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The photoluminescence band in porous Si is found to shift monotonically toward lower energy at a rate of $-(18 \pm 5)$ meV/GPa if a hydrostatic pressure of up to 5 GPa is applied with liquid argon, in contrast to a convex behavior of the shift observed when a methanol–ethanol mixture is used as the pressure-transmitting medium. The data show that the electronic energy gap relevant to the luminescence is intrinsically reduced by the hydrostatic compression but has a distinct solvatochromic character. © 1995 American Institute of Physics.

Photoluminescence (PL) in porous Si is known to be sensitive to hydrostatic pressure.^{1–6} Despite a great deal of effort, the pressure dependence of the peak position is not established yet because the reported data differ from author to author. We meet similar difficulty in identifying the origin of the PL itself. So far a variety of experimental studies have provided evidence for the quantum size effect of Si nanocrystallites.⁷ Nevertheless, since the characteristics of PL are critically dependent on sample preparation and processing methods, there remain alternative arguments about the origin of PL.^{8,9}

It has been realized that porous Si is adsorbent of organic molecules, and that the PL spectrum is affected by the adsorption.^{10–13} This phenomenon suggests that PL has a solvatochromic character originating from contact interaction between the pore surface and organic solvent. In a high-pressure optical experiment, an organic fluid such as a mixture of methanol and ethanol is usually used as the pressure-transmitting medium. Therefore, the observed pressure effects could partly be due to the solvatochromic effects.

In this article we present new data on the solvent and hydrostatic pressure effects. In the pressure experiment we employ condensed argon, as well as a methanol–ethanol mixture, for the first time as the pressure-transmitting medium. Since argon is inert and known to function well as the hydrostatic medium not only in the liquid phase but also in the solid phase above 1.2 GPa, it allows one to explore the intrinsic effects of hydrostatic pressure. Our concern is to see how the pressure dependence of PL is influenced by the solvatochromism.

Free-standing porous Si films with a weight porosity of 65% are prepared from *p*-type (100) substrates with a resistivity of 10 Ω cm by the same method as described in Refs. 6 and 11. The thickness of the films ranges from 10 to 100 μ m. We deal mainly with the samples for which no intentional oxidation is made during the preparation. In this article we refer to those unoxidized samples unless otherwise noted. For the sake of comparison we deal with the following two kinds of oxidized samples: one is obtained by illuminating the as-grown films with a tungsten-halogen lamp for 24 h

while immersing them in water at room temperature; another sample is obtained by exposing as-grown films to O₂ atmosphere at 750 °C for 30 s. The samples are evacuated for at least 1 h prior to the PL measurement.

Pressure is generated with a diamond anvil cell. To liquefy argon in the pressure cell we have the argon gas flowing in the diamond anvil cell while cooling the cell with liquid nitrogen. The detail of the apparatus will be described elsewhere.¹⁴ The 488 nm light of an Ar-ion laser is used to excite the luminescence. The luminescent light is collected with an infrared microscope (Olympus IR), and is fed into a polychromator (Ritsu MC30ND) through an optical cable of bundled silica fibers. The dispersed light is detected with a CCD camera (Photometrics CH250). The spectral sensitivity of the system is calibrated using a standard lamp (Optronic OL245C). The value of pressure is obtained by the ruby-fluorescence method. All the measurements are performed at room temperature.

Figure 1 shows the PL spectra taken while keeping the samples dry, wetted with water and methanol, and immersed in liquid argon at 0.3 GPa. At 1 atm the peak position of the dry sample is located around 1.6 eV. We note that at a sufficiently low pressure liquid argon does not cause significant changes in the spectrum, as expected. Water and benzene cause only a small shift of ± 0.05 eV at most. If methanol is occluded, on the other hand, the spectrum shifts toward higher energy by about 0.14 eV; furthermore, the intensity is reduced by an order of magnitude. Similar changes occur also if ethanol is occluded. Figures 2 and 3 show the peak position and intensity, respectively, relative to the values of dry samples at 1 atm, where the electric dipole moment of solvent molecule is chosen as the variable. The solvatochromism due to methanol and ethanol is remarkable. In Figs. 2 and 3 are plotted for comparison the results concerning the main PL band of oxidized samples. In the oxidized samples the solvent effects are weak and rather independent of the species of the solvent. Evidently the pore surface is protected from solvents by oxide.

Figure 4 shows the PL spectra at several pressures in the environments of argon and a methanol–ethanol 4:1 mixture. We see that the peak position exhibits a weak red shift if the sample is pressurized with argon. As shown in Fig. 5 the pressure coefficient of the shift is $-(18 \pm 5)$ meV/GPa. In

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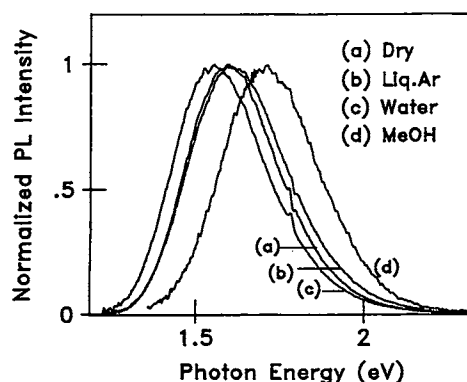


FIG. 1. Normalized PL spectra of unoxidized porous Si taken while keeping the sample (a) dry at 1 atm, (b) immersed in liquid Ar at 0.3 GPa, and wetted with (c) water and (d) methanol at 1 atm. The relative normalization factors are 1.0, 0.54, 0.69, and 0.07 for (a), (b), (c), and (d), respectively, within the accuracy of $\pm 30\%$.

contrast, if the methanol-ethanol mixture is used, the peak position shifts toward higher energies with increasing pressure, reaching a maximum around 2 GPa followed by a low-energy shift at higher pressures. In addition, the intensity is reduced further. Compared to the results obtained with argon, it is apparent that pressure enhances the solvatochromism due to the methanol-ethanol mixture. To see the effects of adsorption of water, we have measured PL of the unevacuated samples, which may be adsorbed with atmospheric moisture, by using argon as the pressure medium. An example of the results is shown in Fig. 5. The peak position clearly exhibits blue shift, while the degree depends on samples.

In the present experiment we monitor the near-edge interband absorption spectrum whenever the experimental condition is changed. In all the cases only a subtle change occurs in the photon energy and exponential slope of the interband

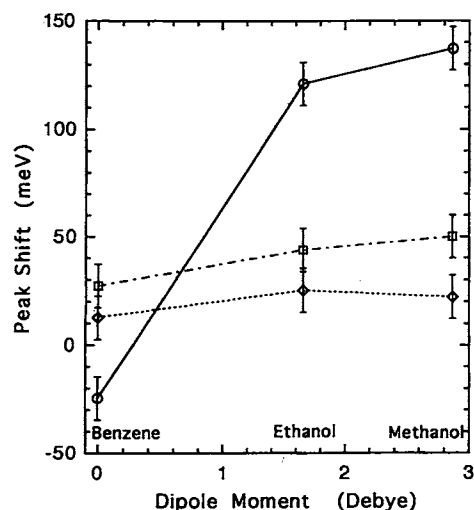


FIG. 2. Shift of the peak position of PL of (O) unoxidized, (□) illumination-oxidized, and (◇) rapid-thermal-oxidized samples vs dipole moment of the solvent molecule.

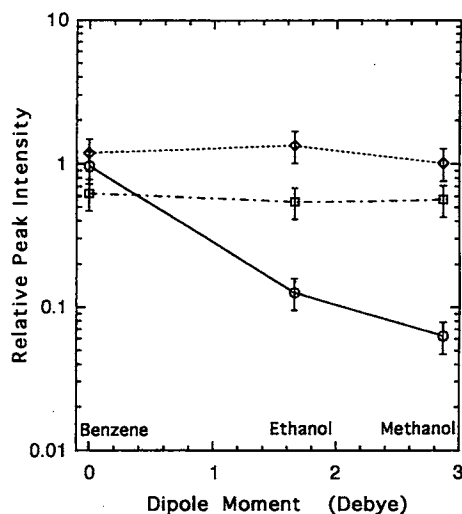


FIG. 3. Relative peak intensity of PL of (O) unoxidized, (□) illumination-oxidized, and (◇) rapid-thermal-oxidized samples vs dipole moment of the solvent molecule.

absorption spectrum of an Urbach-type.⁶ The pressure coefficient of the energy gap is estimated to be smaller than -30 meV/GPa. Furthermore, there appear no clear features of subsidiary absorption around the photon energy of the peak position of PL.

Under hydrostatic pressures of the methanol-ethanol mixture the peak energy of PL almost always shows a maximum around 2 GPa, as shown in Figs. 4 and 5. The blue shift of order of 0.1 eV at 2 GPa cannot be ascribed to the size effect of nanocrystallites, as mentioned below. In the previous studies, therefore, this phenomenon has been interpreted in terms of the Jahn-Teller effect² and band-crossover effect³ in nanocrystallites. It is evident, however, from the present results that the phenomenon is not an intrinsic pressure effect but is dominated by the contact interaction between alcohol and the pore surface. Undoubtedly the remarkable reduction of the PL intensity results from dissipation of photoexcited electrons and holes caused by this interaction.

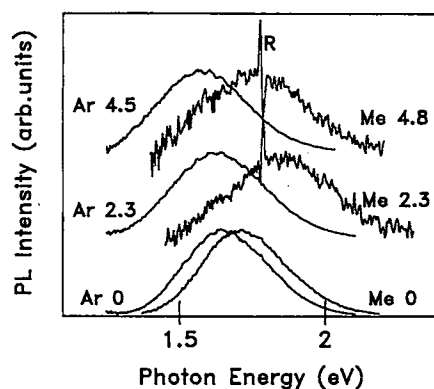


FIG. 4. PL spectra of the unoxidized sample under several pressures of argon (Ar) and methanol-ethanol mixture (Me). Numerals denote values of pressure in GPa. A sharp feature R around 1.79 eV is due to the R lines of ruby.

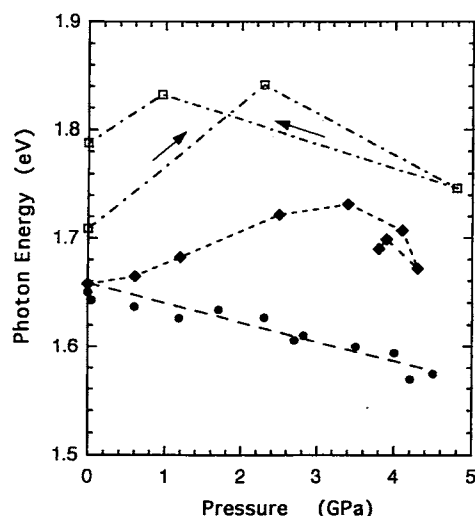


FIG. 5. Peak position of PL vs pressure. The points marked by ● and ◆ are the data of the H₂O-free and H₂O-adsorbed samples, respectively, under pressure of argon; □ are the data under pressure of a methanol-ethanol mixture. The data at 0 GPa of ● and ◆ are taken at 1 atm before liquefying argon in the diamond anvil cell.

The blue shift observed when the H₂O-adsorbed sample is compressed with argon must be dominated also by the contact interaction, which may be related to the large electric dipole moment of the water molecule.

The optical energy gap of amorphous and crystalline Si has a comparatively weak pressure dependence of -10^{15} and -14 meV/GPa,¹⁶ respectively: The energy gap of a nanocrystallite Si is expected to have a negative pressure coefficient slightly smaller than the value of crystalline Si, i.e., about -10 meV/GPa.⁵ Our findings of the weak sensitivity of the PL energy of the H₂O free, unoxidized samples to the hydrostatic pressure of argon is reconciled with the notion that PL originates from the nanocrystallites and/or amorphous matrix. The negative pressure coefficient of the absorption edge is also in favor of this notion. Another striking finding of the present experiment is the fact that the PL energy of the unoxidized samples under pressure is very sensitive to the pressure-transmitting medium as well as the surface condition. This fact affirms that the surface of pores is essential to the luminescence processes.

At present a widely accepted empirical model for the luminescence origin is the bound states supported by an interfacial, structurally relaxed, Si layer between the core and surface of nanocrystallites.^{9,17,18} In addition, the concept of quantum percolation has been theoretically put forward to explain the stretched-exponential decay behavior of the afterglow.^{19,20} This concept concerns the percolation of photoexcited electrons in random networks of $-\text{Si}-\text{Si}-$ back-

bonds of pores¹⁹ or among randomly aggregate nanocrystallites.²⁰ One may easily imagine that the relaxation processes of electrons are influenced strongly by the presence of polar molecules nearby the percolation paths. Viewed from the high sensitivity of the peak position and intensity of PL to the polar molecules such as methanol, particularly under high pressures, the quantum percolation concept seems to give a good basis of physical and practical considerations.

Recently Zeman *et al.*⁴ have found that PL persists even in the metallic phase obtained by applying a very high pressure up to 15 GPa. It is unknown if in that circumstances the above-mentioned interfacial Si layer or the networks of the backbonds remain untransformed and still support the bound states. Therefore, a firm identification of the surface states responsible for PL must await detailed studies on the properties of the high-pressure phase.

In conclusion, surface states play an essential role in the luminescence processes of porous Si and thus methanol and ethanol cause a high degree of solvatochromism on the PL spectrum. The behavior of the PL spectrum under the environment of argon demonstrates that the energy gap of the surface states is reduced intrinsically by hydrostatic pressure.

- ¹ W. Zhou, H. Shen, J. F. Harvey, R. A. Lux, M. Dutta, F. Lu, C. H. Perry, R. Tsu, N. M. Kalkhoran, and F. Namavar, *Appl. Phys. Lett.* **61**, 1435 (1992).
- ² X. S. Zhao, P. D. Persans, J. Schroeder, and Y. J. Wu, *Mater. Res. Soc. Symp. Proc.* **283**, 127 (1993).
- ³ J. M. Ryan, P. R. Wamsley, and K. L. Bray, *Appl. Phys. Lett.* **63**, 2260 (1993).
- ⁴ J. Zeman, M. Zigone, G. Martinez, and G. L. J. A. Rikken, *Europhys. Lett.* **26**, 625 (1994).
- ⁵ J. Camassel, E. Massone, L. Lyapin, J. Allegre, P. Vicente, A. Foucaran, A. Raymond, and J. L. Robert, *Proceedings of the 21st International Conference on the Physics of Semiconductors, Beijing, 1992* (World Scientific, Singapore, 1992), p. 1463.
- ⁶ N. Ookubo, Y. Matsuda, and N. Kuroda, *Appl. Phys. Lett.* **63**, 346 (1993).
- ⁷ D. J. Lockwood, *Solid State Commun.* **92**, 101 (1994); see also the references therein.
- ⁸ G. G. Qin and Y. Q. Jia, *Solid State Commun.* **86**, 559 (1993).
- ⁹ L. Tsybeskov and P. M. Fauchet, *Appl. Phys. Lett.* **64**, 1983 (1994).
- ¹⁰ J. M. Lauerhaas, G. M. Credo, J. L. Heinrich, and M. J. Sailor, *Mater. Res. Soc. Symp. Proc.* **256**, 137 (1992).
- ¹¹ N. Ookubo, Y. Matsuda, Y. Ochiai, and N. Kuroda, *Mater. Sci. Eng. B* **20**, 324 (1993).
- ¹² J. K. M. Chun, A. B. Bocarsly, T. R. Cottrell, J. B. Benziger, and J. C. Yee, *Mater. Res. Soc. Symp. Proc.* **283**, 329 (1993).
- ¹³ M. Ben-Chorin and A. Kux, *Appl. Phys. Lett.* **64**, 481 (1994).
- ¹⁴ Y. Matsuda and N. Kuroda (unpublished).
- ¹⁵ B. Welber and M. H. Brodsky, *Phys. Rev. B* **16**, 3660 (1977).
- ¹⁶ B. Welber, C. K. Kim, M. Cardona, and S. Rodriguez, *Solid State Commun.* **17**, 1021 (1975).
- ¹⁷ F. Koch, *Mater. Res. Soc. Symp. Proc.* **298**, 319 (1993).
- ¹⁸ V. Petrova-Koch, T. Muschik, A. Kux, B. K. Meyer, F. Koch, and V. Lehmann, *Appl. Phys. Lett.* **61**, 943 (1992).
- ¹⁹ S. Sawada, N. Hamada, and N. Ookubo, *Phys. Rev. B* **49**, 5236 (1994).
- ²⁰ M. Ceschini and L. Pavesi, *Proceedings of the 22nd International Conference on the Physics of Semiconductors, Vancouver, 1994*, edited by D. J. Lockwood (World Scientific, Singapore, 1995), Vol. 3, p. 2165.