ОБМІН ПРАКТИЧНИМ ДОСВІДОМ, ТЕХНОЛОГІЯМИ ТА ОБГОВОРЕННЯ

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O. SHUIABOV, A. MALININA, V. DANYLO
State Higher Educational Institution "Uzhhorod National University"
V. CHYHIN
National Lend Forces Academy, Lviv

SOURCE OF BACTERIOCIDIC ULTRA-VIOLET RADIATION AND FLOW OF NANO-PARTICLES OF ZINC AND COPPER OXIDE FOR APPLICATIONS IN MICROBIOLOGY, MEDICINE AND NANOTECHNOLOGY

The use of gas-discharge sources of bactericidal ultraviolet radiation in biomedical engineering, such as lamps on vapor or amalgam of mercury, xenon and inert gas halide molecules, has recently received significant development. In addition to the ultraviolet radiation factor in various applications in medicine, biology and agrotechnologies, other factors of the gas discharge that are realized in open sources based on atmospheric pressure air are also important. Thus the characteristics of the source based on the flare corona, whose use for plasma pretreatment of lettuce seeds, showed that the germination of the treated seeds increases by more than 25% after the treatment. Characteristics of an open, overvoltage nanosecond discharge in air at atmospheric pressure between copper electrodes with an ectonic mechanism for introducing copper vapor into the discharge gap. This discharge is a point source of ultraviolet radiation in the spectral range of 200-230 nm. A more detailed study of this discharge revealed that, simultaneously with ultraviolet radiation, it is a source of a stream of copper oxide nanostructures deposited on a glass substrate. Nanostructures based on zinc and copper oxides are characterized by a pronounced antimicrobial effect. Therefore, the development of new methods for the simultaneous production of bactericidal ultraviolet radiation and fluxes of transitional metal nanoparticles, which allow to strengthen the inactivation and antimicrobial properties of gas-discharge air plasma, are of considerable interest for applications in microbiology, medicine and agricultural technologies. This report presents the pulsed plasma-chemical reactor device, the parameters and optical characteristics of the plasma of over-stressed nanosecond discharge between copper and zinc electrodes, and the results of the investigation of nanostructure characteristics of these metals oxides.

***Keywords**: gas-discharge, ultraviolet radiation, halide molecules, plasma-chemical reactor, copper and zinc electrodes*

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Problem statement

The use of gas-discharge sources of bactericidal ultraviolet radiation in biomedical engineering, such as lamps on vapor or amalgam of mercury, xenon and inert gas halide molecules, has recently received significant development [1, 2]. In addition to the ultraviolet radiation factor in various applications in medicine, biology and agrotechnologies, other factors of the gas discharge that are realized in open sources based on atmospheric pressure air are also important.

Analysis of recent researches and publications

Thus, in [3] the characteristics of the source based on the flare corona, whose use for plasma pretreatment of lettuce seeds, showed that the germination of the treated seeds increases by more than 25% after the treatment. Characteristics of an open, overvoltage nanosecond discharge in air at atmospheric pressure between copper electrodes with an ectonic mechanism for introducing copper vapor into the discharge gap [4]. This discharge is a point source of ultraviolet radiation in the spectral range of 200–230 nm. A more detailed study of this discharge revealed that, simultaneously with ultraviolet radiation, it is a source of a stream of copper oxide nanostructures deposited on a glass substrate [5]. Nanostructures based on zinc and copper oxides are characterized by a pronounced antimicrobial effect [6, 7]. Therefore, the development of new methods for the simultaneous production of bactericidal ultraviolet radiation and fluxes of transitional metal nanoparticles, which allow to strengthen the inactivation and antimicrobial properties of gas-discharge air plasma, are of considerable interest for applications in microbiology, medicine and agricultural technologies.

The purpose of the work is to create the pulsed plasma-chemical reactor device, and to investigate the parameters and optical characteristics of the plasma of over-stressed nanosecond discharge between copper and zinc electrodes, and nanostructure characteristics of these metals oxides.

Device of gas discharge reactor.
Technique and conditions of experiment

The design of pulsed gas-discharge reactor based on a bipolar overvoltage nanosecond discharge in atmospheric air is shown in Fig.1. Electrodes with a diameter of 5 mm and a length of 30 mm made of zinc or copper were installed in a sealed chamber of a dielectric with a volume of 3 litres. The radius of curvature of the working end part of electrodes was 3 mm. The discharge for all types of electrodes was investigated at atmospheric air pressure.

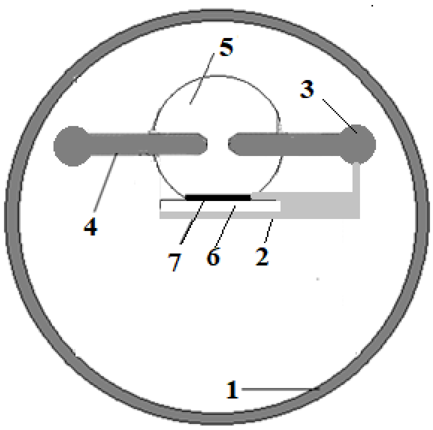

Fig. 1. The scheme of a pulsed plasma-chemical reactor: 1 — dielectric discharge chamber casing, 2 — substrate fixation system for thin film spraying, 3 — interelectrode distance control system, 4 — metal electrodes, 5 — film deposition zone, 6 — glass substrate, 7 — film

To ignite the discharge, high-voltage bipolar pulses with a total duration of 50–100 ns and an amplitude of ± (20–40) kV were applied to the metal electrodes. At the same time, between the tips of the electrodes, a uniform discharge was ignited with an amplitude of current pulses of 50-170 A [8, 9]. The plasma volume did not exceed 5-10 mm^3. The voltage pulses at the discharge gap and the discharge current were measured using the wideband capacitive divider, the Rogowski belt, and the 6-LOR 04 wideband oscilloscope. The time resolution of this recording system was 2-3 ns.

The investigation of spatial characteristics of the discharge was carried out using a digital camera. The pulse repetition rate was varied in the range of f=35-1000 Hz. To record the plasma emission spectra, the MDR-2 monochromator, the FEU-106 photomultiplier, the DC amplifier, and the electronic potentiometer were used. The radiation of discharge plasma was analysed in the spectral range of 200–650 nm.

The transmission spectra of radiation by thin nanostructured films, which were deposited on glass substrates, were recorded using an OCEAN OPTICS USB 2000 spectrometer. The films were deposited for 30–60 minutes with a glass substrate installed at a distance of 30 mm from the center of the discharge gap at an interelectrode distance of 1-3 mm. The image of the surface of thin nanostructured films was recorded using a Cross Beam Workstation Auriga (Carl Zeis) scanning electron microscope. The Raman scattering spectra were excited using an argon ion laser, which generated radiation at a wavelength of 514.5 nm. The Raman spectra of radiation scattering on copper and zinc oxide thin films were studied using an nVia Renishaw spectrometer.

Characteristics and Parameters of Overvoltage Nanosecond Discharge. Let us consider the results of the study of the characteristics and parameters of the plasma of an overvoltage nanosecond discharge in the air between zinc and copper electrodes under the condition of microtip explosions on the surface of the electrodes and the formation of the corresponding ectons. Photos of the discharges at the voltage pulse repetition rate (f = 40-1000 Hz) for all types of electrodes (Zn, Cu) or their combinations, when the distance between them was within 1-3 mm were the same as for the discharge between copper electrodes [4, 10]. At the repetition frequency of the discharge pulse in the range of 35-150 Hz, a diffuse appearance occurred. The diameter of the plasma in the interelectrode gap was approximately equal to the interelectrode distance. In the range of intervals 400–1000 Hz, the diameter of the plasma of an overstressed nanosecond discharge increases by a factor of 3–4. Under the condition of ignition of a fairly homogeneous diffuse discharge under the conditions of these experiments, they were considered in [4].

Figure 2 shows oscillograms of voltage and current pulses for a discharge between copper electrodes.

Similar waveforms were also obtained for discharges between zinc electrodes. The duration of the main part of the voltage pulse train reached 50-120 ns. Bipolar voltage impulse peaks had an amplitude of a positive and negative component up to 20-30 kV. The discharge current pulses were a sequence of current pulses with an amplitude of positive and negative pulses of 120-150 A.

The total length of a sequence of current pulses with an amplitude falling in time, reached 150–200 ns. By graphically multiplying the oscillograms of the current pulses and the oscillograms of the voltage, the time distribution of the pulse contribution of energy to the plasma of the discharge under study was obtained. The maximum pulse power of the discharge was observed in the initial stage of the breakdown of the discharge gap and reached 2-4 MW.

Integration over time of the pulse power made it possible to determine the electrical energy that was introduced into the plasma of a nanosecond discharge during one sequence of voltage and current pulses. For the conditions of our experiments, the energy that was deposited in the plasma in one pulse reached E = 100 mJ. The spectra of ultraviolet radiation of the plasma of the investigated discharge between copper electrodes and the results of their identification are given in [4], and the emission spectra of the discharges between the electrodes of zinc and stainless steel are shown in Fig.3. Approximately 90% of the plasma radiation power in the spectral range of 200–1000 nm for discharges between zinc and copper electrodes is concentrated in the spectral range of 200–260 nm. For the overvoltage nanosecond discharge between copper electrodes, the spectral lines of copper ions in the emission spectrum were the main ones; in the UV spectra of the discharge between zinc electrodes, the spectral lines of zinc atoms and ions were: 202.6; 206.2 nm Zn II; 250.2; 255.8 nm Zn I. The nanosecond discharge plasma parameters for a mixture of copper and air vapor at atmospheric pressure (component ratio 30: 101 kPa, respectively) were determined numerically and calculated as full integrals of the electron energy distribution function (EEDF). The EEDFs were found numerically by solving the kinetic Boltzmann equation in the two-term approximation. Calculations of the EEDF were performed using the program [11]. On the basis of the EEDF, the average electron energy and electron mobility were determined. The ratio of copper vapor concentrations and gas concentrations of the standard atmosphere at a pressure of 1001 kPa: argon, carbon dioxide, oxygen, and nitrogen was as follows: 0.3: 7: 0.27: 159: 599. The calculations were carried out in dependence of the plasma parameters on the ratio of the electric field intensity (E) to the total concentration of copper, argon atoms and carbon dioxide, oxygen and nitrogen molecules, (N). The range of variation of the parameter E / N = 1-1300 Td ($1 \cdot 10^{-17}$ - $1 \cdot 10^{-15}$ V cm^2). The integral of electron collisions with atoms and molecules takes into account the following processes: elastic electron scattering on copper atoms, excitation of energy levels of copper atoms (threshold energy 1.500 eV, 3.800 eV, 5.100 eV), ionization of copper atoms (threshold energy 7.724 eV); elastic scattering of electrons on copper atoms, excitation of the energy level of argon atoms (threshold energy 11.50 eV), ionization of argon atoms (threshold energy, 15.80 eV); elastic scattering and excitation of energy levels of carbon dioxide molecules: vibrational (energy threshold: 0.083 eV, 0.167 eV, 0.252 eV, 0.291 eV, 0.339 eV, 0.422 eV, 0.505 eV, 2.5 eV), electronic (energy threshold: 7.0 eV, 10.5 eV), dissociative electron attachment (threshold energy 3.85 eB), ionization (threshold energy 13.30 eV); elastic scattering and excitation of energy levels of oxygen molecules: vibrational (energy threshold: 0.190 eV, 0.380 eV, 0.570 eV, 0.750 eV), electronic (energy threshold: 0. 977 eV, 1.627 eV, 4.500 eV, 6.000 eV, 8.400 eV, 9.970 eV, dissociative electron sticking (threshold energy - 4.40 eV) ionization (threshold energy - 12.06 eV); elastic scattering and excitation of energy levels of nitrogen molecules: rotational – threshold energy 0.020 eV, vibrational (threshold energy: 0.290 eV, 0.291 eV, 0.590 eV, 0.880 1.170, 1.470, 1.760, 2.060, 2.350; electronic: 6.170 eV, 7.000, 7.350, 7.360, 7.800, 8.160, 8.400, 8.550, 8.890, 11.03, 11.87, 12.25, 13 .00, ionization (threshold energy - 15.60 eV).

The data on the absolute values of the effective cross sections for these processes, as well as their dependences on the electron energy, are taken from the database [18]. The concentration of electrons (Ne) was calculated by the known formula [19]: $N_e = j/e \cdot V_{dr.}$, where j – density of the current in the discharge, e – electron charge, $V_{dr.}$ – electron drift velocity. The electron drift velocity was determined from the expression: $V_{dr} = \mu_e \cdot E$, where μe is the electron mobility, E is the field strength on the plasma. The field tension on the plasma E was calculated by the formula: $E = U_{pl.}/d$, U_{pl} – voltage on the plasma, d - value of the discharge gap. The average energy of the discharge electrons most strongly depends on the parameter E/N = 1-400 Td, while it linearly increases from 0.15 to 8.77 eV. For the range of the reduced electric field strength of 615 Td - 820 Td, at which experimental studies of the electrical T and the optical characteristics of the discharge were carried out, the average electron energies varied within 12.6 - 16.5 eV.

The results of calculating the average electron energies make it possible to determine their temperature in the gas-discharge radiator plasma from the well-known formula [19]: $\varepsilon = 3/2 \cdot kT$, where ε is the electron energy, k – the Boltzmann constant, T – temperature in Kelvin. It increases from 146160 K to 191400 K when the parameter E/N changes from 615 to 820 Td, respectively.

The electron mobility, as follows from the numerical calculation data, varies within $1.1130 \cdot 10^{24} \cdot N$ - $1.031 \cdot 10^{24} \cdot N$ (1/m/V/s) when the E/N parameter is changed in the range of 615 Td - 820 Td, which gives the values of electron drift velocities of $6.8 \cdot 10^4$ m/s and $8.4 \cdot 10^4$ m/s, respectively, for a plasma field tension of $15.0 \cdot 10^6$ V/m and $20.0 \cdot 10^6$ V/m, the value of electron concentration $70.3 \cdot 10^{21} m^{-3}$ - $56.9 \cdot 10^{21}$ m^{-3} at a current density of $765 \cdot 10^6$ A/m^2 on the surface of the electrode of the radiation source ($0.196 \cdot 10^{-6}$ m^2).

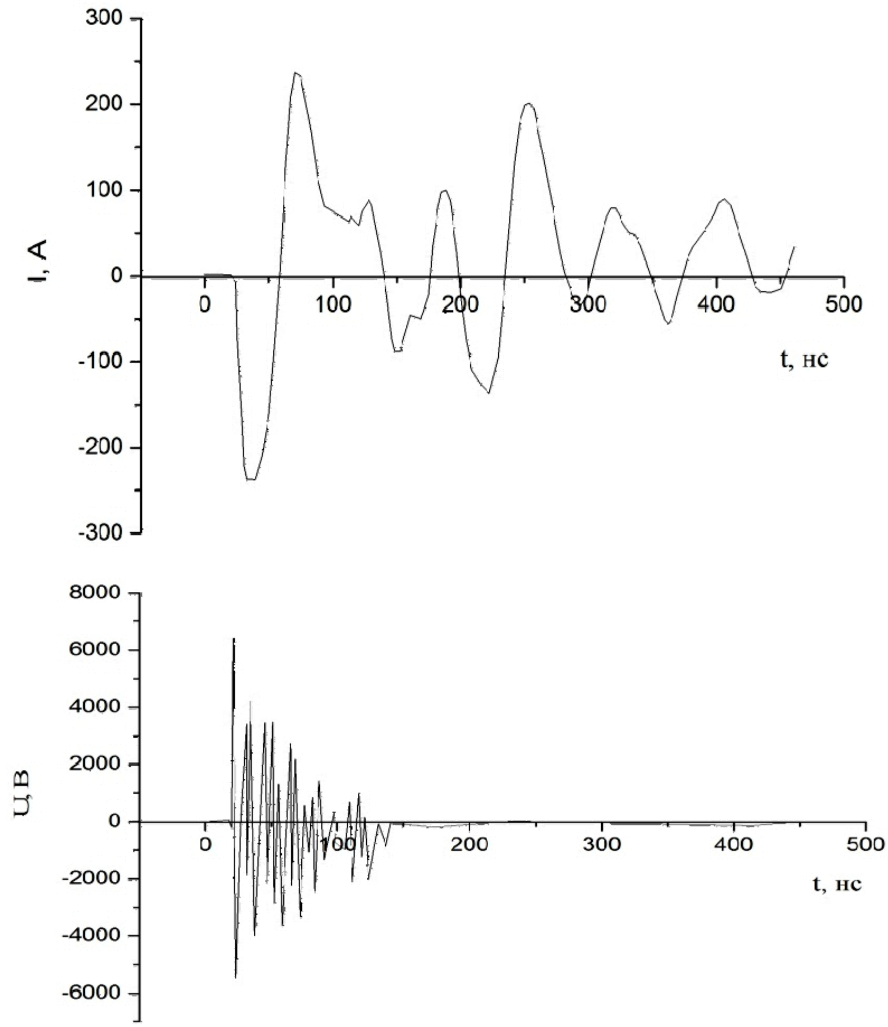

Fig. 2. Oscillograms of current and voltage of an overstressed nanosecond discharge in air between a copper electrode and a stainless steel electrode (interelectrode distance d = 3 mm)

Under the conditions of this experiment, the main mechanism for the entry of zinc, copper, and iron vapor into the plasma is ectonic (an explosion of microtips on the surface of electrodes), in which the electron density of the plasma can reach 10^{16}-10^{17} cm^{-3} [12]. Therefore, an important contribution to the mechanism of formation of excited atoms and transition metal ions can be made by the excitation of metal ions in the ground state by electrons, as well as electron-ion recombination processes. The effective cross sections for these processes, for example, for zinc and cadmium ions, are large enough and reach 10^{-6} cm^2 [13].

Characteristics of thin nanostructured films based on oxides of zinc, copper and iron

Let us consider the main results of the study of the characteristics of nanostructures based on zinc and copper oxides, which are deposited on a glass substrate near the discharge gap.

In Fig. 4 the photograph of the film surface deposited on a glass substrate from the products of erosion of copper electrodes and products of dissociation of air molecules in an overvoltage nanosecond discharge is presented. To determine the size of nanostructures, a gel was deposited on the surface of the film on the basis of standard gold nanostructures of spherical shape with a diameter of 20 nm (they are highlighted in photos in yellow). A comparative analysis of the sizes of spherical gold nanostructures and nanostructures synthesized from products of a nanosecond discharge between copper electrodes in air showed that the sizes of synthesized nanostructures are in the range of 2–20 nm. The transverse dimensions of nanostructures based on zinc oxide were in the range of 2-50 nm, but the formation of large zinc agglomerates with sizes of 1–10 μm was also observed. With increased air pressure and high energy deposition into the plasma (when nanosecond discharges in liquid or air are used to synthesize nanostructures), predominant formation of nanovisexors or nanostructures of transition metal oxides of a more complex form is observed.

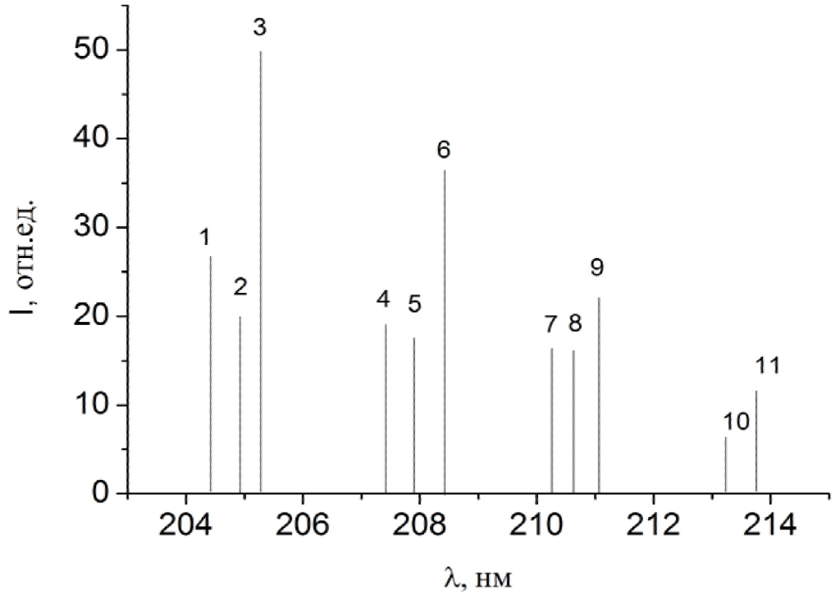

Fig. 3. A portion of the plasma emission spectrum of a nanosecond discharge between zinc electrodes with the most intense spectral lines of atoms and zinc ions (d = 2 mm; f = 100 Hz)

This was confirmed by studying the spectra of Raman scattering of laser radiation with a wavelength of 514.5 nm nanostructures of oxides of zinc or copper, synthesized in the investigated discharge and comparing them with the corresponding Raman spectra of nanowiskers of other researchers. For example, in [14], zinc oxide nanostubes of boules were obtained as a result of the action of a powerful gas-discharge laser on KrF molecules, which emitted at a wavelength of 248 nm, on the surface of a ceramic ZnO target. As can be seen from [5], the Raman spectrum of Ar + laser radiation recorded by us correlates well with the corresponding spectrum obtained in [14], where Raman scattering of the same laser radiation on zinc oxide nano-columns with a diameter of 8-35 nm was studied. Therefore, we can assume that, under the conditions of our discharge, the synthesis of zinc oxide nano-columns occurs perpendicular to the surface of the glass substrate.

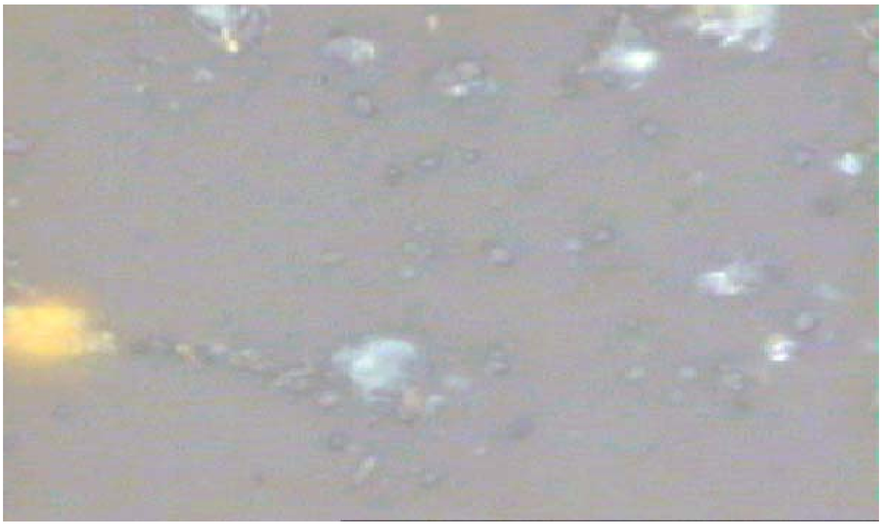

Fig. 4. The structure of the surface of the film synthesized on a glass substrate from the products of sputtering copper electrodes in atmospheric air for 30 minutes under the action of a high-current nanosecond discharge (d = 1 mm and f = 100 Hz)

In Fig. 5 the transmission spectrum of copper oxide nanostructures is given. The transmission of such films increased with an increase in the wavelength in the visible region of the spectrum and the shape of the continuum without maxima and minima in the range from 500 to 650 nm. It correlates well with the spectrum of passing copper oxide (Cu_2O) nanostructures [15]. The absorption band of the film in the wavelength range of 550–580 nm corresponds to the absorption band of copper nanostructures [16, 17]. The narrow bands of film clarification in the blue region of the spectrum (at wavelengths of 420 and 450 nm) are probably associated with the action of ultraviolet discharge radiation in the spectral range 200-230 nm on the film during its synthesis. The same bands of enlightenment were observed for films based on zinc oxide. The cause of the appearance of such bands of enlightenment can be radiation defects of films of copper oxide zinc and the formation of new energy levels in these compounds. The most intense were the transmission bands of nanostructures based on zinc and copper oxides, which was correlated with selective and intense plasma radiation of zinc and copper vapors in the spectral range 200-230 nm.

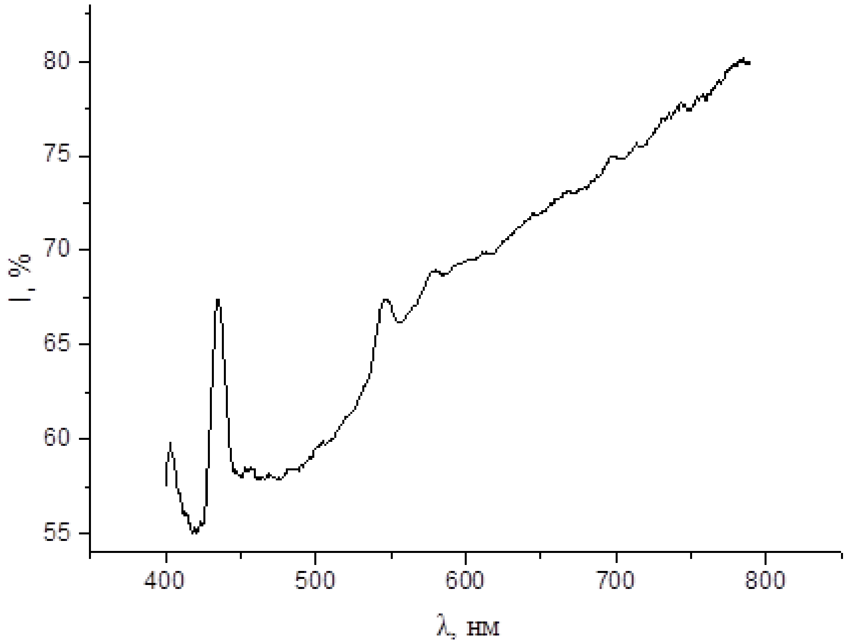

Fig. 5. The transmission spectrum of radiation in the center of the film obtained by sputtering copper electrodes in air for 30 minutes (d = 1 mm and f = 100 Hz)

Conclusions

It has been established that overvoltage nanosecond discharge in atmospheric pressure air between copper or zinc electrodes is the selective source of radiation of atoms and ions of zinc and copper in the spectral range 200–230 nm; at the same time, plasma is the source of copper or zinc oxide nanostructures streams, which can be used in microbiologists, medicine and agrotechnologies, and when automatically assisted by ultraviolet radiation of plasma, thin nanostructured films based on oxides of zinc and copper characterized by transparency windows in the blue spectral range are synthesized, which can be used in optoelectronics.

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