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Localization Behavior at Bound Bi Complex States in $GaAs_{1-x}Bi_x$

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Abstract

While bismuth-related states are known to localize carriers in $GaAs_{1-x}Bi_x$ alloys, the localization behavior of distinct Bi pair, triplet and cluster states bound above the valence band is less well understood. We probe localization at three different Bi complex states in dilute $GaAs_{1-x}Bi_x$ alloys using magneto-photoluminescence and time-resolved photoluminescence spectroscopy. The mass of electrons Coulomb-bound to holes trapped at Bi pair states is found to increase relative to the average electron mass in the alloy. This increase is attributed to enhanced local compressive strain in the immediate vicinity of the pairs. The dependence of energy transfer between these states on composition is also explored.

Ideally, the electronic structure of GaAs can be tailored by alloying with Bi. The addition of just one atomic percent Bi to GaAs induces a 88 meV decrease in the bandgap energy and a comparable increase in the spin-orbit splitting energy.[1,2] Tunability over a wide energy scale with only a small change in composition (and lattice constant) makes dilute bismide alloys good candidates for optoelectronic applications, including multijunction solar cells, infrared LEDs and lasers, and sensors. In reality, the behavior of these alloys is dominated by carrier localization and scattering. Photoluminescence (PL) peaks are typically very broad (> 60 meV), and their peak energies exhibit s-shaped temperature dependencies associated with de-trapping of localized carriers at higher temperatures.[3,4] It is generally understood that holes are localized at Bi pair, triplet and cluster states (hereafter referred to as Bi complexes) that are bound above the valence band edge, analogous to electron localization of N complex states bound below the conduction band edge in $GaAs_{1-x}N_x$.[5,6] However, localization behavior at Bi complex states has been difficult to probe, in part because the PL spectra rarely exhibit sharp emission features associated with individual complex configurations. Overlap between Bi complex states also tends to broaden their emission features in alloys with more than an atomic percent Bi. Consequently, it is known that hole localization and scattering at bound Bi complex states collectively plays an important part in the behavior of dilute $GaAs_{1-x}Bi_x$ alloys, but we know very little about the specific localization behavior at individual Bi complex states.

Recently, we have been able to improve the growth of dilute $GaAs_{1-x}Bi_x$ with less than an atomic percent Bi to the point where emission from several different bound Bi complex states can be clearly identified.[7,8] This improvement in material quality now allows us to more thoroughly explore carrier localization at isolated Bi complexes. In this letter, we present an investigation into the localizing potential of these states. Magneto- and time resolved PL measurements carried out at low temperature indicate that local strain around the Bi complexes alters the behavior of electrons that are Coulomb-bound to trapped holes. Additionally, high magnetic fields were found to restrict energy transfer between Bi complex states. These findings have interesting implications for the interpretation the behavior of $GaAs_{1-x}Bi_x$ alloys.

$GaAs_{1-x}Bi_x$ epilayers with 0.30 – 0.48% Bi were grown on semi-insulating GaAs substrates by molecular beam epitaxy following the procedure detailed in Reference 8. The samples with 0.30% and 0.46% Bi were grown under irradiation from a pulsed KrF excimer laser, while the sample with 0.48% Bi was sectioned from a part of the substrate that was not directly irradiated. Light-stimulated epitaxy of $GaAs_{1-x}Bi_x$ was found to enhance near band edge luminescence and alter the distribution of bound Bi-related states.[8] The compositions were verified by x-ray diffraction (XRD) measurements. Magneto PL spectra were measured at 1.5 K in a 65 tesla pulsed magnet at the National High Magnetic Field Laboratory at Los Alamos National Laboratory. Spectra were acquired continuously at 500 Hz throughout the 50 ms magnetic field pulse. The excitation source was a 515 nm solid-state laser. Laser light was delivered to the sample through a 550 micron diameter optical fiber at a total power of 1.8 mW, and the PL was collected through the same path. Time resolved PL (TRPL) spectra were measured at zero magnetic field at 4.9 K. Frequency-doubled pulses at 405 nm from a Ti-sapphire laser (~150 fs, 0.66 pJ/pulse) were used as the excitation source.

Magneto PL spectra for the three samples are shown in Fig. 1. The highest energy peak,

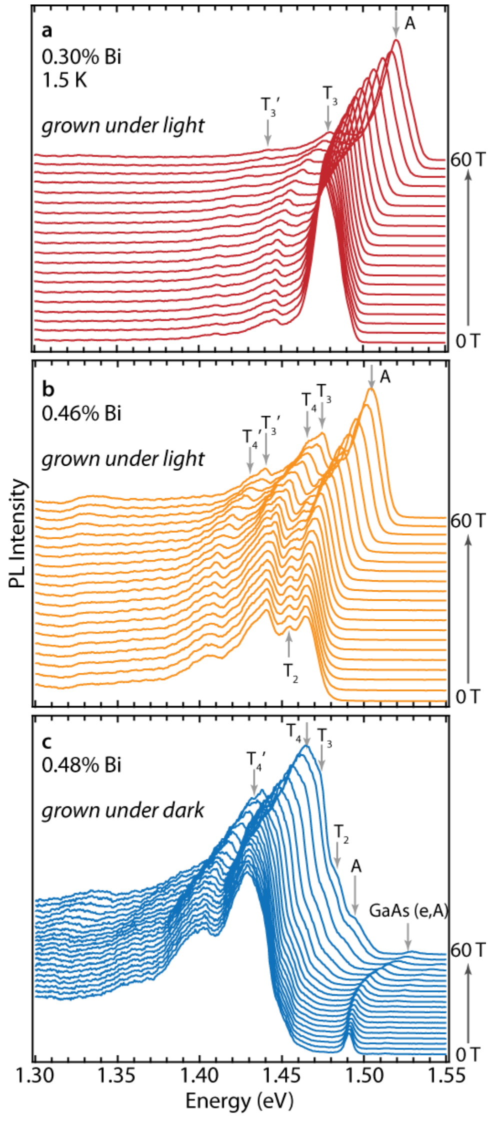

Fig. 1 Magneto-PL spectra between 0 T and 60 T for $GaAs_{1-x}Bi_x$ epilayer samples with (a) 0.30% Bi, (b) 0.46% Bi and (c) 0.48% Bi. The origins of the transitions are marked.

labeled *A*, follows the GaAs$_{1-x}$Bi$_x$ bandgap energy and is associated with recombination involving a shallow acceptor state. Similar transitions have been observed in GaAs$_{1-x}$Bi$_x$ samples reported in previous studies.[5] The nature of this transition will be discussed below. The peaks labeled T_2, T_3 and T_4 are attributed to recombination of excitons bound to Bi complex states.[7] Given their sharp emission peaks and proximity to the valence band edge, we speculate that they are associated with nearest or next-nearest neighbor pairs or triplets rather than larger clusters, although their exact configurations are not known. Phonon replicas of the T_3 and T_4 peaks, labeled T_3' and T_4', are also present in the spectra. We note that the T_2 peak in the sample with 0.46% Bi in Fig. 1b is difficult to see at high magnetic fields because it is slightly obscured in this plot by the *A* peak in the spectra measured at lower fields. In the sample with highest Bi concentration (0.48% Bi), peaks *A* and T_2 only emerge at high magnetic fields, and T_3 appears only as a shoulder on the T_4 peak.

We point out that, unlike the localized N-related complex states in GaAs$_{1-x}$N$_x$, the energies of the T_i peaks of GaAs$_{1-x}$Bi$_x$ shift with Bi concentration. This occurs because the conduction band edge of GaAs$_{1-x}$Bi$_x$ decreases with Bi concentration, and the conduction band to Bi complex state transition energy shifts accordingly.[7,9]

Diamagnetic shifts of the *A*, T_2, T_3 and T_4 PL peaks of the GaAs$_{1-x}$Bi$_x$ epilayers that could clearly be discerned are presented in Fig. 2 in addition to the PL peaks associated with the free electron to acceptor, (*e,A*), (see Fig. 1c) and neutral acceptor bound exciton A^0X transitions in the GaAs buffer (from spectra not shown in Fig. 1). The reduced masses, μ, were calculated by fitting the diamagnetic shifts across the entire magnetic field range to the exact numerical solution for an isotropic exciton in a magnetic field, given in Reference 10, which follows a quadratic dependence at low magnetic fields and a linear dependence at high magnetic fields. The fits are included in Fig. 2

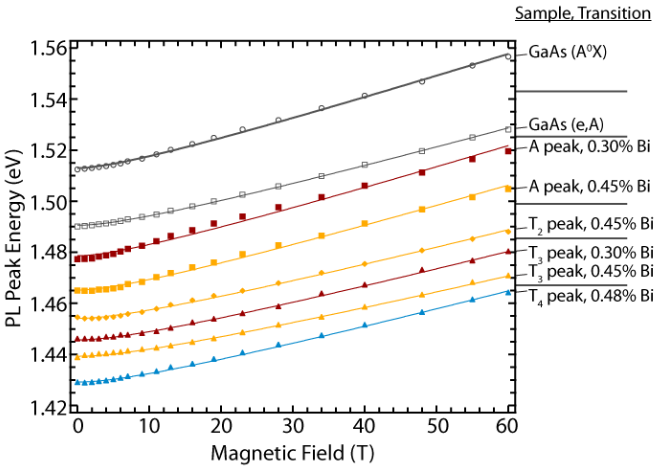

Fig. 2 PL peak energies as a function of magnetic field.

Table I. Reduced mass and radiative recombination lifetimes for two different time ranges after excitation pulse.

		Extracted Reduced Masses	Recombination Lifetimes	
	Transition	**μ (m_0)**	**τ (Early)**	**τ (Late)**
(A^0X)	GaAs	0.060		
(e,A)	GaAs	0.068		
A	0.30 %Bi	0.062		
A	0.46 %Bi	0.064	13 ns	
T_2	0.46 %Bi	0.073	24 ns	134 ns
T_3	0.30 %Bi	0.075		
T_3	0.46 %Bi	0.075	52 ns	173 ns
T_4	0.48 %Bi	0.071	63 ns	191 ns

* Determined in the high field range above 25 T.

for each transition and the extracted mass values are listed in Table I. The reduced mass determined from the diamagnetic shift of the GaAs (*e,A*) peak (0.068 m_0, where m_0 is the free electron mass) is roughly equal to that of the electron effective mass, m_e, in GaAs reflecting the fact that the energy of the acceptor-bound hole exhibits negligible diamagnetic shift compared to the conduction band.[11,12] Likewise, the reduced mass determined from the shift of the GaAs A^0X peak is 0.060 m_0. This is consistent with expectation for an exciton in GaAs with m_e = 0.068 m_0 and heavy-hole mass, m_h, = 0.51 m_0.[13]

The reduced masses extracted from the shift the $GaAs_{1-x}Bi_x$ *A* PL peaks fall in between μ for the (*e,A*) and A^0X transitions of GaAs and are close to the exciton reduced mass determined by magneto-PL measurements, reported in Ref. 14 for $GaAs_{1-x}Bi_x$ with 0.6% Bi measured at 200 K. We therefore assign the *A* peak in our samples to a shallow acceptor bound excitonic transition. The slight increase in μ of the *A* peak compared to the A^0X transition in GaAs is likely due to a combination of increases in m_e and m_h as well as exciton localization at potential fluctuations throughout the crystal. As reported in Ref. 15, low temperature Shubnikov-de Haas measurements show that the electron masses in $GaAs_{1-x}Bi_x$ films with less than 0.5% Bi increased slightly (~0.002m_0) compared to the GaAs reference. Bismuth-induced modification to the valence band structure is also expected to produce some increase in m_h, although reliable measurements of the magnitude of this increase have not yet been carried out.[16] Finally, exciton localization due to random alloy fluctuations and possibly even composition non-uniformities is also probable at 1.5 K, which can affect the PL peak diamagnetic shift. Due to this combination of factors, it is difficult to reliably extract both m_e and m_h values from the A peaks in these measurements.

The diamagnetic shifts of the T_2, T_3 and T_4 peaks are weaker than the A peaks. Assuming that the hole is completely localized at the Bi complex state such that its mass is effectively infinite[14], the increase in μ of excitons bound at these states reflects an apparent increase in m_e. These mass values vary between 0.071 and $0.075m_0$. Given that multiple measurements show that m_e only increases by ~$0.002m_0$ for Bi concentrations up to 0.5% Bi, the higher m_e values measured from the T_i transitions can only be explained by a change in the local environment that the electron observes in the presence of the Bi complex. In particular, the large Bi atoms introduce local compressive strain in the lattice, which has been experimentally observed in the electromodulated reflectance spectra of $GaAs_{1-x}Bi_x$.[17] Hydrostatic compressive strain is well-known to modify the conduction band structure and cause an increase in m_e in GaAs.[18,19] In the present case, compressive strain is most acute in the immediate vicinity of the Bi complexes, leading to a local modification of the conduction band structure and the mass of the Coulomb-bound electron. Using the pressure dependencies of m_e for GaAs[19], we estimate that a hydrostatic strain around a Bi complex required to cause an increase in m_e from $0.068m_0$ to $0.075m_0$ is roughly 0.8%. By comparison, the average hydrostatic component of the biaxial strain in these pseudomorphically strained epilayers is only 0.05% for a composition of 0.46% Bi. It is quite reasonable to expect that at a Bi complex, a Coulomb-bound electron with an orbiting radius of several nanometers could experience an average strain of ~0.8% given that individual Ga-Bi bonds are estimated to have ~7.5-8% strain.[17,20] It has been understood for some time that isoelectronic Bi impurities and bound Bi complex states profoundly affect hole behavior through modification of the valence band structure and localization, respectively.[21,22,23] However, these results provide experimental evidence that the electron behavior is altered in the immediate presence of Bi complex states as well.

Hole localization at bound Bi complex states also leads to long radiative recombination lifetimes.[22,24] Figure 3 shows the PL spectrum of the sample with 0.46% Bi as well as the PL decay curves from several distinct regions within that spectrum. The average power used during these measurements was low enough that the low energy Bi complex states were mainly populated, and the A peak was not fully excited. The radiative recombination lifetimes extracted from fitting the PL decay curves in Fig. 3b at two different time intervals are listed in Table I. Recombination from the A peak remained somewhat fast but non-exponential. Emission from progressively deeper states became increasingly slower. The T_2 peak also exhibited a very non-exponential decay, with lifetimes ranging from 24 ns at the beginning of the decay to 134 ns near the end. The decay curve

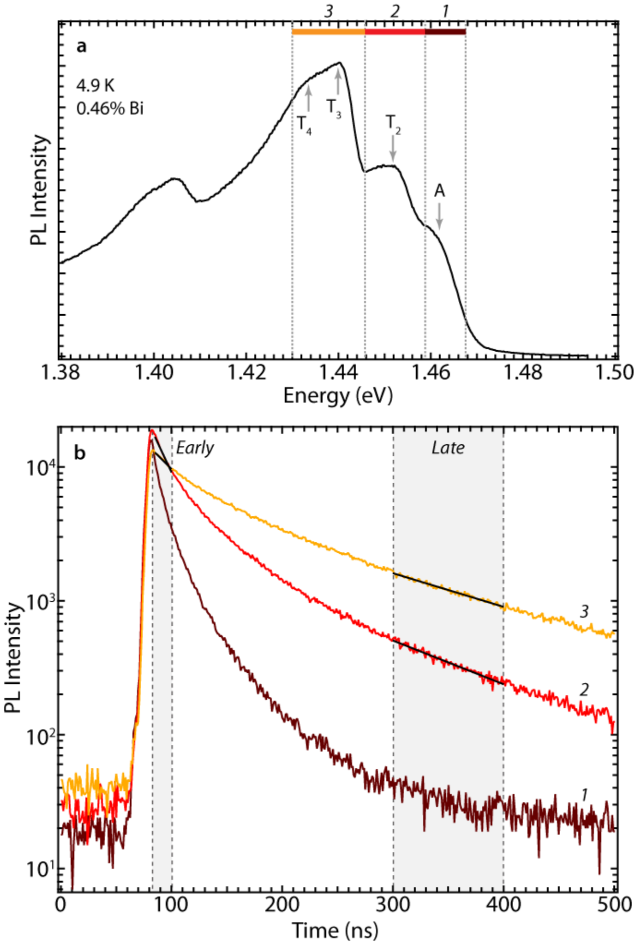

Fig. 3 (a) Time integrated PL spectrum of the sample with 0.46% Bi. (b) Time resolved PL decay curves for regions of the spectrum marked in (a).

of the T_3 peak was somewhat more exponential over a greater time range, but the lifetimes near the end of the decay curve reached similar values of 173 ns.

Radiative recombination lifetimes of free and shallow acceptor-bound excitons in MBE-grown GaAs is typically on the order of a few nanoseconds. The slightly longer and non-exponential decay of the *A* peak region (region *1* in Fig. 3a) suggests recombination dynamics are influenced by relaxation of excitons, otherwise referred to as energy transfer, to lower energy states as well as some localization. Excitons initially generated near the band edge can either radiative recombine over short timescales or hop to nearby states of lower energy, where they may recombine over longer timescales. This behavior has long been observed in dilute nitride alloys, such as $GaAs_{1-x}N_x$ and $GaP_{1-x}N_x$[25,26,27] and more recently in $GaAs_{1-x}Bi_x$.[28] Recombination of the shallow-bound excitons that contribute to the *A* peak is expected to occur on a relatively fast timescale, although some localization by band edge fluctuations associated with alloy disorder can cause the tail at long times in the PL decay curve. The longer lifetimes of excitons recombining from the T_2 (*2* in Fig. 3a) and especially T_3 and T_4 (*3* in Fig. 3a) states are typical in cases of strong hole localization at bound states above the valence band edge.[22,29] The slightly shorter and more non-exponential radiative decay from the T_2 state is also attributed to energy transfer to the lower energy states T_3 and T_4 states. The more exponential decay of the emission from the T_3 and T_4 states indicates that the energy transfer process to even lower lying states is less pronounced perhaps due to a lower density of T_3 and T_4 states and a lack additional transfer pathways.

While some amount of energy transfer is observed in the TRPL behavior of all samples studied here, evidence of substantial energy transfer can also be observed directly in the magneto-PL spectra of the sample with 0.48% Bi. Growth under nominally dark conditions appears to more strongly promote Bi pair formation[8], so this sample may have a greater distribution of Bi pairs compared to the sample with 0.46% Bi (nearly the same composition). Figure 1c shows that the T_2 and *A* peaks do not appear until higher magnetic fields above ~35 T. We suggest that the density of T_2 pairs has reached a point where overlap between states is sufficient enough to strongly promote energy transfer *through* the T_2 states to the lower-lying T_3 and T_4 states such that radiative recombination largely does not occur from the T_2 state themselves. High magnetic fields act to reduce the exciton Bohr radius, thus reducing overlap and restoring T_2 and eventually *A* emission. We have previously observed energy transfer through bound N pair states GaAsN[25,30] as well as the suppression of energy transfer in that alloy at high magnetic fields under similar experimental conditions.[31] In the case of $GaAs_{1-x}N_x$, the percolation of N pair states occurred around 0.23% N, whereas the present results suggest that energy transfer occurs at higher impurity concentrations > 0.46% Bi in $GaAs_{1-x}Bi_x$.

The magneto-PL and TRPL results presented here lead to two conclusions. First, the diamagnetic shift data suggests that local strain around the Bi pair states affects the behavior of Coulomb-bound electrons. Second, the evolution of the emission spectrum and radiative recombination lifetimes indicate that energy transfer through Bi pair states can substantially affect the optical properties of $GaAs_{1-x}Bi_x$. These two findings have interesting implications for the interpretation of $GaAs_{1-x}Bi_x$ behavior and our ability to tailor its properties. First, local compressive strain around Bi pairs will produce potential variations that will scatter electrons. Scattering will be especially apparent at low temperatures, which is consistent with previous electron mobility measurements of n-type $GaAs_{1-x}Bi_x$ epilayers.[32] However, these potential fluctuations should be considered at higher temperatures as well. Additional investigation is needed to determine the extent to which these effects influence the properties of $GaAs_{1-x}Bi_x$. Second, energy transfer enhances carrier localization, since it aids carriers in finding the deepest states in the lattice. The onset of energy transfer through bound Bi-related states at higher impurity concentrations compared to $GaAs_{1-x}N_x$, at least at the dilute Bi concentrations studied here, may make $GaAs_{1-x}Bi_x$ appear as a more attractive semiconductor alloy for long wavelength applications than $GaAs_{1-x}N_x$. However, significant energy transfer is still observed at higher Bi concentrations.[5]

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