



# Electrical Characterization of Nanomaterials

# 10

Artem Kozlovskiy, Inesh Kenzhina, Maxim V. Zdorovets, Kayrat K. Kadyrzhanov, and Alex V. Trukhanov

## Abstract

To date, a key area of research in the field of nanostructured materials science and methods of obtaining nanostructures is the study of the effect of physicochemical and structural properties on their conductive characteristics. In contrast to macro-objects for nanostructures, factors such as the size of grains and the concentration

A. Kozlovskiy (✉)

L.N. Gumilyov Eurasian National University, Nur-Sultan, Kazakhstan

The Institute of Nuclear Physics, Almaty, Kazakhstan

Research School of Chemistry and Applied Biomedical Sciences National Research Tomsk Polytechnic University, Tomsk, Russia

e-mail: [kozlovskiy.a@inp.kz](mailto:kozlovskiy.a@inp.kz)

I. Kenzhina

L.N. Gumilyov Eurasian National University, Nur-Sultan, Kazakhstan

The Institute of Nuclear Physics, Almaty, Kazakhstan

e-mail: [kenzhina@physics.kz](mailto:kenzhina@physics.kz)

M. V. Zdorovets

L.N. Gumilyov Eurasian National University, Nur-Sultan, Kazakhstan

The Institute of Nuclear Physics, Almaty, Kazakhstan

Ural Federal University, Yekaterinburg, Russia

e-mail: [mzdorovets@inp.kz](mailto:mzdorovets@inp.kz)

K. K. Kadyrzhanov

L.N. Gumilyov Eurasian National University, Nur-Sultan, Kazakhstan

A. V. Trukhanov

National University of Science and Technology MISiS, Moscow, Russia

SSPA “Scientific and Practical Materials Research Centre of NAS of Belarus”, Minsk, Belarus

South Ural State University, Chelyabinsk, Russia

of their boundaries, dislocation and defect densities, the degree of ordering of the structure, etc. have a tremendous effect on the conducting properties, as well as the magnitude of the resistance. In this case, in most cases, nanosize can lead to extraordinary changes in the conductivity of nanostructures. The purpose of this chapter is to present the results of the influence of various conditions for the synthesis of copper nanostructures, as well as various methods of modification using ionizing radiation on their conducting properties.

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**Keywords**

Nanotubes · Conductivity · Electrochemical synthesis · Defects · Ionizing radiation

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## 10.1 Introduction

In the past few years, great attention has been paid to methods for producing metallic nanostructures of various geometries, such as cubes, spherical particles, tubes, wires, dendrites, etc. (Sharma et al. 2018; Yang et al. 2015; Matschuk et al. 2010; Bhanushali et al. 2015; Qiu et al. 2009). Such an increased interest in nanostructured materials is primarily due to the possibility of obtaining new data on the nature of quantum forces at the nanoscale, when the size effects begin to play a major role, as well as the wide potential of application as a basis for miniature devices, the demand for which is increasing every year. The use of nanostructures in microelectronics has made a breakthrough in the field of information storage, sensorics, energy storage, etc. Special attention in this direction is paid to nanowires and nanotubes, which, due to their high flexibility in terms of length, diameter, and their aspect ratio, open up broad prospects in the study of the properties of nanomaterials, as well as their practical application (Alia et al. 2013; Jiang et al. 2002). The most promising material among all metals is copper and its oxide forms. Interest in these types of nanostructures is due to their high electrical conductivity and resistance to degradation. Copper nanostructures are widely used as a basis for emitter bases, anode materials, and semiconductor devices (Zang et al. 2018; Zhang et al. 2019).

Among the variety of synthesis methods, a special place is occupied by the method of galvanic or electrochemical synthesis, which allows not only to control the geometry of the obtained nanostructures with high accuracy through the use of template matrices of a given geometry but also to scale this technology on a semi-industrial scale. This synthesis method makes it possible to obtain nanostructures of various lengths, which can vary from 100 nm to 100  $\mu\text{m}$  or more, as well as diameters from several nanometers to tens of microns. In this case, the geometry of the synthesized nanostructures is completely specified by the template matrix, which is used for synthesis. At the same time, varying the synthesis conditions makes it possible not only to control the geometry of the synthesized nanostructures but also to control their phase and elemental composition, the main crystallographic characteristics, such as the crystallite size, crystal lattice parameter, dislocation

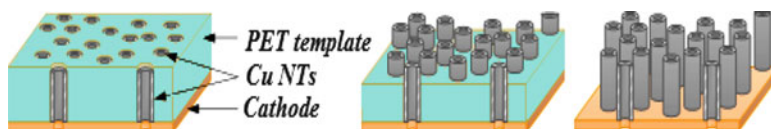
density, degree of crystal structure perfection, etc. A change in all these parameters primarily has a significant effect on the conducting characteristics, while it can be both positive, associated with an increase in conductivity and a decrease in resistance, and negative, due to a sharp deterioration in conducting properties. In this case, the size effect plays an important role in determining the conducting characteristics of nanomaterials, since electron transport in metallic nanostructures, the size of which is comparable to the electron path length, is of great interest, both from a fundamental point of view and for practical application in microelectronics in order to increase the conductivity of nanostructures.

Another important factor in determining the conducting characteristics of nanostructures is their resistance to external influences, degradation as a result of interaction with acids or alkaline solutions, natural aging and oxidation in air, partial amorphization, etc. At the same time, an important task for researchers in this field is to find the optimal conditions for modification and increase the resistance to degradation of nanomaterials. A distinctive feature between nanomaterials and bulk analogs is the presence of a large number of point defects, nonequilibrium phases, which can have a negative effect on the conductive properties of nanostructures, as well as the ballistic nature of charge transfer.

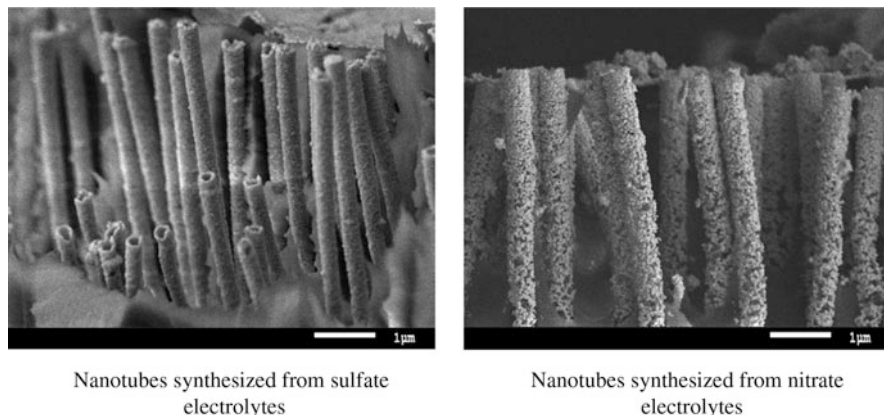
However, despite a large number of studies in this area, there are still many questions associated primarily with the possibility of directed modification of nanostructures, as well as an increase in resistance to degradation, which will further help open up new promising opportunities for the use of nanostructures. This chapter is devoted to the consideration of such issues as the effect of synthesis conditions and the geometry of nanostructures on the conducting properties, assessing the prospects of using various types of ionizing radiation for targeted modification and increasing the conductivity of nanostructures and assessing the potential use of copper nanostructures as a basis for amplifying an electrical signal.

## 10.2 Influence of Synthesis Conditions and Geometry on the Conducting Characteristics of Nanostructures

Figure 10.1 shows a schematic representation of the production of Cu nanotubes in the pores of a template matrix and the subsequent release of their polymer template. In most cases, polymer matrices based on polycarbonate or polyethylene terephthalate, as well as based on aluminum oxide, are used as templates. At the same time, the choice of polymer matrices makes it possible to obtain nanostructures with diameters in the range from 30 to 50 nm to several microns, while matrices based on aluminum



**Fig. 10.1** Schematic representation of the template technology for producing Cu nanotubes



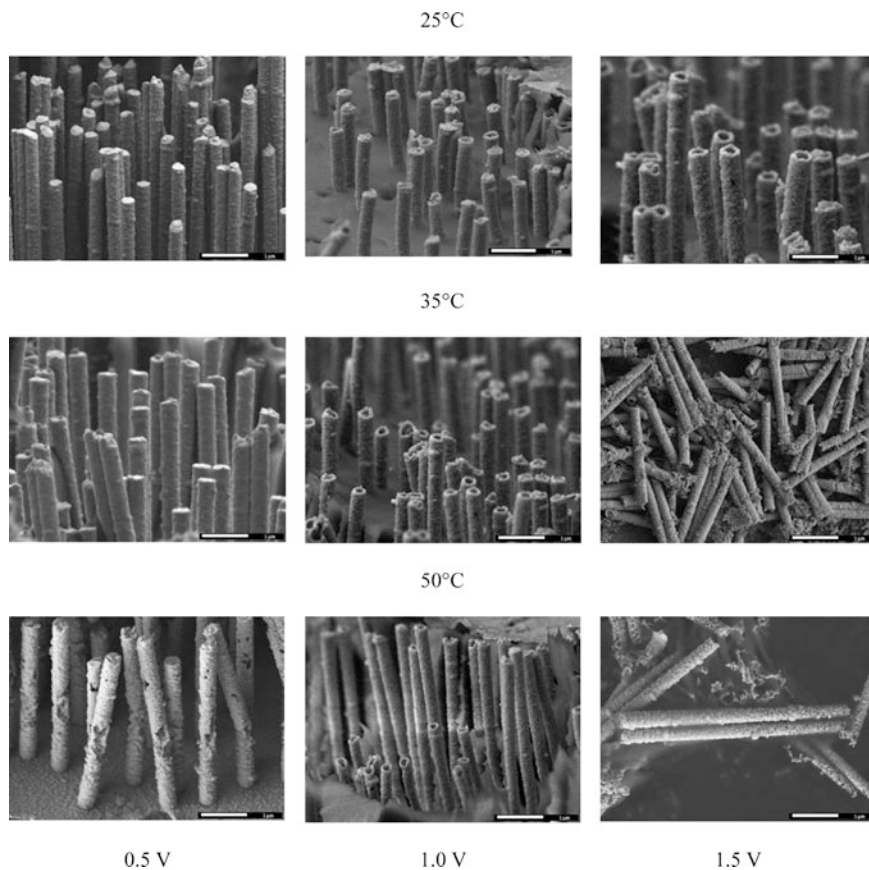
**Fig. 10.2** Typical images of synthesized nanotubes from various electrolyte solutions

oxide limit the possibilities of obtaining ordered arrays of nanostructures with diameters greater than 300–500 nm, which is associated with the processes of anodizing matrices and etching of the matrix diameters.

In most cases, to obtain Cu nanostructures, copper sulfate salts ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ) with the addition of sulfuric acid ( $\text{H}_2\text{SO}_4$ ) are used to increase the acidity level. In this case, the range of applied potential differences in various works varies from 0.3 V to 2.0 V. The authors of various works associate such a wide range of applied potential differences with the possibility of obtaining both nanotubes and nanowires. Also, for the synthesis of Cu nanostructures, electrolyte solutions based on nitrates are used; however, in this case, the synthesized nanostructures have a low degree of crystallinity and order (see Fig. 10.2).

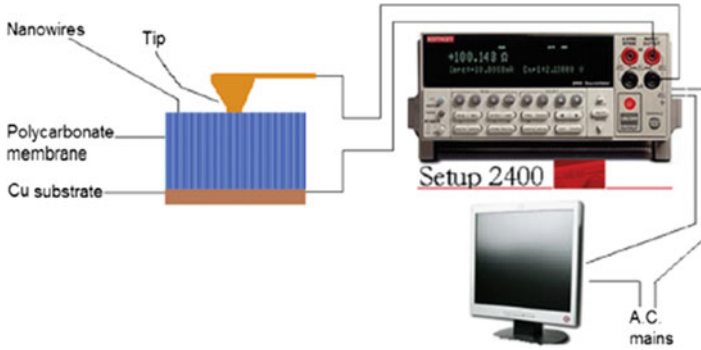
In this case, the presence of disordering regions, as well as the weak bonding of grains, has a negative effect on the conduction mechanisms.

Also, an important role, in addition to the salts used to prepare electrolyte solutions, is played by the synthesis conditions themselves, such as the difference in applied potentials, the temperature of the electrolyte, and the acidity of the solution. Thus, in (Kenzhina et al. 2018), the dependence of the change in the geometry of the obtained nanostructures on the synthesis conditions was shown. The authors varied not only the potential difference but also the temperature of the electrolyte. In this case, the choice of synthesis conditions was based on theoretical data on the deposition potential of copper structures by the electrochemical method, as well as on the conditions for creating an overvoltage gradient in the electrolyte solution. The range of deposition potentials for the search for optimal conditions was 0.5–1.5 V. The temperature range of 25–50 °C was based on the possibility of accelerating the reduction of metal ions in an electrolyte solution, as well as increasing the deposition rate. However, as it was found experimentally, an increase in the electrolyte temperature above 35 °C leads to uneven filling of the template pores with metal due to the uncontrolled growth of nanostructures, as well as a large number of amorphous inclusions resulting from the introduction of oxygen into the



**Fig. 10.3** Typical images of synthesized nanotubes obtained under different synthesis conditions (Kenzhina et al. 2018)

sites and interstices of the lattice during deposition. Amorphization or the formation of disordered regions as a result of the introduction of oxide impurities occurs due to the violent uncontrolled growth of nanostructures and a large amount of oxygen that is released during the deposition process. Also, at high electrolyte temperatures, air bubbles appear, which passivate the pores, thereby complicating the deposition process. In the case of high deposition potentials at high temperatures, the overvoltage gradient sharply increases, which leads to strong distortions and deformations of the structure, as well as the formation of regions of disorder. In this case, according to the authors, the optimal conditions, according to the experimental studies carried out, are an applied potential difference of 1.0–1.5 V at an electrolyte temperature of 25 °C and an applied potential difference of 1.0 V at an electrolyte temperature of 35 °C. These conditions make it possible to obtain nanotubes with a given geometry and wall thickness. The use of synthesis conditions of 0.5 V and an electrolyte



**Fig. 10.4** Typical circuit for measuring current-voltage characteristics (Kaur and Chauhan 2014a)

temperature of 25 °C makes it possible to obtain ordered arrays of nanowires (Fig. 10.3).

Unlike bulk samples for which the measurement of the conducting properties is a fairly simple method, which includes various methods for measuring both current-voltage characteristics and directly the resistivity or conductivity, most methods are unacceptable for nanostructures, and methods for measuring conducting characteristics in most cases are difficult. Amandeep Kaur and R.P. Chauhan were among the first to propose measuring the current-voltage characteristics of nanostructures (Kaur and Chauhan 2014a). Their method is based on measuring the current-voltage characteristics of nanostructures located in a polymer matrix with a metal substrate deposited on one of the sides, which acts as an electrode. A probe with a diameter of several hundred microns is used as the second electrode, which allows simultaneous measurement of the current-voltage characteristics of several hundred nanostructures parallel to each other in a polymer matrix (see Fig. 10.4).

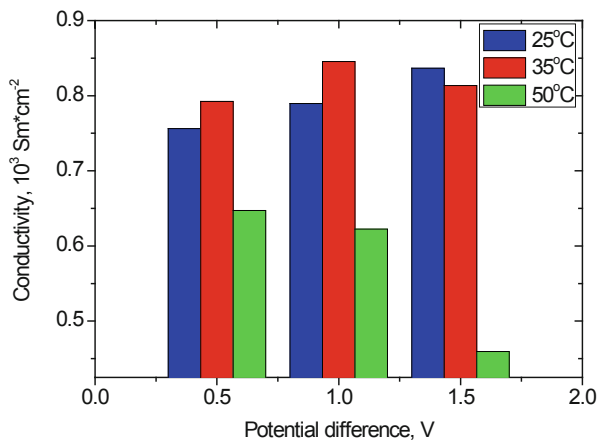
According to the proposed technique in (Kaur and Chauhan 2014a), the authors of (Kenzhina et al. 2018) measured the current-voltage characteristics of the synthesized nanostructures, and using expression (10.1), the values of the specific conductivity were calculated, which are shown in Fig. 10.5.

$$\sigma = \frac{dl}{dU} \frac{l}{A}, \quad (10.1)$$

where  $l$  is the length of the nanotubes,  $A$  is the area, and  $dl/dU$  is the tangent of the  $I$ - $U$  slope.

As can be seen from the presented diagram of the change in the value of the specific conductivity depending on the synthesis conditions, in the case of an increase in the applied potential difference at an electrolyte temperature of 25 °C, it leads to an increase in the conductivity, which the authors of (Kenzhina et al. 2018) associate with an increase in the degree of structural ordering and, consequently, a decrease in concentration of obstacles to the ballistic movement of charge carriers. A decrease in resistance and an increase in conductivity are due to structural orderings,

**Fig. 10.5** Diagram of changes in the conductivity of nanostructures (Kenzhina et al. 2018)



as well as an increase in the size of crystallites, which leads to a decrease in the defect structure and a decrease in the density of dislocation defects. With the ballistic nature of the movement of electrons in the structure of nanotubes, a decrease in the dislocation density and concentration of defects with a change in the synthesis conditions leads to an increase in the conductivity of electrons by reducing the number of obstacles in their path. However, in the case of the formation of oxide nanostructures, which are obtained under synthesis conditions of 1.0–1.5 V and an electrolyte temperature of 50 °C, the value of the specific conductivity decreases sharply, which indicates a deterioration in the conducting properties.

## 10.3 Radiation Modification of Nanostructures to Increase Conductivity

### 10.3.1 Mechanisms of Interaction with Ionizing Radiation

One of the ways to change the physicochemical properties of nanostructured materials is radiation modification. One of the urgent problems of the radiation modification of nanomaterials is the controlled formation of defects in the crystal structure and their recombination in order to improve the strength and conductive properties of nanostructures (Empizo et al. 2015; Chauhan et al. 2016; Kumari et al. 2014). In this case, an important factor is the further migration of defects, which can significantly change the structure of materials. Meanwhile, it is these processes that determine the disturbances in the crystal lattice during irradiation or ion implantation of nanomaterials. In this case, point radiation defects can annihilate or flow down the grain boundaries. Radiation effects arising in nanomaterials under the action of ionizing radiation have a number of features that differ from similar effects in micro- and macro-sized objects. In this case, the presence of a large number of grain boundaries and joints, which serve as sinks for the removal of radiation defects,

contributes to an increase in the stability of nanomaterials in comparison with bulk materials. The use of electronic and gamma radiation for modifying nanostructures is an effective tool for changing the physicochemical properties of nanostructures.

In this regard, it is of great interest to study the effect of ionizing radiation, in particular, the flux of high-energy electrons, gamma quanta, and heavy ions on the structural and conductive properties of Cu nanotubes.

The mechanisms of radiation modification are primarily associated with the processes of formation of radiation defects and their subsequent time evolution, which proceeds in several stages. At the first stage, the energy of the incident particles is transferred to the recoil nuclei for very short periods of time  $\sim 10^{-18}$  s, as a result of which a primary knocked out atom can form. In this case, the condition for the formation of a primary knocked out atom is the excess of the threshold value of the binding energy upon collision and subsequent knockout of the atom from the site of the crystal lattice (Choudhary and Chauhan 2016).

The second stage consists in the transfer of energy from the initially knocked out atom to other atoms of the crystal lattice with the subsequent formation and development of branching cascades of atomic displacements in times not exceeding  $\sim 10^{-13}$  s.

The third stage is characterized by the formation of local atomic rearrangements caused by the spontaneous recombination of defects in a time of  $\sim 10^{-11}$  s. In this case, the formed point defects can migrate along the crystal lattice with subsequent recombination or the formation of clusters and regions of disorder. Energy transfer from incident particles to lattice atoms occurs through elastic scattering and energy losses on electrons and nuclei, as well as inelastic collisions with electrons, followed by ionization of lattice atoms and excitation of the electronic subsystem.

In the case of irradiation with heavy ions with energies above 1 MeV/nucleon, a colossal amount of energy is transferred into the crystal structure. At the same time, the intensity of the “injection” of energy into the electronic subsystem is 100–1000 times higher than into the nuclear one. As a result, the contribution of electronic excitations to the processes of defect formation is much greater. In this case, the density of energy losses along the trajectory of ion movement is 10–50 keV/nm. As a result, the formation of amorphous inclusions, phase transformations, and the appearance of shock waves is observed in the irradiated structures.

In turn, for copper nanostructures, the main processes of defect formation are elastic collisions under irradiation with heavy ions with energies up to 100 MeV. The main factor determining the mechanisms of defect formation upon irradiation with heavy ions is the relaxation of strong electronic excitations created as a result of elastic and inelastic collisions and the subsequent transfer of part of the energy into the crystal lattice.

Unlike ions, electrons have a significantly lower mass, and therefore structural defects such as atomic displacements can be observed only when irradiated with high-energy electrons. In this connection, the description of the interaction of electrons with matter and their motion is carried out within the framework of relativistic quantum mechanics. The relativistic kinetic energy of an incident electron can be calculated by the formula (10.2):



$$E = \frac{m_{0e}c^2}{(1 - v^2/c^2)^{1/2}} - m_{0e}c^2, \quad (10.2)$$

where  $m_{0e}c^2$  is the rest energy (0.51 MeV). For electrons with energies above 500 keV, which can lead to the formation of atomic displacements, the screening effects are neglected, and the Coulomb potential is used to describe the interaction processes. In this case, the loss of energy as a result of a collision with the nucleus can be written as:

$$T = \frac{2E(E + 2m_{0e}c^2)}{M_2c^2} \sin^2\left(\frac{\varphi}{2}\right), \quad (10.3)$$

where  $E$  is the energy of the incident electron. The maximum energy transferred to an atom in elastic collision is calculated using (10.4):

$$T_{\max} = \frac{2E(E + 2m_{0e}c^2)}{M_2c^2}, \quad (10.4)$$

According to the data presented, as a result of collisions of electrons with energies of 1–5 MeV,  $T_{\max} = 180\text{--}250$  eV, which leads to the formation of single defects, since the energy of the primary knocked out atom is insufficient to create cascades of secondary defects. This circumstance served as the basis for the use of electron radiation for the radiation annealing of defects in the crystal structure of materials.

In the case of irradiation with electrons with an energy of more than 10 MeV, which exceeds the energy of the threshold of nuclear reactions, it is necessary to take into account structural disturbances as a result of the inelastic effects of recoil nuclei, gamma quanta, and nucleons. In this case, a significant contribution to the energy losses is made by the deceleration of electrons due to radiation losses in the electric field of nuclei. The emerging bremsstrahlung X-ray radiation in this case can lead to ionization with the subsequent formation of electron-positron pairs and the formation of avalanche-like electron-photon showers in the structure.

In the case of irradiation of gamma quanta, the main feature is the small amount of absorption, as a result of which the depth of penetration and damage is much greater than that of electrons and heavy ions. In this case, the interaction of gamma quanta with energies up to 10 MeV is carried out through three mechanisms: the photoeffect, the Compton effect, and the effect of the formation of electron-positron pairs. The photoelectric effect is typical for the energy range from 10 to 100 keV, the Compton effect is a characteristic for the region from 100 keV to 5 MeV, and the formation of electron-positron pairs is observed at energies above 10 MeV. As a result of the absorption of gamma quanta in the process of the photoelectric effect and the ejection of an electron, the atom passes into an excited state, which is removed by internal electronic transitions. The Compton effect is the elastic scattering of gamma quanta by electrons.

In general, gamma quanta, when interacting with the crystal structure, do not create a large number of atomic displacements. The maximum energy that a gamma quantum is able to transmit as a result of collision can be written as:

$$T_{\max} = \frac{2E_{\gamma}^2}{M_2c^2 + 2E_{\gamma}} = E_{\gamma} \left( 1 - \frac{M_2c^2}{2E_{\gamma}} \right)^{-1}, \quad (10.5)$$

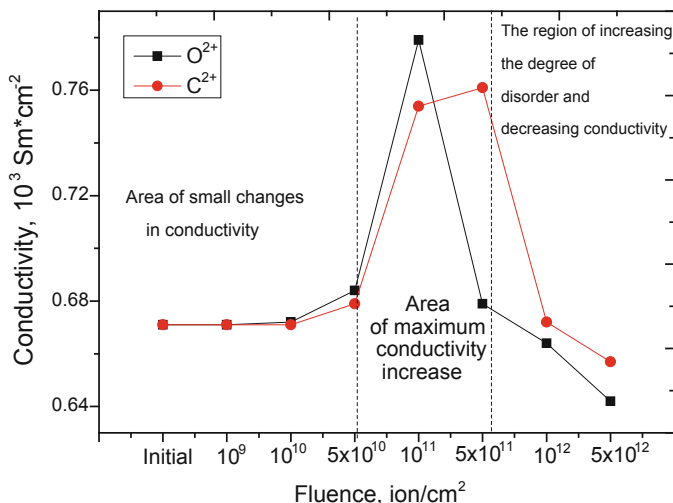
On average, the value  $T_{\max} = 10\text{--}50$  eV, which is significantly less than the energy required to create a large number of structural defects. In this case, the displacement of atoms can occur only in the case of elastic collisions of Compton electrons with target atoms. In this case, most of the gamma quanta are spent on ionization, followed by the release of heat in the form of thermal energy.

### 10.3.2 Examples of the Use of Ionizing Radiation for the Modification of Nanostructures

At the moment, the priority direction of development of the possibility of using ionizing radiation for peaceful purposes is the use of ionizing radiation to modify the properties of nanostructures. These processes are based on changes in the concentration of defects in the structure of nanomaterials during irradiation and the interaction of an ionizing substance with target atoms (Zhao et al. 2017; Tuboltsev and Räsänen 2009; Kaur and Chauhan 2014b). In this case, in the case of high-energy heavy ions, the energy losses, which can lead to the formation of displacement cascades, are not always applicable for modification. For example, in (Kozlovskiy et al. 2019), the effect of irradiation with  $C^{2+}$  and  $O^{2+}$  ions with an energy of 1.75 MeV/nucleon and doses of  $1 \times 10^9$  to  $5 \times 10^{12}$   $\text{cm}^{-2}$  on the change in the degree of structural ordering and conductive properties of Cu nanotubes obtained by the method of electrochemical deposition was considered. During the experiments, the authors established a three-stage nature of the change in conducting properties depending on the radiation dose and the type of ions (see Fig. 10.6).

The first stage is characterized by the retention of the specific conductivity, which is due to the insignificant contribution of the formed single defects to the change in the structural characteristics and conducting properties. An increase in the irradiation fluence from  $5 \times 10^{10}$  to  $5 \times 10^{11}$   $\text{ion/cm}^2$  leads to an increase in the specific conductivity and corresponds to the second stage. The change in the conductive properties is due to a decrease in the concentration of disordered regions and an increase in the degree of perfection of the crystal structure as a result of radiation annealing of defects and stresses arising in the course of synthesis, as well as a change in the density of dislocations and free charge carriers in the nanotube structure.

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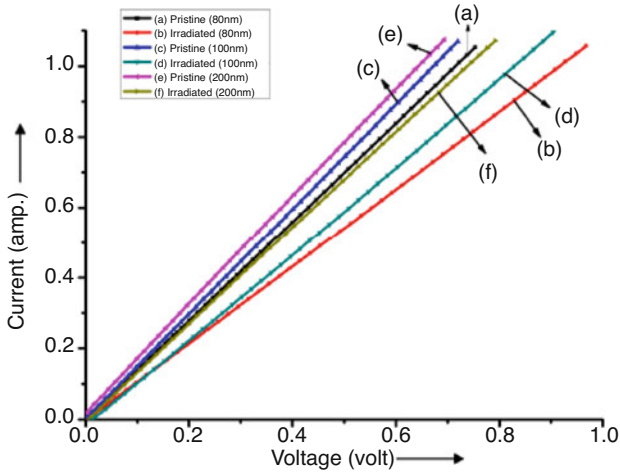
**Fig. 10.6** Graph of changes in the conductivity of nanostructures (Kozlovskiy et al. 2019)

fluence from  $5 \times 10^{10}$  to  $5 \times 10^{11}$  ion/cm<sup>2</sup> leads to an increase in the specific conductivity and corresponds to the second stage. The change in the conductive properties is due to a decrease in the concentration of disordered regions and an increase in the degree of perfection of the crystal structure as a result of radiation annealing of defects and stresses arising in the course of synthesis, as well as a change in the density of dislocations and free charge carriers in the nanotube structure.

The most promising methods of irradiation are fluxes of gamma rays and electrons, which lead to the so-called processes of electron annealing of defects and an increase in structural ordering (Nagel and Balogh 1999). Below is a series of studies devoted to assessing the possibility of using ionizing radiation for directional modification.

*The effect of gamma irradiation on electrical properties of Cu nanowires* (Rana et al. 2014) considered the production of copper-based nanowires with diameters of 80, 100, and 200 nm, obtained by electrochemical deposition, as well as the effect of gamma radiation with different radiation doses (100 and 150 kGy) on the change in the current-voltage characteristics of nanostructures. Polycarbonate membranes were used as template matrices. After irradiation with gamma rays, there is a change in the linearity of the current-voltage characteristics shown in Fig. 10.7, which leads to an increase in resistance.

*Size and irradiation effects on the structural and electrical properties of copper nanowires* by Pallavi Rana and R.P. Chauhan (Rana and Chauhan 2014) considered the influence of size effects and gamma ray learning on changes in the structural and electrical properties of copper nanowires of various diameters (80, 100, and 200 nm). The authors found that after irradiation, the volt-ampere characteristics of nanowires



**Fig. 10.7** Current-voltage characteristics of the samples under study before and after irradiation (Rana et al. 2014)

with a diameter of 80 nm change more strongly than that of nanostructures with a larger diameter.

Based on the data obtained, it can be concluded that the change in the conducting characteristics of Cu nanostructures is influenced not only by the geometry and synthesis conditions but also by ionizing radiation. At the same time, the use of irradiation with specified characteristics and doses can be considered as one of the promising methods for modifying nanostructures in order to increase their conducting characteristics.

## 10.4 Potential Applications of Nanostructures

In recent years, the use of the field emission effect for the generation of free electrons has limitations in comparison with thermionic emission, which is actively used in scanning electron microscopy. This effect is based on the creation of electric field gradients ( $E \geq 10^7$  V/cm) in order to obtain high values of the emission current. Special attention is paid to determining the high electric field strength, which must be achieved at sufficiently low-voltage values. However, despite all these remarks, the field emission effect has a number of useful functions that can be used to create emitting devices with a current density of  $10^6$  A/cm<sup>2</sup>, nanodiodes with a response time of no more than  $10^{-13}$  s, etc.

In this case, the main requirements for micro and nanostructures used as elements of microelectronics are high values of the electric field strength obtained at low applied voltages (about 100–200 V). In this case, an important condition is a small interelectrode distance between the emitting tips and the surface of the receiver.

The phenomenon of cold field emission is based on the effect of quantum tunneling of electrons that are inside a grounded conductor and an external electric field. Using quantum mechanical calculation methods, it is possible to determine the dependence of the current density on the electric field strength  $E$ , which is called the Fowler-Nordheim relation (10.6):

$$J = C_1 E^2 \exp(-C_2 / E), \quad (10.6)$$

where  $C_1$  and  $C_2$  are parameters expressed through the value of the work function of the electron  $\varphi = 3.63$  eV, the charge and mass of the electron.

$$C_1 = \frac{e^3}{8\pi h t^2(y)\varphi}, \quad C_2 = \frac{8\pi\sqrt{2m}}{3he} \varphi^{3/2} \theta(y),$$

$$t(y) = 1, \quad \theta(y) = 1 - y^2, \quad y = \frac{e(eE)^{1/2}}{\varphi}$$

The Fowler-Nordheim relation describes the situation when the emitting surface is an infinite plane perpendicular to the direction of the external electric field. The value of  $E$  in the immediate vicinity of the apex of the nanostructure can be calculated using the analytical formula (10.7):

$$E = \frac{2U}{r \ln\left(\frac{4d}{r}\right)}, \quad (10.7)$$

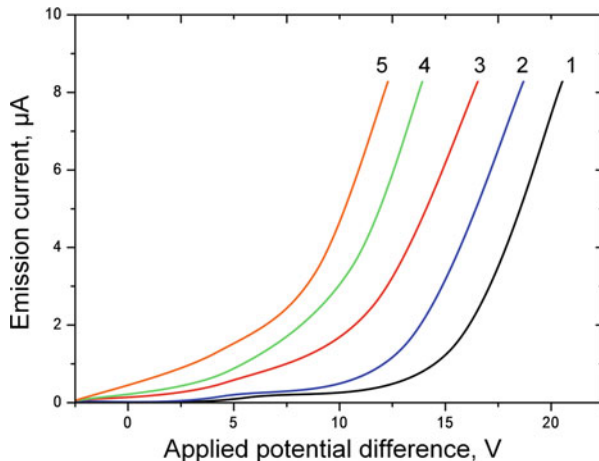
where  $U$  is the applied voltage,  $r$  is the radius of the nanostructure, and  $d$  is the distance between the electrodes. The factor influencing the calculation of the Fowler-Nordheim dependence is the Schottky effect, based on the assumption of the interaction of an emitted electron from the emitter surface and its mirror image, leading to a decrease in the potential barrier, which is created by an external electric field. The correction taking into account this effect is contained in the function  $\theta(y)$ .

The most convenient way to analyze the obtained experimental data determined using (10.6) is based on the logarithmic representation of this equation, to which there is a proportional relationship between the ratio  $I/E^2$  and the inverse value of the electric field strength  $1/E$  (10.8):

$$\ln\left(\frac{I}{E^2}\right) = C_1 - \frac{C_2}{E}, \quad (10.8)$$

The nature of the dependence indicates the mechanism of electron emission associated with field emission. The results obtained show that the emission properties of nanostructures are well described by the Fowler-Nordheim relation. Figure 10.8 shows the dependence of the change in the emission current for various Cu nanostructures irradiated with various types of ionizing radiation.

**Fig. 10.8** Dependence of the change in the emission current on the difference in applied potentials for various nanostructures: (1) initial Cu nanostructures; (2) irradiated with a flux of gamma quanta with a dose of 100 kGy; (3) irradiated with an electron beam with an energy of 5 MeV with a dose of 100 kGy; (4) irradiated with  $C^{2+}$  ions with a fluence of  $10^{11}$  ion/cm<sup>2</sup>; (5) irradiated with  $O^{2+}$  ions with a fluence of  $10^{11}$  ion/cm<sup>2</sup>



As can be seen from the data presented, for modified nanostructures, the achievement of a given value of the emission current is observed at lower applied voltages, which indicates a more efficient enhancement of the emission current by modified nanostructures. An increase in the emission current for irradiated nanostructures is due to an increase in the concentration of charge carriers, as well as an improvement in the structural characteristics and a decrease in the amorphous regions leading to an increase in the conductive and emission properties of nanostructures.

One of the important properties of nanotubes used as emitters is a high aspect ratio (length to diameter ratio). Due to this feature of nanostructures, the value of the electric field  $E$  in the vicinity of the tip of the nanostructures is many times higher than the average value of  $E_0$ —the ratio of the applied voltage  $U$  to the distance between the tip of the nanostructure and the anode.

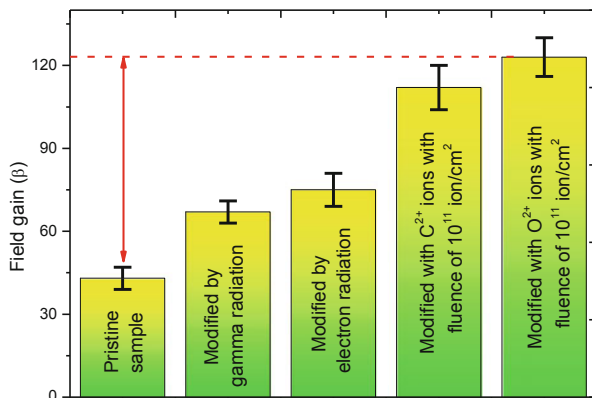
Expression (10.9) allows us to determine the ability of the emitter to amplify the electric field, which is characterized by the field gain  $\beta$ :

$$\beta = \frac{E}{E_0} = \frac{Ed}{U}, \quad (10.9)$$

Since the aspect ratio for nanostructures reaches  $\sim 10^2$ – $10^3$ , the field emission of nanotubes is observed at lower applied voltages than in the case of traditional cold field emitters. Figure 10.9 shows a graph of the dependence of the change in the field gain for various types of nanostructures.

As can be seen from the presented graph, the modification of nanostructures leads to an increase in the value of the field gain, which is due to a change in the crystal structure as a result of irradiation. High values of the gain make it possible to study the Stark effect in order to determine the intramolecular forces and make it possible to explain the dielectric properties of molecules, etc.

**Fig. 10.9** Graph of field gain variation for different types of nanostructures



## 10.5 Conclusion

Despite a large number of works devoted to methods of obtaining and modifying nanostructures, there are still no effective methods for the large-scale production of ordered arrays of copper nanostructures with the same morphological and structural characteristics. The main difficulties in the synthesis are short length, nonlinear morphology, polydispersity, low crystallinity, and low content of nanostructures in matrices (no more than 5–7% of the matrix weight).

A promising method for modifying nanomaterials and their properties is the use of beams of heavy ions or gamma rays and electrons. In this case, in the case of irradiation with ionizing radiation, in contrast to thermal annealing, the modification of properties occurs locally within the structure. By controlling the energy and radiation dose, it is possible to modify the properties of nanomaterials at any depth, as well as significantly increase the resistance of nanostructures to external influences, by means of radiation hardening and changes in structural properties.

This chapter briefly shows the prospects of using various types of ionizing radiation for the targeted modification of copper nanostructures in order to increase the conducting characteristics, which have potential use as emitter bases and anode materials for lithium-ion batteries.

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