Photoluminescence decay times of the defect-induced bound-exciton lines in GaAs grown by molecular-beam epitaxy

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(Received 4 August 1989)

Photoluminescence decay transients of the defect-induced bound-exciton lines frequently observed in GaAs grown by molecular-beam epitaxy were studied in detail in an effort to resolve discrepancies in the published results. In particular, the same high-quality sample previously used in other measurements was obtained in order to eliminate the possibility of sample variability. The nonresonantly excited transient results presented here agree with our earlier measurements made on a different sample, but differ substantially from the results reported by others for the same sample. Finally, new resonantly excited transient results are found to be quite different from the nonresonant case and lead to a clearer picture of the dynamics of this unusual system.

Künzel and Ploog[1] were the first to report on a series of intense and sharp photoluminescence (PL) emission lines in nominally undoped p-type GaAs layers grown by molecular-beam epitaxy (MBE). These lines, which we will refer to as the KP lines, were observed in the 1504–1511-meV spectral region and were attributed to excitons bound to defects.[2] The origin and properties of these luminescent features have since been the subject of numerous investigations and controversies.

Following the introductory work of Künzel and Ploog, more highly resolved PL spectra have been observed by other groups, who have tried to introduce specific models to explain the details of the structure, without as yet any satisfactory conclusion being reached as to the origin of the binding centers. Reynolds *et al.*[3] interpreted these lines as discrete donor-acceptor–pair transitions resulting from preferential pairing. In another investigation, Eaves *et al.*[4,5] fitted the KP PL emission spectrum with a model of excitons bound to acceptor pairs of varying separation. In their original model, the high-energy line observed at 1511.2 meV (henceforth called the g line or line 47) was attributed to an isolated unidentified acceptor bound exciton (BE),[6,7] and the line lowest in energy (1505.0 meV, also called the V line or line 1), was assigned to the nearest-neighbor acceptor-pair BE. However, following the detailed studies of Skolnick *et al.*,[8,9] who reported that most of the PL in this region was strongly polarized parallel to one of the $\langle 110 \rangle$ directions, Eaves and coworkers[10] introduced a modified model. In this revised model the line at 1507 meV (line 14), which was found to be the most intense and strongly polarized of the series, was assigned to be the nearest-neighbor pairs.

Beye and co-workers[11] concluded, from their selectively excited PL and excitation experiments, that there were at least two distinct recombination processes involved in this excitonlike luminescence band. Their experimental results supported an exciton recombination at axially oriented complex defects to be at the origin of the KP series. Such centers were suggested to be complex defects acting as isoelectronic centers. In a more recent paper,[12] the same authors claimed to distinguish at least four sets of BE complexes related to distinct defect centers. An isoelectronlike defect model was again proposed to be most consistent with their experimental results.

However, Charbonneau *et al.*,[13,14] by extending the work of Skolnick *et al.*,[9] have conclusively proved the acceptor BE nature of the KP lines. Their conclusion was reached from the observation of BE two-hole transitions to excited states up to $n=5S$ for lines 8–46. From these higher excited states, accurate acceptor binding energies were determined and used to prove that the broader, lower-energy d_n lines[15] originated from the same family of acceptor defects as the KP lines.

Although the cw spectroscopy of the KP lines is now fairly well understood, their transient behaviors are currently controversial. Information on the lifetimes is very useful in understanding the decay mechanism of BE's. Skolnick, Halliday, and Tu[16] (hereafter SHT) recently made a brief but seemingly definitive negative comment on the results and conclusions of an earlier transient PL study by Steiner, Thewalt, Koteles, and Salerno (hereafter STKS).[17] SHT claimed that the transient PL results of STKS were unreliable due to poor sample quality, and that the true KP transient behaviors were given by Skolnick *et al.*[8] They described the lifetimes as increasing smoothly from 1.5 ns at line 47 to 12 ns for line 14 and below, but the PL decay data have never been published. These results[8] are in themselves surprising, since the large lifetime change, from 1.5 to 12 ns, over such a relatively small range in binding energies is difficult to reconcile with a BE model.

The aim of this paper is to present additional information on the transient behavior of these lines. The nonresonantly excited transient results presented here agree with earlier measurements of STKS on a different sample, although the present results are much clearer and more comprehensive, but differ substantially from the results obtained by SHT for the same sample. New resonantly

excited transient results are obtained which lead to a clearer picture of the recombination mechanism involved in this unusual system.

In order to test the sample-quality hypothesis raised by SHT, the sample studied in the present work (CO3160) was obtained from the same wafer used by Skolnick and co-workers.[8,9,16] The sample was immersed in superfluid helium for the PL measurements. The excitation source was provided from a mode-locked Ar-ion laser synchronously pumping a dye-laser system (pulse width of <30 ps). The laser dye (Exciton LDS 821) provided a tuning range of approximately 800–880 nm, covering the entire region of interest for resonant and nonresonant excitation. The mode-locked laser used in this work has an intrinsic repetition rate of 82 MHz, corresponding to a period between pulses of ~ 12 ns. A cavity dumper was used in order to reduce the repetition rate to 4 MHz. 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 the luminescence decay curves were obtained with the usual time-to-amplitude converter– pulse-height analyzer combination. The total instrumental response to the dye-laser excitation pulses was 250 ps. By operating the system under computer control, eight spectra corresponding to different time windows after the laser pulses could be collected simultaneously.

A series of time-resolved spectra of sample CO3160 using above-band-gap excitation is shown in Fig. 1. This series of spectra clearly shows that the carbon acceptor BE (C^0,X) and line 47, with its low-energy wing, decay much more quickly than the lower-energy *KP* lines, in agreement with the earlier results of STKS. The luminescence decay curves for some of these individual lines were recorded using above-band-gap excitation and are shown in Fig. 2. The (C^0,X) line (not shown in Fig. 2), along with line 47, were found to have identical lifetimes of 1.2 ns. However, an important change in the shape of the decay curve is observed in going from line 47 to line 27. In fact, all the *KP* lines below line 47 showed decay transients which are strongly non-single-exponential, but can be well described by a double-exponential decay process. This observation was also reached by STKS using a less pure sample, but contradicts the assumption used by Skolnick *et al.*[8,16] who described the decay transients of each line of the series as being single exponential. Further, as reported by STKS,[17] the lifetimes of the two decay components do not vary strongly across the *KP* series (excluding line *g* or 47), but the relative amplitude of the slow component grows for the lower-energy *KP* lines. By fitting a double-exponential decay to the transient curves

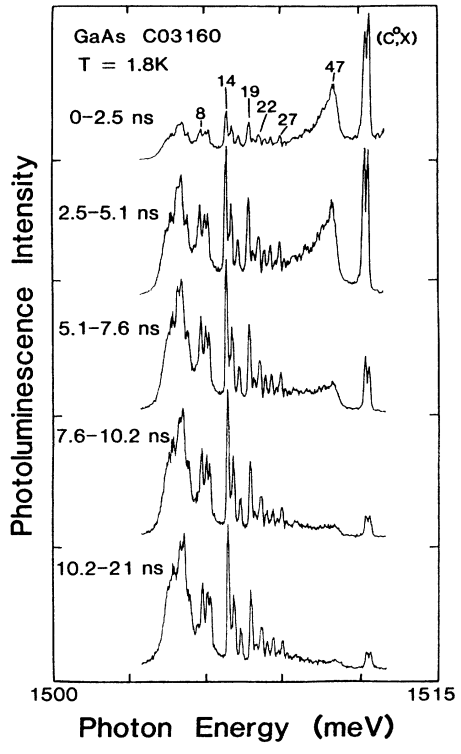

FIG. 1. Series of time-resolved spectra taken at 1.8 K. The time windows are indicated on the figure. The sample was excited by 814-nm radiation at a repetition rate of 4 MHz with an average excitation density of 50 mW/cm^2. After the initial fast decay of the acceptor bound exciton (C^0,X) and line 47, the shape of the spectrum remains unchanged during later time windows.

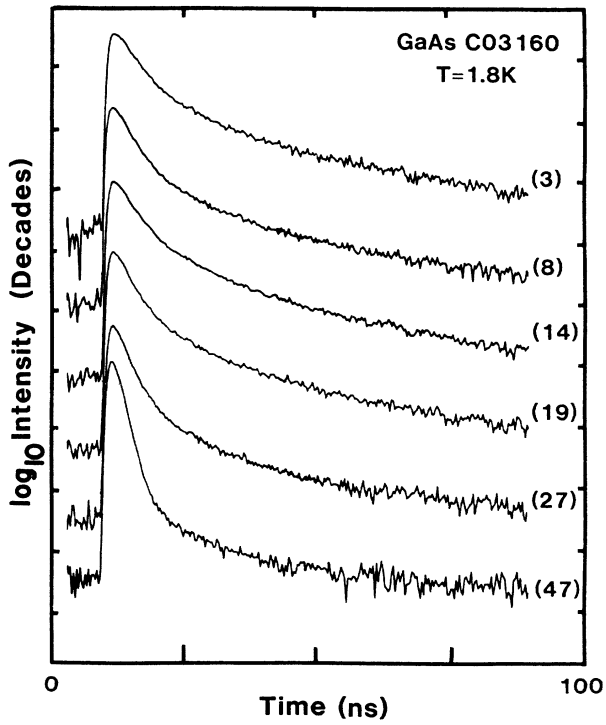

FIG. 2. Luminescence decay measurement of selected lines shown in Fig. 1 under identical experimental conditions. The lifetimes, corresponding to the initial exponential decays, are 3.2, 3.1, 3.0, 2.8, 2.0, and 1.2 ns, corresponding to lines 3–47, respectively. The long-lived component varied from 13 ns for line 27 to 17 ns for line 3.

of Fig. 2, a range of fast components between ~2 and ~3 ns, and slow components from ~13 to ~17 ns, were obtained in going from line 27 to 3.

As postulated by STKS, the double-exponential decay of the *KP* PL likely results from a feeding of the radiative transitions from some long-lived reservoirs. To be more specific, we believe that these reservoirs are the essentially nonradiative excited states of the *KP* BE, whose relaxation to the ground state appears to be quite slow. This is perhaps not surprising for such axial BE defects, since transient PL measurements on BE systems split by uniaxial stress have previously revealed a lengthening of the transition times between the stress-split BE components.[18]

To test this possible explanation of the unusual PL decay curves obtained from nonresonant excitation of the *KP* lines, we have performed the first resonant-excitation measurements of the *KP* PL decay transients using the same high-quality sample. This was done by directly exciting the *KP*-line energies with a tunable mode-locked, cavity-dumped dye laser, and monitoring the signal from the appropriate *KP* BE two-hole transition (2*S* replica). Under resonant-excitation conditions the *KP* BE PL decays were found to be both fast and single exponential (more than one-and-a-half decades) in nature, as shown in Fig. 3. These decay lifetimes did increase relatively smoothly from 1.2 ns near line 47 to 1.6 ns at line 14, representing the true radiative lifetimes of the *KP* BE

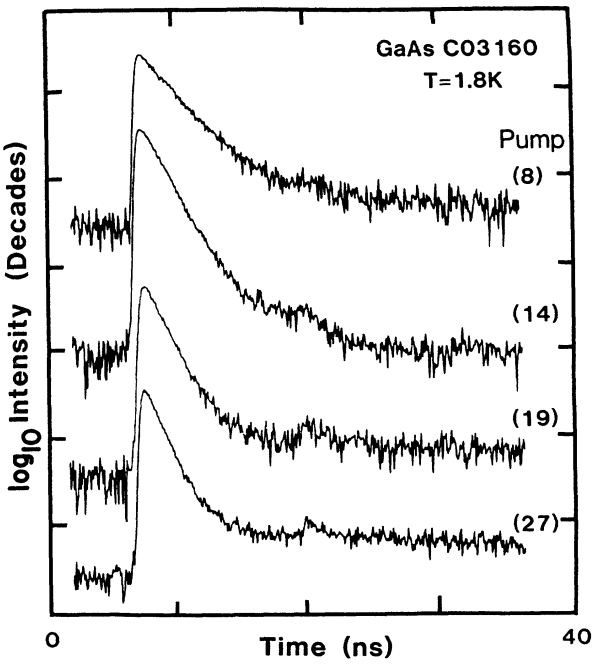

FIG. 3. Luminescence decay measurement of the BE 2*S* two-hole replicas while resonantly exciting lines 8, 14, 19, and 27. Experimental lifetimes of 1.8, 1.6, 1.4, and 1.3 ns were obtained for the various lines. The weak luminescence pulse seen at ~12 ns after the main peak is an experimental artifact arising from the leakage pulses from the cavity dumper. No long-lived component was detected in this emission, except for a weak background contribution.

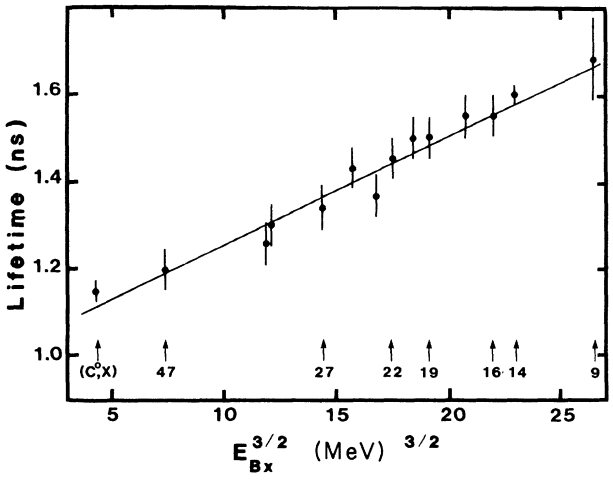

FIG. 4. Summary of the transient results obtained on the 2*S* BE two-hole transitions. The vertical axis represents the lifetime of the 2*S* replicas in nanoseconds, while the horizontal axis is the exciton-localization energy (E_{BX}) to the three-halves power. Some lines of the exciton series are indicated on the horizontal axis.

when created in their ground-state configurations, independent of the capture time required for the exciton to get trapped by the binding centers or the relaxation from higher-lying BE excited states. These results bear no resemblance to the nonresonantly excited transient results reported by either SHT (Ref. 8) or STKS (Ref. 17).

The lifetimes of the 2*S* two-hole transitions obtained here were found to increase in going from line 47 to 8, as one would expect from the general consideration of lifetime versus exciton-localization energy (E_{BX}). This increase in lifetime can be understood qualitatively if the hole becomes more localized with increasing E_{BX}, leading to a decrease in electron-hole overlap and thus an increase in lifetime. A theory put forward by Rashba and Gurgenishvili[19] predicts a three-halves dependence of the exciton-localization energy on the BE lifetime. Such a dependence has been observed, and the results are summarized in Fig. 4, where the lifetimes of the individual defect-bound-exciton 2*S* replicas are plotted as a function of $(E_{BX})^{3/2}$.

In summary, the PL decay measurements presented here support the excitonic nature of the *KP* series and the earlier results of Steiner *et al.*[17] The quite different transient behavior described by Skolnick *et al.*[8,16] is an artifact of the measurement technique used in that study; namely, intensity measurements at only two delay times coupled with the assumption of a single-exponential decay.[20] Whether these axial defects result from two nearby single acceptors[4] or from a double acceptor coupled with an isoelectronic defect[9,16] remains an open question.

ACKNOWLEDGMENTS

We are indebted to T. D. Harris for supplying the MBE-grown GaAs sample discussed here. This work was supported by the Natural Sciences and Engineering Research Council of Canada.

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