Available online at www.sciencedirect.com
SCIENCE DIRECT®
Thin Solid Films 455–456 (2004) 410–416
thin solid films
www.elsevier.com/locate/tsf

Characterisation of porous silicon composite material by spectroscopic ellipsometry

M. Gaillet[a], M. Guendouz[b], M. Ben Salah[b], B. Le Jeune[c,*], G. Le Brun[c]

[a]*Jobin Yvon S.A.S. Thin Film Division Horiba Group, ZI de la vigne aux loups – 5, avenue Arago – 91380 Chilly Mazarin, France*
[b]*Laboratoire d'Optronique (UMR CNRS 6082), Université de Rennes 1, IUT de Lannion, BP 150, 22302 Lannion Cedex, France*
[c]*Laboratoire de Spectrométrie et Optique Laser, Université de Bretagne Occidentale, 6 Avenue Le Gorgeu, BP 809, 29285 Brest Cedex, France*

Abstract

Porous silicon materials are currently under intense investigation for optoelectronic applications. Spectroscopic ellipsometry (SE) was used to study the optical properties of layers of composite material composed by porous silicon and disperse red one (a red dye which is well known for its non-linear properties) in the UV–IR spectral range (0.75–4.5 eV). P-doped silicon substrate was first electrochemically etched in a dilute HF electrolyte solution in order to obtain porous silicon films. Then these films were oxidised to produce a thin (5 μm) transparent layer of SiO_2 on the silicon substrate with negligible optical anisotropy. After the oxidation, disperse red one (DR1) molecules diluted in a solution of THF (tetrahydrofurane) were introduced in the porous material. The DR1 is uniformly distributed inside the porous silica layer and the amount of dye was estimated by an effective medium approximation. The orientation of the dye molecules was tested after poling by a static electrical field.

Keywords: Porous silicon; Spectroscopic ellipsometry; Optical properties

1. Introduction

Several organic molecules with conjugated chain structure (as disperse red one, DR1, molecules used here) are known to possess non-linear optical properties, which are used to elaborate optical functions such as optical modulators or switching devices [1,2], and ordered mesoporous silica can host such small organic molecules and then be efficient for the photonic applications mentioned above.

Spectroscopic ellipsometry (SE) was used to characterise the various stages of the composite material process composed by oxidised porous silicon filled with DR1 dye. The optical properties and the anisotropy of the composite material were determined from the SE data analysis with the aim to model its non-linear behaviour to investigate its intrinsic non-linear properties.

Firstly, the preparation and the structural properties of the samples are presented. Then, the technique used (spectroscopic ellipsometry) for the optical characterisations is exposed, and in a third part, the elaboration of the composite material is followed connected to the analysis of its linear optical properties. Finally, perspectives are discussed.

2. Experimental

2.1. Sample preparation and structural properties

Porous silicon layers were obtained by the electrochemical anodisation of (100)-oriented p^+ silicon substrates (5 mΩ.cm) in a 20% HF electrolyte solution composed of HF(40%):H_2O:C_2H_5OH (3:1:2). An anodisation current density of 100 mA cm^{-2} was applied during 115 s in order to obtain porous silicon films. Under these conditions, the porosity of the layer is approximately 80% (gravimetric measurements) and the porous layer (measured by optical microscopy and reflectivity) is approximately 5 μm. Previous studies [3] have shown that the surface of porous-Si film formed from p^+ substrates is covered by a 0.2-μm thin parasitic film of low porosity; such a film prevents the pores from filling with the DR1 solution. So this layer was

*Corresponding author. Tel.: +33-2-98-01-73-78; fax: +33-2-98-01-82-13.
E-mail address: bernard.lejeune@univ-brest.fr (B. Le Jeune).

0040-6090/04/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2004.01.028

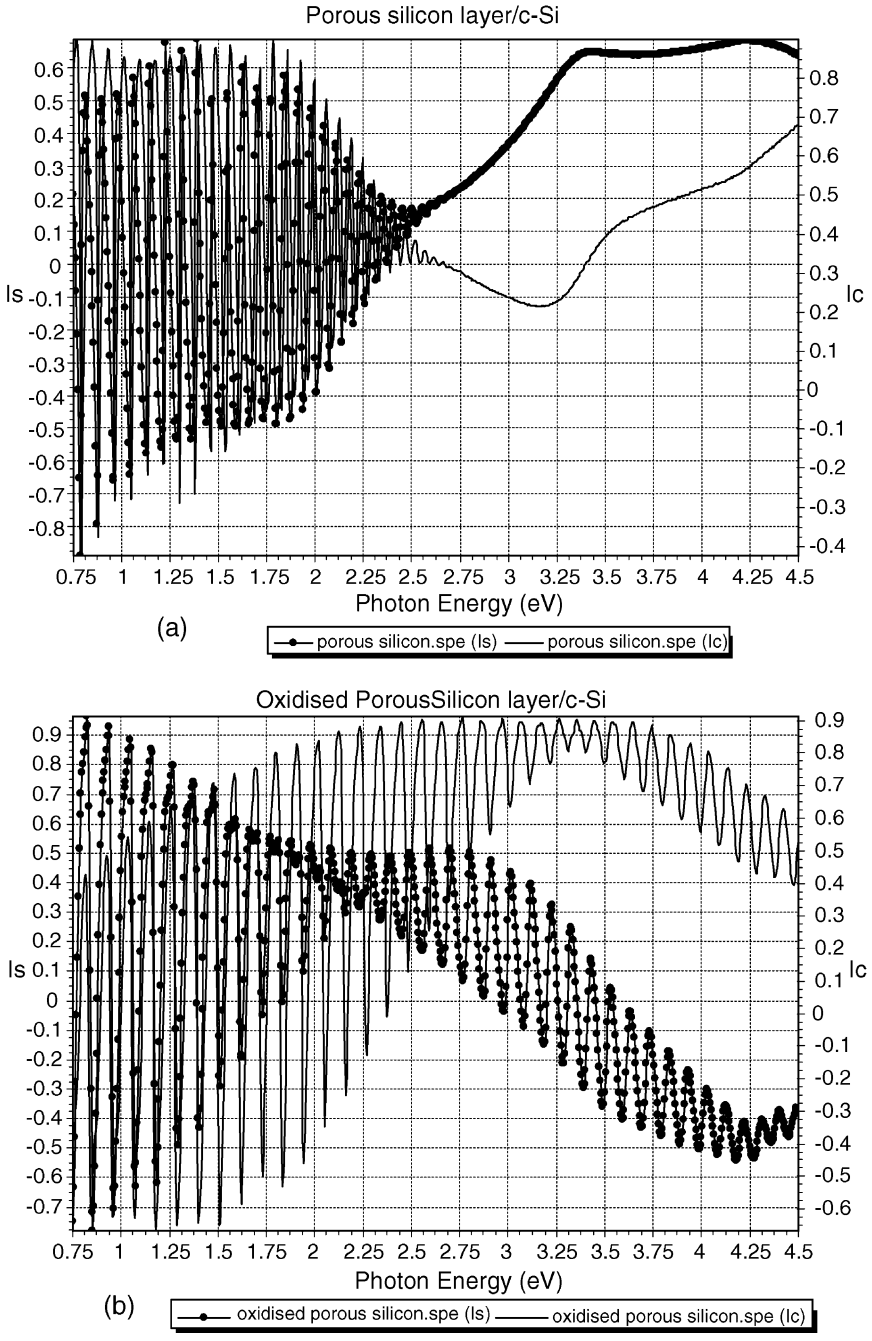

Fig. 1. (a) Spectroscopic measurements $(I_s, I_c) = f(E)$ for a porous silicon layer on a P-doped silicon substrate. (b) Spectroscopic measurements $(I_s, I_c) = f(E)$ for an oxidised porous silicon layer on a P-doped silicon substrate.

removed by SF_6 plasma etching to facilitate filling. Then the samples were pre-oxidised at 300 °C for 1 h followed by a wet oxidation step at 900 °C for 1 h. After this complete oxidation, the residual porosity is 56%, as deduced from the refractive index measured by 'm-line' method and Bruggeman model [4,5].

Indeed the porous silicon was completely transformed to the porous silica (SiO_2) after 30 min and the refractive index of this layer reach a constant value [6].

The DR1 molecules (4-[*N*-ethyl-*N*-(2-hydroxyethyl)] amino-4′-nitraozobenzene) were dissolved in various solvents such tetrahydrofurane (THF), with 20 g/l concentration [3]. Then, the solution was introduced into the oxidised porous silicon films with a micro-syringe.

We have undertaken the systematic examination of the filled oxidised porous layers using Micro-Raman and optical reflectivity techniques. This study [3] dem-

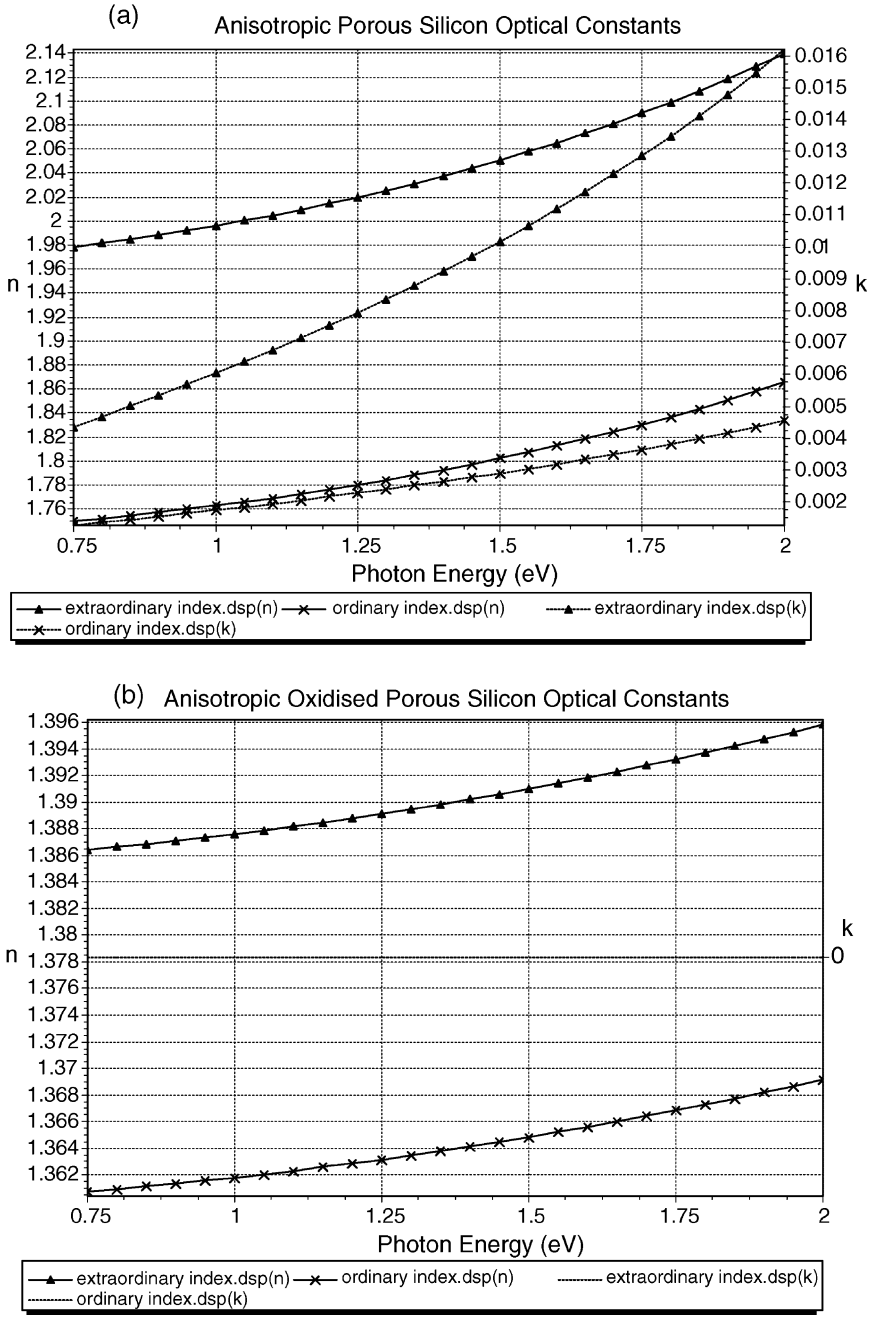

Fig. 2. (a) Complex refractive index ($n+ik$) for the porous silicon layer. (b) Complex refractive index ($n+ik$) for the oxidised porous silicon layer.

onstrated the uniform distribution of the organic molecules (DR1) from the surface up to the silicon interface.

The length of DR1 molecules (4-[*N*-ethyl-*N*-(2-hydroxyethyl)] amino-4′-nitraozobenzene), is not higher than 2 or 3 nm. SEM observations showed that the pores have a columnar structure perpendicular to the surface of the films. The pore diameters of such anodised Si material were evaluated as ranging between 30 and 50 nm. After oxidation the diameters decrease due to the increase of volume of the silicon walls resulting from the silicon transformation in silica. In this case, pore diameters were evaluated between 10 to 20 nm. That means that DR1 molecules could be easily introduced into the oxidised porous silicon layers.

2.2. Optical characterisation

Ellipsometry measurements were performed by using a spectroscopic phase modulated ellipsometer (Jobin Yvon, Model UVISEL NIR). Ellipsometric data were

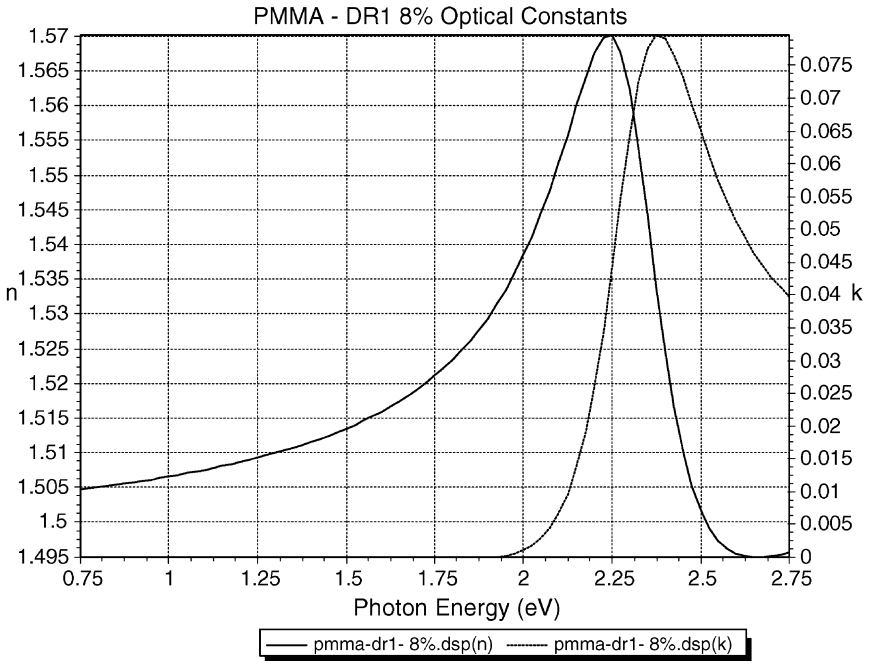

Fig. 3. Complex refractive index $(n+ik)$ for a PMMA – DR1 layer at 8% DR1 concentration.

acquired at an angle of incidence of 70° in the range 0.75–4.5 eV with a step of 0.005 eV. The SE spectra present (I_s, I_c) variables functions of the (Ψ, Δ) ellipsometric angle measurements defined from the fundamental equation of ellipsometry:

$$\frac{r_p}{r_s} = \tan\Psi \cdot e^{i\Delta}$$

I_s and I_c equations are given by:

$$I_s = \sin 2\Psi \cdot \sin\Delta \quad \text{and} \quad I_c = \sin 2\Psi \cdot \cos\Delta$$

A large spectral range was necessary for the complete characterization of the composite material elaboration, which exhibits strong absorption in the UV and visible range. Optical properties (complex refractive indexes) and thickness of the composite structure were extracted from the SE data analysis [7]. During the various stages of the composite structure process, the optical constants of the different films have been determined using single or multiple Lorentz oscillator dispersion formula.

2.3. Results and discussion

During the first step of the process, the p^+-doped silicon substrate is covered by a 5 μm porous silicon layer. Fig. 1a shows the spectroscopic measurements (I_s, I_c) as a function of photon energy (eV) of this sample which exhibit two different parts. Between 0.75 and 2.5 eV, the porous silicon layer is transparent and the thick film introduces a large number of oscillations. At a higher energy level, the film becomes completely absorbent. The optical properties of the layer were extracted over the reduced transparent range (Fig. 2a). The columnar structure of the layer introduces uniaxial optical properties (with an optical axis perpendicular to the surface) [8]: the birefringence is quite strong (> 0.2) in the 0.75–2 eV range due to the strong doping of the silicon, which could be used to control the polarisation state of light in a wide spectral range [9]; one can note that the absorption is not negligible for the same reason [10].

The second step consists of the oxidation of the porous silicon layer in order to obtain a porous SiO_2 layer. The experimental data presented in Fig. 1b exhibit oscillations over the whole spectral range resulting from the transparency of the layer, and Fig. 2b shows that the absorption is effectively negligible in the fitting spectral range of interest. The found refractive index is lower than before and the birefringence is quite small (in the order of 0.02–0.03). These properties are quite interesting to elaborate guiding structures, which are polarisation insensitive.

In the third stage, the DR1 was introduced in the oxidised porous silicon layer. The refractive indexes of different PMMA (polymethyl methacrylate)-DR1 mixture were obtained and the effective medium theory (Bruggeman model) has been used to provide the refractive index of the DR1, which is approximately 1.8 at $\lambda = 1.3$ μm (confirmed by a M-lines set-up [11]). Fig. 3 presents an example of the optical properties

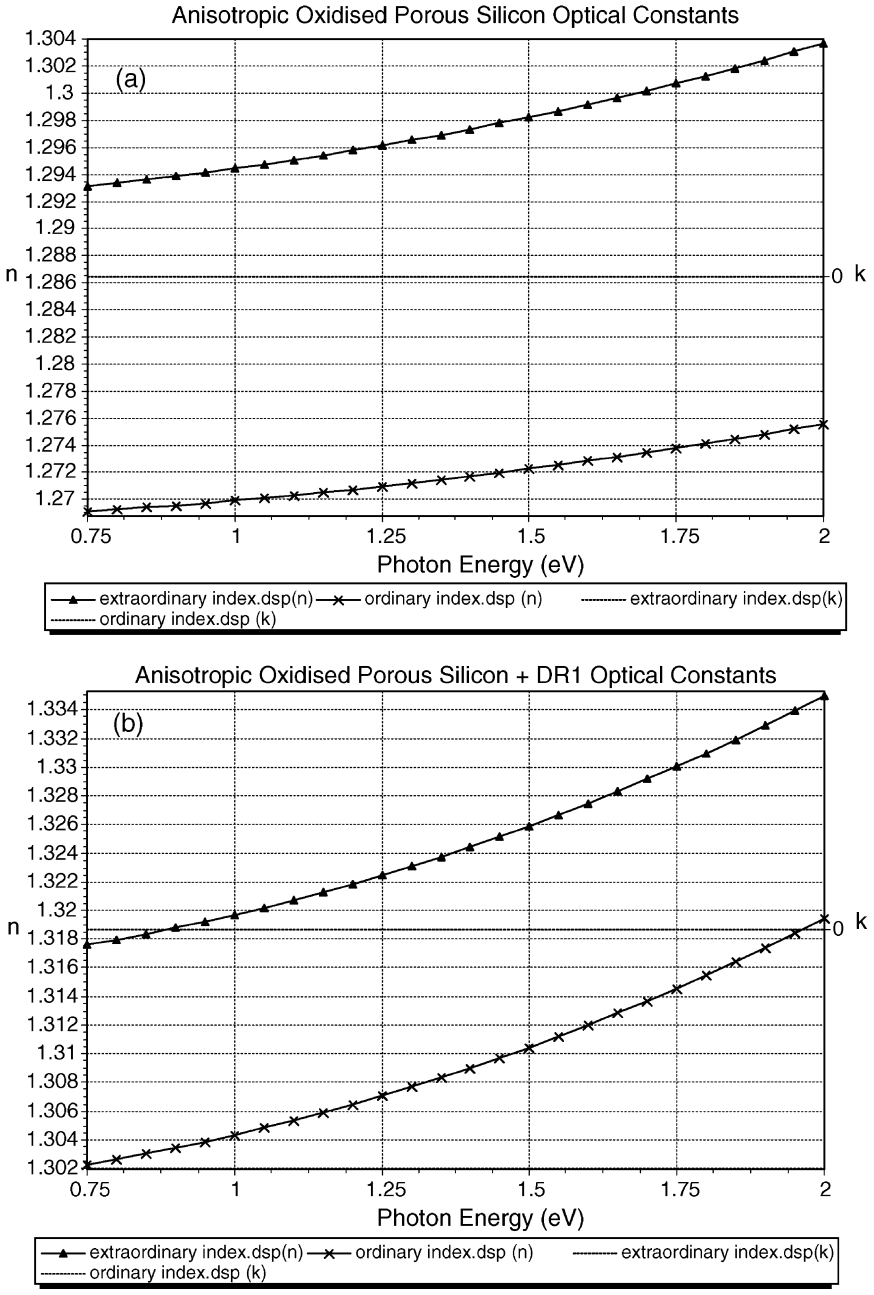

Fig. 4. (a) Complex refractive index ($n+ik$) for the oxidised porous silicon layer before filling by DR1. (b) Complex refractive index ($n+ik$) for the oxidised porous silicon layer after filling by DR1.

obtained by spectroscopic ellipsometry for a layer of a PMMA-DR1 mixture at 8% DR1 concentration. We can see the strong extinction coefficient peak centred approximately 2.4 eV, characteristic of the DR1 absorption range.

A three layer model accurately describes the oxidised porous silicon sample (without and with DR1). It takes into account a dense SiO_2 interface and also a surface roughness described by a mixture of 50/50 void and film material based on the effective medium approximation. The optical constants of the oxidised porous silicon layers are displayed on Fig. 4a,b, respectively, without DR1 and with DR1. From these two spectra, an estimation of the filling rate has been carried out via the Bruggeman model, which in this case is approximately 3.8%.

Finally, the effect of poling post-treatment (performed by static electrical field equal to 1000 V/50 μm) was tested on DR1 molecules. This treatment tends to align DR1 molecules perpendicularly to the surface [12]. It is worth noticing that all the experimental spectra are the same ones after a 90° sample rotation around the normal

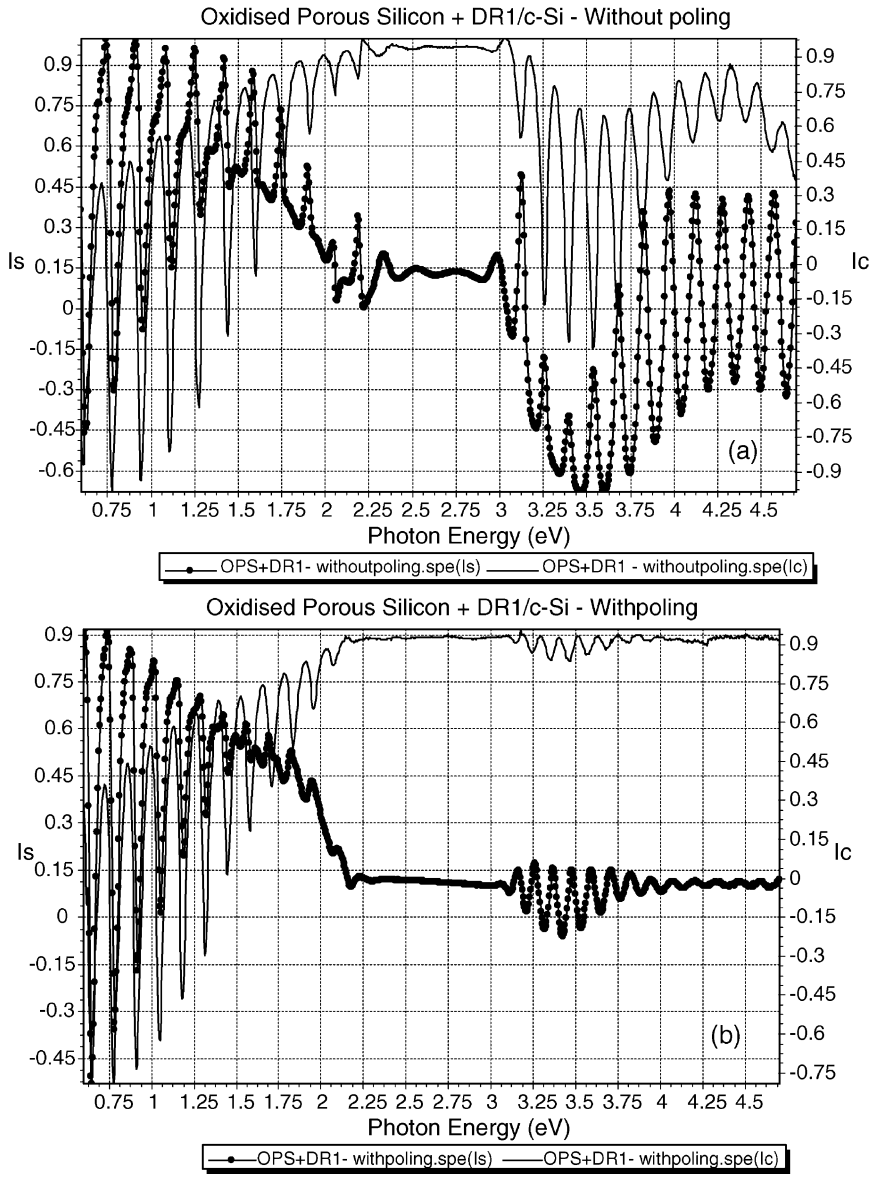

Fig. 5. (a) Spectroscopic measurements $(I_s, I_c) = f(E)$ for an oxidised porous silicon layer on a P-doped silicon substrate filled by DR1 before poling by a static electrical field. (b) Spectroscopic measurements $(I_s, I_c) = f(E)$ for an oxidised porous silicon layer on a P-doped silicon substrate filled by DR1 after poling by a static electrical field.

to the surface, pointing out the normal as a symmetry axis. Fig. 5a,b provide a comparison of the composite material spectroscopic measurements before and after poling post-treatment, respectively. One can observe the effect of poling on the widening of the DR1 absorption range. But at this stage additional analyses are necessary to extract the optical properties of the composite material with poling post-treatment.

3. Conclusion and perspectives

Complete characterization of the composite material process was successfully carried out by spectroscopic ellipsometry. Accurate determination of the composite porous silicon layer optical constants has been performed in the NIR–VIS range in order to investigate the non-linear properties of the material.

Preliminary results have shown the spectroscopic ellipsometry sensitivity to the extinction coefficient anisotropy, which characterise the DR1 molecular orientation.

However, additional work is necessary to accurately characterize the effect of poling on optical properties. Correlation between poling, optical properties and second harmonic experiments will be investigated in the next future with the aim to reach a detailed description of the film mesostructure.

Acknowledgments

The authors wish to thank Dr. R. Benferhat from Jobin Yvon SAS for his interest in this work, Dr. M. Stchakovsky and Dr. R. Ossikovski for helpful discussions. The authors also wish to thank the Conseil Régional de Bretagne and the Conseil Régional des Pays de Loire for financial support.

References

[1] J. Ziss (Ed.), Molecular Nonlinear Optics: Physics and Devices, Academic Press, New York, 1994.
[2] O. Nuyken, C. Scherer, A. Baindi, A.R. Brenner, U. Dahn, R. Gärtner, S. Kaiser-Röhrich, P. Matusche, R. Kollefrath, B. Voit, Prog. Polym. Sci. 22 (1997) 93.
[3] M. Guendouz, N. Pédrono, R. Etesse, P. Joubert, J-F. Bardeau, A. Bulou, M. Kloul, Phys. Status Solidi (A) 197 (2) (2003) 414–418.
[4] D. Buttard, G. Dolino, D. Bellet, T. Baumbach, Mater. Res. Soc. Proc. 452 (1997) 437.
[5] D.A.G. Bruggeman, Ann. Phys. 24 (1935) 636.
[6] J. Charrier, E. Le Gorju, L. Haji, M. Guendouz, Low loss optical waves guides fabricated from oxidized porous silicon, J. Porous Mater. 7 (2000) 243–246.
[7] A. Yariv, P. Yeh, Optical Waves in Cristals, John Wiley and Sons (Ed.), 1984.
[8] I. Mihalcescu, G. Lerondel, R. Romestain, Thin Solid Films 297 (1997) 245.
[9] N. Künzner, D. Kovalev, J. Diener, E. Gross, V.Yu. Timoshenko, G. Polisski, F. Koch, Opt. Lett. 26 (16) (2001) 1265.
[10] S.E. Aw, H.S. Tan, C.K. Ong, J. Phys. Condens. Matter 3 (1991) 8213.
[11] R. Ulrich, R. Torge, Appl. Opt. 12 (12) (1973) 2901.
[12] M.A. Mortazavi, A. Knoesen, S.T. Kowel, J. Opt. Soc. Am. B6 (4) (1989) 733.