

MODIFICATION OF SILICON SURFACE WITH SILVER, GOLD
AND PALLADIUM NANOSTRUCTURES VIA GALVANIC
SUBSTITUTION IN DMSO AND DMF SOLUTIONS*Orest Kuntiy^{1, *}, Mariana Shepida¹, Lubov Sus¹, Galyna Zozulya¹, Serhiy Korniy²*<https://doi.org/10.23939/chcht12.03.305>

Abstract. The investigation results of silver, palladium and gold nanoscale particles deposition on the silicon surface in the DMSO and DMF media are presented. The influence of organic aprotic solvents on the geometry of metal particles and their distribution on the substrate is described. It is shown that solutions of stable metal complexes ($[\text{Ag}(\text{CN})_2]^-$, $[\text{AuCl}_4]^-$) are the main factor in the formation of discrete nanoparticles with a small range of sizes and uniform distribution along the substrate surface, as well as nanostructured films. It has been established that the increase in temperature from 313 to 343 K changes the structure of the gold deposit from the film to the dispersed one, occurred due to a significant increase in the rate of the electrogenerating reaction on the silicon surface microanodes and desorption of organic solvents molecules from the metal nuclei.

Keywords: galvanic substitution, silver, palladium, gold, silicon, DMF, DMSO.

1. Introduction

Galvanic substitution is one of the promising methods of the silicon surface modification with metallic nanoparticles and nanofilms [1-18]. Silver [1-4], gold [4-10], platinum [11-13], and platinum metals [14-16] are widely used for this purpose. Copper [17, 18] is used seldom. Nanoparticles of noble metals in the M/Si surface system are effective for "metal" etching of silicon in HF based solutions to obtain a homogeneous porous layer or nanowires [11-13, 15, 16]. This method is the basis for the formation of antireflective semiconductor surface to produce effective solar cells; the metallization of the silicon surface with gold is widely used to apply the electrical contacts on them [6-10]. In the M/Si surface

system the silicon substrate causes the formation of electron-deficient nanoparticles of metal that increases catalytic activity, as shown, for example, for palladium [14] and silver [3]. Moreover, the antibacterial activity of silver nanoparticles on porous silicon surfaces [2] is known to be increased.

Galvanic substitution is a spontaneous process, in which the rate of electrochemical reactions on microcathodes and microanodes depends on many factors [19]. Naturally, the formation of nanoparticles on the surface of the substrate-reducing agent and the metal precipitate as a whole is a multiple-factor process. In view of the fact that galvanic substitution is performed predominantly in aqueous solutions, the complexity of controlled synthesis of nanoparticles and nanostructured deposits is conditioned by the side processes on microelectrodes and in solution. For example, at low concentrations of deposited metal ions on the microcathodes the side reaction of hydrogen electroreduction (1) takes place and, consequently, the pH value changes in the near-surface layers.



In order to reduce and avoid the undesirable processes on the metals surface, the study of galvanic substitution in the environment of organic solvents [20], namely aprotic ones [5, 21, 22], is of great interest in the last decade. Such processes involving silicon were investigated only in aqueous solutions, that do not provide controlled synthesis of metals nanoparticles on the substrate surface. Therefore, the purpose of the work is to study the modification of the silicon surface by nanostructured silver, palladium and gold deposits by galvanic substitution in DMSO and DMF solutions.

2. Experimental

The metals deposition was carried out by galvanic substitution on the silicon surface from solutions of their compounds in the presence of HF (3 wt%): silver from 0.1M AgNO_3 (AgNO_3 , 99.9 %, Alfa Aesar) and 0.1M

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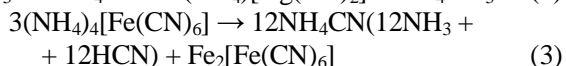
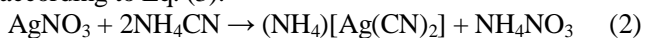
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(NH₄)[Ag(CN)₂] in *N, N*-dimethylformamide (DMF, 99 %, Alfa Aesar), gold – 0.004M (HAuCl₄·3H₂O, 99.99 %, Alfa Aesar) in dimethylsulfoxide (DMSO, 99 %, Alfa Aesar), palladium – 0.004M (Pd(NO₃)₂, Alfa Aesar) in DMSO.

Dimethylformamide solution (NH₄)[Ag(CN)₂] was prepared according to Eq. (2), passing of gaseous NH₄CN (stoichiometric mixture NH₃+HCN) through 0.1M AgNO₃ in DMF. The stoichiometric mixture was synthesized *via* thermal decomposition (473–623 K) of ammonium hexacyanoferrate(II) in the nitrogen medium according to Eq. (3).

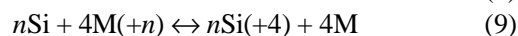
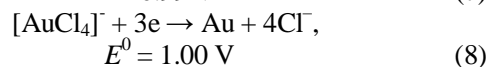
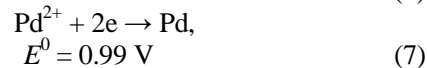
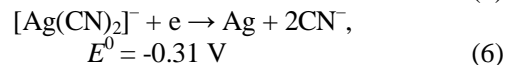
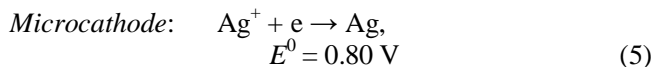
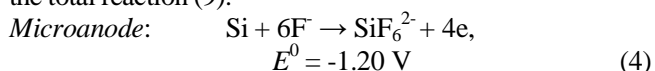


For investigations we used p-type Si(100) plates (Crystec company) with a resistivity of 7–12 Ohm·cm. The silicon plates were divided into squares 1x1 cm². The silicon surface was pre-washed with isopropanol and then etched in 1 % solution of fluoride acid and DMSO (DMF). The samples were immersed in metal salts solutions and kept under a hydrostatic mode at the temperature of 293–333 K for 5–20 min. After applying the metals, the samples were successively washed with corresponding organic aprotic solvent, isopropanol, acetone and dried in the air at 293 K.

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 the energy of 20 kV. The chemical composition of the deposits was investigated using energy dispersion analysis (EDX).

3. Results and Discussion

According to EDX data the silver, palladium and gold deposits are formed *via* galvanic substitution on the silicon surface in DMF and DMSO solutions in the presence of fluoride ions (Fig. 1). Their nanostructuredness indicates that the nucleation rate of reducing metals is higher than their growth rate. Thus, in the medium of organic aprotic solvents, as aqueous solutions, the electrochemical systems Si | [SiF₆]²⁻ || [M(+n)] | M (M = Ag, Au, Pd) possess large electromotive force ΔE^0 ($E_{M(+n)/M}^0 - E_{[\text{SiF}_6]^{2-}/\text{Si}}^0 \geq 2 \text{ V}$). In these systems the electrogenerating half-reaction (4) on microanodes and the half-reactions (5-6) on microcathodes occur providing high cathode current densities and, accordingly, the high rate of the total reaction (9).



During the recovery of metals from [Ag(DMF)_n]⁺ and [Pd(DMSO)_m]²⁺ solvated ions, where cathode polarization is insignificant, discrete metal particles (Fig. 1a) or their agglomerates with a relatively uniform distribution along the surface (Fig. 1c) are formed. However, there is a large range of their sizes – from several tens of nanometers to ~200 nm.

Under metals reduction from [Ag(CN)₂]⁻ ($K_n = 8 \cdot 10^{-22}$) and [AuCl₄]⁻ ($K_n = 1 \cdot 10^{-19}$) complex ions, the high stability of which causes significant cathode polarization, there is a tendency to the formation of nanoparticles up to 100 nm with a relatively small range of their sizes. Moreover, the formation of discrete particles is characteristic of silver (Fig. 1b) and nanostructured porous films – for gold (Fig. 1d). The porosity of the films is caused by the mechanism of galvanic substitution. The electrogenerating reaction (4) occurs only if F⁻ ions are supplied from the solution to the anode sections of the silicon surface and simultaneous removal of the formed SiF₆²⁻ ions from the substrate. Therefore, the presence of pores in the formed film deposit is a necessary condition for the galvanic substitution process.

Regardless of the nature of the reducing metal ion, there is a predominant 2D filling of the silicon surface with particles. Adsorption of high-donor molecules DMF or DMSO (L) on the metals nuclei with the formation of surface complexes *via* donor-acceptor mechanism $\text{M} \square \leftarrow \text{L}$ partially contributes to this phenomenon. For nanoscale particles with large surface energy this bond will be particularly strong. Therefore, the same as for electrochemical deposition in the medium of organic aprotic solvents [23], the nanoparticles are blocked, complicating the supply of reducing metals ions to their surface and inhibiting the further growth of nuclei. Moreover, this phenomenon provides the formation of new nuclei mainly on the silicon surface. The formation of surface complexes can also explain a peculiar “smoothing” effect. This effect determines the spheroidal geometry of the formed nanoparticles, regardless of the ions nature. However, it is extrinsic in aqueous medium. Thus, in the absence of surface active substances on the silicon surface the dendritic and needle deposits of silver or gold can be observed in aqueous solutions of simple salts, for example AgNO₃ and even the complex compound

$\text{H}[\text{AuCl}_4]$ [4]. So, the medium of organic aprotic solvents contributes to the formation of spherical metal particles during galvanic substitution on the silicon surface. However,

the galvanic substitution with the participation of a stable metal complex is the decisive factor to apply on the substrate only nanoparticles with a small range of size.

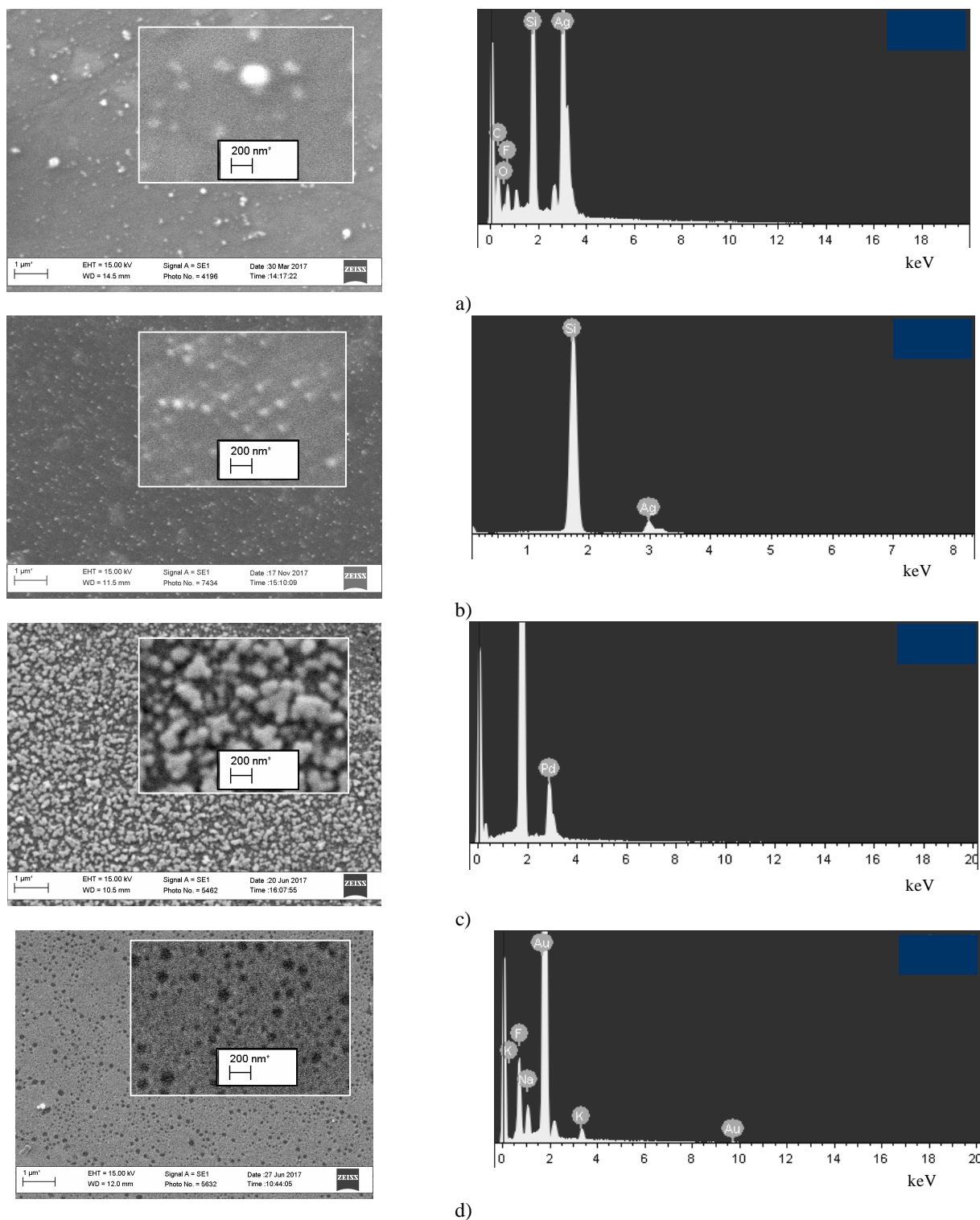


Fig. 1. SEM images of the silicon surface with silver (a, b), palladium (c) and gold (d) deposited *via* galvanic substitution in 0.1M AgNO_3 (a) and 0.1M $(\text{NH}_4)[\text{Ag}(\text{CN})_2]$ (b) in DMF; 0.004M $\text{Pd}(\text{NO}_3)_2$ (c) and 0.004M $\text{H}[\text{AuCl}_4]$ (d) in DMSO and EDX precipitates of the corresponding metals

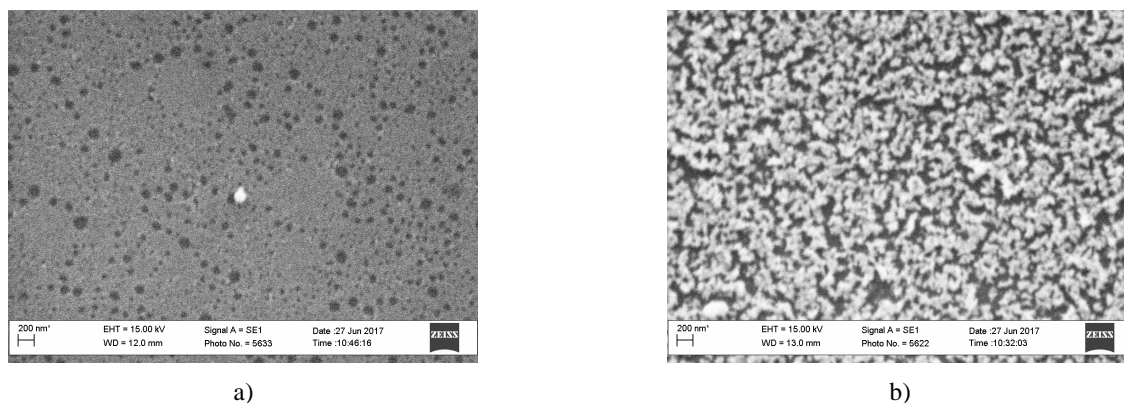


Fig. 2. SEM images of the silicon surface with gold deposited from a solution of 0.004M $\text{H}[\text{AuCl}_4]$ via galvanic substitution in DMSO at 313 K for 1 (a) and 6 (b) min

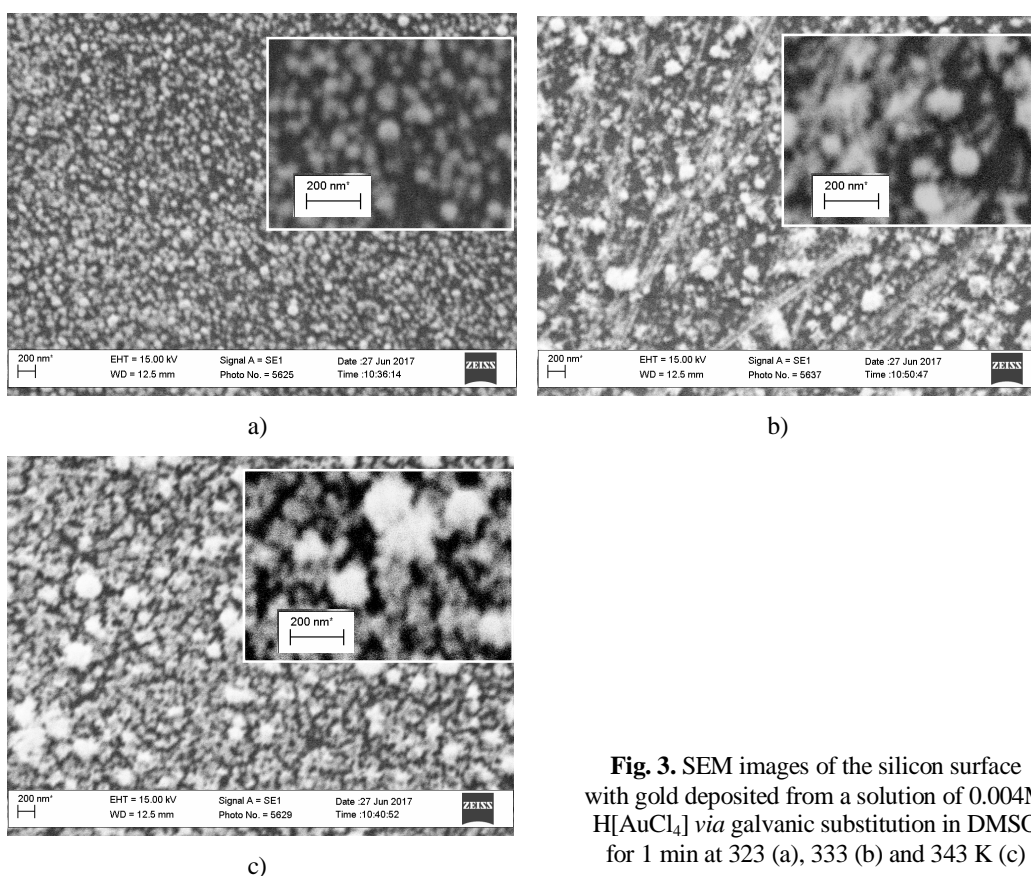


Fig. 3. SEM images of the silicon surface with gold deposited from a solution of 0.004M $\text{H}[\text{AuCl}_4]$ via galvanic substitution in DMSO for 1 min at 323 (a), 333 (b) and 343 K (c)

As the silicon surface is filled with the particles of reducing metal, there is a tendency toward 3D growth of the deposit and particles size, as can be seen, for instance, for gold (Fig. 2). At this stage the adsorption of organic aprotic solvent molecules affects only the shape of individual particles and their agglomerates due to the “smoothing” effect. Thus, the growth of dendritic deposit is prevented allowing to form relatively smooth multilayer metal films.

When comparing the SEM image of gold formed on the silicon surface at the increase of temperature from 313 to 343 K, we observe a change in the deposit structure from film (Figs. 2a, 3a) to the dispersion one (Figs. 3b, 3c). Such a significant influence of the temperature is caused by the significant increase in the electrogenerating reaction rate (see Eq. 4). This fact, in turn, causes an intensification of cathode processes due to the sharp increase in the currents densities on microcathodes (i_{cathode}),

which is typical of galvanic substitution. So, with the increase in temperature by 10 K, the rate of gold reduction by aluminum increases by 1.3–2 times [24]. Since in the medium of organic aprotic solvents side reaction (1) does not occur, the generated current is directed only to metal reduction according to Eq. (8). The latter passes under the diffusion control, therefore, at low concentration of $[\text{AuCl}_4]^-$ ions the limit values (i_{cathode}) are reached. As a result, rough film and dispersed deposits are formed, which is typical of metals electrochemical deposition and reduction *via* galvanic substitution under high values of i_{cathode} [25]. Moreover, with the increase in temperature the adsorption of organic aprotic solvent molecules with gold nanoparticles becomes weaker, the inhibitory effect of the surface complexes on the growth of nanoparticles decreases, and the “smoothing” effect is neutralized.

4. Conclusions

Silver, palladium and gold nanostructured deposits are formed *via* galvanic substitution on the silicon surface in DMF and DMSO solutions in the presence of fluoride ions. When reducing metals from $[\text{Ag}(\text{DMF})_n]^+$ and $[\text{Pd}(\text{DMSO})_m]^{2+}$ solvated ions, discrete metal particles or their agglomerates with relatively uniform surface distribution, but a large range of their sizes (from tens of nm to ~200 nm) are formed. Under metals reduction from $[\text{Ag}(\text{CN})_2]^-$ and $[\text{AuCl}_4]^-$ complex ions the tendency to the formation of nanoparticles up to 100 nm with a relatively small range of their sizes is observed. The medium of organic aprotic solvents promotes the formation of spherical metal particles and 2D fillings of silicon surfaces during galvanic substitution, as well as prevents the occurrence of side processes. With the increase in temperature, there is the tendency towards 3D filling of the substrate with metal nanoparticles with the formation of rough and dispersed deposits. The reason is the significant rate increase of electrogenerating reaction of the silicon dissolution on microanodes. The current density on microcathodes increases to the values that cause high diffusion polarization.

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МОДИФІКАЦІЯ ПОВЕРХНІ КРЕМНІЮ НАНО-СТРУКТУРАМИ СРІБЛА ЗОЛОТА І ПАЛАДІЮ ГАЛЬВАНІЧНИМ ЗАМІЩЕННЯМ У DMSO І DMF

Анотація. Наведено результати досліджень процесу осадження нанорозмірних частинок срібла, паладію та золота на поверхню кремнію в середовищі DMSO та DMF. Описано вплив молекул органічних апротонних розчинників на геометрію металевих частинок та їх розподіл на підкладці. Показано, що розчини стійких комплексів металів ($[\text{Ag}(\text{CN})_2]^-$, $[\text{AuCl}_4]^-$) є головним чинником формування дискретних наночастинок з невеликим діапазоном за розмірами та рівномірним розподілом по поверхні підкладки, а також наноструктурних плівок. Встановлено, що з підвищенням температури від 313 до 343 K спостерігається зміна структури осаду золота від плівкової до дисперсної, що зумовлено значним збільшенням швидкості електрогенеруючої реакції на мікроанодах кремнієвої поверхні та десорбцією молекул органічних розчинників із металевих зародків.

Ключові слова: гальванічне заміщення, срібло, паладій, золото, кремній, DMF, DMSO.