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Analysis of optical and thermal properties of thermally oxidized mesoporous silicon layers

D. Ben Hlel [a,*], I. Gaied [a], N. Sghaier [a,b], A. Gharbi [b], H. Fitouri [c], N. Yacoubi [a]

[a] Equipe photo thermique et composants électroniques (UR/99/13-22), Institut Préparatoire aux Etudes d'Ingénieurs de Nabeul (IPEIN), 8000 Merazka, Nabeul, Tunisia
[b] Institut des Nanotechnologies de Lyon (site INSA UMR 5270), Bât. Blaise Pascal, 7 Avenue Jean Capelle, 69621 Villeurbanne Cedex, France
[c] Unité de recherche sur les Hétéro-Epitaxies et applications, Faculté des Sciences de Monastir, 5019 Monastir, Tunisia

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ABSTRACT

In this paper we will report the evolution of optical and thermal properties of thermally oxidized mesoporous silicon layers. The samples were manufactured by the conventional electrochemical anodization. The modification process including thermally oxidized samples in dry oxygen at different temperatures and duration was conducted. After treatment, the products were characterized by Spectral Reflectance in the wavelength range of 200–1100 nm which served to exclude an important decrease of the optical loss with temperature and duration of oxidation. We noticed that thermal oxidation improved the absorption of the UV light and led to a significant decrease of the average reflectivity. The band gap energy was performed by the Photoluminescence spectroscopy under an excitation at 325 nm and showed a broad emission centered at around 2.1 eV for all the samples. Furthermore, thermal conductivity and thermal diffusivity were determined by Photothermal Deflection Technique by comparing the experimental curves of normalized amplitude and phase of the photothermal signal to the corresponding theoretical ones. It was also found that the increase of both temperature and time of the thermal oxidation process affect the thermal properties of these layers.

1. Introduction

Nowadays, the study of matter at the nanoscale is the subject of an increasing number of research works because of its technological advances in the development and characterization of nanomaterials. These miniaturization and performance requirements have forced the development of special materials. Particularly, the porous silicon (PS), whose pore size is of some nanometers and its unique properties [1], is a promising material. Regarding its pores dimensions, three categories are distinguished: microporous (structures in the scale of 1–2 nm), mesoporous (structures in the scale of 2–50 nm) or macroporous (structures scaling up to 50 nm) [2]. Since the first report of a strong visible photoluminescence in 1990 by Canham [3], this nanostructure has become a widely used material in optics [4], biochemistry [5], microelectronics [6] and photovoltaic applications [7]. In the last two decades, efforts have mainly been focused on the study of meso-PS. This major element in the porous materials family is of a particular interest thanks to the simplicity of its synthesis process [8] which allows us to easily vary the pore's shape and size, the porosity and the pore special arrangement. Despite its success, aging of PS is considered as the main disadvantage of this material: freshly prepared PS is hydrophobic and unstable because the Si-H_x groups of pores surface are very reactive during ambient air exposure. This hydride surface converts to a contaminated native oxide [9]. Characterization techniques need to take the metastability of the freshly anodized layers surface into consideration since the structural, optical and electrical properties of PS can consequently change with time upon exposure to ambient air [10,11]. That is why it is important to stabilize the surface of PS for many device applications. Various treatments can stabilize this surface. The two major methods proposed until now are either using Si–C bonds or Si–O bonds to replace Si–H bonds. As for the latter method, most of the researches use thermal oxidation process [12] which remarkably stabilizes the PS layer and this is confirmed by the photoluminescence spectra (PL) which are identical [13]. Despite the numerous process of oxidation, the effect at higher temperatures on PS structure has been little studied.

This paper reviews the effect of thermal treatments on optical and thermal properties of meso-PS layers after two steps of oxidation: a pre-oxidation at 300 °C during 1 h 30 min and an oxidation at two higher temperatures (800 and 1000 °C) for various durations. Concerning the optical properties, we used PL spectra to

* Corresponding author.
E-mail address: dhouhabenhlel@yahoo.fr (D. Ben Hlel).

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determine the band gap energy. Spectral Reflectance (SR) is used in the domain range from 200 to 1100 nm to investigate the optical loss of the PS guiding structures. Thermal conductivity and diffusivity measurements have been carried out by the use of Photothermal Deflection Technique (PTD), which is a non-contact and a non-destructive method.

2. Experimental details

2.1. Sample preparation

The PS monolayers were obtained from a p^+,<100> oriented monocrystalline silicon substrate using a conventional electrochemical anodization process with an ethanoic solution of 25% HF. For all samples, the applied current density and the etching time were fixed at 200mA cm^{-2} and 15 s, respectively. The thermal treatment to oxidize the PS layers is characterized by two steps. At first a pre-oxidation at 300 °C for 1 h 30 min to stabilize and preserve the porous nanostructure during annealing procedures at higher temperature [14,15]. The second step is to exhibit an oxidation at two higher temperatures, 800 and 1000 °C for various durations. The overall process of PS oxidations was performed in a standard oxidation furnace SEMCO under atmospheric pressure in dry oxygen. The specific features of realized PS samples are shown in Table.1.

2.2. Photothermal Deflection Technique

Photothermal Deflection Technique (PTD) was introduced by Claude Boccara et al. [16] in 1979. The present PTD measurements were carried out in the transverse probe geometry at room temperature. The experimental setup shown in Fig. 1, is described elsewhere [17,18]. It consists of heating the bottom side of a sample with a modulated excitation pump beam. The optical absorption of the sample will generate a temperature gradient in the sample and the surrounding fluid, then a refractive index gradient that deflects a probe laser beam (He–Ne) skimming the sample surface. The amplitude and phase of the deflected beam are analyzed thanks to a position photodetector sensor linked to a lock in amplifier. In the conventional PTD theory, the expression of the probe beam deflection is given by [19,20]:

$$\Psi = \frac{L}{n}\frac{dn}{dT}\sigma_f T_0 \exp(-\sigma_f z_0) = |\Psi| \exp(\omega t + \Phi) \quad (1)$$

where L is the sample width in the laser beam direction, n is the fluid refractive index (in our case the fluid is the air), z_0 is the distance between the probe beam axes and the sample surface, $\sigma_f = (1+j)/\mu_f$ and $\mu_f = (D_f/\pi f)^{1/2}$ is the thermal diffusion length of the fluid, D_f is the thermal diffusivity of the fluid and f is the modulated frequency of the heating beam. The amplitude $|\Psi|$ and phase of the probe beam deflection are given by:

$$|\psi| = \frac{L}{n}\frac{dn}{dT}\frac{\sqrt{2}}{\mu_f}|T_0| \exp(-\sigma_f z_0) \quad (2)$$

$$\phi = \frac{-z_0}{\mu_f} + \frac{\pi}{4} + \theta \quad (3)$$

For numerical analysis of experimental PTD spectra and with a sample composed of a substrate and a layer whose thermal properties are different from those of the substrate, two layer models of the photothermal signal was used. In the case of uniform heating, a one dimensional treatment of the thermal wave is sufficient. By assuming that the fluid and the backing are not absorbent, the heat equations in each medium: fluid, layer, substrate and backing (Fig. 2) are written as follow:

$$\frac{\partial^2 T_f}{\partial z^2} = \frac{1}{D_f}\frac{\partial T_f}{\partial t} \quad \text{if} \quad l_c \le z \le l_c + l_f \quad (4)$$

$$\frac{\partial^2 T_c}{\partial z} = \frac{1}{D_c}\frac{\partial T_c}{\partial t} - A_c \exp(\alpha_c z)(1 + \exp(j\omega t)) \quad \text{if} \quad 0 \le z \le l_c \quad (5)$$

Table 1
Preparation conditions of the samples.

Sample	Initial porosity (%)	Oxidation conditions
1	57	Pre-oxidation at 300 °C for 1 h:30
2	57	Pre-oxidation at 300 °C for 1 h:30 Oxidation at 800 °C for 2 h
3	57	Pre-oxidation at 300 °C for 1 h:30 Oxidation at 800 °C for 4 h
4	57	Pre-oxidation at 300 °C for 1 h:30 Oxidation at 1000 °C for 2 h

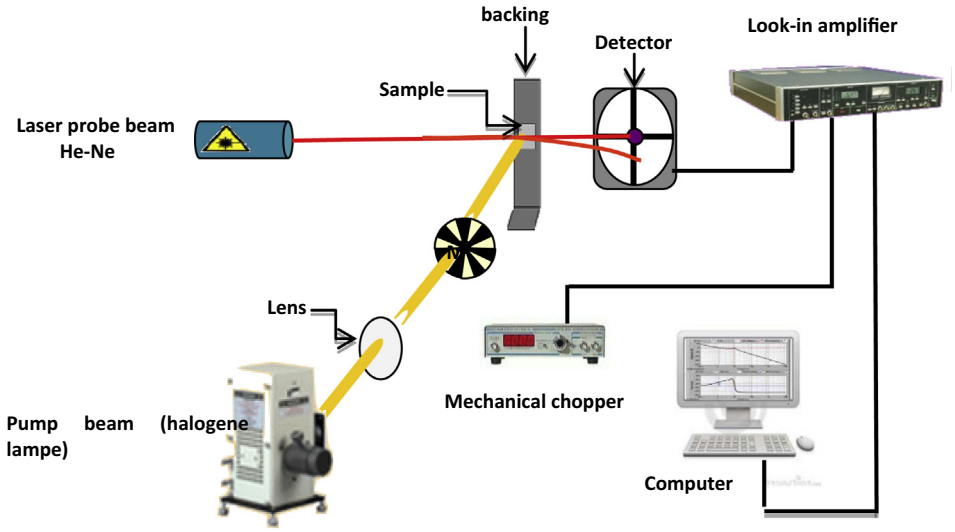

Fig. 1. PTD experimental setup.