

Radiative decay of excitons bound to chalcogen-related isoelectronic impurity complexes in silicon

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We report the observation and characterization of near-infrared optical emission from selenium-doped crystalline silicon. The spectrum, radiative lifetime, external quantum efficiency, and thermal dissociation energy of the observed emission are strikingly similar to those we reported earlier [T. G. Brown and D. G. Hall, *Appl. Phys. Lett.* **49**, 245 (1986)] for sulfur-doped silicon. We attribute the emission to the radiative decay of an exciton bound to a Se-related isoelectronic complex, and suggest that oxygen is a participant in this complex.

The radiative decay of excitons bound to isoelectronic (i.e., isovalent) impurities is an important mechanism in both direct and indirect band-gap semiconductors. This process was first observed and reported by Dietz *et al.* in connection with unknown impurities in ZnTe, a direct-band-gap II-VI compound semiconductor.¹ Hopfield *et al.* subsequently showed that the observed emission near $h\nu=2$ eV originates with the decay of an exciton bound to an oxygen atom substituting isoelectronically for a tellurium atom.² Bound-exciton emission has been reported for two types of isoelectronic impurity centers in the indirect-band-gap III-V compound semiconductor GaP. The first occurs when a single, group-V, atom, nitrogen or bismuth, substitutes for a phosphorus atom.³ The second, sometimes called an *isoelectronic molecule*, occurs when oxygen substitutes for phosphorus and either zinc or cadmium substitutes for an adjacent gallium atom. In this way, an exciton is bound to a nearest-neighbor donor-acceptor pair, either zinc-oxygen or cadmium-oxygen, that replaces a gallium-phosphorus pair, preserving the number of valence electrons (eight) associated with the latter.⁴

The situation for silicon, another indirect band-gap semiconductor, is rather different than that for GaP. It appears that single, group-IV, substitutional isoelectronic impurities do not create bound-exciton states in Si,⁵ but that multiatom isoelectronic complexes do create such states. Isoelectronic bound-exciton (IBE) emission from silicon was first identified rather recently (1979) in connection with an indium-related impurity complex.⁶ This type of emission is characterized by a long radiative lifetime (~ 200 μ s in the case of indium-doped crystalline silicon), which indicates stability against nonradiative Auger processes, and high radiative quantum efficiency. Indium alone cannot form an isoelectronic impurity center in silicon, so it is thought that other atoms, such as oxygen,⁷ also play a role in this complex. Since 1979, IBE emission associated with complexes containing Be, Cu, Li, Tl, and other as yet unidentified impurities has been reported.⁸⁻¹² Only in the case of Si:Be has the nature of the complex been completely identified (Be pairs).

We report here the observation and characterization of what appears to be IBE emission from selenium-doped crystalline silicon (*c*-Si:Se). This newly observed photoluminescence (PL) is interesting by virtue of its striking similarity to that which we reported earlier for silicon doped with another of the group-VI elements (chalcogens), sulfur.¹³ As we describe, the spectra, radiative lifetimes, external quantum efficiencies, and thermal dissociation energies for the emissions from *c*-Si:S and *c*-Si:Se are very similar. In addition, we find that the strength of the emission from *c*-Si:Se is positively correlated with the presence of oxygen during sample processing, consistent with our findings for *c*-Si:S.¹⁴ This behavior is reminiscent of that observed for substitutional-substitutional Zn-O and Cd-O pairs in GaP and supports our hypothesis that the observed PL originates with substitutional-interstitial S-O and Se-O pairs.

The sample preparation techniques for Si:S were described elsewhere,¹³ so we concentrate here on those for Si:Se. Selenium was introduced into Czochralski-grown silicon wafers by either ion implantation or diffusion. In the first method, wafer segments were implanted with 200-keV Se ions at a dose of 3×10^{14} cm^{-2} . Each sample used in the PL experiments was sealed in a quartz tube with a partial pressure of oxygen and annealed at 1200°C for 70 min. Samples annealed in this way were found to yield greater luminescence than samples annealed in vacuum or in the presence of nitrogen or hydrogen. The final preparation step consisted of a heating and quenching procedure, in which each sample was first held in the flame of a propane torch for ~ 1 s and then quickly immersed in an ethylene glycol bath. This heating and quenching procedure was reported by Thewalt *et al.* and by Weber *et al.*¹⁵ to increase dramatically the bound-exciton *P*-line luminescence from *c*-Si:In; we have found that this procedure has the same effect for both *c*-Si:S (Ref. 13) and, in the present case, *c*-Si:Se.

In the second method, thermal diffusion, each sample of *c*-Si starting material was sealed in a quartz tube with a small amount of 99.99% pure Se and a partial pressure of oxygen. The quartz tube was then heated at 1200°C for

approximately 90 min, after which time the sample was removed from the quartz tube and subjected to the same heating and quenching procedure described above. Following the quenching procedure, each sample was given a short etch in hydrofluoric (HF) acid to remove any significant SiO_2 coverage that developed during processing. Each sample was then mounted onto the cold finger of a closed-cycle helium cryostat (Air Products), which allows the sample temperature to be varied in the range $15 < T < 300$ K. The samples were excited using either the 752-nm line from a (cw) krypton-ion laser or the 595-nm line from a (pulsed) nitrogen-pumped dye laser. The PL signal was dispersed using a McPherson 270 monochromator and detected using liquid-nitrogen-cooled germanium detectors (North Coast E0817L for cw measurements and E0817P for transient measurements). A total of 500 lifetime measurements were averaged using a Tektronix 7854 waveform processing oscilloscope. Continuous-wave measurements were made by chopping the PL signal at 100 Hz and using standard lock-in amplifier detection techniques.

The measured PL spectrum, corrected for detector response, from *c*-Si:Se is shown in Fig. 1. Samples prepared by both the ion-implantation and diffusion procedures exhibited the same photoluminescence spectra. Identically treated control samples (no Se) exhibited none of the characteristic PL signal. Two distinct luminescence systems were observed, each reaching maximum intensity at a different temperature. The dominant luminescence for $T < 50$ K is a narrow line, with several weaker phonon sidebands, at wavelength $\lambda = 1.579 \mu\text{m}$. As the temperature increases above $T \sim 50$ K, a phonon-broadened system near $\lambda = 1.34 \mu\text{m}$ becomes dominant and the narrow line system disappears. Figure 2 shows a comparison of the spectra obtained from Si:Se and Si:S for two temperatures. It is clear that they are very similar, with that for Si:Se shifted to longer wavelength from that for Si:S. Furthermore, the basic character of both emission spectra in Fig. 2 is much the same as that observed for IBE emission from ZnTe:O and GaP:Cd-O: a

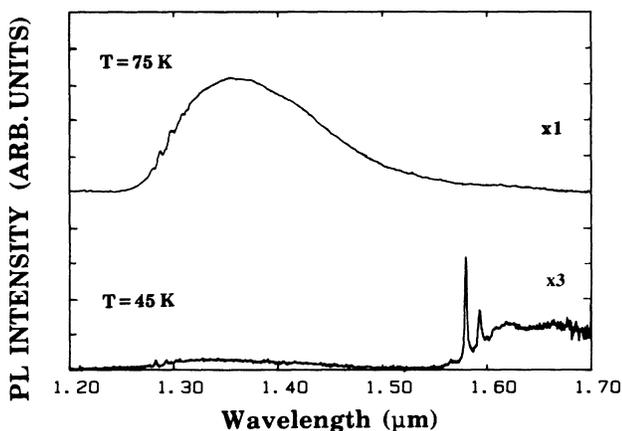


FIG. 1. Photoluminescence (PL) spectrum from *c*-Si:Se for two temperatures: $T = 75$ K (top) and $T = 45$ K (bottom).

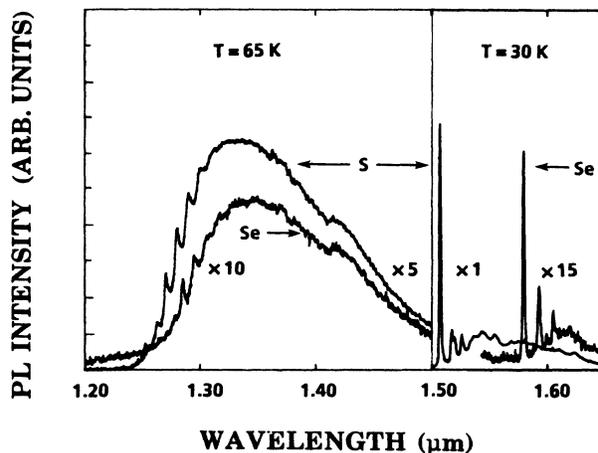


FIG. 2. Comparison of the PL spectra from *c*-Si:S and *c*-Si:Se for $T = 65$ K ($1.2 < \lambda < 1.5 \mu\text{m}$) and $T = 30$ K ($1.5 < \lambda < 1.65 \mu\text{m}$).

no-phonon line on the high-energy side accompanied by successively broader phonon replicas that merge into a broad emission band.^{1,4} Figure 3 shows the temperature dependence of both emission features for Si:Se. It appears that one system grows at the expense of the other. The high-temperature intensity fall off of the broad, shorter wavelength system, when fitted to the standard form $\exp(\Delta E/kT)$, yields a thermal dissociation energy $\Delta E \sim 113$ meV for Si:Se, as compared with $\Delta E \sim 139$ meV for Si:S.¹³

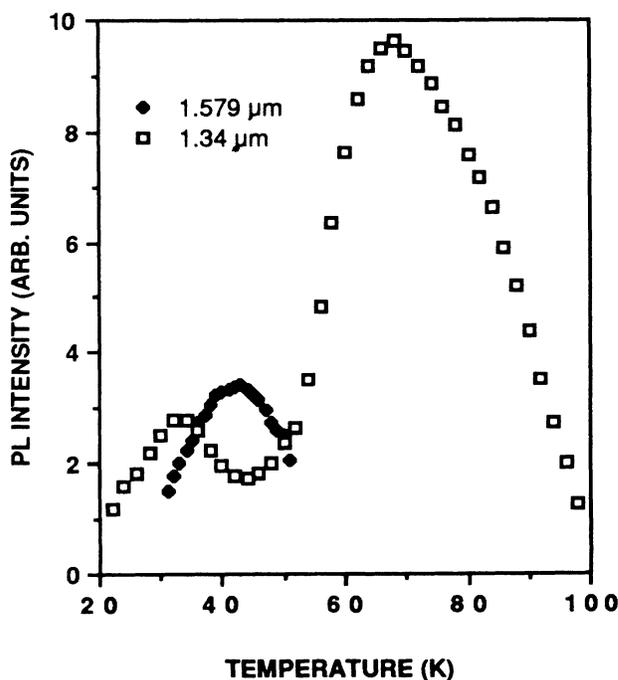


FIG. 3. Temperature dependence of the intensity of the photoluminescence from *c*-Si:Se for two wavelengths: $\lambda = 1.34$ and $1.579 \mu\text{m}$.

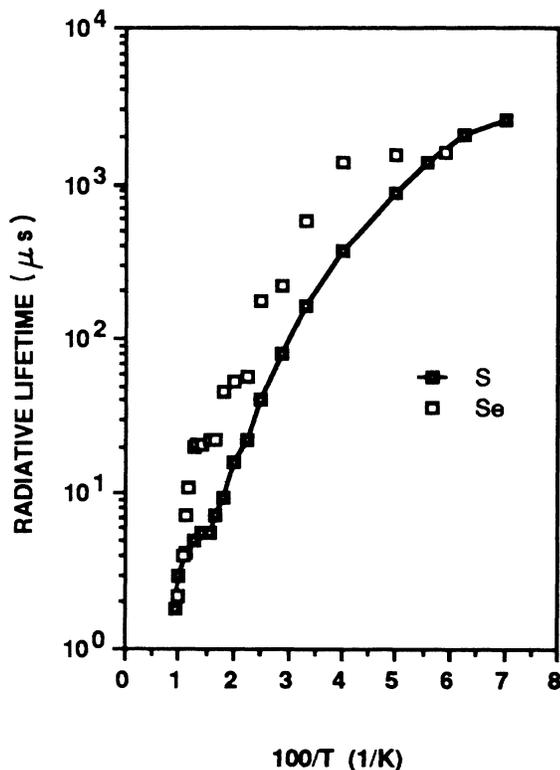


FIG. 4. Temperature dependence of the radiative lifetime of the integrated PL from *c*-Si:Se.

Figure 4 shows the measured radiative lifetime (average of 500 measurements) τ for the integrated luminescence as a function of inverse temperature for the emission from both Si:Se and Si:S. At low temperatures, the lifetime is quite large, $\tau \sim 1$ ms, which shows that the center has a metastable lowest excited state. Near $T \sim 70$ K, the temperature for which the emission intensity is a maximum, $\tau \sim 5$ – 10 μ s for both the Si:S and Si:Se emission. A measurement of the external quantum efficiency η was obtained by comparing the photon flux (assumed Lambertian) from the sample into a fixed solid angle to that from a 1000°C calibrated blackbody source of identical aperture placed in the same position as the sample relative to the collection optics. The measurements result in $\eta \sim 2\%$ for Si:Se and $\eta \sim 5\%$ for Si:S in typical samples for $T \sim 70$ K.

The data presented here for *c*-Si:Se bear a clear resemblance to those we reported earlier for *c*-Si:S. The emission spectrum for each consists of both a narrow and a broadband system that appear to compete with each other for excited state population. The spectral features for *c*-Si:Se are shifted toward longer wavelengths from those for *c*-Si:S by $\Delta\lambda = 0.072$ μ m for the narrow, longer wavelength component and by $\Delta\lambda = 0.015$ μ m for the broad, shorter wavelength component.¹⁶ The lifetime, the external efficiency, and the dissociation energy ΔE (113 meV for *c*-Si:Se and 139 meV for *c*-Si:S) are also very similar. The facts suggest that a common mechanism is responsi-

ble for the observed emission. The long radiative lifetimes and rather large radiative quantum efficiencies lead us to suggest that the emission is produced by the radiative decay of an exciton bound to an isoelectronic impurity complex.

We reported recently that the emission from sulfur-doped *c*-Si is correlated with the presence of oxygen in the sample, and suggested that the isoelectronic complex responsible for the emission might consist of a substitutional sulfur atom and an interstitial oxygen atom.¹⁴ We find, as mentioned earlier in this paper, that the intensity of the optical emission from selenium-doped *c*-Si is also correlated with the presence of oxygen during the sample annealing process. It is natural, then, to suggest that a selenium-oxygen isoelectronic pair might be responsible for the observed emission, in direct analogy with the case of the sulfur-related emission. Beeler *et al.* have recently shown that the stable site of isolated S and Se impurities is substitutional,¹⁷ and it is most likely that oxygen occupies an interstitial site.¹⁸ The existence of S-O and Se-O pairs in silicon is an interesting possibility, particularly when viewed within the context of current theoretical attempts to understand the mechanisms responsible for chalcogen pairing in silicon.¹⁹

The situation reported here is reminiscent of the observation of red luminescence from gallium phosphide (GaP) doped with either Zn or Cd. In this case, both zinc-oxygen and cadmium-oxygen pairs form isoelectronic "molecular" complexes in GaP,⁴ with the associated bound-exciton emission from the latter (Cd-O) appearing at a slightly longer wavelength than that from the former (Zn-O). Cd is directly below Zn, just as Se is directly below S, in the Periodic Table. The Si and GaP systems must differ in detail, of course, but it can be said that the ability of oxygen to join with another impurity in a semiconductor to form an isoelectronic complex that binds an exciton is well established in GaP, and consistent with the results of our experiments on Si. Thewalt *et al.* recently reported IBE emission from an oxygen-related impurity center in silicon that is somewhat associated with the presence of the so-called "thermal donor" in oxygen-rich silicon.²⁰ The role played by oxygen in isoelectronic complexes in silicon clearly deserves much attention.

To summarize, we have described the properties of what appears to be a new photoluminescent impurity complex associated with the presence of selenium in crystalline silicon. The PL spectrum consists of two components, one near the wavelength $\lambda = 1.579$ μ m and the other near $\lambda = 1.34$ μ m. The emission is efficient ($\eta \sim 2\%$) and exhibits a long lifetime ($\tau \sim 1$ ms) at low temperatures. These facts, along with the pronounced similarity between the emission spectra from *c*-Si:S and that from *c*-Si:Se, led us to suggest that the emission originates with the radiative decay of an exciton bound to a Se-related isoelectronic complex.

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