Impurity-related photoluminescence from silicon at room temperature

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We report results for photoluminescence studies of an impurity-related defect system in 450 °C annealed Czochralski-grown silicon resulting in optical emission with a wavelength near 1.7 μm. The photoluminescence emission is found to have a significant intensity that persists to room temperature. The external quantum efficiency at 300 K is measured to be approximately 2.5×10^{-5}.

Photoluminescence (PL) arising from impurity defects in silicon has been extensively studied for many years.[1] Recent interest has been largely prompted by the desire to identify efficient mechanisms by which indirect-band-gap group-IV materials can be made to emit photons with energies smaller than that of the band gap, with a view to integrating photonic devices with Si and Si/Ge electronics. Much of the work in this field has drawn its inspiration from the success achieved with impurity-related luminescence from GaP, another indirect-gap semiconductor.[2]

The chalcogen impurities sulfur[3,4] and selenium[5] have each been shown to be involved in defect centers which can produce strong emission in the near-infrared region of the spectrum. These complex centers are distinguished by their high external PL quantum efficiency, which can be as high as 5%. Relatively efficient electroluminescence has also been reported.[6] The measured radiative lifetimes suggest that the emission is caused by the radiative decay of excitons bound to isoelectronic impurity complexes. The spectra associated with these impurity centers are similar in nature. They both exhibit a narrow-band component which dominates the spectrum at low temperatures ($T\sim35$ K) and a distinctly different broad component which peaks in intensity at considerably higher temperatures ($T\sim60$ K). This component can persist to temperatures up to $T\sim150$ K.

We present here the results for what appears to be another chalcogen-related system in Czochralski- (CZ)-grown silicon. The PL signal from this system also exhibits two distinct bands whose relative intensities vary with temperature. This system is remarkable, however, in that the high-temperature band has a significant PL signal strength which persists to room temperature. Reports in the literature of room-temperature luminescence in silicon are rare. While phonon-assisted free-carrier combination is observed in Si, the efficiency of this process is understandably low, with a measured[7,8] internal quantum efficiency (QE) of 10^{-4}–10^{-6}. Recently, band-edge recombination at room temperature in a SiGe/Si quantum-well structure has also been reported[9] to have an electroluminescent internal QE of 2×10^{-4}. Spectra have been shown for room-temperature luminescence from Er-doped silicon,[10] but we know of no literature reports of the QE to date.

Figure 1 shows PL spectra for temperatures $T=30$, 130, and 300 K for a typical sample which, in this case, consisted of a portion of a $\langle 100\rangle$-oriented, p-type (resistivity = 40 Ω cm) CZ Si wafer manufactured by Monsanto. The sample was prepared for this experiment by heating it in air at $T=450$ °C for 72 h. The PL spectra were obtained with the sample mounted in an Air Products closed-cycle He cryostat and excited with the 676-nm line of a Kr$^+$ ion laser. The resulting PL signal was chopped at 100 Hz, dispersed using a McPherson 0.35-m grating monochromator, and detected using a North Coast liquid-nitrogen-cooled Ge detector and a Stanford Research Systems lock-in amplifier.

As in the case of the other chalcogen impurity centers described above, the spectrum contains two distinct components. The peak near wavelength $\lambda=1.6$ μm (energy = 0.767 eV) in the $T=30$ K spectrum is the well-known P line.[11] As the sample temperature is raised, we find

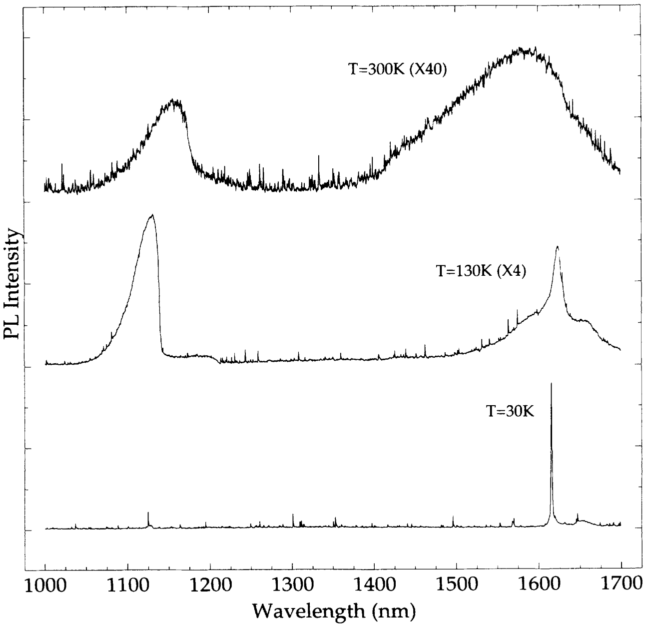

FIG. 1. Measured PL spectra at $T=30$ 130, and 300 K for CZ-grown Si annealed at $T=450$ °C. The data were obtained using a Ge photodetector.

that the P line broadens somewhat while a new, much broader emission band rises from the background. These two components are clearly evident in the $T=130$ K spectrum. At yet higher temperatures, the P line diminishes with respect to the broad band such that, at room temperature ($T=300$ K) only this band is evident. The apparent shift to higher energies (shorter wavelengths) of the emission peak as the sample temperature is raised from $T=130$ K to $T=300$ K is actually an artifact introduced by the declining sensitivity of the Ge detector for $\lambda > 1.6$ μm. To show that this is indeed the case, we measured the PL spectrum at $T=300$ K for the same sample using a Judson Infrared liquid-nitrogen-cooled InAs detector. The result appears in Fig. 2. This detector is noisier and less sensitive than the Ge detector, but its spectral response is nearly flat over the spectral extent of the broad peak. The room-temperature PL clearly peaks near $\lambda=1.7$ μm, demonstrating the above-mentioned shift to shorter wavelengths is indeed a detector artifact. Another interesting feature of the higher-temperature spectra in Fig. 1 is the presence of a strong PL component near the band edge. We find that, for this sample at $T=300$ K, this band is enhanced by about two orders of magnitude over that of an unannealed control sample from the same wafer.

Note that while we present spectra for a single sample in Fig. 1, we have observed identical features (with varying intensities) from a large number of commercial CZ-grown Si samples, regardless of conductivity, type, or orientation. We do not, however, observe either the enhanced band-edge emission or the longer-wavelength PL component from magnetic-CZ-grown or float-zone-refined wafers, or from layers grown by a number of epitaxial techniques. This strongly suggests that the luminescence results from a defect complex in which oxygen plays a pivotal role.

Figure 3 shows a plot of the measured peak intensity of the long-wavelength spectral component as a function of the sample temperature. The signal peaks near $T=35$ K where the P line dominates the spectrum, and decreases roughly exponentially with increasing temperature. As noted earlier, the emission persists to room temperature. The inset in Fig. 3 is an Arrhenius plot of the same data. An excellent fit to the exponential high-temperature falloff can be made, indicating that the luminescence is quenched by a thermally activated process where $E_A=23.6$ meV. It deserves mention that there is an earlier brief report of a similar luminescent system produced in silicon annealed under similar conditions to those used in this work.[12] Those authors reported spectra similar to those in Fig. 1 (using a Ge detector), and a similar enhancement of the band-edge luminescence. However, they also noted that the luminescence peaks in strength at $T=280$ K and can be observed at temperatures up to $T=600$ K. Such a temperature dependence is clearly at odds with our own measurements. The behavior shown in Fig. 3 is typical of a large number of samples examined in our laboratory. It is possible that the emission in Ref. 12 arises from a different mechanism than the one at work in our samples, but it is difficult to say that with certainty.

We have measured the external quantum efficiency η of the sample used to obtain the spectra in Figs. 1 and 2. The measurement was made by first determining the spectral responsivity of our detection system using a calibrated blackbody source at $T=1000\,^{\circ}$C. This enabled us to measure the external spectral quantum efficiency of the sample, which was then integrated over the wavelength

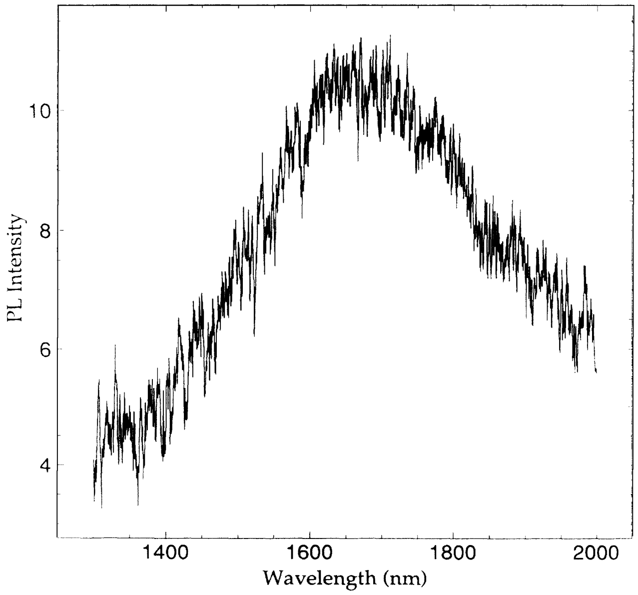

FIG. 2. Measured PL spectrum (arb. units) obtained at $T=300$ K for CZ-grown Si annealed at $T=450\,^{\circ}$C. The data were obtained using an InAs photodetector.

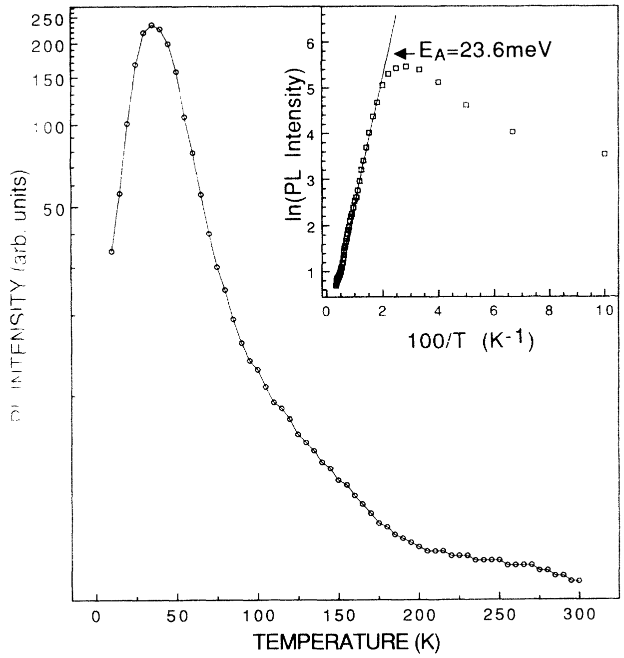

FIG. 3. Temperature dependence of the peak luminescence in Fig. 1. Inset is an Ahrrenius plot indicating an activation energy of $E_A=23.6$ meV.

TABLE I. Electro- (EL) and photo- (PL) luminescence quantum efficiencies at room temperature. Numbers in square brackets are the estimated equivalent external efficiencies.

Material/mechanism	Efficiency at $T=300$ K	Reference
Oxygen-related *P*-line complex	2.5×10^{-5} external, PL	This work
Enhanced band edge	2.5×10^{-5} external, PL	This work
SiGe/Si QW band-edge recombination	2×10^{-4} internal, EL [10^{-5} ext.]	9
Phonon-assisted free-carrier recombination	10^{-5}–10^{-4} internal, EL [6×10^{-7} -6×10^{-6} ext.]	7
Phonon-assisted free-carrier recombination	2×10^{-6} internal, EL [10^{-7} ext.]	8
Porous Si	$<10^{-5}$ external, EL	13

extent of a given spectral feature to yield the total external quantum efficiency of the sample. At $T=77$ K, we obtained for the long-wavelength component of the spectrum $\eta\sim5\times10^{-5}$, and for the enhanced band-edge luminescence $\eta\sim3\times10^{-5}$. At $T=300$ K, the peak intensity of the long-wavelength component is less than at $T=77$ K, but the feature is also broader, resulting in only a small drop in the external efficiency to $\eta\sim2.5\times10^{-5}$. Table I lists the quantum efficiencies at room temperature of a few other radiative processes in silicon for comparison. The annotations PL and EL indicate whether the mechanism measured was photoluminescent or electroluminescent, respectively. In cases where internal efficiencies are reported in the reference we have included in brackets an estimate of the external efficiency given by[14]

$$\eta_{\text{external}}=\left[\frac{1}{n^2}\right]\left[\frac{4n}{(n+1)^2}\right]\eta_{\text{internal}}$$
$$=\frac{4}{n(n+1)^2}\eta_{\text{internal}}\ . \qquad (1)$$

The first factor in the product accounts for the reduction in the solid angle over which the sample radiates due to total internal reflection at the Si/air interface. The second factor is the Fresnel reflection coefficient for near-normal incidence at the interface. Using $n=3.5$ we find that $\eta_{\text{external}}=0.056\eta_{\text{internal}}$. Table II again compares the above sample to some other impurity centers for $T\leq77$ K. It is interesting that the efficiency of the emission reported here is actually comparable, at room temperature, to the efficiency reported for more complex

TABLE II. Electro- (EL) and photo- (PL) luminescence quantum efficiencies at temperature stated. Numbers in square brackets are the estimated equivalent external efficiencies.

Mechanism/impurity	Efficiency	Reference
P line and broad band	5.0×10^{-5} external, 77 K, PL	This work
Enhanced band edge	3.3×10^{-5} external, 77 K, PL	This work
SiGe QW band-edge recombination	0.115 external, 2 K, PL	15
Si:Er	10^{-2} external, 77 K, PL 5×10^{-4} external, 77 K, EL	16
Si:Be	1×10^{-2} external, 40 K, PL	17
Si:S	$(2-5)\times10^{-2}$ external, ~60 K, PL $(2-5)\times10^{-3}$ external, ~60 K, EL	6
Si:Se	2.0×10^{-2} external, 70 K, PL	5
Si:In	10^{-3} external, 15 K, PL 4×10^{-4} external, 15 K, EL	18
Carbon in e^- irradiation damage centers	5×10^{-2} internal, 77 K, EL [3×10^{-3} ext.]	19

structures, such as silicon-germanium/silicon quantum wells.[9] We suspect that the emission described here results from a relatively small concentration of impurity complexes, so there might well be an opportunity to increase the efficiency if the nature of the complex can be determined.

We have found that for every Si sample investigated to date, the appearance of the *P*-line signal at $T = 35$ K is always accompanied by the long-wavelength (near $\lambda = 1.7$ μm) spectral component at room temperature. We have also observed that both of these luminescence features disappear if the sample is heated above 600 °C. The formation kinetics of the *P*-line defect have been carefully studied,[11] with particular attention paid to the similarity to the formation of thermal donors in samples heated to $T = 450$ °C. Early studies led to conjectures that thermal donors might be responsible for the low-temperature *P*-line emission. This was later shown not to be the case based on spectroscopic arguments.[20]

Figure 4 shows the results of an isothermal annealing study in which we have measured the relative peak PL intensities of the long-wavelength luminescence component for $T = 35$ K and $T = 300$ K as a function of anneal time at 450 °C. For comparison, we also measured the change in conductivity which is approximately proportional to the number of thermal donors formed during the anneal. For this study, 11 samples were taken from a single commercially prepared, CZ-grown, 40 Ω cm, *p*-type, $\langle 100 \rangle$-oriented wafer and annealed for various times. A small piece was taken from each sample for the PL measurements at both temperatures. In order to ensure that an accurate comparison could be made between the low- and room-temperature annealing curves, care was taken not to disturb the samples between measurements. In this way, sample-dependent and optical-alignment measurement errors were reduced to a minimum. The remainder of the sample was used to monitor the change in conductivity as measured at room temperature by a standard four-point-probe technique. It is clear from the data that the luminescent centers evolve more rapidly than does the total thermal donor population. It also appears that the *P* line at $T = 35$ K develops slightly more quickly than does the broad, room-temperature feature near $\lambda = 1.7$ μm.

The fact that these two features form in the same samples (which must be oxygen rich) under similar thermal conditions leads us to believe that the defects responsible must be closely related. A spectroscopic study of the *P*-line luminescence in CZ-grown silicon isotopically enriched with ^{13}C and ^{18}O has led to a structural model of the defect which includes an interstitial carbon atom bound to a dioxygen molecule or a related oxygen aggregate.[11] It may be the case that the different bands arise from two metastable configurations of the same defect constituents. This has been shown to be the mechanism leading to the dual-character luminescence described near the beginning of this paper from silicon doped with the chalcogen impurity sulfur.[21]

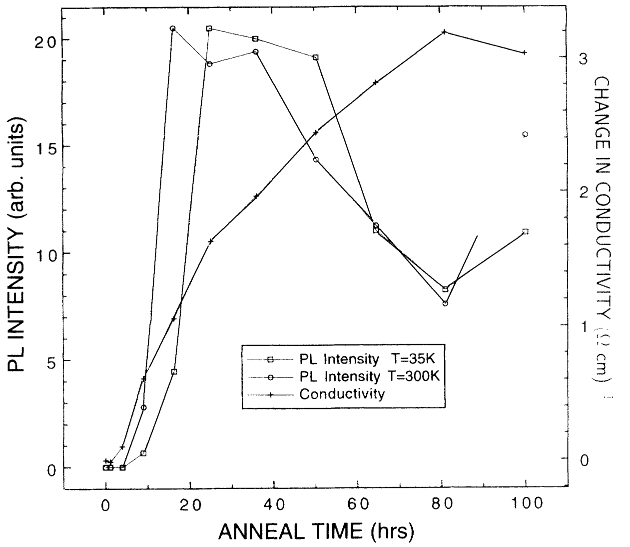

FIG. 4. Dependence of the PL intensity at $T = 35$ and 300 K and the change in conductivity on the isothermal ($T = 450$ °C) annealing time for CZ-grown Si.

That the conductivity rises steadily in Fig. 4 indicates that thermal donor complexes are forming continuously during our 450 °C anneal. ir absorption spectroscopy experiments used to characterize the formation of 450 °C thermal donors have shown that the thermal donor population consists of a family of at least 11 distinguishable defects having slightly different binding energies.[22] When samples are annealed at 450 °C, the concentration of each member defect grows with annealing time until it reaches a maximum concentration, after which time the concentration decreases with further annealing. A comparison of the data shown in Fig. 4 to that appearing in Ref. 22 shows that the growth of both the low- and high-temperature PL intensities conforms to this pattern, even though thermal donors are not thought to be responsible for the *P*-line emission.[20] The situation is admittedly complicated. More work will be required to identify unambiguously the origin of the room-temperature emission near wavelength $\lambda = 1.7$ μm described in this report.

In summary, we have described the characteristics of room-temperature optical PL emission produced by Czochralski-grown silicon annealed at $T = 450$ °C. The measured spectra show that, for $T = 300$ K, the emission occurs near wavelength $\lambda = 1.7$ μm. The intensity of the emission peaks for a sample temperature of $T = 35$ K. At higher temperatures, the luminescence is quenched by a thermally activated process with an activation energy of 23.6 meV. The measured external efficiency at $T = 300$ K was found to be approximately 2.5×10^{-5}. The efficiencies at both low and room temperatures were compared with those reported for several other luminescence mechanisms in silicon.

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