Use of hydrostatic pressure to resolve phonon replicalike features in the photoluminescence spectrum of beryllium-doped silicon

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Photoluminescence (PL) from the recombination of isoelectronic bound excitons in beryllium-doped bulk silicon is measured at 9 K. Pressure tuning demonstrates that two of the PL peaks, which are in the spectral region of phonon replicas previously associated with the recombination of excitons bound to Be pairs, are certainly not phonon replicas of the zero-phonon peak, and likely correspond to the recombination of excitons bound to other Be complexes. This study illustrates the value of applying pressure to a material to elucidate its properties at ambient pressure.

The isoelectronic impurity in Be-doped silicon is thought to be a substitutional-interstitial (SI) pair of Be atoms aligned axially along [111].[1–3] This Si:Be trap has been shown to be an isoelectronic acceptor,[2–5] and serves as a radiative center for exciton recombination. In a recent study of photoluminescence (PL) of Si:Be, Henry *et al.*[3] identified phonon replicas of the main exciton recombination peak involving phonons in the host silicon and local mode vibrations associated with Be_2. In several cases, the structure of the phonon replica was found to be very similar to that in the zero-phonon peak (near 1078 meV). Specifically, the relative intensity of the A and B lines, due to the electric dipole-allowed $J=1-0$ transition and the lower-energy, "forbidden" $J=2-0$ transition, respectively, was found to be the same for the zero-phonon line and some of the phonon replicas, even as the relative intensity of the A and B lines changed with temperature (4.2, 7, and 20 K). While this similarity was quantitatively true for the local mode feature near 973 meV, it appeared to be only qualitatively true for the more complex spectral region associated with the O^{Γ}, TO, and LO one-phonon features near 1015 meV. By applying hydrostatic pressure to Si:Be at 9 K, PL measurements performed here demonstrate that some of the features near 1015 meV (at ambient pressure) are indeed phonon replicas of the zero-phonon feature arising from the recombination of excitons bound to Be_2. However, other features in this region are clearly not phonon replicas, and may correspond to the recombination of excitons bound to other Be complexes in Si.

Be ions were implanted into bulk silicon with a dose of 2×10^{13} ions/cm^2 at 40 KeV, as described elsewhere.[4] Measurements were conducted in a diamond-anvil cell that was loaded with liquid argon to attain hydrostatic conditions, and maintained at 9 K. Photoluminescence was excited by the 514-nm line from an argon-ion laser (5 mW).

Figure 1 shows PL spectra for pressures ranging from 0.5 to 22.2 kbar. The spectrum at 0.5 kbar, which differs little from that at ambient pressure, looks similar to the PL spectrum in Ref. 3 taken at 7 K. The energy of the zero-phonon peak is seen to decrease with increasing pressure. This pressure dependence is investigated in detail in Ref. 6. The energies of the features labeled O^{Γ}, TO, P, and TA also decrease with pressure, at approximately the same rate as the zero-phonon peak. These features are clearly phonon replicas of this large peak and, as is seen in Fig. 2, near ambient pressure they are replicas of the A line. At ambient pressure the energies of these four features are, respectively, 64, 59, 28, and 19 meV below the zero-phonon A peak. The TO and TA energies correspond to the phonon energies at the Δ point.[7] The energy of the P peak apparently does not correspond to the LA phonon at Δ, which is 46 meV,[7] so the identification of this peak as the LA-phonon replica

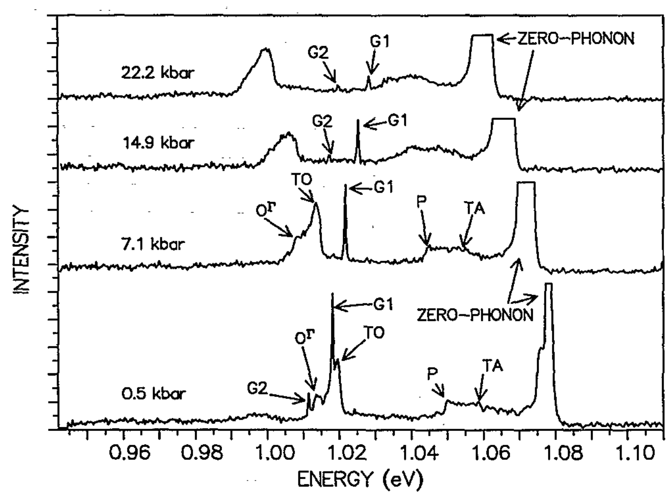

FIG. 1. PL spectra at four "lower" pressures, with an expanded vertical scale to show the phonon replicas of the noted zero-phonon peak and the two peaks $G1$ and $G2$.

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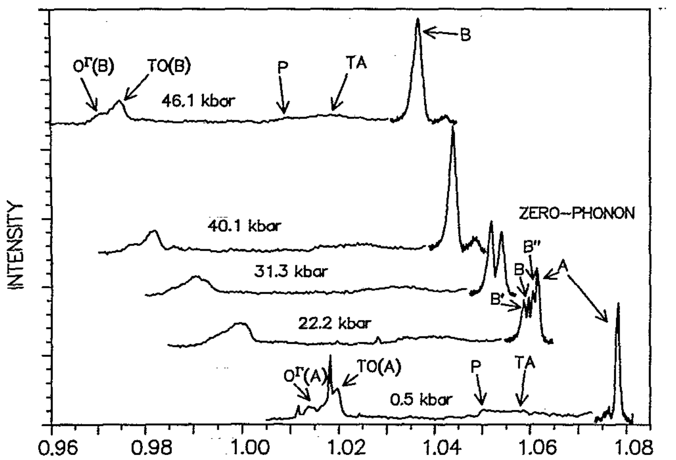

FIG. 2. A comparison of the phonon replicas and the zero-phonon lines at selected pressures. The intensity scale for the zero-phonon peaks (0.2-meV resolution) has been reduced by a factor of 10 vis-à-vis the phonon replicas (0.4-meV resolution).

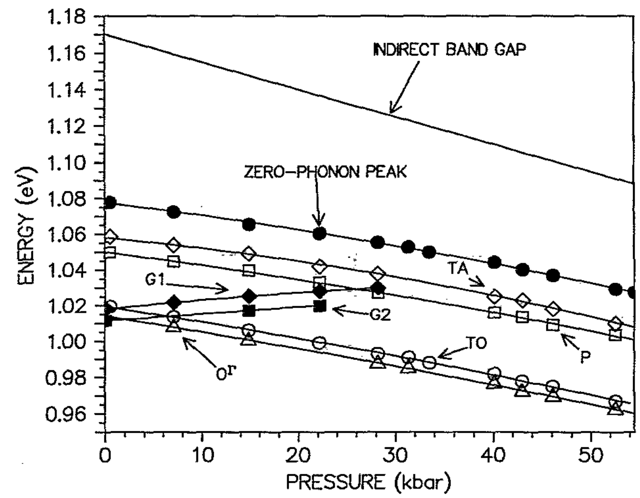

FIG. 3. The dependence of the PL energies of the zero-phonon peak (weighted average) (●), the TA-phonon replica (◇), the P-phonon replica (□), the TO-phonon replica (○), the O^Γ-phonon replica (△), and the $G1$ (◆) and $G2$ (■) peaks as functions of pressure at 9 K. The pressure dependence of the indirect band gap is also shown for comparison. The data points are plotted, along with curve fits using the parameters listed in Table I.

in Ref. 3 is in doubt. Since the energies of the local modes of the Be pair are 38 and 107 meV,[2,3] the P peak is not due to these modes. While the P peak is apparently a phonon replica, its origin is not clear.

In contrast to the pressure dependence of these phonon replicas, the energies of two sharp features labeled $G1$ and $G2$ are seen to increase with pressure in Fig. 1. Near ambient pressure the $G1$ and $G2$ peaks overlap the O^Γ and TO features, with the O^Γ peak being between these two peaks and the TO peak at an energy slightly higher than the $G1$ peak. The widths of these two peaks are about the same as that of the zero-phonon peak, and are much smaller than those of the phonon replicas. In Ref. 3, peaks at the same energies as $G1$ and $G2$ were identified as the TO and O^Γ phonon replicas of the B line, respectively.

Figure 2 displays the PL spectra at even higher pressures. Above ~30 kbar the $G1$ and $G2$ peaks are no longer seen, while the peaks identified as phonon replicas still track the zero-phonon peak. Details of the structure of the zero-phonon peaks are observable in this figure because their intensities have been reduced in magnitude. (The line-shape changes with pressure are discussed in Ref. 6.) When the zero-phonon peak is relatively sharp, e.g., for the dominating A peak at 0.5 kbar and B peak at 40.1 and 46.1 kbar, the O^Γ and TO phonon replicas are resolvable. When the zero-phonon peak is relatively broad, e.g., with contributing A, B, B', and B'' features at 22.2 and 31.3 kbar, the O^Γ- and TO-phonon replicas are not resolvable.

Figure 3 shows the energy of the $G1$ and $G2$ peaks as a function of applied pressure, along with that of the zero-phonon peak (weighted average), the O^Γ-, TO-, P- and TA-phonon replicas, and the indirect band gap of Si. Table I gives the parameters that characterize the fits used in Fig. 3. The slope α of the zero-phonon peak differs from that of the band gap because pressure changes the binding energy of the exciton, as is detailed in Ref. 6. The differences in the slopes for the zero-phonon peak and its phonon replicas are due to the changes in phonon energy with pressure. α is more negative for the TO and O^Γ phonon replicas than for the main peak because the mode Grüneisen parameters for these phonons are positive,[8] while it is less negative for the TA peak because its mode Grüneisen parameter is negative.[8]

The $G1$ and $G2$ peaks are clearly not phonon replicas. They do not track the main peak, and they disappear at pressures at which the main peak and its phonon replicas can still be seen. Further, the intensities of $G1$ and $G2$ change with laser power differently than do these phonon replicas, as is seen in Fig. 4(a). This is clearly true for the $G1$ peak, which is as strong as the TO-phonon replica for 60 mW, but much weaker for 5 mW. Part of the effect of the laser at these higher powers is clearly to heat the sample. Figure 4(b) shows that the intensities of $G1$ and $G2$ and the zero-phonon peak and its phonon replicas all vary with temperature the same way for a fixed laser

TABLE I. Energy positions and pressure coefficients for the zero-phonon peak (weighted average), $G1$ and $G2$ peaks, and the phonon replicas, using the fit $E(P)=E_0(P=1\ \text{bar})+\alpha P+\beta P^2$, where P is the pressure in kbar.

	E_0 (eV)	α (meV/kbar)	β (10^{-3} meV/kbar^2)
Zero phonon	1.078±0.001	−0.67±0.03	−4.6±0.6
Peak $G1$	1.018±0.004	0.56±0.08	−4.8±0.3
Peak $G2$	1.011±0.001	0.39±0.01	−0.6±0.1
TO	1.019±0.001	−0.83±0.03	−3.0±0.7
O^Γ	1.014±0.001	−0.86±0.04	−2.3±0.7
TA	1.058±0.001	−0.50±0.05	−7.7±0.9
P	1.050±0.001	−0.70±0.04	−3.7±0.7
Indirect gap in Si	1.17	−1.5	

power; they first increase and then decrease as temperature increases. (Because of the relatively large exciton binding energies, this decrease at higher temperatures may not be due to thermal detachment or decay of the exciton, but due to more rapid nonradiative decay.) Still, the differences with laser power changes suggest that $G1$ and $G2$ are not due to excitons bound to the Be pair but to excitons bound to a different site, probably one with different laser saturation properties.

Because their energies increase with pressure ($\alpha \sim 0.4-0.6$ meV/kbar), while the indirect gap in silicon decreases with pressure (-1.5 meV/kbar), $G1$ and $G2$ are possibly associated with a deep defect. With the Γ_c-Γ_v gap varying as $\sim 0.48-1.39$ meV/kbar[9,10] and the L_c-Γ_v gap varying as 5.5 meV/kbar,[11] it is possible that this defect is associated with the Γ_c-Γ_v gap. However, the observed transition energies are very different from the Γ_c-Γ_v energy difference, which would suggest that the emission peaks for these defect levels would be broad, in contrast to observations.

$G1$ and $G2$ may be associated with the recombination of excitons bound to impurities in Si other than the isoelectronic Be SI (substitutional-interstitial) pair. One possibility is binding to single substitutional Be-atom double acceptors or to nearest-neighbor double acceptors, which have been identified in Refs. 12 and 13. (These atoms constitute $\sim 10\%$ of all Be, while the SI pairs constitute $\sim 90\%$.[12]) Using a Coulomb model to bind holes to these sites,[6] the exciton binding energy is expected to increase with pressure. This, along with the decreasing indirect band gap with pressure, suggests that the PL energies should decrease with pressure, which is contrary to observations.

Tarnow *et al.*[2] showed that isoelectronic (neutral)

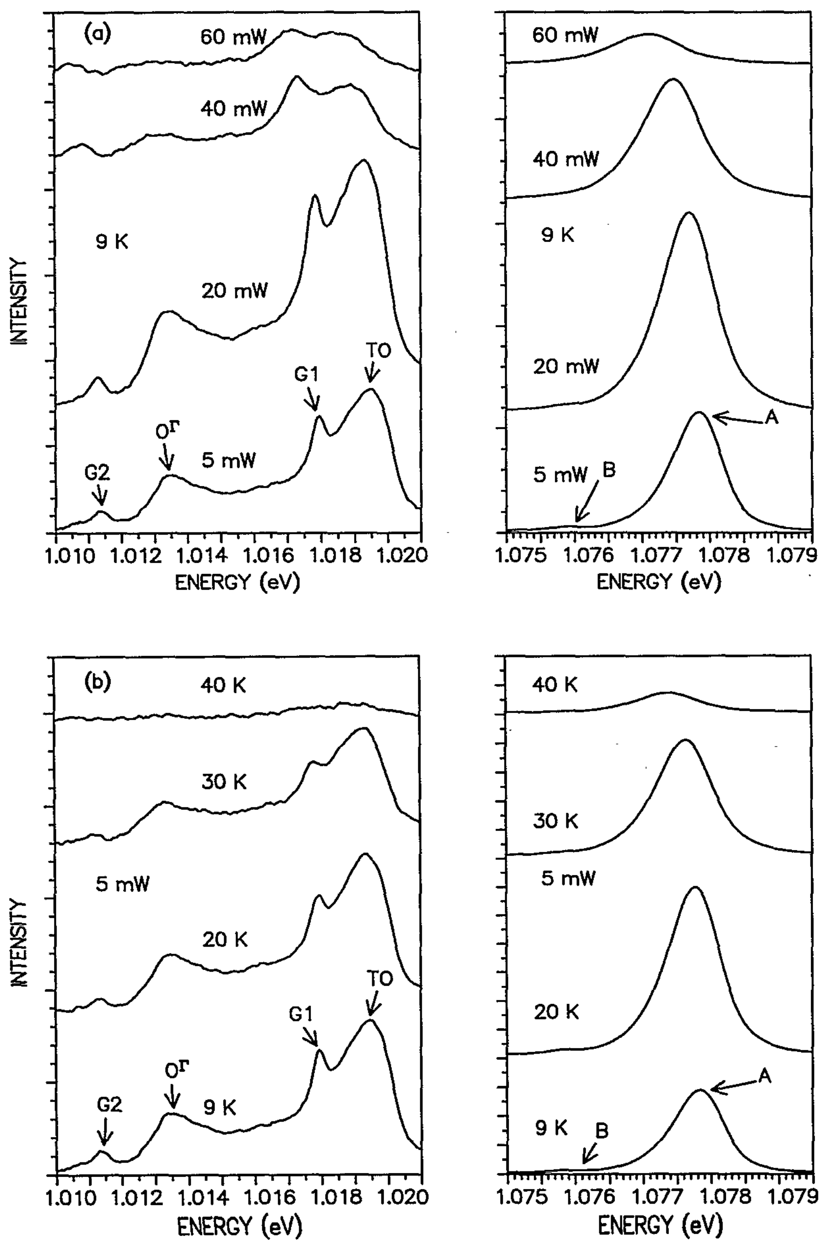

FIG. 4. Photoluminescence as a function of (a) laser power at 9 K and (b) temperature for 5-mW laser power. The spectra on the right are in the zero-phonon peak region and those on the left are in the phonon-replica region. The vertical scales are the same for all spectra on the left, and they are the same for all spectra on the right. The scale for the spectra on the left has been expanded by 25 times relative to that on the right.

three and four-atom clusters have low energies of formation; the four-atom cluster consists of nearest-neighbor SI pairs. Although these clusters have apparently not been detected optically or electrically, perhaps they are present in small concentrations and are responsible for the $G1$ and $G2$ lines.

Binding energies of excitons bound to these larger clusters can be estimated by using the variational analysis used to describe binding to a Be pair in Ref. 6. The electron is assumed to bind to any Be atom in the cluster by a central spherical well with depth V and radius a, which has a tail that decreases as $\sim 1/r^3$, and the hole is assumed to bind to the bound electron with an energy of 43 meV.[5] This model predicts the binding energy for the Be pair at ambient and elevated pressures when $V=6.167$ eV, $a=1.18$ Å, and the pair separation $d=1.9$ Å, and when a and d are allowed to scale with pressure as does the Si lattice constant.[6] When this model is applied to the three-atom cluster using these parameters and the geometry described by Tarnow *et al.*,[2] the PL energy is predicted to be 0.38 eV at ambient pressure, which corresponds to an exciton binding energy of 0.79 eV. This model also predicts an α of 0.7 meV/kbar. The binding energy of each of the $G1$ and $G2$ lines is smaller (0.152 and 0.159 eV), and α is smaller, though also positive. For the four-atom cluster, the exciton binding energy is predicted to be 1.43 eV at ambient pressure, which would shift the level into the valence band.

This model does not rule out the possibility that $G1$ and $G2$ correspond to excitons bound to three-atom clusters. It should be mentioned that the assumption that electrons bind to each Be atom with the same potential is uncertain for the Be pair, as well as for the three- and four-atom clusters. Also, it is unclear whether the pair potentials are transferable to these other clusters.

Although the PL spectrum near 1015 meV (at 1 bar) is very nearly the same here and in Ref. 3, it is uncertain whether the peaks identified as the TO and O^{Γ} replicas of the B line in Ref. 3 were correctly identified there or whether they are the same as $G1$ and $G2$ as labeled here. It is possible that the observation of additional peaks at the same energies here is purely coincidental. Although in both samples the density of Be pairs is $\sim 10^{16}$/cc in the probed region, perhaps the densities of larger Be clusters are different in the two studies because of differing sample fabrication procedures. It is not clear whether the PL spectra taken at different temperatures in Ref. 3 support or disprove the presence of $G1$ and $G2$ in their work. Still, it is clear that the $G1$ and $G2$ peaks observed here are not phonon replicas associated with recombination at the substitutional-interstitial [111] Be pair.

In conclusion, pressure tuning has been able to demonstrate that two of the weak peaks ($G1$ and $G2$) in the PL spectrum of Si:Be are not phonon replicas associated with the Be pair dopant, because their energies increase with increasing pressure, while the energy of the zero-phonon peak decreases with pressure. The $G1$ and $G2$ peaks may be the zero-phonon lines of excitons bound to larger Be complexes, or to other as yet unidentified impurities. This study illustrates the value of applying pressure to a material to improve the understanding of its properties at ambient pressure.

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