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Resonant photoluminescence studies of the growth-induced defects in GaAs grown by molecular beam epitaxy

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The origin of the series of luminescence lines observed in the 1504–1511-meV region in GaAs grown by molecular beam epitaxy has been the subject of considerable recent study. Using high-resolution, high-sensitivity resonant excitation measurements, we conclusively prove the nature of these lines to be due to excitons bound to a series of acceptors. A firm link between these acceptor bound excitons and a series of broader, lower-energy lines will also be established showing that both of these two spectral regions have a common origin.

Künzel and Ploog[1] were the first to report on a series of defect-related photoluminescence (PL) lines in nominally undoped *p*-type GaAs layers grown by molecular beam epitaxy (MBE) in which the arsenic source was As_4. They attributed these lines to optical transitions resulting from excitons bound to point defects with the simultaneous incorporation of an impurity inherent to the MBE growth process, probably carbon.[2] The origin and properties of these luminescent features, which we will refer to as the *KP* lines, have since been the subject of numerous investigations. Up until now, no satisfactory conclusion has been reached as to the origin of the binding centers. Briones and Collins[3] first suggested that the *KP* lines were due to excitons bound to *defect complex* acceptors, and that the lower-energy transitions (d_n lines),[4] observed at $\sim$1470 meV, were free-to-bound (e,A^0) and donor-acceptor pair (DAP) transitions involving the same *defect complex* acceptors responsible for the *KP* series. The correlation between the *KP* and d_n lines was further supported by the polarized PL measurements of Skolnick, Tu, and Harris.[5]

Many other models have been proposed to explain the many line features of the *KP* series. Recently, Zeeman spectroscopic investigations of the *KP* lines[6–8] revealed that, while the bound exciton (BE) ground states (initial state in PL) were magnetically split, the *binding center* ground states (final state in PL) involved in the *KP* transitions were not. This result implied a total angular momentum of $J=0$ in the final state of the PL transition. Out of the various possibilities for the recombination mechanisms giving rise to the *KP* lines, relatively few satisfy the requirement of having a $J=0$ final state. Certainly a model involving a simple, single-acceptor BE is ruled out. There remain three types of models which have been proposed to account for the large number of lines in the spectra, and the spectral range over which the lines occur. Reynolds *et al.*[9] interpreted these lines as discrete DAP transitions resulting from preferential pairing. Although this recombination process does have a $J=0$ final state, since there are no electronic particles involved in this state several arguments against it have been presented in detail, showing that this model is inconsistent with the observed results.[10] A second model that could explain both the Zeeman spectra and the d_n lines was the axial double-acceptor bound-exciton model proposed by Skolnick,[6] which encompassed both the earlier proposal that the binding centers consisted of pairs of single acceptors,[11,12] along with the new possibility of isoelectronic defect-double-acceptor pairs. Skolnick *et al.*[5] supported this model by detecting satellites of some of the *KP* lines which they interpreted as the 2*S* two-hole transitions of the double-acceptor bound excitons, but in the absence of other transitions in the two-hole series this assignment was not definitive. Finally, Beye, Gil, Neu, and Vèrié[13] very recently proposed an isoelectronic bound-exciton model as the origin of the *KP* lines.

The aim of this Rapid Communication is to present additional information on the nature of these transitions. Our high-resolution selectively excited PL spectra reported here provide the first direct proof of the acceptor BE nature of the *KP* lines by revealing an entire series of acceptorlike excited states in the two-hole replicas of many of the *KP* lines. Using the accurate acceptor binding energies determined from these measurements, we demonstrate that the d_n line spectra can be quantitatively accounted for by the same distribution of acceptor defects.

The sample studied in the present work was obtained from the same wafer used by Skolnick and coworkers.[5,6,10] The excitation source used for the resonant PL experiment was a mode-locked cavity-dumped (4-MHz) dye laser system with a full width at half maximum (FWHM) $\simeq$0.05 meV. The laser dye (Exciton LDS 821) provided a tuning range of approximately 800–880 nm, covering the entire region of interest for resonant excitation. For the above-band-gap excitation, the luminescence was dispersed by means of a $\frac{3}{4}$-m double spectrometer and detected by a Varian VPM-159A3 cooled photomultiplier tube. Signals were processed in the photon-counting mode, and time-resolved spectra collected for different time windows after the laser pulse could be obtained with the usual time-to-amplitude converter–pulse-height analyzer combination.[8] For the resonant excitation experiments, a parallel optical multichannel analyzer based upon an imaging photomultiplier tube (PMT) (ITT Mepsicron) was used. The signal, which was dispersed across the detector by a 1200 grooves/mm grating operat-

ed in first order in a $\frac{3}{4}$-m spectrograph, was again processed in the photon-counting mode. Using a novel time-rejection technique,[14] we were able to discriminate between fast and slow recombination processes while simultaneously making use of the parallel collection capabilities of the detector, allowing us to observe the weak but fast *KP* two-hole replicas on top of the much longer-lived DAP luminescence.

PL spectra in the 1460–1480-meV region for a number of different excitation energies are shown in Fig. 1. All the curves represent only the photons emitted in the first 5 nsec after the laser pulse. As the dye-laser position is brought to be resonant with the various peaks of the *KP* series, a number of sharp satellites are observed. In the figure, we compare the acceptor excited-state spectrum of carbon, as obtained from the resonantly excited carbon acceptor bound exciton (C^0, X) two-hole spectrum, with typical resonant PL spectra obtained by pumping seven of the *KP* lines. In the figure the luminescence photon energy scale corresponds to the resonant spectrum of line 19 (bottom spectrum). The other spectra have been shifted in energy so as to line up the 3*S*, 4*S*, and 5*S* excited states of the two-hole replicas. The discrepancies, as in the position of the 2*S* excited state, can be explained by the different acceptors having different central-cell corrections (chemical shifts), and to interaction of the 2*S* states with the optical phonons. The observation of these two-hole series for many of the *KP* lines proves conclusively the acceptor BE nature of these lines, and the need of at least one hole in the final state of the luminescence transitions. The shaded lines labeled LO and TO represent the Raman lines or phonon-assisted BE transition, while the band labeled Δ_{LO} is the LO phonon replica of the satellite observed in the broad structure underlying peaks 1–4, and will be discussed in detail elsewhere.[8]

Figure 2 summarizes the results, with the luminescence energy of the satellites being plotted as a function of the pump energy. Note that all the experimental points are

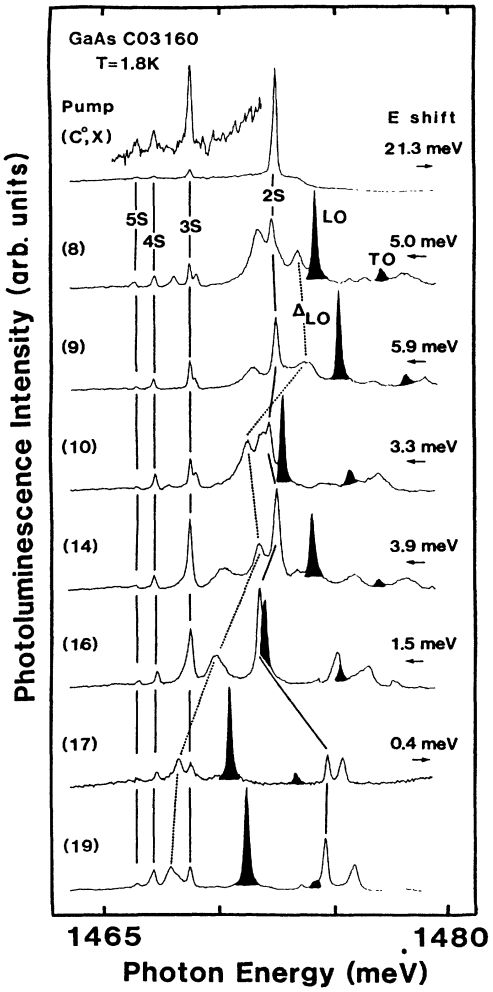

FIG. 1. Selectively excited PL spectra with the laser tuned successively to resonance with different lines of the *KP* series (numbered on the left) and compared with that of the carbon acceptor BE (top). The spectra, taken at 1.8 K, correspond to photons emitted in the first 5 nsec after the laser pulse. The 4*S* and 5*S* transitions have all been aligned—the energy scale applies to the bottom (line 19) spectrum while the energy shifts required to align the other spectra are shown on the right. The shaded lines are the LO and TO phonon Raman lines, while Δ_{LO} is the LO phonon replica of the selectively excited Δ transition.

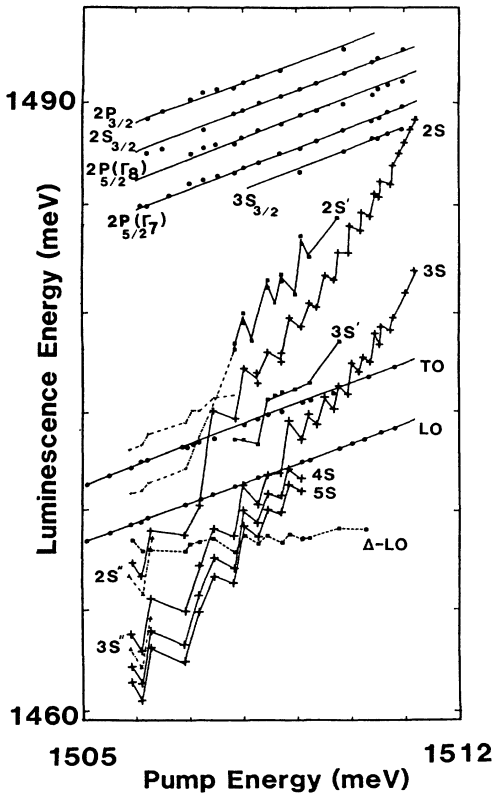

FIG. 2. Summary of the resonant PL measurements in the two-hole replica region. The five straight lines at the top of the figure correspond to selectively excited carbon acceptor-donor pair luminescence. The TO and LO are the phonon Raman lines, which follow the energy of the pump laser. The series 2*S*, 3*S*, 4*S*, and 5*S* are identified as the resonantly excited two-hole satellite of the various defect BE. Δ_{LO} is the LO replica of the selectively excited Δ transition.

included in this figure. The TO and LO Raman lines occur at a constant separation of 33.8 and 36.8 meV from the laser line. The five lines at the top of the figure labeled $2P_{3/2}$, $2S_{3/2}$, $2P_{5/2}(\Gamma_8)$, $2P_{5/2}(\Gamma_7)$, and $3S_{3/2}$ can be ascribed to selectively excited pair luminescence (SPL) of carbon acceptor-donor pairs[15] and are independent of the *KP* series. Many of the 2*S* and 3*S* *KP* two-hole transitions were observed to be split into doublets (e.g., $2S-2S'$), as can also be seen in the some of the Fig. 1 spectra, but no pattern could be ascertained with regard to the magnitude of this splitting. Finally, when the laser was tuned to lower energy than line 8, no structure besides the LO and TO lines was observed, confirming that the broad feature underlying lines 1–4 observed in PL arises from a final-state splitting in the PL experiment. This was also confirmed by means of PL excitation spectra.[8] A similar study was undertaken by Skolnick *et al.*,[5] who resonantly excited the different peaks in the 1504–1512-meV region. They also observed low-energy satellites when the laser was brought in resonance with the defect-bound-exciton lines but could not explain the origin of the various satellites as the structure became more and more complicated with decreasing laser energy. However, they followed the evolution of one line in the satellite region when pumping resonantly lines 32 to 22, and assigned it to the 2*S* two-hole transitions of each of the individual defect BE, which is in agreement with our findings.

The binding energies of the different acceptors responsible for the KP lines can be estimated from the observed 1*S*-2*S* energy separation but the higher excited states should give more accurate results due to reduced central cell effects. The binding energies of the different centers were calculated from the 3*S* two-hole transitions and were used to provide a *Hayne's rule*[16] plot of the BE binding energy vs acceptor binding energy in Fig. 3. This linear dependence likely results from the close similarity within this family of defect acceptors, as proposed by Skolnick *et al.*[5]

The accurate defect acceptor binding energies determined here can also be used to conclusively demonstrate that the d_n lines originate from the same family of acceptor defects as the *KP* lines. Skromme *et al.*[4] used temperature and excitation intensity-dependent PL measurements to demonstrate that these low-energy d_n lines are DAP and free-to-bound in nature, involving normal shallow donors and at least four different acceptor levels. We have used time-resolved spectroscopy to discriminate between the two different kinds of radiative processes. The decay time of free-to-bound transition is known to be much faster than the DAP emission,[17] so by setting different collection time windows it was possible to discriminate the longer-lived DAP from the shorter-lived (e,A^0) transitions. In Fig. 4(a), a typical d_n spectrum is shown along with the higher-lying free-to-bound (e,C^0) and DAP (D^0,C^0) transitions. In Fig. 4(b) the faster free-to-bound transitions are enhanced by using a short time window, while in 4(c) the longer-lived DAP transitions are enhanced with a delayed time window. In Figs. 4(a) and 4(c) the d_n PL is simulated by convolving the observed carbon-related PL with the distribution of defect acceptor binding energies and concentrations as determined from the *KP* line spectroscopy. This fit, which involves no adjustable parameters, is seen to be in excellent agreement with the observed d_n spectra in both cases, proving that indeed the series of peaks at 1471–1491 meV can be correlated with the *KP* lines, both involving the same acceptor defects.

In summary, we have provided the first definitive proof of the acceptor BE nature of the *KP* lines, and of the direct connection between these and the d_n lines. In spite of the new results presented here, a number of unresolved

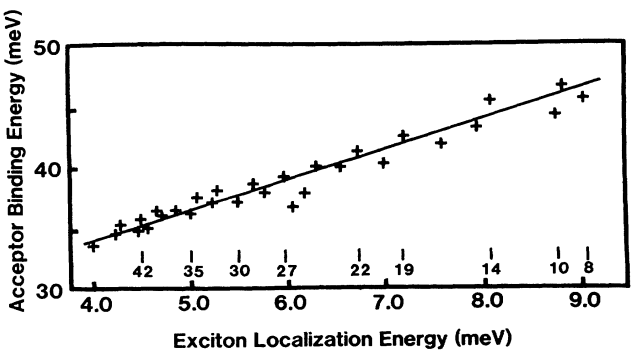

FIG. 3. A comparison of the BE localization energy for the *KP* lines (numbered at bottom) vs the acceptor binding energies as determined from the 3*S* two-hole replicas.

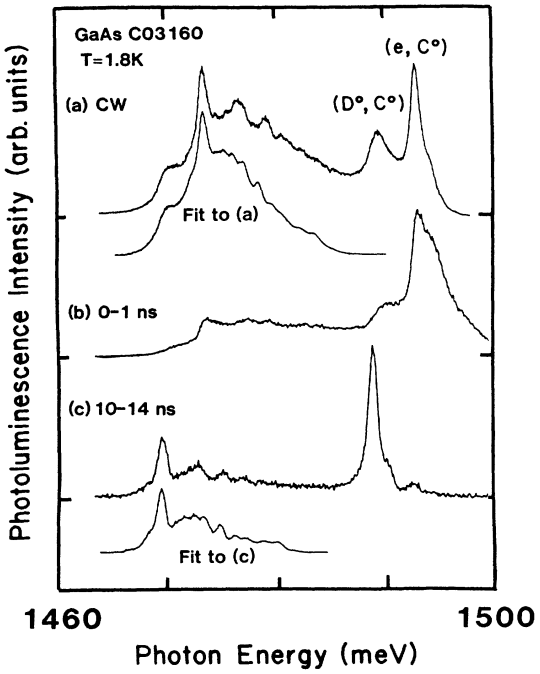

FIG. 4. (a) Shows a typical PL spectrum for CW above gap pumping, revealing the d_n lines lying below the carbon DAP (D^0,C^0) and free-to-bound (e,C^0) bands. Curves (b) and (c) correspond to two different time windows taken after the laser pulse. The d_n spectra in (a) and (c) are seen to be in excellent agreement with simulated spectra generated by convolving the observed carbon spectrum with the distribution of defect acceptors as determined from the *KP* line spectroscopy.

problems still remain in the analysis of these spectra. While the donor-acceptor pair model[7] and the isoelectronic bound-exciton model[13] are ruled out by our results, both the single acceptor pair model and the double acceptor-isoelectronic defect pair model encompassed by the proposal of Skolnick[6] remain viable possibilities. Further progress will likely require the identification of the chemical species involved in these complex defects.

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