Defect Reactions in GaP:(Zn,O)

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We have observed photoinduced reactions between pairs of zinc and oxygen impurities in gallium phosphide. From photoluminescence studies we find that the nearest-neighbor (Zn, O) pairs are dissociating, after which they re-form as further separated pairs. The activation energy for the dissociation is found to be 0.60± 0.07 eV for the photoinduced reaction, and 2.6± 0.6 eV for the purely thermal reaction. We tentatively identify the photoinduced reaction as being due to excitation of local phonon modes by nonradiative electron-hole recombination.

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Defect complexes in semiconductors can play a very important role in determining the electrical and optical characteristics of the material. One simple complex which commonly occurs is a pair of donor and acceptor impurities. The energy of the luminescence emitted from donor-acceptor (DA) pairs depends on the separation of the impurities,[1] and so a luminescence spectrum provides information about the number of pairs of each possible separation.

In this work we use photoluminescence to monitor the relative positions of Zn_{Ga} and O_P impurities in GaP. When the GaP is subjected to laser excitation at high temperatures, we observe reactions in which the impurities diffuse through the lattice to occupy new substitutional sites. This is the first time DA luminescence has been used as a microscopic probe of defect reactions. From low-temperature studies we identify these reactions as being the dissociation of nearest-neighbor (Zn, O) pairs and the formation of further separated pairs. Such a dynamic process of reactions among lattice defects of known initial and final chemical type has not previously been observed in a semiconductor. The photoluminescence spectra reported here provide valuable information about those phonon modes which are likely to be responsible for the (Zn, O) dissociation. Most other studies of defect reactions in semiconductors have not included any observations of the vibrational modes of the defect.

The samples used in this work were liquid-phase-epitaxially grown *pn* junctions on *n*-type GaP (single crystal). The growth technique is described by Saul, Armstrong, and Hackett.[2] The exposed 50-μm-thick layer of the junction is *p* type, doped with Zn and O. The (substitutional) O concentration is about 10^{16} cm^{-3} and the Zn concentration is about 3×10^{17} cm^{-3} (based on the crystal-growth conditions). Other impurities include N and S. The photoluminescence spectra were obtained using above-band-gap Ar^+ laser excitation and a liquid-N_2-cooled *S*-1 type photomultiplier.

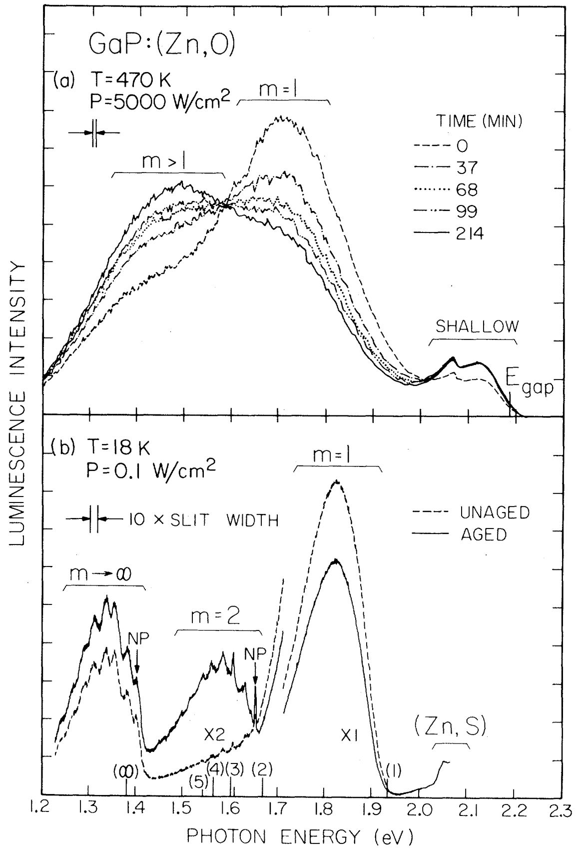

FIG. 1. Photoluminescence spectra at various temperatures (*T*) and laser power densities (*P*); (a) time-resolved spectra showing defect reactions in progress and (b) the initial and final states of the reaction. The labels *m* denote luminescence from an *m*th-nearest-neighbor (Zn, O) pair. NP refers to a no-phonon-assisted transition. Theoretical predictions for the line positions are shown on the abscissa (also in Fig. 2).

Figure 1 shows several high- and low-temperature photoluminescence spectra. In Fig. 1(a) the time between successive scans is about 30 min. We see that the spectra are changing with time. This is a direct observation of a reaction in progress. We refer to this reaction as an "aging" process. The initial and final spectra shown are similar to those seen by Dapkus and Henry.[3] These authors showed that the aging reaction is due to photoinduced destruction of nearest-neighbor (Zn, O) pairs, and they speculated that these pairs were in fact dissociating and forming further separated pairs. Here, we prove that this speculation is correct.

To identify the luminescence bands we go to the low-temperature spectra shown in Fig. 1(b). From the work of previous authors[4-7] we identify the band centered at 1.82 eV as being due to nearest-neighbor pairs $(\mathrm{Zn, O})_{m=1}$, and the band centered at 1.35 eV as due to far-separated pairs $(\mathrm{Zn, O})_{m\to\infty}$. The breadth of these bands is due to phonon-assisted radiative transitions. The (Zn, S) DA luminescence at about 2.05 eV is constant in intensity between the unaged and aged material, which indicates that the low-temperature minority carrier concentration is also constant. Thus, the reduced intensity of the $m=1$ band in the aged material must be due to a reduction of the $(\mathrm{Zn, O})_1$ concentration.[3] Similarly, the $(\mathrm{Zn, O})_{m\to\infty}$ concentration has increased. Centered at 1.59 eV is a luminescence band which is seen in the aged sample, but barely visible in the unaged material. The breadth of this band is similar to those of $(\mathrm{Zn, O})_1$ and $(\mathrm{Zn, O})_{m\to\infty}$ and the resolved phonon structure is characteristic of a complex involving O. Furthermore, if we compare the no-phonon transition location with theoretical predictions,[1,8] we see that the position of this new band is as expected for $(\mathrm{Zn, O})_2$. We thus identify the new luminescence as being due to second-nearest-neighbor $(\mathrm{Zn, O})_2$ pairs. The reduction in $m=1$ pair concentration has been accompanied by an increase in concentration of $m>1$ pairs. From the observed luminescence intensities, and calculations (following Ref. 9) of the initial distribution of pair separations, we find that the increase in concentration of $m>1$ pairs is roughly equal to the decrease in concentration of $m=1$ pairs. We also note that in Fig. 1(a) the $m>1$ band is increasing at the same rate as the $m=1$ band is decreasing. Thus, we conclude that the nearest-neighbor pairs are dissociating and forming further separated pairs.

In Fig. 2 the discrete DA lines for second nearest neighbor and further separated pairs are resolved. All except the $m=2$ and $m=3$ lines have previously been reported,[7] although we reidentify a few of the lines as phonon-assisted transitions. Replicas of the $m=2$ line are seen involving phonons of energies 9.2, 21.7, 27.2, and 46.8 meV. The 46.8-meV mode is probably very similar to a bulk optical (O) mode and we have labeled it as such. The lower energy modes are local modes (resonances) of the (Zn, O) complex. These modes form a broad band at ~20 meV from the no-phonon band in the $m\to\infty$ DA luminescence [Fig. 1(b)]. Similar localized phonons of energy ~25 meV are seen for the isolated neutral O don-

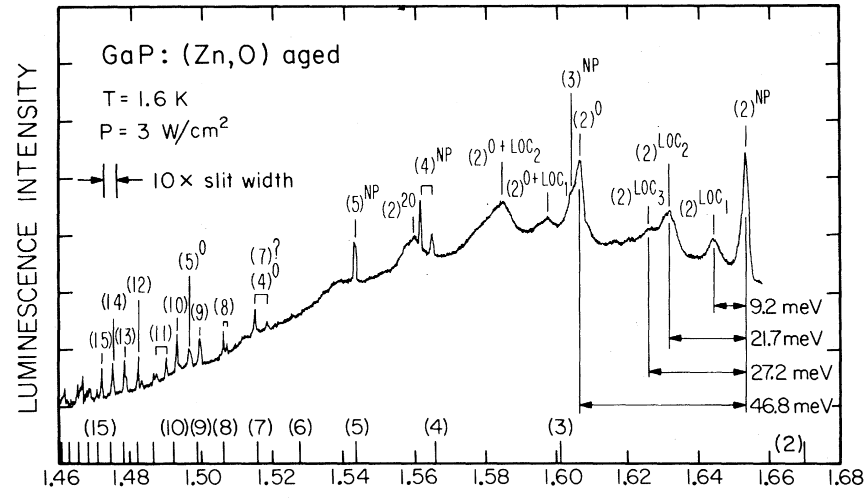

FIG. 2. Low-temperature donor-acceptor pair luminescence. The lines are labeled by (m) for mth-nearest-neighbor pairs with a superscript indicating the type of phonon involved in the transition (O = optical, LOC = local, NP = no-phonon). Those labels with no superscripts refer to no-phonon transitions.

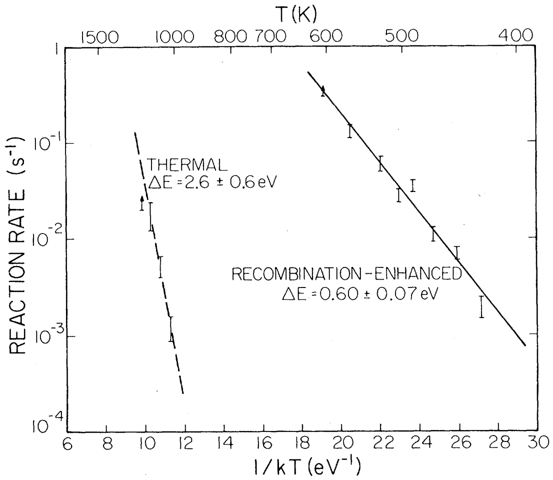

FIG. 3. The dissociation rates of nearest-neighbor (Zn, O) pairs. The rates labeled "recombination enhanced" are for photoinduced dissociation of the pairs, in the limit of high incident light intensity. The rates labeled "thermal" are for pair dissociation by purely thermal means.

or.[10] For a defect with small mass, a localized low-energy phonon mode implies a reduced spring constant. From the phonons observed here, we estimate that the O-Ga spring constant is about 30% of the P-Ga spring constant. This certainly implies a reduction in the O-Ga bond strength compared to that of P-Ga. A weak O-Ga bond seems reasonable considering the small size and large electronegativity of O compared to P.

The mechanism responsible for the $(\mathrm{Zn,O})_1$ dissociation can be identified by measuring the activation energies for the photoinduced and purely thermal reactions.[11,12] We have performed these measurements and a complete account of them will be given elsewhere. The results are shown in Fig. 3. We find activation energies of 0.60 ± 0.07 eV for the photoinduced dissociation and 2.6 ± 0.6 eV for thermal dissociation of the pairs. The difference between these activation energies is roughly equal to the recombination energy (~1.9 eV). Thus, we identify the $(\mathrm{Zn,O})_1$ dissociation to be a "recombination-enhanced" reaction in which the energy available from electron-hole recombination is transferred to localized vibrational modes which leads to a reaction. The strong phonon coupling which is required for recombination-enhanced reactions is clearly evident in the photoluminescence spectrum, Fig. 1(b). The broad $(\mathrm{Zn,O})_{m=1}$ band is primarily composed of a series of 6.0-meV phonon replicas,[4,5] and multiple occupation of this 6.0-meV mode probably provides the "critical reaction path" for the dissociation to proceed.

In conclusion, we have observed photoinduced dissociation of nearest-neighbor (Zn, O) pairs in GaP, and the formation of further separated pairs. As a result of the strong electron-phonon coupling in the $(\mathrm{Zn,O})_{m=1}$ system, it is possible that the dissociation proceeds by the oxygen (or zinc) ion jumping from a substitutional to an interstitial site and migrating away. The ion is then captured by a vacancy to form a further separated pair with the nearest zinc (or oxygen) ion. From the local phonon-mode energies it seems that the oxygen ion is weakly bound in the GaP lattice, and so we suggest that it may be the oxygen (rather than the zinc) ion which makes the jump in the dissociation. The GaP:(Zn, O) system has provided us a unique opportunity for studying molecular defect reactions occurring in an ordered lattice.

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