxide compounds in the crystal structure and subsequent destruction of samples.

Key words: template synthesis, ion-track technology, electrochemical deposition, nanotubes, nanostructures, growth mechanisms, radiation defects.

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Иондаушы сәулелену арқылы модификацияланған мыс нанотүтікшелердің құрылымдық қасиеттерін зерттеу

Заманауи материалтану, металдық наноқұрылымдардың электрондық шоқтармен сәулелену және гамма-сәулелену ағынымен материалдардың құрылымдық және өткізгіш қасиеттерінің реттелетін түрлендірілуін ынталандырудың тиімді құралы болып табылады. Мақалада полиэтилентерефталат негізінде темплат матрицалардағы электрохимиялық синтез арқылы алынатын мыс нанотүтікшелердің құрылымдық және өткізгіш қасиеттеріне әртүрлі сәулеленудің әсер етуін зерттеу нәтижелері келтірілген. Синтезделген Cu-нанотүтікшелердің қасиеттерін 50 кГр-дегі 50-250 кГр сәулелену мөлшермен, 1.35 МэВ қуатпен γ-кванттармен және 5 МэВ энергиясы бар қуатпен электрондардың ағынымен сәулелену арқылы ЭЛВ-4 сызықты үдеткіште (Курчатов, Қазақстан) жүргізілді. РЭМ, РҚТ және ЭДТ әдістері электрондардың ағынмен және 50 және 100 кГр мөлшері бар гамма кванттармен сәулеленуді нанотүтікшелердің кристалды құрылымын өзгертуге, өткізгіштігін арттыруға және құрылымын бұзбай наноқұрылымдардың кедергісін төмендетуге мүмкіндік береді. Сәулелену дозасының жоғарылауы жоғары энергиялық электрондар мен гамма-квантар үшін өткізгіш қасиеттердің шамалы өзгеруіне немесе кристалдық

құрылымда оксид қосылыстарының пайда болуына және үлгілердің кейінгі бұзылуына байланысты өткізгіш қасиеттердің нашарлауына әкеп соғады.
Түйін сөздер: үлгілі синтездеу, ион-трек технологиясы, электрохимиялық тұндыру, нанотүтікшелер, наноқұрылымдар, өсу механизмдері, радиациялық ақаулар.

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Изучение структурных свойств медных нанотрубок, модифицированных ионизирующим излучением

В современном материаловедении облучение электронными пучками и потоком гамма квантов металлических наноструктур является эффективным инструментом для стимулирования контролируемой модификации структурных и проводящих свойств материалов. В работе представлены результаты исследований влияния различного вида излучений на структурные и проводящие свойства медных нанотрубок, полученных методом электрохимического синтеза в порах темплатных матриц на основе полиэтилентерефталата. Модификация свойств синтезированных Cu-нанотрубок проводилась на линейном ускорителе ЭЛВ-4 (Курчатов, Казахстан) путем облучения потоком электронов с энергией 5 МэВ и γ-квантами с энергией 1.35 МэВ, дозами 50-250 кГр в 50 кГр. Методами РЭМ, РСА и ЭДА установлено, что облучение потоком электронов и гамма квантами с дозами 50 и 100 кГр позволяет модифицировать кристаллическую структуру нанотрубок, увеличивая проводимость и снижая сопротивление наноструктур, не разрушая их структуру. Увеличение дозы облучения приводит либо к незначительному изменению проводящих свойств для высокоэнергетичных электронов и гамма квантов, либо к ухудшению проводящих свойств за счет появления оксидных соединений в кристаллической структуре и последующей деструкции образцов.
Ключевые слова: шаблонный синтез, ионно-трековая технология, электрохимическое осаждение, нанотрубки, наноструктуры, механизмы роста, радиационные дефекты.

Introduction

One of the interesting objects of research in modern materials science is metal nanostructures, which are promising for the production of various electronic sensors with unique properties, recording instruments, creating composite materials, etc. Obtaining such nanostructures on a large scale is one of the key moments in the creation of a whole range of modern nanotechnologies [1-3]. Among all metal nanomaterials, copper is one of the most actual, cause copper nanostructures have high electrical conductivity and has an important role in the development of sensors for electronics [4], and can also be used as catalysts [5]. The possibility of controlled regulation of physical and chemical properties of nanostructures [6-12] contributes to the expansion of their use field. At the same time, the stability of physical and structural properties of nanomaterials is the basis for determining the reliability of devices. One of the ways to change the physical-chemical properties of nanostructured materials is radiation modification. The changes in structural properties of nanomaterials initiated by radiation defects often make their practical use difficult.

At the same time, the formation of radiation defects in metallic nanostructures, especially in combination with other influences (change in temperature, mechanical loading, electric field), allows the directional modification of nanomaterials properties [13-17]. The energy losses of incident ions on electron shells can affect the weakening of ionic motion, the suppression or enhancement of defects formation and their further evolution. Ion modification of nanomaterials is a tool for creating kinetically stable non-equilibrium defects and metastable phases. This allows us to investigate the behaviour and properties of nanostructures far from equilibrium [18-21]. Conducting properties of copper nanostructures can be promising for applications in conditions of external irradiation, for example, in space. Therefore, the study of their radiation resistance, the stability of properties under irradiation and the ability to modify properties by irradiation with fast electrons or gamma quanta becomes a very urgent problem. In this connection, it is essential to study the effect of ionizing radiation, mainly, the flow of low-energy and high-energy electrons, as well as γ quanta, on structural and conductive properties of copper nanotubes.

The purpose of this work is to investigate dynamics of changes in structural and conductive properties of Cu nanotubes under various types of ionizing radiation.

Experimental part

Preparation of polymer templates. Track membranes were prepared of «Hostaphan®» brand polyethylene terephthalate produced by Mitsubishi Polyester Film (Germany). The films were treated at the "DC-60" accelerator of heavy ions (Kazakhstan) by krypton ions with an energy of 1.75 MeV/nucleon and a fluence of 4×10^7 ion/cm^2 [22, 23]. The membranes were etched according to the standard two-sided etching technique in a solution of 2.2 M NaOH at 85 ± 1 °C. The pore size according to SEM and gas porosimetry was 380 ± 10 nm [24].

Electrochemical synthesis of copper in channels of nanoporous PET TM. Electrochemical synthesis in tracks of the template was carried out in the potentiostatic mode at a voltage of 1.0 V. Electrolyte solution consists of $CuSO_4 \cdot 5H_2O$ (238 g/l), H_2SO_4 (21 g/l). The yield of copper in current from sulfuric acid solutions of electrolytes is 100% [25]. The growth of nanostructures was monitored by the chronoamperometry method with the "Agilent 34410A" multimeter. Using magnetron sputtering in vacuum, a layer of gold with a thickness of no more than 10 nm was deposited on one side of the template PET matrix, which later appeared as a working electrode (cathode) during electrochemical deposition.

Investigation of the structure and properties of Cu nanotubes. Investigation of structural characteristics and elemental composition of obtained nanotubes before and after irradiation was carried out using a scanning electron microscope "Hitachi TM3030" with a microanalysis system "Bruker XFlash MIN SVE" at an accelerating voltage of 15 kV. X-ray diffraction (XRD) analysis was obtained on a D8 ADVANCE ECO diffractometer (Bruker, Germany) using CuKα radiation. In order to determine the phases and study the crystal structure, the software BrukerAXSDIFFRAC.EVAv.4.2 and the international ICDD PDF-2 database were used.

Modification of structural and conductive properties of Cu nanotubes. The modification of properties of synthesized Cu-nanotubes was carried out at ELV-4a linear accelerator (Kurchatov, Kazakhstan) by irradiating with electrons flux of 5 MeV energies and γ quanta with of 1.35 MeV energy, doses of 50-250 kGy in 50 kGy increments.

Results and discussion

Figure 1 shows SEM images obtained initial samples. Analysis of electron images showed that the synthesized nanostructures are hollow nanotubes whose height coincides with the thickness of template matrix of 12 μm. The diameter of nanotubes corresponds to pore diameters of 380±10 nm.

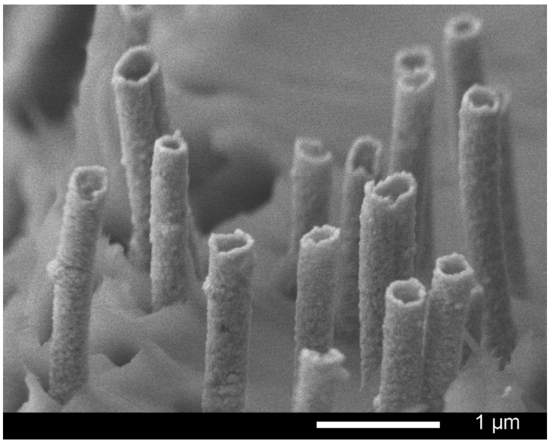
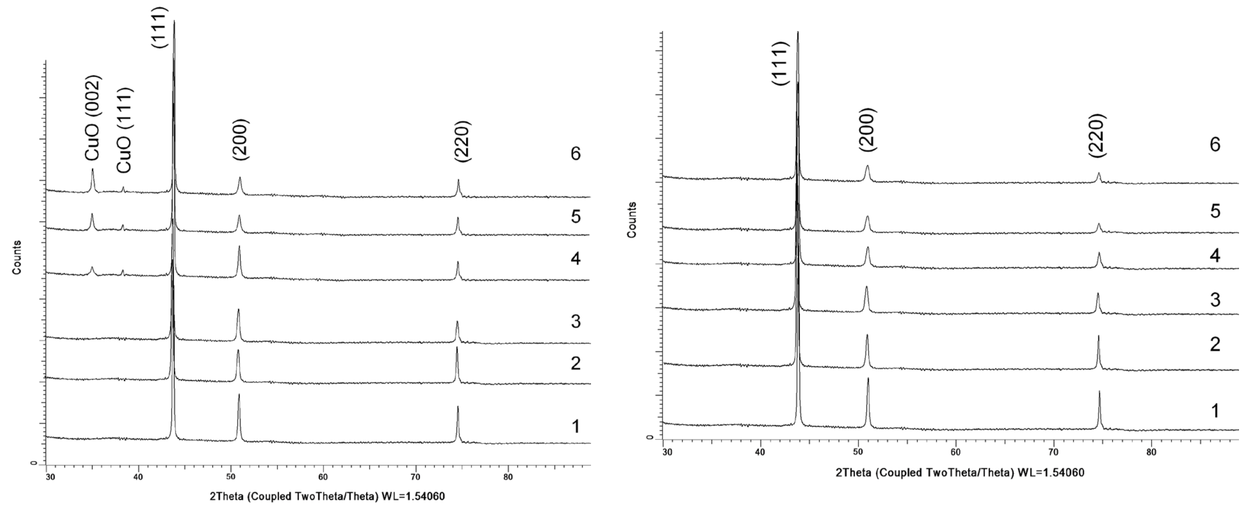


Figure 1 – SEM images of nanotubes

According to EDS data, the obtained nanotubes as a result of electrochemical synthesis are 100% copper, and no peaks characteristic of oxygen were detected. Figure 2 shows XRD patterns of investigated samples before and after irradiation. The type of diffraction patterns of investigated samples is characteristic for polycrystalline nanoscale structures. Analysis of the initial sample diffractogram made it possible to establish that the initial copper nanotubes possess a polycrystalline structure with a fcc phase without the presence of oxide compounds in the structure. According to the XRD data, the unit cell is characterized by a cubic syngony (Fm3m (225)) with a cell parameter a=3.6130, different from the reference value (a = 3.6150, PDF#040836). The difference in the value of the unit cell parameter from the reference value can be caused by microstresses that arise in the structure during the synthesis. When the lines on the diffractogram were approximated by the necessary number of symmetric pseudo-Voigt functions, the width of registered lines at half their height (FWHM) was measured, which allowed characterizing the perfection of the crystal structure and the degree of crystallinity. As a result of the treatment, it was found that the crystallinity of initial sample was 84%.



a) b)

Figure 2 – XRD patterns of Cu nanotubes irradiated by an electron beam with 5 MeV energy (a), (b) γ quanta: 1 – initial, 2 – 50 kGy, 3 – 100 kGy, 4 – 150 kGy, 5 – 200 kGy, 6 – 250 kGy

Analysis of XRD diffractograms of Cu nanotubes irradiated by 5 MeV electron beam, shown in Figure 2a, made it possible to estimate the change in the crystal structure under irradiation. As the irradiation dose is increased, the intensity and peaks shape are changed. That can be caused by a decrease in microstresses contribution to the crystal structure as a result of electron annealing of defects. At the increase in the irradiation dose above 100 kGy, XRD patterns show the appearance of peaks characteristic for copper oxide CuO with Miller (002) and (111) indices. The presence of oxide compounds in nanotubes structure can be caused by the appearance of local heating regions in the crystal structure during the interaction of electrons with nanotubes. Table 1 presents results of the change in the phase state of Cu nanotubes as a result of irradiation with various types of radiation.

Table 1 – Data of phase state changes

Absorbed dose, kGy	e, 5 MeV		γ-rays	
	Cu	CuO	Cu	CuO
0	100	0	100	0
50	100	0	100	0
100	100	0	100	0
150	97	3	100	0
200	97	3	100	0
250	96	4	100	0

As can be seen from Table 1, irradiation with low-energy electrons leads to a change in the phase state of copper nanotubes due to the formation of a CuO oxide compound in the crystal structure. At the same time, at high irradiation doses, a sharp increase in the contribution of oxide phase to the crystal structure is observed. Oxide phase formation can be explained by the local heating of the crystal structure. It is conditioned by the energy losses of electrons in interaction with the crystal lattice of nanotubes. According to the theory, when electrons or ions interact with high energy with the crystal lattice of nanostructures, only a small part of incident particles energy is transmitted to it. In this connection, a small number of additional charge carriers or structural defects arise in nanoscale structures [26, 27]. Moreover, as the energy of incident particles decreases, the number of charge carriers and defects created increases according to the increase in the linear energy transfer and the increase in the cross section for interaction with crystal lattice atoms. But in conventional materials the total number of charge carriers and structure defects decreases with decreasing energy of incident particles.

However, when γ rays of Cu nanotubes are irradiated, according to XRD diffractograms, the appearance of oxide compounds in the structure is not observed (Figure 2b). A feature of γ quanta during passage through a substance is that they collide relatively rarely with electrons and nuclei. But in a collision, as a rule, they sharply deviate from their path, i.e. practically drop out of the beam. Additionally, they have a zero rest mass and, therefore, cannot have a velocity different from the speed of light. This means that the γ quanta in the medium can not slow down: they are either absorbed or scattered, mainly at large angles. For γ-quanta, there is no concept of the path, the maximum range, the energy loss per unit length. As a result of the interaction of γ quanta with the crystal structure, a change in peaks intensity is observed. This leads to a change in the degree of crystallinity and main parameters of the crystal structure. Figure 4a is a graph of dependence of the change in the unit cell parameter from the irradiation dose.

The change in the unit cell parameter, an increase in the parameter is observed with increasing irradiation dose. The greatest increase is observed for samples irradiated by low-energy electrons. For samples irradiated with electrons with energies of 5 MeV and γ quanta, the parameter *a* is increased by 0.12% and 0.15% for electrons and γ quanta, respectively. According to calculations, when irradiation with electrons with an energy of 5 MeV and γ quanta, an increase in the degree of crystallinity is observed, which is due to a change in the crystal lattice. The appearance of oxide compounds in a structure of less than 10% leads to a decrease in the degree of crystallinity. For samples irradiated with low-energy electrons, the change in the degree of crystallinity consists of two stages.

Determination of dynamics of the change in texture planes and the orientation of Cu nanotubes as a result of irradiation was carried out by calculating the texture coefficients using the Harris equation (Table 2).

$$TC_{hkl} = \frac{I_{hkl}}{I_{0hkl}} \Big/ \frac{1}{n}\sum\frac{I_{hkl}}{I_{0hkl}},$$

where I_{hkl} is the experimentally obtained intensity of the reflex, I_{0hkl} is the corresponding intensity according to the JCPDS database, and n is the number of reflexes.

Table 2 – Values of texture coefficients

Dose, kGy	e, 5 MeV			γ-rays		
	111	200	220	111	200	220
0	1.5849	0.8263	1.1456	1.5849	0.8263	1.1456
50	1.6301	0.7311	1.0312	1.7109	0.7835	1.0217
100	1.7507	0.5427	0.9317	1.7345	0.6913	0.9215
150	1.7509	0.5481	0.9137	1.7431	0.6904	0.9119
200	1.7511	0.5391	0.9091	1.7449	0.6834	0.9124
250	1.7502	0.5399	0.9017	1.7356	0.6824	0.9074

Texture coefficients more than one point to the predominant orientation of nanotubes arrays along the corresponding directions, which indicates an increase in the number of grains along these directions. The TC (hkl) values of the initial sample of Cu-nanotubes confirm the assumption of a polycrystalline structure with the dominant direction [111]. At the same time, with an increase in the irradiation dose, a reorientation of the crystal structure is observed for the samples irradiated by the electron beam with an energy of 5 MeV and γ quanta.

For samples irradiated with a low-energy electron flux, a maximum decrease in the resistivity at a dose of 100 kGy is observed. With an increase in the irradiation dose, a sharp increase in the resistance is observed, which is due to local thermal heating of nanotubes, which leads to the destruction of the crystal lattice and samples amorphization.

Conclusion

The dependence of the change in structural and conductive properties of Cu nanotubes from irradiation with various types of ionizing radiation was established. The dynamics of changes in structural and conductive properties as a function of irradiation dose using SEM, XRD, and EDS was studied in detail.

It is established that irradiation with an electron beam and γ rays with doses of 50 and 100 kGy allows us modifying the crystal structure of nanotubes, increasing their conductivity, but not destroying their structure. An increase in the irradiation dose leads either to an insignificant change in conductive properties for high-energy electrons and γ quanta, or to a deterioration of conducting properties due to the appearance of oxide compounds in the crystal structure and subsequent destruction of samples.

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