Photoluminescence Transitions of the Deep *EL*2 Defect in Gallium Arsenide

M. K. Nissen, T. Steiner, D. J. S. Beckett, and M. L. W. Thewalt

Department of Physics, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6

(Received 24 August 1990)

Fourier-transform photoluminescence spectroscopy has been used to obtain detailed and unequivocal information on the two major transitions involving the deep $EL2$ level in semi-insulating gallium arsenide. We report the first observation of a shallow, hydrogenic state of neutral $EL2$, which leads to sharp structure in the luminescence spectrum. This new fine structure should prove extremely useful in perturbation studies of the $EL2$ defect. These new transitions also locate the energy position of neutral $EL2$ within the band gap with unprecedented precision.

PACS numbers: 71.55.Eq, 78.55.Cr

Photoluminescence (PL) spectroscopy is a well developed and widely applied technique for the study of relatively shallow impurities and defects in semiconductors. It is capable of providing detailed information on chemical species, energy levels, symmetries, and, in some instances, concentrations. The use of PL for the study of deep centers is less advanced, since there are often difficulties in reliably associating PL features with specific defects, and in determining the electronic nature of the transition responsible for the PL. In this Letter we demonstrate that the great increases in sensitivity and spectral resolution which can be obtained using Fourier-transform PL (FTPL)[1] can provide a wealth of new information, allowing for the detailed and unequivocal explanation of deep PL processes.

The system under study is the $EL2$ midgap double donor in GaAs. This defect is of great technical importance due to its involvement in pinning the Fermi level in "semi-insulating" (SI) GaAs. It is also of considerable fundamental interest due to its readily accessible inactive metastable state.[2,3] The voluminous literature on $EL2$ continues to be rife with disagreement and controversy; for example, on the question of whether $EL2$ is the isolated As-antisite ($\mathrm{As_{Ga}}$) (Refs. 2 and 4) or the $\mathrm{As_{Ga}}$ plus other constituents,[5] and as to the nature of the lattice relaxation associated with the metastable state.[6,7] The $EL2$ PL literature is similarly characterized by conflicting claims and models. For example, the frequently observed $\simeq 0.63$-eV band has been suggested to arise from neutral $EL2$ recombining with a free hole $(h,EL2^0)$,[7-9] transitions from $EL2^0$ to the $\mathrm{Ga_{As}}$ double acceptor,[7] transitions from a relatively deep ($\simeq 50$ meV) $EL2$ excited state to the ground state,[3] an oxygen-related defect (O),[10,11] some defect other than $EL2$,[12] and finally O in oxygen-containing samples and a free electron recombining with singly ionized $EL2$ $(e,EL2^+)$ in others.[13] The second frequently observed band at 0.68 eV has been assigned to $(e,EL2^+)$ transitions,[3,7] to $(h,EL2^0)$ transitions,[10,11,13,14] and to internal transitions of ionized $EL2$ $(EL2^{+*} \to EL2^+)$.[15]

Our new PL results support the conclusion of Tajima[13] that the $\simeq 0.63$-eV band can be due to either O or $EL2$, and in addition we show clear differences between the two spectra. The fine structure in our $\simeq 0.63$-eV $EL2$ band reveals that at liquid-He temperatures this band results from an electron in a shallow, hydrogenic bound state dropping into the $EL2$ ground state $(EL2^0_{n=2} \to EL2^0_{n=1})$. At higher temperatures ($T \gtrsim 30$ K) the free-to-bound $(e,EL2^+)$ transitions dominate the spectrum. Our results on the structured 0.68-eV band reported by Tajima[14] reveal that at $T \lesssim 35$ K, it is not $(h,EL2^0)$ but rather a donor-acceptor-pair (DAP) transition $(EL2^0,A^0)$ involving carbon (or zinc if present), and the $(h,EL2^0)$ free-to-bound transition occurs only at $T \gtrsim 35$ K. The fine structure of the new transitions allows for determination of the energetic position of $EL2$ in the band gap with unprecedented precision, and we note that the $(h,EL2^0)$ and $(e,EL2^+)$ free-to-bound edges add up to precisely the band-gap energy as they should.

A wide variety of bulk annealed liquid-encapsulated-Czochralski (LEC) GaAs samples were studied. While most were grown by one manufacturer, we emphasize that the O band and the structured ~ 0.63- and 0.68-eV bands reported here were also clearly observed in samples obtained from a second source. A controlling factor in the incorporation of O into LEC GaAs is the moisture content of the B_2O_3 encapsulant.[10,13,16] We refer here to the high-O-content samples grown with wet B_2O_3 as B type (2000 ppm H_2O), and the low-O-content samples grown with dry B_2O_3 as C type (1000–1200 ppm H_2O) and D type (500 ppm H_2O). It is interesting to note that even the addition of Ga_2O_3 to the melt when using dry equipment does not appear to introduce detectable levels of O.

The PL was performed on a Bomem DA3.02 Fourier-transform interferometer using a liquid-nitrogen–cooled Cincinnati Electronics InSb detector. A variety of excitation sources were used, namely, an Ar^+ laser for above-band-gap excitation, a Ti:Al_2O_3 laser for near-gap excitation, and a 1.3-μm diode laser for long-wavelength excitation. All PL spectra have been corrected for instrumental response unless otherwise noted. The photoluminescence-excitation (PLE) spectra were excited by a $LiNbO_3$ optical parametric oscillator system.[17] The samples were mounted in a liquid-helium cryostat that allowed the temperature to be varied from 1.5 K to room temperature.

The first issue to address is the effect of oxygen on the deep luminescence. Figure 1 shows the effect of increasingly lower concentrations of oxygen on the deep PL using above-gap excitation at liquid-helium temperature. The PL spectrum, Fig. 1(a), of the heavily oxygen-doped sample (Ga-O-Ga concentration of 2×10^{15} cm^{-3})[18] is completely dominated by a broad, structureless band at 0.63 eV. We found no evidence of the previously reported structure.[19] In the undoped *B*-type sample, Fig. 1(b), the intensity of the deep PL is approximately 200 times weaker than the near-gap luminescence but is still strong. The peak has shifted down in energy somewhat, but in relation to the width of the band, the change is slight. The deep PL found in the *C*-type and *D*-type samples is, however, dramatically different. The luminescence is much weaker and is unusually long lived, with a lifetime of $\tau\cong5$ ms. The spectrum, Fig. 1(c), is also markedly different: The band now peaks at 0.61 eV and is characterized by sharp structure on the high-energy side of the band. All of the undoped *C*-type and *D*-type samples studied had this same distinctive band and fine structure, whereas the *B*-type samples were normally dominated by the much stronger O-related band at 0.63 eV. In some cases the sharp feature from the deeper band can still be discerned in the *B*-type samples, but it is usually obscured by the O-related 0.63-eV band. We have also verified that the PLE spectra of these bands differ in the way described by Tajima.[13]

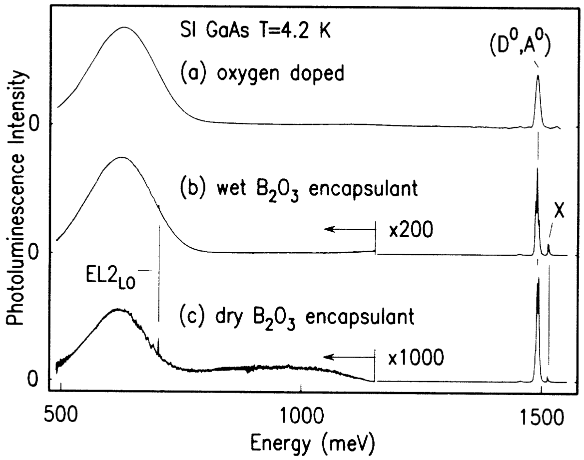

FIG. 1. Spectra at 4.2 K with 515.5-nm excitation showing the effect on the PL of reducing the oxygen concentration. (a) The Ga-O-Ga concentration in the O-doped sample is 2×10^{15} cm^{-3}. The water content of the B_2O_3 encapsulant is (b) 2000 ppm and (c) 500 ppm. The indicated $EL2_{LO}$ transition is present in (b) but is difficult to discern on the strong background. (D^0,A^0) refers to the near-gap donor-acceptor-pair luminescence and *X* the excitonic luminescence. Resolution is 0.5 meV.

The most widely recognized signature of *EL*2 is its unusual bleaching or quenching behavior. The 0.61-eV band is observed to quench completely after the sample is bleached for several minutes with intense light of wavelength near 1 μm, regardless of the wavelength of the light used for exciting the PL. Spectra taken immediately after bleaching show only a much weaker and structureless band centered at 0.66 eV. These spectra were collected quickly when using above-gap excitation because this light slowly regenerates the neutral *EL*2. By bleaching a sample for short periods and measuring both the PL and the 1.039-eV absorption line, the 0.61-eV band was found to bleach at the same rate as the *EL*2 intracenter absorption transition, and complete recovery of both was achieved after annealing at 140 K. As expected, the O-related band could not be quenched when using above-gap excitation for the PL.[13]

The *EL*2 optical cross section, σ_n^o,[20] and the PLE results[13] suggest that the conduction-band-to-*EL*2 PL should be most efficiently pumped by excitation just below the gap. This was found to be the case for the 0.61-eV band and allowed the collection of the low-noise PL spectra of Figs. 2(a)–2(c). An abundance of sharp structure is apparent in the spectrum shown in Fig. 2(a), taken at 4.2 K. The band begins with a weak no-phonon (NP) transition at 739.33 meV which is seen to couple to a wide variety of phonons. The longitudinal-optical zone-center phonon- (LO_Γ) assisted transition is by far the strongest and occurs at 702.82 meV. There is also a transverse-optical zone-centered phonon (TO_Γ) replica, a transverse-acoustic phonon from the *X* point of the Bril-

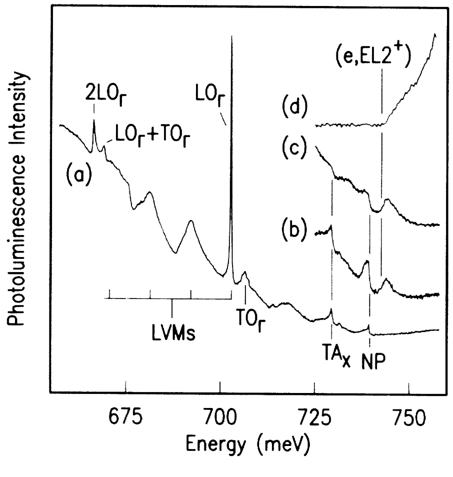

FIG. 2. PL spectra with 840-nm excitation showing (a) the structure on the 0.61-eV band at 4.2 K, and the free-to-bound transition at (b) 20 K and (c) 30 K. These spectra are not corrected for instrumental response. The resolution is 0.12 meV. (d) The PLE of the 0.61-eV band at 1.6 K with approximately 1-meV resolution.

louin zone (TA_X) and $2\mathrm{LO}_\Gamma$ and $\mathrm{LO}_\Gamma+\mathrm{TO}_\Gamma$ replicas. In addition to these lattice phonons, there is strong coupling to local vibrational modes (LVM) of energy 10.8 ± 0.2 meV. These are strikingly similar to the 11-meV LVMs which couple to the 1.039-meV NP transition of the $EL2$ intracenter absorption.[21]

The sharpness of the NP transition and its LO-phonon replica implies that the initial and final states are both localized on the same center. Since $EL2$ is a double donor, it should have shallow Coulombic excited states in the gap analogous to the excited states of the helium atom. On varying the sample temperature, it was noted that the PL was very strongly temperature dependent. The PL intensity of the sharp structure associated with the 0.61-eV band decreased rapidly as the temperature increased, indicating that the initial state was depopulating into another nearby state. PL spectra taken at 20 and 30 K, Figs. 2(b) and 2(c), clearly show a new transition from a thermally populated level, and the Boltzmann-like line shape is indicative of a free-to-bound transition, namely, $(e,EL2^+)$. This is confirmed by the PLE spectrum shown in Fig. 2(d) where the onset of the absorption agrees well with the edge of the free-to-bound transitions in Figs. 2(b) and 2(c). The spectroscopic binding energy of the shallow state is measured to be 3.2 ± 0.5 meV, which puts the $EL2$ ground state at 742.5 ± 0.5 meV below the conduction band at 4.2 K. This is by far the most accurate measurement yet of this important level and is in good agreement with the results of Omling, Silverberg, and Samuelson.[22] We note that the fact that the low-temperature transition couples strongly to LO_Γ while the $(e,EL2^+)$ transition does not results in an anomalous increase in the energy of the center of the band as T increases, from 0.61 eV at liquid-helium temperature to 0.63 eV at 30 K.

As noted by Tajima,[13] the 0.68-eV band is best excited at 1.3 μm, near where the optical cross section σ_p^o reaches its maximum.[20] In contrast to previous work,[14] most of our samples did not show this band. It was found only in samples where the acceptor concentration (N_A) exceeded the shallow donor concentration (N_D) by approximately 1.0×10^{15} cm^{-1}, resulting in a significant concentration of ionized $EL2$. A typical spectrum obtained at 6.0 K is shown in Fig. 3(a). It is very similar to that reported by Tajima.[14] The improved quality allows us to observe that the structure at ~720 meV is not the third LVM replica but rather is dominated by an LO_Γ replica. Once again, the temperature dependence of the PL provides valuable information. In the spectrum collected at 40 K, Fig. 3(b), a free-to-bound transition with an edge at 773.0 ± 0.6 meV is evident, and at 70 K, Fig. 3(c), this initial state is dominant and the broad band has shifted to higher energy by approximately 15 meV. The appearance of this free-to-bound transition and the ~23-meV shift from its edge to the lower edge of the relatively broad NP transition, which peaks at 756 meV, indicates that the 756-meV transition is the NP transition of the $EL2$ to neutral-acceptor $(EL2^0,A^0)$ DAP luminescence (due to carbon with an ionization energy of 27.0 meV) and the 773.0-meV transition is $(h,EL2^0)$. When the energy of the $(h,EL2^0)$ transition edge at 40 K is added to the energy of the $(e,EL2^+)$ edge, a value of 1515.5 ± 1.1 meV is obtained, which compares well to the 40-K band gap, 1516.6 meV.[23]

To conclude, we have presented PL spectra of a band centered at 0.61 eV at liquid-He temperature, with a sharp NP transition at 739.33 meV and strong phonon replicas. The band bleaches and anneals identically to the $EL2$ intracenter absorption and has the same LVMs as observed in absorption. The band is distinguished from the much stronger, structureless oxygen-related PL band centered at 0.63 eV. At low temperature the PL is due to transitions from a shallow, hydrogenic $EL2$ excited state to the $EL2$ ground state and at higher temperatures transitions involving free electrons to the $EL2$ ground state are observed. The 0.68-eV band is only observed in samples where there are significant concentrations of acceptors, and at low temperature this band is due to DAP recombination involving $EL2$ and shallow acceptors. At higher temperatures the band is due to $EL2$ to valence-band transitions. The narrow linewidth of the transitions in the 0.61-eV band will allow perturbation studies of $EL2$ to be carried out with much greater precision than was previously achievable.

This work was supported by the Natural Sciences and Engineering Research Council of Canada, the Simon Fraser University Center for Systems Science, and the British Columbia Advanced Systems Foundation. The authors thank M. Maciaszek and R. P. Bult of Johnson Matthey Electronics for samples and their cooperation.

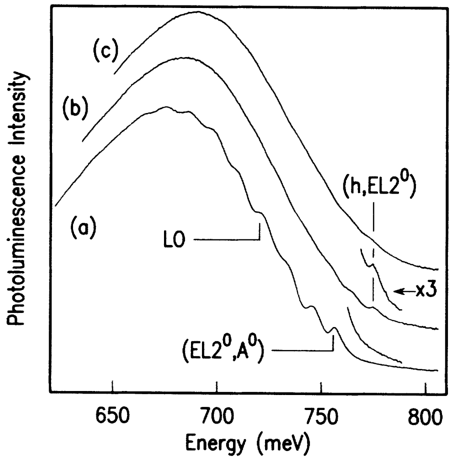

FIG. 3. Spectra of the 0.68-eV band as a function of temperature from a sample with carbon concentration of 5.5×10^{15} cm^{-3} with 1.3-μm excitation. The sample temperature is (a) 6.0 K, (b) 40 K, and (c) 70 K. Resolution is 0.5 meV.

[1] M. L. W. Thewalt, M. K. Nissen, D. J. S. Beckett, and K. R. Lundgren, Mater. Res. Soc. Symp. Proc. **163**, 221 (1990).

[2] U. Kaufmann, in *Festkörperprobleme/Advances in Solid State Physics,* edited by U. Rössler (Vieweg, Braunschweig, 1989), Vol. 29, p. 183.

[3] G. M. Martin and S. Makram-Ebeid, in *Deep Centers in Semiconductors,* edited by S. T. Pantelides (Gordon and Breach, New York, 1986), p. 399.

[4] M. Kaminska, M. Skowronski, and W. Kuszko, Phys. Rev. Lett. **55**, 2204 (1985).

[5] H. J. von Bardeleben, D. Stiévenard, D. Deresmes, A. Huber, and J. C. Bourgoin, Phys. Rev. B **34**, 7192 (1986).

[6] J. Dabrowski and M. Scheffler, Phys. Rev. Lett. **60**, 2183 (1988).

[7] J. C. Bourgoin, H. J. von Bardeleben, and D. Stiévenard, J. Appl. Phys. **64**, R65 (1988).

[8] A. Mircea-Roussel and S. Makram-Ebeid, Appl. Phys. Lett. **38**, 1007 (1981).

[9] P. Leyral, G. Vincent, A. Nouailhat, and G. Guillot, Solid State Commun. **42**, 67 (1982).

[10] P. W. Yu and D. C. Walters, Appl. Phys. Lett. **41**, 863 (1982).

[11] P. W. Yu, Solid State Commun. **43**, 953 (1982).

[12] D. Paget and P. B. Klein, Phys. Rev. B **34**, 971 (1986).

[13] M. Tajima, Jpn. J. Appl. Phys. **26**, L885 (1987).

[14] M. Tajima, in *Defects in Semiconductors,* edited by H. J. von Bardeleben, Material Science Forum Vols. 10–12 (Trans. Tech. Publications, Aedermansdorf, Switzerland, 1986), p. 493.

[15] M. Kaminska, Rev. Phys. Appl. **23**, 793 (1988).

[16] H. Ch. Alt, Appl. Phys. Lett. **54**, 1445 (1989).

[17] M. L. W. Thewalt and D. J. S. Beckett, Can. J. Phys. **66**, 868 (1988).

[18] H. Ch. Alt (private communication).

[19] T. Kazuna, Y. Sawada, and T. Yokoyama, Jpn. J. Appl. Phys. **25**, L878 (1986).

[20] A. Chantre, G. Vincent, and D. Bois, Phys. Rev. B **23**, 5335 (1981).

[21] M. Kaminska, M. Skowronski, J. Lakowski, J. M. Parsey, and H. C. Gatos, Appl. Phys. Lett. **43**, 302 (1983).

[22] P. Omling, P. Silverberg, and L. Samuelson, in *Defects in Semiconductors* (Ref. 14), p. 329.

[23] J. S. Blakemore, J. Appl. Phys. **53**, R123 (1982).