Photoluminescence from the nitrogen-perturbed above-bandgap states in dilute $GaAs_{1-x}N_x$ alloys: A microphotoluminescence study

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Using microphotoluminescence (μ-PL), in dilute N $GaAs_{1-x}N_x$ alloys, we observe a PL band far above the bandgap E_0 with its peak energy following the so-called E_+ transition, but with contribution from perturbed GaAs host states in a broad spectral range (>100 meV). This finding is in sharp contrast to the general understanding that E_+ is associated with a well-defined conduction band level (either L_{1c} or N_x). Beyond this insight regarding the strong perturbation of the GaAs band structure caused by N incorporation, we demonstrate that a small amount of isoelectronic doping in conjunction with μ-PL allows direct observation of above-bandgap transitions that are not usually accessible by PL.

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I. INTRODUCTION

Ga(In)NAs semiconductor alloys containing small amounts of nitrogen have attracted much attention due to their unusual physical properties.[1–4] In addition to the unusually large bandgap reduction with N incorporation,[1] a new electronic transition E_+ has been observed at energy far above the bandgap and shown to blueshift with increasing N composition in modulation reflectance[3,4] (MR) as well as other measurements (e.g., resonant Raman scattering,[5] ballistic electron emission microscopy[6]). The origin of E_+ has been a pivotal issue that affects the understanding toward many other important effects (e.g., the bandgap reduction and the effective mass change). Ever since it was first observed in electro- or photoreflectance,[3,4] the view upon the origin of E_+ has remained highly controversy. Because of its differential spectroscopy nature, MR typically yields a relatively sharp E_+ feature,[3,4] and has therefore created the impression that E_+ is associated with a well-defined state in the conduction band: either the resonant N impurity state N_x in the band anticrossing model,[4,7] or the perturbed GaAs L point.[8,9] The key argument for the L point case was that as $x \to 0$, E_+ extrapolates to the energy close to that of the GaAs L point [at ~300 meV above the conduction band minimum (CBM)] rather than the generally accepted energy for N_x at ~180 meV above the CBM.[10] However, since the N_x level itself was extrapolated from the high pressure data and thus not without uncertainty, it was simply treated as a fitting parameter in the band anticrossing model. There is also some ambiguity in the exact position of the L point, which ranges from 1.815 to 1.84 eV at low temperatures.[11–13] Thus, arguments based on the energy position, as well as the pressure or temperature dependence, of the E_+ feature cannot unambiguously distinguish between the two cases if E_+ is to be associated with one well-defined state. An alternative explanation, based on an electronic band structure calculation using an empirical pseudopotential method,[14] has been offered, that is, E_+ corresponds to the upper edge of perturbed host states. In this work, by using microphotoluminescence (μ-PL), we show that N doping strongly perturbs the host states not just at the vicinity of the L point but in a rather broad spectral range, and MR only emphasizes a small portion of the perturbed states, while other measurements, which often yield somewhat different energy positions than MR does,[5,6] may instead probe these perturbed states differently. Thus, associating E_+ with a single state either N_x or the L point is inappropriate and can only hinder our understanding of the electronic properties of this nonconventional alloy. Although E_+ is indeed the result of perturbed host states, it does not represent the upper edge of perturbed host states.

Modulation spectroscopy is typically used for its high sensitivity in probing the energy of a critical point with singularity in the density of states. Photoluminescence (PL) is energetically less selective, but depends strongly on the thermal distribution of the carriers, and thus generally is not considered as a sensitive technique for probing the states far above the CBM, due to the fast hot-carrier relaxation time for most semiconductors. Despite the extensive studies on the GaAsN alloy and the fact that the E_+ feature has been observed routinely in MR measurements, there has been no report of any above-bandgap emission. By using μ-PL, we observe not only an emission band related to E_+ but also another one associated with the spin-orbit split-off valence band, $E_0+\Delta_0$, in $GaAs_{1-x}N_x$ alloys with x as low as 0.1%, exceeding the detection limit of MR (~0.2–0.3%).[7,8] This surprising finding on one hand is benefited from the higher excitation density and collection efficiency of the μ-PL, and on the other hand, directly manifests the strong perturbation of N doping to the GaAs host. Our results offer valuable insights into the electronic structure of this nonconventional alloy and demonstrate a very sensitive yet simple approach to study the high energy states above the fundamental bandgap in an isoelectronically doped system.

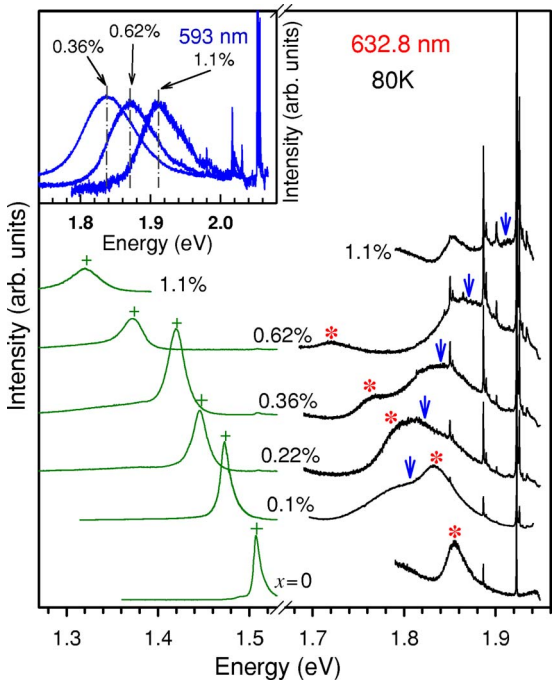

FIG. 1. (Color online) PL spectra of $GaAs_{1-x}N_x$ samples excited by a 633-nm laser at 80 K. The inset shows the PL spectra of three $GaAs_{1-x}N_x$ samples excited by a 593-nm laser. The arrows, stars, and crosses approximately labeled the peak positions of E_+, $E_0+\Delta_0$, and E_0, respectively. The spectra are vertically shifted for clarity.

II. EXPERIMENT

The $GaAs_{1-x}N_x$ samples investigated here, with x ranging from 0.1% to 1.1%, were grown by gas-source molecular beam epitaxy on semi-insulating (001) GaAs substrates. Four samples with $x=0.10\%$, 0.22%, 0.36%, and 0.62% all have an epilayer thickness of 400-nm and a 200-nm GaAs buffer. The epilayer thickness of the sample with $x=1.1\%$ is 100 nm with a 250-nm GaAs buffer and a 20-nm cap. The detailed growth process has been described elsewhere.[15] An undoped GaAs substrate is used as a reference sample ($x=0$). The μ-PL is measured by two micro-Raman systems, Dilor Super Labram (<800 nm) and Dilor HR(>800 nm), in a back-scattering geometry. The systems consist of a LN_2 cooled Si charge-coupled detector or a LN_2 cooled linear InGaAs array detector. A long-working-distance microscope with 50× objective lens is used for a spatial resolution of ~1.0 μm with high signal to noise ratio. The laser excitation wavelengths are 488 nm of an Ar^+ laser, 633 nm of a He-Ne laser, and 593 nm and 671 nm of two diode pumped solid-state lasers, respectively. The typical excitation density is about 100 kW cm^{-2}.

III. RESULTS AND DISCUSSIONS

Figure 1 shows the μ-PL spectra of $GaAs_{1-x}N_x$ samples with x varying from 0 to 1.1% at 80 K, excited by the 633-nm laser. Although only the 80 K data are presented in this paper, the PL line shapes at other temperatures (from 10 to 300 K) remain quantitatively the same as those of 80 K. The PL peaks below 1.55 eV labeled with cross (+) symbols are from the recombination near the fundamental bandgap E_0 of $GaAs_{1-x}N_x$.[16] The E_0 emission in $GaAs_{1-x}N_x$ ($x>0$) exhibits an asymmetrical line shape with a high-energy tail as that observed in bulk GaAs. In addition to the E_0 peak, $GaAs_{1-x}N_x$ exhibits a broad luminescence band that extends a few hundred meV above E_0 together with some sharp Raman lines. For the reference sample ($x=0$), a peak at 1.853 eV is found to exactly match the transition energy from the spin-orbit split-off valence band to CBM, i.e., $E_0+\Delta_0$, with $\Delta_0=0.346$ eV. For samples with $x>0$, the broad emission band in fact consists of two features. One of them, indicated by stars (*) in the figure, tracks E_0 closely with a constant separation Δ_0, and is thus identified as $E_0+\Delta_0$ in the alloy. Δ_0 has been found to be practically independent of x.[3] The other one, indicated by arrows (↓) in the figure, is found to continuously blueshift with increasing x. We believe that this feature is related to the E_+ transition and will be discussed in details below. The two features can be clearly resolved for samples with $x=0.1\%$, 0.36%, and 0.62%, but not resolved for the sample with $x=0.22\%$, which is near the crossing point of the two oppositely moving features. However, for $x=0.22\%$, they can still be separated by deconvolution. The coexistence of the two features in this sample can be further confirmed by varying excitation wavelength and density (to be discussed later). For the sample with $x=1.1\%$, the $E_0+\Delta_0$ feature of the GaAsN layer is too weak to be detected, and the luminescence peak at 1.853 eV is in fact the $E_0+\Delta_0$ mainly from the GaAs buffer layers. The E_+ feature for this sample as well as for those samples with $x=0.36\%$ and 0.62% has a strong interference from the Raman lines associated with the excitation energy. To unambiguously determine the peak position of E_+ for these three samples, a 593-nm laser is used for excitation, and the results are shown in the inset of Fig. 1. Interestingly, the E_+ band also exhibits an asymmetrical line shape with a higher energy tail, resembling that of the band edge emission. We notice that the bandwidth of E_+ is surprisingly large, exceeding 100 meV that is significantly larger than that of E_0, and seems not to vary significantly for the three samples ($x=0.36\%$, 0.62%, and 1.1%), as shown in the inset of Fig. 1.

Distinguishing E_+ from $E_0+\Delta_0$ at the dilute composition limit is critical for revealing the origin of the E_+ feature. We now examine the excitation wavelength dependence of the $x=0.22\%$ sample with unresolved $E_0+\Delta_0$ and E_+ as well as of the $x=0.1\%$ sample with the two less well-resolved features in Fig. 1. The results are shown in Fig. 2. An asymmetrical line shape function similar to that of the $E_0+\Delta_0$ peak in bulk GaAs is used for fitting the above-bandgap PL spectra of the 0.1% and 0.22% samples excited by 593-nm and 488-nm lasers, and the deconvolved spectra are shown in Fig. 2 with dashed curves. We assign the high-energy peak of the 0.1% alloy and the low-energy peak of the 0.22% alloy to $E_0+\Delta_0$, and the other peak to E_+. It is clear that the relative intensity of the two peaks is rather sensitive to the excitation energy. $E_0+\Delta_0$ is relatively enhanced under the near resonant excitation, independent of the relative energy position of the two features. A similar resonant effect for $E_0+\Delta_0$ is also observed in bulk GaAs, where a very weak $E_0+\Delta_0$ peak is

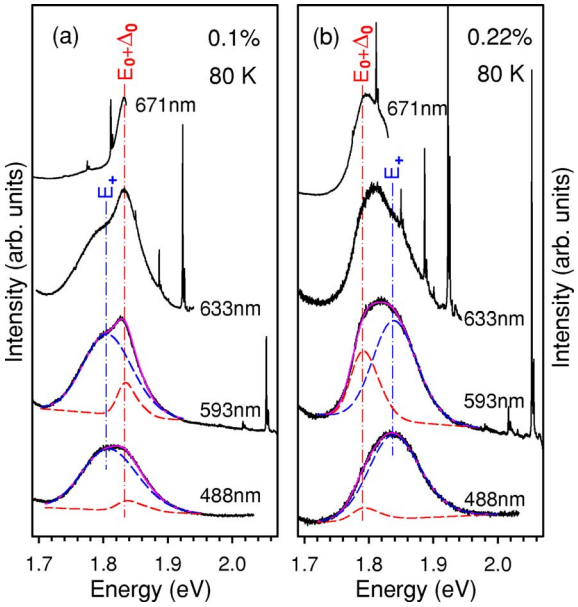

FIG. 2. (Color online) The excitation-wavelength dependence of the above-bandgap PL spectra of 0.1% and 0.22% GaAsN alloys. Two vertical dashed-dotted lines indicate the peak positions of E_+ and $E_0+\Delta_0$. The dashed curves show the deconvolved E_+ and $E_0+\Delta_0$.

observed for a 593-nm excitation in comparison with that excited by 633 nm, and it diminishes for the 488-nm excitation (data not shown). Therefore, the differentiation in their resonant behavior of $E_0+\Delta_0$ and E_+ makes it possible to reliably distinguish the partially overlapped $E_0+\Delta_0$ and E_+ bands in the region of dilute x. This result clearly shows that the bandwidth of E_+ still remains about 100 meV for x being as low as 0.1%, which is much greater than that of E_0.

Next we examine the excitation density dependence of E_+ and $E_0+\Delta_0$ for the two lowest x samples. Figure 3(a) shows the PL spectra of the $x=0.1\%$ sample excited by 633 nm under different excitation powers at 80 K. Although the peak positions vary very little with the excitation power, the relative intensity changes quite significantly, with $E_0+\Delta_0$ being more sensitive to the excitation density. E_+ becomes dominant at the lowest excitation power. The trend is also found true for the $x=0.22\%$ sample, as depicted in Fig. 3(b), despite E_+ is higher in energy, where a forbidden scattering configuration for longitudinal optical phonon at Γ point was used to avoid the strong interference of the Raman lines to the PL peak of E_+. The difference between E_+ and $E_0+\Delta_0$ in either the excitation wavelength or power dependence reflects the different kinetic processes for the two transitions: E_+ is related to the recombination between the high lying conduction band states and states near the valence band maximum, whereas $E_0+\Delta_0$ to the recombinations between the states near the CBM and the split-off valence band. In fact for the 0.62% sample, we have found that the integrated intensities of E_0 and $E_0+\Delta_0$ show nearly the same excitation density dependence, but very different from that of E_+.

Figure 4 summarizes the x dependences of the energies of E_0, $E_0+\Delta_0$, and E_+, along with the energies of Δ_0 and E_+-E_0 versus the bandgap reduction. Our results are in good

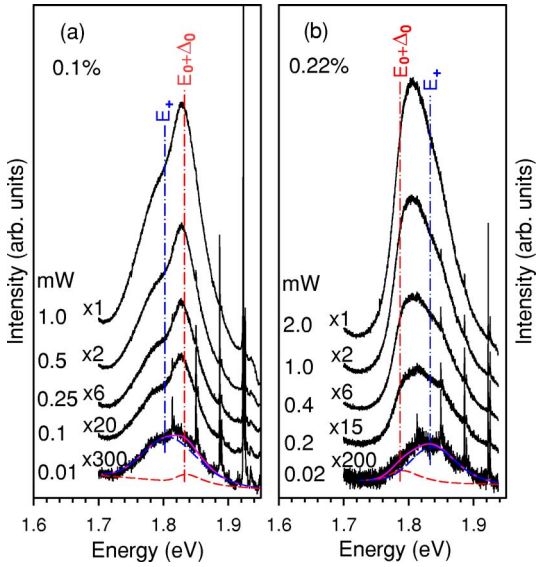

FIG. 3. (Color online) PL spectra of $GaAs_{1-x}N_x$ with $x=0.1\%$ (a) and 0.22% (b) under different excitation powers at 80 K. The positions of E_+ and $E_0+\Delta_0$ are indicated with vertical dashed-dotted lines. The dashed curves show the results of deconvolution.

agreement with those of previous electroreflectance measurement at 77 K or room temperature.[3,8] For E_+, linear extrapolation to the dilute limit yields $E_+(x=0^+)=1.806\pm0.003$ eV [dashed line in Fig. 4(a)], agreeing very well with the extrapolated value of the electroreflectance data.[8] Apparently, $E_+(x=0^+)$ is nowhere close to the generally accepted value 1.68 eV for N_x obtained below 10 K.[17] As a matter of fact, as shown by the PL spectrum in Fig. 1, even the lower energy tail of the E_+ band does not extend below ~1.7 eV for the

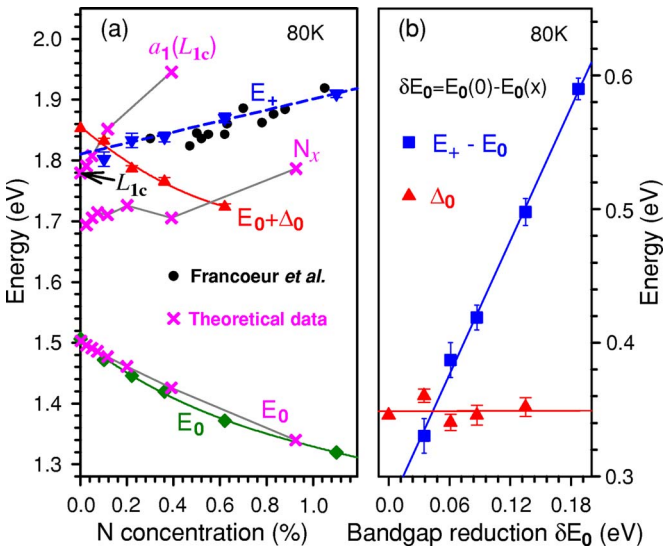

FIG. 4. (Color online) (a) Composition dependence of the optical transition energies in $GaAs_{1-x}N_x$ alloys ($0\leqslant x\leqslant 1.1\%$) measured by μ-PL at 80 K, compared with the theoretically calculated results for E_0, N_x, and $a_1(L_{1c})$ (shown by symbols "×"). The dashed line gives a linear fit to the E_+ data. The circles show the E_+ energies measured by modulated reflectance at 80 K of Ref. 8. (b) The energies of Δ_0 and E_+-E_0 as a function of the bandgap reduction.

sample with the lowest x of 0.1%. A recent pressure study has shown that the composition dependence of N_x is very small if any at such a low composition,[18] agreeing with the theoretical calculation.[19] We also notice that the bandwidth of E_+ is rather large, ~100 meV, much greater than that of E_0. If the x dependence of the N_x level is minimal (at least for the relatively low x region), one should not expect the N_x level would fluctuate much in a sample so as to induce a large bandwidth.

Because E_+ $(x=0^+)=1.806$ eV is very close to the L_{1c} energy of GaAs at 77 K,[11,20] a convenient explanation for the origin of E_+ would be that it is a transition involving the perturbed L_{1c},[8] as proposed by Gonzalez Szwacki and Bogulawski.[9] The underlying argument is that the impurity potential splits the L_{1c} quadruplet into an $a_1(L_{1c})$ singlet and a $t_2(L_{1c})$ triplet,[21] and the Γ component of the $a_1(L_{1c})$ allows the realization of the valence band maximum to L_{1c} optical transition. However, one should notice that this argument is only valid in a supercell calculation with the cell size being an even multiplication of the basic zinc-blende cubic unit cell. For an odd multiplication supercell, the L point will not even be folded into the Γ point.[22] To better understand the origin of the E_+ band, in Fig. 4, we include the theoretically calculated energy levels for E_0, N_x, and $a_1(L_{1c})$ for comparison. These results are obtained using a charge patching method based on a self-consistent pseudopotential approach within a local density approximation (LDA).[23] Empirical corrections to the nonlocal pseudopotential of Ga, As, and N are introduced to fix the LDA errors in the bandgap as well as the intervalley separations (e.g., Γ-L and Γ-X).[19] In a previous publication,[24] the calculated bandgap reductions in the dilute limit have been shown to be in excellent agreement with the experimental data. The N_x level is also found to agree quite well with the generally accepted one.[10] More significantly, the shift of N_x is found to be rather small for $x<0.5\%$, agreeing with the experimental finding that the shift of N_x is minimal if any at $x\sim0.1\%$,[18] which implies that the disorder induced energy fluctuation could not explain the large PL bandwidth of E_+. Also, on increasing x, the exact $a_1(L_{1c})$ deviates significantly from the peak energy of E_+, although they have the same starting point, L_{1c}. Therefore, a more realistic picture should be as follows: the E_+ band is comprised of the contributions of a fairly large set of conduction band states near the L point. These states are perturbed by N doping to different degrees. The broad PL band reflects the convolution of the effects such as the radiative decay rate and the relaxation process for such a set of perturbed host states. Because of the large density of states associated with the L point, the E_+ peak extrapolates to the energy of L_{1c} in the dilute limit. Even though the E_+ transition is indeed associated with the perturbed host states, neither the E_+ energy determined by the modulation spectroscopy nor the peak position of the E_+ emission band reported in this work can be interpreted as the upper edge of perturbed host states. Therefore, this μ-PL study offers a much clearer picture than other techniques and theories, as to what extent the conduction band states have been affected by N doping in terms of the energy range, and indicates that any model based on a single state is unrealistic.

IV. CONCLUSIONS

In summary, the microphotoluminescence (μ-PL) technique has been applied for investigating the evolution of the above-bandgap luminescence in dilute $GaAs_{1-x}N_x$ alloys $(0.1\leqslant x\leqslant 1.1\%)$. Two above-bandgap emission bands are observed, with one being identified to involve the spin-orbit split-off valence band and the other to involve a collection of perturbed conduction band states near the L point. This study illustrates that with the incorporation of a small amount of isoelectronic impurities in a semiconductor, above-bandgap luminescence can be readily measured by μ-PL, which thus offers a relatively straightforward way to study the electronic structure (e.g., the critical point energy) far away from the band edge.

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