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The formation of SiNWs depending on the topology of the metal-catalyst film in the process of metal-assisted chemical etching of c-Si

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Abstract. The method of metal-assisted chemical etching for obtaining silicon nanowires, which consists of two stages, was studied. The conditions and modes for producing layers at both stages of the implemented technology are established, which include (1) chemical deposition of an array of self-organizing Ag nanoparticles on a Si substrate as a catalyst mask and (2) chemical etching of SiNWs to various depths from 110 to 1200 nm. The optical properties and morphology of a metal-catalyst (Ag) film were studied depending on the deposition time and solution concentration. Spectral ellipsometry was used to characterize the samples at all stages of MACE. Using the measured ellipsometric angles, the dielectric functions were determined, as well as the thicknesses and parameters of the fractions of composite layers in a multilayer model by approximating the effective Maxwell Garnett and Bruggeman medium for two-component layers. Samples with Ag nanoparticles with different morphologies were studied using reflection spectrophotometry in the wavelength range from 200 to 600 nm. The results showed that composite Ag-Si structures are promising for obtaining plasmon effects in both the visible and IR spectral regions.

1. Introduction

Silicon is the most popular and widely used semiconductor material due to the intensive development of nanotechnology, which makes a great contribution to electronics (memory chips, buffer layers during epitaxy, thick dielectric layers) [1], optoelectronics [2], photonics (photonic crystals and optical fibers), sensorics [3] and energy (anodes in lithium-ion batteries [4] and solar panels [5]). In recent decades, studies of the unique properties of Si have become relevant, but already in the form of functional objects of small sizes (nanostructures), which have shown the promise of this area of science and technology, as well as the need to develop nanotechnologies for their production.

There are different types of Si nanostructures synthesis. One of the most promising materials is silicon nanowires SiNWs. SiNWs are Si nanostructures of various morphologies with a length of 10 nm and a cross section of 5 to 200 nm, depending on the conditions of their manufacture. There are several methods for obtaining SiNWs: electrochemical, anisotropic etching, laser ablation, vapor – liquid – crystal mechanism and others. The disadvantages of these methods and mechanisms are either the high temperatures of the synthesis of SiNWs or quite long reactions for the synthesis of the resulting structures due to the limited growth mechanisms.

Nowadays metal-assisted chemical etching (MACE) is a counterpart in obtaining of SiNWs, which has gained particular popularity due to its low cost, the absence of the need to purchase expensive



equipment and its applicability to semiconductors with a wide range of characteristics (type of conductivity, degree of doping, orientation). MACE technology is a selective etching of Si using a metal as a catalyst, which allows obtaining single-crystal nanostructures in the form of an array of NWs or structures with a given topology using masks. The development of the 2-step MACE method, compared to the single-stage process, is more promising, due to the ability to control the morphology of SiNWs using a predetermined morphology of Ag nanoparticles (catalyst mask). However, the principle of this etching is poorly understood, there is no clear idea of the etching mechanism, the dependence of the morphology of the resulting structures on the catalyst, the temperature regime, the type of conductivity and crystallographic orientation of the initial silicon wafer and the role of the oxidizing agent in the etching process. Monitoring and managing the process of obtaining SiNWs is important for application use.

Studies of Si nanostructures optical properties are relevant, as they contribute to the development of scientific foundations of nanotechnology and to the fundamental research of nanostructures optics.

2. Experiment

In this work we used wafers of single-crystal silicon p-Si (100) with resistivity of $0.5 \Omega \cdot \text{cm}$ and Si oxide layer thickness of 1 nm. Substrates were washed away from organic matter and natural oxide. After washing, the surfaces of the samples were visually checked for the absence of stains from water droplets. If there are stains, then we need to wash it again. Further, for the immersion deposition of Ag nanoparticles (NPs) on Si, we used a solution of 0.02 M AgNO_3 + 5 M HF in a ratio of 1:1 to 1:10 with a step = 1 in the course of 30 seconds. A new solution was made for each sample. After that the samples were washed in deionized water and dried. Further, for the solution in the ratio 1:1, the influence of the catalyst deposition time (15, 30, 45 and 60 seconds) was investigated. The second stage of the MACE consisted of etching the obtained samples in a solution of 5 M HF + 0.3 M H_2O_2 in a ratio of 10:1 for 60 seconds to obtain a submicron Si nanostructures. The final step is the removal of silver nanoparticles (boiling in nitric acid for 5 minutes).

All samples were studied using a scanning electron microscope (SEM) (JSM 7001F, Jeol, Japan) and multi-angle spectral ellipsometry (Spectroscan, Russia) with a spectral range of $\lambda = 250 - 900$ nm, which corresponds to the photon energy $E = 1.4 - 5.0$ eV and the angle of incidence is $\varphi = 70^\circ$ relative to the normal to the surface from an external medium (air). The basic ellipsometry equation (1), which relates the complex values of the reflection coefficients in amplitude R_p and R_s for p- and s-polarized light and the ellipsometric parameters ψ ($\Psi = \arctg(\frac{R_p}{R_s})$) and Δ ($\Delta = \delta_p - \delta_s$) (phase shift) [6]:

$$\rho = \frac{R_p}{R_s} = \tg(\psi)e^{i\Delta} \quad (1)$$

In the present work, we used an approach in which the permittivity ε [7] of the studied system is determined, including the combined properties of the Ag layer and the properties of the substrate, which is found from the equation (2):

$$\varepsilon = \varepsilon_1 + i\varepsilon_2 = \sin^2(\varphi) \left[1 + \frac{(1-\rho)^2}{(1+\rho)^2} \right] \tg^2(\varphi) \quad (2)$$

3. The formation of SiNWs depending on the topology of Ag film

Silicon nanostructures were obtained depending on the concentration of the silver deposition solution (Figure 1) and the deposition time of Ag on Si wafer (Figure 2).

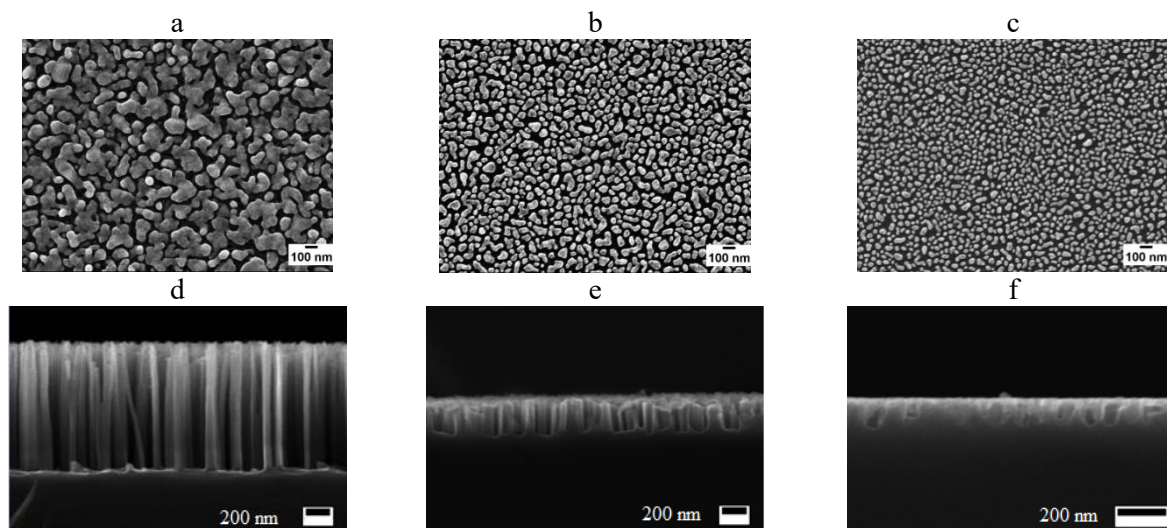


Figure 1. (top view a, b, c) SEM images of Ag NPs on the surface of a c-Si substrate with different concentration of AgNO_3 (1:1, 1:5, 1:10) produced in the 1st stage of MACE and (cross-section d, e, f) Si structures produced in the 2nd stage.

It can be seen that with an increase in the silver nitrate concentration, an increase in size of Ag particles occurs from small spherical $d_{\text{Ag}}=14$ nm (thickness of Ag layer) to multi-tiered structures $d_{\text{Ag}}=48$ nm. As well as an increase in the thicknesses of Si structures from 100 nm pores to 1200 nm SiNWs.

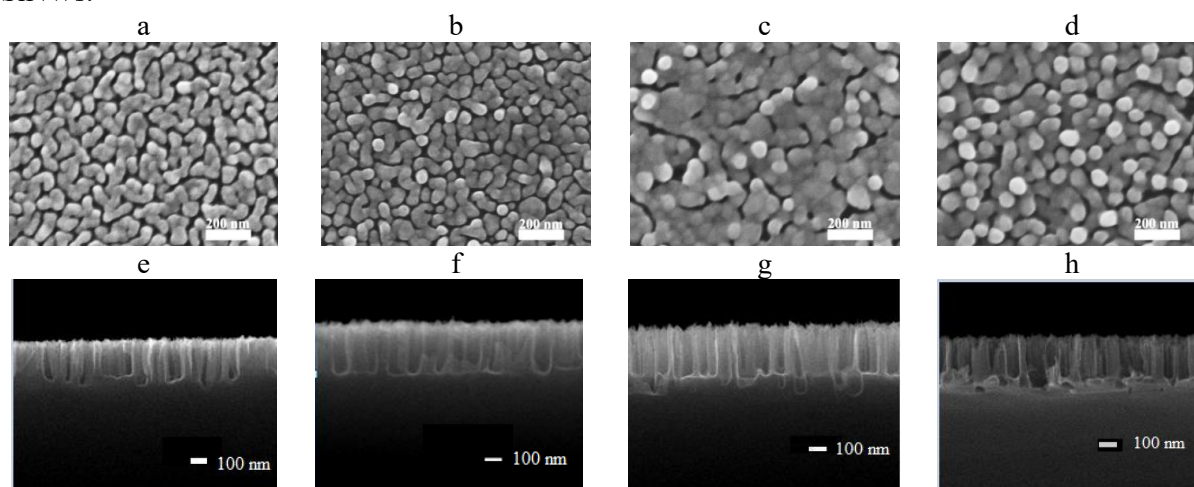


Figure 2. (top view a, b, c, d) SEM images of Ag NPs on the surface of a c-Si substrate with different deposition time (15, 30, 45 and 60 sec) and (cross-section e, f, g, h) SiNWs morphology produced in the 2nd stage.

With an increase in the deposition time, the islet silver film transforms into a multi-tiered developed structure. The dependence of the growth rate of the SiNWs obtained in the MACE process as a function of the catalyst deposition time is nonlinear due to the gradual dissolution of Si in structures with a large amount of Ag. This conclusion is led by the fact that a multilayer catalyst structure is formed on the surface of Si in large quantities with an increase in the deposition time. Highly porous peaks of nanowire structures are formed during the 2nd stage of MACE, in some cases, the upper Si layer is completely etched, which leads to a nonlinear dependence of the etching rate on the amount of catalyst.

4. Investigation of the optical properties of Ag nanoparticles layers

Ellipsometric spectra (Figure 3) for the samples from Figure 1 are presented, which show the difference between them, that explained by different sample morphology.

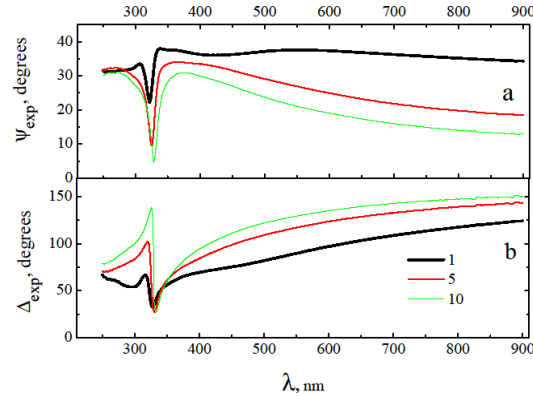


Figure 3. Dependences of the ellipsometric angles ψ_{exp} (a) and Δ_{exp} (b) for samples of Ag NPs layers with different concentration of AgNO₃ (1:1, 1:5, 1:10). Angle of incidence $\varphi = 70^\circ$.

Further, the spectra ψ_{exp} and Δ_{exp} were converted using (2) into the spectra of permittivity ϵ_1 and ϵ_2 , which are shown in Figure 4. The obtained ϵ_1 and ϵ_2 differ from the bulk Ag [8] and both functions have characteristic peaks for $E = 3.8 - 3.9$ eV near the edge of the band of interband transitions.

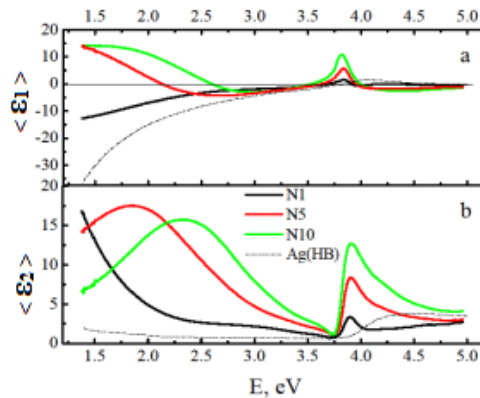


Figure 4. The dependences of the permittivity ϵ_1 (a) and ϵ_2 (b) for samples of Ag NPs layers with different concentration of AgNO₃ (1:1, 1:5 and 1:10) calculated from the experiment from Figure 3. Dash-dotted line for ϵ bulk Ag from the reference [8].

The imaginary part of the permittivity ϵ_2 depends on the morphology of the sample in the visible and near IR ranges, but the position of the peak with an energy of $E = 3.8$ eV does not depend on the morphology, thickness of Ag nanoparticles layers, and, as was studied in [9], on the angle of incidence of light. Therefore, surface plasmon resonance is observed at $E = 3.8$ eV.

According to Figure 1, these layers are composite, consisting of two components: Ag and air. The effective permittivity (ϵ_{eff}) is usually used to describe their optical properties. Spectra and a 3-layer model of an islet silver film on a Si substrate are presented as part of the approximation of the effective Bruggeman medium ($\frac{1}{3} < f_{\text{Ag}} < \frac{2}{3}$) and Maxwell Garnett ($f_{\text{air}} < \frac{1}{3}$) to find the thickness (d) and filling factor (f) of Ag in each layer (Figure 5). This model was obtained with a help of software «Spectr». In our case, the best convergence in the visible and long-wavelength regions of the spectrum was revealed using a 3-layer model, according to which we search for 6 unknown parameters of Ag (3

thicknesses and 3 filling factors). Then, the calculated ellipsometric angles were fitted with experimental values by varying these parameters.

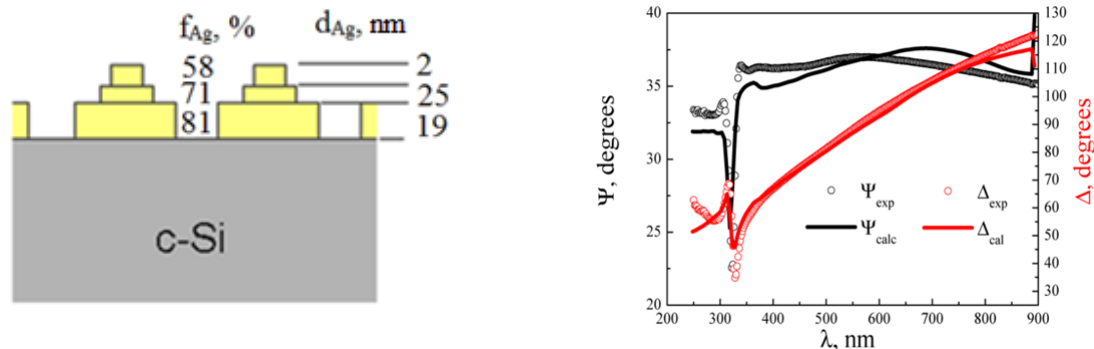


Figure 5. 3-layer model in the framework of the effective media approximation (EMA) for an Ag film. Fitting calculated to experimental ψ and Δ at $\varphi = 70^\circ$ in the framework of the 3-layer model using EMA.

For the lower layer, the Maxwell Garnett model was used, since there is $f_{air} \approx 30\%$, the remaining two layers were approximated using the effective Bruggeman medium. When the best convergence is achieved, we can say that the total thickness of the silver layer is 46 ± 5 nm, which is consistent with the thickness obtained from SEM images.

4.1 Analysis of experimental reflection spectra of «Ag – air» layers

The same samples with arrays of Ag nanoparticles from Figure 1 were investigated using reflection spectrophotometry in the wavelength range from 200 to 600 nm for an angle of inclination of light close to normal ($\sim 9^\circ$) (Figure 6). The calculated spectrum for a 50-nm-thick continuous Ag layer for comparison with the experimental spectrum of an N1 (1:1) 48-nm-thick layer (according to SEM data) is additionally presented, as well as an experimental total reflection spectrum (TR) recorded using a spectrophotometer with an integrating sphere. The measured reflection spectra of sample N1 without and with a sphere show a characteristic dip ($\lambda = 317$ nm) corresponding to the position of the interband transition boundary in the Ag structure, which is detected by both methods in the UV region (~ 320 nm). The effects that occur at the surface boundaries of metal nanoparticles with the external medium are summed into the reflected beam in different directions and collected by the sphere, fixing the amplified plasmon resonance. So, for specimen N1 for mirror reflection, a wide dip is observed from $\lambda = 340$ to 600 nm with a minimum at $\lambda = 380$ nm, also when the total reflection is measured, a wider dip is observed with a minimum at $\lambda = 450$ nm with lower values of calculated spectrum. The spectral position of these minimum is characteristic of plasmon resonances of Ag nanoparticles.

As can be seen from Figure 6, there is weak agreement between the calculated spectrum (50 nm) and N1 (48 nm) with deposition concentration 1:1, because calculation curve was calculated for a continuous silver film and N1 curve was obtained for an island silver film.

It should be noted that the manifestations of bulk plasmon observed in the calculations and experimentally using ellipsometry at inclined angles of incidence were not found in the presented spectra of reflective spectrophotometry, which is explained by the absence of a longitudinal mode in the layers under normal incidence of light on the sample.

In this work, a certain emphasis is placed on the fact that resonances in Ag layers in the UV region can spectrally overlap with interband transitions and this often complicates the interpretation of the results obtained by spectrophotometry. As can be seen in Figure 4, the ϵ_2 spectra for three samples determined by spectral ellipsometry are well differ between each other, both in position and in shape. This is due to two parameters are experimentally determined using spectral ellipsometry, from which we can definitely obtain the values of two permittivity's parameters ϵ (real and imaginary parts). The

conditions of the inclined angles of incidence of radiation on the sample lead to a good separation of optical effects in the spectrum.

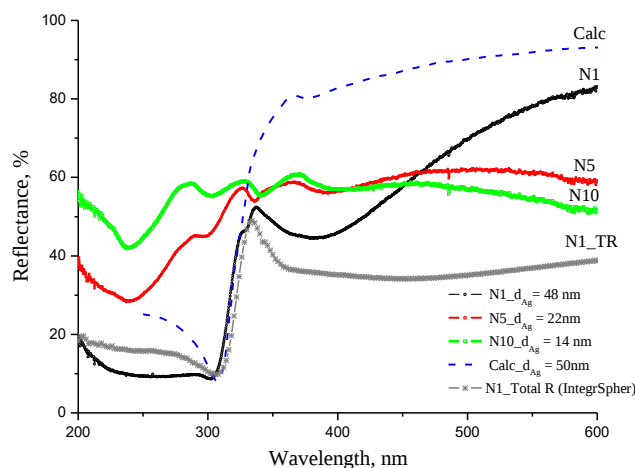


Figure 6. Mirror and total reflection (TR) spectra for layers of Ag NPs obtained by chemical deposition on the c-Si surface (N in the graphs) and calculated spectrum (Calc) for a continuous Ag layer with a 50-nm-thick on the c-Si surface; angle of incidence 9° .

5. Conclusion

A two-step process of MACE of Si was investigated. Vertical threadlike nanostructures obtained by MACE on the surface of single-crystal Si are the basis for the creation of composite nanostructures by the deposition of Ag nanoparticles with plasmon effects in them.

To calculate and interpret the experiment for Ag nanolayers on a c-Si substrate, we used a model in which permittivity ε_1 and ε_2 (real and imaginary parts) are determined. In the calculated spectra ε_2 for the thicknesses of Ag layers from 5 to 60 nm, a peak of surface plasmon resonance is founded at 3.8 eV (Figure 4).

As can be seen from the obtained results, the MACE method is highly sensitive to changes in external conditions. Having fulfilled all the conditions that affect the formation of Si nanostructures will allow us to control the properties of the SiNWs at the initial stages of the MACE process.

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