

## Hole burning spectroscopy of porous silicon

D. Kovalev, H. Heckler, and B. Averboukh

*Technische Universität München, Physik-Department E16, D-85747 Garching, Germany*

M. Ben-Chorin

*Technische Universität München, Physik-Department E16, D-85747 Garching, Germany  
and Department of Chemical Physics, Weizmann Institute of Science, Rehovot 76100, Israel*

M. Schwartzkopff and F. Koch

*Technische Universität München, Physik-Department E16, D-85747 Garching, Germany*

(Received 20 October 1997)

We report on luminescence hole burning experiments that provide a clue for the mechanism of photoluminescence of porous silicon. A large fraction of the light emission is suppressed by an intense resonant pump beam, which introduces an Auger nonradiative recombination. The hole burnt in the luminescence spectrum has two well-defined onsets related to the TO momentum conserving phonons of Si. At low temperatures the hole persists for hours. An increase of the temperature heals the spectral hole, and this is accompanied by a thermoluminescence signal. These results allow us to conclude that most of the luminescence of porous Si arises from radiative recombination between states confined inside the nanocrystals. [S0163-1829(98)00407-X]

The luminescence mechanism in porous silicon (PSi) has been a subject of a long-standing debate. In his first article on PSi luminescence, Canham<sup>1</sup> attributed the photoluminescence (PL) to radiative transitions between quantum-confined levels inside the Si nanoparticles. Some researchers suggested different models,<sup>2</sup> including radiative recombination via surface states,<sup>3</sup> Si-based luminescing compounds like a-Si,<sup>4</sup> siloxene<sup>5</sup> and light emission from certain defects in SiO<sub>2</sub>.<sup>6</sup>

The first spectroscopic evidence that at least part of the luminescence results from quantum-confined states inside the Si nanocrystals came from the experiments of Calcott *et al.*<sup>7</sup> They excited the luminescence resonantly, and observed clear onsets in the PL spectrum. The energy of the onsets is identical to that of the TO and TA momentum-conserving phonons of *c*-Si. Since only two structures are observed (for each phonon) the only possible processes in the absorption-emission cycle involve zero, one, or two momentum-conserving phonons. These processes correspond to no-phonon transitions in both emission and absorption, to a phonon-assisted process in either the absorption or the emission, and to phonon-assisted transitions in both the emission and the absorption. Therefore, Calcott *et al.* concluded that the luminescence arises from states confined inside the Si nanocrystallites.

Several experimental observations, especially regarding the influence of the surface chemistry of PSi on its light emission, are difficult to reconcile with the notion that all the light originates from quantum-confined states. This has led Rosenbauer *et al.*<sup>8</sup> to suggest that most of the light comes from a very efficient luminescence source, which is not the Si nanocrystals. This proposed source is excited only above 2.5 eV, and there is a strong Stokes shift of the emission, so its PL peak is at 1.6–2 eV. The weak luminescence from the Si nanocrystals can be seen only when the excitation of the strong source is impossible (as in the case of the resonant

excitation).<sup>8</sup> In order to support this conjecture, Rosenbauer *et al.* measured the efficiency of light emission under resonant and nonresonant excitations, and found that the luminescence is much weaker under resonant excitation, when the phonon structures are seen. The increase in the luminescence efficiency, as the excitation energy increases, is accompanied by a smearing of the phonon structures. Rosenbauer *et al.* concluded that under usual excitation conditions most of the light does not involve phonon-assisted processes, and therefore it is not a result of radiative transitions between states confined in the Si nanostructures.

In this paper we use luminescence hole burning in order to determine accurately how much of the light is emitted from quantum-confined states. This method has been employed for a variety of the nanocrystal systems (see, for example, Ref. 9). The luminescence is excited by a weak probe beam ( $\hbar\omega = 2.8$  eV). Because of the high energy of the photons all the emitters are excited efficiently. Then an intense pump beam is used to quench the luminescence. If a probe photon is absorbed in a nanocrystal which is already occupied by an electron-hole pair created by the strong pump beam, nonradiative Auger recombination would occur.<sup>10</sup> Therefore, the luminescence due to the probe beam is suppressed by the presence of the pump beam.

In order to identify the light emission from the strong source suggested in Ref. 8, we use a resonant pump beam ( $\hbar\omega \approx 1.8$  eV). At this pump energy the strong source is supposedly not absorbing.<sup>8</sup> Therefore, the fraction of the PL suppressed by the pump beam is emitted from the quantum-confined states. This is confirmed by the observation of onsets due to the TO momentum-conserving phonons in the spectral shape of the “hole” burnt in the PL spectrum. We find that the magnitude of the “hole” reaches 80% in the region of the second phonon step, which implies that most of the luminescence originates from quantum-confined states inside the Si nanocrystals.

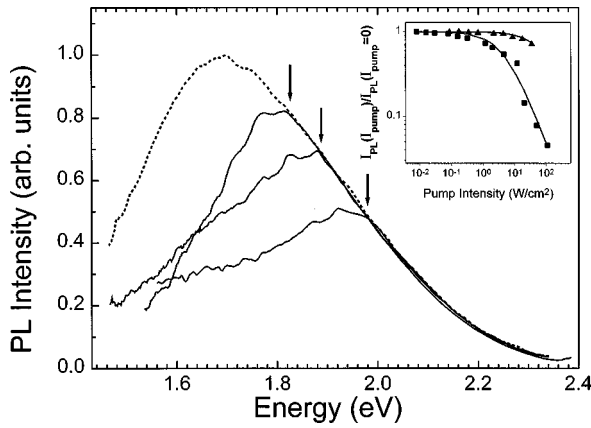


FIG. 1. The PL spectra of PS induced by a weak probe beam at 2.8 eV (dashed line) and its modifications in the presence of an intense pump beam (solid lines).  $\hbar\omega_{\text{pump}}$  are shown by arrows. Inset: The PL intensity as a function of the pump beam intensity. Triangles:  $\hbar\omega_{\text{pump}}=1.946$  eV,  $\hbar\omega_d=1.879$  eV. Squares:  $\hbar\omega_{\text{pump}}=2.54$  eV,  $\hbar\omega_d=1.77$  eV. Solid lines are fits to Eq. 1.

Persistent hole burning is also observed as a result of Auger ionization. If two  $e-h$  pairs simultaneously occupy the same nanocrystal, one pair would recombine nonradiatively via the Auger process. One of the carriers left can gain the energy of the recombined pair and escape from the crystallite. As a result the nanocrystal is charged, and all further radiative recombination inside it is suppressed (due to Auger processes). At low temperatures the nanocrystal remains ionized for long times, resulting in a persistent degradation of the PL.<sup>11–13</sup> We show that Auger-induced charging of the nanocrystallites leads to the persistent hole burning phenomena in the PL with the same phonon onset structure. Increasing the temperature of the sample washes out the hole burnt in the PL spectrum, and this is accompanied by a thermoluminescence signal with similar phonon onsets.

The details of the sample preparation and the optical setup can be found elsewhere.<sup>14</sup> The experiments are done using a pump-probe technique. A dye laser tunable in the spectral range of 600–690 nm is used to excite the PL resonantly, or as a pump beam source. A He-Cd laser (442 nm) beam is used as a probe. The intensity of the probe beam is kept low ( $I_{\text{probe}}=10$  mW/cm<sup>2</sup>) so the PL intensity is in the linear regime. A microscope is used to ensure that the pump spot overlaps completely the smaller spot of the probe laser. The probe beam is modulated at a frequency of 12 Hz, and the PL is measured using conventional lock-in technique at the same frequency. The pump beam is modulated at a high frequency (260 Hz) to achieve quasi-steady-state pumping conditions with respect to the excited carrier lifetimes.<sup>7</sup> To suppress stray light from the pump laser, the entrance slit of monochromator is blocked when the pump beam illuminates the sample. To avoid overheating of the sample by the pump beam all the experiments are done in superfluid He at  $T=1.5$  K, and the intensity of the pump beam is kept below the He boiling threshold ( $I_{\text{pump}}\leq 30$  W/cm<sup>2</sup>).

The PL spectrum under nonresonant ( $\hbar\omega_{\text{probe}}=2.8$  eV) excitation is shown in Fig. 1. The resonant beam suppresses the nonresonant PL intensity at energies below that of the pump photons. The PL intensity at higher emission energies is almost not affected. Two well-defined onsets, separated by

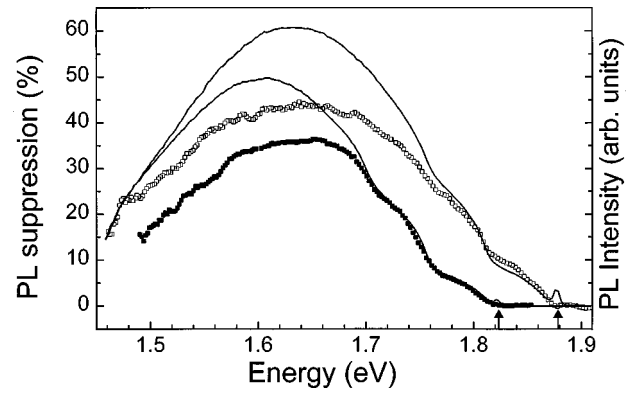


FIG. 2. A comparison between the spectral dependence of the suppression of the nonresonantly excited PL by a pump beam (solid and open squares) and the resonant PL of PS at the same excitation energies. The laser energies are shown by arrows.

56 meV, are seen in the resulting PL spectra. No influence on the PL is observed in the close vicinity of the excitation line. These PL features are related to the TO-phonon replicas and the exciton gap observed in the resonant PL spectrum.<sup>7,15</sup> The maximal suppression we have achieved is as large as 5, and it reaches a factor of 2 in the region of the first phonon step. The effect is far from saturation, and the measured suppression values are limited by the experimental setup (the power of the dye laser). Under a nonresonant pump beam ( $\hbar\omega_{\text{pump}}=2.54$  eV), the maximal suppression value is of the order of 20 (inset of Fig. 1). Note that the actual suppression value is even higher since the detected signal is a result of averaging over the pump laser on and off periods (time ratio is 5:7).

In Fig. 2 we compare the degree of PL suppression (the difference between the PL intensity with and without pump beam) with the resonant PL spectrum. The resonant PL spectra are excited at the same wavelength as that of the pump. There is an obvious correlation between the spectral dependence of the degree of quenching and the resonant PL spectrum. In particular, the two steps in the suppression spectrum coincide with the TO momentum-conserving phonon onsets observed in the resonant PL spectrum. The intensity of the suppressed PL is a large fraction of the PL intensity under nonresonant excitation when all the “emitters” are efficient.

In order to assert that the luminescence hole burning phenomena do not arise from bleaching of the band-edge absorption (due to occupation of the electron or the hole ground states<sup>16</sup>), we looked for changes in the absorption of free-standing layers, induced by the pump beam. However, no induced effect on the absorption is seen within the experimental error. This is probably due to the small fraction of luminescing particles.

The presence of *two* phonon steps in the quenching spectrum proves that the luminescence that has been suppressed also involves momentum-conserving phonons in the emission process.<sup>7</sup> We assume that the probe beam does not induce light emission in a crystallite in which an  $e-h$  pair is excited by the pump beam. The probability of a crystallite to be occupied is proportional to  $\sigma(E_g, \hbar\omega_{\text{pump}})$ , the absorption cross section for photons with an energy  $\hbar\omega_{\text{pump}}$  in a nanocrystal with a “gap”  $E_g$ .  $\sigma(E_g, \hbar\omega_{\text{pump}})$  reflects the average density of electronic states at energy  $\hbar\omega_{\text{pump}}$  in the nano-

crystal. However, since the absorption involves no-phonon and phonon-assisted processes,  $\sigma(E_g, \hbar\omega_{\text{pump}})$  has one phonon onset at  $\hbar\Omega_{\text{phonon}}$  above  $E_g$ . The second phonon onset comes from the emission process. The occupied crystallite does not emit light at  $E_g$  (minus the small exciton gap) and at  $E_g - \hbar\Omega_{\text{phonon}}$ . We point out that if only the absorption takes place inside the nanocrystal, but the emission involves localized states (surface or  $\text{SiO}_x$  defect states), only one phonon step should be seen.

We observe that 80% of the total luminescence is suppressed by the presence of the resonant pump. The spectral shape of the ‘‘hole’’ demonstrates two phonon onsets. Combining these facts, we conclude that the origin of the PL is radiative recombination between quantum-confined states inside the Si nanocrystals.

The observations that the resonantly excited PL is much weaker than that excited at high energies is explained by the difference of the absorption cross sections. In order to give an estimate of the ratio of the absorption cross sections at resonant and non-resonant excitations, we assume that the PL induced by the probe beam at  $\hbar\omega_d$  is proportional to the density of crystallites with a ‘‘gap’’  $\hbar\omega_d$ , which are left unoccupied by the pump beam (at energy  $\hbar\omega_{\text{pump}}$ ). We solve a system of rate equations, and obtain the density of empty crystallites as a function of the pump intensity:<sup>13</sup>

$$N_{\text{empty}}(\hbar\omega_d, I_{\text{pump}}) = \frac{N_{\text{total}}(\hbar\omega_d)}{1 + \tau_R(\hbar\omega_d)\sigma(\hbar\omega_d, \hbar\omega_{\text{pump}})I_{\text{pump}}} \quad (1)$$

Here  $\tau_R(\hbar\omega_d)$  is the radiative lifetime,  $\sigma(\hbar\omega_d, \hbar\omega_{\text{pump}})$  is the cross section for absorption of photons with an energy  $\hbar\omega_{\text{pump}}$  in a nanocrystal with a ‘‘gap’’  $\hbar\omega_d$ ,  $I_p$  is the intensity of the pump light expressed in an areal flux of incident photons. The solid curves in the inset of Fig. 1 are fits using Eq. (1). We neglect the fact that light emission at  $\hbar\omega_d$  originates from crystallites with gaps  $\hbar\omega_d$  (via no-phonon process) and  $\hbar\omega_d + \hbar\Omega_{\text{phonon}}$  (via phonon-assisted emission).<sup>17</sup> Although we used this simplification, the results are fitted very well. Substituting the experimental values of  $\tau_R = 4$  ms we obtain an approximate value of  $\sigma(\hbar\omega_d = 1.88$  eV,  $\hbar\omega_{\text{pump}} = 1.94$  eV) =  $4 \times 10^{-19}$  cm<sup>2</sup>, while for high-energy pumping  $\sigma(\hbar\omega_d = 1.77$  eV,  $\hbar\omega_{\text{pump}} = 2.54$  eV) =  $10^{-17}$  cm<sup>2</sup>. The difference in these values reflects the increase in the density of electronic states with increasing energy above the ‘‘gap.’’ Indeed, the light emission under nonresonant excitation is much more efficient than under resonant one, as claimed by Rosenbauer *et al.*,<sup>8</sup> but this is due to the large difference in the density of states. We point out that this factor we have obtained from the hole burning experiments has a similar magnitude to that deduced from the luminescence intensity by Rosenbauer *et al.*<sup>8</sup>

We turn now to discuss persistent hole burning phenomena. These effects are studied in the following way. After measuring the usual PL spectrum under nonresonant conditions ( $\hbar\omega = 2.8$  eV), we switch off the weak probe beam and expose the sample for 3 h to a strong resonant beam ( $I_{\text{pump}} = 10$  W/cm<sup>2</sup>). The intense resonant pump beam is used to create a long-term degradation of the luminescence via an Auger ionization. After the degradation step, we switch off the strong beam and measure the luminescence again using

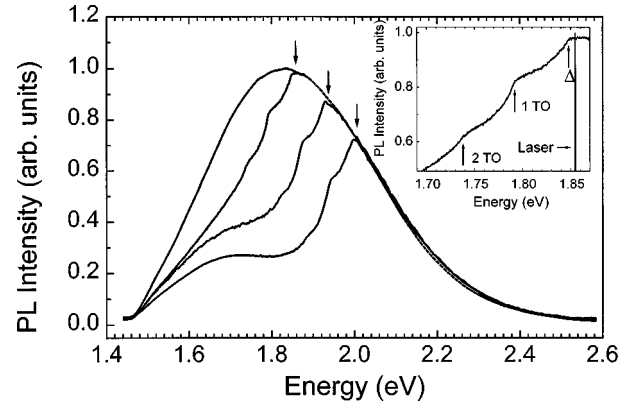


FIG. 3. Persistent hole burning spectra of PS luminescence spectrum at different burning energies (solid lines, the burning energies are indicated by arrows). For comparison the initial PL spectrum is also shown (dashed line). Inset: Detailed PL spectrum in the vicinity of the burning laser energy.

the same weak probe beam. Thermoluminescence is measured during the heating of the sample (after persistent hole burning) using a spectrograph combined with a silicon CCD array.

The burnt luminescence spectra are shown in Fig. 3. They are very similar to those seen in Fig. 1. A clear decrease in PL efficiency is recorded for emission energies below that of the degrading beam, while almost no influence is detected above it. Again two phonon replicas and a forbidden gap (marked  $\Delta$ ) known from the resonant PL measurements are observed (inset of Fig. 3). The degradation becomes less efficient at low detection energies as in the case of the non-resonant fatigue effect.<sup>13</sup> At low temperatures, the spectrum of the ‘‘hole’’ and its magnitude do not change during tens of hours. Heating the sample to 250 K washes out the spectral hole completely.

Electrons or holes ejected from the Si nanocrystals during the Auger ionization process are either captured by surface traps or transferred to a neighboring nanocrystal. When the sample is heated, the trapped carriers can be thermally re-excited into the nanocrystals. A carrier injected into a charged nanocrystal recombines with the carrier which has been left

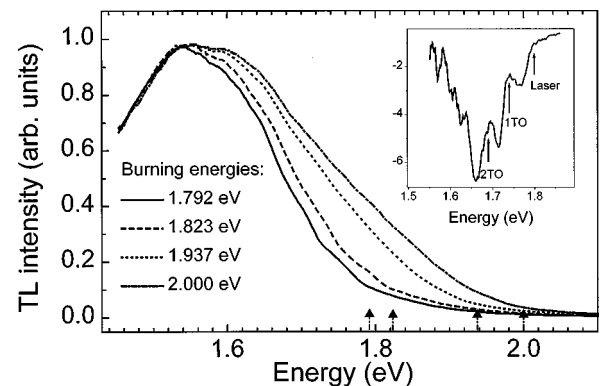


FIG. 4. Thermoluminescence spectra (heating range is 1.5–20 K) measured after spectral hole burning at different energies (shown by arrows). Inset: The first derivative of one of the spectra. A better discrimination of the TO-phonon-related structure is possible.

there. This process restores the initial optical properties of the sample, since the nanocrystals become neutral. If the recombination is radiative a thermoluminescence signal appears. This effect is known for semiconductor-doped glasses.<sup>11</sup>

The thermoluminescence from a sample that has been exposed to resonant light at 1.5 K is measured while the sample is heated to 20 K. The spectra are shown in Fig. 4, and demonstrate the same spectral features seen in the hole burning experiments. The emission spectra shift with the burning light energies. Furthermore, two TO-phonon onsets are seen as well. These TO-phonon replicas are seen better in the first derivative of the thermoluminescence spectrum (the inset of Fig. 4). The presence of a weak anti-Stokes thermoluminescence at energies above the burning energy indicates that a part of the carriers is reexcited via Auger process to crystallites with higher band gaps. According to our estimates, the total number of photons emitted during the heating procedure is roughly equal to the number of photodegraded nanocrystals. The spectrally integrated thermoluminescence signal measured at a constant heating rate has a broad temperature distribution from 1.5 to 250 K, with a maximum at 150 K. Following the procedure described in Ref. 18, we deduce an average activation energy of 300 meV. This energy is in a good agreement with measured energy positions of surface

traps in porous silicon.<sup>19</sup> It is slightly smaller than the activation energy of the dc transport (about 0.5 eV).<sup>20</sup>

The fact that the hole burnt at low temperatures persists for a few hours, and that heating can cause thermoluminescence, has important implication for the understanding of the mechanism of P*Si* luminescence. In several of the suggested models for the PL, it is argued that electrons and holes, optically excited in the core of the nanocrystal, relax in energy to different types of localized states, from which they recombine radiatively. The relaxation energy is assumed to be about 0.3–0.5 eV, thus explaining the Stokes shift of the nonresonantly excited PL. Indeed, such trap states could exist as it is evident from the thermoluminescence data. However, the lifetime of captured carriers is very long (of the order of tens of hours at low temperatures). Radiative recombination between these states is impossible at low temperatures, and thus the light emission cannot involve such transitions.

To summarize, we demonstrated that Auger nonradiative processes result in spectral hole burning in the PL of P*Si*. At low temperatures the hole can persist for long times, and its healing is accompanied by thermoluminescence. The presence of two phonon steps as a general feature in all these phenomena allows us to conclude that the luminescence of porous Si arises from radiative transitions between quantum-confined states inside the Si nanocrystals.

<sup>1</sup>L. T. Canham, *Appl. Phys. Lett.* **57**, 1046 (1990).

<sup>2</sup>L. T. Canham, *Phys. Status Solidi B* **190**, 9 (1995).

<sup>3</sup>F. Koch, in *Silicon-Based Optoelectronic Materials*, edited by M. A. Tischler, R. T. Collins, M. Thewalt, and G. Abstreiter, MRS Symposia Proceedings No. 298 (Materials Research Society, Pittsburgh, 1993), p. 319.

<sup>4</sup>R. P. Vasques *et al.*, *Appl. Phys. Lett.* **60**, 1004 (1992).

<sup>5</sup>M. Brandt *et al.*, *Solid State Commun.* **81**, 307 (1992).

<sup>6</sup>S. M. Prokes *et al.*, *Phys. Rev. B* **45**, 13 788 (1992).

<sup>7</sup>P. D. J. Calcott *et al.*, *J. Phys.: Condens. Matter* **5**, L91 (1993).

<sup>8</sup>M. Rosenbauer *et al.*, *Phys. Rev. B* **51**, 10 539 (1995).

<sup>9</sup>T. Kawazoe and Y. Masumoto, *Phys. Rev. Lett.* **77**, 4942 (1996).

<sup>10</sup>I. Mihalcescu *et al.*, *Phys. Rev.* **51**, 17 605 (1995).

<sup>11</sup>A. I. Ekimov and Al. L. Efros, *Phys. Status Solidi B* **150**, 627 (1988).

<sup>12</sup>V. Grivickas *et al.*, *Thin Solid Films* **255**, 208 (1995).

<sup>13</sup>D. Kovalev *et al.*, *Phys. Rev. Lett.* **77**, 2089 (1996); Al. L. Efros *et al.*, *Phys. Rev. B* **56**, 3875 (1997).

<sup>14</sup>D. Kovalev *et al.*, *Appl. Phys. Lett.* **67**, 1585 (1995).

<sup>15</sup>T. Suemoto *et al.*, *Phys. Rev. Lett.* **70**, 3659 (1993).

<sup>16</sup>Y. Masumoto, *J. Lumin.* **70**, 386 (1996).

<sup>17</sup>Since we would like to get an order of magnitude estimate of the ratio between the cross section at nonresonant and resonant excitation we can assume safely that the cross sections at  $\hbar\omega_d$  and  $\hbar\omega_d + \hbar\Omega_{\text{phonon}}$  are the same, and therefore it can be replaced by an average value.

<sup>18</sup>D. Curie, *Luminescence in Crystals* (Methuen, London, 1963).

<sup>19</sup>M. Ben-Chorin *et al.*, in *Microcrystalline and Nanocrystalline Semiconductors*, edited by L. Brus, M. Hirose, R. W. Collins, F. Koch, and C. C. Tsai, MRS Symposia Proceedings No. 358 (Materials Research Society, Pittsburgh, 1995), p. 575.

<sup>20</sup>M. Ben-Chorin *et al.*, *Phys. Rev. B* **49**, 2981 (1994).