Morphological and magnetic features of columnar nanostructures CuO

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Abstract. Columnar nanostructures (CNS) were grown by plasma chemical synthesis at a gas mixture pressure of 90\% He + 10\% O\textsubscript{2} 200 Pa and substrate temperatures of 340K (sample 1) and 370K (sample 2). The effect of substrate temperature on the morphological, crystalline, magnetic, and impedance properties of CNS was studied. Scanning microscopy (SEM) showed that the morphology of CNS varies significantly from dendritic to wire structure. Energy dispersive X-ray spectroscopy (EDS) showed a change in the stoichiometry of the deficiency samples (Cu\textsubscript{52}O\textsubscript{48}) to an excess of oxygen (Cu\textsubscript{42}O\textsubscript{58}). X-ray diffraction analysis (XRD) and Rietveld fitting showed that samples 1 and 2 have a monoclinic crystal structure with a large proportion of the amorphous phase, the size of coherent scattering regions (CSR) was 26 nm (sample 1). Magnetic measurements showed that sample 1 exhibits ferromagnetic behavior, and at 6 K a magnetic hysteresis loop appears. Sample 2 from 250 K to room temperature exhibits diamagnetic behavior. A connection was found between the appearance of diamagnetism and a jump in the dielectric constant of sample 2. An assumption was made about the electron-ionic nature of the diamagnetism of sample 2.

1. Introduction

Recently, considerable research efforts have been aimed at studying the magnetic and electrical properties of nanoparticles (NPs) of transition metal oxides (NiO, MnO, CuO). The increased interest in them is caused by their great importance both in fundamental and applied sciences. Such materials are used as additives in high-temperature superconductors [1, 2], in highly sensitive sensors [3-5], capacitors [6, 7], as solid electrolytes [8-10], in a spin valve and tunnel devices [11]. Interest in CuO-based nanoparticles is due to the fact that, with a decrease in particle size, a semiconductor with antiferromagnetic (AFM) ordering turns into a superparamagnet [12], exchange bias effects (EB) appear [13], and the AFM ordering temperature decreases. Many physical and mathematical models have appeared to explain the observed effects. The appearance of ferromagnetism (FM) was explained by uncompensated spins on the surface of nanoparticles due to the large number of oxygen vacancies and variable valency [14]. The complex exchange interaction of the AFM nucleus and the FM shell causes the EB effect [13]. These effects are characteristic not only for nanoparticles, but also for films and nanowires [15].

The study of magnetoelectric properties is complicated by a number of factors associated with the size of the nanoparticles. The properties of nanoparticles are affected by the method of preparation, surface contamination of nanoparticles with traces of interaction with the atmosphere and chemical
reactions, significant agglomeration due to high surface energy. The dependences of the magnetic and electrical characteristics, as a rule, do not have pronounced peaks, indicating, for example, phase transitions. The study of nanoparticles obtained in a plasma of a low-pressure arc discharge is associated with all of the above difficulties. However, the effects that are manifested in materials in the nanoscale state are amplified many times, due to the purity of the medium and the materials used, high hardening rate, high speed of plasma-chemical reactions. CuO nanoparticles exhibit an abnormally high polarization in the electric field associated with ionic conductivity [16], high ferromagnetism [17], which correlates with residual stresses [18]. CuO nanowires grown on the surface of granules of a high-temperature superconductor are effective pinning centers [19]. In the present work, an attempt is made to study in detail the effect of high-speed hardening and substrate temperature on the morphological and magneto-electric properties of CNS.

2. Experimental details
CNS CuO was grown on a stainless steel substrate in a plasma chemical reactor described in detail in [20]. The temperature of the substrate was kept constant with water. The process of plasma-chemical synthesis of oxide nanoparticles in a plasma of a low-pressure arc discharge was described in detail in [21]. It was shown that the residual stresses and the average nanoparticle size mainly depend on the pressure and type of plasma-forming gas. A physical and mathematical model is also presented, which is in good agreement with the results. The essence of high-speed quenching is that supersonic plasma jets, consisting of multiply ionized atoms, clusters, and a microdrop fraction, collide with a buffer (inert) gas and heat it, which leads to a sharp increase in the electron temperature of the near-cathode plasma and intensification of plasma-chemical synthesis processes. The plasma quenching rate depends on the thermal conductivity of the buffer gas; therefore, helium was chosen in this work. Heated buffer gas has a significant effect on the agglomeration and growth of nanoparticles on the surface of the substrate. The main parameters of plasma-chemical synthesis are given in the table. The cathode was made of high purity copper (99.99%).

The morphological composition of the samples was studied using a JSM 7001F scanning electron microscope with an Oxford Instruments microanalyzer system and a JEOL JEM-2100 transmission electron microscope. The crystal structure of CNS was studied using an Advance D8 X-ray diffractometer in CuKα monochromatized radiation and a PDF4 + database. The fitting and analysis of the obtained X-ray spectra was carried out using the full-profile analysis program Powder Cell 2.4. Magnetic measurements were carried out using a SQUID magnetometer (Quantum Design) in the temperature range from 5 to 300K. Electrical measurements were performed using the Elins 1500 and Agilent E5061B impedance analyzers in the frequency range from 0.1 Hz to 100 MHz and the temperature range from 100 to 300K. As a capacitive type sensor, a polycor plate with a thickness of \( h = 1 \) mm and a size of \( 10 \times 12 \) mm with counter silver comb electrodes deposited on it was used. The sample for measurement was pressed at a pressure of 20 MPa. The sample size corresponded to the sensor. To prevent the effect of condensed moisture on the measurements, the sample was heated to 370 K in a stream of dried air. The voltage amplitude was 250 mV. The frequency dependences of the impedance modulus \( |Z(\omega)| \) and the phase shift angle \( \varphi(\omega) \), which allows one to construct the Nyquist hodographs and the temperature dependence of the dielectric constant of the samples. Hodographs were simulated using equivalent circuits in the EIS Spectrum Analyzer program.

| Table 1. The main parameters of plasmachemical synthesis. |
|----------------------------------------------------------|
| Arc current                                             | 100 A                      |
| Magnetic field strength of the focusing coil             | 800 A/m                    |
| The distance between the cathode and the anode          | 50 mm                      |
| Cathode diameter                                        | 80 mm                      |
| Pressure in a plasma chemical reactor                    | 200 Pa                     |
| The ratio of buffer and reaction gas                     | 90%He+10%O₂                |
3. Results and discussion

Figure 1 shows SEM and TEM images of samples 1 and 2. As can be seen from the figure, the morphology of the samples is significantly different. The structure of sample 1 is predominantly dendritic; dendrite dimensions are difficult to determine. Studying TEM images allows us to estimate the average size of ~ 30 nm. Sample 2 consists of weakly agglomerated wires with a diameter of ~ 50 nm and a length of ~ 1.5 μm.

The reason for such significant differences is directly related to the features of plasma-chemical synthesis and deposition of the obtained nanoparticles and clusters on a substrate [22]. Interaction with oxygen occurs under thermodynamically nonequilibrium conditions leading to defects in the crystal structure, in this case stoichiometry is violated, large residual stresses appear. The thermal state of the resulting CNS is determined by the temperature of the substrate, the buffer gas, and the condensing nanoparticles and clusters. However, for nucleus particles, the temperature of the substrate plays a decisive role. The lower the temperature of the substrate, the more isotropic particle growth becomes. The optimum temperature for producing nanoparticles is less than 300 K. At a substrate temperature above 450 K, a porous coating forms on the substrate. EDS analysis showed that sample 2 is non-stoichiometric with a deficit in Cu (Cu₄₂O₅₈), and sample 1 is almost stoichiometric (Cu₄₈O₅₂).

![SEM images of samples 1 and 2. The inset shows the TEM image of sample 1.](image)

**Figure 1.** SEM images of samples 1 and 2. The inset shows the TEM image of sample 1.

Figure 2 shows the XRD spectra of samples 1 and 2 in the range of 2θ from 30 to 80 deg.
In the XRD spectrum presented, against the background of the halo X-ray amorphous phase (especially for sample 1), reflections appear corresponding to the monoclinic structure of CuO (JCPDS data, No. 45-0937). No other crystal structures were found. An increase in the temperature of the substrate leads to a substantial decrease in the fraction of the amorphous phase and an increase in the crystallinity of CNS. Microstructural characteristics, unit cell parameters, CSR size, and residual crystallite stresses were determined by broadening the spectral lines using full-profile fitting in the PowderCell program. The results of processing XRD spectra are presented in below.

Table 2. Lattice parameters, CSR size, residual stresses in CuO nanoparticles.

| Sample | a(Å)   | b(Å)   | c(Å)   | D (nm) | ε (MPa) |
|--------|--------|--------|--------|--------|---------|
| 1      | 4.6764 | 3.4212 | 5.1245 | 27     | 690     |
| 2      | 4.6728 | 3.4102 | 5.1003 | 38     | 220     |

As can be seen from the fitting results, the lattice parameter decreases in both samples, the change for sample 2 is especially noticeable. There are many reasons for such deformation in CNS: the effect of capillary forces, static displacements due to uneven deformation in particles, uneven crystallization and the presence of an X-ray amorphous phase, increased concentration oxygen vacancies due to the explosive nature of crystallization from the amorphous phase, bombardment by high energy ions, high pressure is exerted by surface energy. The fitting of the XRD spectrum of sample 2 revealed a significant texture in the (111) plane. Apparently, the predominant growth of the wire structure in CNS occurs precisely in this plane. This is also indicated by a significant decrease in the amorphous phase and residual stresses.

Figure 3 shows the isothermal dependences of the magnetization $M(H)$ of sample 1 at temperatures of 6, 100, and 300 K.
Figure 3. a) Field dependence of the magnetization $M(H)$ of sample 1 at 6, 100 and 300 K. The inset shows hysteresis loops. b) Temperature dependence of the magnetization $M(T)$ of sample 1 at magnetic fields of 50 and 500 Oe in the ZFC and FC modes.

The behavior of the curves is typical for AFM nanoparticles with a ferromagnetic shell or for superparamagnetic nanoparticles. Such curves are well described by the extended Langevin function [23]: $M(B) = M_0 L(x) + \chi_a B$, where $M_0$ is the saturation magnetization, $L(x)$ is the modified Langevin function with the variable $x = \frac{\mu_p B}{k_B T}$. The variable $x$ includes the temperature $T$, the Boltzmann constant $k_B$, and the magnetic moment of the particle $\mu_p$. The $\chi_a B$ term describes the canting of the AFM sublattices of the particle "core", $\chi_a$ is the magnetic susceptibility of the "core" of randomly oriented particles. The fitting is carried out taking into account the relationship between the parameters $M_0 \sim N \cdot \mu_p$, where $N$ is the specific number of particles. The calculations showed a large discrepancy between the prediction of the theory and the obtained curves for a temperature of 100 K. With increasing temperature, the discrepancy is even greater. Apparently, there is a complex exchange interaction in the dendritic subsystem. It is also necessary to take into account magnetoelastic anisotropy (table 2). The contribution from these interactions can be significant. The relationship between magnetoelastic anisotropy and ferromagnetism in nanowires was studied in [24, 25]. As the temperature decreases to 6 K, a hysteresis loop with a coercive force of ~ 0.5 kOe appears on the $M(H)$ curve (inset in figure 5). The residual magnetization was ~ 0.06 emu/g. No features, for example, the effect of exchange bias, were found in the hysteresis loop, which also indirectly confirms the magnetoelastic nature of ferromagnetism in sample 1. The complex exchange interaction was reflected in the dependence $M(T)$ (figure 3b) in different constant magnetic fields of 50 and 500 Oe and various thermomagnetic prehistory (ZFC and FC). As can be seen, the behavior of the magnetization curves strongly depends on the magnetic prehistory and the applied magnetic field. For the fields of 500 and 50 Oe, the irreversibility between the $M_{FC}(T)$ and $M_{ZFC}(T)$ curves starts estimated at 320 and 300 K, respectively. Wide peaks can be distinguished in the $M(T)$ curves: for $M_{FC}(T)$ at $T \sim 100$ K, the $M_{ZFC}(T)$ curve shows a maximum in the range of 90-190 K. The inset shows the difference susceptibility in a magnetic field of 500 Oe. With decreasing temperature, the susceptibility increases. In the field of 50 Oe, the discrepancy between the $M(T)$ curves of the ZFC and FC modes is much larger than in the field of 500 Oe and with a further increase in the magnetic field strength up to 10 kOe, this trend remains. As the magnetic field increases, the character of the temperature dependence $M(T)$ also changes. The Néel temperature for sample 1, obtained from the peaks in the graphs $\frac{\partial \chi(T)}{\partial T}$, where $\chi(T)$ is the susceptibility in a magnetic field of 500 Oe, is 160 K, which is significantly lower than that of a bulk sample. In [26], the authors also note that the Néel temperature decreases significantly for nanoparticles, which is associated with the quantum-size effect, a decrease in the exchange interaction energy, and oxygen vacancies. A study of the susceptibility in a 50 Oe magnetic field showed that the $M_{ZFC}(T)$ curve has a broad maximum in
the region of 80-210 K, and the derivative \( \frac{\partial \chi(T)}{\partial T} \) has a maximum at 180 K, therefore, with a decrease in the magnetic field strength Neyel's temperature rises.

Thus, we can speak of the heterophase magnetic state of sample 1. At low temperatures and high magnetic field intensities, the AFM contribution is dominant and the magnetization curves demonstrate an almost linear dependence without reaching saturation. With increasing temperature, the main contribution to the magnetization is made by ferromagnetic impurities in the form of residual stresses and oxygen vacancies; therefore, the magnetization curves reach saturation in weak magnetic fields. It should be noted that at room temperature the magnetization curve exhibits a negative slope in strong magnetic fields, which is apparently associated with the manifestation of a third magnetic state - diamagnetism. Since the large contribution of the X-ray amorphous halo (figure 2) does not allow us to strictly determine the crystal structure of sample 1, we can assume the presence of contamination in the form of Cu₂O, which appears in small concentrations during plasma-chemical synthesis [27].

Figure 4 shows the isothermal dependences of the magnetization \( M(H) \) of sample 2 at temperatures of 150, 250, and 300 K.

The presented graph shows a significant difference between the isothermal behavior of the samples in a magnetic field. Sample 2 demonstrates the mixed behavior of ferromagnetism and diamagnetism over the entire temperature range without the formation of hysteresis loops. An increase in temperature leads to a nonlinear increase in the diamagnetic susceptibility. Saturation is not achieved even in strong magnetic fields. The diamagnetism of sample 2 cannot be explained by the presence of phase impurities, since only one phase is present in the XRD spectrum, therefore, it can be interpreted as the Landau diamagnetic contribution and the existence of graphene-like structures in CNS CuO with a certain density of free conduction electrons. This assumption is indirectly confirmed by the presence of texture in the crystal structure of sample 2 (figure 2) and non-stoichiometry in oxygen. In [28], the magnetic behavior of CuO nanoparticles was studied over a wide temperature range. At room temperature and a magnetic field strength of 3 kOe, a phase transition occurs and the nanoparticles become diamagnetic, and at 6 kOe a diamagnetic hysteresis is observed. It was suggested that the cause of the anomalous diamagnetic moment is local eddy currents due to the high concentration of oxygen vacancies on the surface of the nanoparticle. X-ray photoelectron spectroscopy (XPS) confirmed this assumption. In the O1s spectrum, the second Ob component was found in the form of a well-defined shoulder with a binding energy \( E_b(O1s) = 531.2 \text{ eV} \) associated with \( O^2^- \) ions in oxygen-deficient regions. In [16], the electrophysical properties of CuO nanoparticles were studied by impedance spectroscopy (EIS) at room
temperature. In the low-frequency region, an abnormal increase in permeability and an increase in conductivity were detected. The discovered effect is explained by the accumulation of electric charges at the boundaries of the nanoparticles and near the electrodes with the formation of a double electric layer. In the nanoparticles, electronic and ionic conductivity of the hopping type was detected. With increasing frequency of the electric field, the conductivity grows according to a power law.

Figure 5 shows the Nyquist hodograph of sample 2 for characteristic temperatures. One can see a significant difference between the lines for different temperatures. For simulations using equivalent electrical circuits, lines can be split into two independent parts. A low-frequency beam describes the electrical processes of the intergranular and near-electrode region, and a clear semicircle describes the intragranular processes of conductivity and polarization [30]. The high-frequency areas for the lines are different. The boundary frequencies \( \omega_g \) for temperatures of 250 and 300 K are presented in Table 3.

### Table 3. Boundary frequencies and fitting parameters using an equivalent electrical circuit.

| T(K) | \( \omega_g \) (kHz) | A(Ohm\(^{-1}\)s\(^{\alpha}\)) | \( \alpha \) | R (kOhm) |
|------|----------------------|------------------|---------|----------|
| 250  | 31.6                 | 5.23\(\times\)10\(^{-7}\) | 0.68    | 189      |
| 300  | 32.3                 | 7.5\(\times\)10\(^{-7}\) | 0.65    | 167      |

The high-frequency region of both lines is described by a simple equivalent circuit for parallel connection of the constant phase element (CPE) and resistor \( R \), since the center of the semicircle is offset relative to the \( Z' \) axis.

The impedance CPE is given by the following formula \( Z_{\text{CPE}}(\omega) = (A(\omega)^{\alpha})^{-1} \), where the constant \( A \) does not depend on the frequency, \( \alpha \) - the exponent varies depending on the frequency-dependent element described by the impedance.

The introduction of the CPE element emphasizes the physical fact that the granule volume (in our case, CNS) is heterogeneous and has a high concentration of oxygen vacancies. The obtained values of the exponent \( \alpha \) allow us to suggest that the CNS volume can be considered as an imperfect electric capacity. The relatively low resistance of the resistor \( R \) is associated with high conductivity due to internal currents. The inset in figure 5 shows the temperature dependence of the real part of the dielectric constant \( \varepsilon(T) \) of sample 2 at a frequency of 33 kHz. The dielectric constant is calculated from the value of the electric capacitance. At low frequencies, the main contribution to the capacitance is made by the double electric layer formed due to poor exchange of charges with the electrodes [30, 31]. In this case, the diffuse impedance of Warburg arises, which is clearly visible in figure 5 in the form of a beam at an angle of 45°. At high frequencies, the increase in capacitance is due to the processes of polarization and ion-electron conductivity inside the granules [32]. The resulting curve has the form characteristic of ionic conductors. A sharp increase in the temperature range of 180-220 K is associated with an increase
in the concentration of ionic charge carriers. Based on the shape of the temperature dependence, we can assume the existence of a phase transition. The obtained dependence corresponds to the diamagnetic behavior of CNS CuO shown in figure 4. A high concentration of vacancies leads to the appearance of ionic conductivity, which leads to phase separation of the antiferromagnetic matrix and the appearance of diamagnetism. Eddy ion currents occur in an alternating electric field, leading to the appearance of magnetic induction and a jump in the dielectric constant.

4. Conclusions

Thus, an increase in the temperature of the substrate in a plasma-chemical reactor leads to the synthesis of fundamentally different CNS CuO. At a substrate temperature of 340 K, a dendritic structure is formed with an average dendrite size of 30 nm. The crystalline structure is predominantly amorphous. The magnetic state over the entire temperature range is heterophasic, with predominant ferromagnetism in the region of high temperatures. At a substrate temperature of 370 K, a non-stoichiometric (Cu_{67}O_{68}) wire structure is formed with a diameter of ~ 50 nm and a length of ~ 1.5 μm. The crystalline structure is predominantly monoclinic with a small fraction of the amorphous phase. A decrease in the lattice parameter and texture in the (111) plane were detected. Sample 2 demonstrates the mixed behavior of ferromagnetism and diamagnetism over the entire temperature range without the formation of hysteresis loops. The study of impedance properties showed the presence of mixed electron-ion conductivity and jumps in permittivity in the range of 180-220 K. A comparison of the magnetic and electrical properties made it possible to draw a conclusion about the vortex nature of diamagnetism.

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