Sedimentation of Silver and Palladium on the Silicon Surface by Galvanic Replacement

Maryana Shepida[1], Oksana Dobrovetska[2]

1. Chemistry and Technology of Inorganic Substances Department, Lviv Polytechnic National University, UKRAINE, Lviv, S. Bandery street 12, E-mail: maryana_shepida@ukr.net

2. Chemical Engineering Department, Lviv Polytechnic National University, UKRAINE, Lviv, S. Bandery street 12, E-mail: oksanadobrovetska@gmail.com

Abstract – The results of investigations of the process of precipitation of micro- and nanosized particles of silver and palladium on the surface of silicon by electroplating substitution are presented. The conditions of the process, in which a nanosized precipitate is formed in the environment of organic aprotic solvents, is established. The influence of the concentration of metal ions in the solution, temperature and duration of galvanic substitution on the morphology of the modified surface, the geometry of the sediment particles and their distribution in size have been studied.

Keywords – galvanic replacement, nanoparticles, silver, palladium, silicon surface, aprotic solvents.

I. Introduction

In the last decade, great attention is paid to modifications of the surface of silicon by micro- and nanosized particles of metals by galvanic substitution [1-6]. This method is easy to implement and in providing equipment [7].

The process of galvanic substitution on the surface of silicon occurs by the electrochemical mechanism and therefore it is characterized by the same electrode processes, as in electrodeposition:

microanode: $Si + 6\ F^- \rightarrow SiF_6^{2-} + 4\ e$;

microcatode: $Me^{n+} + n\ e \rightarrow Me$;

$\sum$: $nSi + 4\ Me^{n+} \leftrightarrow nSi^{4+} + 4\ Me$.

However, the spontaneity of the electroplating substitution process makes it difficult to obtain nanoparticles with given characteristics – geometry, size distribution, component content. Therefore, it is important to establish the basic parameters that affect these characteristics. This will be the basis for the creation of scientific principles for controlled synthesis of nanomaterials by electroplating substitution.

The purpose of the research was to study the process of depositing micro- and nanosized particles Pd and Ag on the surface of silicon by galvanic substitution in an environment of organic aprotic solvents.

II. Research results

Deposition of silver and palladium on the surface of silicon in solutions of organic aprotic solvents DMSO and DMF was investigated. Such environment, as shown by the authors [8-9], prevents the course of a number of side chemical processes. This ensures a uniform distribution of particles of deposited metal by size on the floor of the substrate. In addition, high-donor properties of such solvents cause the formation of surface complexes on the embryos of recovered metals, which also positively affects the sediment nanostructure.

Relatively simple composition of the solution ($AgNO_3$ + DMF; $Pd(NO_3)_2$ + DMSO) was used to obtain nanosized particles. It is shown that nanosized particles of silver and palladium (Fig. 1, a-b) are formed on the surface of silicon in a wide range of ions of reducing metals.

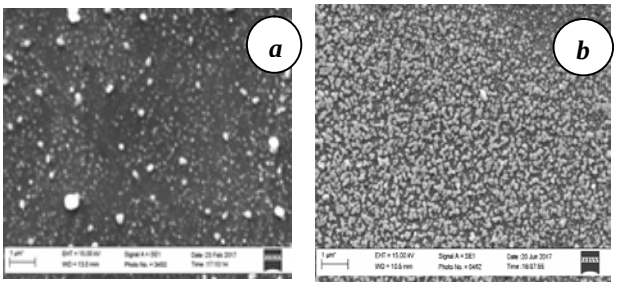

Fig.1 SEM image of the surface of silicon deposited with silver (a), palladium (b) by galvanic replacement in solutions of 0.01M $AgNO_3$ in DMF, 0.004M $Pd(NO_3)_2$ in DMSO.

The concentration of the corresponding metal ions, temperature and duration of galvanic substitution are the main factors influencing the sediment morphology and the size of its structural particles.

The tendency to decrease of the size of deposited particles of silver and palladium with a decrease in the concentration of the corresponding metal ions in solutions of organic aprotic solvents DMSO and DMF was found.

As the temperature increases due to cathodic depolarization, the particle size increases. At the same time, there is a tendency to 3D growth of sediment. Moreover, 2D growth prevails, which contributes to the uniform filling of the substrate (Fig. 2, a-b).

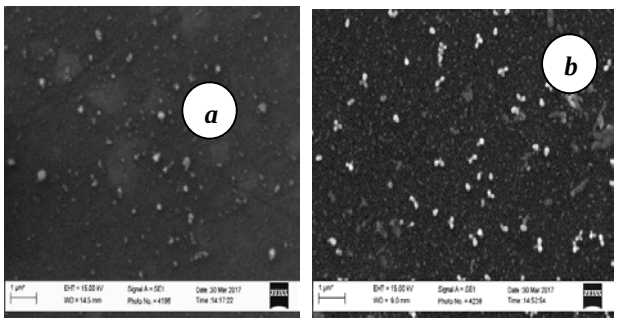

Fig.2 SEM – an image of silver deposited with a galvanic substitution from the solution 0.01M $AgNO_3$ + 3% HF in DMF on the silicon surface for 1 min at a temperature 23(a), 40(b) ^{0}C.

As the length of the galvanic substitution process increases, the size of the particles of the recovered metals increases. This is due to nucleation almost exclusively in the initial period, that is, during the formation of microcatodes and microanodes on the substrate surface. In the future there is only their growth. Consequently, the long process of galvanic substitution causes the formation of a sintered sediment with a large particle size distribution.

Conclusions

1. The main factors influencing the sediment morphology and the size of its structural particles are the composition of the solution, the temperature and the duration of galvanic substitution.

2. In the environment of organic aprotic solvents DMSO and DMF galvanic substitution on the silicon surface passes without any side processes. This contributes to the formation of nanoparticles of silver and palladium of uniform size and uniformity of their distribution on the surface.

3. The size of the particles of the recovered metals increases with increasing of temperature and duration of the electroplating process on the silicon surface.

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