Silicon nanowires and their characterization in the process of metal-assisted chemical etching of c-Si using spectroscopic ellipsometry

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Abstract. In this work, the preparation of c-Si nanowires was investigated using a two-stage metal-assisted chemical etching process. For characterization of structures at all stages of the process, spectroscopic ellipsometry was used and two approaches were used: a) determining and analysing the complex pseudo-dielectric function $\varepsilon$ and b) determining parameters of simulated multilayer structures using the effective medium approximation. Taking into account the structure parameters measured from SEM images the spectra of $\psi$ and $\Delta$ were calculated and fitted to the experimental ones to obtain best convergence. The study of metal-assisted chemical etching process the Si process is intended for the development of silicon technology for obtaining structures of various topology (morphology) with functional components and creating on their basis sensory elements for bio and chemical reagents, taking into account the possibility of integration with micro and nanodevices on the chip.

1. Introduction

Single-crystal silicon (c-Si) is one of the main materials used in manufacture of photovoltaic converters and other electronic devices [1]. The utilization of the semiconductor and optical properties of silicon is extended in the development of silicon-based nanostructures. At present, nanostructured silicon is an important and highly promising material for development of the silicon industry, especially in such of its fields as nanoelectronics [2], optoelectronics [3], bio- and chemical sensors [4], energy-conversion devices (solar cells [5] and lithium-ion batteries [6]), and biomedicine [7].

During the last decade, a method has been developed in which highly advanced c-Si structures are produced in the form of nanowires or columns (SiNWs) with thicknesses of several nanometers to tens of micrometers and as porous-silicon layers. This method has been named metal-assisted chemical etching (MACE) [8]. The interest in this technique has increased recently because no special expensive equipment is required for its application. The method is based on the etching of silicon in the vicinity of metal particles (catalysts), which are, in turn, deposited on the surface of a silicon wafer. The morphology of silicon nanostructures produced in this way depends on the etching conditions: etching solution composition, temperature, etching time, and Si properties (conductivity type, crystallography, doping level).

There exist two main varieties of the MACE process, which include one (1-step MACE) or two (2-step MACE) stages. In the first case, the catalyst metal is dissolved in hydrofluoric acid, and the metal deposition and silicon etching occur in the same chemical solution. In the 2-step MACE process, metal
nanoparticles or films are deposited onto the surface of silicon before its being etched in HF. Noble metals serve as catalyst-metals, silver being used for this purpose the most frequently.

To understand how the deposited catalyst-metal and the conditions of the subsequent etching enable the purposeful formation of SiNW layers with prescribed structural and optical properties, it is advisable to use a non-contact and non-destructive techniques in all stages of SiNW fabrication. Optical measurements by spectrophotometry, Raman spectroscopy, photoluminescence method, and other conventional optical techniques used to study nanolayers proved to be of little utility for SiNW layers with height smaller than 1 μm [9]. For these layers, it is advisable to use the spectroscopic ellipsometry (SE), which is a highly sensitive and informative noncontact and nondestructive technique and is widely used for characterization of nanosize structures [10]. Quite recently SE has been employed to examine SiNW layers formed by 1-step [11] and 2-step [12] MACE processes.

The results of a study of SiNW layers in the earliest stages of formation of SiNW layers with thickness $d_{\text{SiNW}}$ of ~ 47 and 111 nm were reported in [12]. In this process, the first step is important because the morphology of Ag nanoparticles deposited on the surface of c-Si serves as a mask for the SiNW layer to be formed in the second step. Thus, having obtained a certain coating area in the first step, we can prognosticate and control the morphology of the SiNW layer being formed.

In the present study, we further examined SiNW layers produced by the 2-step MACE and also performed modeling and calculations for layers of Ag nanoparticles. Two approaches were used to interpret the results of ellipsometric measurements: (1) determining the pseudodielectric functions and (2) calculating and fitting to experimental data the parameters of a multilayer model in the effective-medium approximation. In the second approach, microscopic specific features of the structures under study were determined: dielectric functions, layer thicknesses, and component fractions. It was shown that the array of nanoparticles (catalyst-mask) and MACE conditions affect the morphology and the optical properties of the nanostructures obtained.

2. Experiment

We used p-Si (100) silicon wafers with resistivity of 0.5 $\Omega$·cm and Si oxide layer thickness of 1 nm. Prior to deposition of the catalyst, the wafers were subjected to the standard cleaning. The role of a catalyst was played by silver nanoparticles deposited from (1:1) 0.02 M AgNO$_3$ + 5 M HF solutions in the course of 5 min. The next stage consisted in etching in a (10:1) 5 M HF + H$_2$O$_2$ solution for $t = 10$ s to obtain a structure of silicon nanowires with heights of several tens of nanometers, after this stage particles of Ag were dissolved in HNO$_3$ solution in the course of 5 min [12].

Ellipsometric measurements were performed with a Spectroscan spectroscopic ellipsometer [13] at wavelengths in the range $\lambda = 250$-900 nm (photon energy $E = 1.4$ - 5.0 eV) and light incidence angle $\varphi = 70^\circ$ relative to the normal to the surface, from an external medium (air).

The ellipsometric angles $\psi$ and $\Delta$ were determined, where $\tan\psi = |r_p|/|r_s|$ ($r_p$, $r_s$ are the complex Fresnel reflectances), and $\Delta = \delta_p - \delta_s$ is the relative change in phase, experienced in reflection between the p- and s-components (the subscripts p and s correspond to the oscillation components of the electric vector of the light wave, parallel and perpendicular to the plane of light incidence, respectively). The $r_p/r_s$ ratio is described by the basic equation of ellipsometry [14] as

$$\rho = r_p/r_s = \tan\psi e^{i\Delta} \quad (1)$$

The morphology of the layers was examined by scanning electron microscopy (SEM) on microscope JSM 7001F (Jeol, Japan).

3. Study of nanostructures by spectroellipsometric and electron-microscopic methods

3.1. Effect of Ag nanoparticle morphology on how silicon nanostructures are formed

The samples were treated with an AgNO$_3$ + HF solution at its different concentrations (first step of the 2-step MACE), with a discontinuous structure of single or interconnected silver particles formed on the
silicon surface (Fig. 1a). These particles have a certain scatter in shape and, accordingly, in size (30 to 100 nm), but have approximately the same heights (30 - 60 nm), as estimated from SEM images (Fig. 1a). The distances between the silver particles make it possible to estimate the width of the subsequently formed silicon structures and their size scatter. Thus, the spaces between the silver particles are tops of the subsequently formed vertical wire structures. An analysis of the images of the interparticle spaces in Fig. 1a demonstrated that their average sizes were within the range 100 - 200 nm. The etching through the mask of silver nanoparticles yielded structure of silicon nanowires (Fig. 1b).

![Figure 1](image1.png)

**Figure 1.** SEM images of arrays of self-organized Ag nanoparticles on the surface of a c-Si substrate (a), produced in the 1st step of MACE via precipitation from an AgNO₃ solution with morphology intended for obtaining silicon nanowires and obtained silicon nanowires (b).

In all stages, the spectroscopic ellipsometry was used to find $\psi_{\text{exp}}$ and $\Delta_{\text{exp}}$. Because silver particles cover the silicon surface in a discontinuous manner and the height of the particles is small, it can be assumed that the incident light must penetrate as far as the substrate and, being reflected, can carry a response from the substrate, too. This optical response is transformed below for the example of a complex pseudodielectric function. We used the model of light interaction with a semi-infinite medium and calculated for this medium the complex pseudodielectric functions by using the experimentally measured $\psi_{\text{exp}}$ and $\Delta_{\text{exp}}$:

$$
\varepsilon = \varepsilon_1 + i\varepsilon_2 = \sin^2(\phi)\{1+[(1-\rho)^2/(1+\rho)^2]\tan^2(\phi)\} $$

(2),

where $\varepsilon_1$ is the real part of $\varepsilon$, and $\varepsilon_2$, its imaginary part, with $\rho$ defined above in (1).

### 3.2. Study of how a layer of silicon nanowires is formed in the MACE process

The MACE process occurs under Ag particles, which gradually submerge and are situated by the end of the process at the bottom of channels. This is confirmed by the example of the sample in Fig. 2 in which these particles are well seen to be situated at the bottom of the layer of nanowires.

![Figure 2](image2.png)

**Figure 2.** Cross-sectional SEM image of silicon wafer with a wire-like Si layer fabricated by MACE, with Ag nanoparticles at its bottom. $d = 375 \pm 15$ nm
For silicon structures of this kind (SiNWs), we used the above-describe approach in which the complex pseudodielectric function is determined. For example, we found by using expression (2) the functions $\varepsilon_1$ and $\varepsilon_2$, presented in Fig. 3, and also those on performing the MACE process in each of the steps.

![Figure 3](image_url)

Figure 3. Transformation of the real $\varepsilon_1$ (a) and imaginary part $\varepsilon_2$ (b) of the pseudodielectric function for the layer of nanowires (SiNWs), $\varphi = 70^\circ$.

A sharp change in both $\varepsilon$ is observed after the etching, with a layer formed with voids and nanoparticles within the channels.

After we used the second approach with a multilayer model and Bruggeman's multicomponent-medium approximation [14] for samples in each step of the MACE process. In the first step (deposition of a layer of Ag nanoparticles), the three-layer model was used to find the thickness of Ag fraction in each layer. In terms of this model, we calculated the spectra of $\psi_{\text{calc}}$ and $\Delta_{\text{calc}}$ by Fresnel formulas, transfer matrices, and Bruggeman's effective-medium approximation, and then the calculated spectra of $\psi_{\text{calc}}$ and $\Delta_{\text{calc}}$ were fit to those obtained experimentally, $\psi_{\text{exp}}$ and $\Delta_{\text{exp}}$ (Fig. 4).

![Figure 4](image_url)

Fig. 4. Result of fitting of spectra of deposited layer of Ag nanoparticles on silicon wafer obtained by fitting in terms of the three-layer model (fig. 5a) of $\psi_{\text{calc}}$ and $\Delta_{\text{calc}}$ spectra to those obtained experimentally, $\psi_{\text{exp}}$ and $\Delta_{\text{exp}}$. 
Figure 4 (step 1) shows the result of fitting for Ag nanoparticle parameters: total thickness of Ag layer was $d_{Ag} = 46 \pm 5$ nm.

Fig. 5. Schematic representation of layers produced after each step of SiNW formation and model parameters obtained by fitting the calculated $\psi_{calc}$ and $\Delta_{calc}$ to the experimental $\psi_{exp}$ and $\Delta_{exp}$; chemical deposition of Ag nanoparticles (step 1), etching of SiNW layers with Ag nanoparticles, layer of SiNW after the removal of Ag from the layer (step 2); here, $d_{SiNWs} = 345 \pm 15$ nm.

Modeling in SE, as a rule, begins with the selection of the simplest models with the minimum number of unknown parameters, then the procedure for fitting the calculated ellipsometric angles with experimental values by varying these parameters occurs. In our case, we started with a 1-layer model: we looked for 2 unknown parameters (thickness and fraction of voids) and got poor convergence. The use of the 2-layer model (4 parameters) did not improve the convergence, and with the 3-layer model (6 unknown parameters), good convergence of the spectra in the visible and long-wavelength regions of the spectrum appeared, as can be seen from, but with interference fluctuations in the UV region which were not smoothed during the fit.

Figure 6 presents the results of fitting of the spectra of $\psi_{exp}$ and $\Delta_{exp}$, calculated in terms of the three-layer model (fig. 5c) with Bruggeman’s effective-medium approximation. The fraction parameters $f_{Si}$ and $d$ for each of the three layers are presented in the fig. 5c. A part of the fitting spectrum is cut off because interference spectra start to be manifested below 550 nm, whereas the spectra of $\psi_{exp}$ and $\Delta_{exp}$ have no features of this kind. This is due to the imperfection of the model because the thicknesses of each of the three layers, used in the three-layer model, are rather large and give interference maxima and minima. However, the convergence of the spectra is good in a sufficiently wide range of wavelengths, $\lambda = 550 - 900$ nm. The same features in fitting of ellipsometric spectra were noted in [11] where the authors used only the long-wavelength part of the calculated spectra, with the UV spectral range cut off.
Fig. 6. Calculated $\psi_{\text{calc}}$ and $\Delta_{\text{calc}}$ spectra obtained by fitting to $\psi_{\text{exp}}$ and $\Delta_{\text{exp}}$.

The study furnished an understanding of how parameters of the catalyst-mask should be chosen and what technology is to be used to subsequently obtain silicon structures in the form of porous silicon or an array of nanowires (columns). The spectroscopic ellipsometry is a nondestructive and informative procedure for obtaining samples with required parameters.

4. Conclusion

A two-step process of metal-catalytic etching of silicon was investigated, which resulted in the formation of vertical nanostructures in the form of filaments from a substrate (monocrystalline silicon). It is shown that the parameters of inhomogeneous layers can be controlled ellipsometrically (thickness, porosity, dielectric constants, their distribution over the layer). This contributes to the selection of optimal conditions in the MACE process. 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 Si nanowires using a predetermined morphology of Ag nanoparticles (catalyst mask).

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