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The use of a high magnetic field (57 T) to study the formation and evolution of nitrogen (N)

cluster and supercluster states in GaAs:N is demonstrated. A magnetic field- is used to lift

the conduction band edge and expose resonant N cluster states so that they can be directly

experimentally investigated. The reduction of the exciton Bohr radius also results in the

fragmentation of N supercluster states, enabling a magnetic field induced delocalized to

localized transition. The application of very high magnetic fields thus presents a powerful

way to probe percolation phenomena in semiconductors with bound and resonant

isoelectronic cluster states.

Alloying is the primary tool for tuning the electronic properties of semiconductors. In the ideal case of a dilute alloy, these electronic property adjustments result from bandstructure modifications generated by the random distribution of isolated substituent atoms.[1] However, isoelectronic impurity cluster states can also exert a profound influence on the electronic structure of the host semiconductor. This effect is well illustrated in the dilute GaAs:N alloy system. The addition of N to GaAs is known to result in a giant bandgap bowing as well as a severe degradation in the electron mobility.[2,3,4] Isolated N impurity atoms form a resonant state 150-180 meV above the GaAs conduction band edge that interact with the host electronic states and induce a continuous downward shift of the conduction band with increasing N concentration.[4,5] Nitrogen also has a propensity to form clusters, which generate stationary bound states just below the GaAs conduction band edge.[6,7] In the ultra-dilute limit (<0.1% N), localized N cluster states act as deep electron traps that degrade carrier transport. However, at higher N concentrations (> 0.2% N), the clusters interact with the downward shifting conduction band as it sweeps by them and exert a strong effect on the electronic properties.[8] Recent experimental results[9,10] reveal that the optical properties are profoundly altered when the localized cluster states overlap and percolate into a fully extended infinite supercluster, which hybridizes with the host conduction band states.[11,12] This percolation threshold is manifested in a massive and abrupt linewidth broadening of the E_0 and E_1 critical point energies that correspond to interband transitions at the Γ and X points of the Brillouin zone, respectively, and signals the evolution of the impurity-doped semiconductor into an alloy [9,10]

Unfolding the statistical evolution of N cluster states and their influence on the electronic and optical properties of GaAs:N is hampered by the difficulty in probing resonant impurity states as well as supercluster bound states.[7] At the higher doping concentrations (> 0.23% N) when the cluster states begin to exert a dominant influence on the electronic bandstructure, line broadening and spectral overlap obscures attempts at unraveling the individual cluster identities within a supercluster.[7] Resonant N cluster states have previously been detected by shifting them out of the conduction band with the application of high pressure, but this approach also distorts the alloy bond lengths.[6,13,14,15,16] We now report on the use of a high magnetic field to 1) eject resonant N cluster states from the conduction band and 2) tailor the spatial overlap of cluster exciton wavefunctions. Our approach now makes it possible to elucidate the evolution of N superclusters right through the onset of the percolation threshold.[9,10]

Dilute $GaAs_{1-x}N_x$ films were grown by molecular beam epitaxy (MBE) up to thicknesses of 300 nm. The compositions ranged between 0.04% and 0.41% N and were confirmed with x-ray diffraction measurements. Further details of the growths can be found in Ref. 17, and a comprehensive account of their optical properties can be found in Ref. 9 and 10. Magneto-PL measurements were carried out in a 60 T long pulse magnet using a solid-state laser (515 nm, 25 W/cm^2) to excite PL through a 550 μm diameter optical fiber coupled to the sample.[18] Spectra measured at 1.6 K for samples with 0.04% - 0.23% N are shown in Fig. 1. The low temperature and low power excitation density favor population of the localized N cluster bound states but preclude the detection of PL from extended states.[9,10] In the spectra in Fig. 1, the lowest energy extended states (as measured
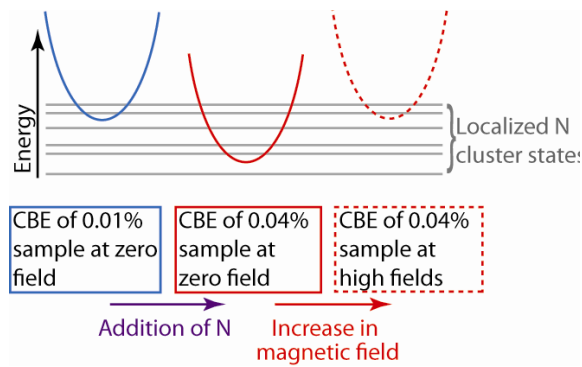
from the top of the valence band) exist in the conduction band in GaAs:N samples before the percolation threshold (N < 0.23%) but in the infinite N supercluster after crossing the threshold. PL peaks from these states will be denoted as *A* and *B*, respectively.[9,10] Zero-field spectra measured under a cw laser high power density of 900 W/cm^{2} so as to reveal the energy of peak *A* are shown for the samples with 0.04% and 0.12% N. In the case of the 0.23% N sample, higher power densities from a mode-locked Ti:sapphire laser were required to excite low temperature PL (peak *B*) from the fully extended infinite supercluster state.[10] The magneto-PL dependences of peaks *A* and *B* were therefore tracked using an elevated temperature of 115 K to populate the extended states.[19]   The energies of peaks *A* and *B* were adjusted to account for the temperature-induced bandgap difference between 115 K and 1.6 K and are marked
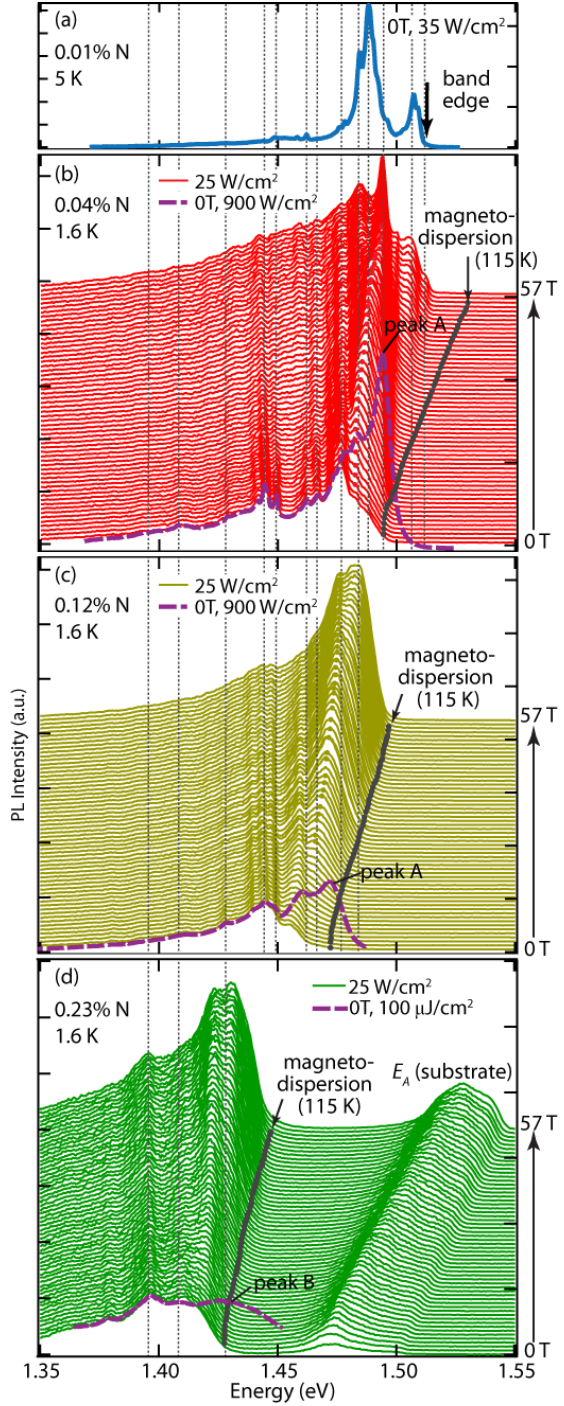
FIG. 1 (Color online). Low temperature PL of GaAs$_{1-x}$N$_x$. (a) 0.01% N measured at zero magnetic field. Magneto-PL spectra measured at fields up to 57 T are shown for samples with N compositions of (b) 0.04%, (c) 0.12% and (d) 0.23% N. Zero magnetic field spectra (dashed lines) measured at high laser intensities are included to show the relative position of peaks A and B (not to scale with the magneto-PL spectra). The magneto-dispersions of peaks A and B (measured at 115 K and shifted in energy to account for the temperature difference) are marked in black dots on the corresponding 1.6 K spectra.

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on the corresponding 1.6 K spectra in Fig. 1b-d.

The highest energy peaks that appear in the magneto-PL spectra in Fig. 1b,c under high magnetic fields are associated with resonant N cluster states that emerge out of the conduction band as bound states when the conduction band shifts to higher energy. The absolute energies of the N cluster states depend on the number of N atoms they contain as well as on their configuration in the lattice.[20] The cluster states at higher energies comprise a smaller number of N atoms but are statistically more abundant. The total N concentration in the $GaAs_{1-x}N_x$ alloy determines the relative position of the conduction band with respect to the N cluster states as well as the statistical distribution of cluster states on the anion sublattice.[7,21] Increasing the N concentration induces a downward shift of the conduction band edge, whilst the N cluster states remain fixed in energy.[7] Thus, a N cluster state that was bound at low N concentrations can become resonant with the conduction band at higher N concentrations if the band edge shifts to an energy below that of the cluster state. This is schematically illustrated in Fig. 2. An applied magnetic field reverses this trend; the conduction band is pushed upward in energy with increasing magnetic field, whilst the localized N cluster states remain dispersionless.[22] Each of the highest energy peaks that appear at high magnetic fields in Fig. 1 emerges from a N cluster state that was resonant with the conduction band at zero field. These can be

FIG. 2 (Color online). Schematic of the effect of composition and magnetic field on the relative positions of the conduction band edge (CBE) and localized N cluster states.

easily identified in the zero-field spectrum of the 0.01% N sample in Fig. 1a, where the conduction band edge lies at a higher energy than the 0.04% and 0.12% N samples. The application of a magnetic field therefore provides a powerful way to expose and study the effect of resonant levels on the electronic structure because it does not involve changing the chemical composition or local atomic environment (as in the case of externally applied pressure).
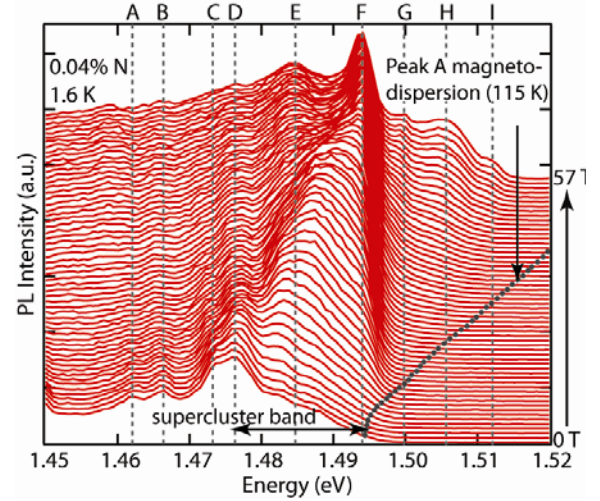
FIG. 3 (Color online). Magneto-PL spectra of the $GaAs_{1-x}N_x$ sample with 0.04% N. The magneto-dispersion of peak A (measured at 115 K and shifted in energy to account for the temperature difference) is marked by black dots.

Besides shifting the position of the conduction band edge so as to expose resonant states, the behavior and interaction of bound states comprising N clusters and superclusters may also be investigated using high magnetic fields. Figure 3 shows the 1.6 K magneto-PL spectra of the 0.04% N sample in Fig. 1b on a magnified energy scale. At low temperatures and zero-field, the lower energy cluster states are preferentially populated and exhibit no magneto-dispersion, indicating that they are highly localized. The higher energy cluster states near the band edge are more prevalent and are also the shallowest states. These states are located at discrete energies, but wavefunction overlap occurs between these states due to their large Bohr radius and close spatial proximity, resulting in the formation of a broad supercluster band (1.475 – 1.495 eV) as denoted in Fig. 3. The spectral weight initially favors the low energy side of this band since carriers are able to

diffuse to the lowest energy states that comprise this spectral region of the broad band.[10]

With increasing magnetic field, the conduction band edge shifts to higher energies and the

overlapping states in the broad band in Fig. 3 behave as deeper states. A concurrent

reduction in the Bohr radius of excitons trapped at the supercluster states increases their

binding energy and decreases the overlap between neighboring cluster states. At high

enough fields, overlap between neighboring cluster states is quenched, and the PL from the

now-localized cluster states forms narrow peaks with zero magneto-dispersion. With

increasing magnetic field, the deepest states succumb to localization first owing to their

greater inter-cluster distance (see line D), and the spectral weight of the broad band shifts

towards the higher energy states that still maintain some degree of spatial overlap and

provide fast recombination channels. With further increase in magnetic field, the next

highest energy states capitulate in succession (lines E and F) until all cluster states

comprising the superclusters (in the broad band that originated at zero-fields) become

localized. Note that the higher energy levels that emerge from the conduction band at high

magnetic fields (lines G – I) were never part of the broad band of PL from superclusters at

zero fields, but remain distinct and localized as they transform from resonant to bound

states.

The evolution of the magneto-PL spectra provides new insight into the behavior of

cluster and supercluster bound states in dilute isoelectronic alloys. Even before the N

cluster states percolate into an infinite supercluster, they form finite superclusters that

provide some degree of delocalized pathways for carrier redistribution from the

conduction band to lower energy cluster states. The application of a high magnetic field

enables the overlap of these cluster states to be tuned independently of isoelectronic impurity concentration. Consequently at high magnetic fields, delocalized pathways for exciton migration can be turned off via field-induced fragmentation of superclusters into individual localized cluster states. Examining the spectra in Fig. 1b-d, the behavior of the 0.12% N sample in Fig. 1c is similar to the 0.04% N sample in Fig. 1b. In Fig. 1c, the peak at 1.483 eV emerges at high magnetic fields from the conduction band whose position at zero field is denoted by peak *A*. But on increasing the nitrogen concentration to 0.23%, in Fig. 1d a peak denoting a cluster emerges at high magnetic fields at an energy of 1.431 eV that exactly coincides with the energy of peak *B* at zero magnetic field. Peak *B* had previously been identified with a newly formed band edge of delocalized states associated with N superclusters.[9] When the nitrogen concentration is increased, the transition from localized to delocalized states that give rise to peak *B* occurs at the percolation threshold for N cluster states when superclusters of infinite size develop.[9] The 1.431 eV peak can be identified as a cluster that at high magnetic fields fragments off the supercluster as it re-crosses the percolation threshold. This is a magnetic field-induced delocalized to localized transition

The application of a high magnetic field also provides insight into the influence of resonant N cluster states on the electronic properties of the conduction band. Previous reports in the literature have suggested that the incorporation of N cluster states into the conduction band with increasing N concentration or decreasing applied pressure induces substantial discontinuous changes in the electron effective mass.[14,23] This conclusion was drawn primarily from diamagnetic shift measurements of the free exciton peak when
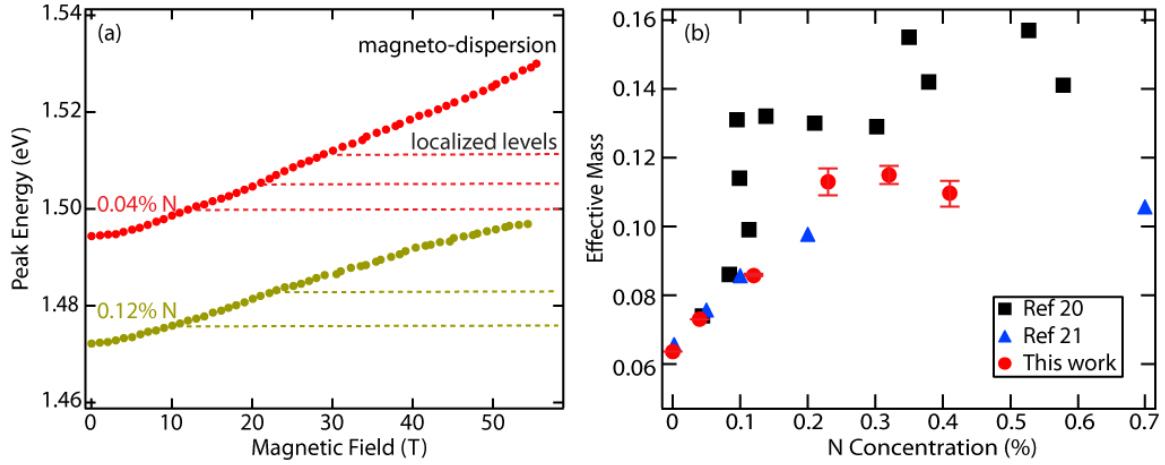
FIG. 4 (Color online). (a) Magneto-dispersions of peak A (115 K) and the energies of the localized levels that emerge from the conduction band at high magnetic fields (1.6 K). The peak A magneto-dispersions were shifted in energy to account for the difference in the temperature. (b) electron effective masses obtained from the diamagnetic shift of peaks A and B measured at 115 K. Values reported in the literature are also shown for comparison.

resonant N cluster states are ejected from the conduction band at high pressures.[14]

However, the magneto-PL measurements presented here suggest otherwise. Figure 4a

displays the magneto-dispersion of band edge exciton peaks for the 0.04% N and 0.12% N

samples measured at 115 K. The energies at which the resonant N cluster states transform

to bound states as the magnetic field is increased, are also indicated. It would be expected

that the slope of the diamagnetic shift would change as each resonant N cluster state

transforms to a bound state, provided that the resonant cluster states did indeed affect the

electron effective mass. But no significant changes in the slopes of the diamagnetic shifts

are observed in our measurements at high fields. Values of the electron effective mass as a

function of N concentration, calculated from the exciton reduced masses found using the

models of Cabib and Zhang and a hole mass of $0.53m_0$, are shown in Fig. 4b along with

those reported in the literature.[23,24,25,26] The present data follows the smooth trend

presented by Mori, *et al.* and does not exhibit the large discontinuous changes reported in

Ref. 23.[24] Presumably, the reason for this is that the relatively low density of impurity cluster states makes only a small contribution to the overall change in the conduction band density of states, while they would be expected to have a bigger impact on electron mobility. Since the application of a high magnetic field is capable of tuning the position of the conduction band relative to the N cluster states without altering bond lengths as occurs in high-pressure studies, it may provide a more accurate way of measuring the influence of cluster states on the electronic properties of dilute isoelectronic alloys such as $GaAs_{1-x}N_x$.

In summary, PL measurements at high magnetic fields provide new insights into the formation and evolution of supercluster states in GaAs:N. Reduction of the exciton Bohr radius results in the fragmentation of N supercluster states, enabling a magnetic field-induced delocalized to localized transition. High magnetic fields also provide an avenue for studying resonant N cluster states by ejecting them out of the conduction band. Finally, we find that the hybridization of localized N cluster states with the conduction band does not give rise to significant fluctuations in the electron effective mass. The ability to controllably adjust the overlap of impurity states presents a powerful avenue for investigating percolation-induced phenomena in a wide range of materials.

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