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Spectroscopic Ellipsometry of Porphyrin Adsorbed in Porous Silicon

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Aqueous solution of meso-tetra(4-sulfonatophenyl)porphine was deposited on electrochemically etched *n*-Si wafers. The morphology of the hybrid systems was investigated by scanning electron microscope and atomic force microscope techniques. The optical response of the hybrid systems was studied by spectroscopic ellipsometry in the range of 1–5 eV. Particular features in adsorption process were revealed for meso-tetra(4-sulfonatophenyl)porphine deposited on variously chemically treated Si substrates. It was found that porphyrin J-aggregates can be intercalated into large pores formed in a bulk *n*-Si as well as into nanopores of luminescent oxide layer.

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1. Introduction

During last decade porphyrins have been extensively studied due to their importance in biological processes and perspectives in various technical applications such as catalysis, photodynamic therapy, biosensors, etc. For example, tetraphenyl porphyrin based thin film transistors were manufactured [1] on thermally oxidized Si substrates. On the other hand, nanostructured porous silicon (por-Si) is a very promising biomaterial, in particular, for a development of devices that are to be linked to the biological systems [2]. From this point of view, the adsorption processes are to be studied making use of non-destructive methods such as ellipsometry. Spectroscopic ellipsometry was shown [3] to be efficient tool to study protein adsorption in por-Si layers.

In this work the system consisting of porphyrin on por-Si layers was studied by means of structural and optical investigations. The regularities of adsorption of porphyrin water solution on the surface of variously chemically treated Si substrates were examined.

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2. Experimental

The aqueous solution of porphyrin of concentration 1×10^{-4} M was prepared by dissolving meso-tetra(4-sulfonatophenyl)porphine (TPPS₄) tetrasodium salt. Adding 0.1 M HCl, the solution of pH=1 was made. In the aqueous medium of this acidity the J-aggregates are formed [4]. The samples were stored at room temperature for 10 days to achieve a stable state with respect to the formation of large J-aggregates.

The (100)-oriented wafers of *n*-Si (0.5 Ω cm) were used as substrates. The wafers were degreased by dimethyl formamide and washed by methanol. Porous layers were produced by electrochemical etching in electrolyte HF:C₂H₅OH (1:1) at 15–35 mA/cm² for 15 min illuminating the back surface of etched sample with 50 W halogen lamp (1200 lx). A droplet (0.1 mL) of porphyrin water solution was put on the sample surface and dried under normal conditions. The morphology of composite structures was investigated by scanning electron microscope (SEM) and atomic force microscope (AFM).

Spectroscopic ellipsometric measurements were carried out by means of the photometric ellipsometer with rotating analyzer operating in the range of 1–5 eV. The measurement results characterize the optical response of the system under investigation in terms of a complex reflection ρ defined as the ratio of complex amplitude reflection coefficients R_p and R_s for light polarized parallel (p) and perpendicular (s) to the plane of incidence:

$$\rho = \frac{R_p}{R_s} = \tan \Psi \exp(i\Delta), \quad (1)$$

where Ψ and Δ are ellipsometric parameters.

The experimental data were interpreted in the approximation of pseudodielectric function $\langle \varepsilon \rangle$, in which the optical response of a complex system (air–film–substrate) is considered as that for isotropic media [5]:

$$\langle \varepsilon \rangle = \sin^2 \theta \left[\left(\frac{1 - \rho}{1 + \rho} \right)^2 \tan^2 \theta + 1 \right], \quad (2)$$

where θ is the angle of light incidence. As a rule, ellipsometric measurements were carried out at $\theta = 70^\circ$.

3. Results and discussion

The results of optical studies are illustrated by Figs. 1 and 2. In the photon energy range under consideration the absorbance spectrum of investigated TPPS₄ aqueous solution (curve 1 in Fig. 1) consisted of three strongest absorption bands located at 1.75, 2.53, and 2.90 eV. The energy and relative intensities of the bands were in good agreement with reference data (see, e.g., [4]). The presence of the first two bands confirmed the formation of J-aggregates [4]. The optical response

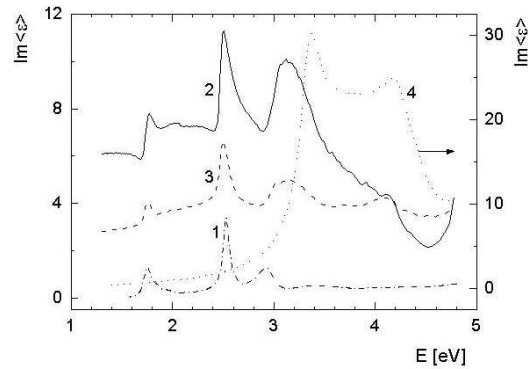


Fig. 1. Optical spectra of TPPS₄ aqueous solution (1), hybrid samples of TPPS₄ on *c*-Si (2), TPPS₄ on por-Si with removed oxide layer (3) and *c*-Si substrate (4). Absorbance of TPPS₄ aqueous solution (1) and imaginary part of pseudodielectric function (2–4) are shown.

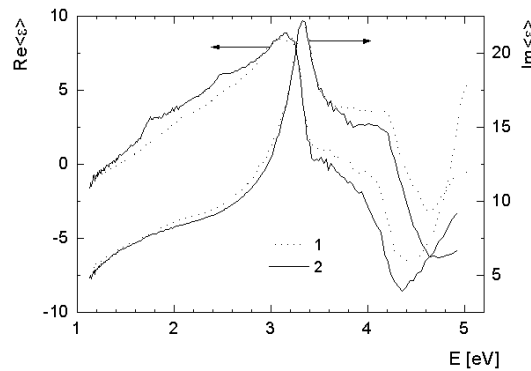


Fig. 2. Pseudodielectric function spectra of as-grown por-Si (1) and hybrid sample of TPPS₄ deposited on por-Si (2).

of a control hybrid sample TPPS₄ on glass was dominated by porphyrin. The fine structure of the spectra for hybrid sample TPPS₄/glass was qualitatively the same though the relative intensity of the absorption bands was slightly changed. For a latter hybrid sample the spectroscopic ellipsometry data were analyzed in a three-media model and the dielectric function spectra of TPPS₄ were determined for the first time. The imaginary part of dielectric function was equal to ~ 2.5 and ~ 5.5 at the maximum of the bands at 1.75 and 2.53 eV, respectively. The uncertainty in the evaluation of numerical values is mainly due to the variation of TPPS₄ layer thickness.

The fine structure of pseudodielectric function spectra $\langle\epsilon\rangle(E)$ for TPPS₄ deposited on crystalline Si wafer (curve 2 in Fig. 1) was mainly caused by porphyrin in the region of lower photon energies. Some interaction between TPPS₄ and crystalline *n*-Si (100)-oriented surface can be proposed from the lineshape analysis

in the range of 2.8–3.5 eV due to overlap of the characteristic peaks in both materials. At higher energies the fine structure of the optical response is caused by Si (curve 4 in Fig. 1). The contribution of TPPS₄ can be modeled as that for a transparent film up to the energy of strong electronic excitations starting at $E > 5$ eV.

Curve 3 in Fig. 1 illustrates the optical response of hybrid sample consisting of TPPS₄ deposited on por-Si with oxide layer removed by etching for 5 min in a 30% water solution of KOH. Immediately before deposition of TPPS₄, the native oxide was removed by etching for 1 min in HF:H₂O (1:1). The lineshape difference for optical features due to porphyrin absorption bands in curves 2 and 3 indicates a different interaction of TPPS₄ with crystalline and porous Si surface. The regularities of the influence of TPPS₄-deposition are well illustrated in the difference spectra between initial and hybrid samples.

The pseudodielectric function spectra for hybrid sample of TPPS₄ deposited on as-formed anodically etched por-Si is presented in Fig. 2. As is seen, the optical features due to TPPS₄ were considerably masked though clearly resolved in the region of ~ 1.7 and ~ 2.5 eV.

AFM studies of TPPS₄/glass samples have shown that parallel fiber-like structures of 0.5–1.0 μm in width and 100–200 nm in height were formed. The structures on the glass surface present a stacking of TPPS₄ mesoaggregates consisting of oblong nanoparticles of \varnothing 100–200 nm and 15–30 nm in height.

SEM studies have shown that a TPPS₄ layer on the surface of crystalline Si was not uniform. Rectangular-like openings of 1–5 μm in size were formed. The openings were oriented along crystallographic axes indicating a strong interaction of TPPS₄ with (100)-surface of crystalline *n*-Si. As follows from AFM observations, the fibers similar to those on glass substrate were formed on the surface of crystalline Si (Fig. 3a) though in this case the flocculated structure of fibers was not so clearly developed. The width and height of fibers were approximately equal to 250 and 30–50 nm, respectively. These fibers were significantly larger than those [4] formed on crystalline Si from aqueous solution with a lower (5×10^{-5} M) concentration of TPPS₄.

The structure of por-Si was typical [6] for *n*-Si. The morphology of por-Si with removed oxide layer investigated by SEM has shown that the pores of size ~ 2 –4 μm and depth ~ 15 μm were formed during electrochemical etching. As follows from Fig. 3b, the fiber-like structure was not formed and porphyrin aggregates were located predominantly inside the pores.

The structural and optical studies have shown that adsorption process of porphyrin aqueous solution was different for various Si surfaces. Large mesoaggregates of TPPS₄ were formed on the surface of glass and crystalline Si resulting in the change of the characteristic absorption bands. Analyzing the whole set of data it was concluded that porphyrin J-aggregates were intercalated into large pores of size 2–4 μm in *n*-Si bulk as well as in the luminescent layer, in which nanopores of

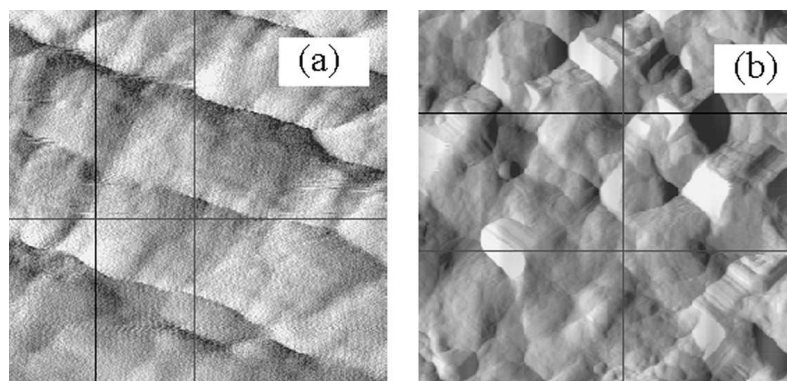


Fig. 3. AFM $1.0 \times 1.0 \mu\text{m}^2$ (a) and $10 \times 10 \mu\text{m}^2$ (b) micrographs of hybrid samples with TPPS₄ deposited on the surface of *c*-Si (a) and por-Si with removed oxide layer (b).

size 10–15 nm [7] were formed during anodic etching. The adsorption of TPPS₄ on Si surface is different in all three investigated cases of monocrystalline wafer and por-Si with and without oxide layer. The results obtained demonstrated that por-Si could be perspective media for intercalation of organic molecules like porphyrin.

Acknowledgments

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