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ELECTRODEPOSITION OF SILVER NANOPARTICLES ON SILICONE SURFACE IN DIMETHYLFORMAMIDE SOLUTIONS OF $(NH_4)[Ag(CN)_2]$

The article presents the results of studies of electrochemical deposition of silver nanoparticles (AgNPs) on the silicon surface in dimethylformamide solutions of 0.025M; 0.05M; 0.1M $(NH_4)[Ag(CN)_2]$. Combination of a pulsed electrolysis mode and an organic aprotic solvent medium (DMF) ensures the formation of 50–150 nm spherical AgNPs with uniform distribution over the silicon surface. It is shown that the main factors influencing the morphology and size of silver nanoparticles are the value of the cathode potential, the concentration of ions $[Ag(CN)_2]^-$ and the duration of electrolysis. With their increase, the size of the nanoparticles and the density of filling the substrate increases. It was found that the deposited AgNPs on the surface of the substrate are activators of chemical etching of the latter to give porous silicon.

Key words: silver nanoparticles, dimethylformamide, silicon surface, electrodeposition, porous silicon.

Introduction

Nanomaterials based on precipitated metal nanoparticles (MNPs) of the Si/MNPs system are characterized by a wide range of functional properties. This makes them promising in nanoelectronics [1], sensors [2−4], photovoltaics [5–7]. The properties of such materials depend significantly on the geometry of the MNPs and their distribution on the substrate surface. Galvanic replacement (GR), which is widely used to produce Si/MNPs, does not always provide controlled formation of Si/MNPs nanostructures [8–10]. Therefore, in the last decade, much attention has been paid to controlled electrochemical deposition of MNPs, in particular nobel metals [11–13]. The latter is due to their resistance to the environment ofsynthesis and operation.Of particular interest is the electrochemical deposition of metal nanoparticles on a substrate in a non-aqueous medium – organic polar solvents and ionic liquids. The absence of side chemical and electrochemical processes in them, in comparison with aqueous solutions, makes it possible to extend the possibilities of controlled production of Si/MNPs nanostructures. Particularly effective is the combination of a non-aqueous medium, in particular organic aprotic solvents, and a pulsed regime of electrochemical deposition [14, 15].

Electrolysis is one of the effective methods of controlled deposition of metal nanoparticles on a semiconductor substrate [16]. It is mostly carried out in aqueous solutions, where in addition to the basic metal recovery process, side processes occur, in particular, the evolution of hydrogen at cathode sites [11, 12, 17–20]. This complicates the formation of metal nanoparticles of a given geometry. Pulse electrolysis in organic aprotic solvents [14–16, 21] eliminates the disadvantages of aqueous solutions. In addition, molecules of organic solvents, by virtue of their electrode donor properties, act as surfactants, affecting the geometry of the nanoparticles and their size distribution.

In the last decade, there has been a tendency to find methods for obtaining functional materials based on silicon, in particular, nanoporous semiconductors [3, 22, 23] and nanowires (SiNWs) [6, 7, 24–26]. One of the effective methods for their preparation is metal-activated chemical etching (MACE) of Si/MNPs nanostructures. It involves pre-deposition on the silicon surface of islet nanoparticles or porous metal films, followed by etching with HF + $+H_2O_2$ based solutions [23].

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Aim of the work

The purpose of the work is the deposition of silver nanoparticles on the silicon surface by pulsed electrolysis in DMF solutions and the use of synthesized Si/AgNPs nanostructures as precursors to obtain porous silicon.

Materials and methods of research

The deposition of silver on the silicon surface was carried out by electrolysis of solutions 0.025M; 0,05M; 0,1M (NH$_4$)[Ag(CN)$_2$] in DMFat temperature 25 ℃. The method of preparation of dimethylformamide solution (NH$_4$)[Ag(CN)$_2$] is described in [8].

The n-type Si (100) silicon wafer of the company Crysteco served as the working electrode with a specific resistance of 4.5 Ohm·cm, size 1x1 cm. Platinum anode plate (S = 2.2 cm^2). The potentials are given relative to the chloride-silver reference electrode. Before electrolysis, the silicon samples were etched for 10 s in HF solution to remove the oxide film from the substrate surface. To ensure reliable electrical conductivity of the silicon surface, a conductive adhesive tape and silver plates were used. The side surface of the specimens was insulated with teflon tape.

The silver nanoparticles were precipitated under pulsed electrolysis using potentiostat IPC-Pro.

Potential pulses were set with a pulse duration of $\tau_{on} = 6$ msand a pause of $\tau_{off} = 300$ $\tau_{off} = 300$, the number of cycles of $\tau_{on}-\tau_{off} = 25, 50, 100$. After electrodeposition, the samples were washed in DMF, ethanol, and dried at 60 °C.

The resulting Si/AgNPssurface was etched in etching solution HF + H$_2$O$_2$ by the method [6].

The morphology of the precipitates obtained on the silicon surface and the silicon surface after MACE was examined using a ZEISS EVO 40XVP scanning electron microscope. Images of the modified surface were obtained by registering secondary electrons by scanning with an electron beam with energy of 15–20 keV. The results were processed using OriginPro 8.0 and 2D computer software.

Results of the studies and their discussion

The studies aimed to determine the dependence of the morphology of electrochemically obtained Si/AgNPs nanostructures and the geometry of AgNPs on the following electrolysis parameters: 1) the value of the cathode potential; 2) ion concentrations [Ag(CN)$_2$]$^-$; 3) the duration of the deposition.

1. The value of the cathode potential

It is shown that in dimethylformamide solutions of 0.05M (NH$_4$)[Ag(CN)$_2$] for cathode potential values in the range E = -1.8...-2.2 V, spherical silver nanoparticles with a relatively small range of them are formed on the silicon surface. sizes (Fig. 1). This is due, first of all, to the high stability of complex ions [Ag(CN)$_2$]$^-$ ($K_n = 1 \cdot 10^{-22}$), which causes significant cathodic polarization. In addition, the formation of such AgNPs geometry is facilitated by the environment of a high-donor aprotic solvent [14, 15, 21].
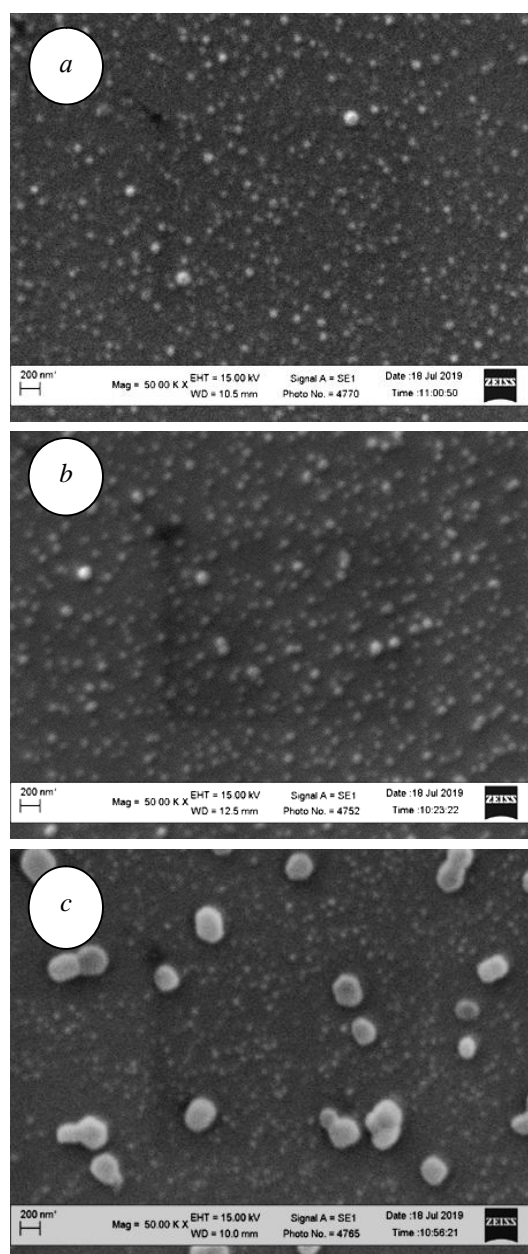

Fig. 1. SEM images of silver nanoparticles on a silicon surface precipitated by 0.05M (NH$_4$)[Ag(CN)$_2$] electrolysis in DMF solution for the duration of deposition of 50 cycles by $E_{cathode}$ (V): -1.8 (a), -2.0 (b), -2.2 (c)

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It is found that as the cathode potential increases, the size of AgNPs increase. However, their shape and density of filling the surface of the substrate is almost unchanged. This can be explained by the prevailing growth rate of AgNPs over their nucleation process.

2. Concentration of ions $[Ag(CN)_2]^-$

It is found that with increasing concentration of ions $[Ag(CN)_2]^-$ size of AgNPs increase practically in proportion (Fig. 2). Thus, nanoparticles of an average size of ~50 nm are precipitated from solutions of 0.025 mol/l, then from 0.1 mol/l – ~150 nm.
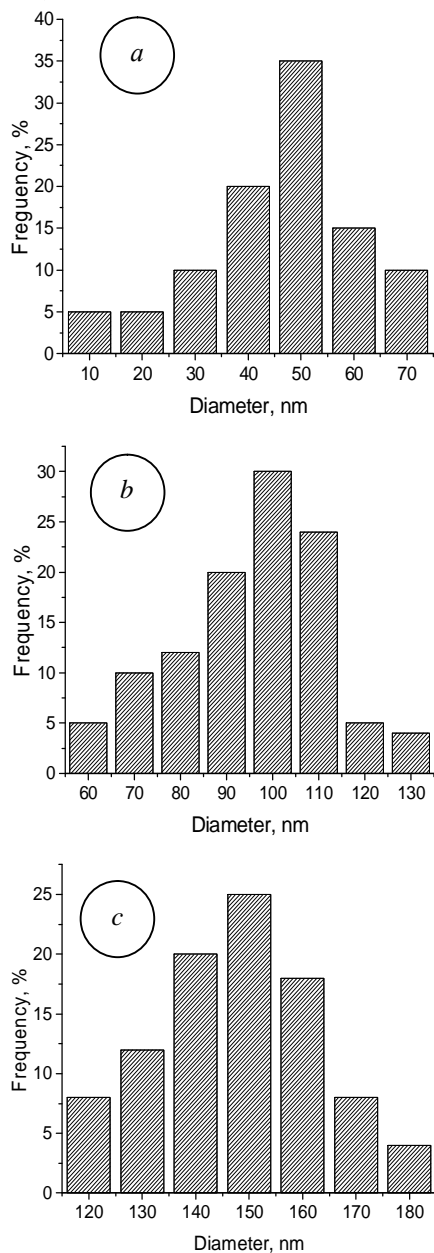

Fig. 2. Histograms of the distribution of AgNPs on the silicon surface by the size obtained by electrolysis in 0,025M (a), 0,05M (б), 0,1M (c) (NH₄)[Ag(CN)₂], in solution of DMF by E = -2,0 V

Therefore, the concentration of ions $[Ag(CN)_2]^-$ is an effective factor in the influence on the morphology of silver nanoparticles, electrochemically deposited on the silicon surface.

3. Duration of deposition

Silver and silicon differ significantly in the parameters of the crystal lattice, so the formation of a precipitate on the silicon surface occurs by the Volmer-Weber mechanism. This involves insulating the nanoparticles with silver nanoparticles. Therefore, as the duration of electrochemical deposition increases, the size of AgNPs increases (Fig. 3).
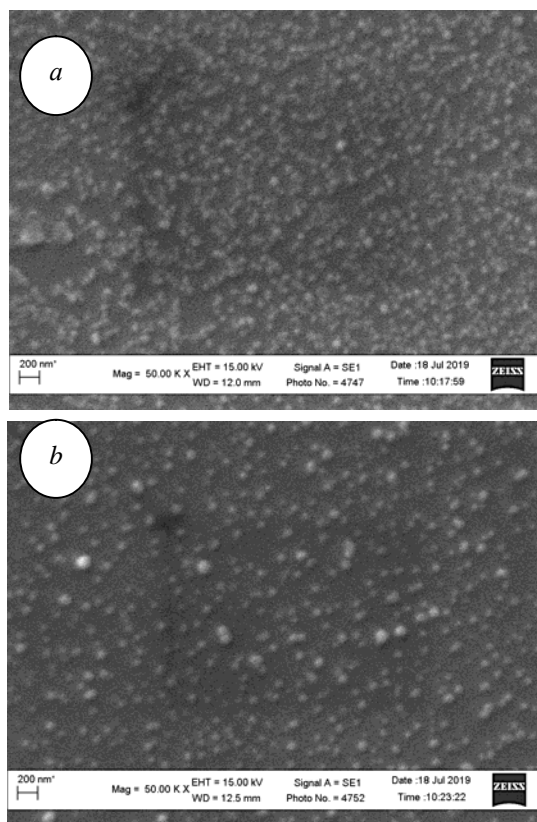

Fig. 3. SEMimages of the silicon surface of silver obtained from 0.05M (NH₄)[Ag(CN)₂] in DMF at E = -2 V for 25 (a) and 50 (b) cycles

Thus, for the duration of electrolysis of 25 cycles, the size of the nanoparticles is ~70 nm, whereas for 50 cycles it is ~90 nm. However, the nature of the substrate filling does not change.

Therefore, the major factors influencing the morphology of the electrochemically obtained Si/AgNPs nanostructure and the size of silver nanoparticles are the value of the cathode potential, the concentration of the deposited metal ions, and the duration of the electrolysis.

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4. Formation of porous silicon from electrochemically obtained nanostructures Si/AgNPs

The obtained nanomaterials Si/AgNPs were investigated for use as precursors of porous silicon. AgNPs nanoparticles in contact with the silicon surface activate the contact corrosion of the substrate in etching solutions, in particular H_2O_2 + HF. However, such electrochemical reactions occur on the anode (1) and cathode (2) sites $[SiF_6]^{2-}$.

$$Si + 6HF \rightarrow H_2[SiF_6] + 4H^+ + 4e^- \qquad (1)$$

$$4H^+ + 4e^- \rightarrow 2H_2 \qquad (2)$$
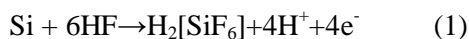
The reaction rate (1) occurring directly near AgNPs is high due to the large value

$$\Delta E^0 = E^0_{Ag^+/Ag} - E^0_{[SiF_6]^{2-}/Si}$$

between silver ($E^0_{Ag^+/Ag}$ = 0,78 V) and silicon ($E^0_{[SiF_6]^{2-}/Si}$ = -1,2 V).

The great importance of ΔE also determines the localization of the process of electrochemical etching by reaction (2). Therefore, the diameter of the pores and their distribution in silicon, respectively, depend on the diameter of the deposited AgNPs and the density of their filling on the substrate. Scanning electron microscopy revealed that nanopores mainly reproduce the shape of metal nanoparticles (Fig. 4).
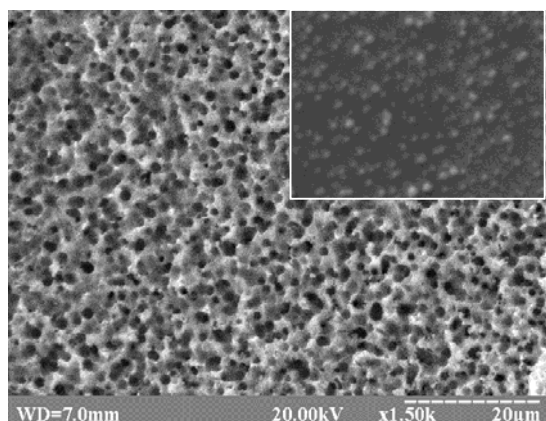

Fig. 4. SEM image of porous silicon, after etching of HF-H_2O_2-H_2O substrate of n-Si(100) coated with AgNPs (inset), applied from a solution of 0.05M (NH$_4$)[Ag(CN)$_2$]

Structures with such porous morphology are used as sensing elements of gas sensors (CO, NH$_3$, CO$_2$, etc.) [27]. Therefore, the controllability of the process of electrolysis of silver nanoparticles on the silicon surface opens the possibility for the development of high-performance modern sensor devices.

Conclusions

Pulse electrolysis on the silicon surface from dimethylformamide solutions 0,025M; 0.05M; 0.1M (NH$_4$)[Ag(CN)$_2$] precipitated silver nanoparticles with an average size of ~50, ~100, ~150 nm, respectively. The main factors influencing the size are the value of the cathode potential, the concentration of ions [Ag(CN)$_2$]$^-$ in solution and the duration of electrolysis. As these values increase, the size of the nanoparticles increases.

Electrochemically obtained Si/AgNPs nanostructures are effective precursors for the production of porous silicon by the MACE method.

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ЕЛЕКТРООСАДЖЕННЯ НАНОЧАСТИНОК СРІБЛА НА ПОВЕРХНЮ КРЕМНІЮ З ДИМЕТИЛФОРМАМІДНИХ РОЗЧИНІВ (NH₄)[Ag(CN)₂]

Наведено результати досліджень електрохімічного осадження наночастинок срібла (AgNPs) на поверхню кремнію у диметилформамідних розчинах 0,025M, 0,05M, 0,1M (NH₄)[Ag(CN)₂]. Поєднання імпульсного режиму електролізу та середовища органічного апротонного розчинника (DMF) забезпечує формування сферичних AgNPs розміром 50–150 нм із рівномірним розподілом їх по поверхні кремнію. Показано, що головними факторами впливу на морфологію та розміри наночастинок срібла є значення катодного потенціалу, концентрація іонів [Ag(CN)₂]⁻ та тривалість електролізу. З їх збільшенням зростають розміри наночастинок і густота заповнення ними підкладки. Встановлено, що осаджені AgNPs на поверхні підкладки є активаторами хімічного травлення останньої з одержанням поруватого кремнію.

Ключові слова: наночастинки срібла, диметилформамід, поверхня кремнію, електроосадження, поруватий кремній.