Green photoluminescence in GaP:Zn,O grown by liquid-phase epitaxy

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A photoluminescence study was made of the green emission band in GaP:Zn,O grown by liquid-phase epitaxy. The spectra are shown to originate from donor-acceptor-pair transitions involving sulfur and zinc. This conclusion is supported by an analysis of the peak energy, peak shape, excitation-intensity dependence of the spectrum, and secondary-ion-mass-spectrometry data. A series of three LO(Γ) phonon replicas are identified. Temperature-dependence measurements of the no-phonon donor-acceptor-pair peak and the Zn-O bound-exciton-complex peak intensities reveal the important role that green transitions play in reducing the recombination rate of the primary red recombination photoluminescence.

GaP doped with the acceptor impurity zinc and donor impurity oxygen is a material suitable for very efficient red-light emitters. This material has revealed the following well-documented radiative recombination mechanisms: (i) a bound-exciton transition[1(a)] occurring at the nearest-neighbor Zn-O complex giving rise to the dominant red emission in the material; (ii) an overlapping pair emission band[1(b)] due to the recombination of an electron bound at the oxygen site of the complex with a hole bound at a remote zinc acceptor site; (iii) electron capture[1(c)] so-called "internal emission," involving an excited-to-ground-state transition for the oxygen donor; (iv) donor-acceptor (DA) -pair recombination involving the oxygen donor and shallow zinc acceptor;[1(d)] (v) bound-free (BF) recombination[1(e)] of a bound electron on an oxygen site with a free hole. The latter three radiative recombination mechanisms result in infrared emission bands, which are weak even at low temperatures. In addition to these mechanisms, liquid-phase-epitaxy (LPE) grown GaP:Zn,O frequently exhibits a green photoluminescence (PL) band, which is pronounced at low temperatures.[1(f)] The intensity of this emission is typically comparable with that of the dominant red PL band. There has been scant work reported on either the origin of this important PL band or on the contribution of recombination processes responsible for this emission on the overall recombination efficiency.

This work is concerned with the identification of the green PL band in LPE grown GaP:Zn,O and with providing some insight into the role that this radiative recombination mechanism plays in determining the efficiency of the dominant red PL process. We report on liquid-nitrogen PL measurements on LPE grown GaP:Zn,O material. Green PL is analyzed and shown to obey a DA-pair recombination scheme: The emission is described by a no-phonon DA-pair peak with a series of associated LO(Γ) phonon replicas. The PL line shape is also shown to be aptly described by standard equations for DA-pair recombination. The donor ionization energy of 104 ± 2

meV is deduced from the pair spectrum and strongly implies that the green PL is attributable to DA-pair recombination involving the donor impurity sulfur and the shallow acceptor impurity zinc. Indeed, secondary-ion-mass spectrometry (SIMS) measurements identified sulfur as a major impurity in our material, lending support to the assignment discussed above. Moreover, the no-phonon DA-pair peak energy is shown to exhibit the expected dependence on excitation intensity. Measurements of the temperature dependence of red and green PL band intensities are discussed. The importance of DA-pair transitions in reducing the visible radiative recombination rate of the primary red recombination photoluminescence is thus highlighted. This phenomenon is found to be especially pronounced at lower temperatures. The essential characteristics of the recombination scheme are shown to revolve around two primary considerations. These are the occupancy of the acceptor level and the relative capture and thermalization rates for the sulfur donor state and the Zn-O bound-exciton-complex electron level.

The role of DA-pair transitions in the photoluminescence of GaP is now well documented.[1(d),2(a),2(b)] Since the first identification of DA-pair spectra by Hopfield *et al.*,[2(a)] spectra involving a wide variety of donors and acceptors have been observed. These spectra result from recombination of electrons bound to donors and holes bound to acceptors, where donors and acceptors are separated by discrete lattice separations, R. The recombination energy, $h\nu$, of the emitted photon may then be written as a function of R in the form[3]

$$h\nu(R) \cong E_g(T) - E_A - E_D + e^2/4\pi\epsilon\epsilon_0 R , \qquad (1)$$

where the energy gap of GaP, $E_g(T)$ $= 2.338 - [6.2\times10^{-4}T^2/(T+460)]$ eV,[4] and E_A and E_D are the ionization energies of the acceptor and donor species, respectively. The last term in Eq. (1) describes the electrostatic interaction between the cores of the ion-

ized donor and acceptor impurities, based on a static dielectric constant, ϵ. The static dielectric constant, which has a value of 11.02 in GaP,[5] is the correct quantity to use in this case, because we are considering the interactions of an electron, for example, with a charge a large distance away compared with the diameter of the bound electron state. At smaller R values a Van der Waals attractive interaction may exist between the neutral donor and acceptor impurities and require an additional term in Eq. (1). This term can take into account the correlation of the electron and hole, but only in the limit of no overlap of the donor and acceptor effective-mass eigenfunctions. Williams has shown that this approach is not valid at small R and negligible at large R.[6] Eigenfunction overlap may well be finite between these two limits, where the Van der Waals term can also be significant. Therefore, in this range this term would not provide a good approximation for the correlation of electrons and holes. In common with most previous studies on this subject, we neglect this term in our analysis.

The expected distribution of pairs as a function of R has been calculated for GaP assuming a random distribution of donors and acceptors separately, for both types of impurity located on similar lattice sites (Ga or P) and dissimilar sites (Ga and P).[7] The distribution in R may then be converted to one in energy by use of Eq.(1).

The transition probability falls off rapidly with increasing R, following an approximately exponential relationship.[2(b)] However, the distribution function for pairs results in a strong increase in the number of pairs with increasing R.[1(d)] Therefore, the DA-pair PL band has a spectral line shape, $I(R)$, governed by the product of these two functions, and can be approximated by

$$I(R) \cong R^6 \exp(-4\pi N_{maj} R^3/3) \ . \tag{2}$$

The capture cross section for ionized pairs is taken to follow $\sigma = cR^2$, where c is a constant. The exponential term describes the probability that there is no acceptor (majority impurity) nearer the studied donor than R. N_{maj} is the majority impurity concentration.

The samples used in this work were grown by LPE on bulk n-type GaP single crystals. Epilayers were grown on the (111)B face at a temperature of 980 °C to a thickness of about 50 μm. The substrate misorientation was ±0.5°. These layers were intentionally doped with zinc and oxygen. The substitutional oxygen concentration is about 1×10^{18} cm^{-3} and the zinc concentration about 2×10^{18} cm^{-3}. SIMS measurements were made using a 14.5-keV Cs$^+$ primary beam and by normalizing published relative sensitivity factors to known implant profiles of respective species. Accuracy of these measurements is estimated to be within a factor of 3. SIMS measurements on this material identify sulfur and silicon as the major unintentionally incorporated impurity species, at concentrations of about 3×10^{16} cm^{-3} and about 1×10^{16} cm^{-3}, respectively. The presence of the aforementioned impurities is mainly attributed to outdiffusion from the substrate during growth and the subsequent prolonged annealing process designed to promote zinc-oxygen pairing. Photoluminescence spectra were obtained using above band-gap Ar$^+$ laser excitation at 488 nm. A flat response

GaAs(Cs) photocathode Hamamatsu R2949P photomultiplier tube was used as a detector. Spectra reported in this work were recorded with a resolution of 0.2 nm.

Figure 1 shows the characteristic 77-K PL spectra in the green emission band region. Not shown in this figure is the dominant red PL band positioned at about 1.850 eV. The spectrum shown in Fig. 1 is composed of a well-defined peak at 2.209 eV, together with a series of successively broader and less intense peaks on the low-energy shoulder of this peak. These results suggest that this broad shoulder originates from the participation of optical phonons in the recombination process.[8] The result is a series of phonon replicas of the no-phonon peak. Two potential recombination mechanisms that could be responsible for the no-phonon PL peak in this p-type material are (i) free to bound (FB) radiative recombination[1(e)] involving a free hole and an electron bound to a donor, usually denoted as (h, D^0); and (ii) DA-pair recombination.[1(d)] In the former case the photon energy resulting from FB recombination without phonon participation is given by $h\nu = E_g(T) - E_D$. Given the peak energy value of 2.209 eV from Fig. 1 and assuming a FB transition, a donor ionization energy of about 130 meV is implied. As discussed earlier, sulfur and silicon are the major unintentionally incorporated donor impurities with ionization energies of about 104 and 82 meV, respectively.[9] It is therefore unlikely that the no-phonon peak in the PL spectrum of Fig. 1 originates from FB carrier recombination. Furthermore, based on Fermi-Dirac statistics the free-hole concentration is quite small at 77 K. Therefore, this radiative recombination mechanism is not expected to be important.

Assuming a DA-pair recombination mechanism, the no-phonon peak shape may be calculated using Eqs. (1) and (2) and the pair distribution function discussed earlier. Ionization energies of $E_A = 64$ meV (for zinc) and $E_D = 104$ meV (for sulfur) are reported.[9] A no-phonon DA-pair peak energy of 2.209 eV is calculated using these values; this value is in good agreement with the one derived from the observed spectrum. The spectrum calculated using the silicon donor ionization energy has a peak energy of 2.231 eV which is over 20 meV displaced from the experimental data. The calculated DA-pair luminescence spectra included thermal broadening by using a symmetric Lorentzian broadening function. The best fit to the observed spectrum was obtained using an E_D value of 104±2 meV. A value of 49 meV for the LO(Γ) phonon energy was assumed.[8] The fit derived using these parameters is shown in Fig. 1. The line intensities of the LO(Γ) phonon replicas can be derived from the probability for the emission of one or more optical phonons, which is described by a Poisson distribution. The calculated replica peak intensities are in reasonable agreement with this distribution based upon a value of 1.1 for the average number of optical phonons emitted in a given radiative recombination. The occurrence of weak or strong phonon replicas[2(a),2(b)] has been shown to depend primarily on the depths of the centers involved and on the site occupied by the donor impurity. Often, phosphorus site donors (e.g., S_P) result in stronger no-phonon bands and weaker replicas than for gallium site donors (e.g.,
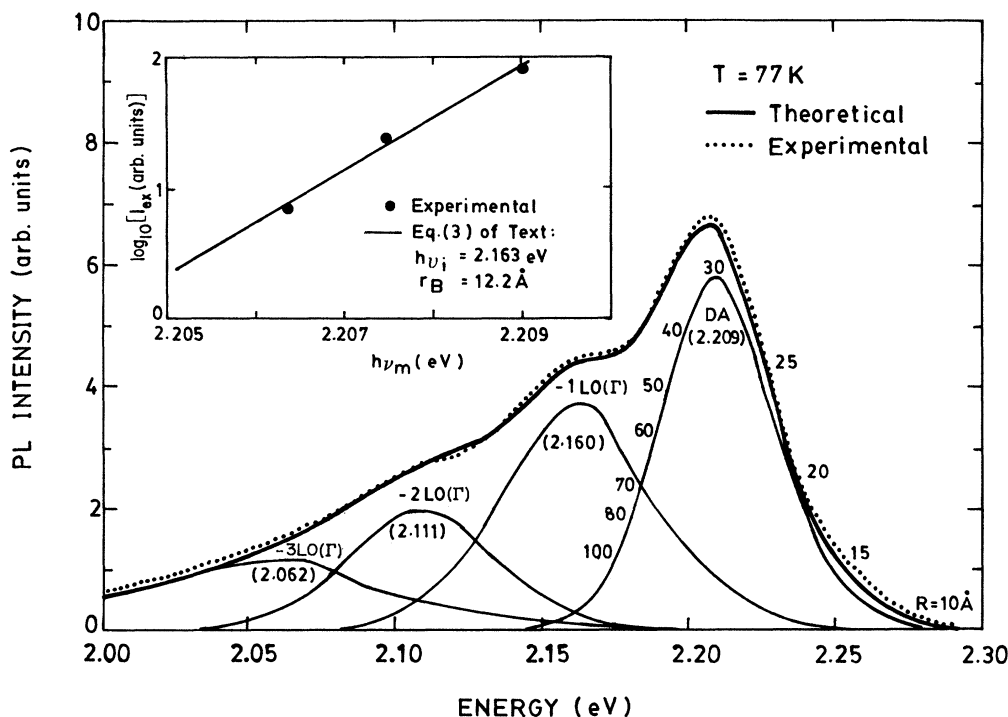
FIG. 1. PL intensity photon energy for the green emission band. Individual theoretical component curves for DA-pair recombination with and without phonon participation, and including broadening (see text) are shown. The total calculated spectrum is shown as a solid line. The experimental data curve is given by the dotted line. The numerals adjacent to the no-phonon DA-pair peak refer to equivalent R values (see text). Peak energies in eV are given in parentheses beneath each peak. The no-phonon peak is labeled as DA and successive phonon replica peaks are identified using the notation $-m\,\mathrm{LO}(\Gamma)$, where m is an integer referring to the number of phonons participating in the transition. The inset to this figure shows the influence of excitation intensity I_{ex} on the DA-pair peak energy $h\nu_m$.

Si_{Ga}). Therefore, in the present case, the strength of the lattice interaction can be attributed principally to the relative depth of the sulfur donor state rather than to the site occupied by this donor. The electron bound to the sulfur donor couples strongly to the lattice. This is responsible for the observed broad phonon-dominated luminescence side bands.

The shape of the PL spectrum shown in Fig. 1 results from the opposing influences of the pair distribution function and the pair recombination transition probability. The data of Fig. 1 indicate that DA pairs which are separated by about 20 to 60 Å are responsible for the majority of the DA-pair transitions in this material. Such pairs are commonly referred to as distant pairs as they originate from shell numbers of about 150 to 1300.[7] Figure 1 also shows that closely spaced pairs (with R less than about 10 Å) do not significantly contribute to the PL signal. One reason for this may be the fact that there are so few of them. Also noteworthy is the fact that far distant pairs separated by as much as 100 Å can contribute significantly to the total emission intensity. This principally reflects the vast numbers of such pairs.

The inset to Fig. 1 shows the influence of excitation intensity, I_{ex}, on the no-phonon DA-pair peak energy, $h\nu_m$. A shift is seen in the DA-pair peak energy to higher energy values with increasing excitation intensity. This shift may be described by the following relationship

for the DA-pair radiative recombination mechanism:[10]

$$I_{ex} = D\left[(h\nu_m - h\nu_i)^3 / (h\nu_B + 2h\nu_i - 2h\nu_m)\right]$$
$$\times \exp[-2(h\nu_B - h\nu_i)/(h\nu_m - h\nu_i)] , \qquad (3)$$

where I_{ex} is the excitation intensity, $h\nu_m$ is the peak energy of the no-phonon DA-pair transition spectrum, and $h\nu_i$ is the emission energy for infinite R, $h\nu_i = E_g - (E_A + E_D)$. The term $h\nu_B$ is defined as follows: $h\nu_B = E_B - h\nu_i$, where $E_B = e^2/4\pi\epsilon\epsilon_0 r_B$, r_B is the shallow impurity Bohr radius, and D is a constant. In the low excitation limit, the DA-pair peak energy approaches $h\nu_i$, while in the high excitation limit, the peak energy approaches $h\nu_i + 0.5E_B$. The extrapolated $h\nu_i$ value is 2.163 ± 3 meV giving a value for E_D of 104 ± 3 meV in agreement with the value determined from the DA-pair peak shape and energy position discussed earlier. This analysis also yields a value of about 12.2 Å for the shallow impurity Bohr radius. The characteristic shift of the DA-pair peak energy with excitation follows from the fact that at high excitation intensities, widely separated pairs will be saturated because of their lower transition probability and concurrently, a larger fraction of small R pairs are excited and decay radiatively due to their higher transition probability. Thus a higher excitation intensity results in an increase in the relative intensity of PL emis-

sion from small R pairs, leading to the observed shift in the DA-pair peak energy to higher energies.

The above findings all lend support to the identification of the green PL emission band in this material as due to a DA-pair recombination mechanism involving S_P-Zn_{Ga} type-IIA pairs,[7] and lattice coupling resulting in a series of three LO(Γ) phonon replicas.

Figure 2 shows the dependence of the red (Zn-O complex) and green (DA-pair) PL peak intensities on inverse sample temperature. The logarithmic sum of these two curves is also shown in this figure. The red peak intensity exceeds that of the green peak over the entire temperature range shown. Two distinct temperature regions are apparent in Fig. 2; these regions are delineated by a critical temperature, T_c, which has a value of about 160 K. For temperatures less than T_c, the red emission intensity is saturated and the green emission intensity is quenched with increasing temperature. The low-temperature green emission quenching behavior is characterized by a thermal activation energy of 64±2 meV. Thus, the red and green PL intensities diverge with increasing temperature. For $T > T_c$, the red emission intensity lies at the onset of quenching, while the slope of the green emission intensity line begins to diminish. As a result, both lines converge with increasing temperature. The activation energy of the logarithmic sum curve for red and green emission is 64±2 meV over the entire temperature range. The regressed line in this case has an associated coefficient of correlation of 0.998. This activation energy

is coincident with that of the zinc acceptor.

In order to understand the above findings, a simple model for the recombination kinetics is discussed. Although it is difficult to express the total DA-pair recombination rate in a simple form because of the dependence of the rate on the spatial separation of each recombining pair, Dishman[11] has used an ensemble-averaging approach to express the DA-pair radiative recombination rate R_{DA} as

$$R_{DA} = B_{DA} N_A^0 N_D^0 , \qquad (4)$$

where B_{DA} is a parameter which is only weakly dependent on temperature and is essentially independent of the free-carrier concentration. N_A^0 and N_D^0 are the concentrations of neutral acceptors and donors in the material, and refer specifically to the impurities zinc and sulfur, respectively. Compensation in this p-type material results in the ionization of donor impurities and the partial ionization of the acceptors. Photoexcitation results in the generation of excess electrons which may be captured by either the sulfur donors or the zinc-oxygen complexes, or shunted through unspecified centers to the valence band. In the case of capture by the complexes, the Zn-O complex acts as a deep electron trap; after trapping an electron the complex becomes negatively charged and can trap a hole by Coulombic attraction. The electron and hole then decay as a bound exciton. Reemission of captured electrons may also occur and will naturally limit ra-
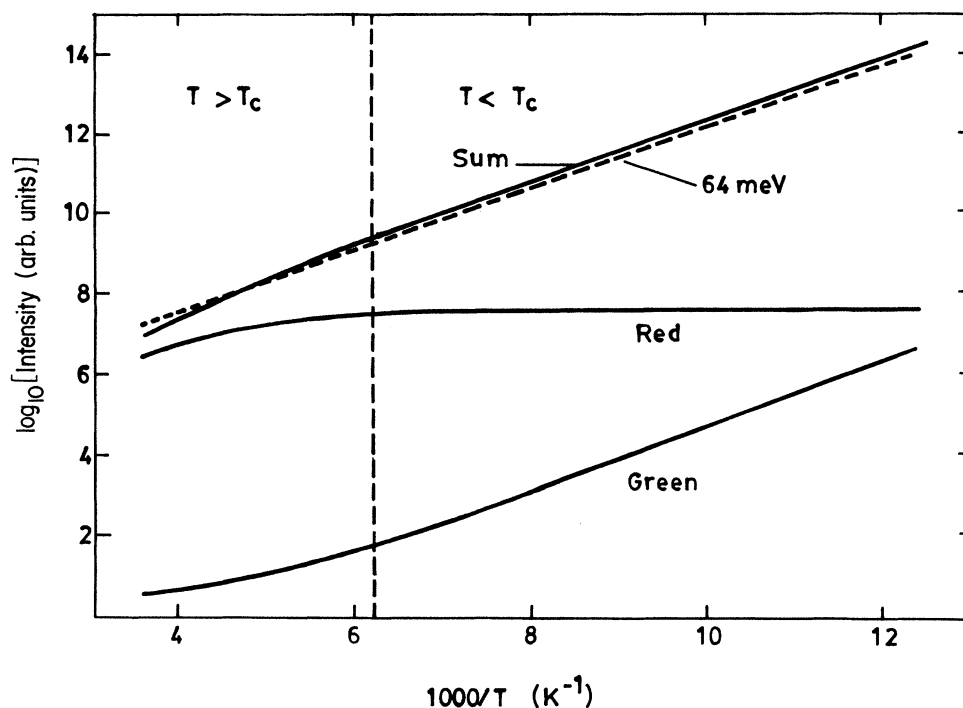

FIG. 2. PL intensity of the red and green PL peaks are given as a function of inverse sample temperature. Also shown is the dependence of the logarithmic sum of the red and green PL peak emission intensities. The dotted line adjacent to the logarithmic sum curve is constructed for a 64-meV activation energy. The position of the vertical dotted line corresponds to $T_c = 160$ K, as specified in the text.

diative recombination efficiencies. These processes are more probable at higher temperatures and for shallower donor states. Thus the detrapping rate of electrons from the zinc-oxygen nearest-neighbor bound-exciton electron state, lying about 300 meV below the conduction-band edge,[9] will be much smaller than for the sulfur donor state. Equation (4) indicates how electrons trapped on these donors contribute to the neutral donor concentration and therefore to the green band intensity. Clearly then, the overall green PL efficiency will depend on the occupancy of the shallow zinc acceptor states at steady state.

A simple approach is used here to establish the dependence of the acceptor level occupancy on temperature using Fermi-Dirac statistics for a typical compensated p-type sample. This approach reveals that at low temperatures, the zinc level occupancy should diminish exponentially with temperature with a 64-meV activation energy. Thus, in this low-temperature region the green PL emission intensity should be quenched with this characteristic energy. For such processes, the onset of luminescence saturation will occur at a critical acceptor level occupancy of 0.5.[12] We use this approach to calculate the critical temperature, T_c, introduced earlier. Using nondegenerate Fermi-Dirac statistics with $N_A > N_D$, the following equation may be derived:

$$N_D \cong N_v(T_c) \exp(-E_a/kT_c) , \qquad (5)$$

where $N_v(T_c)$ is the valence-band density of states at a temperature T_c; values for the hole effective mass of $0.36m_0$ and $E_a = 64$ meV are assumed. A sulfur concentration of about 3×10^{16} cm^{-3} results in a T_c value of about 160 K, in excellent agreement with the value determined experimentally.

The behavior of the red PL emission intensity shown in Fig. 2 will now be discussed. Processes which promote thermal equilibrium cause holes to be continuously transferred from the zinc acceptor states into shallow bound-exciton hole states ($E_h = 39 \pm 4$ meV).[13] The green and red peak intensities reflect on the consumption of excess photogenerated electron-hole pairs. In particular,

electrons are captured as a result of the competition between the donor levels involved in the red and green emissions; this depends on the concentration, capture cross section, and fractions filled at steady-state excitation recombination, for the respective levels. These factors result in the Zn-O complex being far more efficient at capturing minority carriers. Furthermore, reemission from these centers is very inefficient. Therefore, these factors, taken together with an abundant supply of holes (as a result of the rapid communication of the shallow exciton hole level with the valence band), explain the dominant role played by the red band, as can be seen in Fig. 2. In the narrow temperature range above T_c, the onset of red band quenching is apparent and results principally from the diminishing supply of holes to the complex, as the acceptor level occupancy falls below its critical value. Thus, the logarithmic sum curve shown in Fig. 2 exhibits a constant activation energy of 64 meV over the entire temperature range shown. Although measurements above room temperature are not reported in this figure, it is anticipated that at elevated temperatures, the thermalization of electrons from their respective donor levels should become important.

In summary, we report on PL measurements on LPE grown GaP:Zn,O. The green band emission is shown to originate from DA-pair recombination involving sulfur donors and zinc acceptors. A simple model is forwarded to explain the observed temperature dependence of the red and green band PL peak intensities.

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