RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 44, NUMBER 19 15 NOVEMBER 1991-I

0.8-eV photoluminescence band in $Al_xGa_{1-x}As$

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(Received 19 August 1991)

We have investigated the 0.8-eV luminescence band in $Al_xGa_{1-x}As$. The luminescence band is observed in metal-organic vapor-phase epitaxy materials only and is absent in materials grown by liquid-phase epitaxy and molecular-beam epitaxy. Photoluminescence excitation, excitation intensity dependence of luminescence, and two-beam differential photoluminescence measurements indicate that the band originates from the internal transition of a deep defect that is strongly coupled to the lattice.

In recent years, there has been a renewed interest in photoluminescence (PL) of $Al_xGa_{1-x}As$ because of the discovery of *DX* behavior of common donors such as Si, Te, etc.[1] Classically, the PL spectrum of these alloys at low temperatures (≤ 10 K) consists of sharp line features near the band edge which have been attributed to free exciton, bound exciton (D^0X), and donor-acceptor (DA) pair transitions. According to Dingle, Logan, and Arthur,[2] the behavior remains unchanged for alloy compositions up to $x \sim 0.35$ with exciton and pair emission lines following the central Γ valley of the conduction band closely. The exciton peak continues to follow the Γ valley right up to the direct-indirect (Γ to X) crossover at $x \sim 0.45$ and then veers away sharply. On the other hand, the DA peak starts deviating from the Γ band gradually from $x \sim 0.37$, reaches a maximum of 80 meV at $x \sim 0.45$ and then converges to a constant value of about 45 meV from the X valley at $x \sim 0.7$. These results suggest that the optically active donor has a strong band-structure-related character as follows: Γ-like for $x < 0.35$, L-like for $0.35 < x < 0.6$, and X-like for $x \geq 0.6$ depending on the composition of the alloy. As is well known, the main characteristic of the *DX* centers is persistent photoconductivity[1] which suggests that there is an energy barrier which prevents the capture of electrons at the *DX* center at low temperatures. If it is so, then can the *DX* centers participate in continuous radiative transitions? Recently, Montie and Henning[3] reported a new broad PL band in $Al_xGa_{1-x}As$ which is centered at about 0.8 eV. They assigned this emission to a transition between an electron captured at a L-related bistable *DX* level and a hole in the valence band. Alaya, Maaref, and Bourgoin[4] subsequently proposed an alternative model that the emission is caused by an internal transition between the excited state and the ground state of the *DX* center. More recently these assignments have been challenged by Vissar *et al.*[5] They find that the strength of the 0.8-eV band is anticorrelated to the Si donor concentration and therefore cannot be related to the *DX* center. Another significant result of their work is that the energy position of the band does not change with the composition of the alloy material. From these observations, they assign the emission to an internal transition of an unknown defect center. The reports cited above do not investigate the attributes of the transition which give rise to the 0.8-eV band. Furthermore, all the studies so far have been on materials grown by metal-organic vapor-phase epitaxy (MOVPE).

In the present work, we have investigated several properties such as temperature dependence, excitation intensity dependence, and photoluminescence excitation (PLE) spectrum of the 0.8-eV emission band. The detailed characterization is consistent with the model of an internal transition of a localized center that undergoes a large Franck-Condon shift during the transition. We have also probed materials grown by different epitaxial techniques and find that the 0.8-eV band is absent in the materials grown by liquid-phase epitaxy (LPE) and molecular-beam epitaxy (MBE). The 0.8-eV emission therefore is a very special feature related to the conditions under which the materials are grown by MOVPE.

The work reported in this Rapid Communication is mainly on three different types of samples viz. $Al_{0.38}Ga_{0.62}As$:Te grown by LPE, $Al_{0.30}Ga_{0.70}As$:Si grown by MBE, and $Al_{0.29}Ga_{0.71}As$:Si grown by MOVPE. The free-electron concentration measured by the Hall voltage at room temperature is $\sim 10^{17}$ cm^{-3} in all the samples. PL is measured using an Ar-ion laser with the samples kept on the cold finger of a closed-cycle He refrigerator. The sample temperature is varied from 8 to ~ 120 K. Excitation is varied between 1 and 200 mW using neutral density filters and by varying the power input to the laser. The luminescence is detected by using a cooled (77 K) InAs detector and lock-in technique. In a differential measurement of the excitation dependence, the Ar-ion laser is used for setting the bias and a chopped 2.5-mW He-Ne laser for the differential increment. The PLE measurement is done using a quartz iodine lamp and monochromator as the excitation source. A large-area ice-cooled Ge detector is used to measure the total luminescence signal.

Figure 1 shows the PL spectra of the samples used in this work. We observe that the 0.8-eV band is present only in the MOVPE grown samples. The other two samples do not exhibit this emission. We also note that the MBE and the MOVPE samples have very similar compositions and similar Si doping concentration. These observations lead us to infer that the 0.8-eV emission cannot be general property of the donors in $Al_xGa_{1-x}As$, in agreement with the work of Vissar *et al.*[5]

The PL spectrum of the 0.8-eV band at 10 K obtained from the MOVPE grown sample is shown in Fig. 2. The band is rather broad without any prominent structure;

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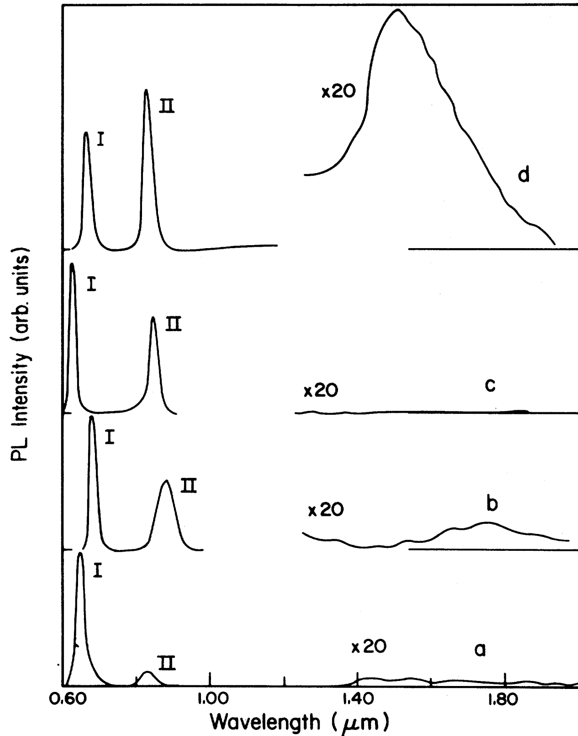


FIG. 1. PL spectra of $Al_xGa_{1-x}As$ grown by various techniques: (a) MBE grown $Al_{0.30}Ga_{0.70}As$:Si, (b) LPE grown $Al_{0.26}Ga_{0.74}As$:Sn, (c) LPE grown $Al_{0.36}Ga_{0.64}As$:Te, (d) MOVPE grown $Al_{0.29}Ga_{0.71}As$:Si. The Te doped sample (c) is on n^+-type GaAs substrate while the others are on semi-insulating GaAs substrate. Peak I is the band-edge emission from the $Al_xGa_{1-x}As$ epilayer and peak II is the emission from the GaAs substrate.

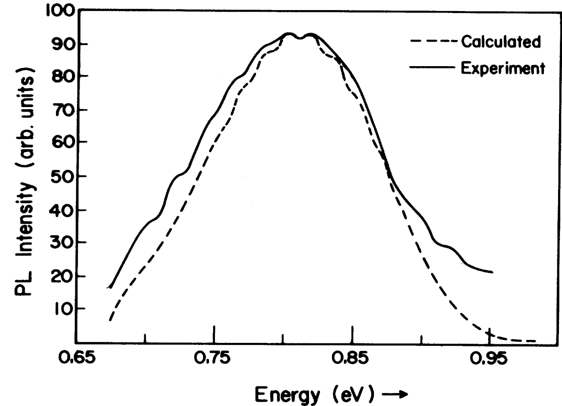


FIG. 2. Observed and calculated spectrum of the 0.8-eV PL band seen in MOVPE grown $Al_{0.29}Ga_{0.71}As$:Si. The parameters used for calculation are $S=13$, $\hbar\omega=0.017$ eV, and zero phonon linewidth is 0.12 eV.

however, a few minor features are observed consistently. The full width at half maximum (FWHM) is ~0.015 eV. The FWHM remains practically constant up to about 50 K and then increases with sample temperature. A plot of FWHM vs $T^{1/2}$ (Fig. 3) shows a behavior characteristic of transitions involving electron-lattice coupling. The intensity of the band reduces on increasing the temperature such that the half width measurement beyond 120 K is not reliable. The variation of the integrated intensity as a function of reciprocal temperature is shown in Fig. 4. The intensity remains practically constant up to about 40 K. The decline is very rapid beyond 60 K and can be described as $e^{\Delta E/kT}$ where $\Delta E \sim 0.04$ eV. The shape of the PL spectrum is independent of the excitation power within the range of our measurement. The strength of the band does not increase linearly with the excitation power as shown in Fig. 5. We have confirmed that the sample temperature does not change significantly by monitering the near band-edge emission at similar power levels. The result of differential measurement confirms the saturation behavior of the emission intensity. Photoluminescence excitation spectrum of the 0.8-eV band measured in the energy range 1.24–2.38 eV shows a sharp turn on near the $Al_xGa_{1-x}As$ band-gap energy. This shows that the center responsible for the 0.8-eV band is excited predominantly through carriers in the bands and the oscillator strength of the direct excitation is small.

In order to understand the experimental results, we assume that the 0.8-eV emission results from an internal transition between the excited state and the ground state of a complex center. To account for the width of the spectrum, we assume that there is strong electron-lattice coupling and analyze the spectral shape within the Huang-Rhys model using a linear coupling. The approximate bandwidth is then given by[6]

$$\Delta(T)=[8\ln2(\hbar\omega)^2 S\coth(\hbar\omega/2kT)]^{1/2}, \quad (1)$$

where a single dominant phonon mode of energy $\hbar\omega$ is assumed and S is the coupling factor. The calculated FWHM by using a fit program is shown in Fig. 3 where $\Delta(0)=[8\ln2(\hbar\omega)^2 S]^{1/2}$ and $\hbar\omega$ are fit parameters. In order to obtain a self-consistent description, the same values of S and $\hbar\omega$ are used to calculate the band spectrum from the superposition of the phonon replica given by[6]

$$I=\frac{S^n}{n!}\exp(-S). \quad (2)$$

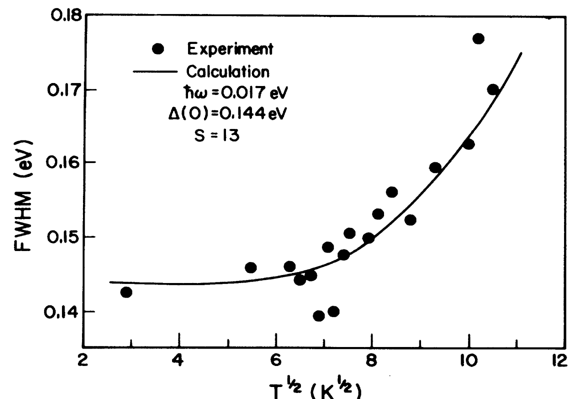


FIG. 3. Observed variation of FWHM with $T^{1/2}$ compared with the calculated value using Eq. (1).

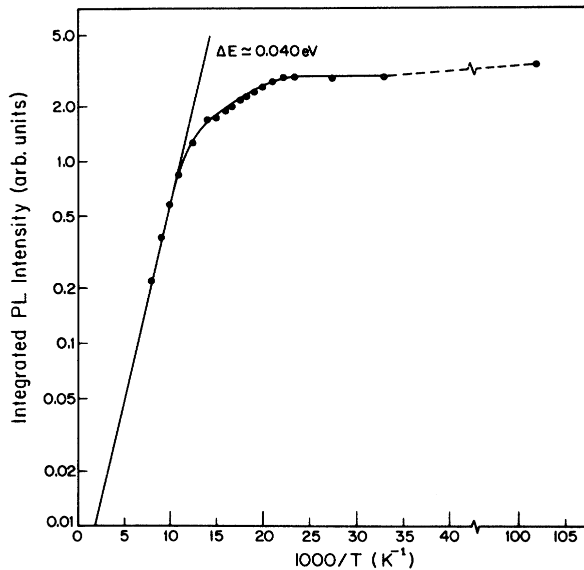


FIG. 4. Plot of integrated PL intensity vs $1000/T$.

The calculated spectrum is shown along with the measured spectrum for a zero phonon linewidth ~0.012 eV. The discrepancy between the calculated and measured spectrum at lower energies may be partly due to the fact that there is some contribution from the semi-insulating substrate. The phonon energy of 0.017 meV obtained from the fit is a local mode since it is much less than the intrinsic LO phonon energies for $Al_{0.29}Ga_{0.71}As$ which are of the order of 0.04 eV.

In order to explain the excitation dependence of the PL intensity we propose a simple model for the excitation of the complex. The incident radiation generates free electron-hole pairs which readily form free excitons at low temperatures. The free exciton can then get captured by the defect to form a bound exciton. This bound exciton can decay either by exciting the defect to a higher energy state or by nonradiative Auger process. The emission at 0.8 eV occurs by the transition from the excited state of the defect to the ground state. A similar process has been envisaged earlier for emission from erbium in $Al_xGa_{1-x}As$.[7] In this model, increase in the luminescence intensity with the excitation power is sublinear because the nonradiative Auger rate is superlinear. Higher excitation increases the bound exciton concentration and simultaneously lowers the Auger lifetime. The latter occurs because of increase in the free-carrier concentration. We have observed that the change in the electron concentration with excitation is negligible because of the persistent photoconductivity and therefore we assume that the Auger transition occurs with the excitation of a hole in the valence band. The hole concentration generated by 10 mW of excitation power is $\sim 10^{15}$ cm^{-3}. This is comparable with the threshold free-carrier concentration needed for Auger quenching as calculated from the relationships given by Langer.[8] The relationship between the emission band intensity and the excitation power can be obtained by using the rate equation

$$\frac{dN_D^*}{dt} = A\tilde{\phi}\frac{P_e}{P_e+Bp} - \frac{N_D^*}{\tau_R}, \tag{3}$$

where N_D^* is the concentration of defects in the excited state, $A\tilde{\phi}$ is the rate of generation of excitons proportional to the excitation $\tilde{\phi}$, P_e is the probability that the defect excited state is created by the exciton decay, Bp is the probability that the exciton decays by the Auger process, and τ_R is the radiative lifetime of the defect excited state. The PL intensity under steady state is then given by

$$\tilde{I} = \frac{N_D^*}{\tau_R} = A\tilde{\phi}\frac{P_e}{P_e+Bp} \sim A\tilde{\phi}\frac{P_e}{P_e+B'\tilde{\phi}}, \tag{4}$$

where in the low-concentration $p \ll n_0$ case the hole concentration is directly proportional to the excitation $\tilde{\phi}$.

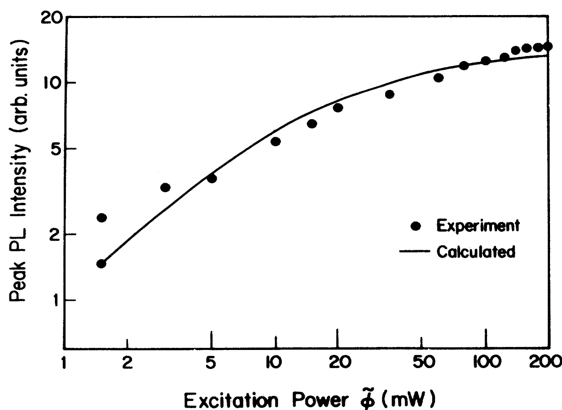


FIG. 5. Variation of luminescence intensity with excitation power $\tilde{\phi}$. The calculated variation using Eq. (4) is indicated by the continuous line.

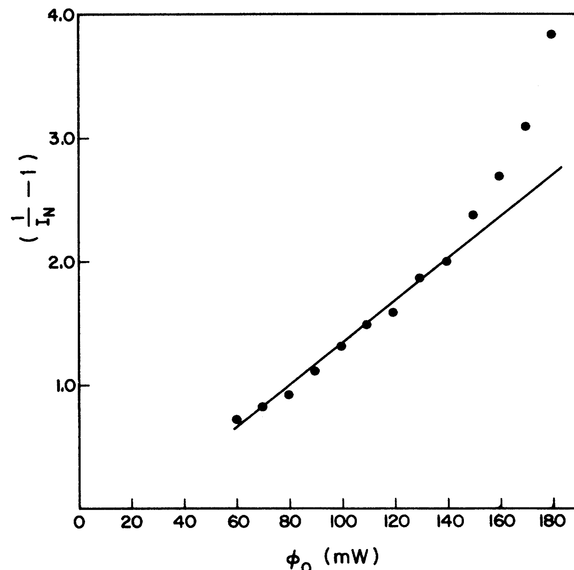


FIG. 6. Plot of differential PL intensity vs bias power ϕ_0. The continuous line is the line of best fit showing that Eq. (6) holds well up to $\phi_0 \sim 140$ mW.

This expression shows that at low excitation power, the PL emission intensity increases linearly. However at higher excitation power, the PL saturates. The excitation dependence calculated from this expression by using P_e and B' as fit parameters is shown in Fig. 5. In differential measurements where the excitation power is increased from $\tilde{\phi}$ to $\phi_0+\tilde{\phi}$ by adding the bias light of power ϕ_o, the differential PL intensity is given by

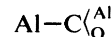
$$\tilde{I}(\phi_0)=A\tilde{\phi}\frac{P_e}{P_e+B'(\phi_0+\tilde{\phi})} . \quad (5)$$

It is seen that the intensity decreases with increase of the bias power ϕ_0 for constant $\tilde{\phi}$. We can rewrite this relationship as

$$\frac{1}{I_N}-1=\frac{\tilde{I}(0)B'}{AP_e\tilde{\phi}}\phi_0 , \quad (6)$$

where $\tilde{I}(0)$ is the PL intensity with bias power $\phi_o=0$ and $I_N=\tilde{I}/\tilde{I}(0)$. Results of the differential measurements are compared with Eq. (6) in Fig. 6. The agreement is seen to be satisfactory except at high power where the measurement uncertainty is large because of the reduced strength of the differential PL signal as given by Eq. (5). Part of the discrepancy at high power levels can also result from the assumed linear dependence of p on $\tilde{\phi}$.

In conclusion, we find that the 0.8-eV emission band can be described fairly satisfactorily as an internal transition of a localized center which undergoes a large lattice relaxation during the transition. We have found that a local mode of energy ~0.017 eV is excited during these transitions. From the evidence presented by Vissar *et al.*[5] and the fact that so far the emission is only in the materials grown by MOVPE, it is certain that this localized center is not related to the *DX* center. In order to visualize the possible structure of the center, we turn to the growth-related aspects. From the literature survey, it is evident that the impurities which are commonly present in MOVPE grown $Al_xGa_{1-x}As$ are C and O. Substitutional C is a shallow acceptor and it is unlikely to result in the wide band emission. This is further substantiated by the fact that this band is not seen in MBE grown materials which are also known to have C. Oxygen is known to be a deep center in $Al_xGa_{1-x}As$ and has been associated with an emission similar to the 0.8-eV band by Tsai *et al.*[9] Another attractive possibility is that the center is a complex involving both C and O. Formation of such a complex can be facilitated by the presence of alkoxides [such as $(CH_3)_2AlOCH_3$] which are difficult to separate from the starting materials [such as $(CH_3)_3Al$] used for growing $Al_xGa_{1-x}As$.[10] A plausible structure of the complex can then be



where C occupies the As site and O an interstitial site. A direct measurement of the far infrared vibrational spectrum may greatly facilitate an accurate determination of the structure of the center.

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