

Photoluminescence from Deuterium Terminated Porous Silicon

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Deuterium terminated porous silicon was fabricated by electrochemical anodization with DF-ethanolD6 isotope electrolyte for the first time. Both deuterium terminated- and hydrogen terminated porous silicons were characterized with TEM analysis, Raman spectroscopy and FTIR spectroscopy. The photoluminescence spectrum of D-PS was different from that of H-PS despite both nanocrystals being the same size. These results indicate that the surface vibration of terminated atoms affects the confinement energy states.

1. Introduction

A great deal of interest has been attracted by the demonstration of intense photoluminescence (PL) from porous silicon fabricated by simple electrochemical dissolution process¹⁾. As the mechanism of strong PL, the quantum confinement effect of excitons is suggested from the points of the higher energy shifts both of the photoluminescence peak and of the absorption edge with increasing chemical dissolution^{1,2)}. However, the blue shift of PL peak is small compared to what is expected from theoretical quantum confinement models³⁾. Furthermore, PL intensity also correlates with surface hydrogen and/or oxygen termination of the nanometer-structure^{4,5)}. Therefore, other alternative models such as siloxene molecules⁶⁾, hydrogenated amorphous Si⁷⁾, or surface states⁸⁾ are also proposed to explain the above points.

Isotope is a powerful tool for searching molecular terminations or kinetics of atoms or molecules. Especially, hydrogen and its isotope are widely used to study the surface structure of bulk semiconductors. A huge number of terminating hydrogen is supplied from hydro-fluoric acid (HF) in porous Si^{9,10)}, therefore by using isotope electrolyte such as deuterio-fluoric (DF) acid, the surface terminations can be changed from hydrogen to deuterium. By comparison of these isotope terminated porous structures, the effects of termination can be clarified without the difficulty of physical characterization in nanometer structure.

In this paper, we report the study of isotope termination on porous Si for the first time. We have fabricated deuterium terminated porous Si (D-PS) using DF-ethanolD6 solution (DF:C₂D₅OD:D₂O=1:1:2). We have characterized the D-PS together with the usual hydrogen terminated porous Si (H-PS) by Raman

spectroscopy. In spite of the same nanometer structure for both samples, D-PS shows shorter PL than that of H-PS. These results indicate that the surface vibration of terminated atoms affects the confinement energy states in porous Si.

2. Experimental Details and Results

Hydrogen terminated porous Si (H-PS), and deuterium terminated porous Si (D-PS) were formed by electrochemical anodizations. The H-PS was fabricated in the dark to avoid the oxidation using HF-ethanol solution (HF:H₂O:C₂H₅OH=1:1:2) by applying positive bias to a p-type 5-10 Ω cm Si substrate with a current density in the range of 100 mA/cm². The D-PS were also fabricated with the same condition except using DF-ethanol-D6 solution (DF:C₂D₅OD:D₂O=1:1:2). Both the porous layers (H-PS and D-PS) have the same 20 μ m-thickness.

The microstructures of these porous Si films were studied using Raman spectroscopy. Figure 1 shows the Raman spectra of H-PS and D-PS taken at 10 K in backscattering configuration with 488 nm line from argon ion laser. Broad and downshift spectra were observed in these samples compared with that of bulk Si crystal. The spectrum peaks near 516 cm⁻¹ with a width (full width at half maximum) of 15 cm⁻¹ for H-PS. In the case of D-PS, the bending mode of D-Si (around 530 cm⁻¹) overlaps the Raman band of Si (516 cm⁻¹), therefore we cannot measure the Raman-spectral width of D-PS; however, the peak of the Si-Raman band lies on the same position. These results show that the micro-bulk structure of H-PS and D-PS is almost the same and can be characterized by nanometer sized Si spheres with the diameter of 3 to 4 nm, which was confirmed by TEM observations.

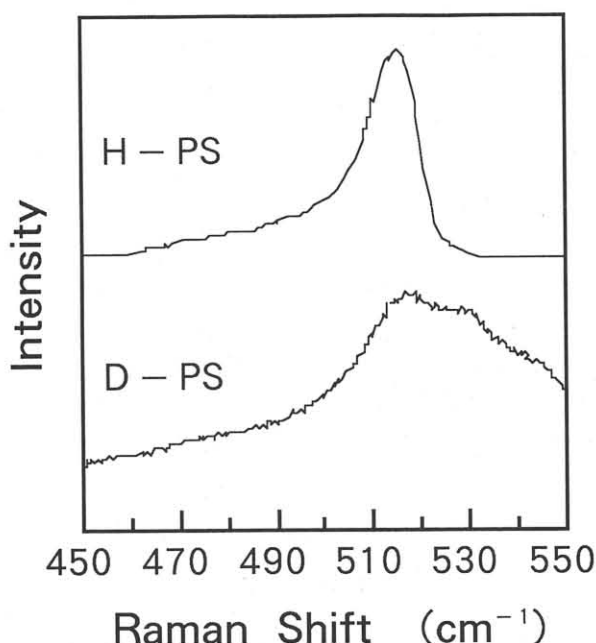


Fig. 1 Raman Spectra of H-PS and D-PS

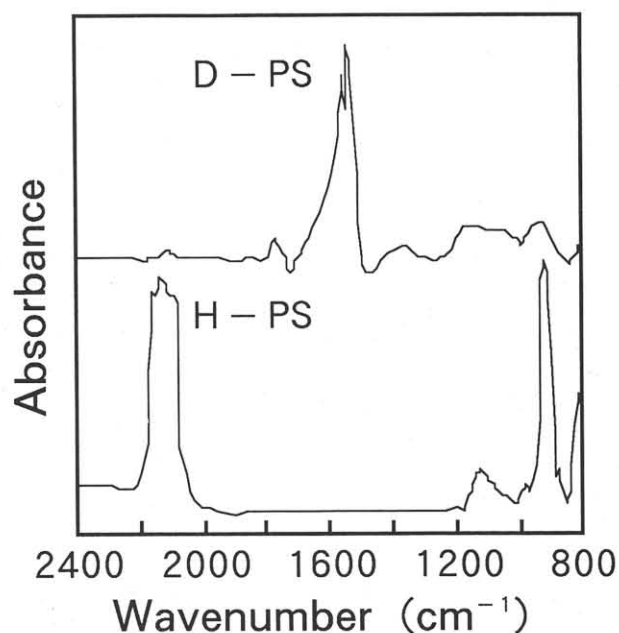


Fig. 2 FTIR Spectra of H-PS and D-PS

The surface chemistry of H-PS and D-PS were studied with FTIR measurements. Figure 2 shows the absorption spectra of these samples. In the H-PS samples, absorbance due to the stretching- (2120 cm^{-1}) and the scissor modes (910 cm^{-1}) of Si hydrides can be observed. In the D-PS samples, both the stretching modes shift to around 1530 cm^{-1} and the scissor modes to 650 cm^{-1} due to deuterium termination. The above results indicate that hydrogen termination is exchanged to deuterium one and that both the Si-H and the Si-D vibrational modes are localized at the surface of nanocrystals.

The above Raman and FTIR measurements, and the same thickness of both the layers show that the electrochemical dissolution process of DF electrolyte is the same to that of HF electrolyte.

Figure 3 shows photoluminescence (PL) spectra of H-PS and D-PS samples. The PL spectra of these porous samples were measured in a vacuum using 325-nm excitation light from helium-cadmium laser. The calibration of the spectral sensitivity was performed using a standard lamp. The peak wavelengths of the PL spectra were 780 nm for H-PS and 700 nm for D-PS. The PL intensities were almost the same for H-PS and D-PS samples. The number of dangling bonds of H-PS was almost equal to that of D-PS, which was confirmed by electron spin resonance experiments.

3. Analysis and Discussion

Despite H-PS and D-PS having the same nanostructure, the observed peak energy of PL is different. This cannot be explained by the simple quantum confinement effects, because the electronic energy states related to coordinate Si atoms such as the band gap of the

nanocrystals, exciton confinement energies or the defect states are the same for hydrogen- and deuterium surface passivations. Furthermore, the electronic states of molecules are also the same for H- and D terminations^{12,13}. The above results show that the surface terminated species around Si nanocrystallites affect the electronic states of nanocrystals.

Taking notice of the frequency difference of surface vibration between hydrogen and deuterium, the difference of the peak PL energy can be understood from the coupling effect of the quantum confined-excited carriers to the vibration of the surface terminated species around Si nanocrystals. The PL peak energy can be calculated by applying Lee-Low-Pines transformations¹³ to the Fröhlich Hamiltonian of a short range interaction¹⁴. It turns out to be

$$E = \frac{\alpha}{L} + 1.1 - \frac{\beta \hbar \omega_s}{L}, \quad (1)$$

where L is the nanocrystallite diameter, $\alpha/L + 1.1$ (α is a constant parameter) is the energy-gap upshift derived from the first principle pseudopotential calculation³, ω_s is a stretching frequency of hydrogen or deuterium terminating on Si nanocrystals, and β is an energy reduction ratio depending on ω_s . Upshifted levels due to the quantum size effects are reduced by $\beta \hbar \omega_s / L$. The energy downshift depends on the stretching frequency of the surface terminated atoms, therefore the PL peak energy is different for hydrogen- and deuterium terminated porous Si in spite of the crystallite size being the same. The above energy reduction indicates that the PL energy upshift is smaller than what is expected from the theoretical calculations, which is clearly shown by Schuppler et al.¹⁵.

Theoretically fitted PL peak energies (broken lines) and the band gap (solid line) as a function of the crystallite size are also shown in Fig. 4 with α as 3.6, β

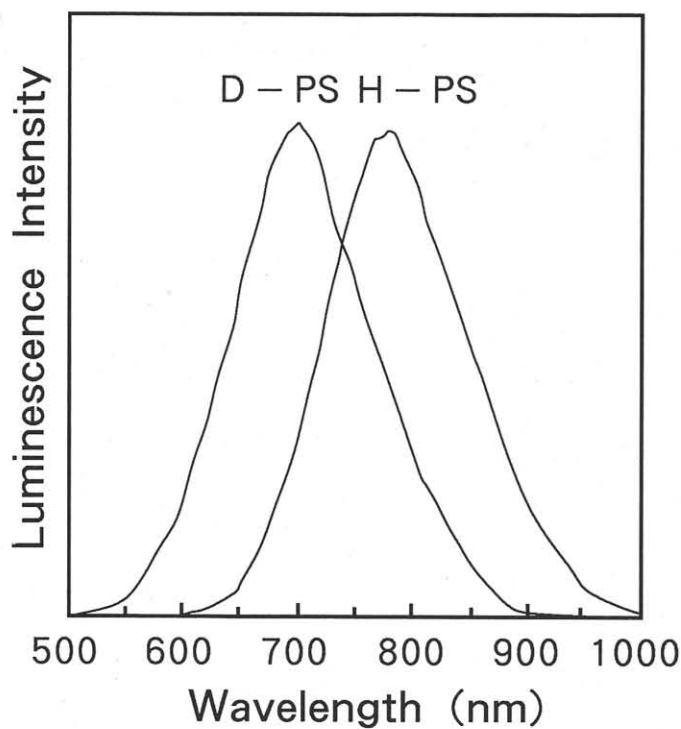


Fig. 3 PL spectra of H-PS and D-PS

as 8.09 for hydrogen termination, and β as 8.54 for deuterium termination. We note here that β is 15.42 in the case of oxidized porous Si. (β varies as the configuration of oxygen on Si nanocrystals changes.) The experimentally observed PL peak energies as a function of crystallite size of H-PS obtained by our experimental results (open squares) and those of oxydized Si nanocrystals (O-Si) obtained by Takagi et al.¹⁶⁾ (solid circles) well agree with these theoretically-calculated lines as shown in Fig. 4.

4. Conclusion

In conclusion, we have fabricated hydrogen- and deuterium terminated porous Si structures and analyzed the experimental results by a coupling effect of confined carriers to the surface vibration. Isotope termination is a powerful method to study the surface effect of nanometer crystallites. Important problems related to many electron systems (or exciton) confined in nanocrystals interacting with surface vibration remain unresolved.

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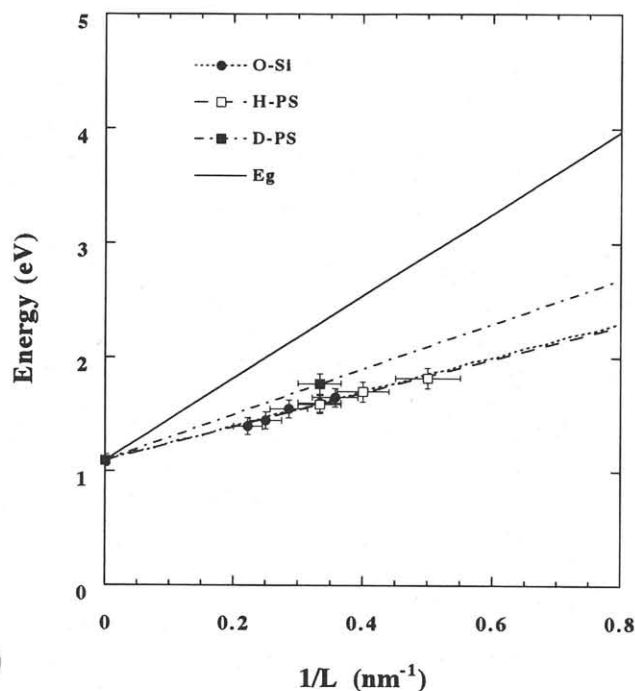


Fig. 4 The size dependence of PL peak energies for H-PS (open squares), D-PS (solid squares) and O-Si (solid circles).

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