Band structure of $In_xGa_{1-x}As_{1-y}N_y$ alloys and effects of pressure

E. D. Jones, N. A. Modine, A. A. Allerman, S. R. Kurtz, and A. F. Wright
Sandia National Laboratories, Albuquerque, New Mexico

S. T. Tozer and X. Wei
National High Magnetic Field Laboratory, Tallahassee, Florida

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$In_xGa_{1-x}As_{1-y}N_y$ is a semiconductor alloy system with the remarkable property that the inclusion of only 2% nitrogen reduces the band gap by more than 30%. In order to help understand the physical origin of this extreme deviation from the typically observed nearly linear dependence of alloy properties on concentration, we have investigated the pressure dependence of the excited state energies using both experimental and theoretical methods. We report measurements of the low-temperature photoluminescence of the material for pressures between ambient and 110 kbar. We also describe a density-functional-theory-based approach to calculating the pressure dependence of low lying excitation energies for low-concentration alloys. The theoretically predicted pressure dependence of the band gap is in excellent agreement with the experimental data. Based on the results of our calculations, we suggest an explanation for the strongly nonlinear pressure dependence of the band gap that, surprisingly, does not involve a nitrogen impurity band. [S0163-1829(99)03731-5]

A semiconductor alloy system, $In_xGa_{1-x}As_{1-y}N$, has been identified as a key candidate material for high-efficiency multijunction solar cells[1,2] and also for long wavelength laser systems.[3,4] The introduction of small amounts of nitrogen ($\approx 2\%$) in GaAs greatly reduces[5,6] the band-gap energy, with reductions approaching 0.5 eV. With the appropriate ratio of indium to nitrogen concentrations, $In_xGa_{1-x}As_{1-y}N_y$ can be lattice matched to GaAs. Lattice matching allows the design of multijunction solar cells without the inherent problems found in strained cells. Of prime importance is the role of the nitrogen isoelectronic atom: (1) What is the origin of the large band-gap reduction? (2) Are the states extended (bandlike) or localized (impuritylike)? In order to answer these questions, a better understanding of the electronic properties of this type of alloy system is required.

In the past, both first-principles[7] and empirical[8] theoretical treatments for this material system have concentrated on understanding the dependence of the band-gap energy on nitrogen composition. In this paper, we present pressure dependent photoluminescence (PL) data together with a first-principles local density approximation (LDA) calculation for the band structure and its pressure dependence. It will be shown that, while it is well known that band-gap energies calculated by the LDA method are not accurate, the predicted pressure dependence of the band-gap energy is in excellent agreement with experiment. Similar observations have been reported for silicon.[9] Because of this good agreement, the character of the states is accurately described and we also have confidence that this technique could be useful for understanding the properties of other low-concentration alloy systems.

The structures were grown in a vertical flow, high-speed rotating disk, EMCORE GS/3200 metalorganic chemical vapor deposition reactor. The $In_xGa_{1-x}As_{1-y}N_y$ films were grown using trimethylindium, trimethylgallium, 100% arsine, and dimethylhydrazine. Dimethylhydrazine was used as the nitrogen source since it has a lower disassociation temperature than ammonia and has a vapor pressure of approximately 110 torr at 18 °C. Unintentionally doped $In_xGa_{1-x}As_{1-y}N_y$ was p type. $In_xGa_{1-x}As_{1-y}N_y$ films for Hall and optical measurements were grown on semi-insulating GaAs orientated 2° off (100) towards ⟨110⟩. Lattice matched ($\delta a/a < 8\times 10^{-4}$) films were grown at 600 °C and 60 torr using a V/III ratio of 97, a DMHy/V ratio of 0.97 and a TMIn/III ratio of 0.12. The growth rate was 10 Å /s. These conditions resulted in films with an indium mole fraction of 0.07 ± 0.005 and a nitrogen mole fraction of 0.022 ± 0.003. The composition was determined by calibration growths of $Ga_xAs_{1-x}N$ and $In_xGa_{1-x}As$ along with double crystal x-ray diffraction measurements. The nitrogen composition of bulk films was also confirmed from elastic recoil detection measurements. A significant increase in photoluminescence intensity was observed from these films following a post-growth anneal. Ex-situ, post-growth anneals were carried out in a rapid thermal anneal system under nitrogen using a sacrificial GaAs wafer in close proximity to the $In_xGa_{1-x}As_{1-y}N_y$ sample. The photoluminescence intensity was a maximum for samples annealed either at 700 °C for 2 min or at 650 °C for 30 min. Similar results have been reported by Rao *et al.*[10] Transmission electron microscopy measurements indicate that the samples are random and no evidence for clustering or phase separation was observed.[11]

The pressure was generated using a small BeCu piston-cylinder diamond anvil cell, 8.75-mm diameter and 12.5-mm height.[12] Methanol, ethanol, and water in a ratio of 16:3:1 was used for the pressure medium.[13] The shift in the fluorescence of a small chip of ruby placed in the pressurized volume was used to calibrate the pressure at 4 K with an accuracy of ± 0.5 kbar.[14] A single 600-μm diameter optical fiber, butted up against one of the diamonds, brought the 1 mW of 5145-nm wavelength laser power to the sample and also collected the PL signal from the sample. A beam splitter system was used to direct the PL signal to an optical monochromator. Depending on the band-gap energy, two liquid-

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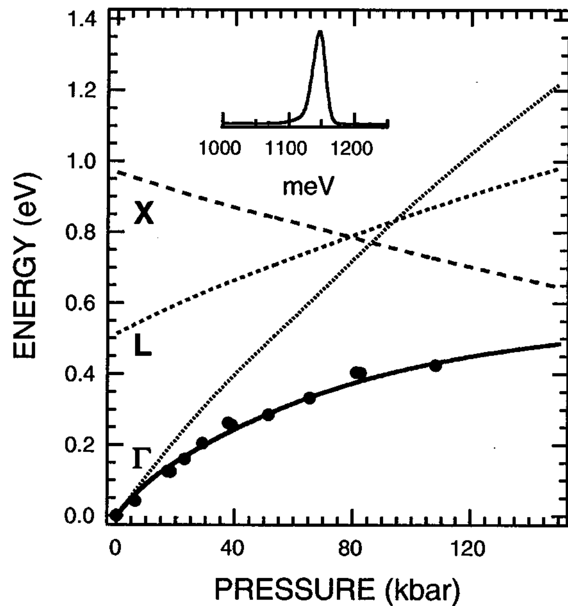

FIG. 1. Experimental (dots) and theoretical (solid line) dependence of the band-gap energy shift versus pressure at 4 K for 2% nitrogen in $In_xGa_{1-x}As_{1-y}N_y$. The dotted lines are the calculated pressure dependencies for the GaAs Γ, *L*, and *X* points. The vertical axes are offset by the respective $In_xGa_{1-x}As_{1-y}N_y$ and GaAs band-gap energies. The inset shows the 4-K ambient pressure photoluminescence spectrum.

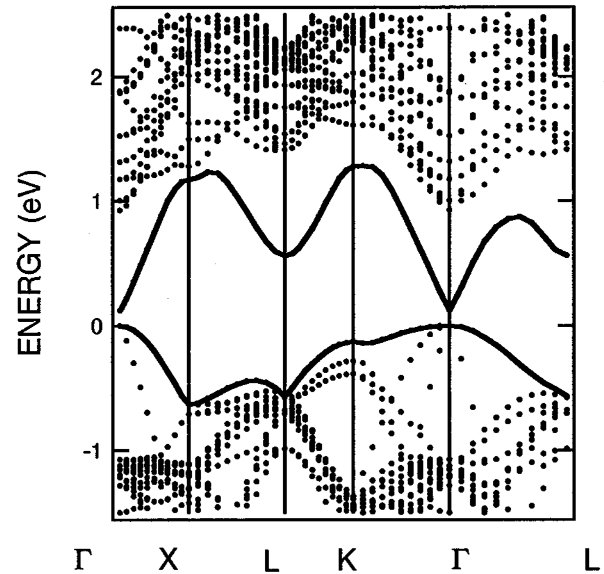

FIG. 2. First-principles local density approximation calculation for the band structure for 3.3% nitrogen $In_xGa_{1-x}As_{1-y}N_y$ alloy. The solid lines, top to bottom, are respectively the conduction and valence-band states.

nitrogen-cooled detectors were used to detect the PL signal. For low pressure regimes, where the band-gap energies were near or below 1 eV, a NORTH-COAST EO-817L Ge-detector was employed, while at higher pressures, a standard charge coupled device (CCD) array was used. A typical low-temperature (4 K) PL spectrum near 1.15 eV is shown in the inset of Fig. 1. The pressure dependence of the band-gap energy shift data, as measured by the peak of the PL spectrum, is shown in Fig. 1 as solid circles. The pressure data ranged between ambient and 110 kbar. The solid curve drawn through the data is discussed below. For comparison between the $In_xGa_{1-x}As_{1-y}N_y$ data and bulk GaAs, the calculated pressure dependencies for the GaAs Γ, *L*, and *X* bands are shown as dotted lines. The calculated pressure coefficients for these GaAs bands are in good agreement with experiment.[15] As can be seen in Fig. 1, the pressure dpendence of the $In_xGa_{1-x}As_{1-y}N_y$ band-gap energy is radically altered with the addition of a small (2%) amount of nitrogen.

In order to model the $In_xGa_{1-x}As_{1-y}N_y$ system, we used the Vienna *ab initio* simulation package[16] (VASP) to perform first-principles electronic structure calculations based on the Kohn-Sham density-functional theory with plane-wave basis sets, ultrasoft pseudopotentials,[17] and the local density approximation for the exchange-correlation functional. In construction of the pseudopotentials, the Ga $3d$ electrons were treated as valence electrons in order to accurately represent any effects of a near resonance with the N $2s$ level that has been observed in GaN.[18] We modeled the $In_xGa_{1-x}As_{1-y}N_y$ system in the experimentally relevant concentration range using a series of supercells of the zincblende GaAs structure each with a single As replaced by a N. The lattice constants of the supercells were varied to simulate the effects of pressure, and for each cell, the ionic positions were relaxed using first-principles forces until the residual forces were less than 20 meV per Å . In all cases, we found that the nitrogen atom remained in the symmetric position during relaxation. In order to compare to experimental data, which is taken as a function of pressure, an *ab initio* calculation of the system pressure was performed. We have investigated supercells with the following stoichiometries: $Ga_{32}As_{31}N$, $Ga_{64}As_{63}N$, $Ga_{108}As_{107}N$, and $Ga_{128}As_{127}N$. These cells correspond to nitrogen concentrations of 3.13, 1.56, 0.93, and 0.78 %, with the nitrogen atoms ordered in simple cubic, fcc, bcc, and simple cubic lattices, respectively. In contrast, the nitrogen atoms in the experimental system are believed to be nearly randomly distributed.[11] However, we found that calculated band structures of our supercells were qualitatively similar despite their differing symmetries, indicating that that the N atoms interact weakly with each other at these low concentrations. Therefore, we believe that our artificially ordered supercells provide an adequate model of the near-band-gap electronic structure of the disordered experimental system. Likewise, we have ignored the presence of In in the experimental system (except for indirect effects due to the change in lattice constant, as will be discussed below). This is justified since experimental studies of $In_xGa_{1-x}As$ alloys indicate that the low concentration of indium found in the experimental $In_xGa_{1-x}As_{1-y}N_y$ system has a small effect on the electronic properties.[3]

Figure 2 shows a representative band structure for the 3.13% system. It should be noted that the band structure is plotted with respect to the Brillouin zone of a 64-atom cell. Since the nitrogen substitution breaks the symmetry of the underlying zincblende structure, there is no uniquely defined way to ''unfold'' the band structure into the Brillouin zone of the primitive 2-atom zincblende unit cell. The high-

symmetry points of the primitive GaAs cell fold into the Γ point of the 64-atom cell, and therefore in the presence of a real symmetry breaking term (such as produced by nitrogen substitution), we can expect interaction between the resulting levels. The valence band and the conduction band are indicated with a heavy solid line. The conduction band is well separated from the other bands throughout most of the Brillouin zone, and it is quite dispersive with more than 1 eV of bandwidth. Likewise, the bands above the conduction band show a substantial amount of dispersion, and there is no evidence of a flat impuritylike band anywhere above the conduction band. The absence of a nitrogen derived impuritylike state is supported by a decomposition of the wavefunctions in terms of atomiclike orbitals, which shows that the conduction band has about 5% of its weight on the nitrogen atom, which is by far the highest fraction of any of the bands above the gap. The calculated band gap is only 0.12 eV, while the experimental band gap is of order 1 eV for this concentration of N. This large error in the band gap is a well-known problem of the LDA. A central result of this paper is that despite this large error in the absolute magnitude of the band gap, the *change* in band gap with lattice constant is in excellent agreement with experiment (see Fig. 1).

Figure 1 compares experimental data to results of our theoretical model. The agreement between theory and experiment is excellent. In order to make a meaningful comparison, some nontrivial analysis of the theoretical calculations is required. The basic principle of this analysis is to treat the lattice constant and N concentration as independent variables, while the band gap and pressure are treated as dependent variables. The dependent variables are then shifted to remove known LDA errors. In order to obtain results applicable to the 2.0% experimental nitrogen concentration, the band gap and the pressure are linearly interpolated between the results of 128-atom (1.56% N) and 64-atom (3.13% N) supercells for each lattice constant. Then, results obtained at the experimental lattice constant of GaAs are taken as the reference (assumed to correspond to the experimental zero of pressure), and we plot the change in band gap against the change in pressure. This procedure compensates for two well known errors of the LDA: (1) The band gap is severely underestimated, as discussed above. (2) The lattice constant is underestimated by about 1%. The second error may seem to be insignificant compared to the errors in LDA results for some other quantities, but it corresponds to about a 20-kbar error in pressure, which is significant on an experimental scale. Since the experimental GaAs lattice constant is used, this procedure also helps to implicitly compensate for neglecting the In, which is added to the experimental system to match the lattice constant to that of GaAs.

The approach described here could prove useful for similar systems. However, we believe that a reason for the success of our approach is that, with the exception of the largest N concentration at the largest lattice constant, all of our model systems have a positive band gap. Previous first-principles calculations for the $Ga_xAs_{1-x}N$ system[7] have used high nitrogen concentrations in order to obtain smaller model systems, which are computationally less demanding. At these higher concentrations, the LDA band-gap error is so severe that computed band structures do not have a band gap. This artificial band-gap collapse leads to unphysical occupations of the electronic states (i.e., conduction-bandlike states are occupied, while valence-bandlike states are unoccupied), producing a significant error in the electronic charge density. In this regime of strongly negative LDA band gaps, we are not confident that our simple LDA-based approach to computing the pressure dependence of excited state energies could be applied fruitfully.

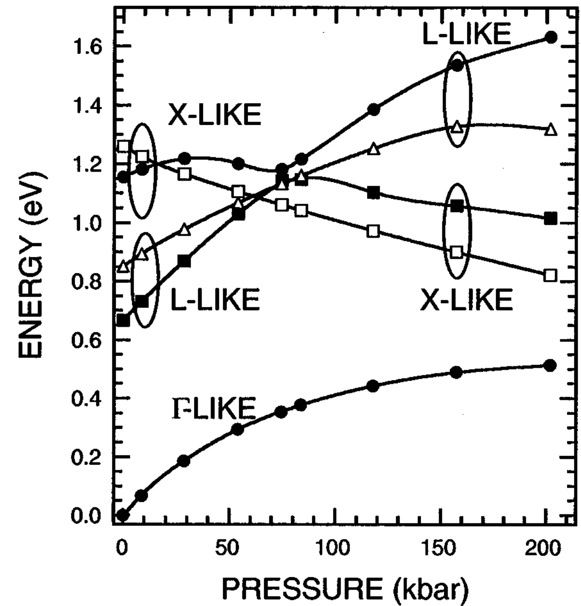

FIG. 3. Theoretical pressure dependence of the conduction bands near the band-gap minimum for 2% nitrogen $Ga_xAs_{1-x}N$ alloy. The points are calculated and there are three singlets (filled points), a doublet (open squares), and a triplet state (open triangles). The figure shows the avoided crossing between the *X*- and *L*-like bands as well as the repulsion between the Γ- and *X*-like bands.

A remarkable feature of Fig. 1 is the strongly nonlinear dependence of the gap on the pressure. This is in marked contrast to the parent GaAs material and provides additional evidence, beyond the large reduction in the band gap, that a few percent of nitrogen is producing remarkable changes in the material. In order to understand this nonlinearity, it is necessary to study additional bands above the conduction band. Figure 3 shows the theoretical pressure dependence of the Γ-point energies of several additional bands treated with the same analysis that was used for the conduction band in Fig. 1. Eight energy bands of the system are shown, but these fall into five degenerate groups. The figure shows three singlet states (filled circles), a doublet (open squares), and a triplet state (open triangles).

A common origin of nonlinear behavior of energy levels as a function of a parameter (such as pressure) is band repulsion. Band repulsion results from the mixing (hybridization) of bands in the same representation of the crystal symmetry group in such a way that level crossings are replaced with nonintersecting horizontal curves separated by a gaplike region. In Fig. 3, the highest singlet on the left and the triplet on the upper right bend downward due to repulsion from higher energy bands that have been omitted from the figure in order to improve its clarity. Whether the upper two singlets cross or repel at about 80 kbar cannot be determined

from the limited number of points that we have calculated, but if they repel, the effect is not very strong. We have chosen to show the bands as crossing in order to aid the eye in following their relationship with the doublet and the triplet. These assignments were chosen by comparing our results for various nitrogen concentrations with results for pure GaAs with the appropriately folded Brillouin zone. This comparison also allows useful, but nonrigorous, assignments of the low-energy $Ga_xAs_{1-x}N$ bands at the Γ point to special points of the primitive 2-atom GaAs Brillouin zone that are folded into the Γ point. For the bands shown in Fig. 3, we propose the following assignments: (1) The bottom singlet corresponds to the Γ point of the fundamental cell. (2) The second singlet on the left hand side (the third singlet on the right) plus the triplet correspond to a split quartet formed from the 4 L-points (111), $(1\bar{1}\bar{1})$, $(\bar{1}1\bar{1})$, and $(\bar{1}\bar{1}1)$. (3) The remaining singlet plus the doublet correspond to a split triplet consisting of the three *X* points (100), (010), and (001). In regions of band repulsion, for example, the character of different bands becomes mixed, and thus these assignments should not be taken too literally. However, we feel that they provide useful labels and help in interpreting the data.

With one exception, all of the bands within a few eV of the gap are observed to regain the degeneracies of pure GaAs to within of a few hundredths of an eV by the time our largest cell (0.78% N concentration) is reached. The exception is the *L*-derived singlet, which remains split off from the triplet by about 0.1 eV. This suggests that this singlet may evolve into the impurity state observed at very low N concentrations.[19,20] However, as mentioned above, this state does not act like an impurity state at the technologically interesting concentrations around 2%. Furthermore, the *L*-derived singlet rises faster than the conduction band throughout the studied pressure range, and we do not see the upward curvature that would be expected if it was repelled by the conduction band. Therefore, we believe that repulsion between the *L*-derived singlet and the conduction band contributes at most a small amount to the nonlinearity of the conduction band. In contrast, Fig. 3 demonstrates almost textbook repulsion between the *X*-derived singlet and the conduction band at pressures over 100 kbar, and it is likely that this repulsion continues to lower pressures, even though the effect is obscured by the additional repulsion between the *X*-derived singlet and a higher state. Based on these observations, we propose that repulsion from the *X*-derived singlet is the chief cause of the experimentally observed nonlinear dependence of the band gap on pressure. Based on the above, we conclude that the nonlinear dependence of the band gap on pressure does not result from localized nitrogen states. Finally, we note that our results are consistent with recent reflectance measurements, which show some of the predicted higher energy states.[21,22]

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