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# Study of composite structure based on Ag and SiNWs

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**Abstract.** In this study, we propose a method for creating a composite structure consisting of an array of vertical silicon nanowires (SiNWs) and silver nanoparticles (AgNPs). To obtain SiNWs, the process of two-stage metal-assisted chemical etching of c-Si was used, and to obtain a uniform distribution of AgNPs in the SiNW array over their entire height, the atomic layer deposition method was used. The structural and optical characteristics of the AgNPs/SiNWs were studied by nondestructive spectroscopic ellipsometry and scanning electron microscopy before and after the preparation of the composite structure. The thickness (from 2.7 to 7.8 nm) of AgNPs layers deposited on a c-Si substrate and their complex dielectric functions were determined within the framework of the Drude-Lorentz model, on which resonance peaks of localized and bulk plasmons are observed. For an array of SiNWs, using a multilayer model and the effective Bruggeman medium approximation, the height of sublayers and the Si fraction in them, as well as the Ag fraction in the Ag/SiNWs composite structure, are determined. The c-Si:Ag composite structure has been characterized by comparing the calculation and experiment. The optical properties of Ag/SiNWs structures with complex spatial geometry are modeled using the COMSOL Multiphysics software package. The expected localization of the electric field is observed on the surface and near the AgNP as a result of the excitation of localized plasmon resonance. The calculated enhanced factor reached $10^{10}$, which suggests that composite AgNPs/SiNWs structure is promising to use as a substrate for surface-enhanced Raman scattering.

**Keywords:** Ag nanoparticles, Si nanowires, atomic layer deposition, metal-assisted chemical Etching (MACE), spectroscopic ellipsometry, localized plasmon resonance

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# Исследование композитной структуры на основе серебра и кремниевых нанонитей

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**Аннотация.** В данной работе мы предлагаем метод создания композитной структуры Ag/Si, состоящей из массива вертикальных кремниевых нанонитей (КНН), декорированного наночастицами серебра (Ag НЧ). Для получения кремниевых нанонитей применен процесс двухстадийного металл-стимулированного химического травления Si, а для декорирования КНН Ag НЧ – метод атомно-слоевого осаждения, с помощью которого было получено равномерное распределение Ag НЧ в массиве КНН по всей их высоте.

**Ключевые слова:** наночастицы серебра, кремниевые нанонити, атомно-слоевое осаждение, металл-стимулированное химическое травление (МСХТ), спектральная эллипсометрия, локализованный плазмонный резонанс

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## Introduction

Localized plasmon resonance (LPR) in metal nanoparticles (NPs) is excited by the interaction of incident light with their electrons [1]. The LPR parameters depend on the shape of the NPs, the distance between them, and their size, as well as on the optical properties of the substrate and the environment, which can be chosen to control the plasmon characteristics. As a rule, metal NPs are deposited on flat substrates made of dielectrics or semiconductors, and air serves as the environment. Of particular interest among semiconductors are Si substrates, which are widely used in nanoelectronics [2] and optoelectronics [3]. Nowadays, high-aspect Si structures can be obtained with a highly developed surface in the form of porous Si [4] or arrays of vertical Si nanowires (SiNWs) [5] by anisotropic [6], electrochemical [4] or metal-assisted chemical etching (MACE) [7] of a single-crystal (c-Si) substrate. The creation and study of the properties of composite structures based on high-aspect Si structures decorated with noble metal NPs is a promising direction in the creation of new functional structures.

A suitable method for the uniform deposition of NPs on such high-aspect Si structures is atomic layer deposition (ALD) [8], which can be used to control the deposition thickness with great accuracy, and without any special requirements on the surface topology compared to the CVD method. In the ALD process, sequential chemisorption of reactant vapors on the substrate surface occurs [9]. The cyclical nature of the ALD processes ensures precise thickness control down to sub-nanometers. In addition, self-limiting surface reactions at the substrate-gas phase interface provide layer-by-layer growth of films and allow conformal deposition of thin films on complex three-dimensional and porous substrates.

The goal of this work was to create Ag/SiNWs composite structures in the form of an array of SiNW decorated with AgNPs using ALD method, to study their structural and optical properties, and to calculate an enhanced factor of a composite structure using the COMSOL Multiphysics software.

## Materials and Methods

To create an array of SiNW, we used p-type c-Si (100) with a resistivity of 10 Ohm·cm. The two-stage MACE method was used to obtain SiNWs [7, 10]. Firstly, Ag island film was deposited onto the surface of the c-Si substrate from a solution of 0.02M $AgNO_3$ + 5M HF (1:1) for 30 seconds (Fig. 1, 1st step). Then the *c*-Si substrate was placed in the electrolyte solution 5M HF + $H_2O_2$ (10:1) (Fig. 1, 2nd step), where etching and formation of SiNWs took place for 10 (sample O1) and 20 (sample O2) seconds to obtain structures of different heights. After the removal of Ag in $HNO_3$ solution, the ALD process was carried out to decorate SiNWs with AgNPs (Fig. 1, 3rd step).

The AgNPs were deposited by ALD with a Picosun R-150 setup as described in [9]. To determine the optimal growth condition the reactor temperatures (142–184 °C), precursor 2,2-dimethyl-6,6,7,7,8,8,8-heptafluorooctane-3,5-dionato) silver(I) triethyl-phosphine (Ag(fod)($PEt_3$), $C_{16}H_{25}AgF_7O_2P$) (98 %, Strem Chemicals, Newburyport, MA, USA), reagents pulse times (2-4 sec) and number of pulses (1-11) in one ALD cycle were varied. The optimal conditions for the growth of Ag on the surface of *c*-Si substrates were determined.

The JSM-7001F Scanning Electron Microscope (SEM) (JEOL, Japan) was used to study the morphology of nanostructures. A statistical analysis of nanostructures was carried out (average size, coverage factor) according to SEM-images and using open-source ImageJ software.

The ellipsometric characteristics were studied using a Semilab SE2000 spectral ellipsometer (Budapest, Hungary) in the wavelength range λ from 400 to 1700 nm at an angle of incidence $\varphi = 70°$.

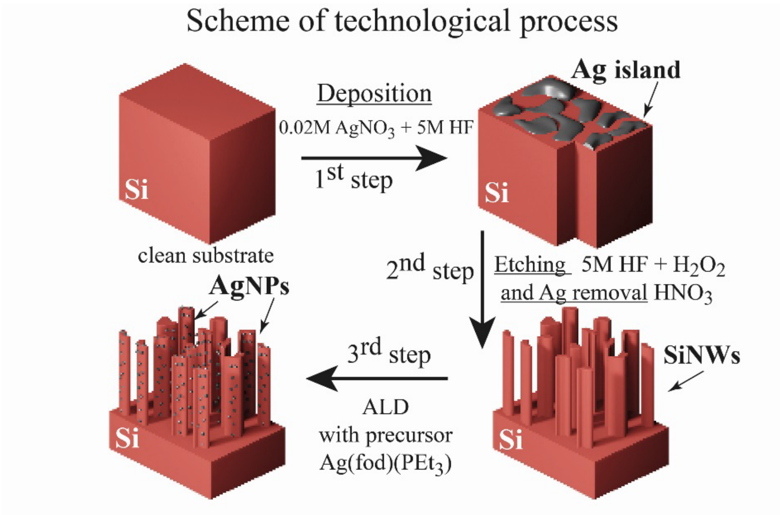


Fig. 1. Schematic representation of the stages for obtaining a composite structure of Ag/SiNWs

The simulation of the electromagnetic field propagation was carried out using the COMSOL Multiphysics software, which applied the 3D Finite Element Method (FEM).

**Results and Discussion**

At the first stage, to optimize the ALD regimes, AgNPs were deposited on flat c-Si substrates (Fig. 2, *a*). As a result of the analysis of this SEM-image in ImageJ software, the average diameter of nanoparticles $d_{Ag} = 22 \pm 3$ nm was obtained with a filling factor of 18 % (Fig. 2, *b*).

The selection of optimal conditions is the most important criterion in the preparation of coatings by the ALD method. Therefore, at the first stage of the search for optimal conditions for the ALD method, the influence of the Ag(fod)($PEt_3$) evaporator temperature was studied. Next, the dependence of the coating growth rate on the reactor temperature was studied and the optimal reactor temperature range of 155–165 °C was established, at which the growth rate was increased and a layer of AgNPs with a thickness of $d \sim 8$ nm was deposited at a number of 2300 cycles. As a result, 3 samples of layers with different thickness were obtained, ($d_{Ag}$ = 2.3, 3.5, and 7.8 nm measured using ellipsometry). By measuring the ellipsometric angles $\psi_{exp}$ and $\Delta_{exp}$ for 3 samples and using the Drude-Lorentz model with the calculated angles $\psi_{calc}$ and $\Delta_{calc}$, they were in good agreement with the experiment. As a result, the parameters of this model were extracted: real ($\varepsilon_1$) (Fig. 2, *c*) and imaginary ($\varepsilon_2$) (Fig. 2, *d*) permittivities and Ag layer thicknesses.

Analyzing the behavior of the function $\varepsilon_1$ for all 3 samples, it can be seen that they are located mainly in the negative region of energy $E$, which is typical for the structure of metals. The imaginary part of the function $\varepsilon_2$ demonstrates a narrow volume plasmon resonance peak at $E$ = 3.9 eV for all obtained AgNPs structures on a Si substrate, and for a sample with $d_{Ag}$ = 7.8 nm.

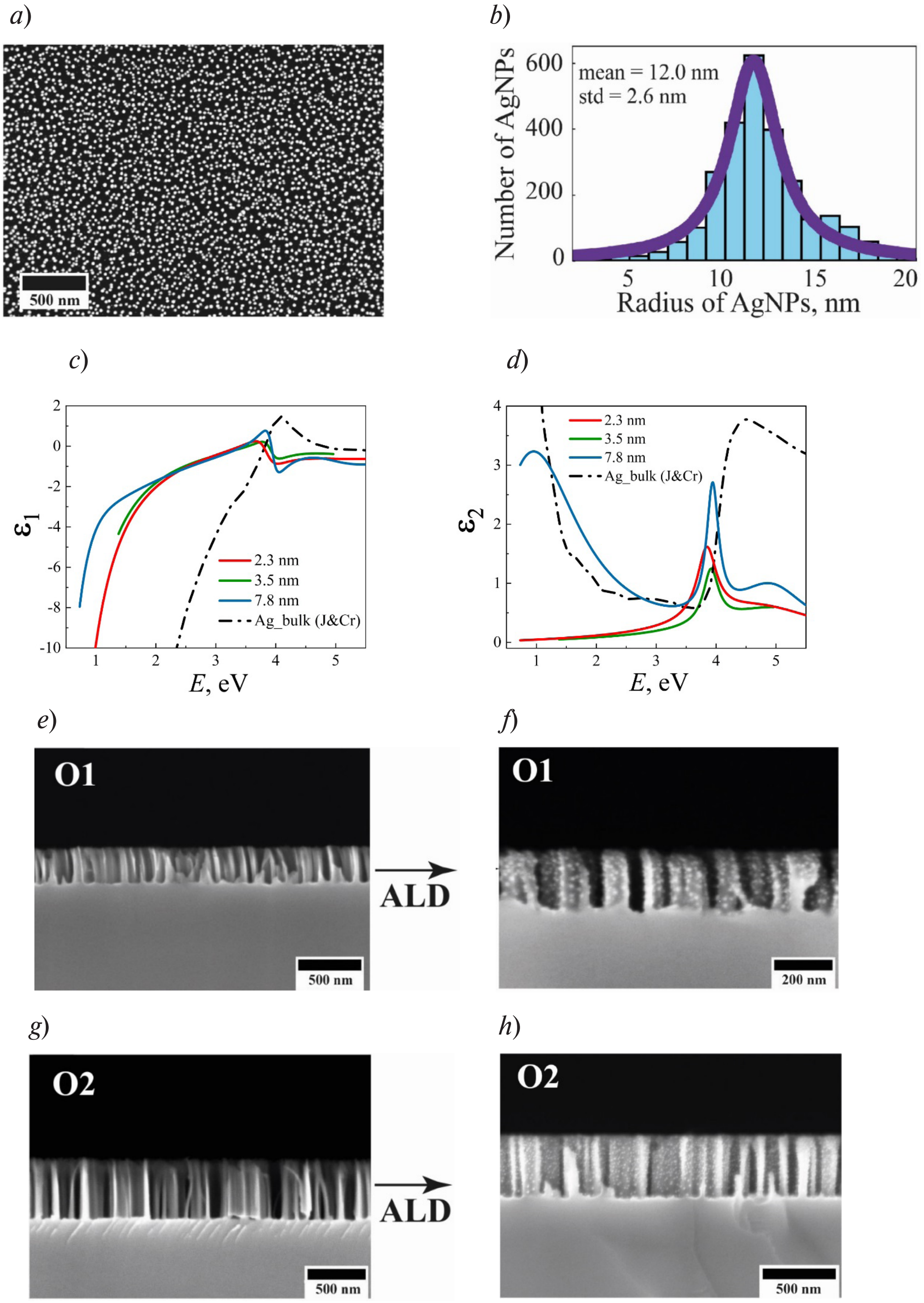


Fig. 2. Top view SEM image of AgNPs deposited by ALD on Si wafer (*a*) and their size distribution (*b*). Spectral dependences of the real part $\varepsilon_1$ (*c*) and imaginary part $\varepsilon_2$ (*d*) of the complex permittivity defined within the framework of the Drude-Lorentz model for three obtained layers of AgNPs with $d_{Ag}$ from 2.3 to 7.8 nm. Cross-section SEM images of the original arrays of SiNW: O1 (*e*) and O2 (*g*). After the deposition of AgNPs by ALD method: Ag/SiNWs (O1) (f) and Ag/SiNWs (O2) (*h*)

The cross-sections SEM-images show the sample O1 (Fig. 2, *e*) with NWs height $h_{SiNWs}$ = 234 nm and the sample O2 (Fig. 2, *g*) with $h_{SiNWs}$ = 469 nm before ALD process.

Both initial samples of SiNWs (O1 and O2) were placed in the same chamber during AgNPs deposition with flat samples to control the thickness of the Ag layers. The cross-section SEM images for these two samples of Ag/SiNWs are shown in Fig. 2, *f*, *h*. The average diameter of AgNPs deposited on SiNWs using the ALD method was 12 ± 2 nm, which turned out to be almost two times smaller than the AgNP diameter deposited on a flat Si substrate.

To interpret the ellipsometric data of SiNW samples before AgNPs deposition, a model with three-dimensional array of vertical rods of cylinders (Fig. 3, *a*) was chosen, structures located on the substrate is divided into several conditional layers with boundaries parallel to the substrate [10]. Thus, it is possible to model each of the layers with the appropriate height parameters. In addition, since each of the layers is located in a certain array, it is separated by a certain medium (in our case, air), such an array can be considered as a composite consisting of Si and air. For such structures, the effective medium approximation (EMA) is usually used. In our case, a three-layers model was used, in which the parameters of the thickness and Si fraction ($h_{Si}$ and $f_{Si}$) of each of the three sublayers were fitted. The value of the $f_{Si}$ and the fraction of voids $f_{voids} = (1 - f_{Si})$ dependent on it were determined in the framework of the Bruggeman EMA (B-EMA) [11]. The optical constants of *c*-Si were taken from the handbook [12].

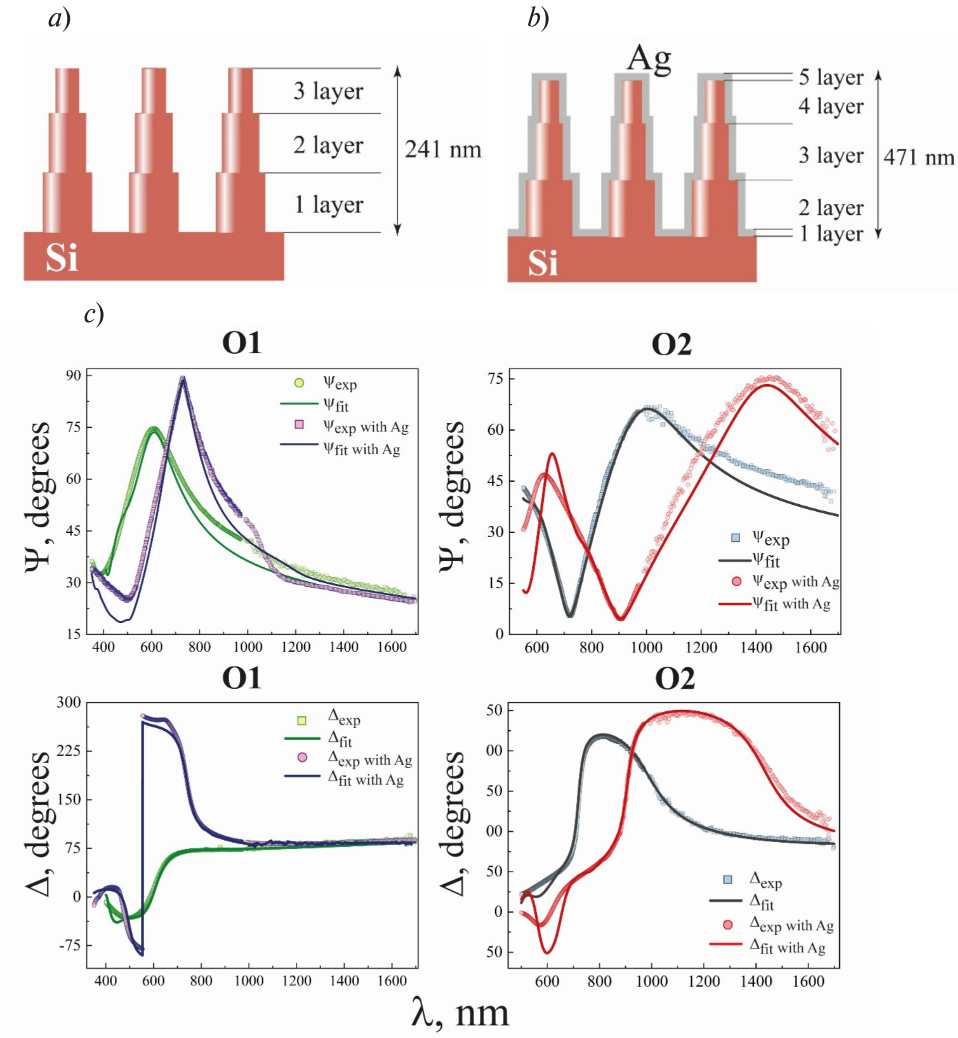


Fig. 3. Schematic model for the structure of SiNWs (sample O1 and O2) (*a*), model for the Ag/SiNW structure with AgNPs layers on the entire surface of SiNWs (*b*). Experimental (exp) and calculated (calc) ellipsometric spectra of SiNWs before (green) and after (violet) AgNPs deposition for sample O1 (*c*). Ellipsometric spectra of SiNWs before (gray) and after (red) AgNPs deposition for sample O2

Calculated ellipsometric angles ($\psi$ and $\Delta$) after fitting for this model are shown in Fig. 3, *c* (green). As a result, $f_{Si}$ and $h_{Si}$ were determined for each of the three sublayers. When summing $h_{Si}$ of all three sublayers, the total height $h_{Si}$ = 241 nm is obtained, which is close to the height of 234 nm obtained from the SEM image in Fig. 2, *e*.

To interpret the ellipsometric data for an array of SiNW with AgNPs, the same model was used as for SiNWs, but with the addition of an AgNPs layer that was deposited on the surface of the NWs (Fig. 3, *b*). According to this model, the AgNPs layer fills a certain volume $f_{Ag}$, which somewhat reduces the $f_{voids}$, while the $f_{Si}$ should remain unchanged. As a result of fitting these parameters in Fig. 3, *c*, the convergence of the experimental and calculated spectra for the O1 sample with AgNPs $\psi(\lambda)$ and $\Delta(\lambda)$ (red), respectively, was obtained. It was found that $f_{Ag}$ = 0.03 for the 1st sublayer, $f_{Ag}$ = 0.04 – 0.02 for layers 2–4, and $f_{Ag}$ = 0.12 for the 5th sublayer. A similar approach in interpreting the ellipsometry data was used for another sample (O2) with a SiNWs height approximately 2 times higher than that of the previous sample. Fig. 3, *c* show the measured spectra of the ellipsometric angles $\psi_{exp}$ and $\Delta_{exp}$, as well as the calculated spectra $\psi_{calc}$ and $\Delta_{calc}$ before (gray) and after (red) the deposition of AgNPs. The total height of each layer in the original SiNWs structure was estimated as $h_{SiNWs}$ = 471 nm. This value is close to the value obtained from the cross-section SEM image of this sample from Fig. 2, *g* with the $h_{SiNWs}$ = 469 nm. As in the previous example, a $f_{Ag}$ is added to each wall of the SiNWs in the B-EMA model, assuming some Ag in the sublayers, including the upper and lower sublayers. Fitting the calculated ellipsometric angles ($\psi_{calc}$ and $\Delta_{calc}$) for this model, the convergence to the experiment was obtained. It was found that $f_{Ag}$ = 0.3 for the 1st sublayer, $f_{Ag}$ = 0.08–0.02 for sublayers 2–4 and $f_{Ag}$ = 0.22 for the 5th sublayer.

On the example of two SiNWs samples, after the deposition of AgNPs on them, a shift of the experimental spectra $\psi(\lambda)$ to the long wavelength region is observed (Fig. 3, *c*), which can be considered a qualitative confirmation of the appearance of an additional component in the structure. And the interpretation of this effect using a multilayer model and of the B-EMA makes it possible to obtain optical data indicating the presence of AgNPs in the Ag/SiNWs composite structure. SEM and non-destructive ellipsometry are complementary techniques for studying arrays of complex high-aspect composite structures.

To numerically calculate the enhanced factor (EF) from the structures under study, we used the model representing a Si substrate on which a cylindrical SiNWs with spheroid AgNPs on its surface were located. A periodic boundary conditions were set on the side faces of the model. The light source is located on the top face of the model. Under the substrate there is a perfectly matched layer that absorbs the radiation falling into it, which makes it possible to reduce the thickness of the simulated substrate. Geometrical parameters (the length of the NW: 250 nm; its diameter: 50 nm; the diameter of the AgNPs: 12 nm and distance between them of 20 nm) were estimated from the SEM image of the experimental sample. As a result, the maximum values of EF = $2\cdot10^6$ at $\lambda$ = 366 nm and $4.9\cdot10^{10}$ at $\lambda$ = 780 nm were obtained for the structure.

## Conclusion

SiNWs samples with heights of 234 and 469 nm were obtained by two-stage MACE method. AgNPs were deposited in the high-aspect SiNWs structure by ALD method with the Ag(fod)($PEt_3$) precursor.

The fabricated SiNW array and AgNPs layers were studied before and after the preparation of the Ag/SiNWs composite structure using spectroscopic ellipsometry and SEM. From the measured ellipsometric characteristics, the structure of SiNWs was determined using a multilayer model and the B-EMA. The height of the SiNW arrays was determined using spectroscopic ellipsometry, which is in good agreement with the cross-sectional SEM images.

The use of a non-destructive ellipsometric technique made it possible to study the optical characteristics of the Ag/SiNWs structure, as well as their morphological features, which ensured the obtaining of setted thickness and properties of AgNPs when implementing precision ALD technology. The parameters of the experimentally obtained samples were used for further modeling. The expected localization of the electric field on the surface and near the AgNP as a result of the excitation of LPR is observed, and the calculated EF reaches $10^{10}$.

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