

## Platinum Nanoparticle Deposition on the Silicon Surface by Galvanic Replacement in DMSO Medium

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The results of studies of the formation of platinum nanoparticles (Pt NPs) on the silicon surface by galvanic replacement (GR) in a fluoride-containing solution of  $H_2[PtCl_6]$  in dimethyl sulfoxide (DMSO) are presented. The conditions of the deposition process of Pt NPs on the substrate surface are established. It is shown that in a wide range of platinum precursor concentrations ( $1-4 \text{ mmol}\cdot\text{l}^{-1}$ ) and temperature ( $30-50 \text{ }^\circ\text{C}$ ), discrete spherical metal nanoparticles (Pt NPs) with a diameter of 20 to 200 nm with uniform distribution on the substrate surface are formed. The main factors influencing the geometry of nanoparticles are the concentration of  $H_2[PtCl_6]$ , temperature and duration of GR. As the values of these factors increase, the particle size increases. Ultrasound accelerates the GR process, which increases the size of Pt NPs and promotes the formation of a metal film on the silicon surface. It is shown that concentrations of platinum ions and DMSO medium during GR are one of the main factors influencing the size of discrete particles with a small size range and uniform distribution on the substrate surface. It was found that with increasing temperature from 30 to 50  $^\circ\text{C}$  there is a change in the structure of platinum sediment from discrete to the formation of agglomerates, which is due to a significant increase in the rate of electrogeneration reaction at the anode surfaces. It was found that increasing the duration of the GR process from 30 to 60 s contributes to the filling density of the silicon surface. The results of studies of the influence of organic aprotic solvent molecules on the geometry of metal particles and their distribution on the substrate surface are obtained. Nanostructures of platinum with good adhesion to the substrate surface were obtained.

**Keywords:** Platinum, Galvanic replacement, Silicon surface, DMSO, Nanoparticles.

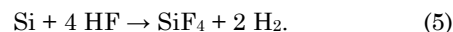
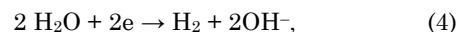
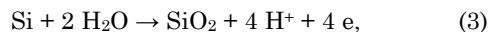
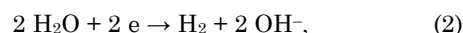
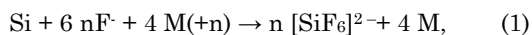
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### 1. INTRODUCTION

The silicon surface modified with nanoparticles and nanostructures of metals has attracted special attention in the last decade due to its effective use in sensors [1, 2], catalysis [3-5], biomedicine [6], optoelectronics [7], solar cells [8], as a photocathode for  $H_2$  evolution from water [9, 10], in fabrication of porous silicon and silicon nanowires [11], etc. The functional properties of silicon/metal nanostructures depend on the geometry of the deposited metal nanoparticles and the overall surface architecture. Therefore, the choice of a method for their preparation is important in terms of maximizing the controlled formation of a certain morphology of a metal precipitate and manufacturability. Methods that meet these criteria include galvanic replacement (GR), which is easy to implement and does not require the use of complex equipment. It is used to modify the silicon surface with nanostructures of noble (Ag, Au, Pd, Pt, Rh, Ru) and non-noble (Cu, Ni) metals [12].

Deposition of metals [3, 6, 8, 12] and, in particular, platinum (Table 1) on the silicon surface by GR is carried out in fluoride-containing aqueous solutions. GR processes follow an electrochemical mechanism that can be represented by the generalized equation (1), where  $M(+n)$  are hydrated or complex metal ions. In aqueous solutions, side processes also occur, which cause passivation of the silicon surface (3), gas evolution (4), (5) and etching of the substrate (5). Organic aprotic solvents have recently been used effectively to prevent them [13-15].



It is of great interest to obtain GR systems of silicon/Pt nanostructures (Table 1) due to their high electrocatalytic properties, which are used in many new areas – fuel cells, biosensors, nanobiomedicine. Due to the increased capabilities of a non-aqueous medium compared to aqueous solutions in the controlled formation of metal nanoparticle geometry, the aim of the study was to investigate the formation of a nanostructured platinum precipitate on the silicon surface by GR in DMSO solutions: precursor concentration, temperature, deposition duration.

### 2. EXPERIMENTAL DETAILS

Materials: *n*-type Si (100) wafers from Crysteco company were used for the research. The specific resistance of the plates was  $4.5 \Omega \text{ cm}$ , the size of the silicon samples was  $1 \times 1 \text{ cm}$ . Hydrogen hexachloroplatinate (IV) (Alfa Aesar, 99.9 %,  $M_w = 409.81 \text{ g mol}^{-1}$ ) and HF (40 %,  $M_w = 20 \text{ g mol}^{-1}$ ).

Solvents: dimethyl sulfoxide (DMSO, 99 %, Alfa Aesar), ethanol (Alfa Aesar), isopropanol (AlfaAesar), acetone (AlfaAesar).

Methods. Deposition of platinum was carried out by GR on an *n*-type silicon sample in (1...4) mM  $H_2[PtCl_6]$  DMSO in the presence of HF (1 wt. %) and its absence. The silicon surface was pre-cleaned in an ultrasonic

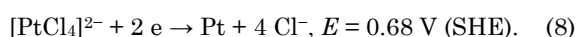
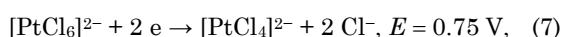
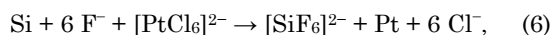
**Table 1** – Conditions for the formation of platinum deposits on the surface of silicon wafers by GR

Type of silicon	Composition of the solution	$t$ , °C	Duration of GR	Morphology of sediment and geometry of particles	Ref.
<i>p</i> -Si	1 mM Na <sub>2</sub> [PtCl <sub>6</sub> ] and 0.25-1 M HF	25	2-10 min	discrete spheroid Pt NPs (40-300 nm)	[4]
<i>n</i> -Si	1 mM H <sub>2</sub> [PtCl <sub>6</sub> ] and 5 M HF	20	5-60 min	height = 100-400 nm; width = 200-1000 nm	[16]
<i>p</i> -Si (100)	3.5 mM PtCl <sub>2</sub> and HF	20	0.5-60 min	nanofilms at [HF]:[PtCl <sub>2</sub> ] < 26; Pt NPs and Pt NCs [HF]:[PtCl <sub>2</sub> ] ≥ 528	[17]
scratched Si wafers	(0.2-10) mM H <sub>2</sub> [PtCl <sub>6</sub> ] and 5 M HF	20	3-60 min	3D Pt nanoflowers	[18]
<i>p</i> -Si (100)	(1-10) mM H <sub>2</sub> [PtCl <sub>6</sub> ] and 2.5 M HF	50	5-60 min	hierarchical Pt nanostructures consisting of pinecone-like, microspherical, flower-like structures	[19]
<i>n</i> -Si	1 mM H <sub>2</sub> [PtCl <sub>6</sub> ] and 0.15 M HF	40	90 s	discrete spheroid particles (~ 50 nm)	[20]
<i>p</i> -Si (100)	2 mM H[AuCl <sub>4</sub> ] 1 mM K <sub>2</sub> [PtCl <sub>6</sub> ] and 0.5 M HF	20	3 min	Pt monolayer decorated Au nanostructured film on the silicon surface	[5]
<i>p</i> -Si (100)	0.3 mM Na <sub>2</sub> [PtCl <sub>4</sub> ]	20	5 min	oblate hemispherical Pt NPs with $\varnothing \approx 40$ nm and height = 10±5 nm	[9]
<i>p</i> -Si (100)	1 mM Na <sub>2</sub> [PtCl <sub>4</sub> ] and 5.7 M HF	22-75	1-30 min	discrete particles (120-250 nm) or dendritic metal structures	[10]
<i>n</i> -Si (100)	1 mM Na <sub>2</sub> [PtCl <sub>6</sub> ] and 4.8 M HF	20	10-960 s	nanoporous Pt NPs (15-100 nm) with high internal surface area	[21]

bath in ethanol and acetone, after which it was chemically etched in a 5 % hydrofluoric acid solution. GR was performed in the temperature range of 30...50 °C with a deposition duration of 30...300 s. After completing the process, the samples were washed with isopropanol, acetone and dried at a temperature of 60 °C. The morphology of the obtained platinum nanoparticles (Pt NPs) on the silicon surface was investigated using a JSM-6060LA analytical scanning electron microscope. Images of the modified surface were obtained by registering secondary electrons and scanning with an electron beam with an energy of 20 keV. The images were displayed using digital software (SEO Scan). The chemical composition of the precipitates obtained was investigated by energy dispersive analysis (EDX). The sizes of the obtained Pt NPs were determined using SEM images by comparing individual particles with the scales presented in the images and using the Axio-Vision V 4.8.2.0 program.

### 3. RESULTS AND DISCUSSION

Deposition of platinum by GR on the silicon surface in a fluoride-containing DMSO solution of H<sub>2</sub>[PtCl<sub>6</sub>] takes place according to the total reaction (6). The authors of [21] emphasize that the reduction of Pt (IV) on silicon occurs in stages (7), (8), but do not indicate differences in the formation of platinum precipitate compared to a single-stage process with PtCl<sub>2</sub> [17] or Na<sub>2</sub>[PtCl<sub>4</sub>] [9, 10]. Due to the values of  $E^0[\text{PtCl}_4]^{2-}/\text{Pt} = 0.68$  V and  $E^0[\text{SiF}_6]^{2-}/\text{Si} = -1.20$  V, the electromotive force of the GR process  $\Delta E^0 = 0.68$  V – (– 1.20 V) = 1.88 V is high for recovery of platinum at a high rate.

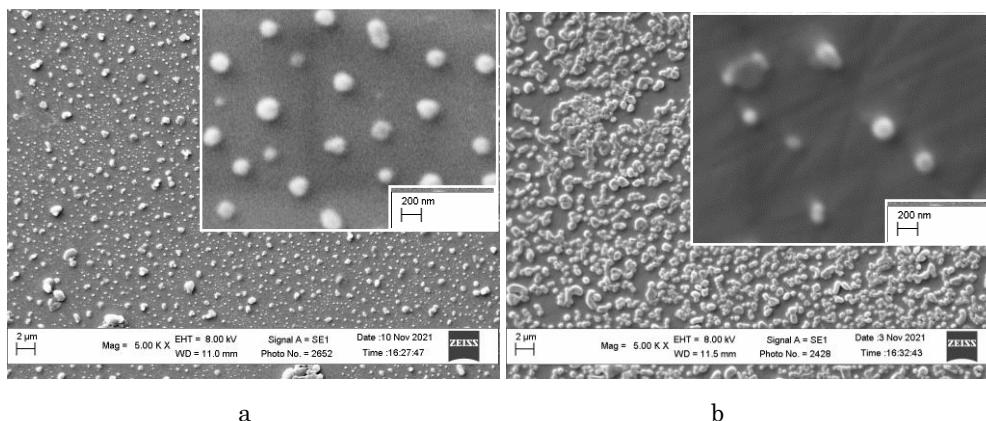


#### 3.1 Influence of Ultrasound

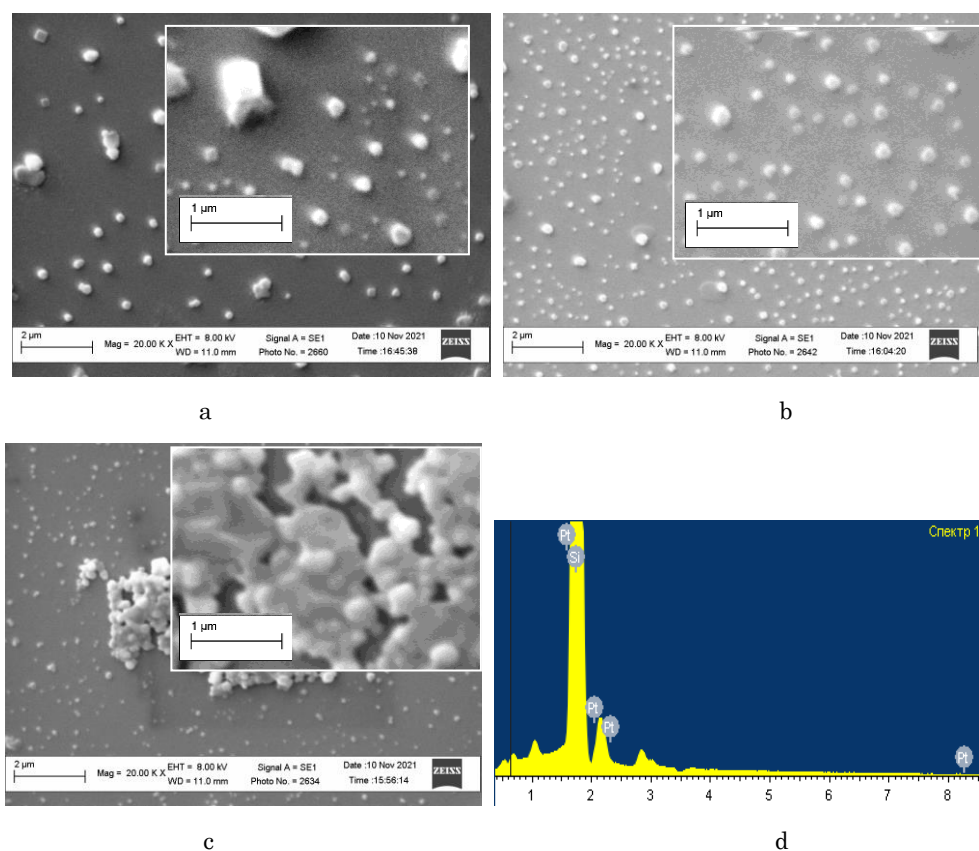
Platinum is deposited on the silicon surface in a DMSO solution in the form of discrete spherical NPs (Fig. 1a). This is characteristic of the formation of metals in DMSO by GR [9, 10]. Spherical NPs are also formed in DMSO solutions during electrochemical deposition [22]. This can be explained by the formation of surface complexes on metal particles due to the high electron-donor properties of DMSO (DN = 29), which creates the effect of a surfactant. During sonogalvanic replacement, particle aggregation in the plane of the silicon surface is observed with a tendency to form a film deposit (Fig. 1b). This is due to many factors influencing electrochemical and chemical processes with ultrasound [23, 24], among which the main ones are an increase in the mass transfer rate, reduction of the adsorption process, and a decrease in the thickness of the electrical double layer. The latter is especially important for accelerating the diffusion of ions to the cathode and anode surfaces and the metal reduction process in general.

#### 3.2 Influence of Temperature

With increasing temperature from 30 (Fig. 2a) to 40 (Fig. 2b) and 50 °C (Fig. 2c), we observe an increase in the size of discrete Pt NPs and their agglomerates. This effect of the temperature factor is primarily due to an increase in the rate of the electrogeneration reaction (9) of silicon dissolution at the anode surfaces, which causes a corresponding increase in the  $i_{\text{cathode}}$  values at the cathode surfaces. As a result, more intense cathodic reduction occurs according to reactions (7) and (8). In addition, the depolarizing effect of temperature leads to a weakening of the adsorption of DMSO molecules on existing Pt NPs, eliminating the factor of surface complexes  $\text{Pt} \leftarrow : \text{DMSO}$ . Therefore, with increasing temperature simultaneously with an increase in the rate of

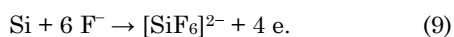


**Fig. 1** – SEM images of the silicon surface after deposition of platinum with 4 mM  $\text{H}_2\text{PtCl}_6$  + HF (1 wt. %) in DMSO at 40 °C for 5 min without (a) and with (b) ultrasound



**Fig. 2** – SEM images of Pt deposited on the silicon surface from 4 mM  $\text{H}_2\text{PtCl}_6$  in DMSO solutions for 60 s at  $t = 30$  (a), 40 (b) and 50 (c) °C and energy-dispersive X-ray spectroscopy (EDXS) of the Si/Pt surface (d)

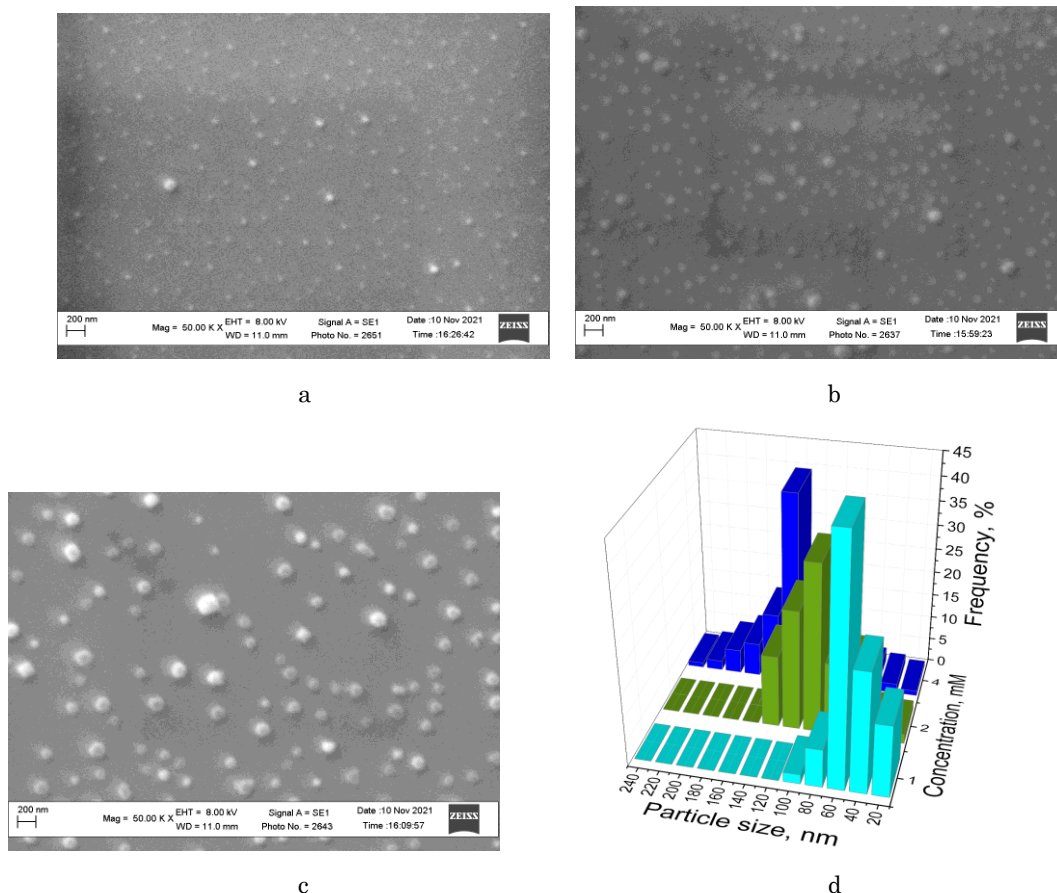
the process of galvanic reduction of platinum, there is a tendency to an increase in the particle size and their agglomeration (Fig. 2c).



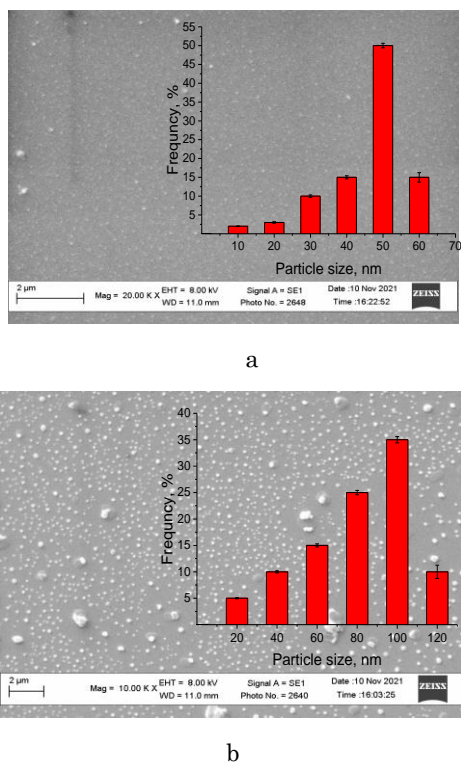
### 3.3 Influence of Platinum Ion Concentration

Spherical Pt NPs are formed in a wide range of platinum precursor concentrations (Fig. 3) with their uniform distribution on the silicon surface (Fig. 3). As their content increases, the size of discrete particles

increases, which is due to a decrease in the cathodic polarization concentration. Thus, in 1, 2 and 4 mM  $\text{H}_2[\text{PtCl}_6]$ , the largest proportion of Pt NPs is in the range of 50-80, 70-100 and 110-140 nm, respectively. There is also a tendency to form agglomerates (Fig. 3c). Thus, the concentration of platinum precursor in the solution is an effective factor influencing the size of Pt NPs during their deposition on silicon by GR. Therefore, solutions with  $\text{H}_2[\text{PtCl}_6]$  concentrations of no more than 1-4 mmol  $\text{l}^{-1}$  should be used to form Pt NPs up to 200 nm in size.



**Fig. 3** – SEM images of the silicon surface after deposition of platinum with 1 (a), 2 (b) and 4 (c) mM  $H_2[PtCl_6]$  in DMSO solutions at 40 °C for 60 s and 3D histogram of Pt NPs size distribution (d)



**Fig. 4** – SEM images of the silicon surface after deposition of platinum with 4 mM  $H_2[PtCl_6]$  in DMSO solutions at 40 °C for 30 (a) and 60 (b) s and histograms of their size distribution

### 3.4 Influence of GR Duration

Comparing the morphology of the platinum precipitate deposited on the silicon surface for 30 and 60 s and the size distribution of Pt NPs (Fig. 4), it is seen that the size of the latter increases with time (Fig. 4b) and the distance between particles increases, while the number of particles practically does not change. This gives grounds to claim that the predominant nucleation occurs in the initial period of the GR process. In the future, almost only the growth of nuclei occurs. Moreover, a kind of 2D filling of the silicon surface is due to the growth of Pt NPs.

## 4. CONCLUSIONS

1. Nanosized discrete spherical Pt NPs are deposited in fluoride-containing DMSO solutions  $H_2[PtCl_6]$  on the silicon surface by GR and are uniformly distributed on the substrate surface.
2. The action of ultrasound accelerates the GR process, which causes an increase in the size of Pt NPs, as well as a tendency to form a film deposit on the silicon surface.
3. The main factors influencing the size of Pt NPs are the concentration of  $H_2[PtCl_6]$ , temperature and GR duration. An increase in the values of these parameters leads to an increase in the particle sizes.

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### Осадження наночастинок платини на поверхню кремнію гальванічним заміщенням в середовищі DMSO

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Наведено результати досліджень формування наночастинок платини (Pt NPs) на поверхні кремнію методом гальванічного заміщення (GR) у фторвмісному розчині  $H_2[PtCl_6]$  в диметилсульфоксиді (DMSO). Встановлено умови процесу осадження Pt NPs на поверхні підкладки. Показано, що у широкому діапазоні концентрацій прекурсора платини (1-4 ммол·л<sup>-1</sup>) і температури (30-50 °С) формуються дискретні сфероподібні наночастинки металу (Pt NPs) діаметром від 20 до 200 нм з рівномірним розподілом по поверхні підкладки. Головними факторами впливу на геометрію наночастинок є концентрація  $H_2[PtCl_6]$ , температура та тривалість GR. Зі збільшенням значень цих факторів розміри частинок зростають. Ультразвук пришвидшує процес GR, що спричиняє збільшення розмірів Pt NPs, а також сприяє формуванню металевої плівки на кремнієвій поверхні. Показано, що концентрація іонів платини та середовище DMSO за GR є одним із основних чинників впливу на розміри дискретних частинок із невеликим діапазоном за розмірами та рівномірним розподілом по поверхні підкладки. Встановлено, що з підвищенням температури від 30 до 50 °С спостерігається зміна структури осаду платини від дискретної до утворення агломератів, що зумовлено значним зростанням швидкості електрогенеруючої реакції на анодних ділянках поверхні. Виявлено, що збільшення тривалості GR від 30 до 60 с сприяє щільності заповнення поверхні кремнію. Наведено результати досліджень впливу молекул органічного апротонного розчинника на геометрію металевих частинок та їх розподіл по поверхні підкладки. Отримано наноструктури платини з доброю адгезією до поверхні підкладки.

**Ключові слова:** Платина, Гальванічне заміщення, Поверхня кремнію, DMSO, Наночастинки.