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Thermal and Optical Properties of Porous Silicon

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Thermal diffusivity and optical absorption have been investigated for porous silicon, at room temperature, using photoacoustic spectroscopy. The experimental results obtained conform well with the existing studies recently published. The value obtained for thermal diffusivity is 0.045 ± 0.002 cm^2/s.The absorption onsets show energy structures, differing from the ordinary semiconductor of bulk type. PACS 51.20.Td; 74.25.Fy; 73.20.Dy; 78.20.Wc; 81.40.Tv

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1. Introduction

Owing to the wide-ranging of possible technological applications in opto-electronic devices[1-27] and biocompatible materials as well[28-33], the interest in characterizing porous silicon (PS) has recently increased very much. Porous silicon has been studied intensively since the discovery by Canham[1], that even at room temperature PS can emit very bright photoluminescence (PL), in great contrast to crystalline silicon (c-Si). Usually, the PS samples are produced by anodic etching of c-Si wafers in hydrofluoric (HF) solution.

A large amount of investigations is devoted to the PL and absorption measurements of PS[1-6,8], but so far there has been a few reports on its thermal properties[7,17,18,34,35]. In this work we have devoted our attention to obtain, by applying the photoacoustic spectroscopy (PAS), the optical absorption and the thermal diffusivity, which is, as other optical properties, an important physical parameter to be considered in device modeling, specially for power dissipation. The PAS spectra are obtained directly from the heat generated in a sample, due to nonradiative absorption processes[36,37]. The fact that the PA signal depends on how the heat diffuses through the sample enable us to measure its thermal diffusivity[7,17,18,38]. The experimental PA setups, consisting of a periodically exciting light source, a photoacoustic cell containing the sample and a microphone are described in details in Refs. 37 and 38 for optical absorption and thermal diffusivity respectively.

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2. Experimental

The samples were produced by etching p-type c-Si wafers of crystal orientation (100) and resistivity 1-30 Ωcm eletrochemycally in 40% HF: ethanol 1:1. The electrolytic cell as well as the etching procedure are described in Ref. 5. Current densities from 5 mA/cm^2 to 25 mA/cm^2 were used and in each case, the current density was always kept constant during etching. Etching times were from 60 to 90 min, so that all samples consisted of a fairly thick layer of PS. Scanning force microscopy (SFM) investigation revealed a typical thickness of around 30 μm.

The SFM measurements were performed using a Digital Instrument Nanoscope III running in tapping mode. In this imaging mode, the SFM tip-cantileve oscillates sinusoidally at high frequencies (300 kHz) with amplitude 10-100 nm, so that the tip contacted the surface once during each period. The data were taken in ambient air at room temperature. The samples were stored in air for a long time (>> 1 month), so that surface oxidation had equilibrated. This implies that the surface structure is fairly reproducibly and does not change in time. Scans were made over areas from

500 x 500 nm to 20 x 20 μm with a resolution of 512 x 512 pixels and the scan rate of 1-2 Hz.

3. Results and Discussion

Figure 1 shows a typical SFM image of p-type PS sample produced with 60 min etching time. In Fig. 2 we show the PA spectrum of the same sample used for Fig. 1. Several spectral features are seen, revealing the complex band system originated from the surface roughness as shown in Fig. 1. The PA energies are respectively 1.603 ± 0.048, 1.668 ± 0.050, 1.751 ± 0.052, 1.882 ± 0.056, 2.025 ± 0.086 and 2.143 ± 0.064eV. Such structures have

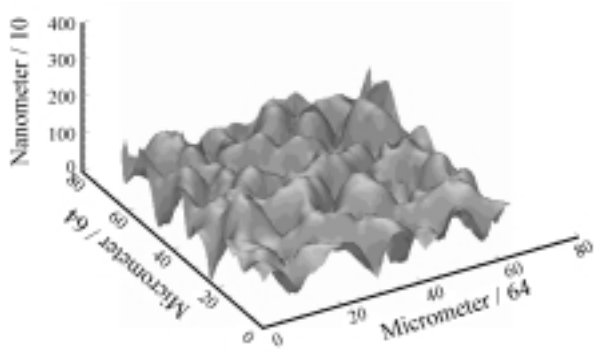

Figure 1. The SFM image of the PS sample. The axes units have been chosen in order to provide a better image presentation. Details in the text.

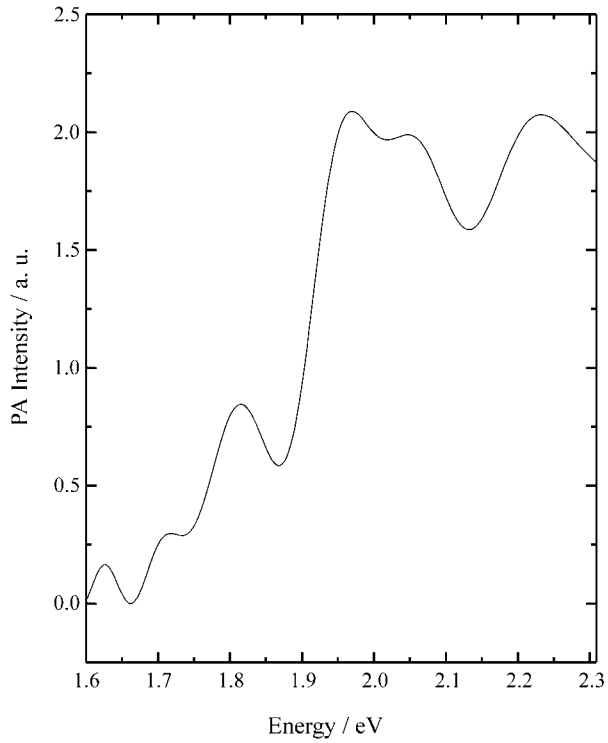

Figure 2. A typical PAS spectrum from a PS sample. The PAS signal is plotted versus the photon energy of the illuminating light. Same PS sample used for Fig. 1.

recently been confirmed by PL, photoluminescense excitation (PLE) and photocurrent measurements[21,26].

To measure thermal diffusivity, the acoustic signal produced in the gas cavity by the sample is detected by a Sunheiser condensed microphone and analyzed in respect to the modulator reference by a lock-in amplifier[38]. For the transmission arrangement, corresponding to the rear-side excitation of a thermally thick sample, the thermoacoustic phase contribution is given by the equation[38].

$$\Phi = \Phi_0 + \arctan \{L_s [(\pi/\alpha_s) f] - 1\}^{-1}, \quad (1)$$

where Φ_0 is the initial phase, α_s is the thermal diffusivity, L_s is the sample thickness (L_s = 530 μm), and f is the chopping frequency. These parameters are determined by a numerical least-squares fitting procedure. In Fig. 3 we show the rear-PA intensity as a function of the chopping frequency f for the PS sample. It is shown that the PA signal intensity S is proportional to f^{λ}, for our best set of measurements λ = -0.92. Figure 4 shows the chopping frequency dependence of rear-signal phase. The solid curve represents the best fit of the data to Eq. (1). The value obtained for the thermal diffusivity, at room temperature is $\alpha_s = 0.045 \pm 0.002$ cm^2/s. This value may be compared to $\alpha_s = 0.047$ cm^2/s and $\alpha_s = 0.053$ cm^2/s recently found[7,18] by Cruz-Orea *et al.*[7] and Calderón *et al.*[18], respectively, with open photoacoustic cell method. It is worthwhile to point out that there are some discrepancies between thermal conductivity values in the literature[7,17,18,25]. Like the thermal diffusivity, the thermal conductivity k is another important parameter to manufacturing devices. The

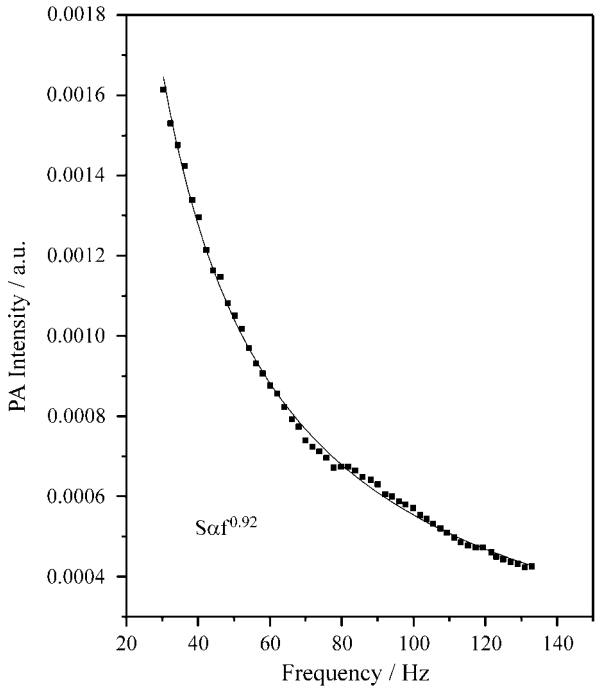

Figure 3. PAS intensity *vs.* chopper frequency for PS sample.

Table 1. Measured values of thermal diffusivity α_s and thermal conductivity k for porous silicon. In the fourth column k_{mean} stands for the computed average. The corresponding average of k for p-type samples is $\alpha_s = 0.032 \pm 0.018$ W/cmK.

Author	α_s (cm^2/s)	k (W/cmK)	k_{mean} (W/cmK) p-type	Sample type
Present work	0.045 ± 0.002	0.075	0.053 ± 0.022	p
		0.031		p
Cruz-Orea[7]	0.047	0.0074	-	n
Caldereón[18]	0.053 ± 0.0035	0.130	-	n
Amato[17]		0.025	0.032 ± 0.013	p
		0.039		p
		0.312		n
Shinoda[25]		0.0100	0.010	p

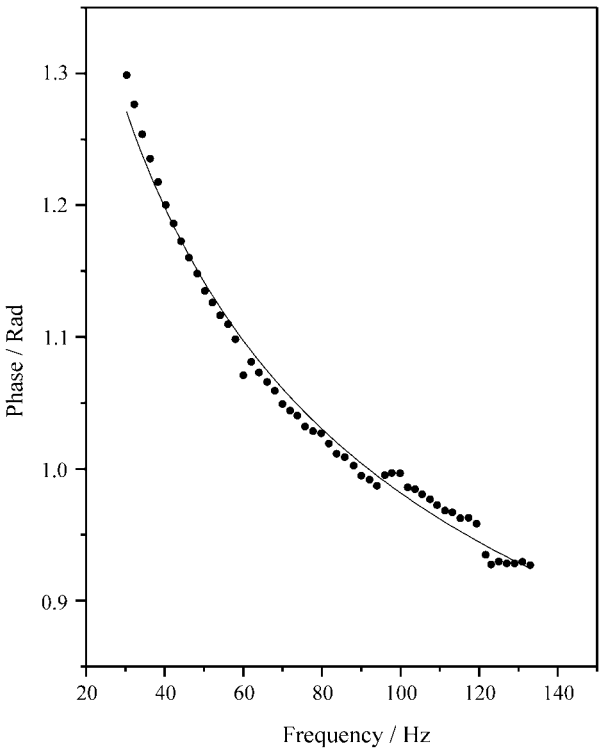

Figure 4. Chopper frequency dependence of the rear signal. The solid curve represents the best fit of the data to Eq. (1). The best value for the thermal diffusivity is $\alpha_s = 0.045 \pm 0.002$ cm^2/s.

measurement of α_s allows us to obtain k, once the density ρ and the specific heat C_v are know. We determine k by the relation $k = \alpha_s \rho C_v$. Cruz-Orea[7] with a spark-process PS found $k = 0.0074$ w/cmK and $\alpha_s = 0.047$ cm^2/s, Calderón *et al.*, with the usual eletrochemical etching process found $k = 0.130 \pm 0.006$ W/cmK and $\alpha_s = 0.053 \pm 0.0035$ cm^2/s respectively. They have used a n-type PS. Amato *et al.*[17], found, for p-type PS the values $k = 0.025$ W/cmK and $k = 0.039$ W/cmK respectively for two different samples, while a value of $k = 0.312$ W/cmK for a n-type PS. Shinoda *et al.*[25], with a thermally induced ultrasonic technique found $k = 0.01$ W/cmK. We may mention that Amato *et al.*[17], have used forheat capacity a value equal to that of c-Si. Using the heat capacity of c-Si, $C_v = 1.67$ J/cm^{3}K and of PS from Shinoda *et al.*[25]. $C_v = 0.7$ J/cm^{3}K we found $k = 0.075$ W/cmK and $k = 0.031$ W/cmK respectively. The results above confirm the good possibility for thermal insulation given by PS layers in contrast to c-Si, which has higher thermal properties, *i.e.*, $\alpha_s = 0.9$ cm^2/s and $k = 1.67$ W/cmK.

In summary, we have obtained through the PAS technique, the complex structure of the band gap energies and the thermal diffusivity of porous silicon. Several absorption features were observed from the PAS spectrum. The positions of these features were found in a range of energy $1.603 \pm 0.048 \leq E \leq 2.143 \pm 0.064$ eV. The thermal diffusivity result is 0.045 ± 0.002 cm^2/s, a value compared to other semiconductors of current technological importance[38]. The results conform well with the existing studies recently published, recognizing PS as a good material with potential to be used, for instance, thermal insulating layers and structures.

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