Resonantly excited photoluminescence from porous silicon:
Effects of surface oxidation on resonant luminescence spectra

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We have studied the photoluminescence mechanism of freshly prepared and naturally oxidized porous silicon by fluorescence-line-narrowing spectroscopy. The surfaces of fresh and oxidized porous silicon are terminated by silicon hydrides and silicon dioxide, respectively. The TO-phonon-related structure in resonantly excited luminescence is clearly observed in H-terminated porous silicon. After surface oxidation, the luminescence intensity increases and a structure in the resonant luminescence appears due to the coupling of excitons and local vibrations at the surface. The effect of surface oxidation on the luminescence spectrum of Si nanocrystals is discussed. [S0163-1829(97)50228-1]

The goal of achieving efficient visible luminescence from Si nanostructures has stimulated considerable efforts in understanding optical properties of group-IV semiconductor nanostructures and producing nanostructure devices.[1] In particular, porous silicon is receiving widespread interest because of its high quantum efficiency of light emission. There are many extensive studies concerning the origin of visible light emission in porous silicon.[2] However, the mechanism of visible luminescence is not clear and is still controversial, because porous silicon shows various optical characteristics.[1,2]

Porous silicon is an inhomogeneous system in the sense that it has broad distributions of nanocrystal size and shape and variations of surface structures. Under blue or violet light excitation, porous silicon shows broad luminescence at room temperature.[1,2] This ''full'' luminescence contains contributions from all nanocrystals in the sample and is inhomogeneously broadened. It shows no fine structures even at low temperatures. However, as in many inhomogeneously broadened systems, resonant excitation (or selective excitation) results in fluorescence line narrowing.[3] Since we suppress the inhomogeneously broadening of the luminescence by selectively exciting a narrow subset of crystallites, the resulting emission is narrow, displaying a well-resolved phonon progression.[3] The resonantly excited luminescence spectrum with fine structures (''resonant'' luminescence) provides an information on the ongoing discussions of the luminescence mechanism. Porous silicon shows the TO-phonon-related fine structures under resonant excitation at low temperatures.[4–7] In contrast to porous silicon, the phonon-related fine structures in the resonant luminescence spectrum are not clearly observed in the size-controlled or size-selected Si nanocrystals with a SiO_2 surface layer.[8,9] The nature of the emitting state and the resonant luminescence in porous silicon and Si nanocrystals has remained controversial.[7–11] In this paper we discuss the effect of surface structure on the full and resonant luminescence in po-

rous silicon by comparing freshly prepared and naturally oxidized porous silicon.

The porous silicon samples were prepared as follows.[12] The substrates were (100)-oriented p-type silicon wafers with a resistivity of $\sim 0.9 \ \Omega$ cm. Thin Al films were evaporated on the back of the wafers to form a good Ohmic contact. The anodization was carried out in HF-ethanol solution ($HF:H_2O:C_2H_5OH = 1:1:2$) at a constant current density of $10 \ mA/cm^2$. It is known that there exist a vertical structure inhomogeneity in the thick porous layer and this structural inhomogeneity affects luminescence properties of porous silicon.[13,14] The vertical inhomogeneity is a consequence of the porous silicon formation mechanism. The top of the porous layer has been in the etching solution longer than the bottom. The crystalline silicon size is then smaller at the top of the layer. After air exposure, the top of the layer is easily oxidized. The size and surface structure of nanocrystals in the top of the layer are completely different of those in the bottom of the layer. Then the porous layer thickness of $\sim 1 \ \mu$m was chosen to provide a uniform optical excitation within the porous layer and a uniform native oxidation within the layer after prolonged air exposure.[15]

The photoluminescence (PL) spectra were measured using a double monochromator, a lock-in amplifier, a photomultiplier, and cw He-Cd, Ar, Ti:Al_2O_3 lasers. The PL spectra were recorded by two different methods. (1) Modulated laser excitation: The excitation laser light was modulated by an optical chopper with frequencies $f(10 \ Hz < f < 1.1 \ kHz)$. The PL spectra depended on the frequency f. (2) cw laser excitation: The excitation laser light was not modulated, but luminescence from samples was modulated by an optical chopper f for the PL spectrum measurement. This PL spectrum did not depend on the frequency and is the time-integrated PL spectrum.

Figure 1 shows Fourier-transform infrared (FTIR) absorption spectra of as-prepared porous silicon and naturally oxi-
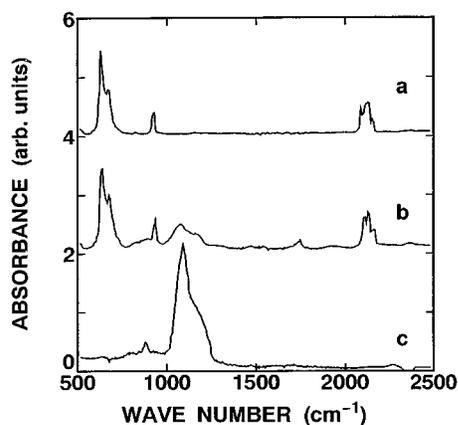
FIG. 1. Infrared absorption spectra of porous silicon samples: (a) as-prepared porous silicon, (b) porous silicon after 15 days air exposure, and (c) oxidized porous silicon. The surface of as-prepared porous Si is covered by hydrogen atoms. After prolonged air exposure, the surface of nanocrystals is oxidized.

dized porous silicon after air storage. For FTIR absorption measurements, we removed the Al electrode on the back of the c-Si wafer substrate and measured the absorption spectrum of the porous Si layer (the absorption due to the c-Si substrate was corrected). In the as-prepared porous silicon sample, the strong absorption peaks are clearly observed around 625, 665, 910, and 2100 cm^{-1}. These peaks are due to the Si-H_n bending mode, Si-H_n deformation modes, the Si-H_2 scissors mode, and the Si-H_n stretching modes.[16] The surface of nanocrystals in as-prepared porous silicon layer is covered by silicon hydrides (SiH, SiH_2, and SiH_3), however, the samples show weak luminescence. After prolonged air storage, a broad peak is observed around ~ 1100 cm^{-1} due to the Si-O-Si stretching mode. The increase in the Si-O-Si band is ascribed to a gradual room-temperature oxidation of the crystal Si skeleton.[15,16] However, even after 15 days in air, the three bands due to the Si-H_n species are clearly observed around 2100 cm^{-1}. The absorption peaks in Si-H bands are larger than those of Si-O bands, although the absorption coefficient of the Si-H band is much smaller than that of the Si-O-Si stretching band.[15,16] Thus this shows that the large area of the sample surface is still covered by silicon hydrides, and the sample of Fig. 1(b) is ''fresh,'' similar to the samples in the previous works.[16–18] Then these samples (used within two weeks) were used as fresh or H-terminated porous silicon. After one year or more, the Si-O bending and the Si-O-Si stretching modes are only observed in the FTIR spectrum. The surface is covered by a SiO_2 layer. These samples were used as oxidized porous silicon.

Figure 2 shows full luminescence spectra of fresh porous silicon and oxidized porous silicon at different temperatures under cw laser excitation. The excitation wavelength was 325 nm from a He-Cd laser, and the excitation intensity is ~ 1 mW/cm^2. Although the surface structures dramatically changed in air storage (see Fig. 1), there is no drastic change in the full luminescence spectrum at room temperature. After surface oxidation, the PL intensity increases significantly (more than one order of magnitude). The PL peak energy in oxidized porous silicon is sensitive to the measurement temperature, compared with the case of fresh porous silicon. The PL peak energy shifts to higher energy at low temperatures.
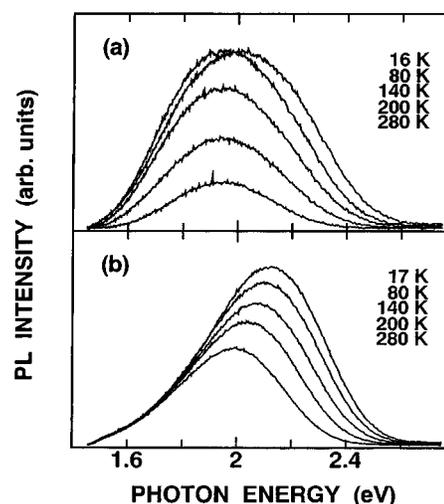

FIG. 2. Temperature dependence of the luminescence spectra of (a) fresh porous silicon and (b) oxidized porous silicon under 3.814-eV excitation. The luminescence peak energy at low temperatures is blueshifted after surface oxidation.

The resonantly excited PL spectra of porous silicon at 2 K are very sensitive to the surface structure of porous silicon, as will be shown below.

Figure 3 shows the modulated frequency dependence of (a) the full luminescence under 3.814-eV excitation and (b) the resonant luminescence under 2.409-eV excitation of oxidized porous silicon, at 2 K. The modulation frequency dependence of the resonant PL spectrum is more clearly observed, compared with the case of the full luminescence. With an increase in the modulated frequency, the PL peak energy shifts to the higher energy region. In particular, the PL spectrum depends on the modulation frequency at lower frequency region ($f < 120$ Hz). These results suggest that the relaxation time has broad time distributions and different PL processes coexist in porous silicon. Thus it is considered that the resonant PL spectra at different modulation frequencies in fresh and oxidized porous silicon samples provides very important information on the PL mechanism of porous silicon and Si nanocrystals.
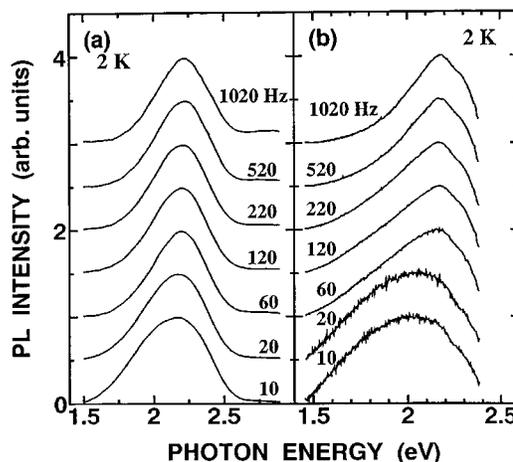

FIG. 3. Modulation frequency dependence of luminescence spectra of surface-oxidized porous silicon at 2 K by using excitation photon energies: (a) 3.814 and (b) 2.409 eV.
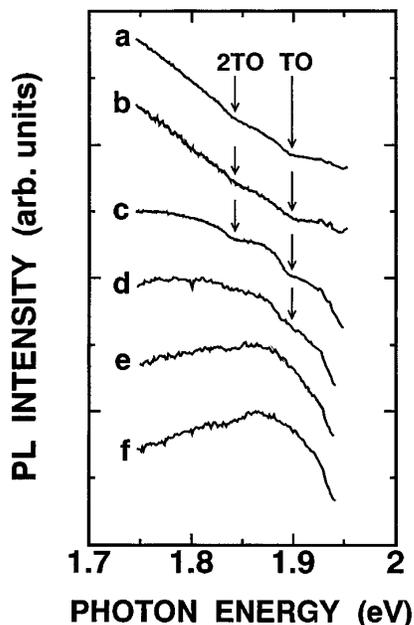
FIG. 4. Resonant luminescence spectra of fresh porous silicon [(a) cw and (b) $f = 120$ Hz] and oxidized porous silicon [(c) cw, (d) $f = 13$, (e) $f = 520$, and (f) $f = 1020$ Hz] at the lower-energy side of the laser line of 1.959 eV at 2 K.
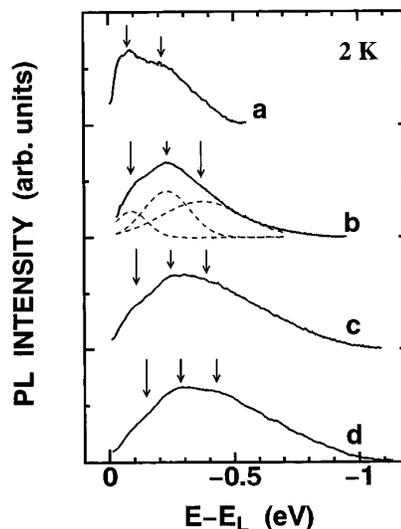

FIG. 5. Resonant luminescence spectra of oxidized porous silicon at 2 K and $f = 130$ Hz by using excitation photon energies: (a) 1.959, (b), 2.409, (c) 2.496, and (d) 2.540 eV. The zero on the abscissa scale corresponds to the excitation laser energy.

Figure 4 shows resonant luminescence spectra of fresh and oxidized porous silicon at different modulation frequencies. The measurement temperature was 2 K and the excitation energy was 1.959 eV which corresponded to the red side of the full luminescence spectra (see, Fig. 2). In the resonant luminescence spectrum under cw laser excitation, the steplike structure can be observed in both fresh and oxidized porous silicon samples. In H-terminated porous silicon samples, the PL spectrum scarcely depend on the modulated frequency. The fine structures in the resonant PL spectrum shown by the arrows in the figure is equal to the TO (~ 57 meV) phonon energy of bulk crystalline Si (c-Si).[5] However, after prolonged air exposure (surface oxidation), the steplike structure becomes unclear with an increase in the strength of the Si-O-Si stretching mode. The resonant luminescence spectrum depends on the modulated frequency. These results suggest that the PL mechanism of surface-oxidized porous silicon is different from that of H-terminated porous silicon and different PL processes coexist in surface-oxidized porous silicon samples.

Figure 5 shows resonant luminescence spectra recorded at 2 K using excitation energies of 1.959 (curve a), 2.409 (curve b), 2.496 (curve c), and 2.540 eV (curve d), where the zero on the abscissa scale corresponds to the excitation energy. The resonant luminescence spectrum shows the peak structure rather than the steplike structure. Broad luminescence spectra with multipeaks are divided by the Gaussian bands, where peaks are shown as the arrows in the figure. A curve fitting program has been used to generate the Gaussian components, which are shown as dashed curves in Fig. 5(b), where the sum curve of the Gaussian bands can reproduce the experimental curve. The energy interval between the Gaussian peaks (135–140 meV) corresponds to the 1100 cm^{-1} Si-O-Si stretching mode, although the intensity ratio of the Gaussian peaks depends on the excitation energy

position in the full luminescence spectrum.[19] Even under laser excitation of the higher energy side of the luminescence band, this structure is observed in oxidized porous silicon. In contrast, in H-terminated porous silicon, the steplike structure is only observed under laser excitation of the higher energy side of the luminescence band, but the peak structure is not observed.[5,9] In oxidized porous silicon samples, a peaklike structure is clearly observed at high chopping frequencies. We observed for the first time that there is a good correlation between the surface oxidation and the resonant luminescence spectrum in porous silicon.

Let us now discuss the PL mechanism of H-terminated and surface-oxidized porous silicon. It is well known that hydrogen termination extremely reduces the surface recombination centers in c-Si.[20] By utilizing H-terminated surfaces, we can minimize the influence of surface states. Moreover, Raman spectroscopy examination implies that H-terminated porous silicon shows the crystalline nature while oxygen-terminated porous silicon shows atomic disorder within the nanocrystals.[17] The PL peak energy in H-terminated porous silicon without air exposure is sensitive to the size of the nanocrystal, compared with the case of surface oxidized Si nanocrystals.[21] In H-terminated porous silicon, the interior c-Si state plays an essential role in the luminescence process. The weak deformation potential interaction between excitons and phonons in c-Si causes the TO-phonon related structure in the resonant luminescence spectrum.[4,5] The steplike structure reflects the phonon-assisted absorption process rather than the light emission process in the c-Si interior state.[4] H-terminated porous silicon samples show their indirect-gap c-Si nature in the resonantly excited luminescence process.

On the other hand, in oxidized porous silicon, the peak structure is observed as shown in Fig. 5. The peak structures with 135–140 meV energy interval cannot be explained by the exciton-phonon coupling in the Si crystallites (~ 57 meV TO phonon) as excitons are highly delocalized within nanocrystals. This energy is almost equal to the local

vibration energy of the Si-O-Si stretching mode,[22] as mentioned above. The strong coupling between localized excitons and vibrations at the surface causes the structure in resonant luminescence, through the Fröhlich interaction between excitons and polar Si-O vibrations.[23] These results indicate that excitons are strongly localized at the Si/SiO$_2$ interface, since the coupling of electronic and vibrational excitations dramatically increases with localization of excitons in smaller dimensions.[24] After surface oxidation, the PL intensity increases significantly and the PL peak energy at low temperatures is blueshifted. The Si-O-Si vibration-modified structure appears in the luminescence spectra. Moreover, the PL peak energy in oxidized porous silicon is not sensitive to the nanocrystal size.[12] Then, oxygen-modified surface states provide the active states for efficient luminescence. Thus it is considered that efficient PL is due to the radiative recombination at the surface state in oxidized porous silicon. However, the steplike structure is also observed in the infrared spectral region. This is because the surface states do not critically affect the PL process in large nanocrystals exhibiting infrared and red PL. These results suggest the coexistence of different PL processes in surface-oxidized porous silicon samples. The PL mechanism of surface-oxidized porous silicon is complicated, compared with H-terminated porous silicon. We believe that the efficient luminescence comes from the oxygen-modified surface states, although other emission mechanisms are active in oxidized porous silicon. Studies of the resonant luminescence in Si nanostructures with an identified surface structure would reveal the nature of the visible luminescent mechanism in inhomogeneous Si quantum structures and materials.

In conclusion, we have discussed the effects of surface structures on resonant luminescence spectrum of porous silicon. There is a good correlation between surface structure and the resonant luminescence spectrum in thin porous silicon samples. H-terminated porous silicon samples clearly show the TO-phonon related structure in the resonant luminescence spectrum. After surface oxidation, the PL intensity increases and the fine structure in the resonant luminescence of surface-oxidized porous silicon depends on the experimental condition such as the photon energy and the modulation frequency of the excitation laser. Both the surface and interior c-Si states contribute to efficient PL in porous silicon.

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