

Electrochemical deposition of silver nanostructures from aqueous solutions in the presence of sodium polyacrylate

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Abstract – The silver nanostructures obtaining was investigated by electrochemical deposition from aqueous solutions (1...10 mM AgNO₃ + 50 mM NaPA) onto graphite substrate. The influence of the concentration of silver ions and cathodic potential values in the range $E = -0,2 \dots -1,0$ V on surface filling degree and geometry of silver particles was (had been) studied. It is shown, the discrete silver particles ranging in size from 50 to 400 nm with a uniform distribution on the surface of the substrate are formed.

It is established that decreasing of the concentration of silver ions and increasing of cathodic potential tends to reduce the particle size.

Key words – silver, nanoparticles, graphite, sodium polyacrylates, electrochemical deposition, SEM.

I. Introduction

Different methods of synthesis of nanosized silver particles are widely studied in the last decade due to their unique physical, chemical and bactericidal properties [1]. The metal nanostructures are prepared by physical and chemical methods. Chemical methods include the following major groups: sonochemical synthesis, photochemical, biochemical, chemical and electrochemical reduction of silver salts [2]. The disadvantages of the silver nanoparticles formation by chemical methods are the difficulty of controlled particle formation and contamination by products of the reaction. So, promising is the electrochemical deposition, especially during the obtaining of discrete nanoscale particles [3].

In the last decade, special attention is paid to study of the influence of polymer stabilizers (polyvinylpyrrolidone, polyvinyl alcohol and sodium polyacrylate) and nature of substrate (graphite, glassy carbon, indium tin oxide coated glass (ITO-glass)) on the geometry of the particles and their distribution on substrate surface [4, 5]. While the polymers, are principally used for obtaining of the “solutions” of stabilized nanosized particles.

This work is devoted to investigation of electrochemical precipitation of silver nanoscale particles fixed on the graphite substrate from solutions containing sodium polyacrylate (NaPA).

II. Results and Discussion

According to the research results the concentration of NaPA 50 mM for the electrochemical deposition of silver nanoscaled particles is optimal. It provides cathodic polarization, which contributes to formation mainly spherical particles on graphite surface. At the same time

the polymer molecules are not fixed on the substrate, thus providing purity of deposit.

The concentration of metal ions is one of the main parameters of influence on the geometry of nanoparticles. It is established, in the presence of NaPA the discrete silver nanoparticles are electrochemically deposited on graphite surface by silver-ion content 1... 10 mM. At the same time, with increasing of silver-ions concentration are observed the next regularities:

- 1) the particles size is increasing;
- 2) the filling surface coefficient and unevenness of particles distribution are increasing;
- 3) the range of particles size is expands.

Thus, with increasing of concentration of silver nitrate from 5 to 10 mM the average size of particles are increased from 50 to 400 nm. Comparing the distribution of silver particles on the surface, obtained from solutions 5 and 10mM AgNO₃, shows that the relative uniformity in the first case is higher (Fig. 1). However, the filling degree is dominated in a solution of 10 mM AgNO₃. The range of particle sizes is as follows: 50...100 nm and 100...300 nm in the solutions of 5 and 10 mM correspondingly. These regularities are explained by the peculiarities of silver ions diffusion to the cathode surface. With higher concentration of metal ions the cathodic polarization is lower. That, in its turn, facilitates the nucleation and growth of particles.

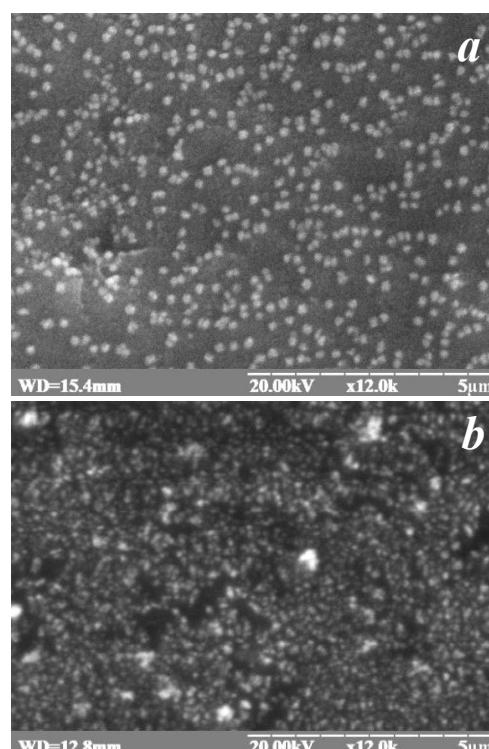


Fig. 1. SEM of particles deposited from solutions of 5 (a) and 10 (b) mM AgNO₃ + 50 mM NaPA at 20°C; E = -0.6 V

Research has shown, the optimal concentration of silver ions for obtaining of nanosized silver particles with a uniform distribution on surface is 2...5 mM. For smaller concentrations observed formation of colloidal deposit, at higher – too wide a range of particle sizes and a large proportion of particles with size over 200 nm.

Another effective influencing factor for the electrochemical deposition of metal nanostructures is the value of electrode potential. In the range of cathodic potentials -0.2...-1.0 V is observed the next trend of the formation of silver particles:

- 1) the tendency to agglomeration is diminished;
- 2) reduce the size of particles;
- 3) decreases the difference in particle size.

For example, at $E = -0.2$ V the deposit characterized like agglomerates of 300...400 nm, whereas at $E = -0.6$ V the discrete nanoscale particles (50...100 nm) are formed (Fig. 2). At the same time, in a wide range of cathode potentials the high uniformity of surface filling is observed.

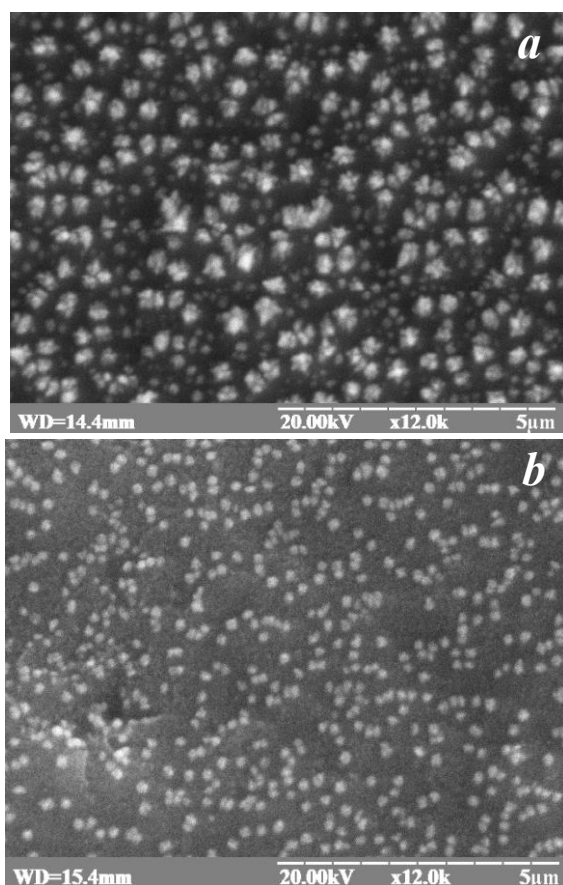


Fig. 2. SEM of particles deposited from 5 mM AgNO_3 + 50 mM NaPA solution at 20°C and $E = -0.2$ (a) and -0.6 (b) V

This regularity is caused by that. The increasing of the cathodic potential causes the growth of the cathodic currents (Fig. 3). For potentiostatic electrodeposition regime this leads to diffusion polarization. As can be seen from the polarization curves, a significant increase of current is observed at potentials above -0.8 V. It can be explained by the formation of deposit with developed surface, i.e., the actual increase of cathode surface area. It is especially noticeable with increasing of concentration of silver ions in solution.

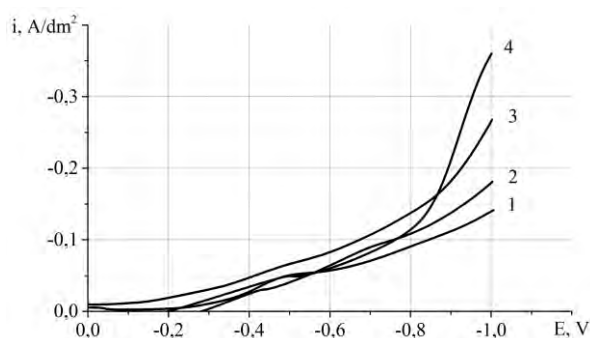


Fig. 3. Cathodic polarization curves of silver in solutions n mM AgNO_3 + 50 mM NaPA, where n : 1 – 1; 2 – 2; 3 – 5; 4 – 10

Conclusion

1. Sodium polyacrylate causes the cathodic polarization of silver, which contributes to the formation of nanoscale particles.
2. Optimal conditions for deposition of uniformly distributed discrete particles of silver are: electrolyte composition (2...5) mM AgNO_3 + 50 mM NaPA; $E = -0.4$... -0.6 V at 20°C.
3. Increasing of the cathodic potential from -0.2 V to -0.6 V is accompanied by the transformation of deposited particles from agglomerates to the discrete spherical particles.

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