Application of photoacoustic spectroscopy in the study of optical absorption in n-type porous silicon

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Abstract

The application of the photoacoustic spectroscopy technique in the study of the optical absorption spectrum in samples of porous silicon n-type is reported. A spectral range of 250 to 800 nm and modulation frequencies of 200 Hz were used. The differential optical absorption spectrum obtained shows two significant absorption bands, one in the visible region and the other in the UV region, which is consistent with the quantum confinement model. These optical absorption remarkable properties give porous silicon a particular importance for its application as a photothermal material.

Keywords: Photoacoustic spectroscopy, optical absorption spectra, porous silicon, thermal waves.

Resumen

Se reporta la aplicación de la técnica de espectroscopía fotoacústica en el estudio del espectro de absorción óptico en muestras de silicio poroso tipo n. Se utilizó un rango espectral de 250 a 800 nm y frecuencias de modulación del haz monocromático de 200 Hz. El espectro de absorción óptico diferencial obtenido muestra dos importantes bandas de absorción, una en la región visible y la otra en la región UV, que es consistente con el modelo de confinamiento cuántico. Estas notables propiedades de absorción óptica dan al silicio poroso una importancia particular para su aplicación como material fototérmico.

Palabras clave: Espectroscopía fotoacústica, espectros de absorción óptica, silicio poroso, ondas térmicas.

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I. INTRODUCTION

Photoacoustic spectroscopy (PAS) is one of the most convenient techniques for non-destructive studies in materials [1] and has fewer obstacles than conventional optical spectroscopy. In PAS, the heat generated by nonradiative decays induced by the absorption of modulated monochromatic light incident on the sample, turns to sound and can later be detected by a sensitive microphone. In this way, the scattering of light is not a problem when we study dust samples because all the absorbed light becomes sound. Besides this, we can analyze the optical absorption spectrum at different depths of the sample [2].

The porous silicon is made from a crystalline silicon wafer by means of an electrochemical etching process in a hydrofluoric acid (HF) solution obtaining a sponge structure with columns and pores, in the micro and nano scale, interconnected with each other. Depending on the density and depth of the pores, different optical, thermal and electrical properties can be obtained, as well as forming p-n semiconductor junctions. Several studies have been reported on the formation of porous silicon showing the use of a variety of solutions and concentrations of HF to increase the formation of porosity, as well as the application of different exposure times and values of current density to the electrochemical process [3, 4].

Several studies have been reported on the modification of the electrical characteristics of transport of carriers in the porous layer due mainly to the considerable surface / volume ratio in this material, which is convenient for the application in sensors. Among the optical properties of porous silicon, luminescent efficiency represents the most important aspect for the development of devices as light emitters [5], however, the optical characteristics of porous silicon have also led to its use as photodetectors [6] and as antireflection layers for solar cells [7].

Even though today there is an advanced knowledge about diverse properties of porous silicon, studies in the literature

on the optical absorption properties of this material are scarce. This work contributes to the knowledge in this important aspect, taking advantage of the important benefits provided by photoacoustic spectroscopy over conventional techniques, especially in the attempt to use porous silicon as photothermal material in the use of solar energy, where high values of optical absorption are desirable in the visible region of the electromagnetic spectrum.

II. EXPERIMENTAL PROCEDURE

The porous silicon samples were prepared by electrochemical etching on (100) oriented, nondegenerated, *n*-type (2.1 x 10^{18} cm^{-3}) crystalline silicon. The samples had an electrical resistivity of 1-5 Ω *cm* and a thickness of 300 μm. The crystalline samples, with an appropriate platinum network electrode attached to them, were immersed in a 150 *ml* Becker filled with fluoridric acid. A current density of 40 mA/cm^2 was then applied to the sample using a dc power supply operating between 5-10 *V*. During the etching period (60 min) the samples were always kept under irradiation of a 250 *W* infrared lamp positioned 20 *cm* away from the etching bath. Figure 1 shows a scheme of the elaboration process and figure 2 shows a side view optical micrograph of a typical n-type porous silicon sample.

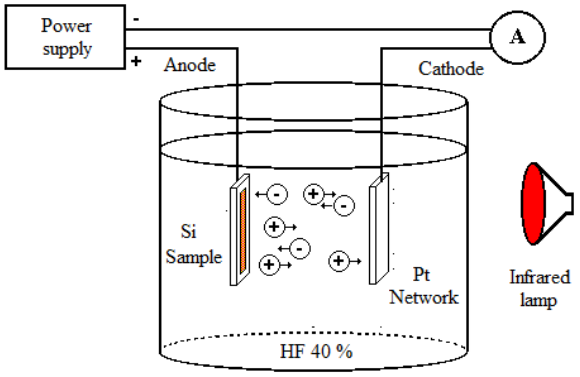

FIGURE 1. Experimental arrangement for the formation of porous silicon from n-type crystalline silicon.

In the photoacoustic spectroscopy technique the continuous beam of white light emitted by a Tungsten Lamp (Spectra Physics 66921) operating at 700 W is intensity modulated at a fixed frequency of 17 Hz with a mechanical chopper (Oriel 75159) after it passes through a monochromator (Spectra Physics 74000) with 1200 lines/mm diffraction grating in order to obtain monochromatic light in the spectral range from 1.5 to 4.5 eV. The light is focused, using an optical quartz fiber onto the quartz window of the photoacoustic cell, in which the sample to be studied was placed. The signal that emerges from the cell is then send to a Lock-in amplifier (SR-850) synchronized at the modulated frequency, where it is measured, and a personal computer is used for the storage and processing of the data that is acquired through an electronic card GPIB (General Purpose Interface Bus), which is controlled by a virtual instrument developed with programming of LabView software of National Instruments. Figure 3 shows the scheme of the photoacoustic spectroscopy technique.

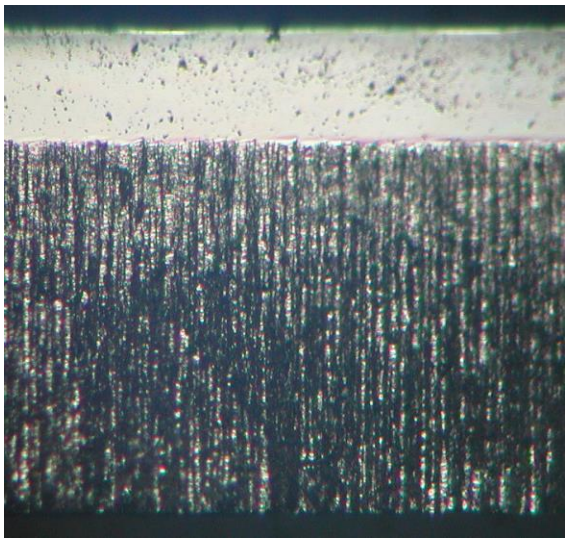

FIGURE 2. Optical microscope side view of cleaved n-type porous silicon sample etc held during 60 min. The thickness of the sample is 300 μm.

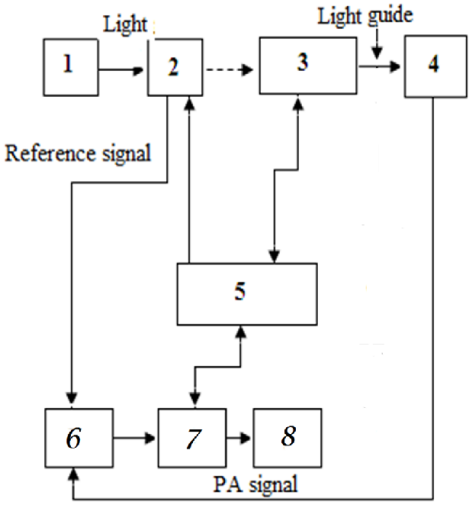

FIGURE 3. Experimental setup of the photoacoustic spectroscopy technique. (1) Xenon lamp, (2) chopper, (3) monochromator, (4) photoacoustic chamber + sample, (5) interface, (6) lock-in amplifier, (7) computer, (8) graph.

III. RESULTS AND DISCUSSION

Figure 3 and 4 show the amplitude and phase of the photoacoustic signal versus the wavelength, respectively, using a graphite as analysis sample. The shape of the

spectrum of Figure 3 contains information on the characteristics of the optical response of the system, that is, the xenon lamp, the focusing lens system, the optical fiber and the photoacoustic cell window. For each given sample, the spectrum obtained must be normalized with that of figure 3 to eliminate the optical response of the system and obtain exclusively the optical response of the sample under study.

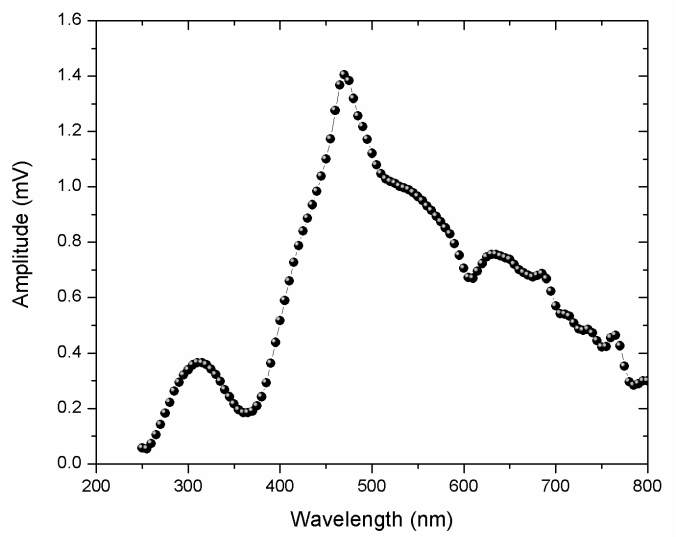

FIGURE 3. Amplitude versus wavelength of the photoacoustic signal using a graphite as analysis sample.

Figure 4 shows the flat behavior of the photoacoustic phase versus wavelength with the graphite as analysis sample. The flat shape is the one expected for a sample that behaves as a black body to the incident radiation.

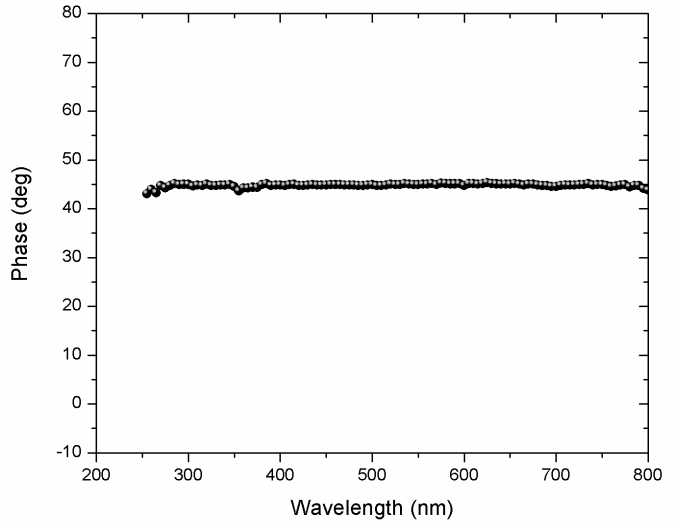

FIGURE 4. Phase versus wavelength of the photoacoustic signal using a graphite as analysis sample.

Figure 5 shows the differential photoacoustic spectrum of n-type porous silicon sample with 60 min of electrochemical attack, obtained using the spectrum of the crystalline silicon substrate as a reference. The presence of a remarkable absorption band is observed in all the visible region of the spectrum and another minor in the ultraviolet region centered roughly in 4 eV. The spectrum obtained is consistent with the quantum confinement model. The size of the remaining silicon nanoparticles in the porous layer is so small that porous silicon can be considered as a direct band gap semiconductor [8].

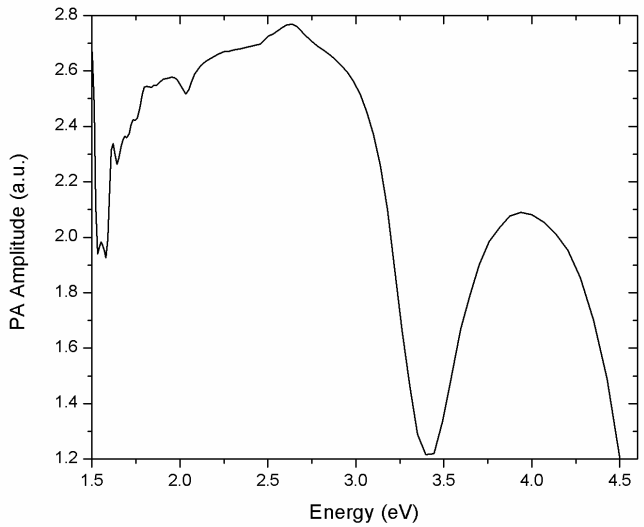

FIGURE 5. Differential photoacoustic spectrum of n-type porous silicon sample with 60 min of electrochemical attack.

V. CONCLUSIONS

The advantages provided by photoacoustic spectroscopy make it particularly useful for samples that are powdered, gels, or amorphous, being the last one the case of porous silicon. The photoacoustic response reveals two significant absorption bands, one in the visible region and the other in the UV region, which is consistent with the small size of the remaining silicon nanoparticles in the porous layer and to the quantum confinement model.

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