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Evolution of the GaN_xP_{1-x} alloy band structure: A ballistic electron emission spectroscopic investigation

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The evolution of the band structure of the GaN_xP_{1-x} alloy, under dilute nitrogen concentrations ($x=0$, 0.0028, 0.0086, 0.0210, and 0.0310), is investigated using ballistic electron emission spectroscopy (BEES). The observation of fine structure in the BEES spectra of GaNP samples is discussed in terms of a possible splitting in the degeneracy of the *X* valley due to the nitrogen induced intense perturbation in the GaP lattice. For an incorporation of 3% of N, the reduction in the band gap is approximately measured to be 300 meV. The data are qualitatively described by the recent perturbed host states model of Kent and Zunger.

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I. INTRODUCTION

Recently it has been discovered that partial replacement of the group V elements with nitrogen (N) leads to dramatic changes in the band structure of III-V semiconductors, specifically GaAs and GaP. The most striking observation in this new class of materials is the large reduction in the band gap of the host semiconductors.[1,2] With 4% of N incorporation in GaAs, it is observed that the band gap reduces by 400 meV, while still retaining the direct band-gap property.[3] Unlike GaAs, GaP is an indirect band-gap semiconductor with a band gap of 2.27 eV at room temperature. The isolated N impurity in GaP provides a localized state in the gap. With the increasing N concentration the optical absorption seems to indicate a lowering of the ‘‘band gap,’’ by as much as 300 meV.[4,5]

There has been intense research activity on both theoretical and experimental fronts to understand the influence of nitrogen on the band structure of these two semiconductors. Shan *et al.* proposed a band anticrossing (BAC) model of two interacting levels E_+ and E_- to explain their pressure-dependent photoreflectance data on GaInNAs alloys.[6] The BAC model states that the incorporation of nitrogen in III-V semiconductors results in the formation of a localized nitrogen state, which is in resonance with the extended states of the conduction band of the host semiconductor. Electroreflectance measurements further confirmed that the nitrogen induced band repulsion is indeed responsible for the band-gap reduction in GaNAs alloys.[7] High-resolution photoluminescence measurements on GaN_xP_{1-x} ($x \leqslant 0.031$) alloys have been interpreted in terms of the evolution of the nitrogen related impurity band due to the isolated N centers, N pairs, and its clusters.[8] The data suggest that the excitonic effect plays a significant role in the impurity band formation and the subsequent band-gap reduction.

Density-functional theory calculations, supported by the pressure-dependent photoluminescence measurements, however, fail to account for any role of the nitrogen related impurity band in the band-gap reduction.[9] Rather, it is due to the repulsion between the *X*-derived singlet state and the conduction band of the host semiconductor. Most recent pseudopotential supercell calculations suggest that the formation of a perturbed host state (PHS) and its subsequent downwards movement with the increasing N incorporation is responsible for the band-gap reduction in the GaNP alloys.[10] It is believed that the PHS possesses some *X* character due to its close proximity to the *X* valley. However, none of the experimental methods mentioned earlier fingerprint either the relative positions of the Γ, *L*, and *X* valleys of the conduction band or the formation of a N-related impurity band, which is crucial in understanding the phenomenon of band-gap reduction. Ballistic electron emission microscopy (BEEM)/spectroscopy (BEES) has proven to be very successful in showing the band-gap reduction in GaNAs alloys and in showing the evolution of the band structure of the III-V alloys.[11] It is the purpose of the present paper to investigate the band-structure evolution of the GaN_xP_{1-x} ($x \leqslant 3.1\%$) alloy semiconductor as a function of nitrogen composition using ballistic electron emission spectroscopy. A part of this work at its preliminary stage was presented elsewhere.[12]

II. EXPERIMENT

The GaN_xP_{1-x} ($x \leqslant 0.031$) samples were grown on (100) GaP substrates by using an r-f plasma enhanced gas-source molecular-beam epitaxy system. Four sets of samples with N compositions $x=0.0028$ (0.28%), 0.0086 (0.86%), 0.021 (2.1%), and 0.031 (3.1%), were grown at ~520 °C. Pd/In/Pd metalization is used as the Ohmic contact for the GaP substrate. 60 Å of gold is used as the Schottky contact on the GaNP epilayer. The details of the BEEM experimental method have been recently reviewed.[13] From the scanning tunneling microscope (STM) tip, hot electrons are injected into the semiconductor sample. Given sufficient kinetic energy, the injected carriers will overcome the Schottky barrier, pass through the semiconductor, and finally reach the collector point (Ohmic contact). A plot of collector current (I_c), as a function of the tip bias (V) constitutes the BEEM spectrum.

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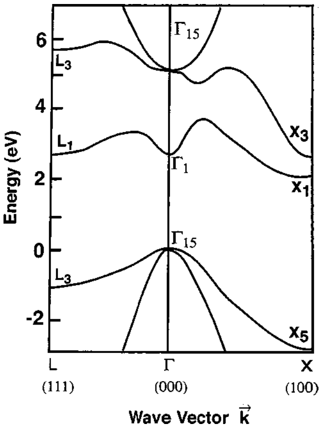

FIG. 1. Band diagram of GaP semiconductor.

A second derivative (SD-BEEM) plot of d^2I_c/dV^2 versus V fingerprints the relative positions of the Γ, *X*, and *L* valleys with the display of an individual peak corresponding to the electron scattering into each of these valleys.[13,14]

One should be cautious while taking the second derivative on the original BEEM spectrum. Even though our I_c-V spectra look clean, to obtain second derivative spectra with high signal-to-noise ratio we took a large number of data points for signal averaging purposes. Hence for each sample, on average, 40 000 of I_c-V spectra, in sets of 200, were collected at several locations on the semiconductor matrix. The fluctuations in the N concentration across any given sample is considered to be less than 0.1% of the total N present. In spite of our success to incorporate N up to 16% in GaP, the samples were highly nonstoichiometric with large variations in the N composition. Thus the samples were unsuitable for BEEM experiments beyond 3.1% N. All the measurements were performed at room temperature in ambient atmosphere. A typical band-structure diagram of GaP is shown in Fig. 1.[15]

III. RESULTS AND DISCUSSION

The BEEM spectra taken on $\mathrm{GaN}_x\mathrm{P}_{1-x}$ samples, for $x = 0-0.031$, at room temperature are shown in Fig. 2. The threshold for the onset of the BEEM current on the I_c-V spectrum of the GaP sample $(x=0)$ is determined as 1.44 ±0.05 eV, corresponding to the ballistic electron transport through the *X* valley of the semiconductor. Recalling that the conduction band minimum in GaP lies at *X* valley and thus the aforementioned threshold represents the Schottky barrier height of the Au/GaP interface, which is in excellent agreement with the previously reported values.[16] No additional thresholds or steplike features can be seen from the I_c-V curve for the higher lying *L* and Γ valleys. With the addition of nitrogen, however, for all the compositions $(x=0.28\%$, 0.86%, 2.1%, 3.1% of N), one can clearly distinguish an inflection point in the BEEM spectra. Thus the appearance of an inflection point in the spectra represents the availability of an additional channel for the current transport in the GaNP alloys. Such an observation, limited to only N doped GaP, is a strong indication of the nitrogen influence on the band structure of GaP. The origin and the nature of this additional transmission channel in dilute nitrides can be better understood by taking second derivatives on each of the I_c-V curves. Such plots are shown in Fig. 3.

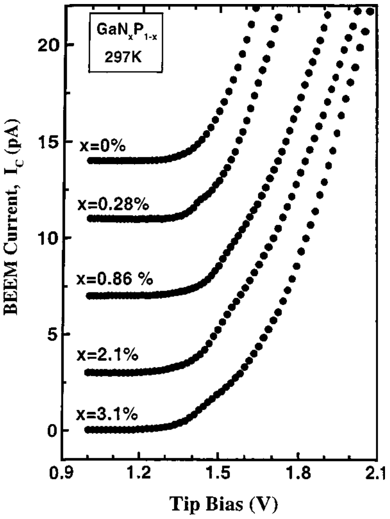

FIG. 2. Room-temperature BEEM spectra for five different nitrogen concentrations. For clarity, the spectra are shifted along the *y* axis.

The second-derivative plot of the GaP sample $(x=0\%)$ shows one broad peak, making the identification of the relative peak positions of the higher lying *L* and Γ valleys diffi-

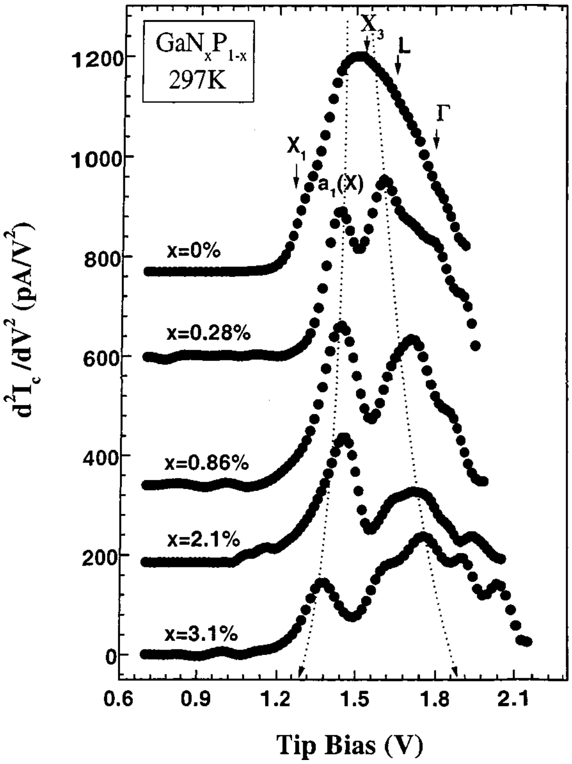

FIG. 3. Room-temperature second derivative of the BEEM I_c-V spectra in exact correspondence to Fig. 1. The spectra are vertically shifted for clarity. Dotted lines guide the eye to increasing separation between the LHS and RHS peaks with the increasing N concentration.

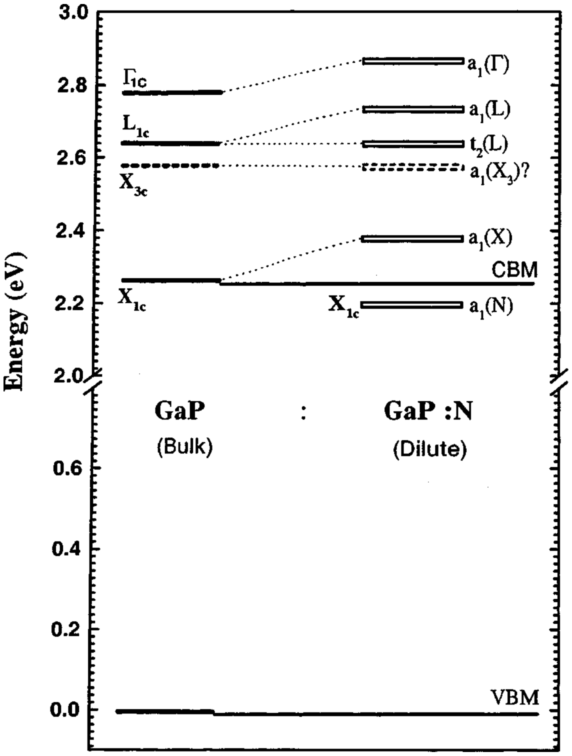

FIG. 4. Schematic of a possible ordering of the X, L, and Γ valleys in pure GaP against GaP:N system under dilute N compositions. Considering the large scattering in the reported values for the relative position of the X_{3c} valley, the possibility for the intermixing of X_{3c} and L_{1c} valleys is not ruled out.

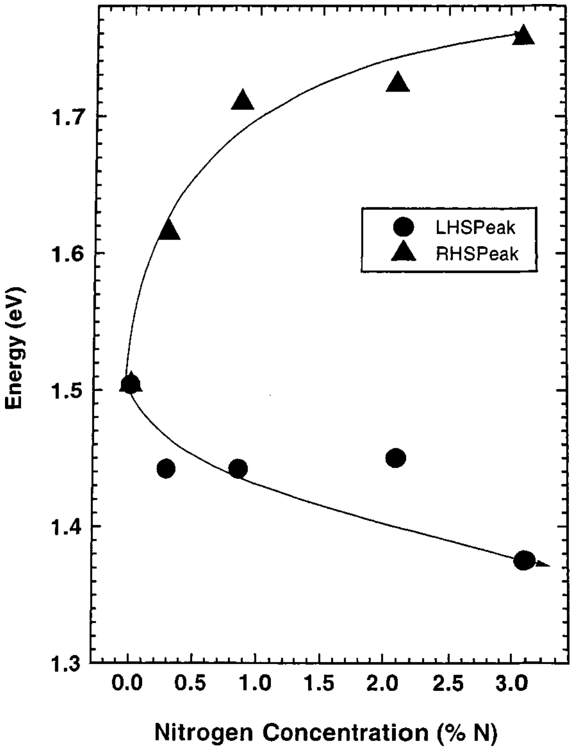

FIG. 5. Compositional dependence of the thresholds observed in the SD-BEEM spectra of GaNP. The solid line is the fit to the experimental data points.

cult. This can be understood by looking at the band structure of GaP, in which the ordering of the conduction-band valleys is $X_{1c} \rightarrow L_{1c} \rightarrow \Gamma_{1c}$, as seen from Fig. 1. The subscript "$1c$" refers to the first Brillouin zone of the conduction band. The energetic separation between $X_{1c} \rightarrow L_{1c}$ and $L_{1c} \rightarrow \Gamma_{1c}$ valleys are widely accepted as 370 and 130 meV, respectively, at room temperature.[15] Interestingly, there is evidence for a higher lying valley, X_{3c}, whose minimum occurs just below that of L_{1c}.[17–19] The $X_{1c} \rightarrow X_{3c}$ separation in pure GaP is measured as 310 meV at room temperature,[17,18] however, theoretically it is estimated as only 285 eV at absolute *zero* temperature.[15] Therefore the ordering should be rewritten as $X_{1c} \rightarrow X_{3c} \rightarrow L_{1c} \rightarrow \Gamma_{1c}$. Within 500 meV, the ballistic electrons will encounter four of these valleys over the voltage range studied.

As seen in Fig. 1, the conduction-band minimum in GaP is located on the (100) axis at the X valley, while the L valley is located on the (111) axis. Since we have employed GaP crystals with (100) crystal orientation for the BEEM experiments, the X valley is on-axis with the direction of the ballistic electron injection, where as the L valley is off-axis with the injection. Unless the Au/GaP interface provides additional transverse momentum to the ballistic electron, the scattering probability into the L valley is considered to be small. Similarly, the scattering probability into the Γ valley is expected to be much smaller due to the lower density of states and the decrease in the mean free path (mfp) with the increasing electron energy. Keeping this and the ordering of the valleys in mind, X_1 and X_3 might be contributing a large portion of the measured BEEM current, when compared to the rest of the valleys.

In contrast with the case of pure GaP, even for a small percentage of nitrogen incorporation (0.28%), the broad peak can be seen as splitting virtually into two or more subpeaks (Fig. 3). The left-hand side (LHS) peak, which appears to be sharp and more pronounced than the right-hand side (RHS) peak, is the derivative product of the inflection point. The broad RHS peak with a weakly resolved multiple structure in it is attributed to various higher lying conduction-band states of the host semiconductor. Before assigning each peak to a particular conduction-band valley, let us understand the role of nitrogen in GaP.

We adopt the description, provided by Kent and Zunger, of the perturbed host states of the GaNP band structure based on a polymorphous description of the evolution of the energy states of the material.[10] The ordering of the primary conduction-band states X_{1c}, X_{3c}, L_{1c}, and Γ_{1c} of GaP are shown in the left-hand side of Fig. 4. The L-related states usually, as mentioned earlier, have a close proximity to the X_{3c} derived states and significant mixing between these states might be expected to occur with the incorporation of nitrogen. The nitrogen derived states, $a_1(N)$, $a_1(X)$, etc., are shown on the right-hand side of Fig. 4. In our case because of the strong sensitivity to the X bands of GaP, we believe the dominant peaks reflect the splitting of the X valley, as proposed by Kent and Zunger, with the additional structure due to higher lying X_{3c}, L_{1c}, and Γ_{1c} valleys.[10] These authors did not include the behavior of X_{3c} derived states in their calculation and it is shown heuristically for completeness in Fig. 4.

Our unique experimental observations, such as inflection point and its associated spectral features in the second derivative BEES, suggest that the host states are perturbed significantly with the incorporation of N in GaP. The LHS peak is thus attributed to the nondegenerate state of the X_1 valley $\{a_1(N)\}$, and the RHS multipeak structure is attributed to the X_3, L, possibly partly due to the intermixing of X_{3c}, L and Γ valleys. This can be seen very clearly in the case of 3.1%-N sample with the display of multiple peaks.

A plot of threshold energies as a function of nitrogen composition, as displayed in Fig. 5, clearly shows that the energetic separation between the LHS and RHS peaks increases with the increasing N composition. Such an increasing separation might be a direct consequence of the downwards movement of the nondegenerate state (X_{1c}) of the X valley with the increasing N concentration. The reduction in the band gap for 3.1%-N incorporation is measured to be 0.28 ± 0.02 eV, which agrees well with the previously reported values.[1–5]

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