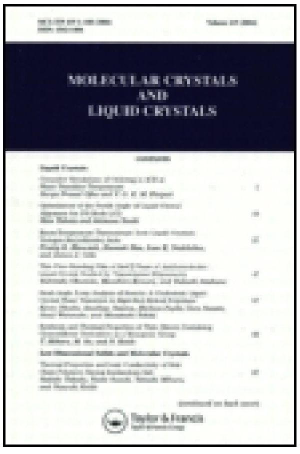

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RADIATIVE RECOMBINATIONS IN Be-DOPED $Al_xGa_{1-x}As$

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Abstract Six types of systematic photoluminescence (PL) measurements ($T \geq 77$ K) were carried out on single crystals of $Al_xGa_{1-x}As$ ($x \sim 0.3$) undoped or doped with Be by LPE or ion implantation. The multimeasurements approach was employed in order to ascertain that the highest-energy radiative recombination was in fact band-to-band (BTB), and consequently to obtain accurate activation energies. LPE doped crystal luminescence consisted of a high-energy BTB peak and a lower energy shoulder (observed near 77K) assigned to free electron to bound (FTB) hole recombination at the Be acceptor center. All Be implanted $Al_xGa_{1-x}As$ specimens had BTB radiative recombinations at $T \geq 77$ K. The lower energy FTB shoulder, observed between 85 and 77K, appeared only for crystals annealed at or above 800°C, i.e., the higher temperatures are necessary to activate the implanted Be dopant in $Al_xGa_{1-x}As$. In addition to the BTB and FTB peaks, a PL peak at ~ 1.29 eV is attributed to implantation damage.

INTRODUCTION

The importance of $Al_xGa_{1-x}As$ in diodes, simple and cascade solar cells, and solid state lasers, etc. is well established. In AlGaAs the Be has, at LPE temperature ($\sim$800°C), a high liquid/solid distribution coefficient (e.g., $K_{Be} = 10$ at $x < 0.4$ and 800°C) and high diffusivity, D ($D = D_0 \exp(-E_0/kT)$, with $D_0 = 11.2\ cm^2$, $E_0 = 2.43$ eV).[3] Thus, LPE prepared junctions could be improved by ion implanting Be, which was carried out, along with thermal annealing. The reason this is anticipated to be favorable is that MBE generated Be gradients[1] in adjoining AlGaAs(Be) layers when heated to 800°C, similar to our T_{AN}, had a low diffusion coefficient ($D \leq 10^{-15} cm^2 sec^{-1}$). In an initial study[4] SIMS profiling of Be implanted AlGaAs showed either very little (fluences $\leq 10^{14} cm^{-2}$) or significant (fluences $> 10^{14} cm^{-2}$) redistribution. While Be implanted GaAs PL work has been published,[5] the present study is the first PL work on implanted Be in AlGaAs. MBE specimens were studied,[1,6] with the highest energy PL band assumed to be BTB, and band broadening was attributed to Be. We undertook our study in order to look for distinct Be related PL peaks, and obtain accurate E_a(Be) values by firmly establishing the highest energy PL as BTB. To achieve the latter six multi-point type PL experiments were carried out.

EXPERIMENTAL

Layers of $Al_xGa_{1-x}As$ ($x \sim 0.3$) were grown on (111) GaAs by LPE using the sliding boat technique. Be ions were implanted (100 KeV) at fluences 5×10^{13} and 1×10^{14} cm^{-2}. The implanted samples were capped with SiO_2 and annealed for one hour at 600°, 700°, 800° or 850°C. After annealing the caps were removed by a 1:1 solution of concentrated HF and water (∿ 10 sec). Two samples were annealed without caps in the LPE reactor. One sample was doped by the LPE growth process. Comparing the PL spectra of the latter with the ion implanted one then revealed the damage from the implantation process.

The photoluminescence apparatus consisted of an Ar^+ laser operated at 5145 Å (with intensity varied from 1 to 20 mw at sample) and a 3/4 meter monochromator set to a bandpass of 3 meV at 1.8 eV. The laser beam was focused to a spot ca. 100 μm diameter at the sample which was mounted on a copper heat sink and placed in a cryogen throttling optical dewar. Temperature spectral cycling showed no excitation damage. The temperature was measured with a chromel-(Au - 7% Fe) thermocouple. The photoluminescence was detected with a Dry Ice cooled photomultiplier tube with an S-1 response. The laser beam was chopped with a mechanical chopper so that, following pre-amplification, phase sensitive amplification of detection could be used with a lock-in amplifier.

The ion implantation was carried out at NRL in Washington, D. C.

RESULTS

Six types of PL measurements were carried out. The PL spectra of undoped (native) AlGaAs were studied before studying the Be doped samples. First, the near band gap PL of native samples consisted of a single peak whose full width at half height (FWHH), or $\Delta_{1/2}$, was directly proportional to sample temperature T over the 80K to 300K range. Over this same T range the peak intensity I_{PL} showed thermal quenching with an activation energy E_a of approximately 28 meV. Also, the energy position $\hbar\omega_o$ of the PL peak changed with temperature. Then, by plotting the $\hbar\omega_o$ versus T, it was found that the curve fitted the relationship of Varshni[7] by using his coefficients of $\alpha(8.871 \times 10^{-4}\ K^{-1})$ and $\beta(5.72 \times 10^2\ K)$ for GaAs, and the calculated band gap, E_o, for AlGaAs at absolute zero. The latter was calculated by using the high energy PL peak as E_g at our T. In addition, I_{PL} increased superlinearly with increasing excitation intensity, I_o ($I_{PL} \propto I_o^{\sim 2}$) but $\hbar\omega_o$ and $\Delta_{1/2}$ remained constant when I_0 was varied (Figure 1).

For the Be-implanted samples, the near band gap luminescence at 77K increased with increasing annealing temperature T_{AN} up to 850°C, the highest T_{AN} used here. On the other hand, I_{PL} never became as large as in the undoped samples. This indicates that even for T_{AN}=800° or 850°C, damage caused by ion implantation is still present.

Observations about lower energy PL bands were as follows. For the sample implanted with a fluence of 5 x 10^{13} ions/cm^2 and T_{AN}=800°C, and the samples implanted with fluences of 5 x 10^{13} and 1 x 10^{14} ions/cm^2 and T_{AN}=850°C, the near band gap PL spectra of these samples consisted of a single peak with a shoulder ca. 15 to 20 meV below (to lower energy of) the major peak, the value depending on Al content (Figure 2).

For the samples annealed in the LPE reactor (capless), T_{AN} of 800°C produced samples whose PL had a shoulder ∿19 meV below the main peak (77K), whereas T_{AN} of 700°C produced only a single PL band.

The PL of AlGaAs doped by LPE also consisted of a near band gap peak with a shoulder ∿19 meV below it.

The temperature dependence of the high energy PL peak of all the Be doped samples was the same as the undoped AlGaAs, i.e., the position, $\hbar\omega_0$, changed with T in the same manner as GaAs. The main PL peak of the samples underwent thermal quenching, with E_a of ∿20 meV being determined by an Arrhenius plot of I_{PL} vs. T^{-1}. I_{PL} of the high energy peak of Be doped AlGaAs increased superlinearly with an increasing I_0. However, the main peak increases faster than the shoulder, until at higher I_0, the main peak strongly dominates the shoulder. However, $\hbar\omega_0$ of the main peak and shoulder remained unchanged with increasing excitation I_0.

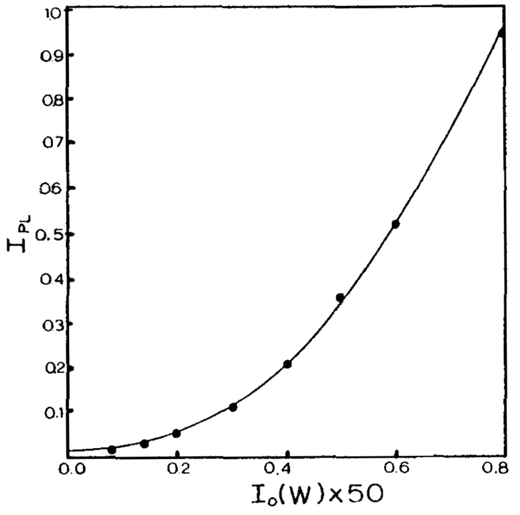

FIGURE 1. I_{PL} vs. I_0 for undoped $Al_{0.25}Ga_{0.75}As$.

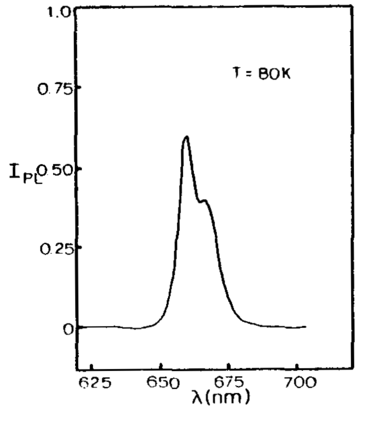

FIGURE 2. I_{PL} vs. wavelength of Be implanted $Al_xGa_{1-x}As$.

In addition to the near band gap radiation, we also detected at 77K two broad band PL peaks centered at ∿1.39 eV and ∿1.29 eV. These two PL bands were not observed for the LPE doped AlGaAs but were present for the ion implanted and annealed samples. Whether both PL bands were present or just one depended on the sample spot probed.

DISCUSSION

Our procedure consisted of studying the PL of undoped crystals, followed by the LPE doped ones, and then finally followed by the ion implanted ones so as to determine the implantation damage. Most fundamental was the need to definitively establish that the highest energy recombination is BTB, since only then can accurate E_a values for lower energy PL processes be determined and used reliably for future applications. For this reason we carried out six types of PL experiments to ascertain the assignment: $\hbar\omega_0$ vs. T, $\Delta_{1/2}$ vs. T, I_{PL} vs. T, I_{PL} vs. I_0, $\Delta_{1/2}$ vs. I_0, and $\hbar\omega_0$ vs. I_0. The findings given in the RESULTS section above will be referred to repeatedly in the present DISCUSSION.

For undoped AlGaAs the single peak PL is initially assigned to be either BTB or FTB (D-VB, CB-A) recombination. This is consistent first with our result that the peak $\hbar\omega_0$ vs. T has the same dependence as for GaAs,[7(a)] and second with the observation that $\Delta_{1/2}$ of the band is directly proportional to T.[7(b)] Also, from our Log I_{PL} vs. T^{-1} relationship, the derived thermal quenching E_a of 28 meV cannot be used to decide between the two assignments, since a BTB transition can be quenched by electrons thermally populating either donor levels or conduction band states[8] both of which would be associated with the higher energy L or X bands, probably close to the Γ minimum for our alloy compositions. Also, the quenching could be the result of thermal depopulation of carriers (holes from A or electrons from D) at impurities. While this carrier depopulation might in principle be associated in AlGaAs with a carbon acceptor (E_a = 26-36 meV, depending[9] on X), the E_a(C) of which matches our 28 meV value best, we show in the next paragraph below that this assignment is actually not possible. Also, donor depopulation cannot be ruled out based on the above data, since in AlGaAs the range[10] of E_a is 6 meV to 300 meV.[11]

The dependence of PL intensity (I_{PL}) on I_0 (factor of 50 variation) gave rise to a superlinear relationship ($I_{PL} = I_0^{\sim 2}$) without ever an onset of saturation, but $\hbar\omega_0$ remained unchanged with changing I_0. The latter is an indication that the recombination mechanism remained unchanged over the I_0 range. The absence of saturation eliminates from consideration residual C acceptors, since the accidental presence and concentration, if there at all, should be very small (the AlGaAs was n-type) and saturable. The same argument is valid for residual donors. Therefore, by elimination, the single PL peak is reliably assignable to BTB, and the quenching process corresponds to carrier transfer from CB to L or X bands. It is also noteworthy that the PL $\Delta_{1/2}$ did not change with this I_0 variation, indicating that the sample was not heating up during these measurements and that the data are valid.

For the Be doped samples the appearance of the lower energy (by 15-20 meV) shoulder in each ~80K PL spectrum indicates that Be is the cause of a radiatively active level in AlGaAs assigned as A_{Be}. The possibility that this level is caused by the implantation and annealing processing is eliminated by the fact that the same shoulder appeared in the LPE doped sample, and also in MBE grown AlGaAs(Be).[6] Three sample E_a(Be) values of different AlGaAs compositions (different E_g) are shown:

E_g (eV)	FTB (eV)	E_a (meV)	Corrected E_a (meV)
1.828	1.812	16	19
1.889	1.869	20	23
1.921	1.905	16	19

where $E_g = E_{BTAc} + E_a - \frac{1}{2}kT$ (∿3 meV at 77K).

With the information that the high energy PL band is BTB, which in turn affirms that our $E_a(A_{Be})$ values from PL are accurate, it remains to confirm the earlier literature approach for obtaining E_a(Be). First, initial experimental electrical properties of AlGaAs(Be) showed E_a(Be) to have a concentration dependence;[2] from that data for a sample closest in composition (x ∿ 0.45) to ours (x ∿ 0.3) we use[2] $\Delta E_a = 63$ meV - 3.1×10^{-5} meV cm^{-1} $N_A^{1/3}$. Using our N_A (10^{18} cm^{-3} from Hall measurement) the calculated E_a is ∿32 meV. However, this E_a value for Be should be corrected[6], since m* of the Be hole depends[9] on x of $Al_xGa_{1-x}As$. In fact, using ε(x = 0.3) from Casey and Panish[12] and m* (x = 0.3),[9] the E_a ∿ 32 meV diminishes[9] to 24.7 meV, in good agreement with our PL experimental 20 meV for the sample. Furthermore, when for 77K we add to 20 meV Eagles' thermal kinetic energy $\frac{1}{2}kT$ (3 meV) of the free carrier[6], our corrected E_a(Be) equals 23 meV, with which the above 24.7 meV value agrees very well. It can be concluded that previously used procedures agree well with ours.

Deep level PL peaks at 1.29 eV and 1.39 eV appeared in AlGaAs only when Be was implanted, and the energies remained independent of Al content (x = 0.201 to 0.336), x was obtained from $E_g(RT) = 1.424 + 1.247x$ (H.C. Casey, J. Appl. Phys., 49, 3684 (1978)). We attribute the 1.29 eV PL to implantation damage, since the backside PL (GaAs) of the substrate, as also some spots on the AlGaAs(Be) front, showed only the 1.39 eV band. This indicates the presence of microcracks in AlGaAs(Be) grown on GaAs. Furthermore, the 1.29 eV PL was absent in LPE AlGaAs(Be). This 1.29 eV PL may in part be due to V_{Ga} such as the E_3 trap observed[13] by DLTS, since the E_3 energy position is also invariant with composition change. Additional work is underway on this problem, however.

In summary, the highest energy PL peak for $Al_xGa_{1-x}As$ was shown to be BTB, accurate E_a(Be) values in AlGaAs were then derivable, and a deep level PL peak at 1.29 eV was assigned to originate from the implantation process of Be. Native, LPE and ion implantation doped $Al_xGa_{1-x}As$ crystals were studied, as was the influence of T_{AN} on Be activation.[14]

REFERENCES

1. M. Ilegems, J. Appl. Phys., 48, 1278 (1977).
2. S. Fujita, S. M. Bedair, M. A. Littlejohn, and J. R. Hauser, J. Appl. Phys., 51, 5438 (1980).
3. K. Masu, M. Konagai, and K. Takahashi, Appl. Phys. Lett., 37, 182 (1980).
4. J. Comas and S. M. Bedair, Appl. Phys. Lett., 39, 989 (1981).
5. (a) P. K. Chatterjee, K. V. Vaidyanathan, W. V. McLevige and B. G. Streetman, Appl. Phys. Lett., 27, 567 (1975). (b) P. K. Chattergee, W. V. McLevige, K. V. Vaidzanathan, and B. G. Streetman, Appl. Phys. Lett., 28, 509 (1976).
6. V. Swaminathan, J. L. Zilko, W. T. Tsang, and W. R. Wagner, J. Appl. Phys., 53, 5163 (1982). Their E_a was calculated from $h\nu$ (obs BTB) = E_a + [$h\nu$ (obs. B-A) - 1/2 kT)] (D. M. Eagles, J. Phys. Chem. Solids, 16, 76 (1960)).

7. (a) Y. P. Varshni, Physica, 34, 149 (1967). He found $E_g = E_0 - \alpha T^2/(T+\beta)$, where T = Kelvin, E_0 is E_g at 0K, and α and β are empirical constants. (b) E. W. Williams and H. B. Bebb, J. Phys. Chem. Solids, 30, 1289 (1969).

8. R. Dingle, R. A. Logan, and J. R. Arthur, Jr., Gallium Arsenide and Related Compounds (Inst. Phys. Conf. Ser. 33A, (1976), p. 210.

9. G. B. Stringfellow and R. Linneback, J. Appl. Phys., 51, 2212 (1980); $m^*(x) = (0.48 + 0.31\ x)m_0$; $\varepsilon(x) = (13.1 - 3.0x)\varepsilon_0$; and $E_a = E_H(\varepsilon_0/\varepsilon_s)^2/(m^*/m_0)$.

10. (a) K. Sugiyama and T. Kawakami, Jap. J. Appl. Phys., 10, 1007 (1971). (b) H. Kressel, F. H. Nicoll, F. Z. Hawrylo, and H. F. Lockwood, J. Appl. Phys., 41, 4692 (1970). (c) Zh. I. Alferov, D. Z. Garbuzov, O. A. Ninua, and V. G. Trofim, Sov. Phys. - Semicond., 6, 982 (1971). (d) J. Shah, B. I. Miller, and A. E. DiGiovanni, J. Appl. Phys., 43, 3436 (1972). (e) B. Monemar, K. K. Shih, and G. D. Pettit, J. Appl. Phys., 47, 2604 (1976). (f) A. I. Keda, L. G. Lunin, and O. D. Lunina, Izv. Vyssh. Uchebn. Zaven. Fiz., 3, 117 (1977). (g) E. Wagner, D. E. Mars, G. Hom, and G. B. Stringfellow, J. Appl. Phys., 51, 5434 (1980). (h) V. Swaminathan, N. E. Schumaker, J. L. Zilko, W. R. Wagner, and C. A. Parsons, J. Appl. Phys., 52, 412 (1981).

11. K. Kaneko and M. Ayabe, J. Appl. Phys., 51, 6337 (1980).

12. H. C. Casey, Jr. and M. B. Panish, Heterostructure Lasers, Part A (Academic, New York, 1978).

13. D. V. Lang, R. A. Logan, and L. C. Kimerling, Proc. 13th Int. Conf. on Phys. of Semi. (1976), p. 615.

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Editors' Note: superlinear=exponential, LPE=liquid phase epitaxy, MBE=molecular beam epitaxy, AN=annealing, D-VB=donor to valence band, CB-A=conduction band to acceptor, DLTS=deep-level transient spectroscopy.