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Band gap of porous silicon

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We observe a quadratic rise of the absorption coefficient with excitation energy in photoluminescence excitation spectra of porous silicon. Extrapolation to $\alpha = 0$ yields an average band gap of microporous silicon about 0.2 eV above the luminescence line. Good agreement is obtained with an estimate of the band gap from the position of the second luminescence line of porous silicon in the infrared spectral region. Further analysis of the line shape using different luminescence detection energies shows that, in addition to the size distribution of crystallites, there exists a second contribution to the linewidth.

During the past years there has been an increased interest in the luminescence properties of porous Si (PS). This material has efficient luminescence in the visible regime even at room temperature.[1] Although many of studies have been devoted to various aspects of PS, it is not yet clear what is the origin of the light emission; this question is still under intense debate.

There are numerous models that have been suggested in the literature. Generally they can be classified into four major categories: Radiative recombination is assumed to occur via quantum confined excitons,[2] localized electronic states on the surface of the crystallites,[3,4] defects in the oxidic coverage of the crystallites,[5] and even within certain Si-based chemical compounds, like siloxene.[6]

Canham[1] was the first to ascribe the visible luminescence to quantum confinement of the excited electron-hole pair inside the small Si structures, resulting in a luminescence energy well above the bulk Si band gap. It was further argued that the nonradiative recombination is much reduced due to the good surface passivation and the fact that the carriers are confined inside the crystallites and cannot diffuse far away to reach a nonradiative center. Calcott *et al.*[2] have shown that the luminescence at low temperature has a phonon structure; they argued that this proves that both the absorption of the light and the reemission occurs within the Si crystallites. However, there is a variety of experiments that cannot be simply explained by this model. For example, it was shown that the chemical environment affects the luminescence properties.[7–9] This result suggests that the enlarged surface area of the PS plays a role in the light emission. The existence of localized states on the surface of the Si network has been shown using various measurements.[3] Furthermore, it was demonstrated that the infrared emission observed from PS is related to a radiative recombination process, which involves a dangling bond state at the surface of a crystallite.[10,11]

The reason for the difficulty in determining the radiative processes in PS is related to the highly nonhomogeneous structure of the material. Crystallites having different sizes and shapes, will result in a broad distribution of confinement energies. Therefore, it is not easy to identify where the absorption as well as the related emission takes place. Several attempts were done to translate the PL spectral shape into a size distribution of the crystallites.[12] However, such an interpretation depends crucially on the model taken for the luminescence transitions and therefore cannot help to identify the mechanism. Absorption studies of PS using transmission or photothermal deflection spectroscopy (PDS) do not show any feature that can be easily correlated with a typical band gap. Therefore, the band gap is often associated with an absorption coefficient of 10^3 cm^{-1}. However it was shown that the PL can occur below or even above this band gap.[13]

In this paper we would like to show that photoluminescence excitation spectroscopy (PLE) allows us to determine an effective band gap for the luminescing crystallites in PS. Furthermore, our results demonstrate that this effective band gap is relevant only for the luminescent parts of the PS size distribution; therefore, the use of absorption or Raman data to conclude about the typical size of the luminescing crystallites is misleading.

The standard samples were prepared from p-type substrates (1–5 Ω cm) using a 1:1 by volume mixture of 50% HF and ethanol and current densities in the 50-mA/cm^2 range. The sample thickness was 10 μm. Higher substrate doping and further dilution of the etching solution was used, when samples with different PL peak position were required. The excitation source for the PLE measurements was a Xe-arc lamp with either 300- or 1000-W electrical power. The light was dispersed by a 22-cm SPEX single monochromator. Optical band pass filters were used to provide suppression of stray light. The excitation light was focused onto the sample using mirror optics to avoid problems with absorption and dispersion of lenses in the ultraviolet spectral range. The lumines-

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cence light was collected by conventional lens optics, and spectrally resolved with a second 22-cm SPEX monochromator. The signal was detected using a Si diode in a standard lock-in technique. To account for the spectral variation of the excitation power, a normalization spectrum was recorded simultaneously with the PLE data using a quartz beamsplitter and a pyrodetector. This type of normalization can be used due to the linearity of the PL intensity with the incident light power. Also the PL spectra were corrected for the spectral sensitivity of the detection system.

Figure 1 shows the PL spectra of a typical aged PS sample taken with various excitation wavelengths. In general the spectrum is peaked around 1.6 eV and has a typical width [full width at half maximum (FWHM)] of about 0.4 eV. The spectral shape of the line depends slightly on the excitation photon energy. On the high-energy side, an increase of the PL intensity is observed for higher excitation energy, which induces a blueshift of the peak position. On the low-energy shoulder of the PL spectra, a smaller effect is observed, resulting in a decrease of the width of the luminescence line for lower excitation energies. This behavior allows us to exclude depth inhomogenieties on a macroscopic scale as a reason for these changes. For an inhomogeneous sample, the spectrum should be wider for lower excitation energies since the sample is more transparent and a wider particle size distribution is excited. So the shifts in the spectra are due to the fact that only with high excitation energies the full size distribution can be addressed while with lower-energy excitation the larger crystallites absorb preferentially.

To determine the absorption characteristics of the luminescing particles we have measured the PLE spectra of the sample. The absorption is deduced from the PLE signal assuming that the quantum efficiency is independent of the excitation energy. The absolute value of the absorption α is derived from spectra at the saturation limit $\alpha d > 1$ (d is the sample thickness). Figure 2 compares for samples with similar substrate doping and porosity the absorption coefficient measured by PDS and transmission (data taken from Ref. 14) with that deduced from PLE. While the PDS transmission data show an exponential dependence on the energy in the 2 eV region, the PLE does not follow the same behavior. Furthermore, the magnitude of the PLE absorption is much below that measured by transmission and PDS, an effect also reported by Ookubo[15] when comparing to absorption data. In the lower part of Fig. 2, the PLE intensity $I_{\rm PLE}$ is shown as $\sqrt{I_{\rm PLE}E}$ as function of excitation energy for three different detection energies. For low excitation energies where the sample is optically thin this is equivalent to plotting $\sqrt{\alpha_{\rm PLE}E}$. In this range for all the detection energies a linear relation is observed. This is the expected behavior for an indirect semiconductor as observed also for crystalline silicon.[16] Moreover, the use of this notation allows us to identify an effective band gap E_g^*, for which the extrapolated absorption vanishes. We point out that our extrapolated band gap is about 0.2 eV above the PL peak position for detection on the luminescence peak.

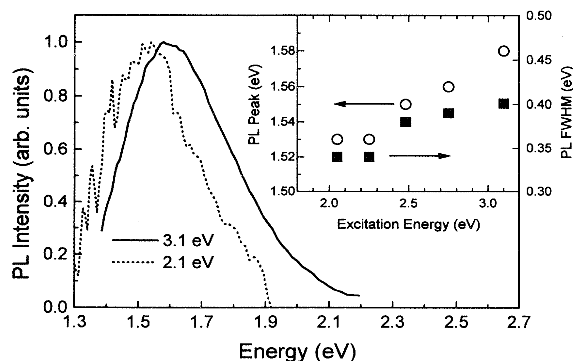

FIG. 1. Photoluminescence spectra of microporous silicon taken at different excitation energies. Inset: Photoluminescence peak position and full width at half maximum (FWHM) as a function of excitation energy.

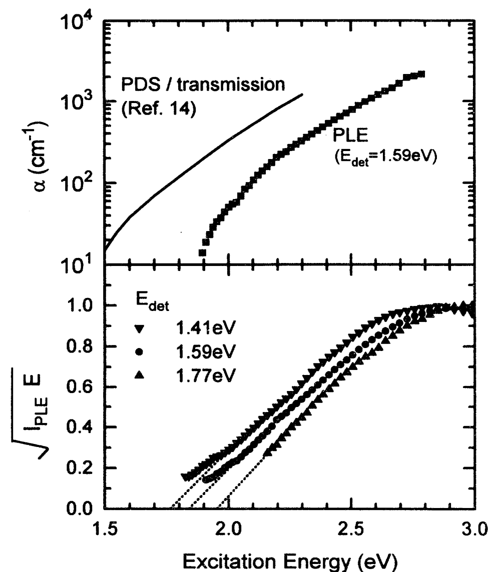

FIG. 2. The lower part of the figure shows the square root of PLE intensity times photon energy vs excitation energy for different detection energies. The dotted lines indicate the extrapolation to the band gap E_g^*. The upper part gives a comparison of the typical absorption behavior obtained by PDS and transmission (data taken from Ref. 14) and PLE.

Due to the size distribution of the crystallites inside the PS, no unique band gap can be defined. This is shown in Fig. 3 where the effective band gap is depicted as a function of detection energy showing a linear increasing dependence. This behavior is easily understood in terms of a size distribution. If we increase the detection energy, only particles with larger band gap will contribute to the luminescence and therefore the average band gap increases.

In the following we present a simple model that accounts for the described observations. We first address the spectral behavior of the PLE. There is a lot of experimental[2,17] and theoretical[18] evidence that the absorption process in PS involves phonons, even at low temperatures. Therefore, the assumption that each of the

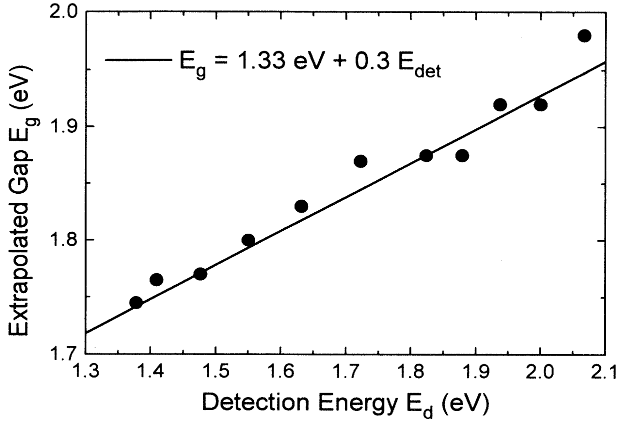

FIG. 3. Extrapolated band gap E_g^* as a function of detection energy. The straight line interpolation follows the relation $E_g = 1.33$ eV $+0.33 E_{\mathrm{det}}$.

crystallites behaves to a large extent as an indirect semiconductor is quite reasonable. For an indirect semiconductor with a well-defined band gap E_g, the absorption coefficient $\alpha(E, E_g)$ as function of photon energy E can be written as

$$\alpha(E, E_g)\ E = \zeta_{\mathrm{abs}}(E_g)\ (E - E_g)^2\ \Theta(E - E_g)\ . \qquad (1)$$

ζ_{abs} allows for a change in the oscillator strength of the crystallites with increasing gap in comparison to the bulk and Θ is the Heaviside step function. Basically for the absorption process one has to take into account phonon emission and absorption processes. In Eq. (1), only the more likely Stokes process is considered. So the gap E_g as defined in Eq. (1) involves a phonon energy.

The application of Eq. (1) to small crystallites requires further consideration. As we have stated earlier, a definition of a band gap for a quantum confined system is not trivial. One simple possibility is to take E_g as the energy difference between the lowest-lying quantum confined state in the conduction band and the highest level in the valence band. However, the $(E - E_g)^2$ dependence of the absorption coefficient is a result of a continuous $E^{1/2}$ density of states. While the lowest-lying quantum levels will be discrete, even for the simplest effective-mass particle in a box approximation, the density of states is quasicontinuous not far above the lowest states due to the many possible transitions even in such an idealized crystallite. More elaborate calculations for Si crystallites show an increase of the absorption roughly proportional to $(E - E_g)^2$ too.[19] We therefore assume that Eq. (1) can be applied to each of the crystallites, bearing in mind that the E_g we get from the extrapolation of our experimental data is not necessarily the gap between the lowest- and highest-lying levels in the conduction and valence bands, respectively. Another complication can arise from the fact that in bulk Si from 2.2 eV another gap starts to contribute to absorption. This gap will be affected by quantum confinement too so that contributions disturbing the quadratic rise of porous silicon absorption should only be found in considerably higher energies.

In the case of PS we have to deal with a broad luminescence line. One source of broadening is certainly the distribution of crystallite sizes or energy gaps, respectively, so we have to introduce a size distribution function into Eq. (1). Another source might be the emission process. Both the relaxation step between the absorbing and emitting states and the emission step can contribute to the broadening. In a quantum confined system, the relaxation energy $E_g - E_{\mathrm{det}}$ is equal to the difference between the lowest-lying light-emitting level and the extrapolated gap E_g plus the excitonic binding energy. This relaxation energy should increase with E_g. Similar behavior is expected if surface states are involved in the emission. However from Fig. 3 one can see that the difference between the extrapolated gap and the detection energy decreases for higher gaps. Therefore, we conclude that the relaxation energy does not change very much as function of the gap and can in the simplest approximation taken to be constant.

If the luminescence line of each of the crystallites was infinitely sharp, then the luminescence detected in one energy is only related to one subset of crystallites, which have the same gap. In that situation, the extrapolated gap should move the same amount as the detection energy. Figure 3 shows that this is not the case. So it is necessary to take into account a quite large linewidth of the luminescence corresponding to one band gap. Such a linewidth may arise from a varying distance of the luminescing states from the extrapolated band gap. The emission intensity I from a crystallite with a gap E_g can be expressed as

$$I(E_x, E_d, E_g) = \alpha(E_x, E_g)\ \eta_{\mathrm{em}}(E_g)\ L(E_d, E_g)\ , \qquad (2)$$

where E_x, E_d are the excitation and detection energies, respectively. $L(E_d, E_g)$ describes the finite emission line shape and η_{em} is the quantum efficiency of light emission, which depends only on the crystallite band gap. Assuming that the simplest type of effective medium theory can be used and all contributions to the absorption can be summed up, the luminescence intensity taking into account a distribution of gap energies is given by

$$\begin{aligned} I(E_x, E_d) E_x &= \int_{1.1\,\mathrm{eV}}^{\infty} dE_g\ f(E_g)\ (E_x - E_g)^2\ L(E_d, E_g) \\ &\quad \times \eta_{\mathrm{em}}(E_g)\ \zeta_{\mathrm{abs}}(E_g) \qquad (3) \\ &= A(E_d)\ \left\{ \left[E_x - E_g^*(E_d)\right]^2 + \Sigma^2(E_d) \right\}\ , \qquad (4) \end{aligned}$$

where $A(E_d)$ is simply a prefactor, E_g^* describes the average gap, while $\Sigma(E_d)$ is the standard deviation evaluated with respect to the distribution function

$$\begin{aligned} f^*(E_g, E_d) &= f(E_g)\ \eta_{\mathrm{em}}(E_g)\ \zeta_{\mathrm{abs}}(E_g)\ L(E_d, E_g) \qquad (5) \\ &= f_g^*(E_g)\ L(E_d, E_g)\ . \qquad (6) \end{aligned}$$

It contains not only the distribution of gaps but also the other gap-dependent quantities $\zeta_{\mathrm{abs}}(E_g)$, $\eta_{\mathrm{em}}(E_g)$, and $L(E_d, E_g)$. Since we cannot separate the effects of size distribution and the efficiencies of absorption and emis-

sion, we have introduced $f_g^*(E_g)$ as product of these factors. For fixed E_x, Eq. (3) describes the luminescence line shape, whereas for fixed E_d we get the spectral behavior of the PLE or the average absorption of the distribution of luminescing particles equivalently.

From Eq. 4 it is clear that for any distribution of particle sizes the effective absorption taken from the PLE spectrum follows the behavior of an indirect band gap semiconductor [Eq. (1)] as observed in Fig. 2. This is independent of the luminescence line shape and the only requirement for it to hold is that the excitation energy will be well above the band gap, so that the integration can be done over the whole distribution of gaps. This is already assumed in Eq. (3) otherwise the upper integration limit should be the excitation energy instead of infinity. In addition the additive term Σ^2 in Eq. (4) must be negligible. It will be shown later that this is the case. Quite contrary, when a measurement is done within the distribution, like in the case of absorption measurements, the details of the measured spectra will depend crucially on the distribution. Therefore, it is not surprising that we observe a square root dependence of the absorption on energy, while PDS (Ref. 14) and transmission measurements[16] show different behavior in lower energies.

In order to get some quantitative estimates of the distribution, we continue by assuming a specific form of $L(E_d, E_g)$ and $f_g^*(E_g)$. We assume that the line shape broadening corresponding to one gap is given by a Gaussian

$$L(E_d, E_g) = \frac{1}{\sqrt{2\pi}\,\sigma_h}\, e^{-\frac{1}{2}\left(\frac{E_d+\delta-E_g}{\sigma_h}\right)^2} . \qquad (7)$$

δ is inserted in order to allow for energy relaxation between the absorption edge and the emission energy. As discussed before it is taken to be constant independent of the excitation and detection energies as well as the crystallite band gap. The behavior of $f_g^*(E_g)$ is more complicated to estimate. In addition to the unknown size distribution it contains also the quantum efficiency and the ζ function, which involve a certain model for calculation. At this stage we would like to assume for the sake of simplicity that it can be quite well approximated by a Gaussian distribution

$$f_g^*(E_g) \sim \frac{1}{\sqrt{2\pi}\,\sigma_g}\, e^{-\frac{1}{2}\left(\frac{E_g-E_{g0}}{\sigma_g}\right)^2} . \qquad (8)$$

In addition, we note that the luminescence line shape is in many cases close to a Gaussian. The convolution of two Gaussians again has Gaussian shape, so this feature of the luminescence line is described by the particular choice for $L(E_d, E_g)$ and f_g^*. Inserting this into Eq. (3), we obtain

$$I(E_d, E_x)E_x \sim e^{-\frac{1}{2}\left(\frac{E_d+\delta-E_{g0}}{\sigma_g^2+\sigma_h^2}\right)^2} \left\{ \left[E_x - E_g^*(E_d)\right]^2 + \Sigma^2 \right\}, \qquad (9)$$

where E_g^* and Σ^2 are given by

$$E_g^* = \frac{(E_d+\delta)\,\sigma_g^2 + E_{g0}\,\sigma_h^2}{\sigma_g^2 + \sigma_h^2} , \qquad (10)$$

$$\Sigma^2 = \frac{\sigma_g^2\,\sigma_h^2}{\sigma_g^2 + \sigma_h^2} . \qquad (11)$$

The effective band gap E_g^* depends linearly on the detection energy as experimentally observed in Fig. 3. Moreover, using the data we can evaluate the two line broadening parameters using Eqs. (9) and (10). The experimental data entering are the width of the luminescence line in the high excitation energy limit for Eq. (9) and the slope of $E_g^*(E_d)$ from Fig. 3 for Eq. (10). We find $\sigma_g = 0.09$ eV and $\sigma_h = 0.14$ eV. This corresponds to FWHM values of 0.2 eV and 0.3 eV, respectively.[20] δ is the difference between the extrapolated gap and detection energy for detection on the PL maximum. Its value is 0.2 eV. For low temperatures (4.2 K), the same behavior of the excitation spectra is found. The width of the luminescence line is increased by a small amount and the line itself shifts to higher energies, but slightly less than the shift of the bulk Si band gap. Both effects might originate from an increased quantum efficiency on the low-energy side of the luminescence line at low temperatures. This results in a higher value for σ_g ($\sigma_g = 0.13$ eV). However, $\sigma_h = 0.11$ eV (corresponding to FWHM 0.25 eV) as well as $\delta = 0.2$ eV are found to be almost the same as at room temperature. The analysis of samples with different luminescence linewidth at room temperature yields constant σ_h while a larger size distribution is found for the sample with broader luminescence. The accuracy of the determined parameters might depend on whether δ is really constant within the luminescence line. Since δ is rather expected to increase with emission energy as discussed, before this would rather diminish further the effect of the size distribution σ_g on the overall linewidth and rise σ_h.

The gap upshift in crystallites is related to the size according to $\Delta E_g \sim L^{-n}$ with an exponent $n \approx 1.5$.[21,12] Thus, the energetic width can be translated into a size fluctuation of ≈ 10 Å. The value for Σ is 0.08 eV, so that the additive term in Eq. (9) is really negligible not far above the luminescence line as required for extrapolating to the gap. Furthermore, the presented model is also able to account for the changes in luminescence peak position and width as a function of the excitation energy observed in Fig. 1.

We have employed the same method of plotting $\sqrt{\alpha E}$ vs E to extrapolate an average band gap from measurements of the photoconductivity. The photoconductivity band gap, $E_g^{\mathrm{PC}} = 1.4$ eV, lies about 0.4 eV lower in energy than the PLE band gap determined with detection on the PL peak (1.8 eV). This indicates that we have a large size distribution of Si crystallites in the samples and any method to determine the absorption responds to another part of this size distribution. Since for the photoconductivity a separation of the carriers is needed to get a signal, the major contribution will come from the larger and better conducting particles. Optical absorption measurements will average the whole distribution and the only method to determine the absorption

behavior of the luminescing particles is PLE. This is also the reason for the low absorption coefficients obtained by PLE (Fig. 2) since only part of the absorption processes results in light emission. In addition this shows that the distribution function f_g^* introduced to analyze the PL and PLE spectra is determined by the quantum efficiency and not by the size distribution function $f(E_g)$ of the particles in the low-energy side of the spectrum.

There is another way to estimate the band gap involving the second luminescence signal of porous silicon observed in the infrared spectral region. It is ascribed to a recombination process via dangling bonds.[10] Since this is a highly localized defect level in the band gap of the material, it remains quite unaffected in its energetical position by quantum confinement effects.[19] So the shift of the infrared luminescence line with respect to its bulk position of 0.82 eV measures either the shift of the valence or conduction states due to confinement. The literature provides experimental[22] and theoretical values for the ratio[19,23] of the shifts of valence (ΔE_v) and conduction (ΔE_c) band. Taking the experimental value $\Delta E_v/\Delta E_c=2$ leads to the conclusion that the observed infrared radiative transition is from the conduction band to a dangling bond, otherwise the calculated band gap would fall below the red luminescence line. So the band gap can be calculated according to[4,24]

$$\begin{aligned} E_g &= 1.17\text{ eV} + \Delta E_c + \Delta E_v \\ &= 1.17\text{ eV} + (E_{\rm IR} - 0.8\text{ eV})\left(1+\frac{\Delta E_v}{\Delta E_c}\right) . \end{aligned} \tag{12}$$

Figure 4 presents the PL peak position of the infrared signal, the band gap calculated from this according to the above considerations, and the band gap extrapolated from the PLE measurements. Both methods to achieve a band gap of porous material give results that are in good agreement for various PL peak positions. The fact that the PLE data are taken at T=300 K while the luminescence spectra were recorded in T=20K does not obscure the comparison of gaps since the energy difference between the PL maximum and the gap deduced for this maximum as detection energy is quite the same at low and high temperatures as mentioned before.

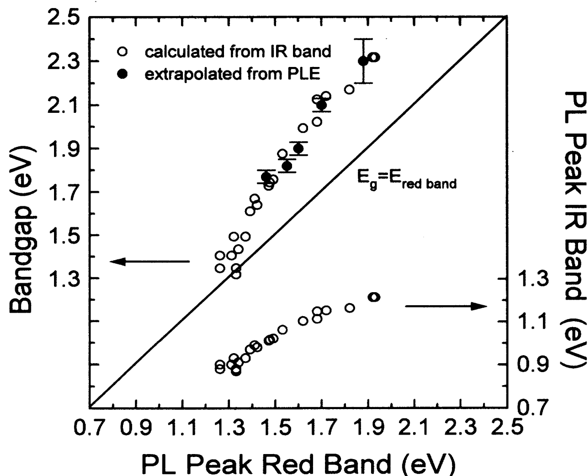

FIG. 4. Band gap of porous silicon for different types of samples as determined from PLE measurements with detection on the PL maximum (solid symbols) and from the position of the infrared luminescence band (open symbols), which is also given in the lower part of the figure. The diagonal straight line indicates the case where the band gap equals the PL peak position of the redband.

The spectral width of the infrared band of $\Delta E_{\rm IR} = 0.3$ eV can be considered within the same model developed for the redline. According to the 2:1 ratio of the changes of valence and conduction band, the same ratio applies for the gap distribution width and the valence band contributes $\sqrt{4/5}$, the conduction band $\sqrt{1/5}$ to the additional line broadening σ_h of the redline.[25] For a total FWHM of 0.4 eV, the actual contributions are 0.30 eV and 0.15 eV, respectively. In addition to the contribution of one of the bands, an inherent width of the infrared line has to be taken into account. Porous silicon prepared from highly p-doped substrate in which quantum size effects are negligible has an infrared linewidth of 0.2 eV.[26] Adding this value to the broadening contributions of the conduction band leads to an estimate of the infrared linewidth for microporous material of 0.25 eV, which is in good agreement with the experimental value of 0.3 eV.

We would like now to discuss the luminescence mechanism in light of the results shown above. Our PLE spectra strongly suggest that the absorption of the excitation radiation takes place in confined crystalline silicon structures. The results demonstrate that the luminescence takes place below the effective band gap, thus a relaxation step is necessary between absorption and emission. We find that during this relaxation about 0.2 eV are lost. We have to take into account that we have implicitly considered only Stokes processes in absorption, so in the end two phonon energies of 56 meV — one for absorption and one for emission — might contribute to the energy difference and in this case only about 0.1 eV have to be attributed to the relaxation process itself.

There are several possibilities to account for this relaxation. In the pure quantum confinement model[2,27] the relaxation step involves the creation of a confined exciton. The binding energy of a free exciton in bulk crystalline silicon is only 14 meV; however, it can become larger via confinement.[28]

A model in which the relaxation is natural, is the surface state model.[3,4] Here, the absorption takes place at the band edges of the crystallites, but it is immediately followed by a relaxation to localized surface states within the same crystallite in which the electron-hole pair has been created. Luminescence will result from radiative recombination of trapped carriers. The observation that the luminescence occurs below the effective band gap and also the finite linewidth for a given gap of the crystallites even at low temperatures are inherent to this type of mechanism. The fact that the relaxation energy is the same for 300 K and 4 K is in disagreement with models suggested for the relaxation in band tails of amorphous semiconductors.

There is another possibility for relaxation that should be considered. It was suggested that carrier diffusion affects the probability of nonradiative recombination

processes.[29] Carrier transport could also be involved in the relaxation process. If the excited carriers are allowed to move and relax to local minima of energy before the creation of an exciton, there should be a difference between absorption energy and luminescence.[30] In a sense, this is similar to the behavior in a-Si, except of a change in the typical length scale of disorder. The weakly confined regions of the silicon skeleton will play the role of band tails states. They are localized because of the energy fluctuations, and excited carriers that are formed somewhere else can relax into them.

In this respect it is interesting to note that when the small crystalline particles are completely disconnected, as in the case of colloidal suspensions, no large difference in the energy of the absorption and the emission is observed.[31] This seems to indicate the importance of transport in the relaxation process. We have tried to examine the role of the transport for relaxation in different ways. At low temperatures where the transport of carriers between crystallites should be suppressed, we find the same energy difference between the energy gap and the luminescence peak as we observe at room temperature. Also in porous silicon subjected to rapid thermal oxidation where structural investigations suggest a loss of interconnectivity of Si crystallites,[32] we find about the same relaxation energy.[33] These observations seem to indicate that in porous silicon the relaxation process is mostly within single particles (geminate recombination) and that we can rule out transport as a viable mechanism for relaxation.

The question then arises what is the difference between the oxidized colloidal particles and PS. The high quantum efficiency of the colloids of about 50% at low temperatures indicates that they are better passivated, and therefore it might be that surface states in this case are not operative as the radiative channel. However, it seems that better passivation is not the answer to this difference, since even by changing completely the PS crystallite coverage from hydrated to oxidized, no change in the relaxation energy is found. One is thus led to look for another explanation for the discrepancy. One possibility is that these colloids consist of nearly perfect spherical particles, while PS crystallites have irregular shapes. This will result in a removal of the degeneracy of levels associated with the spherical shape, and would lead to a more complex band structure of the particles.[34]

We have demonstrated that luminescence excitation is a tool for determining the band gap of the luminescent part of the size distribution of crystallites in porous silicon. For typical PL emission energies of 1.6 eV, this gap lies 0.2 eV above the luminescence line, which is in good agreement with a determination of the gap based on the infrared luminescence of the material. The gap determined from photoconductivity is substantially smaller (1.4 eV) indicating that the size distribution of the crystallites is broader than reflected by the luminescence line shape and that the conducting particles are mainly the nonluminescing ones.

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