Resonant excitation study of ultrasharp emission lines in ordered $Ga_xIn_{1-x}P$

B. Fluegel, S. Smith, Y. Zhang, A. Mascarenhas, J. F. Geisz, and J. M. Olson
National Renewable Energy Laboratory, Golden, Colorado 80401

(Received 29 August 2001; revised manuscript received 7 December 2001; published 28 February 2002)

Narrow-line photoluminescence in the below-gap spectral region of ordered $Ga_xIn_{1-x}P$ is investigated with high-spatial and -spectral resolution photoluminescence excitation and time-resolved spectroscopy. Sharp absorption lines are found both correlated and uncorrelated with emission lines, indicating multiple coupled systems. Saturation and temporal measurements support a quantum dot model.

DOI: 10.1103/PhysRevB.65.115320 PACS number(s): 78.66.Fd, 78.55.Cr, 73.20.Hb

I. INTRODUCTION

Spontaneous ordering in $Ga_xIn_{1-x}P$ (GaInP) results in a reduced band gap as well as a number of electronic and vibrational signatures of the reduced symmetry. Less understood is the appearance in the low-temperature photoluminescence (PL) of a spectrally broad peak approximately 40 meV (depending on growth conditions) below the band-gap excitonic transition. Because this broad peak is absent in randomly alloyed GaInP, it has been attributed to several possible order-related microstructure details. Recent micro-PL measurements[1,2] have shown that while the broad peak is spatially homogeneous on a macroscopic scale, extremely narrow linewidth PL peaks, which vary microscopically, appear in the same energy region and are only resolved with submicron spatial resolution measurements. Because of their δ-function spectral shape and apparent random spatial distribution, comparisons have been made with self-assembled quantum dots (SAQD's), and models of excitons spatially localized at order-related defects have been proposed.[2,3] At this point, the connection between the sharp lines and the broad low-energy peak is unknown. Their common spectral range and their clear connection with ordering first suggested that the broad peak is a continuum of unresolved lines. However, the broad peak is *not* observed to further decompose with lower excitation power or higher spatial resolution[1,2] and important differences have been seen in the magneto-PL behavior[2] of the two signals. In addition, no evidence exists for the coupling that would be expected between multiple states of a single quantum system. In this paper, we investigate these sharp line spectra by resonant excitation and by time resolving the PL.

II. EXPERIMENTS

Two single-variant ordered GaInP samples used here, previously described in Ref. 1, were chosen for their large domain size, ~ 0.5 μm. Details of the metalorganic chemical vapor deposition (MOCVD) growth are shown in Table I. To obtain subwavelength spatial resolution, the 10-μm-thick epilayer was coated with an opaque aluminum mask that contains 0.2-μm-diam holes. Individual holes were illuminated by a cw tunable or a picosecond pulsed laser focused through the window of a 4-K cryostat by a compensated objective. PL was collected in the backscattering direction, dispersed in a double spectrometer, and detected with a Si detector array or a GaAs photomultiplier tube. Similar PL, PL excitation (PLE), and time-resolved results were obtained from both samples.

III. RESULTS

A. Photoluminescence linewidth

Figure 1 shows the low temperature PL spectrum with cw excitation at the band-gap exciton absorption. The macroscopic signal from the unapertured area of the sample, Fig. 1(a), shows an excitonic peak and a broad featureless low-energy peak designated as the low-energy band (LEB). In contrast, the high-spatial-resolution signal from a 0.2-μm aperture, shown in the upper curve of Fig. 1(b), reveals a sharp peak at 1.8692 eV. This and other lines, designated the low-energy line (LEL), are similar to Refs. 1 and 2, but the 60-μeV linewidth is even narrower, limited by our spectrometer resolution. These results confirm the known spatial resolution dependence of the PL: i.e., we find that sharp PL lines begin to be resolved only when the spatial resolution approaches a few μm. This indicates that the LEL arises from excitons bound not to identical substitutional atoms, but instead to energetically variable defect sites whose density is on the order of the inverse aperture and collection size, i.e., 10^{14} cm^{-3}. Further information for the LEL is shown in the other curves of Fig. 1(b), where PL spectra are shown for increasing lattice temperature. The energetic position of the 1.8692-eV line shifts monotonically to the red with increasing lattice temperature, as shown in the inset. This narrow linewidth allows for a more precise determination of the temperature dependence than is usually[4] possible in band-gap exciton PL. Also shown in the inset is the full width at half maximum of this line, which increases by a factor of 2 during the temperature range covered ($T \leqslant 30$ K). In Ref. 2, no such temperature broadening was resolved, and this absence of inhomogeneous broadening in the spectral lines was inter-

TABLE I. MOCVD growth parameters for the two samples used. Both had a growth rate of 4 μm/h and a V/III ratio of 70.

Sample	Growth temperature	GaAs substrate	Orientation
1	690 °C	Si doped	$4° \rightarrow [111]_B$
2	680 °C	Semi-insulating	$6° \rightarrow [111]_B$

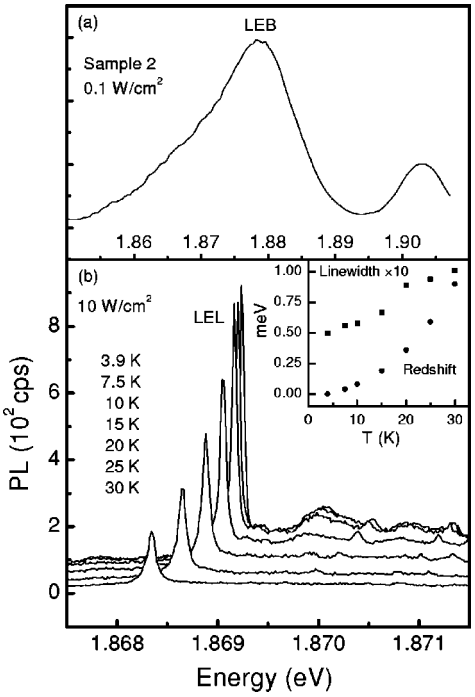

FIG. 1. (a) Macro-PL spectra cw excited at 1.908 eV. (b) Micro-PL from the apertured sample area at lattice temperatures from 3.9 K (largest) to 30 K (smallest). Curves are plotted on the same origin, i.e., *not* displaced. Inset: the linewidth and peak position relative to the 3.9-K peak are plotted as a function of temperature.

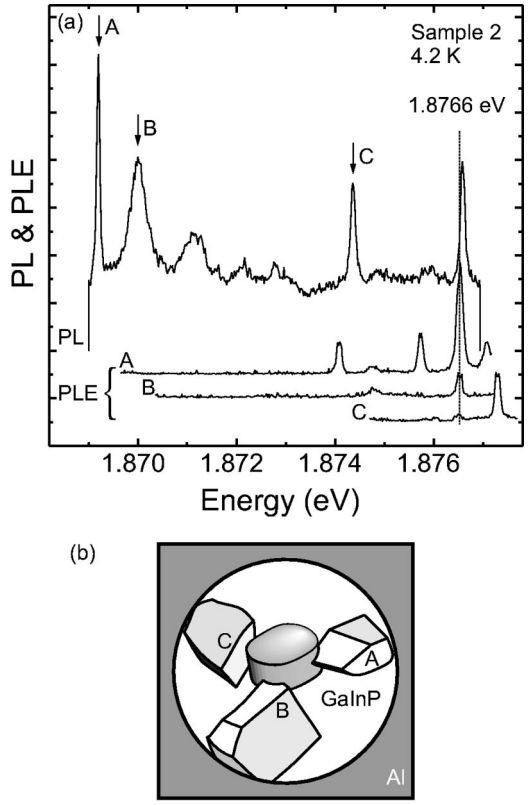

FIG. 2. (a) Sample 2 PLE (lower curves, displaced vertically) detecting at three energies *A*, *B*, and *C* in the PL spectra (upper curve). PL was excited at the exciton peak, 1.9015 eV. (b) Model of diffusively coupled localized regions in ordered GaInP. The shapes schematically represent localization sites of various possible geometries. Tunneling of the electron wave function is possible only between contiguous sites. Sites *A*, *B*, and *C* each emit at ground-state energies corresponding to the peaks in Fig. 2(a). The region labeled 1.8766 eV absorbs at this energy, and the generated excitons can transfer into *A*, *B*, or *C*.

preted as evidence for single quantum dots. The slight broadening of Fig. 1 does not contradict this conclusion, since it is due to acoustic phonon coupling to an isolated state, similar to an isolated impurity[5] rather than a thermal distribution within the line. Its intensity follows a temperature-dependent drop in quantum efficiency very similar to the LEB.

Despite having an experimental spatial resolution smaller than the typical domain size, we do not find apertures that exhibit a single LEL peak; nor do we find multiline patterns that repeat from one aperture to another. This may indicate energy levels that are strongly dependent on the individual defect geometry or a high density of defects. The latter may be expected from the bulk nature of the system. Unlike SAQD's, which are grown in a single two-dimensional (2D) sheet, the GaInP LEL arises from localization at defects throughout the 10-μm-thick epilayer, and spectroscopic measurements at these below-gap energies will penetrate into the epilayer. To further probe the nature of the LEL spectra, we use PLE spectroscopy to selectively excite possible ''excited states'' while looking for emission at selected lower-energy LEL lines.

B. Photoluminescence excitation

Figure 2(a) shows the PLE results. The signal level and spectrometer rejection allowed scanning to within 0.3 meV of the detection energy. Within this detection limit, no absorption peak can be distinguished from the PL peak: i.e., emission energies have a Stokes shift <0.3 meV from any possible corresponding absorption energy, which indicates that the sharp line originates from the recombination of a single exciton bound to a single-defect site.

At higher photon energies, several sharp absorption peaks appear in Fig. 2(a). In some samples, these are found to be as narrow as 0.1 meV, the resolution of the exciting laser. Their spectral location corresponds, in some apertures and samples, to higher-energy PL peaks while other PLE peaks show no correlation with PL peaks. For example, the 50-μeV mismatch between the PLE and PL peaks at 1.8766 eV in Fig. 2(a) is repeatable and above experimental error, indicating that their proximity is probably accidental. Figure 3, in contrast, is an example of an aperture where PLE lines very closely overlap the LEL, as indicated by the dotted vertical lines. Carriers excited at these higher-energy PL lines transfer to lower states, e.g., from 1.9081 to 1.9053 eV, and the excitation occurs at the PL energy to within our laser resolution. This spectrally coincident absorption and emission without a measurable Stokes shift indicates that this transfer rate is comparable to the radiative rate.

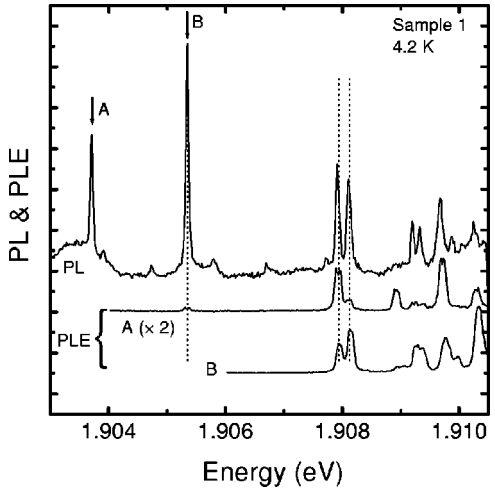

FIG. 3. Sample 1 PLE (lower curves, displaced vertically) detecting at two energies *A* and *B* in the PL spectra (upper curve). PL was excited at the exciton peak 1.927 eV.

Because our ensemble of sample apertures does not show a pattern of common energies or common energies differences, it cannot be determined whether the LEL's of Fig. 3 are the ground and excited states of a single localized system or instead multiple systems capable of carrier transfer. Multiple independent systems are required to explain the data of Fig. 2(a). PLE was measured for detection at the three different PL peaks indicated with vertical arrows. A common excitation is found at approximately 1.876 60 $\pm 0.000\,02$ eV: i.e., all three detection energies are excited by pumping here, as would be expected if *A*, *B*, and *C* were ground and excited states of a single QD. However, this model is not supported by the individual excitation curves: peak *A* is not excited from excitation at *B*, and peak *B* is not excited from *C*. A simple explanation of this using multiple localization sites is shown in Fig. 2(b) where spatially separate sites border each other within the aperture. These shapes are highly schematic, representing various possible line, point, or plane defects in the CuPt ordering, and the intersection between some shapes indicates that these pairs have an overlapping electron wave function resulting in the tunneling of carriers. Here 1.8766 eV excitation is absorbed in the central site, where excitons can then transfer within the radiative decay time into regions *A*, *B*, and *C* that emit at the energies shown in Fig. 2(a). No transfer is possible between *A*, *B*, and *C*, hence no cross excitation is possible among them. A similar phenomenon has long been observed for the excitation transfer among different spatially random distributed impurity sites, for instance, in nitrogen-doped GaP,[6] where an energy transfer was observed for an impurity-center concentration comparable to that of the defect concentration in these ordered samples. This type of energy transfer has been intensively studied for many 2D distributed systems (e.g., in quantum wells with lateral fluctuations and quantum dots), as well as some 3D systems involving impurities.

C. Saturation and time-resolved PL

As noted above, the LEL behavior varies with spatial location across even the same sample. In a third aperture, we again found sharp PLE lines, but in this case, no common excitation energies for different PL peaks and no cross excitation from one PL line to another. However, in this particular aperture, the saturation behavior of the LEL PL resembles, as previously noted in a cw measurement,[2] the multiexciton emission of InAs/GaAs SAQD's.[7] Figure 4 shows these intensity-dependent PL spectra. The first LEL peak to appear, 1.8713 eV, saturates at higher power and even loses amplitude as other LEL peaks appear. Similar results in Ref. 7 were attributed to emission from multiexciton states where exchange energies result in different emission energies for each successive recombination. In particular, the power dependence of the pair of lines labeled *A* and A' in Fig. 4 strongly resembles the lowest-energy group of Ref. 7, which had a separation of 3.5 meV. Cross excitation from *A* to A' would not be expected because of the exchange energy. A key point in the identification of multiexcitonic states, however, would be the time evolution of the PL. Emission from a particular state will not occur until the number of electron-hole pairs decays to the appropriate upper level. With saturating excitation and within one energy group, the lowest-energy line will reach a temporal maximum first and higher-energy lines will have a delayed maximum.[7] Figure 5(a) shows time-resolved PL from the two lines of Fig. 4 using time-resolved single-photon counting with an excitation density of 1 μJ/cm^2. The higher-energy line *A* is seen to peak 300 ps after the lower-energy line A', in qualitative agreement with the multiexciton model.

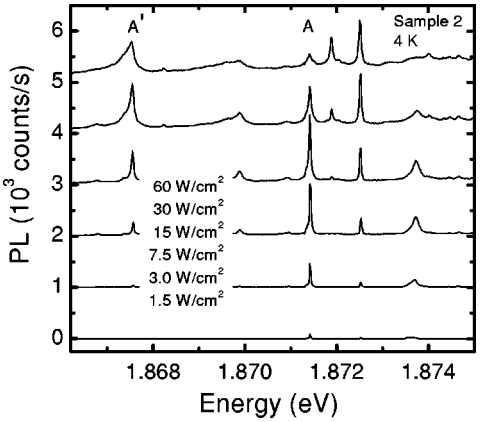

FIG. 4. Excitation-power-dependent PL spectra, exciting at 1.9015 eV. Curves are displaced vertically with increasing excitation power from the lower to the upper curve.

D. Decay rates

The LEB emission has been previously time resolved[8,9] and found to be nonexponential with decay times that depend strongly on excitation power and detection energy. For very low excitation density, decay times of 10^{-4}–10^{-3} sec have been reported, and this has motivated spatially indirect models for the origin of the LEB PL. This same evidence was applied to the LEL PL in the calculation of a spatially indirect ''sequence mutation'' quantum dot that explains long-lifetime sharp-line PL.[3] However, until now, no time-

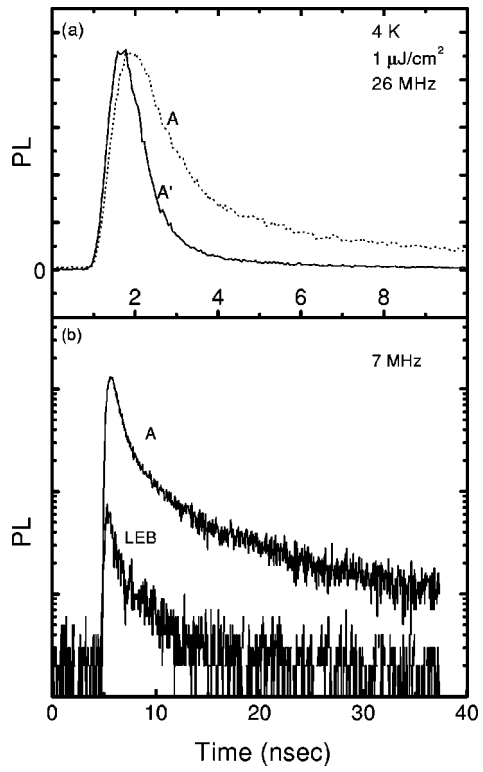

FIG. 5. (a) Normalized time-resolved PL at two LEL peaks of Fig. 4. (b) Logarithmic plot of the PL decay at the ground-state peak and at the LE band.

resolved measurement has been made on the LEL PL as distinct from the LEB PL. In fact, Ref. 2 has emphasized the different nature of the two emissions as demonstrated by magneto-PL. This raises the question of their possible temporal differences.

Figure 5(b) shows a time-resolved comparison between the 1.8714-eV PL line and a similar bandwidth of the nearby LEB continuum. The results are strongly nonexponential and show that the LEL has an initial decay in 1 ns and a longer signal extending to tens of ns. The smaller curve shows the decay of the LEB band and is very similar to the LEL. Other PL lines and other apertures showed similar results, with LEL initial decay times up to a few ns and LEB initial decay times within a factor of 2 of the LEL.

IV. DISCUSSION

The very efficient luminescence at low temperature suggests that the bound exciton decay is primarily radiative. In the temperature dependence of Fig. 1(b), the general increase of PL at lower temperatures results from the freezing out[10] of nonradiative recombination channels $\nu_{\rm nr}$. This reduction of $\nu_{\rm nr}$ saturates at 10 K, and below that, only temperature-independent nonradiative channels are possible. Further evidence of the radiative decay ν_r is seen in the PLE. The PL magnitude obtained by directly exciting a strong LEL line and emitting at a small number of PL lines is nearly equal to that generated at the same energies by pumping at the exciton absorption. Accounting for the fraction of total exciton-pumped PL emitted by the LEL line gives an estimate for the LEL single-line absorption that is 10^{-2} that of the exciton peak. This surprisingly strong absorption points to a direct transition, a large dipole matrix element, and a rapid radiative recombination rate. Thus the short decay times of Fig. 5(b) become significant because they do *not* support a model of spatially indirect quantum dots as in Ref. 3.

In comparing our LEB decay with the published longer lifetimes, difficulties arise from the nonexponential decay and the very strong dependence on power and detection energy, as well as variations in sample quality. If we limit our discussion to modern samples with well-resolved excitonic PLE peaks such as Ref. 8, it can be seen from that data that ms lifetimes occur only in the lowest-energy tail states of the LEB, and in contrast, the $1/e$ decay time at the spectral peak is <1 μs. The samples used in this present work are even faster; by measuring a sample from Ref. 8, we find that under identical excitation conditions of 10^{-7} J/cm^2, our sample 2 had more than an order of magnitude faster decay. The nature of LEB may be very different for different growth facilities.

Our measured LEL characteristics are consistent with other works; however, the specific crystal faults that result in the strong exciton localization may differ. Antiphase boundaries were found to be correlated with LEL in Ref. 2; however, the present two samples and others similarly grown do not show this correlation. Other proposed localization mechanisms are the sequence mutations[3] and edge dislocations.[11]

V. SUMMARY

In summary, we have found sharp absorption lines in the low-energy spectral region of ordered GaInP, both coincident and noncoincident with the LEL PL lines, with some systems showing quantum dot behavior. There is an apparent similarity between the two LEL and LEB signals in their time decay and temperature dependence. However, the similarity is outweighed by other differences: the magneto-PL in Ref. 2, the saturation behavior of Fig. 4, and the complete absence of PLE from the LEB band. In no case could we find absorption between the discrete PLE peaks of Figs. 2 and 3. We therefore conclude that (1) the LEB and LEL signals originate from different sources and (2) the origins of the LEL are likely sample (growth) dependent, and this will have consequences for any attempt to give a unified theory[3] for the below-gap transitions in ordered GaInP. The implications of this study go beyond understanding the controversial origin of the below-band-gap emission in ordered GaInP. In fact, it supplies us with a model system for investigating the inter-defect-site energy transfer in a 3D system.

ACKNOWLEDGMENTS

We would like to thank H. M. Cheong for discussions, C. Kramer for growth of samples, and P. Ernst and C. Geng for use of their sample. This was supported by the U.S. Department of Energy under Contract No. DE-AC36-99GO10337.

[1] H. M. Cheong, A. Mascarenhas, J. F. Geisz, J. M. Olson, M. W. Keller, and J. R. Wendt, Phys. Rev. B **57**, R9400 (1998).
[2] U. Kops, P. G. Blome, M. Wenderoth, R. G. Ulbrich, C. Geng, and F. Scholz, Phys. Rev. B **61**, 1992 (2000).
[3] T. Matilla, Su-Huai Wei, and Alex Zunger, Phys. Rev. Lett. **83**, 2010 (1999).
[4] Yoshihiro Ishitani, Shigekazu Minagawa, and Toshiaki Tanaka, J. Appl. Phys. **75**, 5326 (1994).
[5] D. E. McCumber and M. D. Sturge, J. Appl. Phys. **34**, 1682 (1963).
[6] P. J. Wiesner, R. A. Street, and H. D. Wolf, Phys. Rev. Lett. **35**, 1366 (1975).
[7] E. Dekel, D. V. Regelman, D. Gershoni, E. Ehrenfreund, W. V. Schoenfeld, and P. M. Petroff, Phys. Rev. B **62**, 11 038 (2000).
[8] P. Ernst, C. Geng, F. Scholz, and H. Schweizer, Phys. Status Solidi B **193**, 213 (1996).
[9] M. C. DeLong, W. D. Ohlsen, I. Viohl, P. C. Taylor, and J. M. Olson, J. Appl. Phys. **70**, 2780 (1991).
[10] M. D. Sturge, E. Cohen, and K. F. Rodgers, Phys. Rev. B **15**, 3169 (1977).
[11] P. Ahrenkiel (private communication).