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Impurity-Band Model for $GaP_{1-x}N_x$

B. Fluegel, Yong Zhang, J. F. Geisz, and
A. Mascarenhas

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B. Fluegel, Yong Zhang, J. F. Geisz, and A. Mascarenhas
National Renewable Energy Laboratory, Golden, CO, angelo_mascarenhas@nrel.gov

ABSTRACT

Low-temperature absorption studies on free-standing $GaP_{1-x}N_x$ films provide direct experimental evidence that the host conduction-band minimum (CBM) near X_{1C} does not plunge downward with increased nitrogen doping, contrary to what has been suggested recently; rather, it remains stationary for x up to 0.1%. This fact, combined with the results of earlier studies of the CBM at Γ and conduction-band edge near *L*, confirms that the giant bandgap lowering observed in $GaP_{1-x}N_x$ results from a CBM that evolves purely from nitrogen impurity bands.

1. Objectives

Recently, several new approaches have emerged for high-efficiency solar cell design based on hetero-epitaxy of III-V semiconductors on Si. Some of these approaches are based on using the giant bandgap bowing in $GaP_{1-x}N_x$. An experimental investigation of the electronic properties of $GaP_{1-x}N_x$ is undertaken to determine if this material is better described as an impurity-band system rather than as an alloy. This study will indicate whether the material may be unsuitable for photovoltaic applications. This research relates to the Solar Program Multi-Year Technical Plan objective to increase the performance and lower costs of high-efficiency solar cells by identifying new materials and cell designs.

2. Technical Approach

To probe the indirect (*X*) and direct (Γ) bandgaps of $GaP_{1-x}N_x$, optical absorption was measured on 2-μm-thick, metal-organic chemical vapor deposition (MOCVD) grown $GaP_{1-x}N_x$ epilayers that had been removed from their GaP substrates. For measurements near the indirect excitonic gap E_{gx}, additional samples about 100 μm thick grown by liquid-phase epitaxy (LPE) were also used. The growth and characterization of the MOCVD samples are described in Ref. 1. The epilayers were held freestanding in He vapor at 1.6 K, oriented at Brewster's angle with the light from a tungsten-halogen lamp. For the sensitive measurement of E_{gx}, the epilayer thickness was increased up to 10 μm, and multiple epilayers were stacked to increase the transmission length.

3. Results and Accomplishments

We performed a very precise study of the optical absorption in the vicinity of the indirect gap in dilute $GaP_{1-x}N_x$ where the evolution of the host states can be observed free from overlapping impurity absorption. In this dilute regime, the effect of the nitrogen-impurity-induced perturbation on the host CBM near X_{1C} causes a weak feature referred to as the A_X-line that is attributed to the threshold of the indirect free-exciton energy gap, E_{gx} to become observable in the low-temperature absorption spectrum.[2,3] This feature can be used as a marker for the position of the indirect gap near X_{1C} for dilute N samples as shown in the lower spectra of Fig. 2. The upper spectra track this gap energy as nitrogen is increased. The free-exciton feature, which is broadened as a result of scattering from nitrogen impurities, gets smeared out for concentrations beyond those shown. Figure 3 shows the variation of A_X with N composition in the range from 0.008% to 0.1%. The inset of Fig. 3 contrasts this variation with the variation of the bandgap estimated in Ref. 4 for this region. Evidently, in the 0.008% to 0.1% N composition range, A_X—and therefore, the host indirect CBM near X_{1C}—remains practically stationary, with no evidence of the host CBM plunging down—which, being a symmetry-induced effect should definitely have turned on in the very dilute range investigated. Figure 3 indicates that, were there to be any shift in the 0.008% to 0.1% composition range for $GaP_{1-x}N_x$, it would be two orders of magnitude smaller than that claimed in Ref. 4. This conclusion is based on the results for $GaAs_{1-x}N_x$,[5,6,7] where the repulsion turns on for *x* well below 0.001%, is linear up to ~1%, and only saturates at high nitrogen concentration.[8] A careful examination of the absorption spectra for the more dilute $GaP_{1-x}N_x$ samples in Fig. 1 of Ref. 4 reveals the absurdity of attempting to extract the position of the CBM by modeling the absorption onset, because the absorption from the A line increasingly predominates as the nitrogen concentration decreases. In fact, in ultra-dilute samples, this is the only remaining absorption.

The data of Fig. 3 show no evidence of the downward repulsion of A_X, and thus, contradict the claims of Refs. 4 and 9 for the rapid downward movement of the host CBM near X_{1C} with increasing N as the reason for the anomalous lowering of the bandgap observed for $GaP_{1-x}N_x$. However, our data corroborate the conclusions of the resonance Raman studies of Ref. 1 that the host CBM near X_{1C} remains stationary with increasing nitrogen content. These results for increased nitrogren doping can be combined with those of several other studies, namely: ellipsometry[10] and Raman studies[11] concluding that the E_1 transition—and hence, the conduction-band edge at L_{1C}—does not move rapidly downward; and the conclusions of Refs. 4 and 10 and the present study that the CBM at Γ_{1C} does not move rapidly

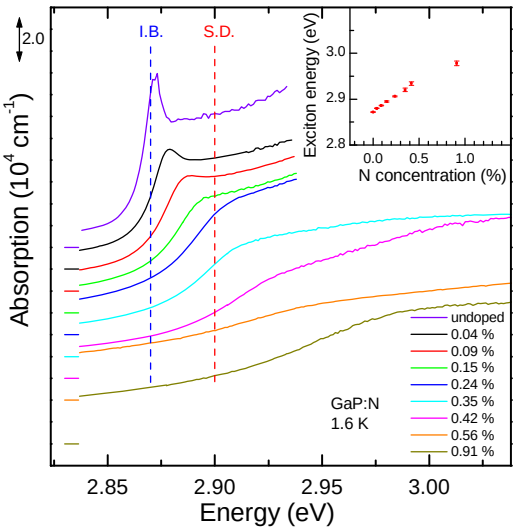

Fig. 1. Low-temperature absorption in the GaP:N direct-bandgap spectral region for increasing nitrogen concentration. Inset: Energy of the excitonic bandgap, $E_{g\Gamma}$, as a function of nitrogen concentration.

downward. Based on these results, we can now assert that: (1) none of the host CBMs plunge downward with increasing nitrogen doping, and (2) the CBM in $GaP_{1-x}N_x$ evolves solely from nitrogen impurity bands, as suggested earlier by resonance Raman studies.[1]

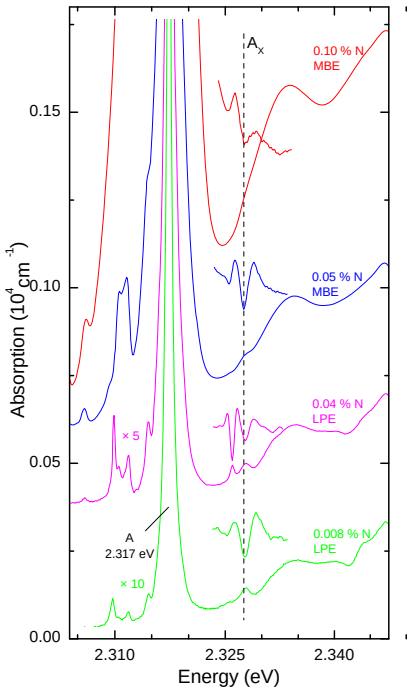

Fig. 2. Expanded plot of absorption near the indirect bandgap in four thick GaP:N samples. The indirect-bandgap exciton is identified by the A_x peak and marked by the vertical line at 2.3275 eV. Limited-range spectra for each sample show the normalized second derivative of absorption used to precisely locate A_x.

4. Conclusions

Our results challenge the validity of the BAC and polymorphous models for $GaP_{1-x}N_x$, but corroborate the conclusion of Ref. 12—that it is unrealistic, due to the dissimilarity between $GaP_{1-x}N_x$ and $GaAs_{1-x}N_x$, to seek a universal model for the bandgap lowering that applies to both the isoelectronic doping systems.

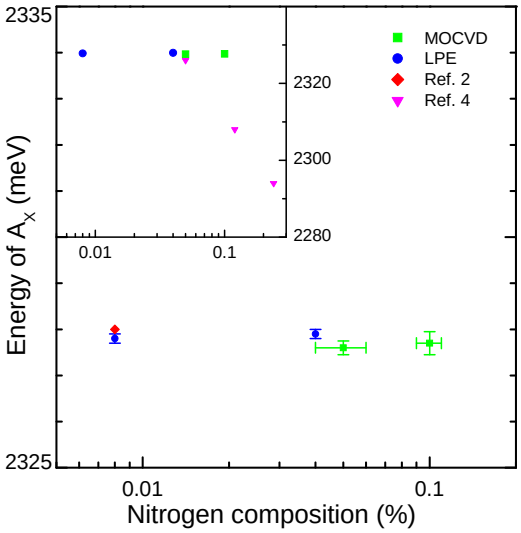

Fig. 3. Measurements of the indirect-bandgap exciton in Fig. 2 as a function of nitrogen. Inset: Vertical axis compressed to show the above data in comparison to the alloy bandgaps extracted from Ref. 4.

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