

Luminescent properties of visible and near-infrared emissions from porous silicon prepared by the anodization method

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Luminescent properties of anodized porous Si are experimentally investigated. An extremely long decay time together with a peculiar temperature dependence due to the competing Auger process are observed for the visible luminescence band indicating an analogous recombination mechanism to that of electron-hole pairs being trapped at spatially separated tail states in *a*-Si:H. Besides this visible luminescence, an intense emission is also detected in the infrared region around 1.1 eV. Its decay time is shorter than that of the visible band and possible recombination mechanisms are discussed.

Visible light emission from porous silicon¹⁻⁵ and related microstructures^{6,7} has been an issue of recent interest from both scientific and technological aspects. In spite of extensive experimental studies, the unique role of the size-quantization effect due to a spatial carrier confinement in the radiative recombination mechanism in anodized porous Si has not been experimentally verified due to the difficulty in directly correlating its photoluminescence (PL) with structural observations. So far, two types of explanation have been presented for the visible light emission, which has much higher energy than the band gap of crystalline Si. One is the carrier recombination in a layer having a modified structure from original Si crystal, for which the mechanism resembles that in hydrogenated amorphous Si (*a*-Si:H) (Ref. 8) or polysilane.⁹ The other is the size-quantization effect experienced by carriers confined in a small dimension of *c*-Si just as in the case of ultrafine Si particles.⁶ The original claim of the latter by Canham¹ is based on the smaller spectral width [full width at half maximum (FWHM) = 0.1 eV] of the emission as compared to those of the visible luminescence from *a*-Si:H (0.3 eV) and polysilane (0.6–0.7 eV). However, this point, which relies on his uncorrected spectra, should be reexamined because different and broader visible emission spectra have been commonly reported by other workers. Gardelis *et al.*⁵ also supported the quantization-effect model based on the analogous features in the decay time and the temperature dependence to those of quantum-confined excitons. Therefore, it is of importance to investigate if their observation is universal. Quite recently, the existence of an intense near-infrared luminescence around 1.1 eV was briefly reported.¹⁰ Study on this emission in conjunction with the one in the visible region should provide an important insight into the understanding of the recombination mechanisms in porous Si.

In this paper, the results of photoluminescence measurements on these two emission bands in porous Si are presented. It is found that the properties of the visible luminescence are peculiar in various aspects and are rather compatible with the spatially separated electron-hole recombination just as those trapped in the tail states of *a*-Si:H. Possible models for the occurrence of the two emissions are also discussed.

We used boron-doped *p*-type Si substrates as the starting material. Before anodization, the back side electrodes were formed by evaporating Al and by subsequently annealing the wafers at 500°C for 30 min. The anodization was performed in a hydrofluoric-acid (HF) solution (49%-HF/ethanol = $\frac{2}{3}$) with a Pt cathode. The maximum dc voltage employed was 3V, which was applied for a period of 120 min.

The luminescent properties were measured in the temperature range between room temperature (RT) and 4.2 K. Either Kr⁺ (351 nm) or N₂ laser (337 nm) was used as the excitation source depending on the purpose of cw or pulsed measurements, respectively. The luminescence was dispersed by a spectrometer with a focal length of 1 m and was detected either by a photomultiplier tube or Ge pin diode. Unless stated, the frequency of chopping the excitation was kept constant at 225 Hz.

Figure 1 shows a typical PL spectrum for the porous Si measured at 4.2 K. The displayed spectrum has been corrected for the optical response of the measurement system. It consists of two dominant emissions with comparable intensities, one with a peak at around 1.7 eV and the other at around 1.1 eV. They are, respectively, referred to as visible and ir bands in the following. Both peak positions agree with those reported by Perry and Lu¹⁰ quite recently. However, the information on the spectral shape of their ir luminescence is not available so that it is not clear at present whether our observation is

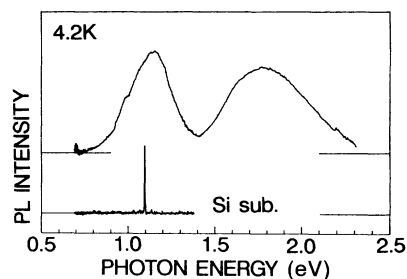


FIG. 1. The upper curve is the photoluminescence spectra for the anodized porous Si measured at 4.2 K, which are corrected for the spectral response of the measurement system. The lower one was obtained by exciting the unanodized crystalline substrate area.

in full agreement. The lower spectrum in Fig. 1 was obtained by exciting the Si substrate (a portion covered with wax during the anodization) for comparison. It is dominated by a sharp emission due to the TO-phonon satellite of a boron-bound exciton and shows a distinct difference from the broad spectral shape of the ir band in the porous Si. Although the temperature dependence was found to be quite different among the visible and ir bands, as described later, it was found to be possible to detect both bands in the whole temperature range studied. Intensities of these bands were recorded as a function of the excitation photon energy (excitation spectra) as shown in Fig. 2. Both bands have a common threshold for excitation around 2.3 eV. This result indicates that the same excited state is involved for the two recombination processes. It was further found that the peak energy of the visible emission shifts to higher energies as the excitation energy is increased. One possible explanation is that this luminescence is excited below the "thermalization edge" of a disordered material.⁸ In such a case, either an electron or a hole is directly generated in the localized tail state so that the recombination energy is expected to show a memory effect of the excitation energy. However, a possibility cannot be ruled out at this stage that the observed peak-energy shift may be brought about by a spatial nonuniformity probed by different penetration depths.

The decay characteristics were also studied and the results are summarized in Table I. With our apparatus, the intensity of the ir band at RT was too weak to allow the time-resolved measurement. The visible band was found to have an extremely long decay time which is in sharp contrast to the results of Gardelis *et al.*⁵ Although our detection system does not have a time resolution in the nanosecond range, it was confirmed that the component in the range of millisecond is dominantly contributing to the cw spectrum at 4.2 K. This was actually checked by measuring the visible PL intensity as a function of chopping frequency. At this temperature, the intensity starts to decrease above 20-Hz chopping and becomes half the original (near-dc) value at 150 Hz. Such an agreement

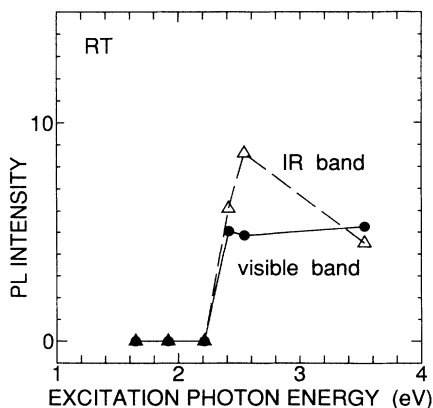


FIG. 2. The luminescence intensities (in arbitrary units) of the visible and ir emissions as a function of the excitation photon energy measured at room temperature.

TABLE I. Decay-time constants for the visible and ir emissions. The ir band at RT was too weak to perform the time-resolved measurements.

| T (K) | τ_{vis} (μs) | τ_{ir} (μs) |
|-------|---------------------------------------|--------------------------------------|
| RT | 46 | |
| 4.2 | ~ 2000 | 2 |

also provides the experimental verification that the effect of high-density excitation which might occur in pulsed measurements is negligible in the present case. By monitoring the phase delay while scanning the detected wavelength within the visible band, it was also found that the decay time becomes monotonically longer for smaller photon energy. The tail-state luminescence in *a*-Si:H shows a similar behavior possibly because the effective Bohr radii become smaller for the carriers localized at deeper states.⁸

Temperature dependencies for the two emissions are shown in the inset of Fig. 3. The ir band has a monotonic enhancement of intensity towards low temperature and reaches a constant value. On the contrary, intensity of the visible band first increases as the temperature is lowered and then shows a quenched behavior when the sample is further cooled down below 100 K. In order to eliminate the possible artifact brought about by the lock-in detection technique when applied to the extremely slowly decaying visible luminescence, the excitation beam was not chopped and the dc detection was employed. The behavior of the visible band below 100 K shows a striking resemblance to that of the luminescence in *a*-Si:H, which is due to the recombination of spatially

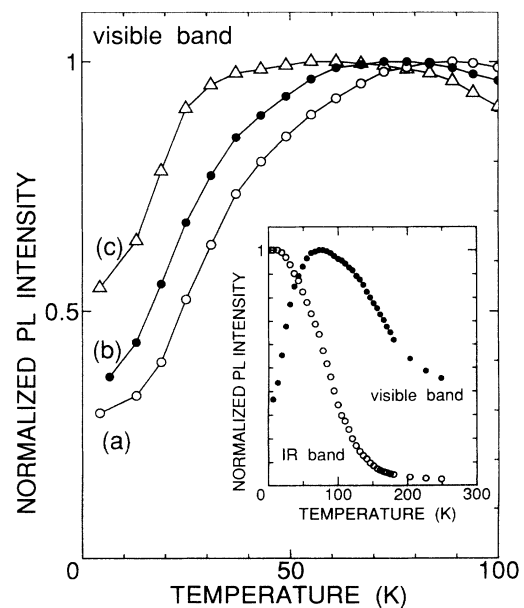


FIG. 3. The inset shows the luminescence intensities of the visible and ir bands as a function of temperature. The results in the low-temperature region for the visible emission are shown under various excitation intensities: (a) 14 mW, (b) 1.8 mW, and (c) 0.15 mW. (b) corresponds to the data in the inset.

separated electron-hole pairs localized at tail states.^{11,12} The temperature-dependent excitation of the Auger process has been proposed by Street¹² for such a system. This effect is important if the separation of the recombining electron-hole pair becomes comparable to the distance to the third carrier.

As is naturally expected and has actually been confirmed for the *a*-Si:H case, the nonradiative rate determined by this mechanism is dependent on the number of photogenerated carriers, and thus the excitation intensity. This is exactly what is observed for the present system as shown in Fig. 3. With a stronger excitation, the quenched portion at low temperatures becomes larger together with a simultaneous shift in temperature which gives the maximum luminescence intensity (T_{\max}). A possibility of laser heating is excluded because both the quenched magnitude and the shifting direction of T_{\max} with changing the excitation power are opposite from what is predicted by such an effect. A separate measurement reveals that it is around 100 K that the decay time starts to rapidly increase towards 10^{-3} -s range so that the observed T_{\max} (60~90 K) is considered to be reasonable. Therefore, our results are consistently explained by assuming that the radiative recombination takes place at spatially separated electron-hole pairs. It should be noted that the recombination time for the carriers localized at tail states of *a*-Si:H ($\sim 10^{-3}$ s) (Ref. 11) at low temperature shows a quantitative similarity to our observation on the visible luminescence in porous Si as already pointed out. In a recent paper by Zheng, Wang, and Chen,¹³ they also reported a nonmonotonic temperature dependence but no change with different excitation power. They attributed the decrease in the intensity to a reduced phonon population at low temperature. However, the drastic quench observed by these authors seems to be inconsistent with their model unless for the explanation on why the phonon-emitting assistance is negligibly small compared to the phonon-absorbing one.

The ir emission, on the other hand, has no indication of strongly localized recombination as revealed in its decay time and the temperature dependence. However, at the same time, it is obviously not due to the underlying bulk Si but is related to the porous region because of its large half-width. Further, a deep-level luminescence (with respect to the visible emission) is unlikely taking into account the ~ 1000 times faster decay than that for the visible. The plausible model thus seems to be the delocalized recombination taking place at the region which is adjacent to the visible-emitting one.

Both of the visible and ir luminescence are found to decrease their intensities after subsequent anneal, but with different rates. The anodized porous Si was annealed at 360 and at 600°C in N_2 ambient. The measured PL intensity is shown in Fig. 4. The horizontal axis represents the relative PL intensity for the visible band measured at RT. After annealing at 600°C, the intensity is drastically decreased and becomes 0.004 times the original value. The vertical axis corresponds to the visible and ir emission intensities measured at 4.2 K. The intensity variation for the visible band observed at 4.2 K linearly follows that measured at RT. Taking into account the fact

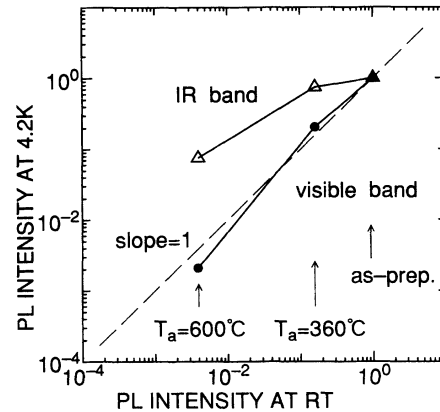


FIG. 4. Summary of the annealing effect on the luminescence intensities (in arbitrary units). The horizontal axis represents the variation of the visible emission measured at RT. The intensities of both visible and ir emissions at 4.2 K correspond to the vertical axis.

that the contribution of the nonradiative process is quite different at these two temperatures, which has been revealed by the temperature dependence of the decay time, it is unlikely that the observed intensity variation is due to the introduction of nonradiative centers. Rather, it is speculated that possible dissociation of hydrogen or surface oxidation during anneal results in a reduction of total volume of the light-emitting region, in other words, the number of localized states responsible for the visible luminescence. The ir band is much less sensitive to the loss of hydrogen but still reflects the effect. This result suggests that this emission does not arise directly from the electron-hole pair within the region emitting the visible light.

Based on the experimental results, the recombination mechanisms in the porous Si are discussed. The visible luminescence is attributed to a spatially separated electron-hole pair just like in the case of the luminescence from the disorder-induced tail states. A delocalized-pair model (or a large-scale exciton) finds difficulty in explaining the observed competition between radiative and non-radiative processes in the 10^{-3} s range. Even if the quantum-well picture, which is convenient in expecting the visible energy for emission, finds a possibility of slow recombination of delocalized pairs reflecting the indirect-band nature of the host, introduction of the third carrier into the same well should result in a huge magnitude of Auger efficiency just like in the system of a neutral-donor bound exciton in GaP ($\sim 10^{-8}$ s). As soon as the carriers are strongly localized, the states should become insensitive to the size of confinement so that it is more likely to be the structural modification, such as incorporation of large concentration of hydrogen or introduction of surface states, etc., rather than a simple reduction in dimensions which causes a visible luminescence. The average radius of the localized carriers can be simply estimated not to be very much larger than ~ 10 Å since, otherwise, the electron-hole separation calculated from the decay time exceeds several nm, a size of microcrystal-

lites whose existence is known to give rise to the visible emission.

Such a strong localization might cause an appreciable coupling of the electronic states to the lattice. A certain portion (but possibly not all) of the broad spectral width of the visible band should be attributed to the lattice relaxation with a large Huang-Rhys factor (i.e., much larger than unity) because the observed width seems to be too large for a simple distribution in the localized state energy (electronic part). Another suggestion of coupling with the lattice has been pointed out in Ref. 13, in which the peak-energy shift according to temperature is demonstrated to be sample dependent possibly reflecting the various phonon spectra.

Although the visible luminescence finds various similarities to that of *a*-Si:H, it should be noted that our model, in a strict sense, only claims that the carriers are trapped at the localized states in (on) an object which has a greater band gap than that of bulk Si. Of course, disorder-induced tail states in hydrogen-enriched *a*-Si is a likely attribution. However, other origins may also be acceptable such as surface-related localized states on the Si microcrystallites because the lack of the size-quantization effect on the radiative initial state does not suddenly exclude the presence of quantized *c*-Si particles itself. A significant role of the surface states has been elucidated for the CdSe microcluster system.¹⁴

The origin of the ir luminescence is speculated to be a narrow-gap region (such as *c*-Si) which is adjacent to the visible-light-emitting region. Taking into account the similar excitation spectra, transfer of excited carriers may take place from the wide-gap region either by diffusion or tunneling. The observed width of 0.3 eV is larger than free or typical bound excitons and also than electron-hole plasma emission from bulk Si. Other candidates that are capable of explaining a large width include the band-bending effect or a model in which one of the carriers is residing in the wide-gap region (namely at the localized state). Since we do not observe a systematic shift in the emission spectrum with changing excitation intensity, the band bending is unlikely. The latter mechanism should not be so efficient as a direct exciton recombination because the carriers are still spatially separated and a total overlap of their wave functions cannot be anticipated. However, we point out a similarity in the lifetime (2×10^{-6} s) to the excitons in a so-called type-II

AlAs/GaAs quantum well (electrons confined in the *X* minima of AlAs and holes in the GaAs) whose decay time is also in the microsecond range.¹⁵ The ir emission may be alternatively attributed to a simple delocalized recombination in *c*-Si weakly disordered by the presence of the adjacent wide-gap region, which might give rise to a strong and broad luminescence with insignificant shift in energy from the bulk energy gap. If so, the size-quantization model for the visible band encounters another difficulty; the largely different recombination energies (among the ir and visible bands) in spite of the similar excited-state energies as observed by the excitation spectra which should have also been shifted by the quantization.

In conclusion, the properties of the two emission bands in anodized porous Si are characterized. A close similarity of the visible luminescence to that observed in *a*-Si:H is found thereby indicating that the electron and hole are localized and spatially separated. The quantum-confinement model is incompatible with such a localized scheme. As for the ir emission, tentative models are presented to explain its faster decay as well as its broad shape, which speculate that the *c*-Si region adjacent to the wide-gap (visible-emitting) region is responsible for this recombination. The observation of the ir band may also serve as an argument against the size-quantization model for the visible luminescence.

Note added: A detailed examination of the recombination process has recently been published by Vial *et al.*¹⁶ They conclude that the decay time of the visible luminescence at room temperature or higher is determined by the (extrinsic) nonradiative recombination. Although we did not specify the reason why we observed a shorter decay time at room temperature than at 4.2 K (Table I), the simplest explanation seems to be the contribution of the nonradiative path with the thermal assistance. Actually, the radiative lifetime estimated by them using their high-temperature data is 1 ms and is in good agreement with our low-temperature value. The final picture they present, however, is not based on the carrier localization.

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