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Photothermal deflection investigation of thermally oxidized mesoporous silicon

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ABSTRACT

In this paper we investigate the thermal oxidation effect on optical and thermal properties of meso-porous silicon (meso-PS) layers using photoluminescence (PL) and photothermal deflection techniques (PDS, PTD). Samples have been successfully prepared by electrochemical anodization process. After a pre-oxidation for 1 h 30 min at 300 °C, layers are thermally oxidized in dry oxygen at different temperatures (800, 1000 °C) and durations. PL measurements show that the annealed layers have comparable spectra with a peak position focused on 2.1 eV. This behavior indicates the formation of luminescent silicon (Si) nanocrystallites with comparable average sizes. From the effective mass theory, the diameter of those nanocrystallites is estimated to be around 2.2 nm. Another estimation of the mean size of the silicon nanocrystallites obtained from the evolution of the thermal conductivity of the meso-PS layers based on photothermal deflection technique (PTD) data was close to the values obtained from the PL results. Photothermal deflection spectroscopy (PDS) measurements show that the thermal oxidation affects the absorption edge of the Si substrate. The optical band gap energy of the started substrates determined from the Tauc's relation is observed to increase with the thermal temperature and duration. The possible origins of this shift are discussed.

1. Introduction

The term miniaturization is widely accepted in our vernacular as a positive step in product development. Reducing components to create less space and to fabricate novel micro-opto-electronic devices is the subject of many research works. Needless to say that the handling and assembly processes during the manufacturing of the electronic devices have to meet requirements of miniaturization as well. For those reasons, and considering porous silicon (PS) properties [1], this material has been therefore a natural candidate for miniaturization of many device applications [2] when starting from a Si substrate. After the curious result proposed by Canham [3] about efficient visible light emission from PS at room temperature, a considerable amount of work has been done to study the properties of porous materials.

This candidate which is a top-down material is produced by etching pores in crystalline Si has a thermal conductivity of about 2 or 3 orders of magnitude lower than that of bulk Si crystal [4]. This is due to its porosity, to phonon scattering on the surface of pores and increased phonon – phonon scattering caused by its nano-scale structure. Its low thermal conductivity [5,6], combined with easy fabrication on Si substrates make PS a good material for thermal insulation in MEMS (micro-electro-mechanical systems) and sensors. Reduced optical losses from front side [7,15], increased band gap energy [8], and ballistic transport [9] are just a few examples of the peculiar properties of PS nanocrystals size in the order of a few nanometers. By way of background and according to the International Union of Pure and Applied Chemistry (IUPAC) guidelines, the PS have been classified depending on the pore sizes as microporous (<2 nm), mesoporous (2 – 50 nm) and macroporous (>50 nm) [10].

Today PS is in the scientific interests of many research teams around the world, attracting the attention of chemists [11], physicists [12], biologists [13] and doctors [14]. Although numerous papers concerning fabrications and physical – chemical properties of PS have been already published [15,16], effects of some fabrication parameters on morphological, optical and thermal properties of PS is not yet well established, due to the complexity of the processed materials [17]. However, it has been observed that the storage in ambient air causes oxidation; the Si partially turns into SiO_2, and consequently the properties of PS are changed [18].

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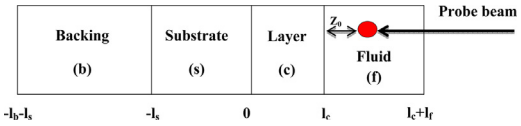

Fig. 1. Schematic representation of the different media.

Therefore, it is important to stabilize its surface. The two major common ways to stabilize the structure are the formation of oxide surface or addition of carbon atoms. Stabilized oxide layer can be achieved in several ways, e.g., by thermal oxidation, anodic oxidation or liquid phase oxidation [19]. These methods create oxide layers of varying thicknesses with varying densities of surface –H and –OH groups. Not only the surface chemistry is affected but also the pore structure changes due to the volume expansion as oxygen is incorporated into the crystal structure of Si [20]. It is very important and necessary to study the optical and thermal properties of PS after thermal annealing. Even if works have already been performed, a comprehensive approach of physical properties of thermally oxidized PS has to be going on to increase the performance in many device applications.

Therefore, we have attempted to explore the effects of heat treatment on the optical properties of meso-PS while temperature varying from 300 to 1000 °C. In order to get better insights in the relationships between these parameters, the meso-PS samples have been fully characterized by PTD and PDS and PL spectroscopy. We examine for the first time, to the best of our knowledge, the PDS behavior of the Si substrate after formation of oxidized PS layer. Our aim is a better understanding of the sample behaviors after passivation process.

2. Theory

The photothermal deflection technique or "Mirage Effect" technique was first introduced in the early 1980s by Bocarra, Fournier, Baldoz [21] and subsequently developed by Aamodt [22], Murphy [23] and by Jackson et al. [24]. This non-contact technique has been proved to be well suitable for investigation of optical and thermal properties of samples [12,25]. The basic phenomena of photothermal deflection technique consists on heating the sample with a modulated light pump beam that creates a thermal diffusion wave inside the sample and induces a temperature gradient leading to a refractive index gradient in the surrounding media of the sample. A probe laser beam skimming the sample surface is then deflected. The deflection is usually estimated by calculating the distribution temperature in the medium due to the heat transfer and then solving the propagation of the beam through an inhomogeneous medium.

For numerical analysis of experimental photothermal deflection technique 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, 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. 1) are written as follows:

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

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

$$\frac{\partial^2 T_s}{\partial z^2} = \frac{1}{D_s}\frac{\partial T_s}{\partial t} - A_s \exp\alpha_s(z+l_c)\exp(-\alpha_c l_c)(1+\exp(j\omega t)) \quad \text{if} \quad -l_s \le z \le 0 \tag{3}$$

$$\frac{\partial^2 T_b}{\partial z^2} = \frac{1}{D_b}\frac{\partial T_b}{\partial t} \quad \text{if} \quad -l_b - l_s \le z \le -l_s \tag{4}$$

where, $\alpha_i$is the optical absorption coefficient, D_i is the thermal diffusivity of the i medium and $A_i = \frac{\alpha_i I_0}{2k_i}$, i = c, s.

By applying the boundaries conditions of temperature and heat flow at different interfaces, one can deduce the expression of the surface temperature T_0 [26]:

$$T_0 = \frac{\begin{array}{c}E_s[(1+b)(1-r_s)\exp(\sigma_s l_s) - (1-b)(1+r_s)\exp(-\sigma_s l_s) \\ -2(b-r_s)\exp(-\alpha_s l_s)] + E_c[(1+b)(1-r_c)\exp(\sigma_s l_s) \\ -(1-b)(1+r_c)\exp(-\sigma_s l_s)][1-\exp(-\alpha_c l_c)]\end{array}}{[(1-g)(1-b)\exp(-\sigma_s l_s) - (1+g)(1+b)\exp(\sigma_s l_s)]} \tag{5}$$

where, $E_s = \frac{A_s \exp(-\alpha_c l_c)}{\alpha_s^2 - \sigma_s^2}$, $E_c = \frac{A_c}{\alpha_c^2 - \sigma_c^2}$ $g = \frac{k_f \sigma_f}{k_s \sigma_s}$, $b = \frac{k_b \sigma_b}{k_s \sigma_s}$, $r_s = \frac{\alpha_s}{\sigma_s}$, $r_c = \frac{\alpha_c k_c}{\sigma_s k_s}$ and k_i is the thermal conductivity of the i medium.

Generally speaking for our system, the beam deflection (Ψ) can be expressed as [12,25,26]:

$$\psi(z,t) = -\frac{L}{n_0}\frac{dn}{dT_f}\frac{\sqrt{2}}{\mu_f}\left|T_0\right| e^{\frac{-z_0}{\mu_f}} e^{j\left(\theta + \frac{\Pi}{4} - \frac{z_0}{\mu_f}\right)} e^{j\omega t} \tag{6}$$

where, L is the sample width in the laser beam direction, n_0 is the refractive index of the surrounding media at room temperature, $\frac{dn}{dT}$ is the change of n_0 with the temperature, $\mu_f = (D_f/\pi f)^{1/2}$ is the thermal diffusion length of the fluid, D_f is the thermal diffusivity of the fluid, f is the modulated frequency of the heating beam, and z_0 is the distance between the probe beam axis and the sample surface.

The amplitude $|\Psi|$ and phase Φ of the probe beam deflection calculated from Eq. (6) are given by:

$$\left|\psi\right| = \frac{L}{n}\frac{dn}{dT}\frac{\sqrt{2}}{\mu_f}\left|T_0\right|\exp(-\sigma_f z_0) \tag{7}$$

and

$$\phi = \frac{-z_0}{\mu_f} + \frac{\pi}{4} + \theta \tag{8}$$

3. Experimental details:

PS samples were fabricated by the conventional electrochemical anodization process of p^+ type Si (100) wafers with an ethanoic solution of 25% HF. The anodization time and current density were kept at 15 s and 200 mA cm^{-2} respectively, for all PS samples. To oxidize the PS layers, two steps of thermal treatment are used. The first step consist in a pre-oxidation at 300 °C for 1 h 30 min to stabilize and preserve the porous nanostructure during annealing procedures at higher temperature [27,28]. 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 conditions of the PS samples preparation employed in the present study and the oxidized fraction are summarized in Table 1.

The experimental PTD setup is described in detail elsewhere [12,42]. The sample under test is heated by a modulated light produced by a halogen lamp of 100 W powers. A probe laser beam (He – Ne) skimming the sample surface is deflected. This deflection is detected by a position photodetector linked to a lock in amplifier. The amplitude and phase of the photothermal signal are redden via an interface from the lock in amplifier and track their variation as a function of square root of modulation frequency using a LABVIEW software.

However for PDS (Fig. 2), we study the evolution of amplitude and phase as a function of wavelength, by incorporating a monochromator between the tungsten – halogen lamp (150 W) and