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Intrinsic band-edge photoluminescence from silicon clusters at room temperature

L. Tsybeskov
Department of Electrical Engineering, University of Rochester, Rochester, New York 14627

K. L. Moore and D. G. Hall
The Institute of Optics, University of Rochester, Rochester, New York 14627

P. M. Fauchet
Department of Electrical Engineering, University of Rochester, Rochester, New York 14627;
The Institute of Optics, University of Rochester, Rochester, New York 14627;
Laboratory for Laser Energetics and Department of Physics and Astronomy, University of Rochester, Rochester, New York 14627

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We report silicon band-edge photoluminescence (PL) with photon energy of 1.1 eV and external quantum efficiency (EQE) better than 10^{-3} in samples prepared by high-temperature oxidation of porous silicon. The integrated PL intensity is insensitive to temperature. The EQE strongly depends on the annealing conditions: temperature, time, and ambient. A model is proposed in which the PL originates from silicon clusters within a nonstoichiometric silicon-rich silicon oxide matrix. [S0163-1829(96)52336-2]

A number of groups have investigated different types of photoluminescence (PL) in crystalline silicon (c-Si) during the last decades. Recent interest has focused on the visible PL that is observed in Si nanoclusters and in porous Si (PSi),[1] the infrared PL in silicon-germanium superlattices,[2] and the subgap PL due to impurities in c-Si.[3] Band-edge PL in bulk Si is inefficient and usually observed at low temperatures only because c-Si has an indirect band gap.[4] However, there are a few reports in the literature of room-temperature band-edge PL in Si.[5] The typical external quantum efficiency (EQE) of this PL is understandably low ($\leqslant 10^{-5}$) but can be increased by better surface passivation.[6] In this work we report a significant increase of the Si band-edge PL EQE to greater than 0.1% and its unexpected weak dependence on temperature. During sample preparation, a large number of parameters may be varied opening additional room for further improvements.

The samples were prepared by anodically etching boron-doped p^+ c-Si wafers with a resistivity $\rho \approx 0.05$ Ω cm in an HF-ethanol solution (1:1) under a current density $J \approx 20$ mA/cm^2. After anodization the samples were annealed in dilute oxygen (10% O_2 in N_2) from 10 min up to 3 h, at temperatures ranging from 800 to 990 °C. Fourier-transform infrared (FTIR) spectra of the oxidized samples show the presence of silicon oxide with an absorption peak near 1080 cm^{-1} and the absence of Si-H bonds. The PL measurements were performed using the experimental setup in Ref. 5.

Figure 1 compares the PL spectra measured over a temperature range from 12 to 300 K for a sample annealed at 950 °C for 30 min. The inset shows a detailed PL spectrum at 12 K with a weak no-phonon (NP) line at 1.158 eV, a TA-phonon line near 1.14 eV, and a TO-phonon line at 1.1 eV with a replica at 1.04 eV. These PL spectral lines are well known in c-Si and tabulated in Ref. 3. The PL spectrum peak is shifted and becomes broader as the temperature is raised. In the temperature region from 12 to 50 K the PL peak undergoes a small blueshift (to shorter wavelength) and at temperatures greater than 70 K the PL peak is redshifted (to longer wavelength). We do not observe any blueshift in the PL spectra attributable to quantum confinement effects.

Increasing the temperature broadens the PL spectra. Figure 2 shows that the intensity of the high-energy tail of the PL spectrum is linear on a semilogarithmic scale. The slope increases linearly with temperature, as expected when the carriers follow a Boltzmann distribution.[7] If $f(E,T)$ is the probability of energy states being occupied and $N(E)$ is the parabolic density of states, then the total broadening of the PL line $\Delta E \sim f(E,T) x N(E)$ is proportional to 2 kT, in agreement with our measurements. The temperature dependence of the PL peak follows that of the energy gap[8] with corrections for the characteristic phonon energy [TO phonon, 58 meV (Ref. 3)] and the thermal distribution of the population. Figure 3 shows the good agreement between the calculated

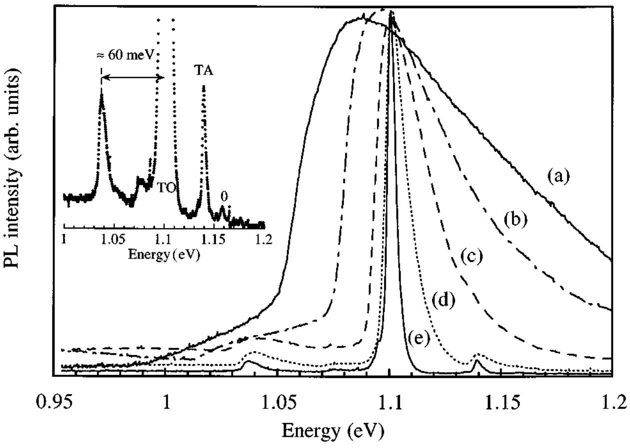

FIG. 1. The PL spectra in oxidized porous Si measured at different temperatures: (a) 300, (b) 200, (c) 100, (d) 50, and (e) 12 K. The inset shows the fine structure of the 12-K PL with typical phonon lines: NP line at 1.158 eV, TA line at 1.14 eV, and TO line 1.1 eV, with a replica at ~1.04 eV.

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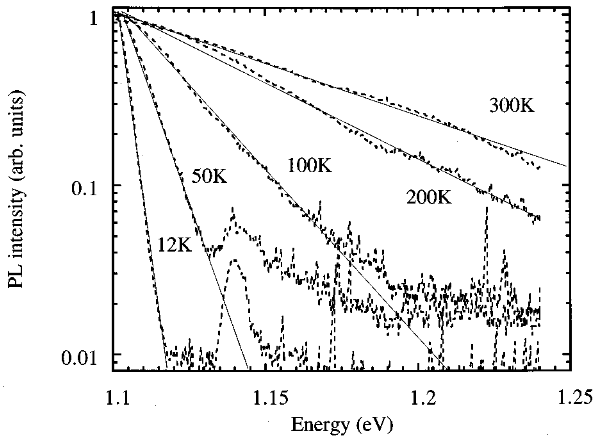

FIG. 2. The short-wavelength part of the normalized PL spectra at different temperatures plotted in a semilogarithmic scale.

temperature dependence of the PL peak and the experimental data.

Bulk *c*-Si exhibits exciton-related PL that is thermally quenched for $T \geqslant 20$ K.[3] This threshold can be shifted to higher temperatures for excitons bound to impurities.[3] When we measure the PL spectra of our samples down to 0.7 eV, we observe no impurity or defect-related transitions [including boron-related PL (Ref. 3) or the oxygen-related *P* line[5]]. The PL temperature dependence in our samples is found to be completely different from that of *c*-Si. Figure 4 shows that whereas the PL peak intensity drops with increasing temperature, the integrated PL intensity is essentially temperature independent from 12 to 300 K.

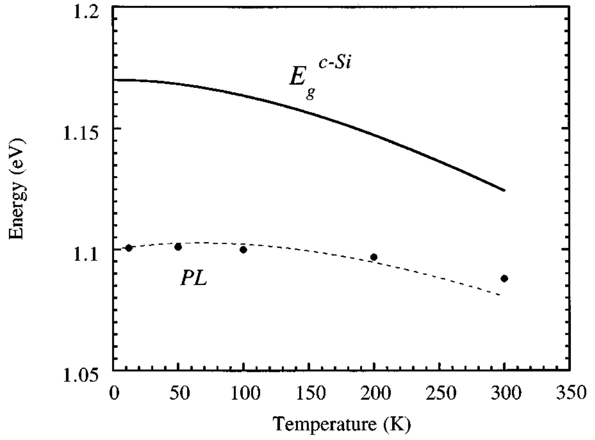

FIG. 3. Temperature dependence of the *c*-Si band gap (solid line) and the PL peak position in oxidized PSi: experiment (dots) and fitting (dashed line). The fitting formula is $E_{\rm PL}(T) = E_g^{c-{\rm Si}}(T) - E_{\rm ph}^{\rm TO} + E_{\rm th}^{c-{\rm Si}}(T)$, where $E_g^{c-{\rm Si}}(T)$ is the temperature-dependent *c*-Si band gap, $E_{\rm ph}^{\rm TO}$ is the characteristic TO-phonon energy (58 meV) and $E_{\rm th}^{c-{\rm Si}}(T)$ is the most probable carrier energy for a thermal population distribution.

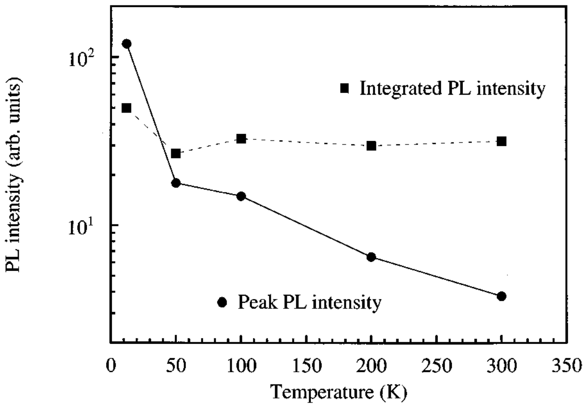

FIG. 4. Temperature dependence of the PL intensity.

The PL intensity exhibits a linear dependence on the excitation intensity over the range of 1–100 W/cm^2. At the maximum excitation intensity (~130 W/cm^2), the PL spectrum becomes broader, which is attributed to local heating by the laser. The local temperature of the sample, calculated using the broadening of the PL spectrum, is found to be ~400 K. However, even at the maximum excitation level, we do not find any deviation from a linear dependence.

The PL external quantum efficiency was estimated by comparing our samples with a sample that exhibits PL in approximately the same spectral region. After ion implantation with Be, bulk *c*-Si has a 1% EQE at 12 K.[9] Under similar experimental conditions, the PL of Si:Be is several times more efficient than that of the samples studied in this work. We estimate the EQE in our best samples to be greater than 0.1%.

The low-temperature PL spectra are similar to that of pure, bulk *c*-Si. The shift and broadening of the PL spectra with increasing temperature can be explained by the temperature dependence of the *c*-Si band gap and the Boltzmann distribution. However, our samples were prepared by thermal oxidation of PSi and contain a significant amount of nonstoichiometric silicon oxide (SiO_{2-x}). Usually, strain is a serious problem for thermally grown SiO_2 on Si, which makes it impossible to grow an oxide with a thickness on the order of 1 μm.[10] The lack of any evidence for the presence of strain in our samples is surprising.

Our PL intensity is strongly sensitive to the oxidation procedure. Table I shows the relative PL intensities for several samples prepared under different oxidation conditions. These results are a key to the explanation of the unusual PL efficiency and temperature dependence in our samples. The most intense PL was found in samples oxidized at 950 °C for 30 min. At this temperature, recrystallization of Si from an amorphous phase or from strongly nonstoichiometric silicon-rich silicon oxide (SRSO) takes place.[11,12] For lower oxida-

TABLE I. All the data are provided for samples annealed in dilute oxygen (10% O_2 in N_2). Variations of ambient (pure O_2 or N_2 and forming gas) lead to a decrease in PL intensity.

Sample #	Annealing T (°C)	Annealing (time)	PL intensity (arb. units)
1	800	1 h	0.1
2	900	30 min	0.3
3	950	30 min	1
4	950	3 h	0.5
5	990	3 h	0.05

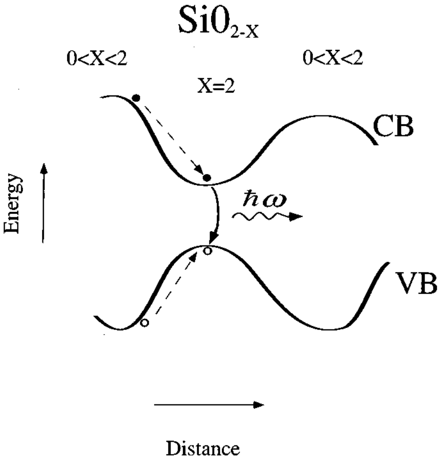

FIG. 5. Proposed band diagram for SRSO. Even if an electron-hole pair is generated in the oxide, excitons rapidly form in the Si clusters where radiative recombination takes place. The presence of traps in the oxide is not important if the exciton formation time is shorter than the trapping time.

tion temperatures, recrystallization is less efficient and a red PL band reminiscent of the PL in porous silicon[13] is observed. Long-time (>10 h), low-temperature (~500 °C) oxidation of *c*-Si also provides room-temperature PL at 1.1 eV, but the dominant PL is the *P* line near 0.77 eV associated with intrinsic defects in *c*-Si.[5] For higher oxidation temperatures ($T \geqslant 1000$ °C) or longer oxidation times (3 h), the PL intensity decreases due to the destruction of the Si clusters by melting and the only PL is the blue PL band that is observed in fully oxidized porous silicon (''porous glass'').[14]

SRSO is a composite material with a variation of the ratio between silicon and oxygen. The band gap of this material varies from 1.1 eV (pure Si) to several electron-volts (SiO_{2-X}) with giant contravariant fluctuations due to different chemical compositions (Fig. 5). These fluctuations are responsible for the confinement of nonequilibrium electrons and holes. Even if the temperature is sufficient for the dissociation of excitons, the electrons and holes cannot leave the potential valleys; eventually, they will form an exciton again and recombine radiatively (Fig. 5). In this model, the PL intensity is insensitive to temperature, in agreement with the experimental observations. We speculate that the smooth transition between the Si clusters and the nonstoichiometric SiO_{2-X} may help to avoid strain.

The Si clusters responsible for the luminescence are large, as no blueshift in the PL spectrum has been observed. Calculations of the increase of the Si band gap with decreasing crystallite size show that the effect of quantum confinement on the band gap becomes measurable near 10 nm.[15,16] Since the PL energy cannot exceed the band-gap energy, the luminescent clusters in our samples are larger than 10 nm. We have studied the surface morphology of samples annealed at 950 °C using an atomic-force microscope (AFM). The surface of the sample was cleaned by a short (~5 sec) dip in 10% HF to remove the SiO_2 on the surface of the film. Densely-packed Si grains with average sizes between 100–150 nm were easily resolved.

The light-emitting properties of SRSO prepared by oxidizing PSi are promising for optoelectronic applications. The electroluminescence (EL) in *c*-Si is as inefficient as the PL. In addition, EL is quenched by an electric field $E \geqslant 10^4$ V/cm due to field-induced dissociation of the exciton.[3] As shown in Fig. 5, the internal field due to band-gap fluctuations is much larger than any reasonable external field, and field-induced quenching will not be important. Since carrier transport due to field-assisted tunneling has already been demonstrated in SRSO prepared by oxidation of PSi,[17] *c*-Si band-edge EL should achievable in this material. Very recently, we have indeed obtained room-temperature EL near 1.1 eV in a device structure made of SRSO.[18]

In conclusion, we have reported room-temperature, Si-band-edge-related PL with external quantum efficiency greater than 0.1%. The PL is insensitive to temperature. According to our model, the PL is due to radiative transitions within large Si clusters immersed in SRSO. Future work needs to be done to optimize the preparation procedure and to demonstrate efficient SRSO-based devices.

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