Impurity-Band Model for GaP\(_{1-x}N_x\)

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

Presented at the 2005 DOE Solar Energy Technologies Program Review Meeting
November 7–10, 2005
Denver, Colorado
NOTICE

The submitted manuscript has been offered by an employee of the Midwest Research Institute (MRI), a contractor of the US Government under Contract No. DE-AC36-99GO10337. Accordingly, the US Government and MRI retain a nonexclusive royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for US Government purposes.

This report was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or any agency thereof.

Available electronically at http://www.osti.gov/bridge

Available for a processing fee to U.S. Department of Energy and its contractors, in paper, from:
U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831-0062
phone: 865.576.8401
fax: 865.576.5728
email: mailto:reports@adonis.osti.gov

Available for sale to the public, in paper, from:
U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
phone: 800.553.6847
fax: 703.605.6900
email: orders@ntis.fedworld.gov
online ordering: http://www.ntis.gov/ordering.htm

Printed on paper containing at least 50% wastepaper, including 20% postconsumer waste
Impurity-Band Model for GaP$_{1-x}$N$_x$

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 freestanding 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 $\Gamma$ and conduction-band edge 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 heteroepitaxy 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 ($\Gamma$) 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. 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$_x$ where the repulsion turns on for $x$ well below 0.001%, is linear up to ~1%, and only saturates at high nitrogen concentration. 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 nitrogen doping can be combined with those of several other studies, namely: ellipsometry and Raman studies concluding that the $E_f$ 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 $\Gamma_{1C}$ does not move rapidly...
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.

ACKNOWLEDGEMENTS

The NREL work was partially supported by the DOE/EERE/NCPV and by DOE/SC/BES/DMS.

---

**ABSTRACT (Maximum 200 Words)**

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 $\Gamma$ 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.