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# ELLIPSOMETRY OF POROUS $n$-Si:(Ni, Co) STRUCTURES

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The composite samples of porous $n$-Si, which have been prepared by anodic etching and embedded with Ni and Co nanostructures by electroless process, were investigated by null-ellipsometry technique. The ellipsometric data were analysed in the multilayer model and the composition of porous layer on the substrate surface was determined. The null-ellipsometry technique was shown to be an efficient tool for nondestructive testing and characterization of porous $n$-Si samples with embedded transition metal structures.

**Keywords:** porous $n$-Si, transition metal nanoparticles, null-ellipsometry

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## 1. Introduction

Porous semiconductors are interesting objects for materials science and promising components in nanotechnology [1]. Much attention has been given to porous silicon (por-Si) since the photoluminescence has been observed at room temperature [2]. In addition, a great interest in por-Si systems stems from other novel physical properties and possible applications in optical, electronic, and magnetic devices [3]. A large number of optical sensors based on por-Si technology were developed for detection of vapours, liquids, and biological molecules [4]. The changes in reflectance [5], interference pattern in porous layer [6], and surface plasmon resonance [7] were shown to be sensitive enough for the operation of por-Si as optical sensors.

Hybrid structures composed of por-Si and metals present additional possibilities for physical studies of composites and their applications. Photoluminescence enhancement and stabilization in Fe-passivated por-Si was indicated [8]. Por-Si matrix was used [9] for production of metal nanorods by electroless process. Hybrid materials composed of magnetic nanoparticles in por-Si were fabricated and an enhanced coercive field of hybrid structures with Co [10] and $Fe_3O_4$ [11] was indicated. Ferromagnetic nanostructures incorporated in por-Si were shown [12] to be suitable for magnetic sensor applications. In particular, metal–por-Si nanocomposites [13] are considered as promising materials in the development of magnetophotonic crystals [14].

Although por-Si has been widely studied for two decades, the fabrication and characterization of hybrid structures with well-defined morphology has been the focus of intense scientific interest only in recent years. In the present work the hybrid por-Si:(Ni, Co) structures were fabricated and characterized by optical and structural properties. Por-$n$-Si was produced by anodic etching technique [1]. As a template-based technique for electrosynthesis of nanomaterials [15, 16], an electrochemical deposition was used to form metal structures in the porous layer of $n$-Si substrate. The morphology of hybrid structures was investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The optical response of the samples was characterized by null-ellipsometry technique [17].

## 2. Experiment

The samples of por-Si were fabricated by standard technology of anodic etching [1]. The (100)-oriented $n$-type Si wafers (KEF 0.5) were etched for 15 min. in an electrolyte of composition HF:$C_2H_5OH$ (1:1) at current densities in the range of 10–25 $mA/cm^2$. During etching procedure, the backside of wafer was illuminated by a light of 800 lx intensity from a standard 75 W bulb. The formed por-Si samples possessed a typical structure, which has been described in detail previously [18]. The upper layer, which is responsible for photoluminescence of por-Si and is composed of Si nanocrystals imbedded in oxide matrix, was removed by etch-


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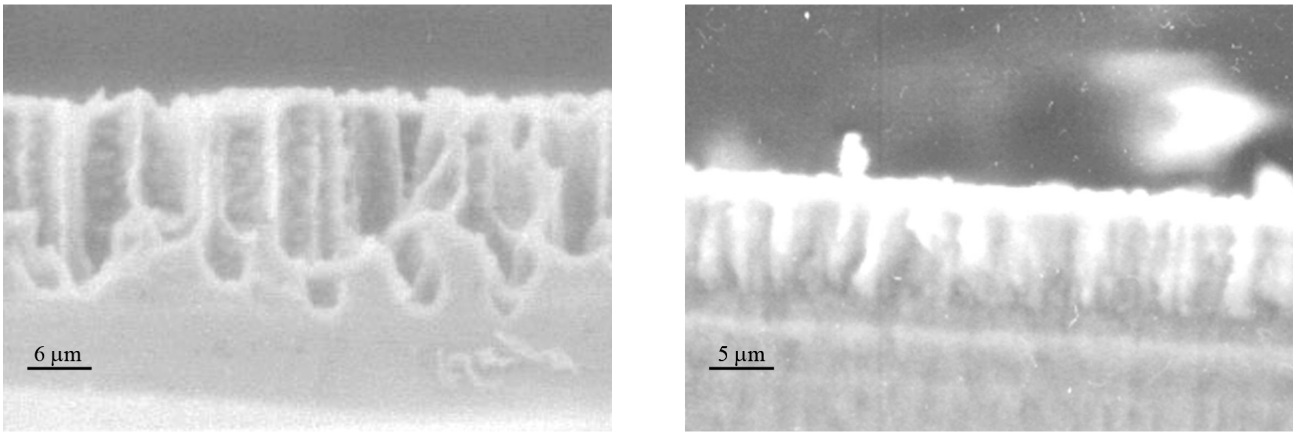



(a) (b)

Fig. 1. SEM micrographs of por-$n$-Si (upper luminescent layer removed), (a) before and (b) after infiltration of Ni.

ing in 1 N KOH solution. After this procedure the substrates with the porous layer on the surface were washed in distilled water and dried in air.

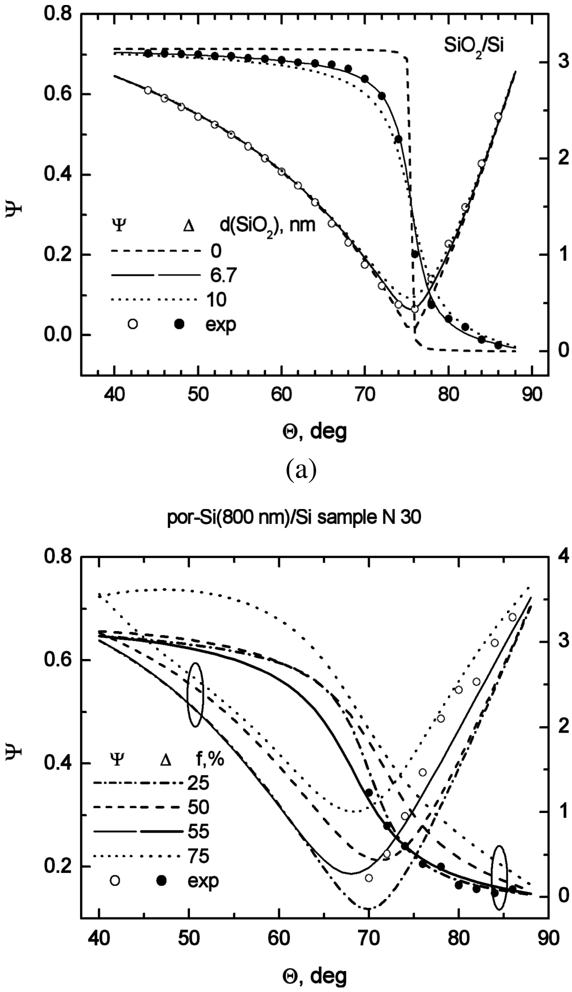
The por-Si structure was infiltrated with Ni and Co by electrochemical technique. Por-Si with infiltrated Ni was formed using electrolyte of composition $NiSO_4{\cdot}7H_2O$ (250 g/l) : $Na_2SO_4$ (100 g/l) : $H_3BO_3$ (10 g/l) : 1 M $C_4H_6O_6$. In this electrolyte, anions are stable therefore Ni-ion complexes are not formed. The electrolyte acidity (pH 4) was controlled by boric acid. Organic component, tartaric acid, improved the metal adhesion on Si surface. During electrochemical process, the current density was equal to 1.5 $\mathrm{mA/cm^2}$ at deposition time which was varied in the range from 2 to 60 s. For Co deposition the electrolyte $CoSO_4{\cdot}7H_2O$ (75 g/l) : $C_6H_{15}NO_3$ (70 ml/l) with pH 2.6 was used at current density 10 $\mathrm{mA/cm^2}$ and deposition time 3–60 s.

The morphology of samples was investigated by means of a scanning electron microscope EM125 operating at 125 kV and AFM Thermomicroscope Explorer. The SEM images for pure por-$n$-Si and that with embedded Ni are presented in Fig. 1.

The ellipsometric studies have been carried out making use of null-ellipsometer LEF-3M operating with He–Ne laser (633 nm). In these measurements the optical response of the sample was characterized in terms of a complex reflection $\rho$ defined as the ratio of complex amplitude reflection (Fresnel) coefficients $R_\mathrm{p}$ and $R_\mathrm{s}$ for light polarized parallel (p) and perpendicular (s) to the plane of light incidence:

$$\rho = \frac{R_\mathrm{p}}{R_\mathrm{s}} = \tan\Psi\,\cos(\mathrm{i}\Delta)\,, \tag{1}$$

where $\Psi$ and $\Delta$ are ellipsometric parameters. The ellipsometric data have been analysed by multilayer model [19]. Analysis of ellipsometric data in por-Si has been described in detail elsewhere [19]. The inverse problem has been solved by model calculations [20] using a transfer matrix technique.




(b)

Fig. 2. Angular dependence of ellipsometric parameters for (a) initial sample of c-Si and (b) for por-$n$-Si with removed surface layer.

## 3. Results and discussion

The morphology of por-$n$-Si depends strongly on the technological procedure [1]. At higher current densities, the pores, which have been formed in the substrate, are randomly distributed with their size varying from 1 to 5 $\mu$m. At lower current densities with backside illumination (Fig. 1(a)), the pores are cylindrically-shaped. According to AFM data, the distance between pores varies in the range of 1–5 $\mu$m and the surface roughness is of the order of 0.5 $\mu$m. The cross-sectional image illustrates the thickness of porous layer which is equal to $\sim$18 $\mu$m for a particular sample shown in Fig. 1(a).

The optical properties of initial and fabricated por-$n$-Si samples were investigated by the optical response measured using null-ellipsometry technique. In Fig. 2 the angular dependence of ellipsometric parameters is presented. The data for starting sample of crystalline $n$-Si (Fig. 2(a)) are well described by a model in which the reference optical data for Si [21] have been used. The presence of natural oxide $SiO_2$ of thickness 6.7 nm on the surface of c-Si wafer was indicated. For comparison and in order to illustrate the sensitivity of the structure analysis using the ellipsometric data, the angular dependence of $\Psi$ and $\Theta$ at various thickness of $SiO_2$ layer is also shown in Fig. 2(a).

The reflectance of por-Si is significantly reduced [19] and increases at larger angles of light incidence (Fig. 2(b)). In the model of multi-layer structure, the $n$th layer is characterized by dielectric function $\varepsilon_n$ and thickness $d_n$. In the case of composite layer consisting of several components, the effective dielectric function $\varepsilon_{\text{eff}}$ can be defined according to Bruggeman model of effective media:

$$\sum_n f_n \frac{\varepsilon_n - \varepsilon_{\text{eff}}}{\varepsilon_n + 2\varepsilon_{\text{eff}}} = 0\,, \qquad (2)$$

where $\sum_n f_n = 1$ and $f_n$ is the volume fraction of $n$th component. In the case of porous layer, Si and pores contribute to the optical response of composite sample according to their volume ratio. Along with experimental data, in Fig. 2(b) the modelled angular dependence of ellipsometric parameters $\Psi$ and $\Delta$ are shown for several values of porosity $f$ defined as the volume fraction of voids. As the pores in the most of fabricated samples of por-$n$-Si were cylindrically-shaped, the approximation of a single porous layer was used for fitting the calculated dependence to experimental one. The sample presented in Fig. 2(b) was characterized by effective layer of thickness 800 nm and porosity equal to 55%.

As follows from the structural investigations, after electrochemical deposition of metal (Fig. 1(b)), the surface of por-$n$-Si was coated by a metal layer and pores were partially filled with metal nanostructures. In order to reveal the particular features of the pores in substrate, the sample of por-$n$-Si was polished to remove the upper metal layer.

The optical response of the finally prepared por-$n$-Si:(Ni, Co) samples of thickness up to 1 $\mu$m was analysed in the three-layer c-Si/por-Si:(Ni, Co)/air model. The results of ellipsometric data analysis for por-$n$-Si with Ni and Co embedded in the substrate pores are presented in Fig. 3. The model calculations fitted to the experimental data are in a reasonable agreement with the mean-squared error (MSE) of order (1–1.5)$\cdot 10^{-2}$. In the case of por-$n$-Si:Ni the data of which is shown in Fig. 3(a), the estimated composition of porous substrate of thickness 300 nm was 0.36, 0.55, 0.09 for Si, voids, and Ni, respectively. For substrate porous layer of thickness 1 $\mu$m in por-$n$-Si:Co (Fig. 3(b)) the corresponding values were 0.22, 0.71, 0.07 for Si, voids, and Co, respectively.

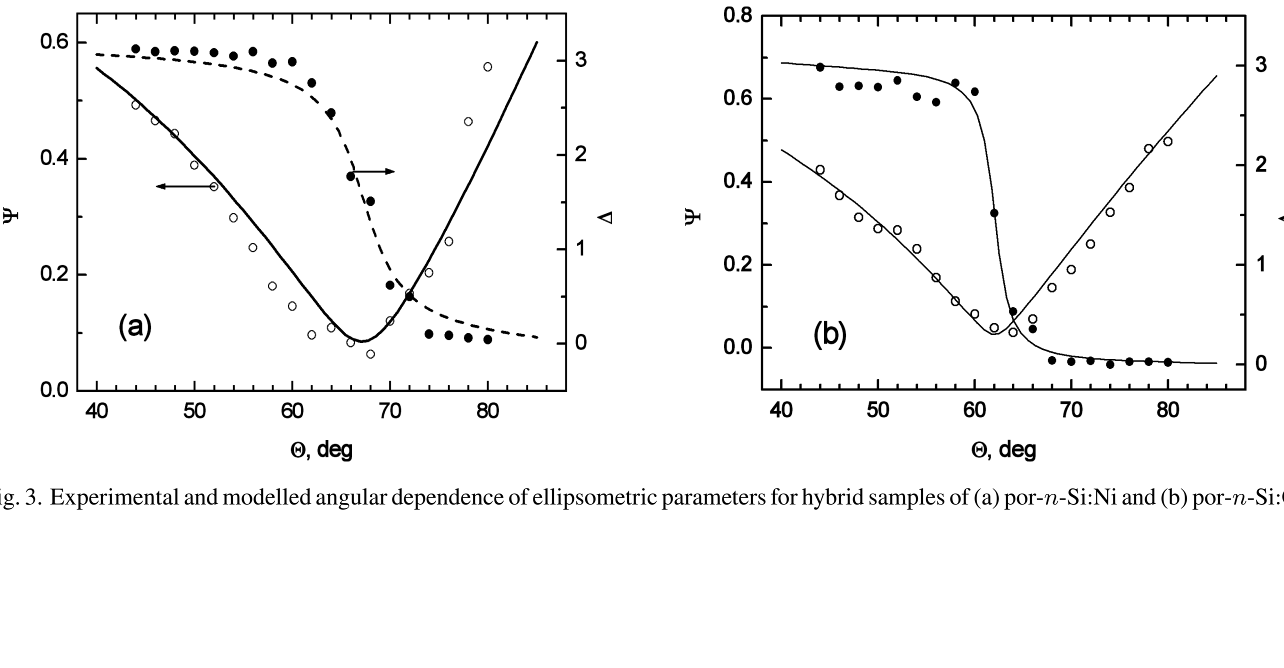



Fig. 3. Experimental and modelled angular dependence of ellipsometric parameters for hybrid samples of (a) por-$n$-Si:Ni and (b) por-$n$-Si:Co.

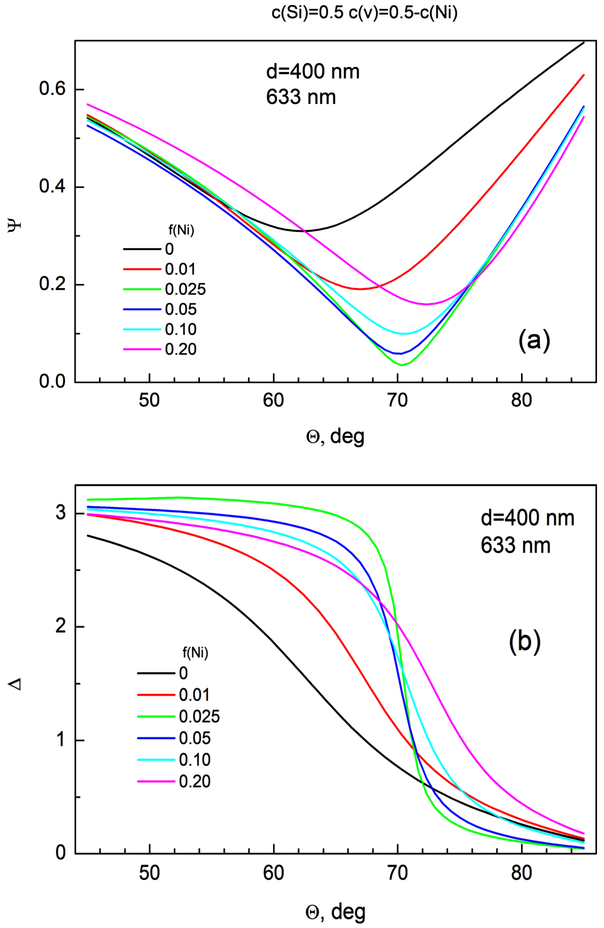



Fig. 4. Model calculations of the angular dependence of ellipsometric parameters (a) $\Psi$ and (b) $\Delta$ at 633 nm for porous layer of thickness 400 nm in por-Si:Ni at a constant volume fraction for Si ($f_{Si} = 0.50$) and various amount of Ni, $f_{Ni} = 0.50 - f_v$, where $f_v$ is the volume fraction for voids.

It should be noted that the thickness of effective layer that has been obtained from analysis of ellipsometric data is smaller than the thickness of porous layer and depends on the accepted structural model discussed below.

The model calculations presented in Fig. 4 illustrate the sensitivity of the ellipsometric method for determination of composition in porous layer. The characteristic changes in the angular dependence were revealed: (i) at small Ni amount ($f_{Ni} < 0.05$) the changes are mainly caused by interference effect; (ii) at higher Ni amount ($f_{Ni} \geq 0.05$), the minimum in the function $\Psi = f(\Theta)$ shifts to the region of higher angles of light incidence. In the angular dependence of the other ellipsometric parameter, $\Delta = f(\Theta)$, the analogous shift to larger $\Theta$ values is observed. Similar regularities were revealed for porous layers of larger thickness. A comparison of modelled and experimental angular dependences of ellipsometric parameters has shown that the composition of porous substrate layer in por-$n$-Si with embedded structures of transition metals is determined with an accuracy of the order of 3–5%.

Several aspects in the studied characterization of por-$n$-Si by null-ellipsometry should be noted. The model calculations have shown that, on the one hand, the MSE is weakly dependent on the assumed thickness of porous layers. On the other hand, the experimental data obtained by null-ellipsometry measurements, which have been carried out at a single wavelength, can be influenced by interference pattern. For this reason, in order to increase the accuracy of determined parameters, it is reasonable to combine the null-ellipsometry studies with spectral ellipsometry and with the results of structural investigations to fix the thickness of porous layer.

The next factor, which is of importance in the analysis of porous structures, is the shape of pores. As noted above, the cylindrical-shaped pores were formed in $n$-Si samples under consideration (Fig. 1). However, depending on the composition of etchant [1], the dendrite-like pores can be also formed in both $n$- and $p$-type Si. In this case, the model of homogeneous porous layer should be replaced by a multi-layer structure [19, 22]. The model calculations have been carried out and cylindrical-shaped pores were replaced by pyramidal model. It was found that this factor results in a small increase of the error which was of order of several percent in por-$n$-Si. In addition, the magnetic nanoparticles, which have been formed in por-Si, can self-organize into fractal dendrite-like structures [23] instead of nanorods [9], which completely fill the pores. This factor can also lead to the deviation from homogeneous cylindrical-shaped model and the composition variation with depth should be taken into account.

Finally, the formation of nanostructures in por-Si with embedded nanoparticles of transition metals can cause the deviation of dielectric function from the values characteristic of bulk materials. This factor is of particular importance and was analysed in [24] for the case of nanostructured materials.

## 4. Summary

The por-$n$-Si layers, which have been formed on the surface of c-Si substrate and embedded with transition metal structures, were investigated by null-ellipsometry technique at 633 nm. It was shown that the optical response of composite structure can be efficiently used for characterization of composite structure. The composition of por-$n$-Si:(Ni, Co) layers of thickness up to

1 $\mu$m was determined with an accuracy of 3–5% by analysis of experimental ellipsometric data in three-layer c-Si/por-Si:(Ni, Co)/air model for cylindrically-shaped pores.

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# PORĖTOJO $n$-Si:(Ni, Co) DARINIŲ ELIPSOMETRIJA

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**Santrauka**

Nul-elipsometrijos metodu ištirti sudėtingosios sandaros porėtieji $n$-Si dariniai, paruošti anodiniu ėsdinimu, su Ni ir Co dalelėmis, įterptomis elektrocheminio proceso būdu. Elipsometriniai duomenys išanalizuoti, pasinaudojant daugiasluoksniu modeliu ir nustatytas porėtojo sluoksnio, suformuoto padėklo paviršiuje, sąstatas. Gauti duomenys parodė, kad nul-elipsometrija yra efektyvus neardantis būdas charakterizuoti porėtojo $n$-Si darinius su įterptomis pereinamųjų metalų dalelėmis.