Optical absorption of free-standing porous silicon films

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The optical absorptions of anodically etched p^+ and n^+ porous silicon (PS) films were investigated by photothermal deflection spectroscopy. Si–H stretching overtones and combination bands of Si–F and Si–H were observed. The defect model in hydrogenated amorphous silicon was used to explain the Urbach edge and the subgap absorptions of PS. The dangling bond defect densities in PS were estimated. © *1996 American Institute of Physics.* [S0021-8979(96)03106-1]

I. INTRODUCTION

Visible photoluminescence (PL) from porous silicon (PS) has generated widespread interest because of the potential application of PS in Si-based optoelectronic technology. Experimental techniques such as transmission measurements, PL, and photothermal deflection spectroscopy (PDS) have been applied to investigate the optical properties of PS.[1–8] PL provides information of radiative recombination of photoexcited carriers while PDS provides complementary information of nonradiative recombination. Transmission measurements have also been used to study the optical properties of PS,[3] but, due to the lack of sensitivity, only blue shifts in the energy gap can be deduced.[4] In contrast, PDS is sensitive to small optical absorption and is capable of measuring the subgap absorption of PS.[5,6] In this study, PDS was applied to investigate the Urbach slope and band tail absorption of PS which are expected to relate strongly to defects in PS.

II. EXPERIMENT

Free-standing porous silicon films were prepared by anodic etching of (100)-oriented boron- and phosphorus-doped (0.01 Ω cm) silicon wafers for 30 min in a HF(48%)–ethanol mixture (3:1 by volume). The current densities were in the range 5–100 mA/cm^2. The PS films were then detached from the substrates by electropolishing under a HF:ethanol mixture (1:7 by volume) with a current density of 0.5 A/cm^2. All PS films were rinsed in ethanol and dried in atmosphere. Film thickness d was determined by scanning electron microscopy (SEM) while the porosity P was determined by gravimetry (sensitivity of 0.01 mg). Free PS films of thickness 10–180 μm and porosities 33%–75% were obtained.

The optical absorption spectra of free-standing PS films were measured by PDS from 0.5 to 1.5 eV. The principle of operation of PDS is well documented.[9] The measurements were carried out with a standard setup consisting of a 1 kW Xe arc lamp and a 1/4 m grating monochromator (Oriel) with selective long-pass filters as a tunable light source.[10] The pump beam was modulated at 23 Hz by a mechanical chopper before irradiating on the sample cell. Carbon tetrachloride was used as the deflecting fluid. A HeNe laser (Uniphase) was directed parallel to the surface of the PS films as the probe laser. A quadrant cell (United Detector Technology) was used as the position sensor for monitoring the photothermal deflection signal which was fed into a lock-in amplifier (Stanford Research Model SR830) for phase-sensitive measurements. All PS films absorption spectra were taken immediately after sample preparation.

III. RESULTS AND DISCUSSION

PDS spectra were normalized to the power spectrum of the pump beam, and were then calibrated by matching the absorbance to absorption coefficients obtained by transmission measurements at large photon energies. The absorption coefficient (α), after correcting for reflection loss, is deduced by solving α in the equation

$$T=\frac{(1-R)^2\,\exp(-\alpha d_{\mathrm{eff}})}{1-R^2\,\exp(-2\alpha d_{\mathrm{eff}})}, \tag{1}$$

where R is the reflectivity and $d_{\mathrm{eff}}=(1-P)d$ is the effective sample thickness. The reflectivity was calculated from the Fresnel equation using the refractive index of PS, n_{PS}, which is approximated by[11]

$$n_{\mathrm{PS}}(E)=P+(1-P)n_{\mathrm{Si}}(E). \tag{2}$$

The absorption spectra of p^+ PS and n^+ PS are shown in Figs. 1 and 2, respectively. The absorption spectra of crystalline Si are also included in the figures for reference. Gradual blueshifts of the fundamental absorption edge (at 1.1 eV) for both p^+ PS and n^+ PS with increasing porosity can be observed. The blueshifts of the absorption edge are in agreement with previous reports and were commonly attributed to quantum confinement effects associated with nanocrystalline structures in PS.[1,12] Moreover, intensive absorption peaks between 0.5–0.8 eV were observed in both p^+ PS and n^+ PS for porosities ranging from 33% to 42%.

The intense peaks in the absorption spectra can be assigned to the vibrational overtone absorptions of Si–H or Si–F. The vibrational absorptions can be described by transitions between anharmonic vibrational levels in a Morse potential. The vibrational energy level E_n is given by[13]

$$\frac{E_n}{hc}=\left(n+\frac{1}{2}\right)\nu_h-\left(n+\frac{1}{2}\right)^2 x\nu_h, \tag{3}$$

where n is the vibrational quantum number, ν_h is the fundamental vibrational frequency, and x is the anharmonicity coefficient. For the 0 to n transition, a linear plot of $\nu_{0,n}/n$ against n can be used to assign the spectral peaks.[13] Here $\nu_{0,n}$

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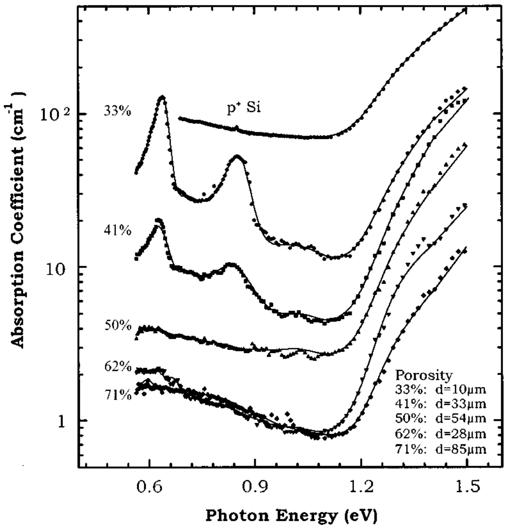

FIG. 1. Optical absorption spectra of p^+ porous silicon with different porosities.

is the absorption in cm^{-1}. Figure 3 shows the best linear fits to the vibrational overtones in Figs. 1 and 2. *The fitting parameters x for the 33%, 41% porosities p^+ PS, and 42% porosity n^+ PS are 0.096, 0.103, and 0.094, respectively. The fitting parameters describe how far the vibrational overtones deviate from a parabolic potential well.* In addition, the respective absorption peaks at 0.639 (5155 cm^{-1}), 0.626 (5051 cm^{-1}), for p^+ PS and 0.639 eV (5155 cm^{-1}) for n^+ PS can be assigned to the second vibrational overtone of Si–H. Similarly, the absorption peaks at 0.849 (6849 cm^{-1}), 0.827 (6667 cm^{-1}) for p^+ PS and 0.855 eV (6895 cm^{-1}) for n^+ PS can be assigned to the combination bands of Si–F stretching mode and the Si–H third overtone. The fundamental stretching modes of Si–F and Si–H are 914 and 2092 cm^{-1}, respectively.[14]

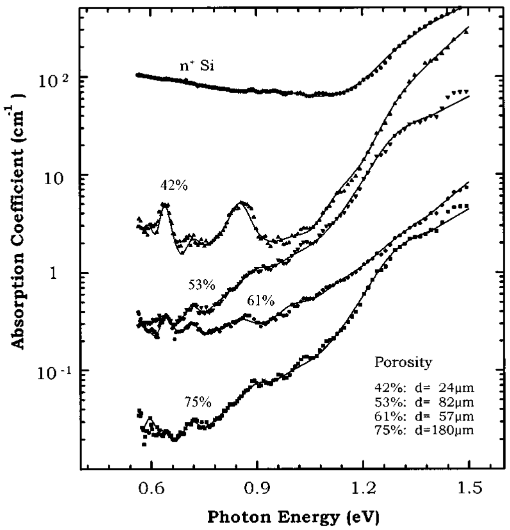

FIG. 2. Optical absorption spectra of n^+ porous silicon with different porosities.

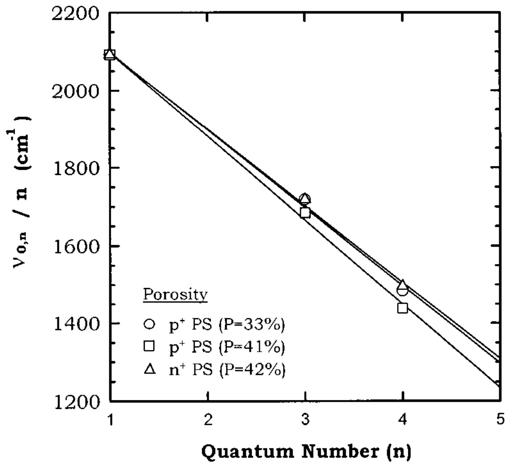

FIG. 3. Plot of $\nu_{0,n}/n$ against vibrational quantum number n.

A highly localized surface state of dangling bond defect was suggested by Koch *et al.* to explain PL in PS.[15,16] The dangling bond defects act as nonradiative recombination centers, and their energy levels are proposed to lie approximately in the midgap position. The defects in PS were suggested to be similar to the dangling bond defects in hydrogenated amorphous silicon (a-Si:H).[17,18] For example, it was demonstrated that in PS, there was an increase in subgap absorption after ultraviolet (UV) light irradiation.[16] The observation is quite similar to the light-induced metastable defect in a-Si:H.[17,19] Based on the similarity above, the correlation between the Urbach edge and the dangling bond defect density in a-Si:H is assumed to be applicable to PS. In a-Si:H, the density of dangling bond defects N_s is closely related to E_0, where E_0 can be determined by fitting the Urbach edge to the function $\alpha = a_0 \exp(E/E_0)$.[18] Experimentally, it was found that N_s is essentially proportional to $\exp(E_0/10 \text{ meV})$. Hence, defect densities in p^+ and n^+ PS can be estimated from E_0. According to Figs. 1 and 2, the values of E_0 are 76–100 meV for p^+ PS, and 151–170 meV for n^+ PS, respectively. The corresponding values of N_s are estimated to be 10^{17}–10^{18} cm^{-3} for p^+ PS and at least 10^{19} cm^{-3} for n^+ PS. The estimation of N_s are based on Fig. 1 of Ref. 19 where the correlation between the dangling bond densities and E_0 for a-Si:H were provided. The lowest dangling bond density for the D^0 state (neutral defect) in PS, determined by electron spin resonance (ESR), was reported to be 10^{16} cm^{-3}.[16] The disagreement is attributed to different preparation conditions and doping level of the anodically etched Si. In addition, ESR is insensitive to charged defects and hence only provides the lower bound for the total defect density.

Similar concentration of the dopants in p^+ Si and n^+ Si are expected to be present in p^+ PS and n^+ PS. For heavily doped crystalline Si, free-carrier absorption is observed for photon energies below the fundamental band gap with rising absorptions towards small photon energies. The absorption due to free carriers below 1 eV can be fit by a power law $\alpha \propto n \cdot E^{-\delta}$, where n is the carrier density and δ is a constant ranging from 1.5 to 3.5.[11,20] In Fig. 1, the subgap absorption of high-porosity p^+ PS films (below 1 eV) increases as photon energy decreases and exhibits the characteristic contribution to absorption due to free carriers. The contribution is in sharp contrast to the report that p^+ PS films, investigated by transmission measurements, did not show any free-carrier absorption and the free holes were assumed to be captured into trap states.[11] The inconsistency can be explained by higher sensitivity provided by PDS measurements in this study. *Absorption by free carriers in PS fabricated from 5 Ω cm p-type silicon wafers was also observed in photoinduced absorption measurements.*[21] Free-carrier absorption is not evident in n^+ PS as shown in Fig. 2. One explanation is that, since the density of dangling bond in n^+ PS is estimated to be much higher than that of p^+ PS, most of the free electrons are captured by deep levels relating to dangling bond states.

IV. CONCLUSIONS

The absorption coefficients of p^+ and n^+ PS films were measured by PDS. Blueshifts of the energy gap were observed. Stretching vibrations of Si–H overtones and combination bonds of Si–F and Si–H were assigned for the resonant absorption peaks. The defect models in a-Si:H were used to explain the Urbach edge and the subgap absorption of PS. Finally, the density of dangling bond defects in PS was deduced from the Urbach slope.

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