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Optical absorption and photoluminescence spectra in the range 1.2–2.2 eV have been measured in free-standing films of porous Si under hydrostatic pressures up to 6.4 GPa at room temperature. The absorption rises nearly exponentially in the low energy region. Under pressure, the whole spectrum shifts toward lower energies with a pressure coefficient of about -90 meV/GPa. The photoluminescence spectrum also exhibits a redshift of about -40 meV/GPa. These results are interpreted by analogy with the pressure-induced shrinkage of the optical energy gap seen in amorphous chalcogenide semiconductors.

Porous silicon prepared by anodization in HF solution shows an intense and wide photoluminescence (PL) band in the visible region at room temperature. Various states have been proposed as the origin of this band, i.e., nanometer-scale Si crystallites,¹⁻⁴ Si-H₂-related materials,^{5,6} molecules like siloxene^{7,8} or amorphous structures.⁹⁻¹³ Electron microscope observation of nanocrystallites suggests quantum confinement effects.¹⁻³ Molecular materials like siloxene closely resemble porous Si in the PL spectrum.^{7,8} The amorphous structure is inferred for the oxidized porous Si, in which the intensity and the decay time of PL are greatly enhanced by the oxidation.^{4,9-12,14}

Recently, the behavior of the PL spectrum under hydrostatic pressure has been studied empirically. According to Zhou *et al.*¹⁵ and Zhao *et al.*,¹⁶ the PL peak shifts toward higher energies at a rate of 40–90 meV/GPa with increasing pressure from 1 atm to about 2 GPa, and then turns to shift toward lower energies as pressure increases above about 2 GPa. Camassel *et al.*,¹⁷ on the other hand, have claimed that the spectrum exhibits a redshift at a rate of -10 to -30 meV/GPa even in the range 0–1 GPa. All of the authors consider their results favorable to the quantum confinement effect. It is apparent, however, that further study of the pressure dependence of the optical properties is needed to clarify the origin of the PL band.

In this letter, we report experimental results on the effects of hydrostatic pressure on the absorption and PL spectra of free-standing porous Si film. The *p*-type Si substrate (boron doped, 10 Ω cm) is anodically etched in HF solution (HF:H₂O:C₂H₅OH=1:4:1) under a current density of 20 mA/cm² for 20 min (sample A) or 110 min (sample B). The porous Si layer thus produced is isolated from the substrate electrochemically by raising the current density to 0.5 A/cm². The thicknesses of samples A and B are 19.1 and 93.7 μ m, respectively. Both samples are oxidized for 48 h in ambient air under illumination by a tungsten lamp.

The samples are cut into pieces with a typical size of $150 \times 150 \mu\text{m}^2$. They are usable without further processing, such as lapping. The absorption and PL spectra are measured with a microscope-spectrometer system equipped

with a metal-gasketed diamond anvil cell. A fluorocarbon fluid (Sumitomo 3M Fluorinert FC40) is used as the pressure medium. The 488 nm line of an Ar-ion laser is used for exciting the luminescence, while a tungsten-halogen lamp is used as the light source for the absorption measurement. The luminescent and transmitted light fluxes are collected with an optical microscope, and are fed into a polychromator through an optical fiber cable. The dispersed light is detected by a CCD camera (Photometrics PM 512). The sample is exposed to the laser beam of a power of about 10 mW for 5–20 s to take the PL spectrum under a given pressure. The sensitivity of the polychromator-camera system is calibrated by measuring PL of which the spectrum shape is already known. The pressure in the diamond anvil cell is obtained from the wavelength shifts of the *R* lines of a small ruby crystal.

Figure 1 shows the absorption spectra of samples A and B at various pressures up to 6.4 GPa. Under atmospheric pressure, the spectrum consists of an exponential tail, i.e., Urbach tail and an appreciable background depending on the sample. The reciprocal of the Urbach slope is 0.23 and 0.30 eV for samples A and B, respectively, at 1 atm. The Urbach tail shifts toward lower energies with increasing pressure. The reciprocal of the Urbach slope appears to increase at a rate of about 0.01 eV/GPa for both samples. Figure 2 shows the photon energies at the optical density of 1.7 for sample A and 3.0 for sample B as a function of pressure. The overall shift of the Urbach tail can be described by a pressure coefficient of about -100 meV/GPa for both samples, though the coefficient seems to change with pressure in the 0–2 GPa region. On reducing the pressure, the absorption tail shifts back toward higher energies with hysteresis, as indicated in Fig. 2. If the pressure is completely released, the spectrum still lies on the lower energy side of the initial spectrum. The pressure coefficient is about -80 meV/GPa in this reverse process.

Figure 3 shows the PL spectrum under various pressures. We note that the intensity is reduced strongly by application of pressure, and is almost quenched under pressures above 4 GPa. If pressure is reduced to 1 atm, the intensity returns to about a quarter of the initial value. At

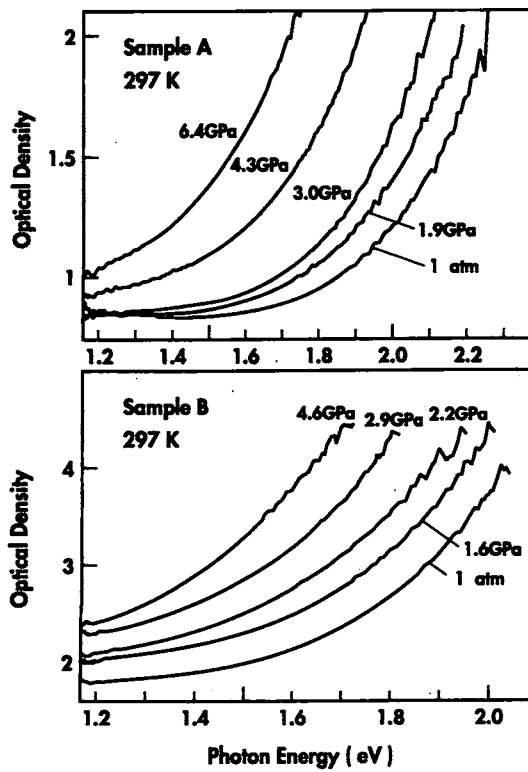


FIG. 1. Optical density spectra at various pressures for samples A and B.

any stage of this experiment, the line shape of the PL spectrum can be described well by a Gaussian function and a weak background. The peak position is plotted in Fig. 2 along with the results of the absorption measurements. It is uncertain from the present data whether the PL spectrum obeys a redshift or a blueshift under low pressures. It is evident, however, that the PL spectrum shifts toward lower energies under pressures above 2 GPa. The pressure coefficient is estimated to be from -30 to -40 meV/GPa.

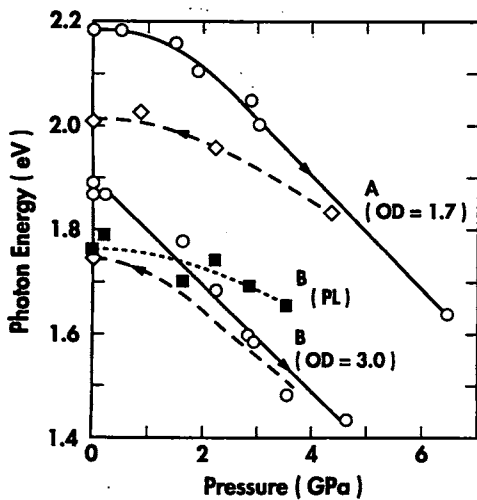


FIG. 2. Photon energies yielding certain optical densities (1.7 for sample A and 3.0 for B) under pressure. The pressure-increasing and pressure-decreasing runs are indicated by the symbols \circ and \diamond , respectively. The photon energies yielding the PL spectrum peak at various pressures are also shown by the symbol \blacksquare .

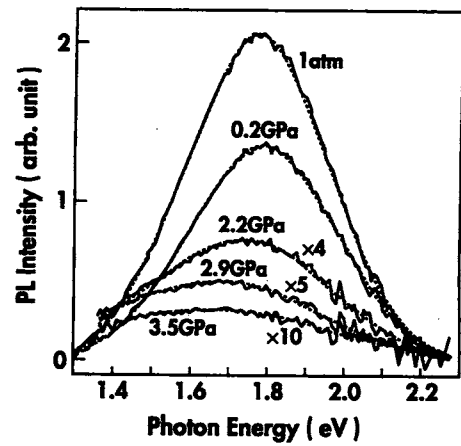


FIG. 3. PL spectra under various pressures. The solid curves are the experimental PL spectra and the dotted curves are Gaussian curves fitted to the experimental spectra. Numbers indicated are the magnification factors for the vertical scale.

On reducing the pressure, the peak position exhibits an appreciable hysteresis. This hysteresis is unlikely to be induced by the laser beam irradiation, because the fatigue caused by laser irradiation alone is negligible for the oxidized sample of porous Si. As mentioned later, the hysteresis in the PL spectrum and the absorption spectrum could reflect the pressure-induced plastic deformation of the porous structure.

Tables I and II compare the pressure coefficients of absorption and PL bands, respectively, in various materials.¹⁸⁻²³

As has been argued by Camassel *et al.*,¹⁷ the molecular materials are unlikely to be the origin since their absorption bands should have positive pressure coefficients. It is also true for the interband absorption of nanocrystallites if a simple "particle in a box" model is concerned. However, each nanocrystallite would have an absorption spectrum dependent on its size, shape, and chemical modifications by hydrogen and/or oxygen. A random distribution of such nanocrystallites might give rise to an exponential absorption tail which shows a large negative pressure coefficient.

Another possible origin for the absorption tail of porous Si is the amorphous structure incorporating oxygen and/or hydrogen. Amorphous semiconductors usually exhibit the Urbach tail, which shifts with a negative pressure coefficient. The Urbach slope is reduced by pressure because of the increased band tailing.²¹ In fact, the present

TABLE I. Pressure coefficients (dE/dP) of absorption for various materials.

Material	dE/dP (meV/GPa)	Energy gap (eV)	Reference
Porous Si	-80 to -100	~ 2.4	This work
Crystalline Si (indirect)	-14	1.1	18
Crystalline Si (direct)	52	3.4	19
α -Si:H	-10	~ 1.2	20
α -GeS ₂	-100	~ 3.1	23

TABLE II. Pressure coefficients (dE/dP) of photoluminescence for various materials.

Material	dE/dP (meV/GPa)	Pressure range (GPa)	Peak energy (eV)	Reference
Porous Si	-30 to -50	2 to 4	~1.77	This work
Porous Si	-10 to -30	1 >	~1.75	17
Porous Si	40 to 90	2 >	~1.85	15
α -Si:H	-18 to -19	8 >	~1.3	22

experiment shows that the Urbach slope of porous Si is appreciably reduced by pressure. A typical amorphous material α -Si:H has a pressure coefficient of the Urbach tail²⁰ appreciably smaller in magnitude than that observed in porous Si. The large pressure sensitivity reminds us of amorphous arsenic and chalcogenide semiconductors²³ which have a pressure coefficient of the order of -100 meV/GPa, comparable to the present observation in porous Si. The uppermost valence band of those amorphous materials is composed of lone-pair nonbonding p orbitals of chalcogenide atoms. These nonbonding orbitals overlap randomly to form the tail states. Compression enhances the overlap between the nonbonding orbitals so that the uppermost valence band is broadened and the energy gap is reduced.²³ If the lone-pair electrons of O atoms in porous Si form the uppermost valence band, as is predicted theoretically for Kautsky-type siloxene crystal,²⁴ the present result can be understood in the same way as in the case of amorphous chalcogenide semiconductors.

The amorphous structure in porous Si contains many vacant sites which may work as barriers to prevent electrons from transferring between lattices.^{4,8} In that case, many localized states with various spatial extensions²⁵⁻²⁷ will appear near the band edges. The vacancies can easily be compressed so that the degree of the overlap between the localized states might sensitively increase with pressure. The enhanced tunneling rate broadens the relevant electronic bands, contributing also to the reduction of the optical energy gap.

The PL spectrum of porous Si responds to pressure by a large decrease in the intensity. This phenomenon may partly come from an increase in the nonradiative recombination rate. The pressure-induced plastic deformation of the porous structure, which is evidenced by the hysteresis seen in both the absorption and PL bands, is likely to serve to produce nonradiative recombination centers, e.g., Si dangling bonds. Further, a possible enhancement of the tunneling rate due to the increase in the overlap between localized states could promote the nonradiative recombination, since the more widely an electron or hole spreads, the more rapidly it would be captured by a nonradiative center. Meanwhile, the pressure coefficient of the shift of the PL band is relatively small. In general, the PL charac-

teristics depend on the relaxation process of the photoexcited electrons and holes, on their population in the radiative states, and on the recombination processes. Very little is known about the effect of pressure on these factors, so it is difficult at present to pursue why the pressure coefficient differs between the PL and the absorption bands.

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