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High-pressure studies of photoluminescence in porous silicon

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Raman scattering and photoluminescence measurements performed on porous silicon at high hydrostatic pressures up to 21 GPa indicate that the phase-transition pressure in this material is porosity dependent and much higher than in bulk crystalline silicon. For porosities higher than 80% the phase transition occurs at 18 GPa followed by unrecoverable suppression of both Raman and luminescence activity. The obtained results are consistent with the quantum-confinement model. [S0163-1829(98)02745-3]

Highly porous silicon, prepared by anodic oxidation of bulk crystalline silicon, has been the subject of intense research since the discovery of its light emitting properties in 1990.[1] Technological interest in porous silicon and silicon nanostructures arises from their potential applications in Si-based optoelectronics.[2–4] Different mechanisms have been proposed to explain light emission.[5] In the quantum-confinement model the photoluminescence is assumed to be due to electron-hole recombination across the nanostructure fundamental band gap. In the present work, we try to investigate the photoluminescence emission mechanism and to test the validity of the quantum-confinement model by experiments under high hydrostatic pressure up to 21 GPa. Structural phase-transitions accompanied by changes of electronic band structure constitute an excellent tool for the study of the photoluminescence emission properties. Bulk silicon undergoes a first-order phase transition towards a metallic β-Sn phase at 12.3 GPa.[6] Porous silicon is, however, expected to show different behavior, due to its nanostructured nature.[7] Raman scattering is an excellent indicator of structural changes. Previous high-pressure studies done by other authors[8–10] gave rise to controversies. To shed more light on this subject, we have studied systematically the pressure dependence of photoluminescence (PL) and Raman scattering (RS) in porous silicon as a function of porosity. We obtained values of the Raman-shift and the PL-energy and intensity which are well reproducible for all measured porosities at all pressures up to a maximum of 21 GPa.

Free-standing porous silicon samples with porosities of 55, 65, 75, 85, and 90 % were fabricated as described elsewhere.[11] Highly porous silicon samples (85–90 %) were especially used in order to obtain nanometer-size crystallites and to reduce size dispersion. The samples were placed in a diamond-anvil cell of the Syassen-Holzapfel type[12] with a sapphire backing plate for Raman scattering.[13] A 4:1 methanol:ethanol mixture was used as pressure transmitting medium. The influence of the pressure transmitting medium on porous silicon has been investigated by other authors[9,14] and no qualitative difference was found between a (4:1) methanol:ethanol solution, an inert gas or an inert liquid. Furthermore, in Ref. 14 it was explicitly shown that the blue-to-red energy shift reversal is also observed when liquid Xe is used. This point will be discussed in detail in the experimental results. Nonhydrostaticity for pressures above 10.5 GPa (solidification of the pressure medium) was not large enough to cause broadening of the ruby lines and it is, therefore, not expected to significantly affect the PL and Raman spectra. Luminescence and Raman emission was excited by the 488 nm line of an Ar^+ laser, analyzed by a double Spex monochromator, and recorded with a photon counting system.

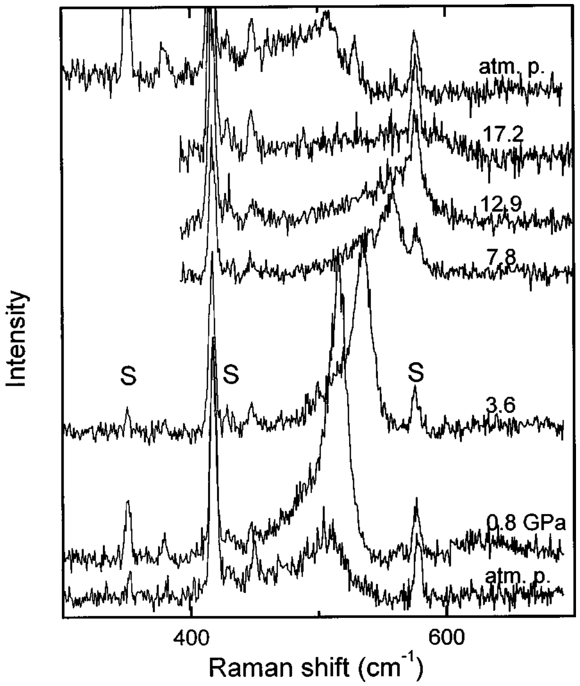

FIG. 1. Raman spectra measured during a pressure cycle on a sample of 85% porosity compressed up to 17.2 GPa. The narrow peaks at 380, 420, and 575 cm^{-1} (marked *S*) originate from the sapphire windows of the diamond-anvil cell.

Both Raman and PL spectra were recorded from the same sample spot.

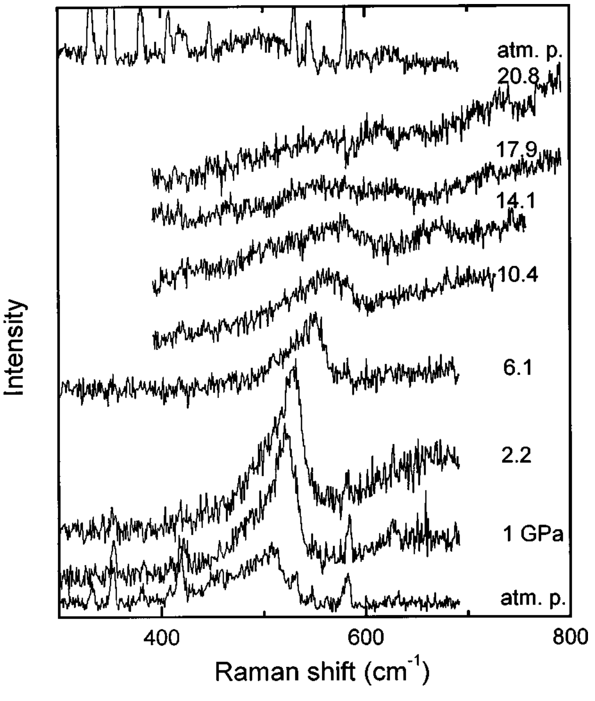

FIG. 2. Raman spectra measured during a pressure cycle on a sample of 90% porosity compressed to a maximum pressure of 20.8 GPa.

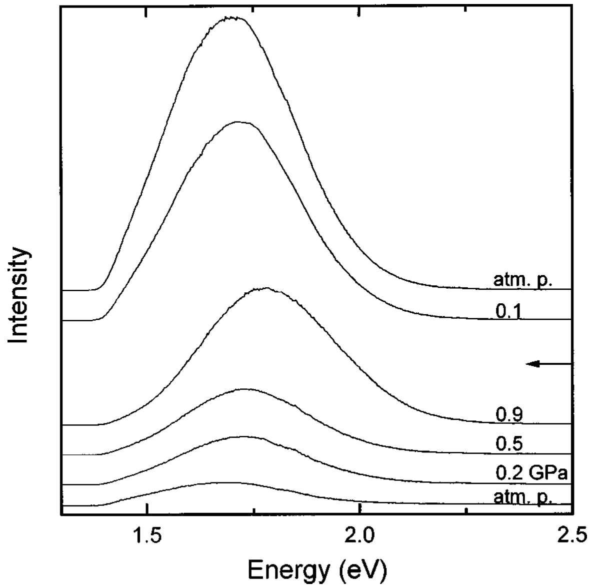

FIG. 3. Photoluminescence spectra measured in the low-pressure region ($\leqslant 1$ GPa) during the increase (below arrow) and decrease (above arrow) of pressure on a sample of 90% porosity.

Representative Raman spectra for 85 and 90 % porosity samples at various pressures during a full pressure cycle are shown in Figs. 1 and 2, respectively. At ambient pressure the Raman frequency of porous silicon $\omega_{\text{porous-Si}} = 510.5\ \text{cm}^{-1}$ is lower than the frequency of crystalline silicon $\omega_{c\text{-Si}} = 520.5\ \text{cm}^{-1}$. The redshift as well as the broadening and asymmetry of the peak, are typical characteristics of porous silicon and are attributed to spatial correlation effects. The Raman shift with pressure was found to be independent of porosity for porosities in the range 55–90 % and it was up to 20% higher than that of crystalline silicon.[15] PL spectra measured on 90% porous samples during fine scanning of the low-pressure region ($\leqslant 1$ GPa) or after pressure release following compression to high hydrostatic pressures are presented in Figs. 3 and 4, respectively. Figure 5 shows the pressure dependence of the mean energy position of the PL band $[M_1 = \int EI(E)dE / \int I(E)dE]$ for 85 and 90 % porosity. In the range up to 1 GPa, the PL intensity increases with pressure by almost one order of magnitude (Fig. 3) and the PL band is shifted to higher energies (Figs. 3 and 5). In the same pressure range the intensity of the Raman peak is also enhanced while the peak becomes narrower and the peak position is shifted to a higher frequency (Figs. 1 and 2). The increase in PL energy and efficiency could be indicative of a reduction and redistribution of sizes in the porous structure, while the narrowing of the Raman peak is characteristic of an increase in typical sizes. The absence of correlation between the PL energy and the porous-Si nanoparticle size determined from Raman spectra has been already pointed out by Lockwood *et al.*[16] This apparent contradiction can be explained by the following phenomenological model, which is fully supported by our experimental results and observations: We assume that within the porous material thin nanowires and nanocrystallites with considerable size dispersion coexist. We then attribute the Raman and PL spectra to different classes of particles of different typical sizes. The estimation of particle sizes was based on a line-shape analysis of Raman spectra according to the spatial correlation model.[17] Nanoparticle sizes were obtained after the phase transformation of large size crystallites (see below). Nanocrystallites with typical sizes below 3 nm build a well-confined system and are

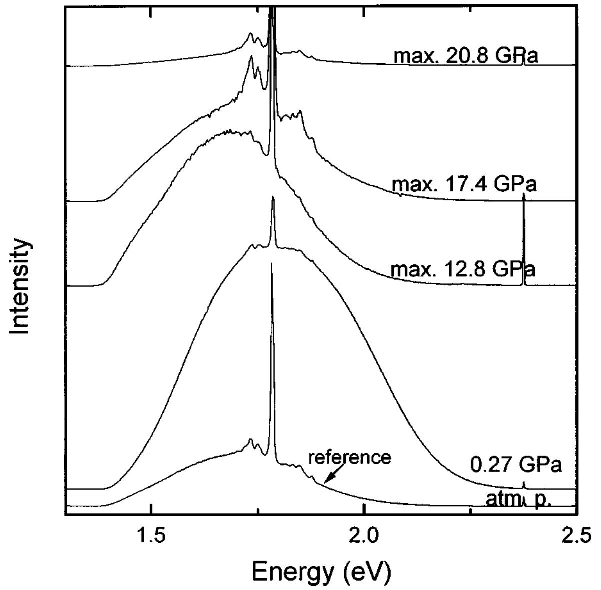

FIG. 4. Photoluminescence spectra of 90 % porous silicon samples recovered at atmospheric pressure after compression to 12.8, 17.4, and 20.8 GPa. Comparison with a reference spectrum measured at ambient pressure before pressure increase, and with the most intense PL signal observed at 0.27 GPa in the direction of increasing pressure. The sharp peaks at 2.38 and 1.78 eV and the structures superimposed to the spectra are interferences from the diamond anvils and the sapphire windows of the cell and from the ruby sensor.

responsible for the photoluminescence emission, while their Raman activity is relatively low. This assumption is in agreement with the results of Schuppler *et al.*,[18] that the optically active structures in porous silicon responsible for the luminescence in the visible range (1.68 eV/740 nm) are particles with sizes between 1.5 and 2 nm. Crystallites or clusters of crystallites with sizes larger than 3 nm and material properties similar to those of bulk silicon (c-Si), have no effective contribution to photoluminescence, but contribute effectively to Raman scattering, since the Raman intensity increases with increasing crystallite size. With increasing pressure, interconnecting nanowires are probably broken. The size distribution of nanocrystallites (<3 nm) is so changed and an increase in the number of nanocrystallites or a decrease in nanocrystallite sizes may occur. The PL blueshift in the low-pressure range could be attributed, therefore, to either a size or a pressure effect, or to the combination of both. Changes in nanocrystal surface chemistry induced by the pressure transmitting medium can be ruled out, since the observed PL blueshift on a 90% porosity sample compressed to a maximum pressure of 0.9 GPa (Fig. 3) is reversible though the intensity enhancement is nonreversible. After the complete release of pressure, the PL intensity at ambient pressure was enhanced by almost one order of magnitude compared to PL intensity before compression, while the PL frequency was reestablished to its initial value. If surface reactions have taken place, they would have caused permanent energy changes. This has been also pointed out by Cheong *et al.*,[19] although in their high-pressure study on porous silicon using liquid helium as the pressure medium only a red PL energy shift has been observed due to the fact that no measurements were done at ambient pressure or in the low-pressure range (<0.5 GPa) where the PL blueshift appears. We attribute the PL blueshift at pressures $\leqslant 1$ GPa to a pressure-dependent reversible deformation of electronic bands, while for the nonreversible PL intensity increase we assume a permanent increase of nanoparticle density through breaking of larger particles to particles with sizes comparable to the average typical nanoparticle size for this pressure range. Further increase in pressure between 1 and 12 GPa results in a reduction in PL efficiency (Fig. 4) and shifts the photoluminescence from blue to red [Figs. 5(a) and 5(b)]. The pressure required for the reversal of the shift is lower than 2 GPa. The pressure coefficient of the red energy shift is similar to that of the indirect gap of crystalline silicon of -17 meV GPa^{-1}.[20] In the same pressure range large crystallites with low surface-to-volume ratio and the same orientation form (probably) clusters with larger typical sizes. With increasing size the Raman peak becomes narrower, approaching a more ''crystalline'' (ordered) structure. Above 12 GPa large crystallites and clusters retaining the properties of bulk silicon undergo a phase transition from the crystalline to a Raman-inefficient metallic phase. Consequently, the contribution of smaller crystallites to Raman scattering becomes important, and the Raman peak is broadened while its intensity decreases as the phase-transformed large particles no longer contribute. The Raman spectra we detect at ambient pressure and their evolution with increasing pressure are significantly different than those published by Zeman *et al.*[9,10] This is possibly due to the fact that our samples (especially the highly porous samples of 85 and 90 % porosity) contain nanocrystallites with narrow size dispersion and smaller typical sizes than those of the spectra presented in Refs. 9, 10 as is evident through a comparison of the relevant Raman results. Our observation, that the photoluminescence

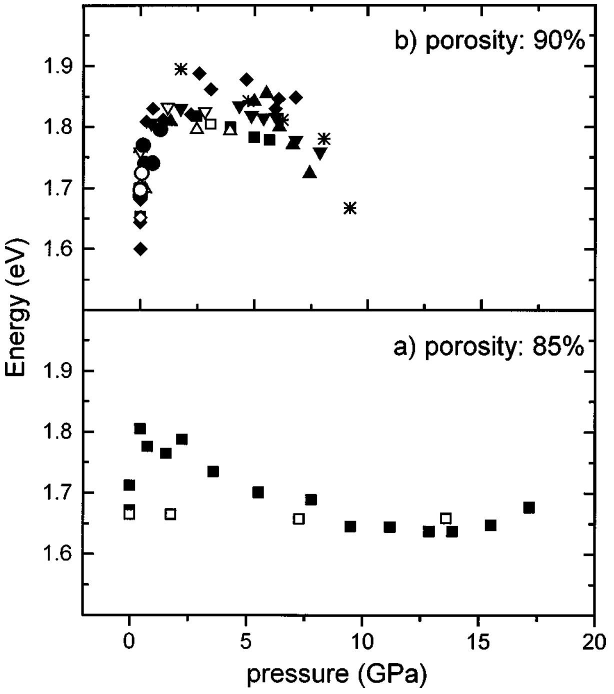

FIG. 5. Pressure dependence of the energy of the porous silicon photoluminescence during the increase (full symbols) and decrease (open symbols) of pressure for two different porosities: (a) 85% and (b) 90%. Different symbols correspond to different samples.

persists above the pressure-induced transformation of larger particles at 12 GPa, is in agreement with the observations of Zeman *et al.*[10] However, our interpretation based on the gradual evolution of Raman and PL bands between 12 and 18 GPa is that PL and RS can be assigned to different classes of particles (nanosize crystallites and crystallite clusters, respectively) and, that the PL emission above 12 GPa can be explained through the phase transformation of nanocrystallites at pressures higher than 12 GPa. Moreover, we observe that photoluminescence spectral changes are reversible for maximum pressures ⩽12 GPa [Figs. 5(b), open symbols], while changes occurring after compression to 17 GPa are irreversible [Fig. 5(a) open symbols] in consistency with the proposed transformation of nanosize crystallites at pressures above 12 GPa. After release of pressure the PL intensity of samples compressed up to 17.4 GPa is higher than the initial values at ambient conditions (Fig. 4) indicating permanent changes in particle sizes. This ''hysteresis effect'' is expected for nanocrystallites that have undergone compression at high hydrostatic pressures. In addition, the PL signal of samples recovered after compression to 17.4 GPa is lower than the signal after compression to 12.8 GPa, indicating that between 12.8 and 17.4 GPa a certain number of crystallites has been gradually phase transformed and no longer contributes to the luminescence. Thus, reversibility of the pressure dependence of the PL energy and intensity depends on the maximum pressure achieved with an irreversibility threshold found to be around 12 GPa. For irreversible paths and maximum pressures slightly below 18 GPa, the PL energy [Fig. 5(a)] does not change during or after pressure release, while the intensity and band shape of the Raman spectra (Fig. 1) confirm the occurrence of permanent structural changes. The same observations regarding the reversibility of the process have been made by Ernst[14] and similar values have been reported. In porous silicon the phase transition is gradually completed at pressures much higher than 12 GPa, since crystallites with different sizes transform at different pressures: the smaller the crystallites, the higher the phase-transition pressure. Our results are consistent with those published by Tolbert *et al.*[7] for Si nanocrystals. The phase-transition pressure of porous silicon depends obviously on porosity. Highly porous silicon (>80%) transforms at 18 GPa. Indicative of the phase transition is the change in color and transparency (the sample becomes totally opaque, almost black) and the diminishing Raman and luminescence activity. For maximum pressures above 18 GPa (after phase transformation of all crystallites), no significant Raman (Fig. 2) and luminescence activity (Fig. 4) is observed during compression between 18 and 21 GPa or after pressure release. This is a strong evidence that the luminescence emission is related to the nanocrystallites present in porous silicon. A successive reduction of the PL efficiency between atmospheric pressure and 14 GPa and a collapse of the photoluminescence intensity of porous silicon above 18 GPa has been also registered by Zeman *et al.*,[10] while Ryan *et al.*[8] and Ernst[14] have qualitatively observed a continuous decrease in luminescence intensity with pressure and complete quenching at high pressures [~17 GPa (Ref. 8) ~18 GPa (Ref. 14)].

To summarize, Raman-scattering and photoluminescence measurements have been performed in porous silicon at various hydrostatic pressures up to 21 GPa for porosities between 55 and 90%. Above 55%, the Raman frequency increases with pressure independently of porosity. Spectral features of both the Raman and PL bands exhibit almost the same transition pressures. The PL band exhibits a blueshift up to ≅2 GPa followed by a redshift up to ≅12 GPa. The observed rates in the redshift of the PL energy are similar to *c*-Si rates. In the direction of decreasing pressure both the Raman and PL spectra recover their initial band shape, if the maximum pressure achieved is less than 12 GPa. On the contrary, after compression to a maximum pressure of 18 GPa, the spectral features of Raman bands indicate permanent structural changes. The experimental results are interpreted in terms of a porous material consisting of a variety of crystallites of different sizes. Nanocrystallites with dimensions less than 3 nm are responsible for carrier localization and efficient photoluminescence, while larger size crystallites and clusters of crystallites contribute mainly to Raman scattering. The phase-transition pressure increases with decreasing crystallite sizes. In highly porous silicon (>80%) the phase transition is completed at almost 18 GPa resulting in irreversibly diminishing Raman and luminescence activity.

In conclusion, according to our experimental studies: (a) Raman scattering and photoluminescence emission of porous silicon are dominated by different size subsets of the nanocrystallites present, and (b) the luminescence emission is related to the nanometer size (<3 nm) crystallites in evident confirmation of the quantum-confinement model.

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[1] L. T. Canham, Appl. Phys. Lett. **57**, 1046 (1990).

[2] A. Loni, A. J. Simons, T. I. Cox, P. D. J. Calcott, and L. T. Canham, Electron. Lett. **31**, 1288 (1995).

[3] L. Tsybeskov, S. P. Duttagupta, K. D. Hirshman, and P. M. Fauchet, Proc. Electrochem. Soc. **95-25**, 34 (1995).

[4] A. G. Nassiopoulos, S. Grigoropoulos, and D. Papadimitriou, Appl. Phys. Lett. **69**, 2267 (1996).

[5] A. G. Cullis, L. T. Canham, and P. D. J. Calcott, J. Appl. Phys. **82**, 909 (1997).

[6] Author, in *Landolt-Börnstein, Zahlenwerte und Funktionen aus, Naturwissenschaften und Technik*, edited by K. L. Schäfer, Neue Serie, Gruppe IV, Bd. $\underline{4}$, S. 49 (Springer-Verlag, Berlin, 1980).

[7] S. H. Tolbert, A. B. Herhold, L. E. Brus, and A. P. Alivisatos, Phys. Rev. Lett. **76**, 4384 (1996).

[8] J. M. Ryan, P. R. Wamsley, and K. L. Bray, Appl. Phys. Lett. **63**, 2260 (1993).

[9] J. Zeman, M. Zigone, G. L. J. A. Rikken, and G. Martinez, J. Phys. Chem. Solids **56**, 655 (1995).

[10] J. Zeman, M. Zigone, G. L. J. A. Rikken, and G. Martinez, Solid State Commun. **96**, 503 (1995); J. Zeman, M. Zigone, G. L. J. A.

Rikken, and G. Martinez, Thin Solid Films **276**, 47 (1996).

[11] G. Kaltsas and A. G. Nassiopoulou, Sens. Actuators A **65**, 175 (1998).

[12] G. Huber, K. Syassen, and W. B. Holzapfel, Phys. Rev. B **15**, 5123 (1977).

[13] K. R. Hirsch and W. B. Holzapfel, Rev. Sci. Instrum. **52**, 52 (1981).

[14] S. Ernst, Ph.D. thesis, Universität Stuttgart, 1994.

[15] D. Papadimitriou, Y. S. Raptis, A. G. Nassiopoulou, and G. Kaltsas, Phys. Status Solidi A **165**, 43 (1998).

[16] D. J. Lockwood, A.-G. Wang, and B. Bryskiewicz, *Proceedings of the 2nd International Symposium on Quantum Confinement, Physics and Applications* [Proc. Electrochem. Soc. **94-17**, 222 (1994)].

[17] I. H. Campbell and P. M. Fauchet, Solid State Commun. **58**, 739 (1986).

[18] S. Schuppler, S. L. Friedmann, M. A. Marcus, D. L. Alder, Y.-H. Xie, F. M. Ross, T. D. Harris, W. L. Brown, Y. J. Chabal, L. E. Brus, and P. H. Citrin, Phys. Rev. Lett. **72**, 2648 (1994).

[19] H. M. Cheong, P. Wickboldt, D. Pang, J. H. Chen, and W. Paul, Phys. Rev. B **52**, R11 577 (1995).

[20] *Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology*, edited by O. Madelung, M. Schulz, and H. Weiss, New Series, Group III, Vol 17a (Springer-Verlag, Berlin, 1982), p. 43.