

June 2004 • NREL/SR-520-36318

Growth and Characterization of GaN As(P) for High Efficiency Solar Cells

**Final Subcontract Report
29 July 1999–28 September 2003**

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Abstract

Scanning Tunneling Microscopy (STM) and Ballistic Electron Emission Microscopy (BEEM) have been used to characterize $\text{GaN}_x\text{As}_{1-x}$ and $\text{GaN}_x\text{P}_{1-x}$ as a function of composition. The reduction in band gap has been measured. Detailed studies of the band structure as a function of N composition has led to a basic understanding of the materials system. The major results of this work include: (i) determination of relative contributions of the Γ - and L-like bands of $\text{GaN}_x\text{As}_{1-x}$ to the BEEM spectra; (ii) determination of the composition dependence of the Au/ Γ - and L-like bands of $\text{GaN}_x\text{As}_{1-x}$ Schottky barrier height; (iii) development of a model to describe the BEEM results at nonepitaxial metal/semiconductor interfaces; and (iv) ballistic electron emission spectroscopy studies of $\text{GaN}_x\text{P}_{1-x}$ samples which demonstrated possible splitting in the degeneracy of the X valley due to the nitrogen. The data were qualitatively described by the recent perturbed host states model of Kent and Zunger.

Project Objective

To characterize $\text{GaAs}_{1-x}\text{N}_x$ and $\text{GaP}_{1-x}\text{N}_x$ alloys using STM/BEEM. To understand the origins of the giant band gap bowing of these compound semiconductor alloys as a function of nitrogen concentration.

Accomplishments

The funding provided through the sub-award from the University of California at Santa Barbara has led to the following significant accomplishments:

1. The STM/BEEM technique has been developed to a high degree of perfection for studying the Schottky barriers and band structure of a range of compound semiconductor alloys that have been of interest to NREL for many years because of their potential applications to solar cells. The technique was perfected through initial studies of the prototypical alloy system $\text{Ga}_x\text{Al}_{1-x}\text{As}$ where the band structure is well known¹ through other spectroscopic techniques. Two major reviews^{2, 3} highlight how this technique can be used for such studies.
2. Having developed a basic understanding of the BEEM technique and its capabilities for studying the band structure, we began a systematic investigation of $\text{GaAl}_{1-x}\text{N}_x$ alloys grown by Molecular Beam Epitaxy (MBE) by Professor Charles Tu at UCSD. During the 2000-2001 time frame we made a series of BEEM measurements of such structures⁴ ranging in composition from $x=0.003$ to $x=0.02$; that is, nearly an order of magnitude. The BEEM spectra clearly showed bands that evolve markedly as a function of nitrogen concentration. Two peaks that could be identified as Γ and L bands were observed, as shown in Fig. 1 for the room temperature BEEM spectra. As the nitrogen concentration increased, the energetic separation between these peaks was found to increase and with a decrease in the

relative contribution of the L band. The Schottky barrier for the Au/GaAsN was found to decrease markedly with nitrogen concentration. The observed Schottky barrier reduction followed the decrease in the Γ - band.

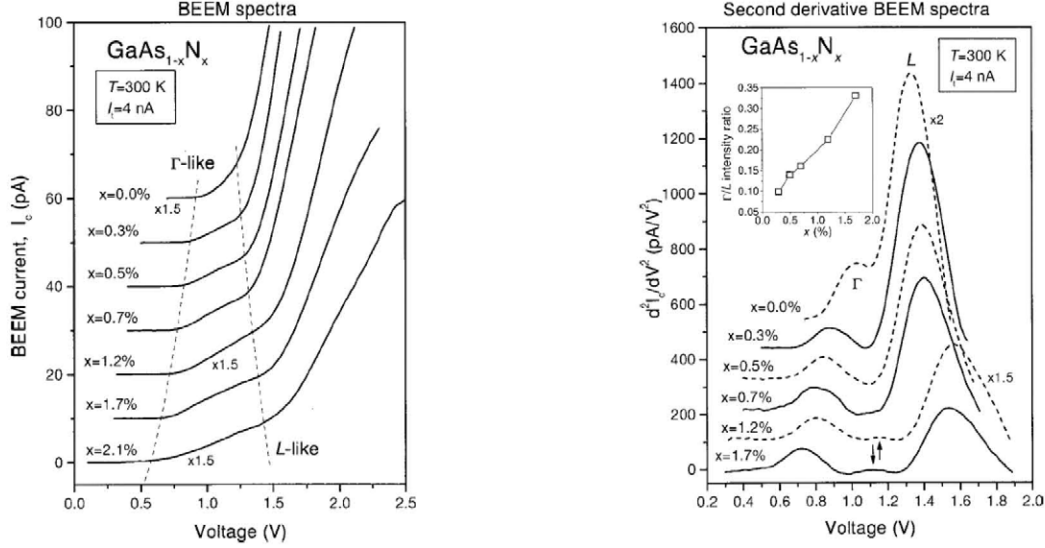


Figure 1 (left) Room temperature BEEM spectra of GaAs_{1-x}N_x for seven different nitrogen compositions; (right) second derivative (SD) BEEM spectra. The inset shows the ratio of the Γ -like peak to the L-like peak as a function of nitrogen content.

A particularly interesting feature of the BEEM data was the observation of a weaker 3^{rd} band for $X=0.012$ and 0.017 and placed approximately ~ 0.40 eV above the Γ band. The BEEM data are the only means to observe such effects and have been interpreted as a splitting of the four-fold L valley into the $a_1(L_{1c})$ singlet and $t_2(L_{1c})$ triplet states. The BEEM results also provided strong evidence for a model of nitrogen induced Γ -L mixing as an explanation for the giant band gap reduction in such alloys.

3. Having developed a basic understanding of GaAsN we explored the comparison case of GaN_xP_{1-x}. This is a particularly interesting case because GaP is an indirect bandgap semiconductor (see the left panel of Fig. 2 for the GaP band structure) as distinct from the direct bandgap material GaAs. The evolution of the band structure⁵ was again studied as a function of nitrogen composition. Typical BEEM spectra are shown in the right panel of Fig. 2. Considerable structure was observed with the dominant X band being the lowest state and moving downwards in energy by as much as 300 meV for 3% N. Additional fine structure was interpreted as a splitting in the degeneracy of the X-valley due to the perturbation in the GaP lattice by nitrogen alloying.

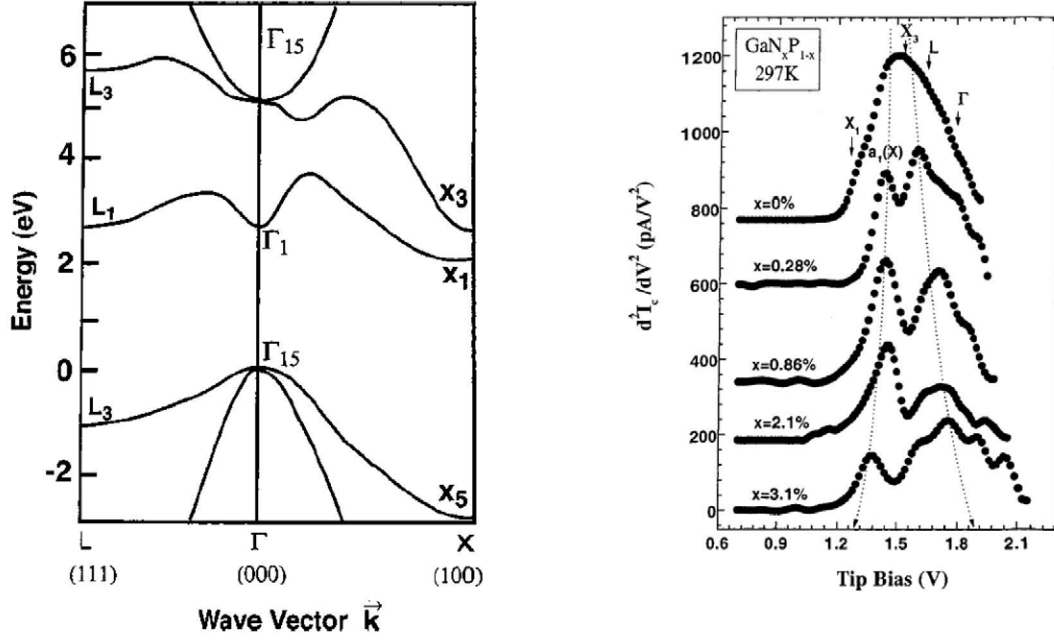


Figure 2 (left) Band structure for GaP. Note, the material is an indirect gap semiconductor and the conduction band minimum occurs at the X-point. (right) BEEM spectra for six different nitrogen compositions in $\text{GaN}_x\text{P}_{1-x}$. Note the downward motion of the X band with increasing nitrogen content. Additionally, note the correspondence of the BEEM peak positions and the band positions shown on the left.

The perturbed states were qualitatively compared with the theory of Kent and Zunger⁶. The ordering of the primary conduction band X_{1c} , X_{3c} , L_{1c} , and Γ_{1c} of states of GaP are shown on the left hand side of Fig. 3. The nitrogen derived states, $a_1(N)$, $a_1(X)$, ... etc., are shown in the right hand side of Figure 3.

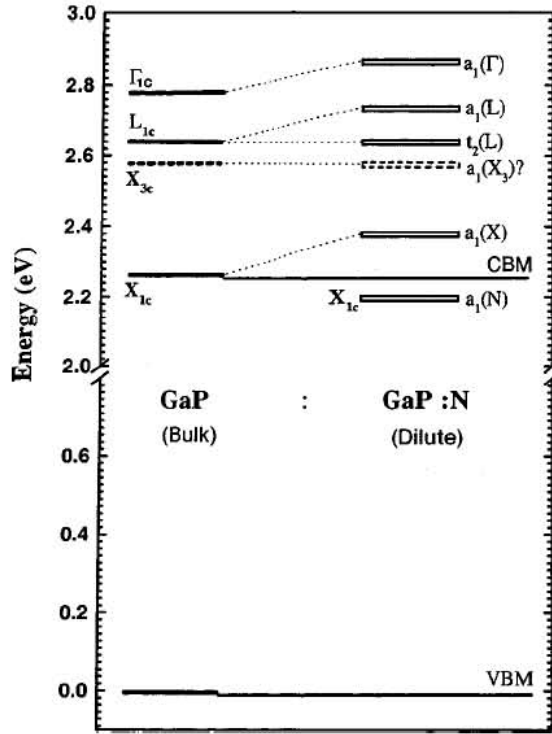


Figure 3
Schematic of a possible ordering of the X, L, and Γ valleys in pure GaP against GaP:N system under dilute N compositions. Considering the large scattering in the reported values for the relative position of the X_{3c} valley, the possibility for the intermixing of X_{3c} and L_{1c} valleys is not ruled out.

4. The BEEM measurements provide a unique and important compliment to optical studies. The selection rules for BEEM are different and allow one to see both direct and indirect dimensions. Combining BEEM with optics would therefore be important to do. We have recently succeeded in seeing BEEM luminescence⁷ from GaAs samples and we can now begin to study simultaneously transport and optical properties.
5. We developed an interface scattering model to describe BEEM results from nonepitaxial metal/semiconductor interfaces. The model starts with a Hamiltonian consisting of the sum of two terms: one term, H_0 which describes an ideal interface for which the interface parallel component of wave vector is a good quantum number, and the second term, δH which describes interfacial scattering centers. The eigenstates of H_0 consist of an incident and a reflected part in the metal and a transmitted part in the semiconductor. The three components of each eigenstate have the same interface parallel wave vector. Because tunneling preferentially weights forward-directed states, the interface parallel component of wave vector is small for the H_0 eigenstates that are initially populated with high probability in BEEM. δH scatters electrons between the eigenstates of H_0 . The scattering conserves energy, but not the interface parallel wave vector. In the final state of the scattering process, states with a large interface parallel wave vector can be occupied with reasonable probability. If scattering is weak, so that the parallel wave vector is nearly conserved, the calculated collector current into conduction-band valleys with zero parallel wave vector at the minimum, such as the Γ valley for GaAs (100), is much larger than the calculated collector current into

conduction-band valleys with a large parallel wave vector at the minimum, such as the L valleys for GaAs (100). However, if scattering is strong, the injected electron flux distribution is redistributed and valleys with zero interface transverse wave vector at their energy minimum are not preferentially weighted. Instead, the weighting varies as the density of final states for the scattering process so that, for example, the calculated L-channel collector current is much larger than the calculated G-channel collector current for GaAs (100). Interfacial scattering reduces the overall magnitude of the calculated BEEM current near threshold for GaAs. We generalize the model to describe buried heterostructures and apply it to the Au/GaAs (100) interface and GaAs/ $\text{Al}_x\text{Ga}_{1-x}\text{As}$ heterostructures buried beneath this interface. Experimental results on these materials are presented and compared with the model. Strong scattering is required to describe the observed BEEM currents for Au/GaAs (100) and buried GaAs/ $\text{Al}_x\text{Ga}_{1-x}\text{As}$ heterostructures.

Summary

As a result of the studies initiated through the GaNAs characterization project, we have:

- 1) established BEEM/STM as a powerful probe of the band structure of compound semiconductor alloys in general;
- 2) we have shown the value of this technique in providing a detailed understanding of the giant bandgap reduction for the specific cases of nitrogen doped compound semiconductors (GaAs and GaP).

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