# Modification of the Silicon Surface by the Gold Nanoparticle by Galvanic Replacement

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***Abstract* – The results of studies of the deposition of gold nanoparticles on the surface of silicon by galvanic substitution are presented. The process conditions under which a nano-sized precipitate is formed in the organic aprotic solvents are investigated. The effect of temperature and duration of galvanic substitution on the morphology of the modified surface, the geometry of the sediment particles and their size distribution is studied.**

Keywords – galvanic replacement, nanoparticles, gold, nanofilm, silicon surface, aprotic solvents.

## Introduction

One of the promising methods of depositing nanoparticles of metals on a semiconductor surface is galvanic replacement. This method is easy to perform and does not require external current source or reducing agent in solution [1-4]. Gold is often used to modify the surface of silicon, due to its unique physical and chemical properties [5-8]. Galvanic replacement on the surface of silicon occurs by the electrochemical mechanism and therefore it is characterized by the same electrode processes, as in electrodeposition. However, the spontaneity of the process makes it difficult to obtain nanoparticles with a given geometry and size distribution. Therefore, it is important to establish the basic parameters that affect these characteristics. In order to reduce and avoid the flow of undesirable processes on the surface of silicon, in the last decade there is an interest in the study of galvanic substitution in the environment of organic solvents [9], in particular aprotic [10, 11]. 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.

The purpose of this work is investigate the influence of the composition, temperature and duration of the process on the size and shape of deposited gold nanoparticles on the surface of silicon by galvanic replacement in dimethylsulfoxide (DMSO) solutions.

## Experimental

The metals deposition was carried out by galvanic replacement on the silicon surface from solutions of their compounds in the presence of HF (3 wt%): gold – 0.004M ($HAuCl_4 \cdot 3H_2O$, 99.99%, Alfa Aesar) in dimethylsulfoxide (DMSO, 99%, Alfa Aesar).

For investigations we used p-type Si(100) plates (Crysteco company) with a resistivity of 7–12 Ohm·cm. The silicon plates were divided into squares 1x1 $cm^2$. The silicon surface was pre-washed with isopropanol and then etched in 1% solution of fluoride acid and DMSO. The samples were immersed in metal salt solution and kept under a hydrostatic mode at the temperature of 40-70 $^oC$ for 1 min. After applying the metals, the samples were successively washed with corresponding organic aprotic solvent, isopropanol, acetone and dried in the air at 60 $^oC$ [10].

The morphology of the resulting deposits on the silicon surface was investigated using ZEISS EVO 40XVP scanning electron microscope. The images of the modified surface were obtained by recording secondary electrons using an electron beam with energy of 20 kV. The chemical composition of the deposits was investigated using energy dispersion analysis (EDX).

## Results and Discussion

Deposition of gold on the surface of silicon in an environment of organic aprotic solvents, in particular dimethylsulfoxide DMSO, has been investigated. Such environment, as shown by the authors [11], ensures even distribution of nanoparticles by size over the substrate's surface.

For the recovery of metal from complex ions - $[AuCl_4]^-$ ($K_{н} = 1 \cdot 10^{-19}$), the high stability of which causes significant cathode polarization, there is a tendency for the formation of nanoparticles up to 100 nm with a relatively small range of their sizes. Moreover, for gold the formation is characteristic - nanostructured porous films (Fig.1).

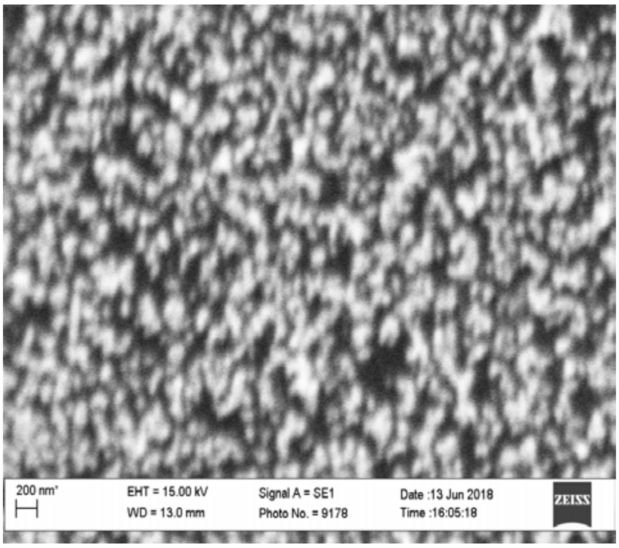

Fig.1. SEM images of n-Si (100) surfaces of silicon with gold deposited by galvanic replacment in DMSO solutions at the temperature 40 $^{o}$C

Compared the SEM image of gold formed on the surface of silicon with a temperature rise of 40 to 70 °C, observe a change in the structure of the sediment from the film (Fig.1.) To the dispersion (Fig. 2, b, c). Such a significant effect of the temperature factor is due to a significant increase speed of the electrically generating reaction. This, accordingly, causes an intensification of cathode processes due to the sharp increase in the densities of currents on microcatodes ($i_{cathode}$), which is typical for galvanic replacement. So, with an increase in temperature by 10 $^{o}$C, the rate constant for the recovery of gold increases in 1,3 ... 2 times [10]. Since there are no side processes in the environment of organic aprotic solvents, the generated current is directed only to the recovery of the metal. The last reaction passes through the diffusion catheter, therefore, at low concentration of ions $[AuCl_4]^-$ the limit values ($i_{cathode}$) are reached. As a result, rough film and dispersible precipitates are formed, which is characteristic of electrochemical precipitation of metals and their renewal by galvanic replacement in high $i_{cathode}$. In addition, as the temperature rises, adsorption of organic aprotic solvent molecules with gold nanoparticles becomes weaker. Accordingly the inhibitory effect of the surface complexes on the growth of nanoparticles decreases, and the "smoothing" effect is leveled. As a result of cathodic depolarization, the size of the particles increases. At the same time, there is a tendency towards 3D growth of siege. Moreover, 2D growth prevails, which contributes to uniformly filling the substrate (Fig. 2, a, b, c).

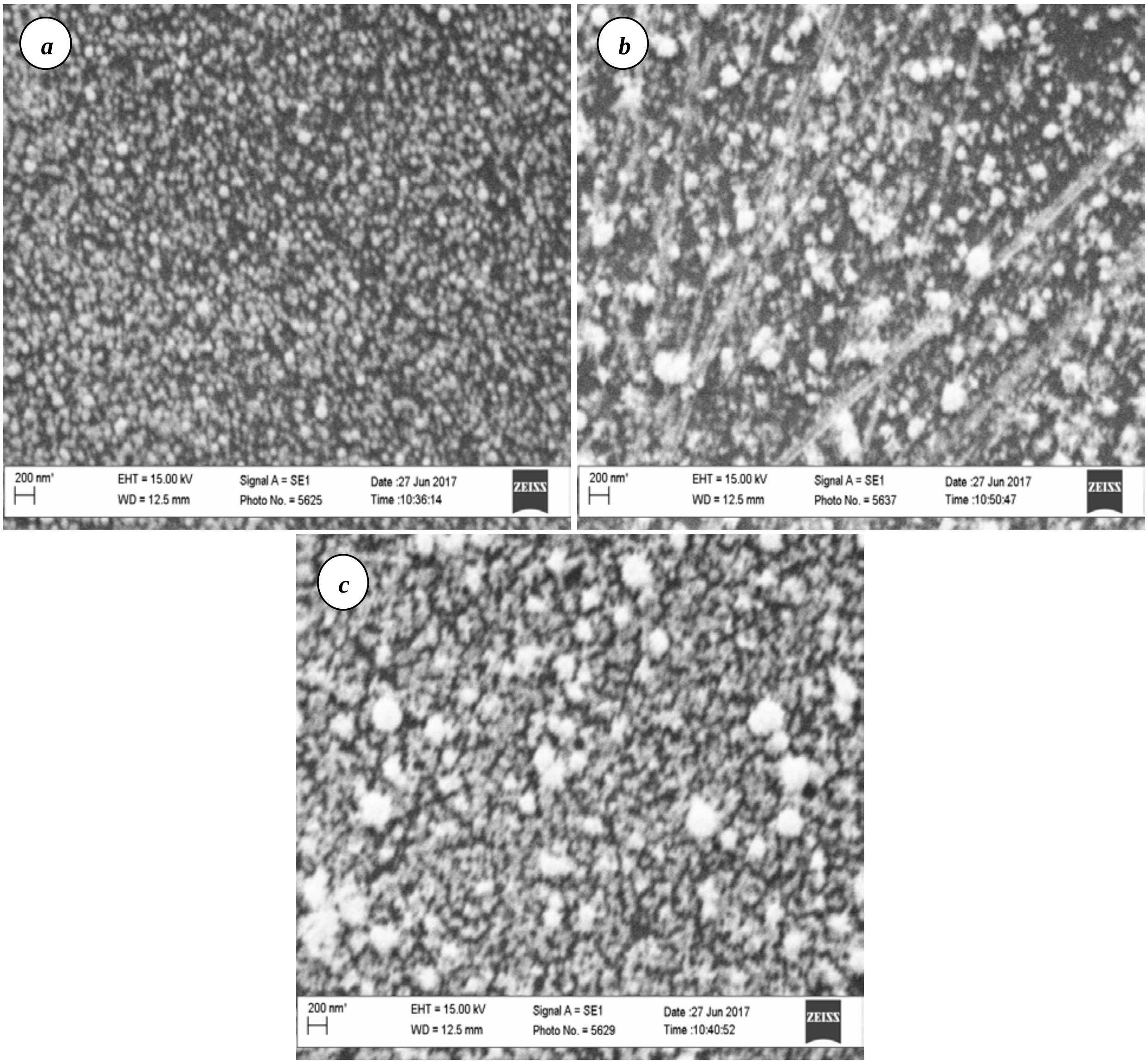

Fig.2. SEM - images of gold nanoparticles deposited from a solution of 4 mM $HAuCl_4$ in DMSO on a silicon surface for 1 min at a temperature of 50 (a), 60 (b), 70 (c) $^{o}C$

As the length of the galvanic replacement process increases, the size of the nanoparticles of the recovered metal increases. This is due to nucleation almost exclusively in the initial period 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 replacement causes the formation of sintered precipitate with a large dispersion of nanoparticles in size. 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 replacement.

## Conclusion

1. With the temperature increase, there is a tendency to 3D fill the substrate with nanoparticles of metals to form rough and disperse sediments. This is due to the significant increase in the speed of the electrenergizing reaction of the dissolution of silicon on microanodes. Accordingly, current densities on microcatodes increase to values that cause high diffusion polarization.

2. In the environment of organic aprotic solvents, namely DMSO galvanic replacment on the silicon surface passes without any side processes. This contributes to the formation of gold nanoparticles and homogeneous in size and evenness of their distribution on the surface.

3. The tendency of decreasing the size of deposited gold particles is revealed by decreasing the concentration of the corresponding metal ions.

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