

Infrared photo-induced absorption spectroscopy of porous silicon

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The quantum confinement model, which assigns some of the luminescence features in porous silicon to size quantization in Si nano-crystallites, also predicts quantization of both the conduction and valence bands into sub-levels. In order to resolve this effect we have used a new experimental technique called "photo-induced infrared absorption spectroscopy". Here, a pump, visible laser, optically induces carriers in the conduction/valence band. Optical transitions between the quantized sub-levels are resolved by a probe, infrared beam in the energy range 50–300 meV. A broad photo-induced absorption signal has been observed in the 60–250 meV spectral range, in agreement with the prediction of the quantum confinement model. However, the photo-induced absorption signal decreases with the decreasing temperature, resolving activation energy of about 10 meV. This behavior can be understood if the allowed optical transitions are from the exciton singlet state only. Also, we found additional features in the photo-induced absorption spectrum that are correlated with the Si=O vibrational modes. Our results indicate a strong coupling between bulk excitonic states and surface states in small Si nano-crystallites.

1 Introduction The extensive research over the last decade on porous silicon (PS) structures is driven by the unique optical properties of PS, particularly the strong room temperature photoluminescence (PL) from PS that can be utilized for developing silicon based optoelectronic devices [1, 2]. However, despite many attempts to explore the origin of the luminescence from PS, this topic is not yet fully addressed. Presently, there are two main disciplines for explaining the origin of the PL: (1) Quantum confinement (QC) model [1, 3] that assigns the luminescence to radiative recombination of long-lived highly localized excitons in nanometer-size silicon crystallites. (2) Surface states model [4] that assigns the luminescence to localized states/centers on the surface or in an interfacial region between the Si crystallites and the host matrix. Deep or shallow surface states as well as chemical complexes such as siloxene and its derivatives [5–7] have been proposed as the source of radiative centers. At the present, none of the experimental techniques reported so far, has provided indisputable conclusion to the controversy regarding the origin of the luminescence.

In this work we describe a new experimental technique, based on photo-induced infrared absorption (PIA) spectroscopy, which can resolve the above puzzle. In brief, the QC model, which provides a nice explanation to the blue shift of the PL relative to that of bulk Si, also predicts the quantization of both the conduction and the valence bands of the Si nano-crystallites. In a dot-like model both the conduction and the valence bands are split into sub-levels. Apparently, inhomogeneous broadening due to distribution of sizes and shapes of the Si nano-crystallites is expected to significantly broaden the spectrum of optical inter-sub-level (ISL) transitions. We would like to emphasize that ISL transitions in quantum dots are a

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pure quantum confinement effect. In bulk Si with any complex surface structure or interfacial matrix there *should not* be a signature of these optical transitions.

There is, however, one important experimental aspect that should be addressed. Since PS is essentially an insulator, carriers (electrons and holes) are not available for optical ISL transitions. Therefore, we have used a pump-probe technique, in which a visible pump laser induces electron-hole pairs (excitons). Due to the long lifetime of the carriers, it is possible to populate many crystallites in the ground state of both the conduction and the valence bands. These carriers are now available for inter-sub-level spectroscopy and a second mid-infrared probe beam was utilized to detect the induced infrared (IR) absorption.

2 Experimental and results The PS layers were prepared by electrochemical etching of (100) 10–30 Ω cm, Boron-doped, Si substrates. Anodization was performed in a 1:1 solution of HF (48% wt.) and C_2H_5OH with a current density of 75 mA/cm². The anodization time was set to 30 seconds. This gives porous samples of 75%–80% porosity and 4 μ m in thickness. Next, the samples were rinsed in ethanol, dipped in pentane and dried with nitrogen gas blow. All the prepared samples were aged for 1 month in ambience before optical measurements, so that a certain degree of stability was achieved. The backside of the substrates was mechanically polished to allow infrared absorption measurements.

Direct IR spectroscopy was performed using a Perkin-Elmer 2000 Fourier Transform Infrared (FT-IR) spectrometer. For PIA measurements a pump-probe setup, with a pump Ar^+ ion laser operating at a wavelength of 488 nm (with a 4 mm diameter spot) and a probe IR beam from a blackbody source that is focused in a normal incidence geometry (to the PS surface), was utilized. The samples were placed in a cryostat where temperature was controlled between 4 K and room temperature. The IR beam was dispersed by a 1/8 m Oriel monochromator and detected by either InSb detector or HgCdTe detector, depending on the wavelength range. Spectra were recorded between 3 and 20 μ m. Either the pump or the IR beams were mechanically modulated, in order to measure photo-induced absorption or IR transmission spectrum respectively and the signal was recorded with a phase sensitive lock-in amplifier. This differential technique permits us to detect absorbance as low as 10^{-6} . The PIA spectrum taken at room

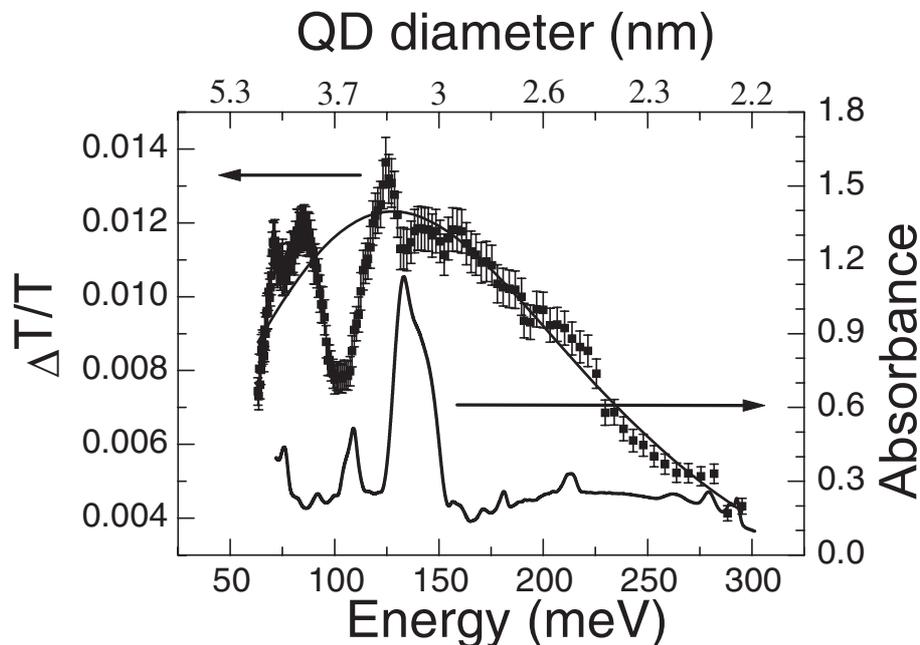


Fig. 1 Room temperature photo-induced absorption spectrum (squares) and linear absorbance of porous silicon layer. The upper scale corresponds to an approximation of inter-sub-level transitions in a spherical quantum dot (QD) with infinite barrier.

Table 1 Vibration modes recognized in the absorption spectrum of PS.

Si=O stretch	1220 cm ⁻¹	151 meV
Si-O-Si asym. stretch	1070 cm ⁻¹	133 meV
Si-O-H bend doublet	880 cm ⁻¹	109 meV
	840 cm ⁻¹	104 meV
Si-H _n bend (<i>n</i> = 1, 2, 3)	600 cm ⁻¹	74 meV

temperature together with the linear absorption spectrum is shown in Fig. 1. The optically induced differential transmission, normalized to the sample transmission gives directly the photoinduced absorbance as $\Delta T/T = 1 - \exp(-\Delta\alpha d) \approx \Delta\alpha d$ for small values of PIA, where $\Delta\alpha$ is the photoinduced absorption coefficient and d is the thickness of the PS layer.

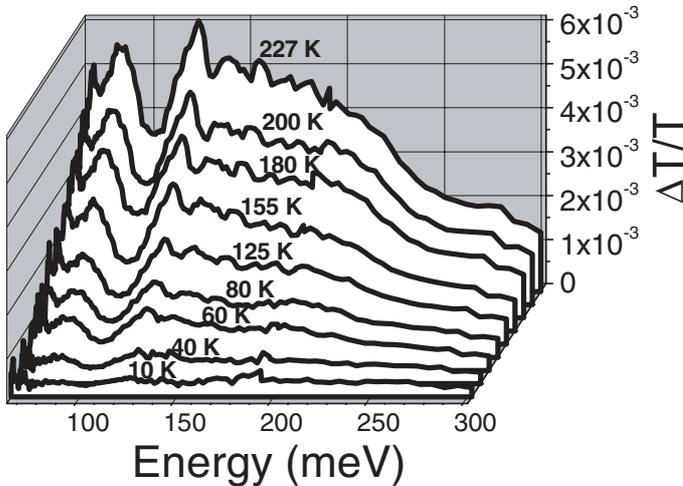
A very broad PIA signal is clearly distinguished in the spectrum of Fig. 1. The PIA gives a maximum at ≈ 150 meV and a linewidth of 100 meV with a strong asymmetric line shape. We attribute this line to ISL transitions inside the silicon nanocrystals. The width of the line is consistent with the expected inhomogeneous broadening due to a broad distribution of nanocrystal sizes present in the PS layer. In addition to a broad absorption line, some spectral features are observed in the low-energy part of the spectrum. These features are strongly correlated to the IR molecular absorption lines summarized in Table 1 [8]. This subject will be fully addressed in the following sections.

Photo-induced absorption spectra were recorded between room temperature and 4 K. Some of these spectra are shown in Fig. 2. A monotonic decrease of PIA is observed from room temperature down to 30 K. Fig. 3 shows a plot of the integrated PIA signal versus temperature. Three different regimes are recognized: below 30 K, no change of the integrated PIA is observed above the experimental error; from 30 K to 150 K a thermally activated process dominates PIA with an activation energy ≈ 10 meV; and above 150 K, a second thermally activated process with a higher activation energy is observed.

3 Discussion

3.1 Inter-sub-level transitions To obtain a rough estimate of the crystallite sizes corresponding to the measured ISL transitions, we approximate the electronic states to that of a spherical quantum dot with infinite barrier. In this approximation, the energy difference between the first two levels is

$$\Delta E \approx 20 \frac{\hbar^2}{m_e D^2}. \quad (1)$$

**Fig. 2** PIA spectra recorded at temperatures between 10 and 227 K.

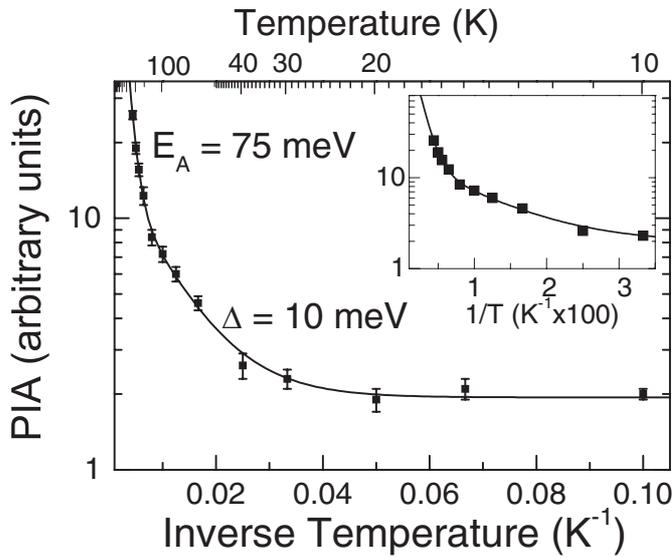


Fig. 3 Temperature dependence of integrated photo-induced absorption spectrum (in a logarithm scale). The inset is an expansion of the high temperature part of the plot.

Where m_e is the electron mass (the free electron mass was taken as an approximate value) and D is the crystallite diameter. This estimate gives only a thumb-rule idea of the expected values of the PIA spectrum.

Under this approximation we find the size of the crystallites to distribute from 2.3 to 5 nm diameters. Notice that in this approximation we have assumed constant oscillator strength of the transitions as well as we ignored larger nanocrystallites that cannot be detected by our setup. In spite of these approximations, our results seem to be consistent with transmission electron microscopy (TEM) measurements performed on highly luminescent porous silicon [9].

Calcott et al. [2] found that with the decreasing temperature, the radiative lifetime of the excitons increases very rapidly. Hence, one would expect the density of carriers in the ground sub-levels to increase in proportion to radiative lifetime. As a result, the PIA signal should also increase with the increasing number of photo-excited carriers. In our experiment, opposite behavior has been found, e.g. the PIA signal decreases with the decreasing temperature. This can be explained in this manner: Following Calcott et al., we assumed that the exciton state is splitted into an upper lying singlet and a lower lying triplet states, separated by the exchange interaction by an energy Δ . If we denote by A_S and A_T the PIA from the singlet and the triplet respectively, then the total PIA signal is given by the following expression.

$$\text{PIA} = \frac{3A_T + A_S \exp(-\Delta/kT)}{3 + \exp(-\Delta/kT)}. \quad (2)$$

The solid line in Fig. 3 represents a least-square fitting of the experimental data to this expression. From the fitting we find $\Delta = 10$ meV and $A_S/A_T = 28$. The splitting energy, Δ , is in a good agreement with that measured by time resolved PL [2, 10, 11]. We conclude that ISL transitions from the singlet are allowed, while ISL transitions from the triplet are forbidden. To our best knowledge, this is the first observation of such selection rules for ISL transitions in Si quantum dots.

In addition, we observed a second thermally activated process at temperatures above 150 K with activation energy of about 75 meV. Notice that a similar phenomenon has also been observed in time resolved PL [12, 13].

3.2 Localized excitons From Fig. 1 one can see that in addition to the broad PIA signal, there are additional narrower spectral features in the 70–150 meV range. These narrow lines that superimpose the broad ISL absorption are strongly correlated with the vibrational modes observed in the linear absorption

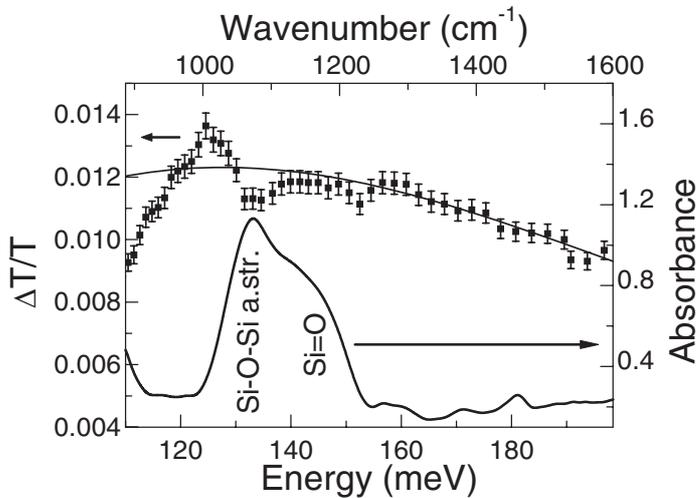


Fig. 4 Room temperature photo-induced absorption spectrum (squares) and linear absorbance between 110 and 200 meV (expansion of Fig. 1).

spectrum. Figure 4 is an expansion of the 110–200 meV PIA spectrum showing the correlation of the PIA signal with the Si=O and Si–O–Si stretching bands. Notice that the PIA signal first decreases with a minimum at 133 meV followed by an increasing signal at 125 meV. A similar, but somehow smaller, effect appears at 150 meV.

We assign this observation to an energy shift of the Si=O vibrations due to interaction with the bulk states of the quantum dot. Following Wolkin et al. [14], we assume that for large Si nano-crystallites ($d > 3$ nm) excitons are quantum confined by the quantum dots. For such a large nano-crystallites, the energy separation between conduction sub-levels is small and no coupling to surface vibrational states is expected. However for crystallites of smaller diameter, the energy separation between conduction sub-levels increases and resonance coupling with surface vibrational states occurs. This is consistent with the model proposed in reference [14], where electrons are trapped on the surface of small nano-crystals.

Our experimental results suggest that electrons are trapped at the surface (i.e. highly surface localized exciton) once that energy separation between the quantized sub-levels is close to resonance with the surface vibrational modes. The measured energy shift of the Si=O vibrations (between the linear absorption and the PIA spectrum, see Fig. 4), of about 8 meV provides an estimate of the coupling strength between quantum confined and surface states.

Similar, but somehow weaker and less pronounced effects appear for the Si–O–H and Si–H_n ($n = 1, 2, 3$) vibration modes. This is because at those energies two-phonon absorption screens these effects.

4 Conclusions Photo-induced infrared absorption spectroscopy of luminescent porous silicon layers provided important experimental evidence of quantum confinement in Si nanocrystals and surface trapped states at the interface with the host matrix. Intra-band transitions between sub-levels in the conduction and valence bands were observed. These transitions provide a support to the model of highly localized excitons in silicon nanocrystallites. Furthermore, our results suggest that quantum confined states are coupled to surface localized states in small nanocrystallites.

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