

# Photoluminescence of shallow acceptors in epitaxial $\text{Al}_x\text{Ga}_{1-x}\text{As}$

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The low-temperature (2 K) photoluminescence (PL) of  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  ( $0 < x < 0.25$ ) was studied in an effort to characterize shallow acceptors in material grown by organometallic vapor phase epitaxy and liquid phase epitaxy techniques. The dominant shallow acceptor in nominally undoped  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  specimens grown by both techniques was identified as Carbon, with  $E_A = 26$  meV for  $x = 0$ .  $E_A$  was observed to increase with increasing  $x$  to  $\sim 36$  meV at  $x \sim 0.20$ , as expected for an effective mass like center where  $E_A \propto [m^*(x)/\epsilon(x)^2]$ . The PL peak due to the conduction band to acceptor transition was found to become progressively broader with increasing  $x$ , which is attributed to increasing donor plus acceptor concentration. The acceptor Ge was studied in intentionally doped LPE specimens. It also behaves as a simple effective masslike center, with  $E_{\text{Ge}} \sim 40$  meV for GaAs and 55 meV for  $\text{Al}_{0.2}\text{Ga}_{0.8}\text{As}$ , contrary to earlier reports of anomalous behavior.

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## I. INTRODUCTION

$\text{Al}_x\text{Ga}_{1-x}\text{As}$  is an important material for many optoelectronic applications, particularly where lattice-matched heterostructures are required, such as for lasers and solar cells. A great many papers have been written about crystal growth and device fabrication and performance in this alloy system. However, many properties of  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  are still not well understood. In particular, a number of questions have been raised recently about acceptors in  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ . Material grown by liquid phase epitaxy (LPE) and organometallic vapor phase epitaxy (OMVPE) has been found<sup>1</sup> to be increasingly compensated with increasing  $x$ . Carbon has been suggested<sup>2</sup> to be present in high concentrations, particularly in OMVPE  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ , but to date this has not been conclusively demonstrated. In a separate context, the suggestion has been made that the behavior of Ge in  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  is unusual, i.e., electrical measurements are interpreted to indicate that the depth of the Ge acceptor increases rapidly with increasing  $x$ .<sup>3</sup>

The low-temperature ( $\leq 4$  K) photoluminescence (PL) of GaAs has been extensively studied and is quite well understood.<sup>4</sup> Luminescence measurements on samples with  $n \leq 10^{16}$  cm<sup>-3</sup> or  $p < 10^{17}$  cm<sup>-3</sup>, for  $n$ - and  $p$ -type material, respectively, can be used to identify the dominant acceptors present by indexing the energies of the conduction band to acceptor ( $e, A^0$ ) and shallow donor to acceptor to ( $D^0, A^0$ ) pair luminescence peaks to those observed in intentionally doped material.<sup>4</sup> In nominally undoped material grown by LPE and chloride VPE C, Si, Zn, and sometimes Ge and Sn are identified.<sup>4</sup>

Several problems might be anticipated in an effort to apply the low-temperature PL techniques which are so useful in GaAs to alloys such as  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ . The acceptor energies may shift with alloy composition, thus prohibiting the identification of acceptor levels from the information

available for GaAs. In addition, the PL lines may exhibit alloy broadening sufficient to make impossible the positive identification of the acceptor involved. An example of this is the thoroughly studied case of the recombination due to excitons bound to N in  $\text{Ga}_x\text{In}_{1-x}\text{P}$ ,<sup>5</sup>  $\text{GaAs}_{1-x}\text{P}_x$ ,<sup>6</sup> and  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ .<sup>7</sup> Few low-temperature PL data exist in the literature for  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ ,<sup>8-11</sup> and no attempts to systematically study carbon by PL have been published.

In the present study, samples of  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  with  $x < 0.3$  grown by OMVPE and LPE were used for PL studies at  $\sim 2$  K to determine the feasibility of using PL to identify the acceptors, to study the composition dependence of the PL due to residual acceptors in  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ , to compare the residual acceptors in material grown by the OMVPE and LPE techniques, and to study the composition dependence of the depth of the acceptor Ge in lightly doped LPE  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  specimens.

## II. EXPERIMENTAL

The samples used in these studies were grown either by LPE or OMVPE on  $n^+$  or semi-insulating Cr-doped substrates. The LPE layers were grown by slow cooling in a conventional slider-type apparatus. The organometallic growth technique used is described in detail in Ref. 12. It is basically an rf-heated cold-wall system using trimethylaluminum and trimethyl-gallium as the metal sources and  $\text{AsH}_3$  as the As source in a flowing  $\text{H}_2$  ambient.

The photoluminescence experiments were performed with the samples immersed in pumped liquid helium to produce a temperature of  $\sim 2$  K. The PL was excited with the 6471-Å line of a Kr laser focused to a spot of area  $\sim 10^{-3}$  cm<sup>2</sup>. The power was typically 1–10 mW. For GaAs specimens, which have the sharpest lines, PL measurements were also made at lower excitation intensities with no change in PL spectrum, indicating that the lines are not broadened or shifted due to a too high excitation intensity. The spectrometer used was a Spex double monochromator with a resolution of  $\sim 1$  Å with 200-μm-wide slits. The detector was a cooled GaAs photocathode photomultiplier (RCA

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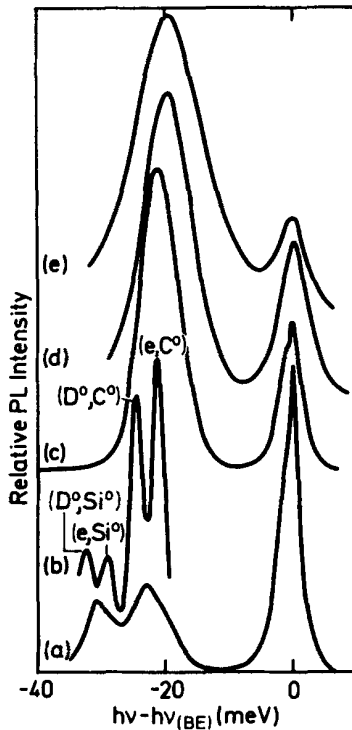


FIG. 1. Photoluminescence spectra at 2 K for various OMVPE and LPE specimens: (a) MO40, LPE,  $x = 0$  (b) Spectrum of high-purity GaAs from Ashen *et al.*<sup>4</sup> (c) LS179, OMVPE,  $x = 0$  (d) AL9, LPE,  $x = 0.036$ , (e) LS105, OMVPE,  $x = 0.040$ .

C31034A) which has a relatively flat response for wavelengths between 3000 and 8800 Å, which is the range of interest for GaAs and  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ .

### III. RESULTS AND DISCUSSION

#### A. Undoped GaAs

To establish a connection between this work on  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  and previous work on GaAs, it is useful to first consider the spectrum measured for undoped LPE GaAs. In Fig. 1, curve (a), the PL intensity for sample MO40 is plotted versus  $h\nu$  on a scale where the zero of energy is taken to be the peak of the higher-energy (bound exciton) line. This is done for ease of comparison of the spectra for  $\text{Al}_x\text{Ga}_{1-x}\text{As}$

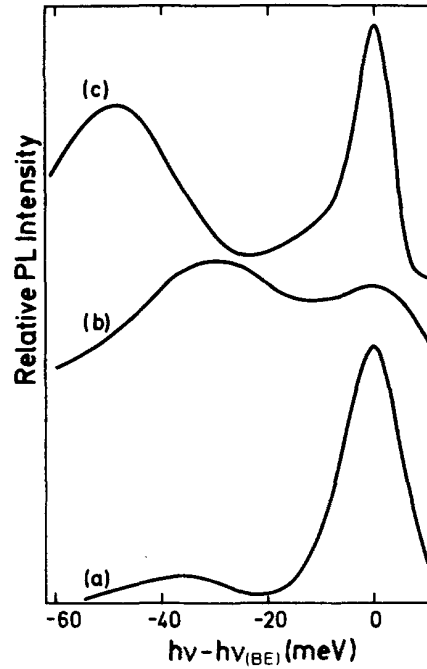


FIG. 2. Photoluminescence spectra at 2 K for higher  $x\text{Al}_x\text{Ga}_{1-x}\text{As}$  specimens: (a) AL10, LPE,  $x = 0.21$  (b) LS115, OMVPE,  $x = 0.23$  (c) D329, LPE,  $x = 0.21$ , Ge doped.

with different values of  $x$ . The actual values of  $h\nu$  can be obtained from Table I where values of other relevant parameters are also listed for all samples used in Figs. 1 and 2. Since the residual doping level,  $n = 4 \times 10^{15} \text{ cm}^{-3}$  from Hall effect measurements, for sample MO40 is somewhat greater than that needed for optimum resolution,<sup>4</sup> we see only a single high-energy peak with a maximum at 1.5144 eV and a shoulder indicative of a peak at 1.5129 eV. From the detailed study of Heim and Hiesinger<sup>13</sup> we identify these peaks as being due to the recombination of an exciton bound to a neutral donor ( $D^0, X$ ) and neutral acceptor ( $A^0, X$ ), respectively. If this identification is correct, then this weak excitation must be presumed to create a measurable number of neutral acceptors since none should exist at equilibrium. Similarly, Heim and Hiesinger observed ( $D^0, X$ ) lines in  $p$ -type samples of GaAs and both ( $D^0, X$ ) and ( $A^0, X$ ) lines in semi-insulating specimens.

TABLE I. Summary of properties of key samples.

| Sample | Growth technique | Doping | $x$   | $n$ ( $\text{cm}^{-3}$ ) | $N$ ( $\text{cm}^{-3}$ ) | $h\nu(\text{BE})$ | $h\nu(e, A^0)$ | $\Delta w$ (meV) | $\gamma$ (meV) |
|--------|------------------|--------|-------|--------------------------|--------------------------|-------------------|----------------|------------------|----------------|
| MO40   | LPE              | $U$    | 0     | $4.3 \times 10^{15}$     | $1.0 \times 10^{16}$     | 1.5144            | 1.4914         | 8.0              | 9              |
| LS179  | OMVPE            | $U$    | 0     | $3.1 \times 10^{14}$     | $4.79 \times 10^{15}$    | 1.5136            | 1.4925         | 7.3              | 12             |
| AL9    | LPE              | $U$    | 0.036 | $7.1 \times 10^{15}$     | $2.5 \times 10^{16}$     | 1.5562            | 1.5366         | 9.2              | 12             |
| LS105  | OMVPE            | $U$    | 0.040 | $5.0 \times 10^{15}$     | ...                      | 1.5619            | 1.5425         | 13.6             | ...            |
| LS95   | OMVPE            | $U$    | 0.059 | $1.8 \times 10^{16}$     | ...                      | 1.5854            | 1.5604         | 15.7             | 21             |
| LS176  | OMVPE            | $U$    | 0.103 | $7.2 \times 10^{16}$     | ...                      | 1.6420            | 1.6208         | 12.8             | ...            |
| AL10   | LPE              | $U$    | 0.21  | $3.1 \times 10^{15}$     | $6.0 \times 10^{16}$     | 1.7790            | 1.7432         | 20.9             | 25             |
| LS115  | OMVPE            | $U$    | 0.23  | $1.7 \times 10^{16}$     | ...                      | 1.7925            | 1.7640         | ...              | ...            |
| D329   | LPE              | Ge     | 0.21  | $4.7 \times 10^{17,p}$   | ...                      | 1.7760            | 1.7280         | 28.9             | ...            |
| M515   | LPE              | Ge     | 0.102 | ...                      | ...                      | 1.6387            | 1.5994         | 18.0             | ...            |
| M516   | LPE              | Ge     | 0.164 | ...                      | ...                      | 1.7163            | 1.6716         | 22.5             | ...            |
| M517   | LPE              | Ge     | 0.190 | ...                      | ...                      | 1.7487            | 1.6989         | 23.0             | ...            |

Two peaks are observed for sample MO40 at lower energy, 1.4914 and 1.4836 eV, which can be identified as being due to C and Si acceptors, respectively. For comparison, curve (b) is a spectrum for a high-purity ( $N_D + N_A < 10^{15} \text{ cm}^{-3}$ ) GaAs sample taken from the work of Ashen *et al.*<sup>4</sup> It shows separate ( $e, A^0$ ) and ( $D^0, A^0$ ) peaks for both C and Si. The spectrum for sample MO40 shows only single peaks because as will be discussed below, the donor level merges with the conduction band for specimens with  $N_D + N_A \geq 10^{16} \text{ cm}^{-3}$ .

The spectrum for an OMVPE GaAs sample ( $n = 3.1 \times 10^{14} \text{ cm}^{-3}$ ) is shown as curve (c) in Fig. 1. It is virtually the same as for the LPE specimen except that the only acceptor peak is due to C. The ratio of the ( $e, A^0$ ) peak to the bound exciton (BE) peak is larger for the OMVPE specimen. The relatively low liquid nitrogen Hall mobility of 21 000  $\text{cm}^2/\text{V s}$  indicates that  $N_D + N_A = 5 \times 10^{15} \text{ cm}^{-3}$  which explains the rather broad peaks.

## B. Undoped $\text{Al}_x\text{Ga}_{1-x}\text{As}$

PL spectra for nominally undoped  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  specimens with low values of  $x$  can now be compared to the GaAs spectra. In Fig. 1, curves (d) and (e) are PL spectra for OMVPE and LPE specimens, respectively, with  $x \approx 0.04$ . Because the low-temperature PL peaks are much narrower than those measured at 300 K, the PL at 2 K will be a much more accurate measure of  $x$ . Uncertainties in the exact origin of the BE emission, whether it is due to ( $D^0, X$ ) or ( $A^0, X$ ), for example, give rise to potential errors of  $\sim 3 \text{ meV}$ . This represents an error in  $x$  of only  $\sim 0.002$ . From the data of Dingle *et al.*<sup>11</sup> we determine  $x$  to be given as

$$x = \alpha [h\nu_{\text{BE}}(x) - h\nu_{\text{BE}}(0)] \quad (1)$$

in the range  $0 < x < 0.35$ , where  $\alpha = 0.8032$  and  $h\nu_{\text{BE}}(0) = 1.512 \text{ eV}$ . The depth of the acceptor level is determined as  $h\nu_{\text{BE}} - h\nu_{(e, A^0)} + 5.4 \text{ meV}$ . Again, the BE peak is assumed to be a good relative measure of the energy band gap  $E_G$ , with  $E_G - h\nu_{\text{BE}}$  being 5.4 meV, independent of composition. This approximation is accurate to within the  $\sim 3\text{-meV}$  variation in the ( $e, A^0$ ) line from sample to sample estimated<sup>4</sup> for the fairly high doping level ( $\sim 10^{16} \text{ cm}^{-3}$ ) of these samples.

The spectra for the low  $x$  alloys shown in Fig. 1 are virtually identical to the curves for GaAs, indicating that C is the main acceptor. It is likely that a small amount of Si would be contained in these specimens, but the small Si peak would be obscured by the tail of the much more intense C peak. The spectra for OMVPE specimens with higher values of  $x$  show a distinct broadening and a shift of the carbon peak to lower energy relative to the bound exciton peak. The ( $e, A^0$ ) peak also shows a definite increase in intensity relative to the BE peak.

In Fig. 2 the PL spectra for LPE and OMVPE specimens [curves (a) and (b), respectively] with  $x = 0.2$  are plotted. The continued broadening of the peaks make identification of the acceptor less certain, but the simplest interpretation is that the broadening and apparent increase in  $E_A$  is a continuation of the pattern established at lower values of  $x$ . This is confirmed in Fig. 3 where  $h\nu$  of the two

peaks is plotted versus composition for all specimens for which PL was measured. The peak halfwidths are indicated as error bars on the data points. This plot clearly shows the continuous change in  $h\nu_{\text{BE}} - h\nu_{(e, A^0)}$  with composition.

We can understand the variation in ionization energy using the effective mass theory of shallow impurity states where the depth of the level is proportional to  $m^*/\epsilon^2$ , namely

$$E_A = (\epsilon_0/\epsilon_s)^2/(m^*/m_0)E_H, \quad (2)$$

where  $m^*$  is the electron effective mass,  $\epsilon$  is the dielectric constant, and  $E_H$  is 13.6 eV, the hydrogenic ionization energy.

The actual values of acceptor binding energies calculated using simple effective mass theory are of course not exact because of the need for central cell corrections, but the variation with composition in  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  should be accurate. The value of  $m^*$  in the alloy was taken to be<sup>14</sup>

$$m^*(x) = (0.067 + 0.083x)m_0, \quad (3)$$

and  $\epsilon$  was taken to be<sup>14</sup>

$$\epsilon(x) = (13.1 - 3.0x)\epsilon_0. \quad (4)$$

Both are obtained by linear interpolation between values for GaAs and AlAs. The change in  $E_A$  with  $x$  is seen more clearly in Fig. 4 where the energy difference between the bound exciton and conduction band to acceptor peaks is plotted versus  $x$ . Also included in this plot are data from Makita *et al.*<sup>7</sup> and Shah *et al.*<sup>10</sup> for undoped  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ . The present data for  $x < 0.3$  are consistent with the behavior expected for the acceptor carbon as indicated by the solid line. This would

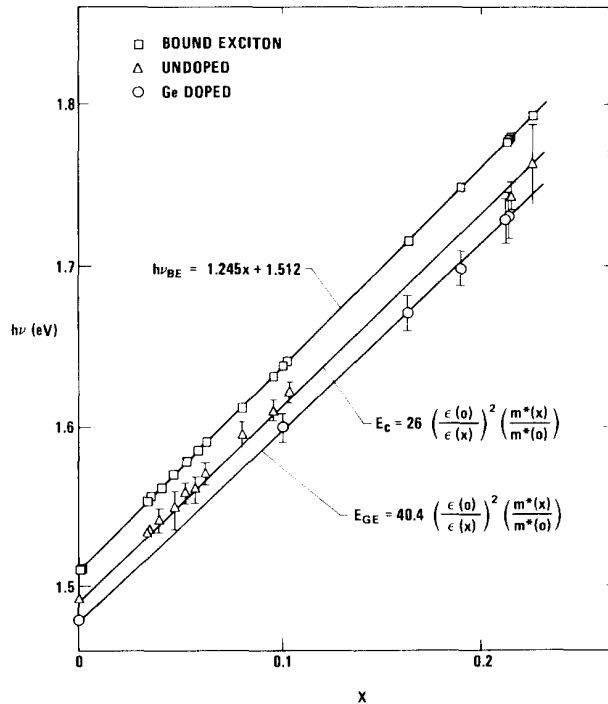


FIG. 3. PL peak energies versus composition determined from  $h\nu_{\text{BE}}$ . The data are for both LPE and OMVPE nonintentionally doped specimens ( $\Delta$ ), and for LPE Ge-doped specimens ( $\circ$ ). The error lines represent the depth expected from effective mass theory based on the experimental values of  $E_c$  and  $E_{\text{Ge}}$  for GaAs.<sup>4</sup>

indicate that C is the dominant acceptor in nominally undoped  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  grown by both OMVPE and LPE. However, some data at low values of  $x$  and the data of Makita *et al.*<sup>7</sup> and Shah *et al.*<sup>10</sup> fall significantly below the line. The reason for this deviation is not clear. The emission is probably not due to another acceptor, since C is the shallowest known acceptor in GaAs.

### C. Ge-Doped $\text{Al}_x\text{Ga}_{1-x}\text{As}$

The PL spectra of lightly Ge doped  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  specimens were investigated in an effort to clarify earlier peculiar behavior reported for the acceptor Ge is LPE  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ .<sup>3</sup> A typical spectrum for a Ge doped LPE  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  specimen is plotted as curve (c) in Fig. 2. The spectrum for this sample with  $x = 0.21$  is similar to the results for undoped specimens, except that the  $(e, A^0)$  peak is shifted to lower energy relative to the bound exciton peak. The peak energies for Ge doped specimens are also plotted in Figs. 3 and 4. In Fig. 4 we plot for comparison the results of Kressel and Ladany<sup>15</sup> for PL measurements obtained at 77 K. Also included is the expected behavior assuming that the bound exciton peak is a constant 5.4 meV below the band-gap energy and that the composition dependence of Ge acceptor level measured relative to the valence band edge may be expressed as

$$E_{\text{Ge}}(x) = 40.4[\epsilon(0)/\epsilon(x)]^2[m^*(x)/m^*(0)](\text{meV}), \quad (5)$$

where 40.4 meV is the depth of the Ge acceptor in GaAs.<sup>4</sup> Viewed in this way Ge is found to behave exactly as expected for a shallow effective mass like center in  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  with  $x < 0.2$ . At higher  $x$  the Ge may be slightly deeper than expected from the effective mass theory.

SpringThorpe *et al.*<sup>3</sup> measured the free hole concentration  $p$  versus temperature for relatively heavily doped  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  LPE specimens ( $N_A - N_D \approx 2 \times 10^{18} \text{ cm}^{-3}$ ). The slope of the  $p$  versus reciprocal temperature curve was

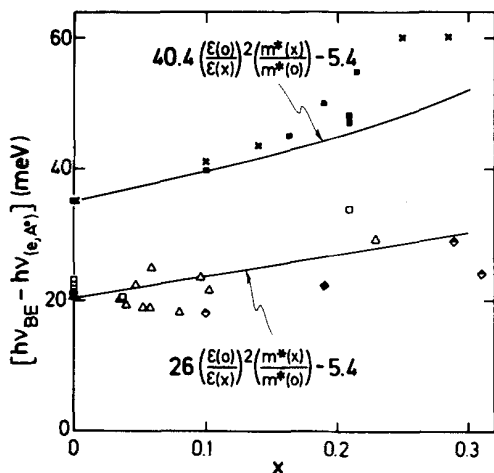


FIG. 4. Difference in energy of the free to bound  $(e, A^0)$  peak and the bound exciton peak versus composition for undoped  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  ( $\Delta$ , OMVPE;  $\square$ , LPE;  $\blacklozenge$ , Shah *et al.*<sup>10</sup>;  $\blacklozenge$ , Makita *et al.*<sup>7</sup>) and Ge doped  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  ( $\blacksquare$ , LPE;  $x$ , Kressel and Ladany<sup>15</sup>). The solid lines are calculated assuming  $E_C = 26 \text{ meV}$ ,<sup>4</sup>  $E_{\text{Ge}} = 40.4 \text{ meV}$ ,<sup>4</sup> and using the effective mass theory to predict the variation with  $x$ .

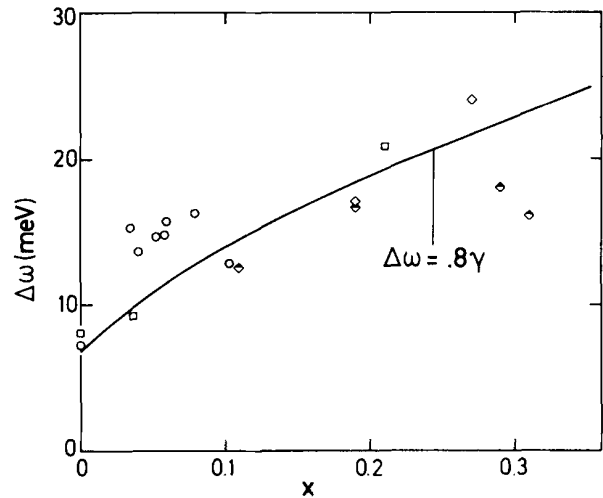


FIG. 5. PL peak half-width (2 K) versus  $x$  for undoped  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  grown by OMVPE ( $\Delta$ ) and LPE ( $\square$ ) and data points obtained from Alferov *et al.*<sup>8</sup> ( $\diamond$ ), Shah *et al.*<sup>10</sup> ( $\blacklozenge$ ) and Makita *et al.*<sup>7</sup> ( $\diamond$ ) for LPE material.

used to obtain  $E_{\text{Ge}}$  for a series of samples with  $x$  varying from 0 to 0.6. They found  $E_{\text{Ge}}$  to vary linearly with  $x$  in this entire composition range,

$$E_{\text{Ge}} = 175x + 10 \text{ (meV)}. \quad (6)$$

These values of the Ge ionization energy are much different than those obtained here. The difference may be due to the heavy doping of the SpringThorpe *et al.* specimens. The activation energy of 10 meV for GaAs is much smaller than the value of 40.4 meV obtained at lower Ge doping levels from PL studies.<sup>4</sup> It is concluded that these data for heavily doped samples cannot be interpreted to give values of activation energy representative of individual Ge acceptors.

Early PL studies of Alferov *et al.*<sup>16</sup> which were construed to indicate a new type of behavior, are in fact probably consistent with the effective mass like increase of the Ge ionization energy reported here.

### D. Broadening of PL peaks

The PL spectra for LPE and OMVPE GaAs samples with  $N_D + N_A \sim 10^{16} \text{ cm}^{-3}$  have relatively broad  $(e, A^0)$  peaks ( $\Delta\omega = 7\text{--}8 \text{ meV}$ ) which prevents the resolution of the  $(D^0, A^0)$  and  $(e, A^0)$  peaks. This behavior is consistent with the results of Ashen *et al.*,<sup>4</sup> who conclude that for impurity concentrations of  $> 10^{15} \text{ cm}^{-3}$  in  $n$ -type specimens the  $(e, A^0)$  and  $(D^0, A^0)$  peaks cannot be resolved. In the  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  alloys the peaks become considerably broader with increasing  $x$  as shown in Fig. 5, becoming  $\sim 20 \text{ meV}$  for  $x = 0.2$ . Also included in this plot are results from Makita *et al.*,<sup>7</sup> Shah *et al.*,<sup>10</sup> and Alferov *et al.*<sup>8</sup> for low-temperature PL of undoped LPE  $\text{Al}_x\text{Ga}_{1-x}\text{As}$ . From the values of  $h\nu_{\text{BE}} - h\nu_{(e, A^0)}$ , we conclude that the peaks are probably due to C for these specimens so the results may be compared directly to our own.

In alloys the most obvious potential source of PL broadening is due to the variation local field due to local compositional fluctuations. The broadening of the so-called  $A$  line due to recombination of excitons bound to isoelectronic  $N$  in  $\text{Ga}_x\text{In}_{1-x}\text{P}$  (Refs. 5 and 17) and  $\text{GaAs}_{1-x}\text{P}_x$  (Refs. 6 and

18) alloys is well established. However, in the very spectra where the  $A$  line is observed to broaden, the  $C$  line, due to excitons bound to neutral sulfur donors, shows essentially no broadening due to alloying. Garbuzov *et al.*<sup>5</sup> attribute the difference in behavior to the relatively large spatial dimensions of the wave functions of carriers bound to coulombic centers as opposed to the more strongly localized carriers bound to the isoelectronic center  $N$ . Thus the lattice potential is averaged over large volumes for the coulombic centers resulting in very small variations in potential from donor to donor and in little alloy broadening.

A more likely explanation for the broadening with increasing  $x$  observed for  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  alloys is ionized impurity concentration broadening. For both LPE and OMVPE samples the value of  $N_D + N_A$  deduced from the temperature dependence of electron mobility is found to increase with increasing  $x$  in undoped alloys.<sup>1</sup> This trend can be observed for the data in Table I for the specimens where  $N_D + N_A$  has been determined.

Physically, the reason for the broadening of optical transitions involving either donors or the conduction band is that at impurity concentrations such that the separation between the donors and other ionized centers is less than the Bohr radius of the electron bound to the donor, the donor level broadens, eventually forming a continuum with the conduction band. The acceptor center also broadens but only at higher concentrations, since the Bohr radius for holes is smaller due to the larger effective mass:

$$r_H = (\epsilon m_0 / m^*) (0.53 \text{ \AA}). \quad (7)$$

The broadening of the donor states in GaAs as a function of doping has been carefully studied using Hall coefficient analysis and the donor binding energy determined from far infrared photoconductivity measurements.<sup>19</sup> A shift of the donor ionization energy is observed for concentrations as low as  $\sim 10^{14} \text{ cm}^{-3}$ . At  $5 \times 10^{15} \text{ cm}^{-3}$  an impurity band has formed.

In compensated  $n$ -type Ge, Debrege and Shlimak<sup>20</sup> observed a broadening of the ( $D^0, A^0$ ) line for concentrations of  $> 10^{16} \text{ cm}^{-3}$ . Equivalent broadening should occur at lower concentrations in GaAs with its lower electron effective mass.

For  $p$ -type Zn-doped GaAs, Pankove<sup>21</sup> observed values of  $\Delta w$  for 4.2 K cathodoluminescence of  $\sim 10 \text{ meV}$  for samples of the lowest doping level and a broadening of  $\sim 20 \text{ meV}$  only for  $p \sim 10^{19} \text{ cm}^{-3}$ . For his excitation conditions (24 keV,  $4.5 \text{ A/cm}^2$ ) broadening at low  $p$  concentrations was probably related to the high excitation intensity. The reasons for the small amount of broadening in the  $10^{17}$ – $10^{18} \text{ cm}^{-3}$  range as compared to the present results and the results of Debrege and Shlimak are (1) that the samples were  $p$  type, hence he would see the broadening of the acceptor level which occurs at higher values of  $N_D + N_A$  and (2) that the material is not compensated. Compensated samples would be expected to produce more broadening due to the reduced screening of the ionized centers.

From this discussion it is clear why the ( $D^0, A^0$ ) and ( $e, A^0$ ) lines cannot be resolved in the GaAs specimens with  $N_D + N_A \sim 10^{16} \text{ cm}^{-3}$ , and qualitatively it is clear that we

should expect broadening in the alloys due to the increase in ionized impurity concentration with increasing  $x$ . A number of attempts have been made to quantitatively explain the magnitude of the broadening due to tail states formed in the conduction band due to ionized impurities. Following early work by Keldish and Proshko,<sup>22</sup> Shklovskii and Efros<sup>23</sup> obtained a quantitative expression for the mean square potential of the randomly distributed, screened impurities:

$$\gamma = \frac{1}{2\sqrt{\pi}} \frac{e^2}{r_0 \epsilon} (N r_0^3)^{1/2}, \quad (8)$$

where  $r_0$  is the Debye length

$$r_0 = (\epsilon k T / n e^2)^{1/2}. \quad (9)$$

In these expressions  $N = N_D + N_A$  and  $n = N_D - N_A$ . The potential  $\gamma$  determines the width of the impurity band and is hence related to the half-width of the PL emission.

Considering the nonequilibrium distribution of electrons in these tail states Levanyuk and Osipov<sup>24</sup> have attempted to calculate PL line shapes for compensated, nondegenerate semiconductors, the case of interest here. The results are complex and depend on the particular temperature and value of  $\gamma$ , but under certain conditions they predict that  $\Delta w \approx \gamma$ .

In Table I the values of  $\gamma$  calculated for samples for which  $N$  is known are listed for comparison with the measured values of  $\Delta w$ . From this limited set of data we would conclude that the half-width is indeed governed by  $\gamma$  and that  $\Delta w / \gamma \approx 0.8$ . By using the composition dependence of  $N$  from Ref. 1:

$$N_D + N_A = 1.32 \times 10^{16} + 4.0 \times 10^{17} (\text{cm}^{-3}) \quad (10)$$

and assuming  $n = 10^{16} \text{ cm}^{-3}$  (a safe assumption since  $n$  varies only by a factor of 10 for all samples measured and  $n$  enters only to the  $\frac{1}{2}$  power), we can calculate  $\gamma$  as a function of  $x$ . The calculated value of  $0.8 \gamma$  is plotted for comparison with the experimental data in Fig. 5. This estimate of half-width gives a good qualitative explanation for the experimentally observed increase in half-width with increasing  $x$ . We conclude that the increase in half-width for ( $e, A^0$ ) transitions for the OMVPE and LPE  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  samples studied is not due to alloy broadening caused by local variations in composition, but is rather broadening due to the increasing  $N_D + N_A$  with increasing  $x$  deduced from mobility measurements.<sup>1</sup>

#### IV. CONCLUSIONS

We conclude from 2-K photoluminescence measurements that nominally undoped  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  alloys grown by either OMVPE or LPE contain carbon as the major shallow acceptor. The depth of the carbon acceptor is found to have a simple dependence on alloy composition, consistent with the effective mass theory,

$$E_c = 26[\epsilon(0)/\epsilon(x)]^2 [m^*(x)/m^*(0)] (\text{meV}). \quad (11)$$

The conduction band to acceptor PL peak is observed to broaden with increasing  $x$ . This is attributed to the increase in the total ionized impurity concentration with increasing  $x$  which we deduce from the temperature dependence of electron mobility. The composition dependence of half-width is

found to be described well by taking  $\Delta w = 0.8 \gamma$ , where  $\gamma$  is the calculated root mean square potential of the randomly distributed, screened impurities.

The ionization energy of the acceptor Ge intentionally introduced into LPE  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  is found to have a composition dependence similar to that observed for carbon in the nominally undoped material. It can be described as being equal to 40.4 meV for GaAs with  $E_{\text{Ge}} \propto m^*(x)/\epsilon(x)^2$  in the alloys with  $x \leq 0.2$ . This resolves the problems of earlier reports of apparent anomalous behavior of the ionization energy of Ge in  $\text{Al}_x\text{Ga}_{1-x}\text{As}$  alloys.

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<sup>1</sup>G.B. Stringfellow, J. Appl. Phys. **50**, 4178 (1979).

<sup>2</sup>G.B. Stringfellow, Ann. Rev. Mater. Sci. **8**, 73 (1978).

- <sup>3</sup>A.J. SpringThorpe, F.D. King, and A. Becke, J. Electron Mat. **4**, 101 (1975).
- <sup>4</sup>D.J. Ashen, P.J. Dean, D.T.J. Hurle, J.B. Mullin, and A.M. White, J. Phys. Chem. Solids **36**, 1041 (1975).
- <sup>5</sup>D.Z. Garbuzov, S.G. Konnikov, Pls., Kop'ev, and V.A. Mishurnyi, Sov. Phys. Semicond. **8**, 998 (1975).
- <sup>6</sup>D.J. Wolford, B.G. Streetman, W.Y. Hsu, J.D. Dow, R.J. Nelson, and N. Holonyak Jr., Phys. Rev. Lett. **36**, 1400 (1976).
- <sup>7</sup>Y. Makita, Ijuin, and S. Gonda, Appl. Phys. Lett. **28**, 287 (1976).
- <sup>8</sup>Zh. I. Alferov, D.Z. Garbuzov, O.A. Ninua, and V.G. Trofim, Sov. Phys. Semicond. **5**, 982 (1971).
- <sup>9</sup>K. Sugiyama and T. Kawakami, Jpn. J. Appl. Phys. **10**, 1007 (1971).
- <sup>10</sup>J. Shah, B.I. Miller, and A.E. Digiovanni, J. Appl. Phys. **43**, 3436 (1972).
- <sup>11</sup>R. Dingle, R.A. Logan, and J.R. Arthur Jr., Inst. Phys. Conf. Ser. **33a**, 210 (1977).
- <sup>12</sup>G.B. Stringfellow and G. Hom, Appl. Phys. Lett. **34**, 794 (1979).
- <sup>13</sup>U. Heim and P. Hiesinger, Phys. Status Solidi (B) **66** 461 (1974).
- <sup>14</sup>H.C. Casey Jr. and M.B. Panish, *Heterostructure Lasers, Part A*, (Academic, New York, 1978).
- <sup>15</sup>H. Kressel and I. Ladany (unpublished); as reported in H. Kressel and J.K. Butler, *Semiconductor Lasers and Heterojunction LEDs*, (Academic, New York, 1977), p. 375.
- <sup>16</sup>Zh. I. Alferov, D.Z. Gabuzov, O.A. Ninua and V.G. Trofim, Sov. Phys. Semicond. **5**, 986 (1971).
- <sup>17</sup>H. Mariette and J. Chevallier, J. Appl. Phys. **48**, 1200 (1977).
- <sup>18</sup>D.J. Wolford, B.G. Streetman, R.J. Nelson, and N. Holonyak Jr., Solid State Commun. **19**, 741 (1976).
- <sup>19</sup>G.E. Stillman and C.M. Wolfe in *Characterization of Epitaxial Semiconductor Films*, edited by H. Kressel (Elsevier Scientific Publishing Co., New York, 1976) pp. 76-79.
- <sup>20</sup>V.P. Dobrego and I.S. Shlimak, Sov. Phys. Semicond. **1**, 1231 (1968).
- <sup>21</sup>J.I. Pankove, Jpn. J. Appl. Phys. **21S**, 298 (1966).
- <sup>22</sup>L.V. Keldysh and G.P. Proshko, Sov. Phys. Solid State **5**, 2481 (1964).
- <sup>23</sup>B.I. Shklovskii and A.L. Efros, Sov. Phys. Semicond. **4**, 249 (1970).
- <sup>24</sup>A.P. Levanyuk and V.V. Osipov, Sov. Phys. Semicond. **7**, 727 (1973).