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Synthesis of Copper Nanoparticles by Cathode Sputtering in Radio-frequency Plasma

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The paper describes the design features of the synthesis of copper nanoparticles by the cathode sputtering method in radio-frequency plasma. The dependence of the size and number of Cu nanoparticles on the plasma power, sputtering time, gas flow and pressure was studied. Optimal parameters for obtaining copper particles with an extended fractal structure were determined.

Keywords: Copper, Copper nanopowder, Nanoparticles, PVD method, RF plasma, Synthesis, Cathode sputtering.

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1. INTRODUCTION

Obtaining of nanoparticles in RFCD (radio-frequency capacitive discharge) plasma is one of the promising methods for the synthesis of nano-particles from various materials. Magnetron sputtering was used by Hahn and Averbak to produce nanoparticles of pure metals, alloys, binary intermetallic compounds and ceramics, which could not be obtained by ordinary thermal evaporation [1].

Copper nanopowders are widely used to create nanostructured functional materials [2]. Interest in such materials is due to the fact that their properties differ significantly from the properties of materials obtained using coarsely dispersed copper powders. Copper nanopowders can improve the sintering process in powder metallurgy; they are capable to maintain high and stable conductivity and can be used for miniaturization of parts in communication technology and electronics; they can act as catalysts of reactions in the chemical industry, provide electrical conductivity and improve the mechanical properties of polymers, etc. [3].

2. EXPERIMENTAL

As a spraying substance, a copper target of cylindrical shape with a purity of 99.9999 % was used.

RFCD is formed between the two electrodes. The upper electrode is a copper target, which has the shape of a circular plate and is connected to a high-frequency generator. The second electrode of cylindrical shape is grounded.

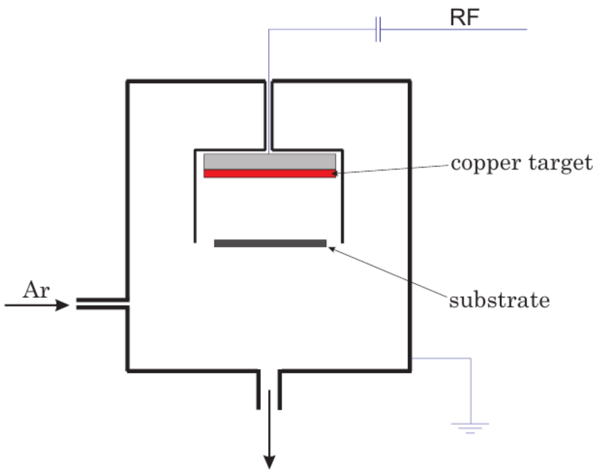

Fig. 1 – Principal scheme of cathode sputtering in RF plasma

Plasma burning between the electrodes was observed only in the central part ~ 5 – 5.5 cm in diameter. The RF generator was connected to the upper electrode through an impedance matching network and a coupling capacitor. Plasma parameters: power 5 – 150 W, working gas flow 20 – 200 sccm, pressure 50 – 400 mTor.

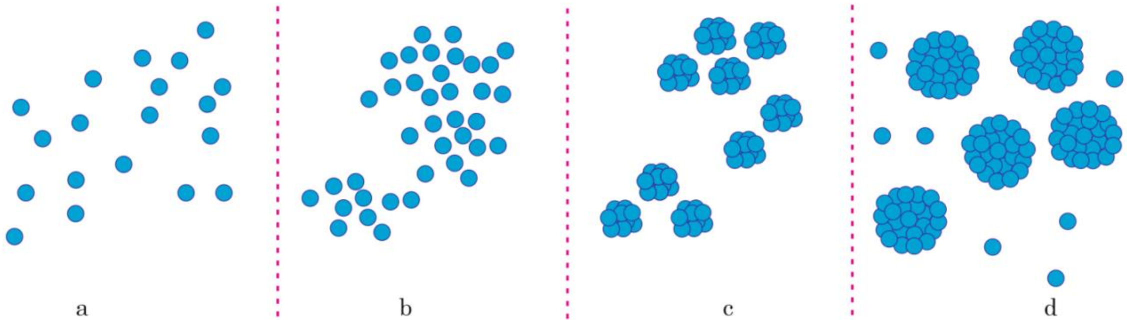

Fig. 2 – Mechanism of growth of nanoparticles in RF plasma: nucleation phase (a), saturation phase (b), coagulation phase (c), surface growth phase (d)

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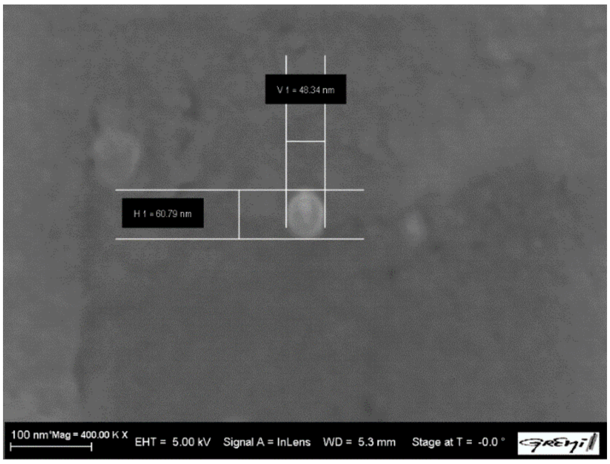
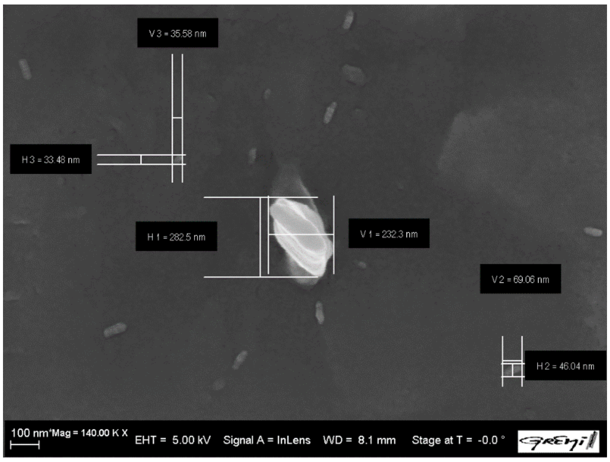
There are following stages of synthesis of nanoparticles and microparticles. The working gas Ar is injected through the gas inlet valve, the gas passing through the grid forms a laminar flow in the region of the interelectrode space, which is constantly evacuated by the pump. When RF voltage is applied to the electrodes an electrical breakdown is formed in the gas and the plasma is ignited. Then, during the ionization process, the ions of the gas bombard the copper target and knock out the copper atoms. In the course of physical reactions, nanoparticles are formed according to the well-known mechanism presented in Fig. 2 [4-5].

3. RESULTS AND DISCUSSION

In the synthesis of copper nanoparticles by the cathode sputtering method in RFCD plasma, two main ways of nanoparticle formation are observed.



a



b

Fig. 3 – SEM images of copper nanoparticles: power 100 W (a), 150 W (b)

The first more widespread growth mechanism, which is observed at the majority of experimental parameters (plasma power, working gas flow, pressure in the working chamber, synthesis time, synthesis intervals), consists of three stages. The first stage is the phase of nucleation, the second stage is the saturation phase and the third stage is the coagulation phase (see Fig 2 a, b, c). Then these nanoparticles settle on the substrate (since they have a large specific surface area, they adhere to the substrate). Fig. 3 shows such nanoparticles that were synthesized with the following parameters: pressure 40 Pa, time 50 minutes (5 times 10 minutes), gas flow 200 sccm, voltage 350 V, power 100 W (see Fig. 3 a) and 150 W (see Fig. 3 b).

The second rarer mechanism of nanoparticles growth is more interesting in terms of practical application, because, in this case, nanopowders are formed and they do not adhere to the substrate and can be used in a wide range of applied problems. The growth mechanism is shown in Fig. 3. In contrast to the first mechanism, the formation of nanoparticles has a fourth stage - phase of the surface growth. Thus, powders are formed, preferably of a spherical shape with a developed surface as shown in the illustration below (Fig. 4).

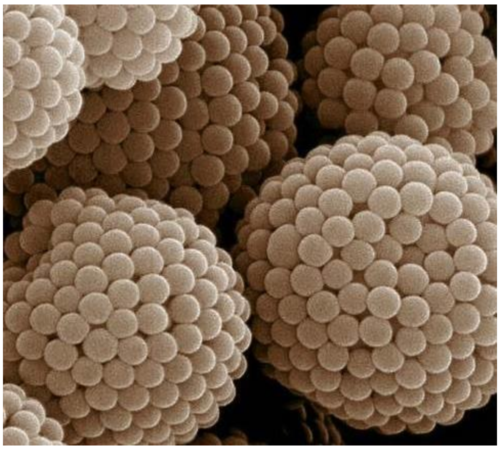


Fig. 4 – Visualization of a extended fractal surface

To obtain separate (not adhering to the substrate) copper nanoparticles with a developed surface, it is necessary to select very finely the experimental parameters: the working gas flow, the pressure, the time and the power of the plasma.

We managed to obtain copper nanoparticles with a developed fractal surface. The SEM image of such a powder is shown in Fig. 5. It is seen that the powders have sizes from 100 to 500 nm, the powders are formed from the agglomeration of nanoparticles with dimensions of about 50 nm. These nanopowders were synthesized at the following parameters: pressure 35 Pa, time 5 times 10 minutes with an interval of 5 minutes, power 150 W, gas flow 120 sccm, voltage 340 V. For the growth of nanopowders it is important to control not only the pressure, but also the flow of working gas. Since a strong gas stream can carry copper clusters formed inside the plasma from the working chamber, There may be other physical processes that affect the growth of clusters that remain to be determined during the course of the investigation.

Table 1 – Chemical composition of copper nanopowder

Element	Wt%	At%
OK	18.82	47.94
CuK	81.18	52.06
Matrix	Correction	ZAF

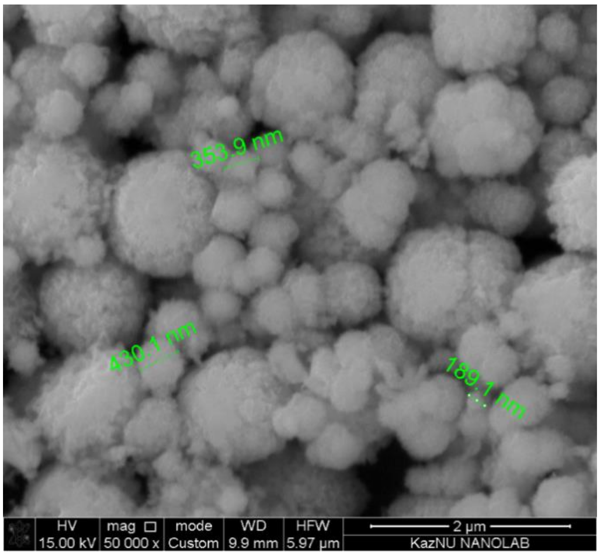


Fig. 5 – SEM image of copper nanopowder

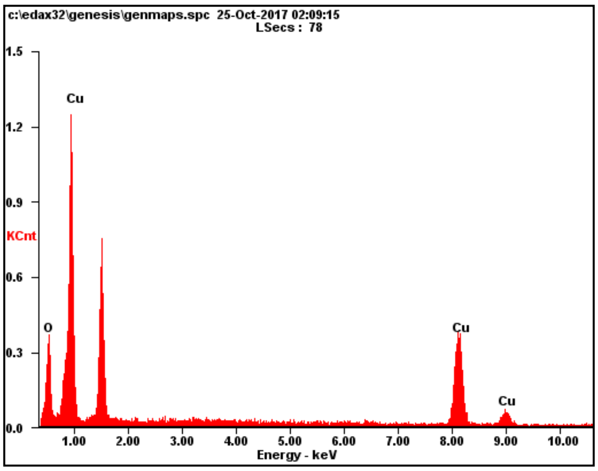


Fig. 6 – The energy dispersive spectrum of copper nanopowders

Fig. 6 shows the energy dispersive spectrum of copper nanopowders obtained by the method of cathode sputtering, it is seen that the main element is copper 81.18 Wt % or 52.06 At %, the rest is oxygen. Oxide appears on the surface of clusters at the opening of the working vacuum chamber, this is also shown by the diffractogram measured on Dron-7 (Fig. 9).

Depending on the supplied power of discharge, it is possible to obtain nanoparticles of a certain size. As the discharge power increases, the energy of the electrons rises and the ionization rate of the gas increases, as a result of which the ion concentration and ion bombardment energy is higher, which leads to a rapid growth of the nanoparticles. This process is well described on the curves presented in Fig. 7.

The amount of nanoparticles depends on the pressure and flow of the working gas. The results are shown in Fig. 8, where it can be seen that at low powers the number of particles is low, since the ionization process itself requires a certain time. After the gas is ionized, the ions in this plasma begin to bombard the target and knock out the copper atoms. As a result of the atoms interaction, nanoparticles appear.

And at high power, the process of ionization of gas occurs faster and the number of nucleated particles increases. Also, the number of particles is strongly affected by the flow of working gas, because with a strong flow some part of the particles are blown out of the chamber. This dependence is shown in Fig. 8, the plasma power is 150 W, and the time is 50 minutes.

As can be seen from the curve (see Fig. 7), at low plasma power the number of particles decreases, since the ionization process itself needs a certain time. And at high power, the gas ionization process is faster and the amount of nucleated particles increases [6].

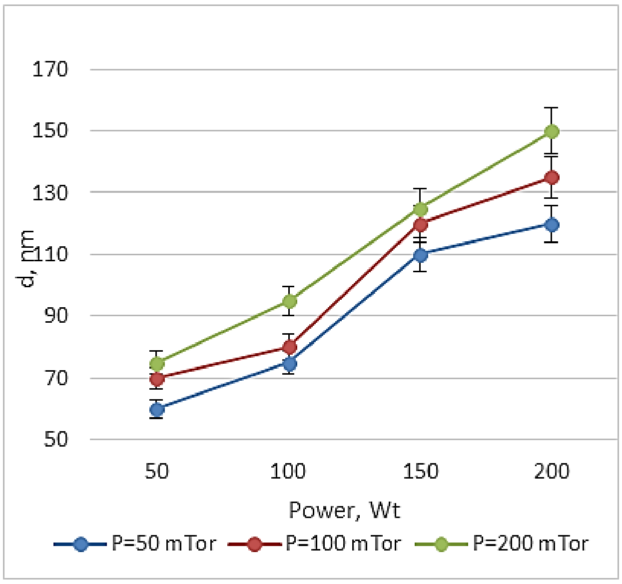


Fig. 7 – Dependence of the diameter of synthesized particles on the power of discharge

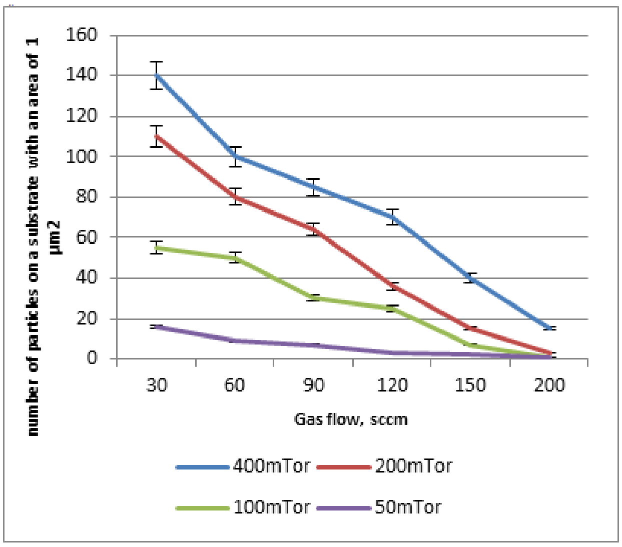


Fig. 8 – Dependence of the number of particles on the working gas flow

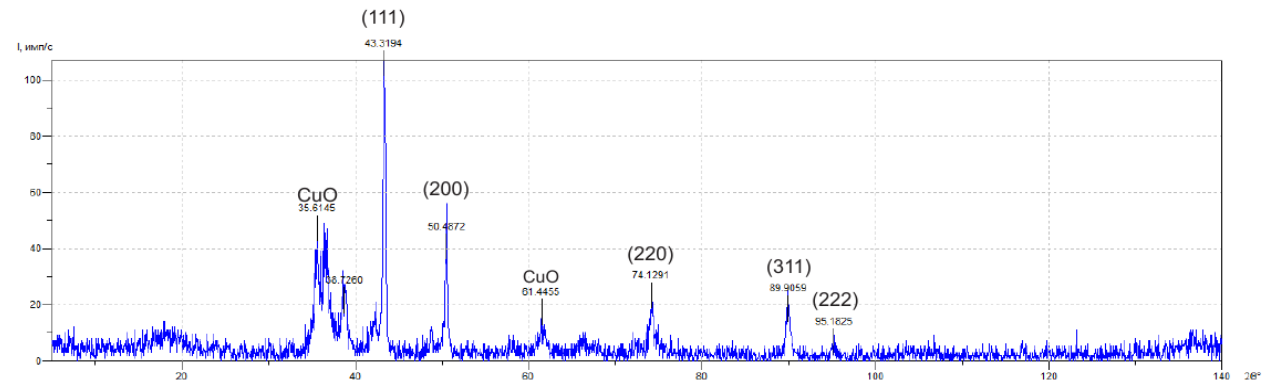


Fig. 9 – XRD pattern of copper nanopowders

4. CONCLUSIONS

Nanoparticles and copper nanopowders were obtained by the PVD (physical vapor deposition) method in RF plasma. The influence of plasma parameters on the growth and the number of nanoparticles was determined. The number of nanoparticles is related proportionally to the working pressure, the plasma power and inversely proportional to the flow of the working gas. The fine-tuned parameters, at which separate copper particles with extended fractal structure appear, were found.

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