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PHOTOACOUSTIC TECHNIQUE FOR MEASURING BAND-GAP ENERGY OF POROUS SILICON LAYER ON n-Si SUBSTRATE.

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ABSTRACT

The porous silicon layer was prepared on n-type Si wafers using electrochemical-etching method. The current density was varied from 16 mA/cm^2 to 40 mA/cm^2. The surface morphology measured using SEM confirms the formation of porous layer on the silicon substrate. The photoacoustic (PA) absorption band and optical band gap energy were determined from PA signal intensity spectra measured at three different modulation frequencies (i.e. 15 Hz, 23 Hz and 33 Hz). The absorption band and energy gap of porous silicon gradually shifted towards higher energy region as the increase of current density thus confirming the porosity dependence of band gap on sample porosity.

INTRODUCTION

Porous silicon (PSi) has emerged as a promising material for fabrication of optoelectronic devices since the discovery of its room temperature photoluminescence effect. The development of PSi has initiated a considerable effort in order to characterize and understand the optical and physical properties of the light emitting material (Canham 1990; Loni et. al. 1994).

Photoacoustic (PA) spectroscopy is a photothermal method, which provides direct information of non-radiative de-excitation energy channels in materials. Measurements of optical absorption spectra using conventional method could only be performed on freestanding films of PSi layer. However, freestanding PSi layer can only be produced by supplying current density as higher as (500 - 1000) mA/cm^2 and substantially distorted the luminescence properties of PSi. The advantage of PA technique over conventional transmission studies is that the optical absorption spectra of PSi layer and Si substrate could be simultaneously measured by adjusting the thermal diffusion length. This can be done by monitoring photoacoustic signals at different modulation frequencies. Thus, the optical properties of PSi layer can be characterized without removing the porous layer from the substrate (Rosencwaig and Gersho 1976; Rosencwaig 1980). Therefore the objective of this paper is to demonstrate that the photoacoustic measurement carried out at three chosen modulation frequency can be used to measure the energy gap of both, porous layer and silicon substrate simultaneously.

MATERIALS AND METHOD

Porous silicon layer was prepared by electrochemical etching on phosphorous-doped (10 - 20) Ωcm n-type silicon (n-PSi) silicon wafer. An electrolyte mixture of hydrofluoric acid (HF) and ethanol (1:1 by volume) was used with etching time of 20 minutes. In the present work the n-PSi samples were prepared at five different anodization current densities i.e. (16.98, 22.64, 28.29, 33.96 and 39.62) mA/cm^2. After etching, the PSi sample was rinsed in distilled water for 10 minutes to avoid superficial cracks. In order to stabilize the properties of the porous silicon, the samples were dried in air and stored in the dark for 24 hours prior to the PA measurements. The photoluminescence (PL) measurements were carried out to confirm the formation of the porous layer on the surface of Si substrate. The energy gap measurement were done by recording the photoacoustic (PA) signal as a function of excitation energy. The experimental set up for PA measurements was similar to the one described by Toyoda et al. 2000a. The energy gap of the samples was determined by the following equation.

$$(Ih\nu)^{1/2} = A(h\nu - E_g) \quad (1)$$

where h is the Planck's constant, ν and I represent the frequency of light and the PA signal intensity, respectively. E_g and A are band gap energy and material coefficient (Da Silva et al. 1995; Toyada et al. 2000b).

RESULTS AND DISCUSSION

Figure 1 depicts the PL spectra of n-PSi samples while Figure 2 shows the normalized PA signal intensity spectra obtained at modulation frequencies of 23 Hz and 33 Hz. It could be observed that the PA spectra exhibit a broad absorption band at lower wavelength region. The absorption peaks were located at 405, 402, 399, 395, and 392 nm respectively corresponding to current densities of 16.98, 22.64, 28.29, 33.96 and 39.62 mA/cm^2.

Figure 3 shows the $(Ih\nu)^{1/2}$ versus photon energy ($h\nu$) at modulation frequencies of 33 Hz and 23 Hz. At high modulation frequency (Fig 4a) which imply that the small thermal diffusion length of the photoacoustic signal was contributed by photon absorption in porous layer. However at lower modulation frequency (15 Hz.) the PA signal was contributed by Si substrate. The energy gap of n-PSi layers was determined in the higher energy region of 33 Hz and 23 Hz modulation frequency. The energy gaps are 1.70, 1.74, 1.78, 1.82 and 1.86 eV for n-PSi samples fabricated at current densities of 16.98, 22.64, 28.29, 33.96 and 39.62 mA/cm^2, respectively. These values are higher than the energy gap of Si substrate (E_g = 1.11 eV) and exist in the visible luminescence region (Toyoda et al. 2000b). In the lower energy region the PA signal measured at 15

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Hz and 23 Hz posses energy gap values of 1.11 eV, which is due to the energy gap of Si substrate (Todorovic et al. 2001; Marin et al. 2001).

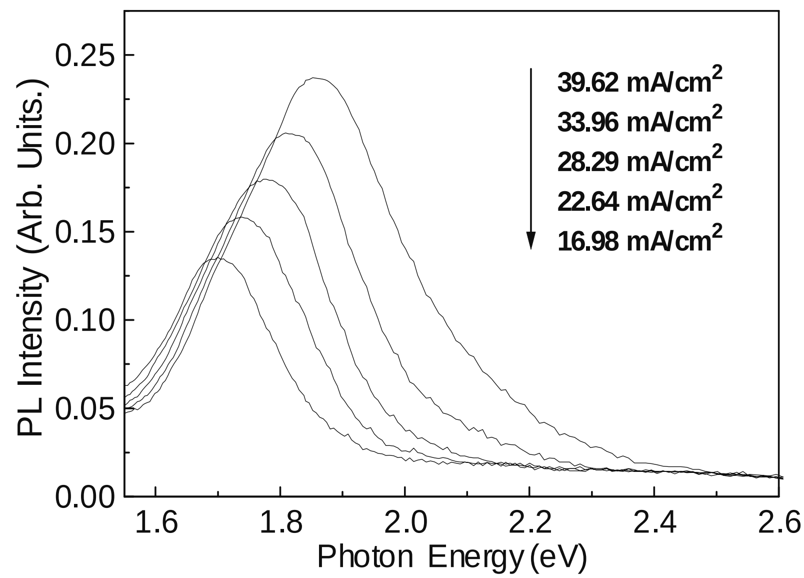

Figure 1: Photoluminescence (PL) spectra of n-PSi samples prepared at different current densities.

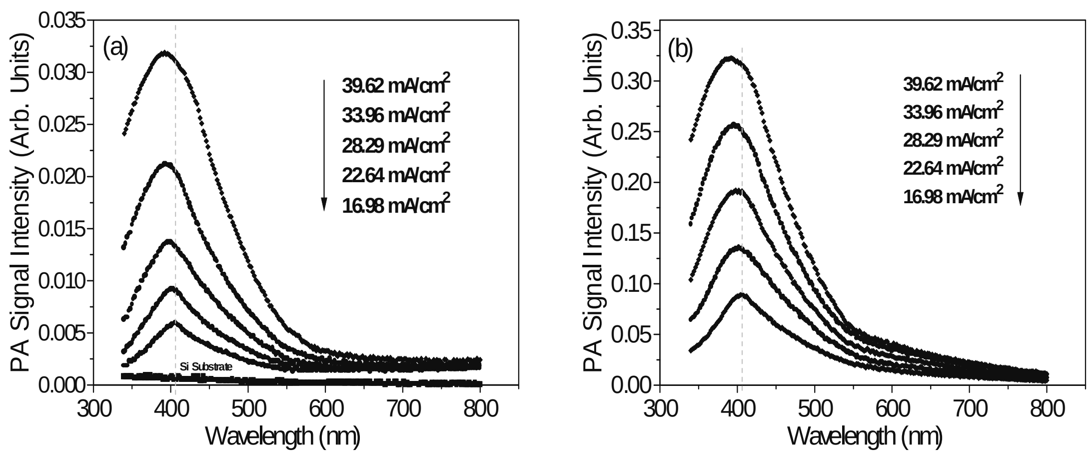

Figure 2: Normalized PA signal intensity spectra of n-PSi samples (a) 33 Hz and (b) 23 Hz.

The $(Ih\nu)^{1/2}$ versus photon energy ($h\nu$) measured at modulation frequency of 15 Hz is shown in Figure 4. This signal was entirely contributed by the Si substrate in which the energy gap was determined as 1.11 eV.

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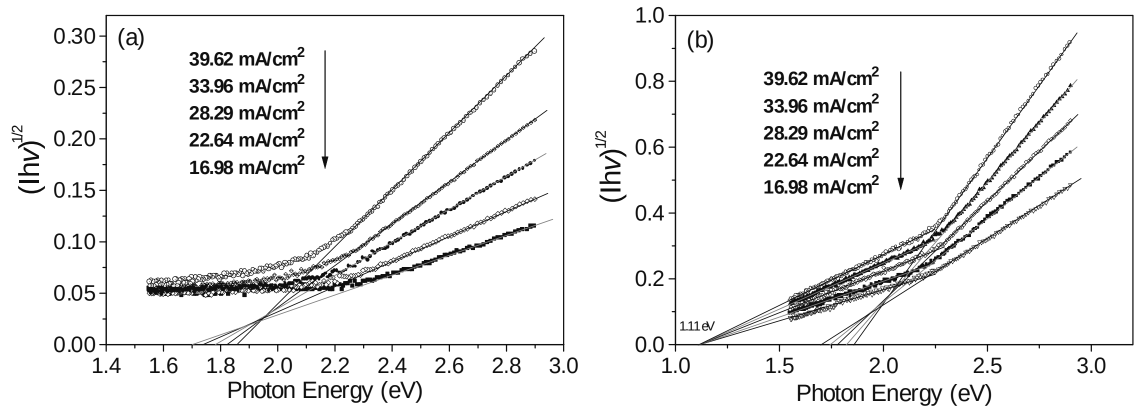

Figure 3: $(Ih\nu)^{1/2}$ versus photon energy for n-PSi samples measured at modulation frequencies of: (a) 33 Hz and (b) 23 Hz.

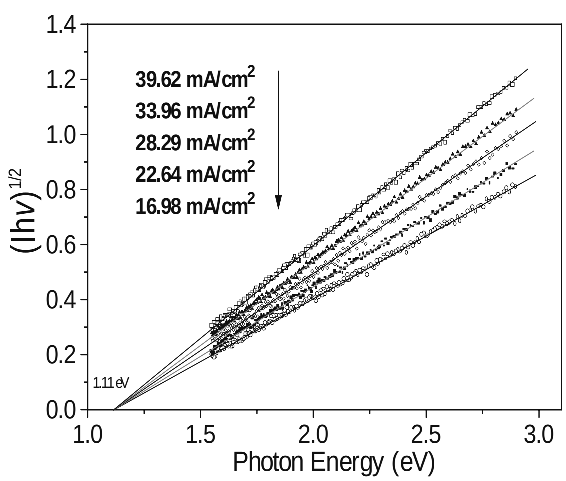

Figure 4: $(Ih\nu)^{1/2}$ versus hν collected at chopping frequency of 15 Hz.

Figure 5 shows the dependence of energy gap on porosity for the n-PSi samples measured at three different modulation frequencies, 15 Hz, 23 Hz and 33 Hz. This implies the energy gap of n-PSi layer could be obtained at higher modulation frequencies i.e 23 Hz and 33 Hz. which increases with the increasing of surface porosity. The gradual blueshift of energy gap towards higher energy region is due to the enhancement of luminescent Si-oxygen bonds impregnated inside the enlarged micropores at higher porosity (Canham 1990; Smith and Collins 1992; Hipwell and Tien 1999). This phenomenon was confirmed from SEM micrographs and EDX spectra of the samples.

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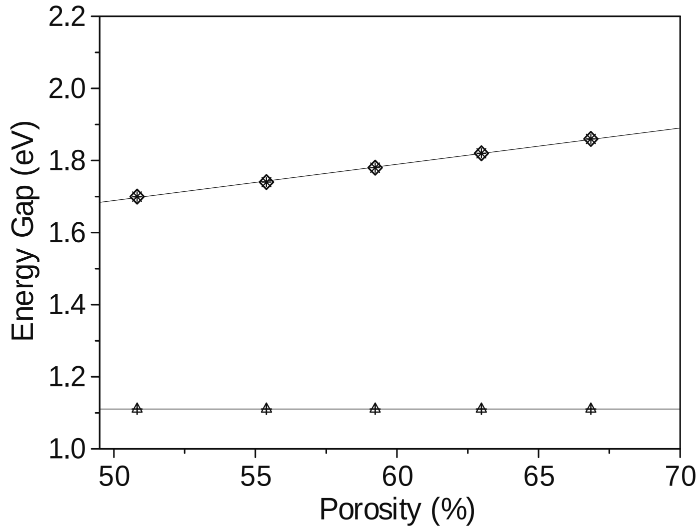

Figure 5: Porosity dependence of energy gap measured at modulation frequencies of 33 Hz (◇); 23 Hz (✳) 15 Hz (△) .

CONCLUSION

The PA technique has been used to determine the optical absorption band and energy gap of porous silicon prepared on silicon substrate (n-PSi). The broad optical absorption band was observed on PA signal intensity spectra at lower wavelength**.** The energy gap values of n-PSi layer are determined at modulation frequency of 23 Hz. and 33 Hz, whereas the energy gap of silicon substrate (i.e. 1.11 eV) was determined at 15 Hz. and 23 Hz. The energy gap of n-PSi were blueshifted gradually against sample porosity as the increase of anodization current density.

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