Electrical band-gap energy of porous silicon and the band offsets at the porous-silicon/crystalline-silicon heterojunction measured versus sample temperature

J. T. Frederiksen, P. G. Melcher, and E. Veje
Oersted Laboratory, Niels Bohr Institute, Universitetsparken 5, DK-2100 Copenhagen, Denmark
(Received 26 February 1998; revised manuscript received 18 May 1998)

Photocurrent measurements have been carried out on a series of samples consisting of porous silicon on top of crystalline silicon, in the temperature range 10–300 K. From the experimental data set, the electrical band-gap energy of porous silicon is deduced to be (1.80 ± 0.01) eV, independent of sample temperature. In contrast to this, some temperature variations are observed for the band offsets, reflecting qualitatively the temperature dependence of the fundamental band-gap energy of crystalline silicon. However, whereas the latter decreases monotonically for increasing temperature, a maximum is observed at around 125 K for the conduction-band offset together with a corresponding minimum for the valence-band offset. The results are discussed with the conclusion that for the samples studied here, the electrical band gap in porous silicon is of a molecular nature and cannot be related to quantum-confinement properties of nanocrystals of elemental silicon. [S0163-1829(98)06336-X]

I. INTRODUCTION

Crystalline silicon (c-Si) is well suited for production of electronic components, but is in itself useless for the production of light-emitting devices, due to the indirect nature of the fundamental bandgap in c-Si. This property of c-Si has the implication that photoluminescence (PL) from it is extremely weak, even at low temperature. Therefore, porous silicon (PS) has attracted a great deal of interest since Canham, in 1990, reported[1] observation of bright PL from PS, even at room temperature, see, e.g., Refs. 2–4 and references cited therein. PS can be produced by electrochemical etching of c-Si in hydrofluoric acid.[1]

It has been discussed at length whether the bright PL from PS is of molecular origin or is related to quantum confinement in nanocrystallites of c-Si in the PS layer. For overviews of experimental and theoretical work on PS, with references to preceeding review articles, see, e.g., Refs. 5–7. Andersen and Veje[8] studied PS with PL, photoluminescence excitation, and photoabsorption, and from their data set, they concluded that for their samples, the PL properties were of a molecular nature, and could not be related to quantum confinement. Also, from their data, they constructed an energy-band diagram related to the luminescence, consisting of four bands, and they suggested that the two bands, within which the radiative recombinations take place, may be surface bands. This unusually complex band system has recently been confirmed[9,10] with the use of photoacoustic spectroscopy, which is an alternative technique to those used by Andersen and Veje.[8] To this can be added that Gole *et al.*[11] have in a detailed and convincing work been able to relate the PL to a silicon oxyhydridelike fluorophor bound to the PS surface, providing evidence for the existence of a common radiative center associated with a moleculelike species bound to the surface of the PS framework. This is fully consistent with the conclusions given in Refs. 8–10.

Romstad and Veje[12] have carried out photovoltaic and photocurrent measurements on PS at room temperature. From their data they deduced the electrical band-gap energy of PS and the conduction-band and valence-band offsets at the PS/c-Si heterojunction at room temperature. Still, the question remains as to whether the electrical bandgap of PS is of a molecular nature or is relatable to the properties of nanocrystallites of c-Si in the PS layer. Such crystallites are known to be present in the PS layer.[5,7] Whereas the PL emission may well result from radiative recombination at surface sites, presumably the electrical conductivity is a bulk property and may thus differ in origin from the optical emission properties. In addition, in a recent compilation of properties of PS edited by Canham[13] it is seen that the overall situation concerning the photoelectric properties of PS is unclear, calling for further studies. Therefore, we have decided to carry out photocurrent measurements from 10 to 300 K, the results of which are reported and discussed in this monograph. Throughout this article, with photocurrent (PC), we mean electric current induced above the dark current level by photon illumination.

II. EXPERIMENT

The samples were produced by etching boron-doped, p-type c-Si wafers of crystal orientation (100) electrochemically in hydrofluoric acid; the electrolytic cell as well as the etching procedure are described in detail in Ref. 8. Current densities from 5 mA/cm^2 to 25 mA/cm^2 were used, and, in each case, the current density was kept constant during etching. Etching times were from 30 to 60 min so that all samples consisted of a fairly thick layer of PS, to avoid direct contact between the electrode on the top surface of the PS layer and the c-Si wafer. For some of the samples, the thickness of the PS layer was studied with scanning electron microscopy. Mainly, samples of thickness from a few μm up to around 10 μm were used here. The limiting thickness, which is determined by equilibrium between the formation

 © 1998 The American Physical Society

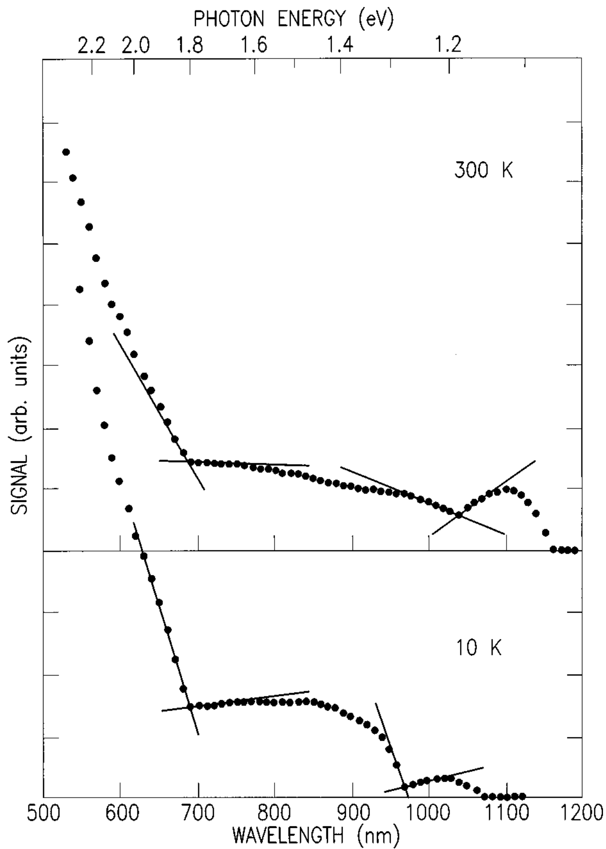

FIG. 1. Typical PC signals in arbitrary units plotted vs the wavelength (lower scale) and photon energy (upper scale) of the illuminating light. The upper curve was recorded with the sample at 300 K, and the lower curve was recorded at 10 K.

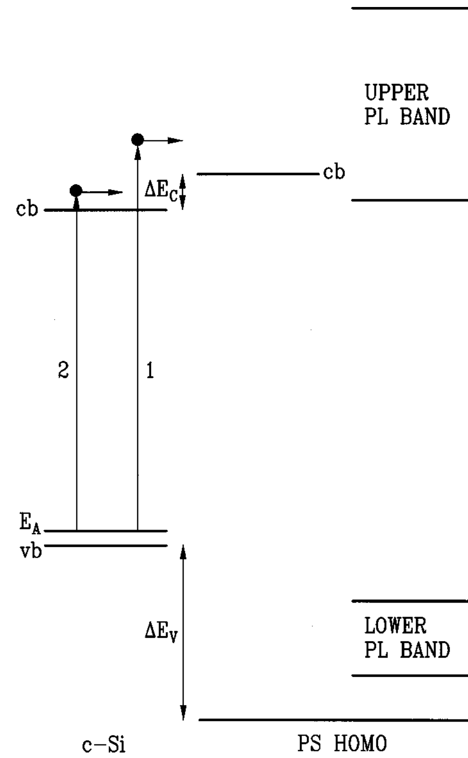

FIG. 2. The figure shows the energy-band structure for *c*-Si (left) and PS (middle and right sections) at room temperature. The band structures are on the same scale, and the band edges have been aligned in accordance with the band-offset data at room temperature. In the figure are also sketched photoexcitations in *c*-Si followed by a ballistic injection into the PS layer (process 1) and photoexcitations in the *c*-Si layer to energies below the height of the conduction-band edge in PS (process 2). The figure is a reproduction of Fig. 4 in Ref. 12, for further details, see Ref. 12.

and dissolution processes seems to be of the order of 50 μm. The samples were dried and stored in air at room temperature for several days before they were used, so that they were in equilibrium with their surroundings.

The *c*-Si wafer back side of each sample was glued onto a small copper plate with the use of a drop of silver paste. Thereby, good electrical contact between the back side of the sample and the copper plate was created at the same time as the sample was fixed to the sample holder. The electrical contact to the top surface of the PS layer consisted of a thin metal wire glued onto the surface with a droplet of silver paste. The contacts were stable in time and yielded reproducible results.

The samples were mounted in a closed-cycle helium refrigeration system and studied between 10 and 300 K. The samples were illuminated with light from a 250-W halogen lamp coupled to a McPherson model 207 scanning monochromator ($f=0.67$ m). The power of the monochromatic light reaching the sample was a few μW, so that heating as well as photochemical modification of the sample during illumination could safely be ignored. The output photon fluence from the monochromator was measured versus the wavelength passing through the monochromator, and all data have been normalized to the same photon fluence. The current through the sample was measured with a picoammeter with dark current suppression. The technical details of the photocurrent facility with data collection device are described in detail in Ref. 12.

III. RESULTS

In Fig. 1 are shown two typical PC spectra, one obtained at a sample temperature of 300 K (top), the other recorded at 10 K (bottom). In both spectra are seen two discontinuities of the slope, one being located at 690 nm (1.80 eV) and the other at 1042 nm (1.19 eV) in the PC spectrum recorded at 300 K, and correspondingly at 690 nm (1.80 eV) and 961 nm (1.29 eV) at 10 K. These two features have previously been observed at 300 K and interpreted as follows.[12] The feature at 690 nm (1.80 eV) is the onset for photoexcitation across the electrical band gap in PS, and consequently, the photon energy at this onset (i.e., the position in photon energy of the discontinuity in the slope) is identical to the electrical band-gap energy of PS. The onset at 1042 nm (1.19 eV) in the room-temperature spectrum is caused by electrons that are photoexcited in the *c*-Si backing layer and subsequently, due to the electric field, are injected ballistically from the *c*-Si layer into the conduction band in the PS layer. This process is in Fig. 2 indicated with a system of two arrows labeled 1 (for details, see Ref. 12). Previously, we also concluded[12] that the PC signals seen at wavelengths above this onset have been caused by a PC induced in the *c*-Si at sections of the

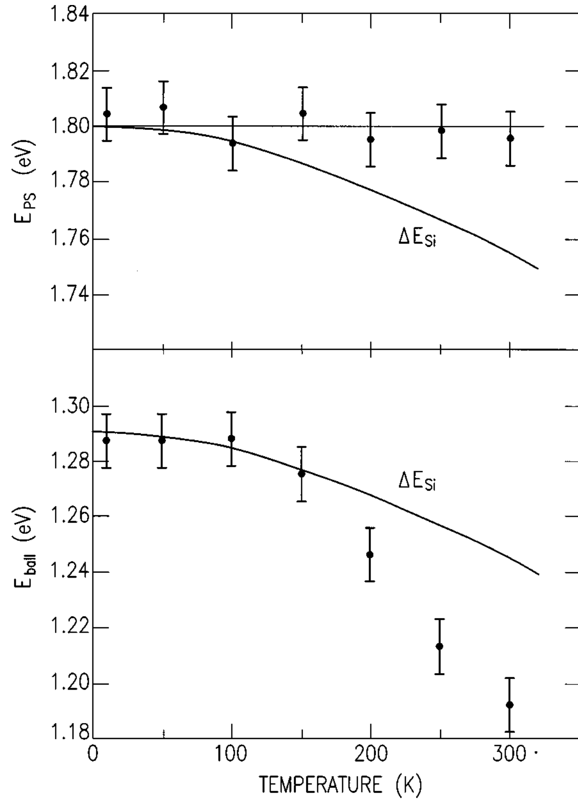

FIG. 3. The upper panel of the figure shows the experimental results for the electrical band-gap energy of PS, E_{PS}, vs sample temperature (filled circles), together with the average value, 1.80 eV, represented by a horizontal line. Included is also a full-drawn curve, labeled ΔE_{Si}, showing the temperature variation of the fundamental band-gap energy of c-Si, as given in Ref. 14, and shifted so that its value at 0 K equals the average electrical band-gap energy of PS. The lower panel shows the results of the photon energy threshold for ballistic injection of photoexcited electrons from the c-Si layer into the PS layer, E_{ball}, vs sample temperature, together with a full-drawn curve labeled ΔE_{Si}, showing the temperature variation of the fundamental band-gap energy of c-Si.[14]

sample where the electrical contact on the top surface had direct connection to the c-Si wafer, thus shorting out the PS layer. Such a process is labeled 2 in Fig. 2. This interpretation was confirmed by carrying out PC measurements on unetched p-type c-Si samples, which yielded a much stronger response with a relative curve shape similar to that seen in the wavelength region 1100–1200 nm. For details, again see Ref. 12, in which also a detailed description of our procedure for data treatment is given.

In the present work, we have recorded PC spectra at a number of sample temperatures between 10 and 300 K, and from the spectra, we have derived the temperature variations of the positions in photon energy of these two onsets. The results are shown in Fig. 3 and are also given in Table I together with the uncertainties we relate to the results.

In Ref. 12 it was argued that the conduction-band offset ΔE_c at the c-Si/PS heterojunction (i.e., the discontinuity in the conduction-band edges at the interface) equals the difference between the photon-energy threshold to create ballistic injection of electrons from the c-Si into the PS layer (process 1 in Fig. 2) and the threshold for creating the PC signal that is solely related to processes in the c-Si backing (i.e., process 2 in Fig. 2, which is related to the signals at the longest wavelengths in Fig. 1). This is because both processes result from excitation from the same level in c-Si (for details, and also for a discussion concerning possible band bendings at the heteroface, see Ref. 12). In this way, we have experimentally deduced the magnitude of the conduction-band offset from 10 to 300 K. These values are given in the fourth column in Table I and shown in the upper panel of Fig. 4. Finally, we have determined the valence-band offset ΔE_v (i.e., the discontinuity in the valence-band edges at the c-Si/PS heterojunction) from the relation given in Ref. 12, which also is evident from Fig. 2,

TABLE I. The first column gives the sample temperatures, at which the PC measurements have been carried out. The next column presents the experimental values obtained for the electrical band-gap energy E_{PS} of PS, and the results of the photon energy threshold for ballistic injection of photoexcited electrons from the c-Si layer into the PS layer, E_{ball}, are shown in the third column. The conduction-band offset values ΔE_c and the valence-band offset values ΔE_v are given in the last two columns. The uncertainty related to each value listed in the second and third columns is 0.01 eV, and the uncertainty related to each value listed in the two last columns is 0.02 eV.

T (K)	E_{PS} (eV)	E_{ball} (eV)	ΔE_c (eV)	ΔE_v (eV)
10	1.804	1.287	0.137	0.509
50	1.807	1.287	0.160	0.488
100	1.794	1.288	0.194	0.458
150	1.805	1.275	0.198	0.462
200	1.795	1.246	0.177	0.492
250	1.798	1.213	0.154	0.525
300	1.796	1.192	0.128	0.564

$$\Delta E_v = E_{\mathrm{PS}} - E_{\mathrm{Si}} - \Delta E_c .$$

E_{PS} is the electrical band-gap energy of PS, and E_{Si} is the fundamental band-gap energy of c-Si. Concerning the latter, the values used here were obtained from the data presented in Ref. 14, and concerning E_{PS}, the average value, 1.80 eV, was used throughout, instead of the specific value obtained at each temperature. As seen from Fig. 3, within uncertainty limits, E_{PS} is constant in the temperature range used, and by using the average value, the scattering of ΔE_v versus temperature was reduced. Our values for ΔE_v are presented in column five in Table I, and are shown in the lower section of Fig. 4.

IV. DISCUSSION

A. The electrical band-gap energy versus temperature

Evidently, from the upper panel of Fig. 3, as well as from the second column in Table I, for the samples studied here, the electrical band-gap energy of PS is seen to be independent of the temperature of the sample, within the overall uncertainty of 0.01 eV quoted. In the upper section of Fig. 3 is also included a horizontal line representing the average value of the data points, which equals (1.80 ± 0.01) eV, and it is seen that the individual data points are distributed randomly around this line rather than they tend to indicate some

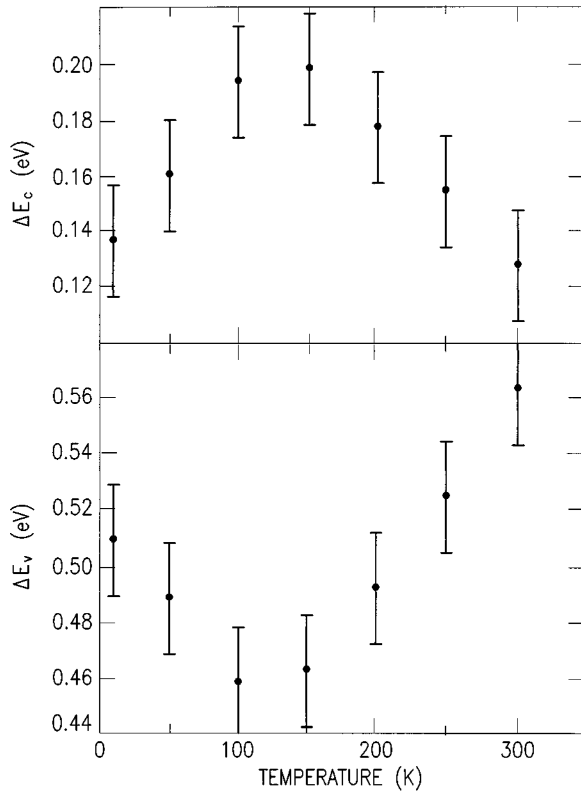

FIG. 4. The figure shows the conduction-band offset ΔE_c and the valence-band offset ΔE_v at the c-Si/PS heterojunction, vs the sample temperature.

more systematic decrease or increase with increasing temperature. In the upper part of Fig. 3 is furthermore drawn a curve showing the variation of the fundamental band-gap energy of c-Si, ΔE_{Si}, as given in Ref. 14, and shifted to match the horizontal line at 0 K. It is clearly seen that the electrical band-gap energy of PS does not tend to follow this curve.

As stated in the introduction, one of the models proposed to account for the bright PL from PS is based on the existence of geometrically small, well-confined regions of c-Si, so-called nanocrystallites of c-Si. The presence of such structures may enhance the PL emission intensities, because electrons and holes are confined spatially (for an overview of theoretical works, see Ref. 6). For such nanocrystallites, a series of localized quantum states are formed, rather than extended bands, and the eigenenergies of such states will increase with the decreasing size of the confinement region. However, the eigenenergies of these states must follow the temperature variation of the fundamental band-gap energy of c-Si, which is reduced by 0.046 eV (cf. Fig. 3) when the temperature is increased from 0 to 300 K (Ref. 14). Consequently, if the electrical band-gap energy of PS was relatable to properties of the nanocrystallites of c-Si present in the PS layer, it should follow such a temperature variation, and evidently, this is not the case (cf. Fig. 3, top). Thus, the temperature invariance we observe experimentally for the electrical band-gap energy of PS is incompatible with models based on quantum confinement. Rather, the temperature invariance we observe makes us conclude that the electrical band gap of PS is of a molecular nature, and this is fully in accordance with the conclusion in Ref. 8 concerning a band system related to the PL of PS as well as with the thorough investigation of Gole *et al.*[11] In other words, the temperature invariance observed here is fully consistent with the temperature invariance of the PL spectral distribution reported by Andersen and Veje.[8] At the same time, we want to point out, that the electrical band-gap energy of 1.80 eV is clearly larger than the threshold energy of 1.59 eV for PL, reported in Ref. 8 (i.e., the optical band-gap energy of PS). The optical band-gap energy of PS as well as the upper and lower PL-related bands, as reported in Ref. 8, are included to the right in Fig. 2. At the time of writing, the PL-related band system is being confirmed,[9,10] and although there is as yet no safe experimental evidence, there are indications[10] that the upper and lower PL-related bands are surface bands, whereas the conduction band of PS naturally is of bulk nature. Such an interpretation is fully in accordance with the work by Gole *et al.*[11] at the same time as it offers an explanation for the fact that the threshold energy for PL (Refs. 8–10) is markedly below the threshold for photoexcitation across the electrical bandgap.

In a number of cases, the question has been raised, as to whether the band-gap system of PS is of a direct or indirect nature. Here we wish to emphasize that this may be a wrongly posed question. Long-range order is definitely lost in PS and therefore, the k vector and thus the concept of a direct or indirect gap no longer have any precise meanings. Rather, the concept of electric dipole allowed or forbidden processes should be applied.

B. Conduction-band and valence-band offsets versus temperature

The conduction-band and valence-band offsets, ΔE_c and ΔE_v, are, in Fig. 4, plotted versus the sample temperature (upper and lower panel, respectively). Both of these quantities change in a smooth way with temperature, rather than showing a random scattering, and both have an extremum in the temperature interval 100–150 K, a maximum and a minimum, respectively. It is worth noting that with the uncertainties quoted, it would be incorrect to conclude that ΔE_c and ΔE_v change monotonically with temperature, and we permit ourselves to believe that the uncertainties we relate to our data are fairly conservative. Therefore, we tend to conclude that the extrema seen for ΔE_c and ΔE_v at around 125 K are real. This is supported by the fact that the temperature variation of E_{ball} is monotonically decreasing with increasing temperature, see Fig. 3. Thus, the three quantities from which ΔE_c and ΔE_v have been deduced, namely E_{PS}, E_{ball}, and E_{Si}, all change monotonically with the temperature, and the data sets for the two of these quantities that have been determined experimentally here, namely, E_{PS} and E_{ball}, do not show any appreciable scattering. Figures 3 and 4 have been drawn on identical scales to put the temperature variations of ΔE_c and ΔE_v in Fig. 4 in contrast to the temperature variations shown in Fig. 3.

Since the band-gap energy of c-Si decreases by 0.046 eV when the temperature is raised from 0 to 300 K, and the band-gap energy of PS is independent of temperature, there must be a temperature variation in one or both of the band-gap offsets. From Fig. 3, it is seen that the temperature-related reduction in band-gap energy for c-Si mainly results

in an increase in ΔE_v, leaving ΔE_c less affected. However, as stated above, the detailed changes in ΔE_c and ΔE_v versus temperature are complicated, showing extrema at around 125 K. It has been pointed out that it cannot be answered in general whether or not the band offsets are related entirely to bulk electronic properties of the individual constituents.[15] It is indeed the case for a large class of systems of ordinary semiconductor materials,[15] but there are also semiconductor compounds, for which electronic interface states influence the offsets, and this makes a discussion entirely in terms of bulk electronic properties meaningless.[15] Evidently, this is the case for the PS/c-Si heterojunction, and this is no surprise, since we deal with two bandgaps, one depends on the temperature, the other does not, one of the materials is elemental, having a well-ordered crystal structure, the other material being a disordered compound. Therefore, we shall not proceed a discussion any further here, but only mention, that according to Ref. 16, for the GaAs/AlAs system, the temperature dependence of the valence-band offset has a minimum at around 150 K, in other words, it is possible that the temperature variation of a band offset has an extremum.

Summarizing briefly, we have carried out PC measurements on a series of PS samples on top of c-Si, from 10 to 300 K. From the PC spectra, the electrical band-gap energy of PS is found to be (1.80 ± 0.01)eV, independent of the temperature of the sample. This is discussed in terms of current models for the electronic structure of PS, and it is concluded that the electrical bandgap of PS is of a molecular nature and cannot be related to the properties of nanostructures of c-Si. In addition, the conduction-band and valence-band offsets at the c-Si/PS heterojunction are determined as functions of the sample temperature, 10–300 K. The band offsets show somewhat complicated temperature relations with extrema at around 125 K.

ACKNOWLEDGMENTS

This work has been supported by the Danish Natural Science Research Council, the Carlsberg Foundation, Director Ib Henriksens Foundation, and the NOVO Nordic Foundation. All of the grants were highly appreciated.

[1] L. T. Canham, Appl. Phys. Lett. **57**, 1046 (1990).
[2] D. A. B. Miller, Nature (London) **384**, 307 (1996).
[3] K. D. Hirschman, L. Tsybeskov, S. P. Duttagupta, and P. M. Fauchet, Nature (London) **384**, 338 (1996).
[4] R. T. Collins, P. M. Fauchet, and M. A. Tischler, Phys. Today **50** (1), 24 (1997).
[5] Y. Kanemitsu, Phys. Rep. **263**, 1 (1995).
[6] G. C. John and V. A. Singh, Phys. Rep. **263**, 93 (1995).
[7] A. G. Cullis, L. T. Canham, and P. D. J. Calcott, J. Appl. Phys. **82**, 909 (1997).
[8] O. K. Andersen and E. Veje, Phys. Rev. B **53**, 15 643 (1996).
[9] E. Veje, A. Ferreira da Silva, K.-F. Berggren, I. Pepe, and A. V. Batista da Silva, Proc. Electrochem. Soc. **97-7**, 242 (1997).
[10] R. C. Egeberg, E. Veje, A. Ferreira da Silva, I. Pepe, and A. Santos Alves, J. Porous Mater. (to be published).
[11] J. L. Gole, F. P. Dudel, D. Grantier, and D. A. Dixon, Phys. Rev. B **56**, 2137 (1997).
[12] F. P. Romstad and E. Veje, Phys. Rev. B **55**, 5220 (1997).
[13] *Properties of Porous Silicon*, edited by L. Canham, EMIS Datareview Series No. 18 (INSPEC, London, 1997), Chapters 6, 7, and 10.
[14] C. D. Thurmond, J. Electrochem. Soc. **122**, 1133 (1975); and as quoted in G. E. Jellison, Jr., and D. H. Lowndes, Appl. Phys. Lett. **41**, 594 (1982); in N. Do, L. Klees, P. T. Leung, F. Tong, W. P. Leung, and A. C. Tam, *ibid.* **60**, 2186 (1992).
[15] N. E. Christensen, Phys. Rev. B **38**, 12 687 (1988).
[16] K. J. Malloy and J. A. Van Vechten, J. Vac. Sci. Technol. B **9**, 2212 (1991).