

ELLIPSOMETRIC CHARACTERIZATION OF HYBRID SAMPLES COMPOSED OF IRON PORPHYRIN ON Si

G.J. Babonas, I. Šimkienė, A. Rėza, and J. Sabataitytė

Semiconductor Physics Institute, A. Goštauto 11, LT-01108 Vilnius, Lithuania

E-mail: jgb@pfi.lt

Received 31 January 2006

Hybrid organic–inorganic system composed of iron porphyrin deposited on Si substrate was investigated by spectroscopic ellipsometry. A series of samples with (100) and (111)-oriented Si wafers and various acidity of aqueous solution of iron porphyrin deposited on Si substrates were fabricated and investigated. Experimental data were analysed in various models in order to reveal the general regularities of the hybrid system. It was determined that in hybrid samples, the mesostructures of iron porphyrin formed from both acid and base aqueous solutions possess similar electronic excitation bands. It was proposed that a major part of iron oxo-dimers were destroyed on the Si surface due to formation of the chemical bonds between Si substrate covered by native oxide and iron porphyrin.

Keywords: optical properties of composite materials, organic–inorganic hybrid nanostructures

PACS: 78.66.Sq, 81.07.Pr

1. Introduction

Recently, hybrid inorganic–organic structures were widely studied due to their potential applications in molecular electronics [1]. In this respect, self-assembly of organic molecules on metal surfaces was mostly investigated [2]. The chemical bonds between Si and organic molecules are assumed [3] to be stronger than metal–molecule bonds and hence the hybrid Si-based structures are expected to be promising in the development of molecular electronic devices [4]. The properties of such hybrid structures can be varied by altering, on the one hand, the dopant type, concentration, orientation, and surface treatment of Si substrate and, on the other hand, the acidity, concentration, and aggregation state of organic compound solution.

In the development of hybrid structures, the characterization of complex samples becomes an urgent problem. Along with direct structural studies, the optical technique is widely used to characterize the chemical composition of hybrid samples by infrared measurements of vibration spectra as well as a standard UV-vis-near-IR spectroscopy. The ellipsometric technique was also applied for determination of thickness of thin organic layers [5] and for determination of the optical constants of organic films [6], e. g., optical parameters of porphyrin derivatives metal phthalocyanines

[7]. In this work the optical response of hybrid structure composed of iron porphyrin (FeTPPS) on Si substrate was analysed. Spectroscopic ellipsometry investigations have been carried out in order to develop the model, which could be used for analysis of the optical response of these complex samples, and to investigate the aggregation state of FeTPPS in various hybrid structures under consideration by altering the characteristics of the substrate and acidity of deposited aqueous solution of FeTPPS.

2. Experimental

The substrates for preparation of hybrid samples were *n*-type Si wafers with surface planes (100) or (111). The Si (100)-oriented wafers (0.5 Ω cm) were degreased by boiling dimethylformamide whereas the (111)-oriented wafers were not additionally treated. The surface of Si substrates was covered by native oxide layer, which could be detected and characterized by spectroscopic ellipsometry [8]. The thickness of the surface layer, which was estimated from spectroscopic ellipsometry measurements assuming the layer to be composed of pure silica, was 0.8 and 2.8 nm for (111) and (100)-oriented Si substrates, respectively. The untreated air-exposed Si (111) surface is more hydrophobic due to adsorption of carbon compounds.

The degreased and ethanol-rinsed SiO₂/Si(100) surface should be less hydrophobic as a thicker oxide layer containing OH[−] groups is formed because of the influence of non-absolute ethanol.

Aqueous solutions of concentration 10^{−4}–10^{−3} M were prepared from Fe(III) meso-tetra(4-sulfonatophenyl) porphine chloride C₄₄H₂₈FeN₄O₁₂S₄Cl. The acidity of the solutions was varied in the pH range 1–12 by adding 0.1 M NaOH and 0.1 M HCl. A droplet (~0.1 ml) of aqueous solution of FeTPPS was spotted on Si and dried at room temperature. Control optical measurements have also been carried out on the hybrid samples obtained at the deposition of FeTPPS on glass substrates and aqueous solutions of various acidities at different cuvette length *l*.

The morphology of hybrid samples was studied by a standard atomic force microscopy (AFM) technique (Thermomicroscope Explorer). On the basis of these observations, several typical structural features were determined: (i) the presence of contact line at the boundary of the dried drop of FeTPPS aqueous solution, (ii) formation of macro- and nano-aggregates, (iii) occurrence of micrometre-size rings typical of porphyrin and its derivatives [9]. The morphology of the structures on the surface of hybrid samples was quite similar in all the samples under consideration.

The main difficulty in the interpretation of experimental optical results was the non-homogeneity of the surface layer because of the occurrence of defects leading to a rough surface relief. Thus, for the interpretation of optical response it was reasonable to accept a general common model based on the effective media approximation. It should be noted that the light beam spot (up to 5 mm at angle of incidence $\Theta \sim 70^\circ$) in the set-up used was significantly larger than the size of macro-aggregates.

The optical response of hybrid samples was investigated by spectroscopic ellipsometry. The spectral ellipsometer with rotating analyzer operating in the range of 1–5 eV was used. In the experimental run, the complex reflectivity ρ of the sample is determined,

$$\rho = \frac{R_{\parallel}}{R_{\perp}} = \tan \Psi \exp(i\Delta), \quad (1)$$

where R_{\parallel} and R_{\perp} are reflectance coefficients for light polarized in parallel (\parallel) and in perpendicular (\perp) to the plane of light incidence, respectively, and Ψ , Δ are ellipsometric parameters. In the case of isotropic bulk sample, the complex reflectivity is directly related to

the dielectric function ε of material under consideration:

$$\varepsilon = \sin^2 \Theta \left[\left(\frac{1 - \rho}{1 + \rho} \right)^2 \tan^2 \Theta + 1 \right]. \quad (2)$$

In the case of complex sample, the dielectric function calculated according to (2) is denoted as pseudodielectric function $\langle \varepsilon \rangle$. Details of the set-up and measurement procedure as well as the modelling of the optical response for a multilayer system were described in [10, 11].

The optical response of hybrid sample FeTPPS/Si can be analysed in several models. In the empirical three-media ambient/film/substrate model *I*, the contribution of FeTPPS layer to optical response of the sample FeTPPS/Si was assumed to be equal to the experimentally determined pseudodielectric function of the composite hybrid structure FeTPPS/SiO₂. In the latter system the fine structure of the spectra of ellipsometric parameters is mainly caused by the FeTPPS layer.

Figure 1(a) shows the results of modelling, in which the thickness of the FeTPPS is considered as the variable parameter. As is seen, the contribution of FeTPPS clearly manifests itself in the spectra of pseudodielectric function $\langle \varepsilon \rangle$ of composite system FeTPPS/Si. The peak E_1 at 3.4 eV ($\Lambda_3 \rightarrow \Lambda_1$ transitions) in Si [12] is suppressed by the main Soret band in FeTPPS at 400 nm (3.1 eV) [13]. In contrast, the contribution of the dominant peak E_2 at 4.2 eV ($X_4 \rightarrow X_1$ transitions) in Si is relatively increased in experimental spectra for hybrid sample FeTPPS/Si as compared to those in modelled data. The analysis has shown that the shape of the spectra for hybrid sample FeTPPS/Si is quite well reproduced and the thickness of the complete effective surface layer ($d \sim 30$ nm for this particular sample) can be determined. However, numerical values of experimental and calculated data differ significantly for the real part of effective dielectric function $\langle \varepsilon \rangle$ because the influence of glass substrate was neglected in the model calculations.

In the improved version (model *II*) the contribution of FeTPPS was also calculated from the optical response of hybrid sample FeTPPS/glass. However, the inverse problem for ellipsometric parameters of the hybrid system FeTPPS/Si was solved with adjustable parameters d (thickness) and w (where w is the “weight” defined as $w = 1 - P$, where P is porosity, i. e. P is the volume fraction of voids in the FeTPPS layer) for the effective FeTPPS layer. In order to achieve a reasonable fitting between experimental and calculated data

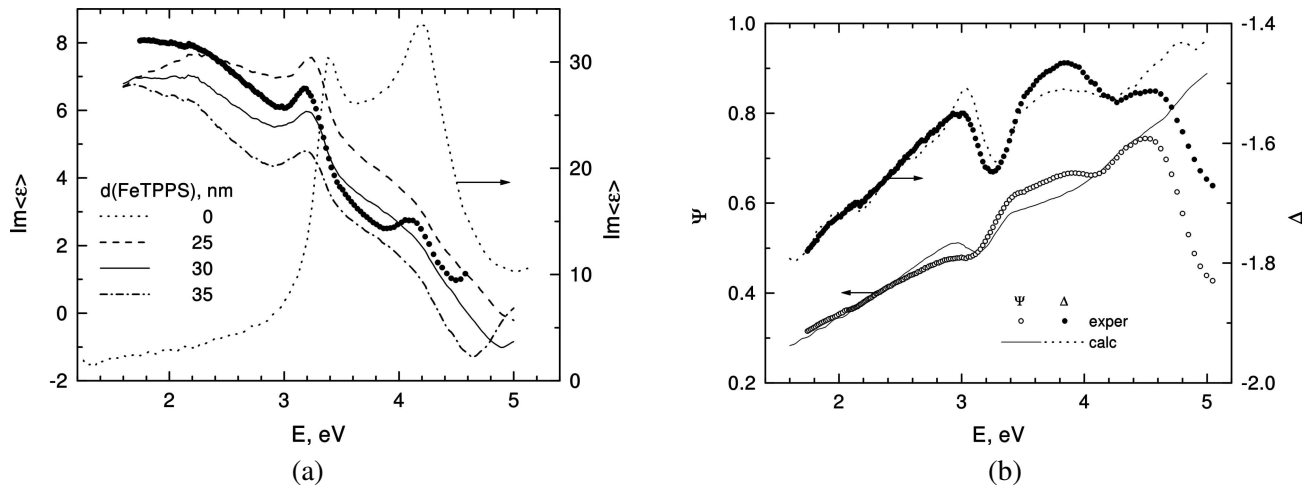


Fig. 1. Experimental (points) and modelled (curves) spectra of (a) pseudodielectric function and (b) ellipsometric parameters of hybrid sample FeTPPS/Si produced from aqueous solution of FeTPPS (1.0 mM, pH 9.0). Dielectric function of FeTPPS layer was taken to be equal to pseudodielectric function of the system FeTPPS/SiO₂. (a) Model I: the thickness of complete FeTPPS layer was a variable parameter. (b) Model II: thickness and porosity of the FeTPPS sublayers were adjustable parameters.

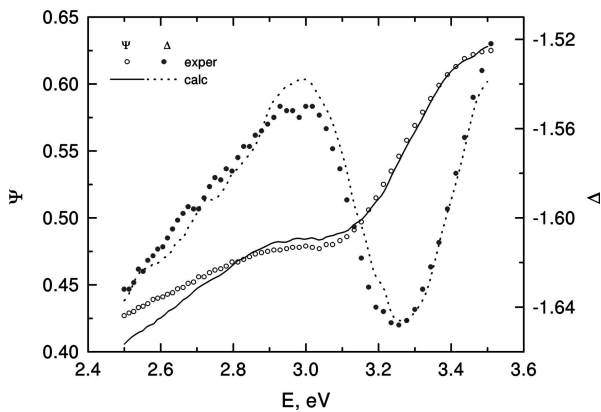


Fig. 2. Experimental (points) and calculated (curves) spectra of ellipsometric parameters for hybrid sample FeTPPS/Si(111) in model III, in which the data were considered in the region of the Soret band of FeTPPS.

in the vicinity of main optical features at 1.7–4.5 eV (Fig. 1(b)), a three-layer stack of FeTPPS film was assumed with d in the range of 45–105 nm and w varying from 0.04 to 0.95.

A more adequate model III was applied for hybrid sample FeTPPS/Si when experimental data were considered in a narrow spectral range, e. g., in the vicinity of the main absorption band of FeTPPS (Fig. 2), where the optical response of the hybrid sample dominated. In this model the fitting of experimental data was more accurate (purpose function was less than 0.01). According to the model, the TPPS layer on Si was non-homogeneous with dense ($w = 0.93$ –1.5) and porous ($w = 0.03$) sublayers of total thickness ~ 55 nm.

In the last model IV, a stack of layers simulated by three Lorentzian lines represented the effective FeTPPS film on Si (Fig. 3). As is seen from Fig. 3(a), the cal-

culational results fit perfectly the experimental data for hybrid sample FeTPPS/Si(100) produced from aqueous solution of FeTPPS of concentration $1 \cdot 10^{-3}$ M and pH 9.0. The energy of simulated absorption bands in sublayers of surface film for hybrid sample FeTPPS/Si (Fig. 3(b)) agrees well with Soret bands for both FeTPPS monomers (at 392 nm, pH 3.3) and O-(FeTPPS)₂ dimers (415 nm, pH 11.2) [13]. In contrast, dimers are mainly responsible for the optical absorption of FeTPPS with high pH values in aqueous solution and in hybrid sample FeTPPS/glass. Figure 3(b) shows also the E_1 peak of Si which can influence on the shape of the optical response in FeTPPS/Si.

The analysis of various models has shown that spectroscopic ellipsometry can be effectively used in the studies of hybrid systems like FeTPPS deposited on Si and in determination of regularities of the interaction between surface layer and substrate. However, a unified model should be applied for the series of samples under consideration.

3. Results and discussion

3.1. Influence of Si-substrate orientation

As noted above, thin (1–3 nm) film of native silica oxide layer occurs on Si wafers masking the influence of the substrate orientation. Nevertheless, the effective dielectric functions representing the contribution to optical response originating from FeTPPS on Si (111) (Fig. 3(b)) and Si (100) (Fig. 4) are somewhat different. As is seen from Fig. 4, two surface sublayers of 3 nm (upper) and 25 nm (lower) thickness were determined

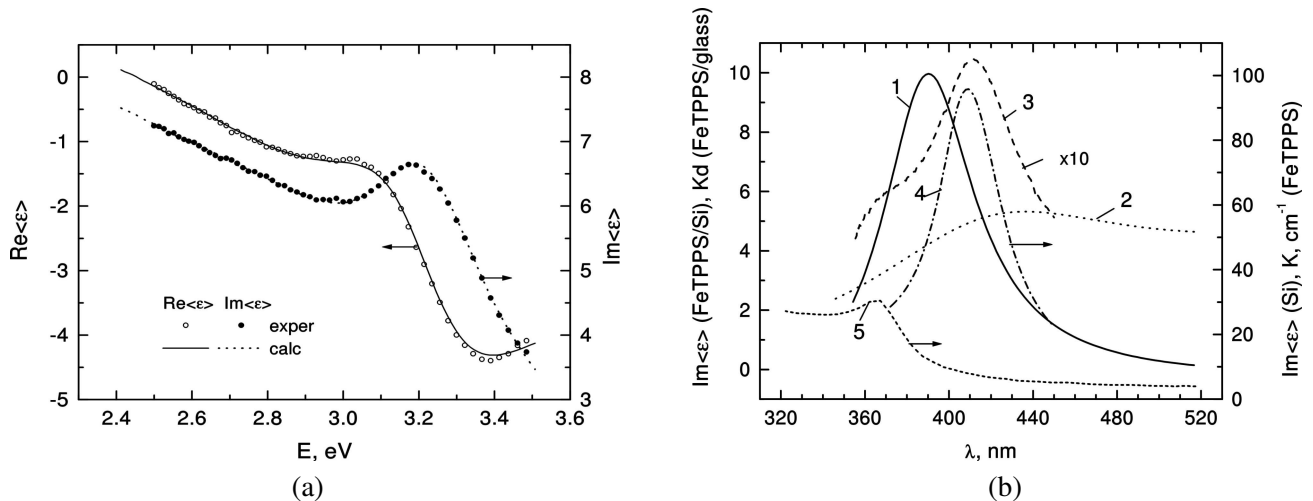


Fig. 3. (a) Experimental (points) and calculated (curves) spectra of pseudodielectric function for sample FeTPPS/Si(111) simulated by Lorentzian-type lines (model IV). (b) Modelled spectra of $\text{Im}\langle\epsilon\rangle$ of the porphyrin upper (4 nm, 1) and lower (26 nm, 2) sublayers in FeTPPS/Si, absorption of surface layer in FeTPPS/glass (3) and in FeTPPS aqueous solution (1 mM, pH 9.0, $l = 0.12$ mm, 4), and $\text{Im}\langle\epsilon\rangle$ of Si (5).

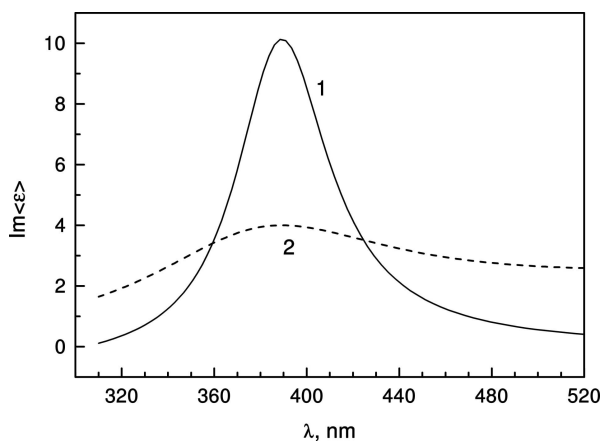


Fig. 4. Spectra of imaginary part of pseudodielectric function $\text{Im}\langle\epsilon\rangle$ for upper (1) and lower (2) surface sublayers calculated for hybrid sample FeTPPS/Si(100) processed from aqueous solution with pH 8.7.

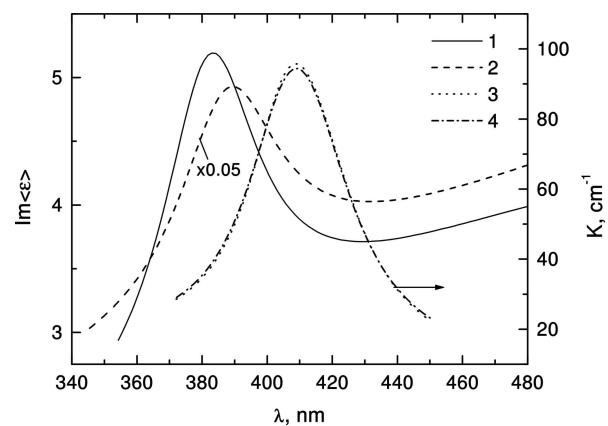


Fig. 5. Spectra of $\text{Im}\langle\epsilon\rangle$ calculated in the one-layer model for FeTPPS deposited on Si (111) (1) and (100) (2) and absorption spectra of aqueous solution ($l = 0.12$ mm) with pH 9.0 (3) and 8.7 (4).

from fitting of experimental data in model IV. From the location of the absorption bands it was reasonable to suggest that the bands were caused by electronic excitations attributed mainly to monomers of FeTPPS, though some contribution from dimers could not be excluded in the formation of the broad second band.

The optical data for FeTPPS in aqueous solution with high pH values and in hybrid samples with differently oriented Si substrates are presented in Fig. 5. Experimental data were analysed in the model of one effective layer on substrate. The spectral dependence of dielectric function for a single effective surface layer was simulated by a set of three Lorentzian-type lines. As is seen from Fig. 5, the absorption bands were al-

most identical for FeTPPS in aqueous solutions with pH values equal to 8.7 and 9.0. However, a slight shift should be noticed for the FeTPPS films of 10 and 27 nm thickness, respectively, on (100) and (111)-oriented Si substrates. It was possible to assume that for two studied orientations of Si substrate, the main contribution to the optical response originated from electronic excitation of monomers. The difference in the spectra for samples on Si (100) and Si (111) could be caused by a strain induced in the surface layers of porphyrin. It should be noticed that from general considerations it follows that Si (100) surface is more active than Si (111).

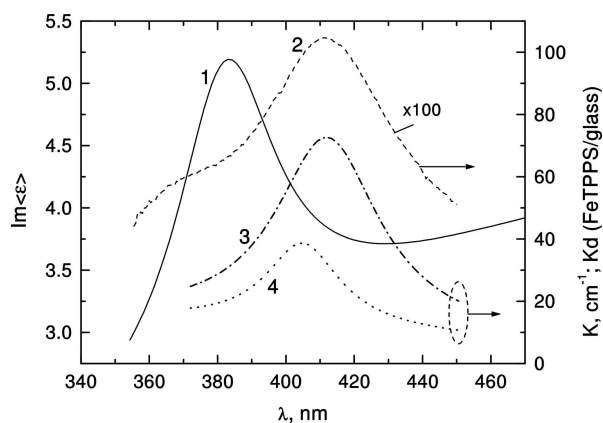


Fig. 6. Spectra of $\text{Im}(\epsilon)$ for FeTPPS in hybrid sample on Si (111) (1), absorption spectra for hybrid sample FeTPPS/glass (2), and two components (3, 4) of Soret band in aqueous solution of FeTPPS (pH 9.0, $l = 0.12$ mm).

3.2. Influence of substrate type

As followed from Fig. 3(b), the contribution of FeTPPS (pH 9.0) layer on substrate in the *multilayer* model IV was characterized by dominating peaks at 390 and 410 nm for hybrid samples on Si (111) and glass substrates, respectively, in the case of porphyrin with high pH values. In Fig. 6 the contribution of a *single* FeTPPS surface layer for a hybrid sample on Si (111) is shown. In a single layer model, the blue shift of the FeTPPS band in hybrid FeTPPS/Si sample with respect to that in FeTPPS/glass is clearly seen. In the aqueous solution, the most intensive broad absorption band of FeTPPS (pH 9.0) was observed at 410 nm and it was decomposed into components at 405 and 415 nm. The results of experimental optical investigation can be interpreted as the redistribution of oscillator strength with enhanced monomer and dimer components for samples of FeTPPS (high pH values) deposited on Si (111) and glass substrates, respectively.

A similar set of experimental data was obtained for samples produced from aqueous solution of FeTPPS of high acidity (Fig. 7). The optical parameters of the modelled FeTPPS layers deposited on Si (100) and glass from acid aqueous solution (pH 1.8) are presented in Fig. 7. As is seen from Figs. 6 and 7, the main regularities are similar for FeTPPS aqueous solution with both low and high pH values: the shorter wavelength component is stronger for hybrid samples with Si substrate.

3.3. Influence of acidity of FeTPPS aqueous solution

In Fig. 8 the data for two hybrid samples FeTPPS/Si and the corresponding aqueous solutions of FeTPPS

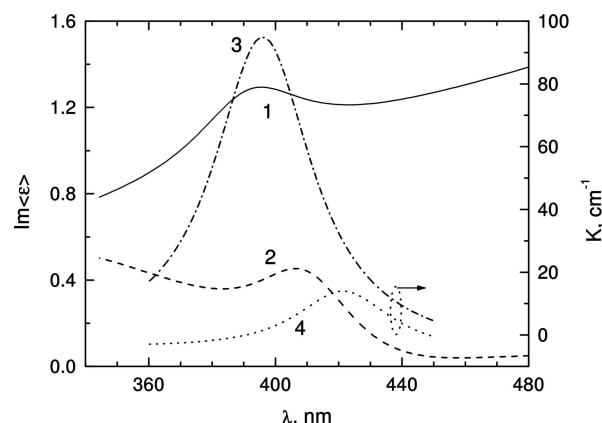


Fig. 7. Spectra of $\text{Im}(\epsilon)$ for FeTPPS in hybrid sample on Si (100) (1), absorption spectra for hybrid sample FeTPPS/glass (2), and two components (3, 4) of Soret band in aqueous solution of FeTPPS (pH 1.8, $l = 0.12$ mm).

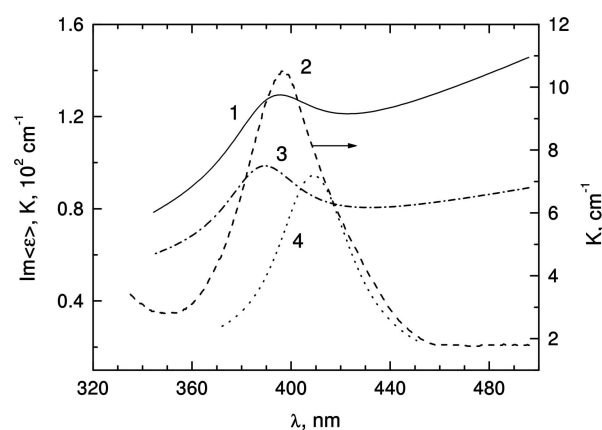


Fig. 8. Main Soret band in hybrid FeTPPS/Si samples (1, 3) and FeTPPS aqueous solutions (2, 4) with pH values equal to 1.8 (1, 2) and 8.7 (3, 4).

are presented. As is seen, the blue shift of the Soret band in FeTPPS in hybrid sample with respect to FeTPPS aqueous solution with pH 8.7 is clearly seen. In contrast, the location of the main band is close for both FeTPPS aqueous solution at pH 1.8 and hybrid sample FeTPPS/Si.

The location of the main Soret band in FeTPPS/Si hybrid samples indicates that similar mesostructures of porphyrin were formed from both acid and base solutions. These dominant optical features correspond mainly to monomers in acid FeTPPS aqueous solutions. However, it is worthwhile to note that weak bands at ~ 600 nm typical of dimers in solution [13] were observed in FeTPPS/Si samples formed from near-neutral and base aqueous solutions (Fig. 9). On the basis of the observations it is reasonable to suggest that a major part of oxo-dimers have been destroyed on the surface of Si substrate, most probably because of the formation of chemical bonds Si–O–FeTPPS.

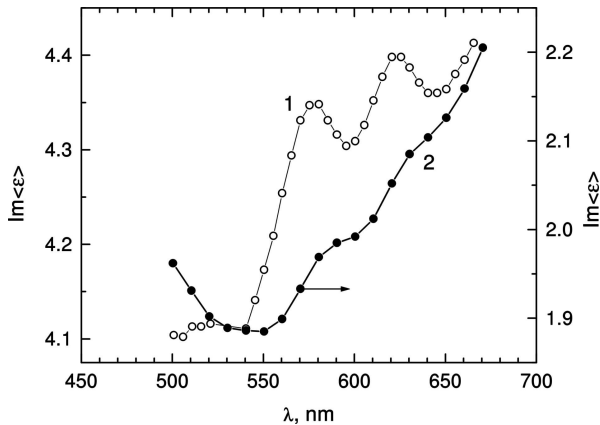


Fig. 9. Experimental spectra of $\text{Im}(\epsilon)$ for hybrid sample FeTPPS/Si with thick (1) and thin (2) layers produced from FeTPPS aqueous solution (pH 6.5).

Acknowledgement

Support from EU project PHOREMOST (N 511616) is gratefully acknowledged.

References

- [1] K.S. Kwok and J.C. Ellenbogen, Molecular electronics: Future electronics, *Mater. Today* **5**, 28–37 (2002).
- [2] M.A. Ratner, Introducing molecular electronics, *Mater. Today* **5**, 20–27 (2002).
- [3] J.M. Buriak, Organometallic chemistry on silicon and germanium surfaces, *Chem. Rev.* **102**, 1271–1308 (2002).
- [4] N.P. Guisinger, M.E. Greene, R. Basu, A.S. Baluch, and M.C. Hersam, Room temperature negative differential resistance through individual organic molecules on silicon surfaces, *Nano Lett.* **4**, 55–59 (2004).
- [5] C.A. Richter, C.A. Hacker, L.J. Richter, and E.M. Vogel, Molecular devices formed by direct monolayer attachment to silicon, *Solid-State Electron.* **48**, 1747–1752 (2004).
- [6] A.B. Djurišić, T. Fritz, and K. Leo, Modelling the optical constants of organic thin films: Impact of the choice of objective functions, *J. Opt. A* **2**, 458–464 (2000).
- [7] A.B. Djurišić, C.Y. Kwong, T.W. Lau, Z.T. Liu, H.S. Kwok, L.S.M. Lam, and W.K. Chan, Spectroscopic ellipsometry of metal phthalocyanine thin films, *Appl. Opt.* **42**, 6382–6387 (2003).
- [8] D.E. Aspnes and A.A. Studna, Optical detection and minimization of surface overlayers on semiconductors using spectroscopic ellipsometry, *Proc. SPIE* **276**, 227–232 (1981).
- [9] L. Latterini, R. Blossey, J. Hofkens, P. Vanoppen, F.C. De Schryver, A.E. Rowan, and R.J.M. Nolte, Ring formation in evaporating porphyrin derivative solutions, *Langmuir* **15**, 3582–3588 (1999).
- [10] G.J. Babonas, A. Niilisk, A. Reza, A. Matulis, and A. Rosental, Spectroscopic ellipsometry of TiO_2/Si , *Proc. SPIE* **5122**, 50–55 (2002).
- [11] I. Simkiene, J. Sabataityte, G.J. Babonas, A. Reza, and J. Beinoras, Self-organization of porphyrin structures on Si, *Mater. Sci. Eng. C* **26**, 1007–1011 (2006).
- [12] D.E. Aspnes and A.A. Studna, Dielectric functions and optical parameters of Si, Ge, GaP, GaAs, GaSb, InP, InAs, and InSb from 1.5 to 6.0 eV, *Phys. Rev. B* **27**, 985–1009 (1983).
- [13] E.B. Fleisher, J.M. Palmer, T.S. Srivatsava, and A. Chatterjee, Thermodynamic and kinetic properties of an iron–porphyrin system, *J. Am. Chem. Soc.* **93**, 3162–3167 (1971).

HIBRIDINIŲ GELEŽIES PORFIRINO ANT Si DARINIŲ ELIPSOMETRINIS APIBŪDINIMAS

G.J. Babonas, I. Šimkienė, A. Rėza, J. Sabataitytė

Puslaidininkų fizikos institutas, Vilnius, Lietuva

Santrauka

Spektroskopinės elipsometrijos metodu buvo tiriama hibridinė organinė–neorganinė sistema, sudaryta iš geležies porfirino, nusodinto ant Si padėklų. Buvo pagaminta ir išnagrinėta serija bandinių ant Si (100) ir (111) plokštumomis orientuotų padėklų su nusodintais ant jų įvairaus rūgštingumo geležies porfirino vandens tirpalais. Siekiant išryškinti bendrus hibridinės sistemos dėsningu-

mus, eksperimentiniai duomenys buvo analizuojami, panaudojant įvairius modelius. Nustatyta, kad hibridiniuose dariniuose tiek iš rūgštinių, tiek iš šarminių tirpalų susidaro geležies porfirino dariniai su panašiomis elektroninių sužadinių juostomis. Manoma, kad didžioji geležies okso-dimerų dalis ant Si paviršiaus yra suardoma, formuojantis cheminiams ryšiams tarp Si padėklo, padengto savuoju oksido sluoksniu, ir geležies porfirino.