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Evolution of $GaAs_{1-x}N_x$ conduction states and giant $Au/GaAs_{1-x}N_x$ Schottky barrier reduction studied by ballistic electron emission spectroscopy

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The evolution of $GaAs_{1-x}N_x$ band structure at low nitrogen concentrations (up to $x=0.021$) is studied by ballistic electron emission microscopy (BEEM) spectra of $Au/GaAs_{1-x}N_x$ heterostructures. Two peaks observed in the second derivative BEEM spectra are identified with the contribution from the Γ- and L-like bands of $GaAs_{1-x}N_x$. As the nitrogen concentration increases, the energetic separation between these peaks increases, with a relative decrease of the L-like band contribution to the BEEM current. In addition, we found a strong decrease of the $Au/GaAs_{1-x}N_x$ Schottky barrier with the nitrogen incorporation, from $\sim$0.92 eV at $x=0$ down to $\sim$0.55 eV at $x=0.021$. The observed Schottky barrier reduction approximates the $GaAs_{1-x}N_x$ band-gap reduction.

The alloying of semiconductor materials is often used to alter their physical properties such as the band gap (E_g) and the lattice constant in a gradual manner, and to make them suitable for specific applications. Recently, a class of III-V alloys, where small amounts of nitrogen replace the group-V element, has attracted a great deal of attention because of the observation of a giant band-gap reduction. In the case of dilute $GaAs_{1-x}N_x$, for example, the band gap is reduced by more than 0.4 eV at $x\sim0.04$, indicative of a colossal band-gap bowing parameter.[1–5] Such a large tuning range also suggests a great potential for such alloys for a variety of optoelectronic applications.[6,7]

Very recently there has been a flurry of activity involving optical methods to study the band structure of $GaAs_{1-x}N_x$ and $Ga_{1-y}In_yAs_{1-x}N_x$ alloys. An anomalous pressure dependence of the band gap and/or an energy state (labeled E_+ in Ref. 8) located several hundred meV above the lowest conduction state (labeled E_0 in Ref. 8) has been observed in electroreflectance,[8] photomodulation[9] and photoluminescence[10] spectroscopies. As the nitrogen fraction increases, the E_+ optical transition strengthens and the splitting between E_0 and E_+ increases.

Concurrent with the experimental measurements, there have been initial attempts to develop both heuristic[9] and first-principles[10,11] theoretical models to explain the anomalous behavior. The authors of Ref. 9 proposed a two-level anticrossing model, wherein the interaction between the extended Γ conduction state of $Ga_{1-y}In_yAs_{1-x}N_x$ and the localized resonant nitrogen level (N level) located in the conduction band results in a splitting of the conduction band into two subbands E_0 and E_+. In contrast, first-principles calculations in the frame of the local-density approximation[10] showed that the nonlinear pressure dependence of the band gap is due to the nitrogen-activated mixing of the Γ, L, and X valleys without involving the localized resonant N level. Along with this, recent theoretical calculations conducted on large supercells[11] suggest that in order to explain the experimental E_0 and E_+ compositional and pressure dependencies, a significant intermixing between all GaAs-originated conduction bands (Γ, L, and X) and the N level should be considered.

To shed light on the band structure, here we report measurements of the electron transport in the conduction band of these alloys using the ballistic electron emission microscopy (BEEM) technique.[12] This technique has recently proved to be highly successful for studying the electronic band structure and Schottky barrier formation in the prototypical $Al_xGa_{1-x}As$ system.[13,14] In the BEEM technique, a metal tip is used to inject hot electrons into a metal film deposited on the semiconductor material to be studied. The electron energy distribution is simply changed by changing the tip potential. Variation in second derivative (SD)-BEEM current as a function of tip-to-base bias can be related directly to the band structure of the material under study.[14,15] Unlike optical studies of interband transitions, BEEM studies separately probe the conduction- and valence-band states. Thus BEEM transport and spectroscopy provide insight into the semiconductor band structure, and complement optical studies.

A 1000-Å undoped $GaAs_{1-x}N_x$ layer and a 1000-Å n^+-GaAs buffer layer were grown on n^+(001)-oriented GaAs substrates by gas source molecular-beam epitaxy at 420 °C (the details of the growth conditions were published elsewhere[16]). A detailed analysis is presented here for the nitrogen compositions of $x=0$, 0.003, 0.005, 0.007, 0.012, 0.017, and 0.021. The composition of $GaAs_{1-x}N_x$ layers was determined from dynamic simulations of the x-ray-diffraction spectra. High-resolution x-ray-diffraction data also demonstrate that these layers are indeed single-phase alloys, in accordance with previous photoluminescence stud-

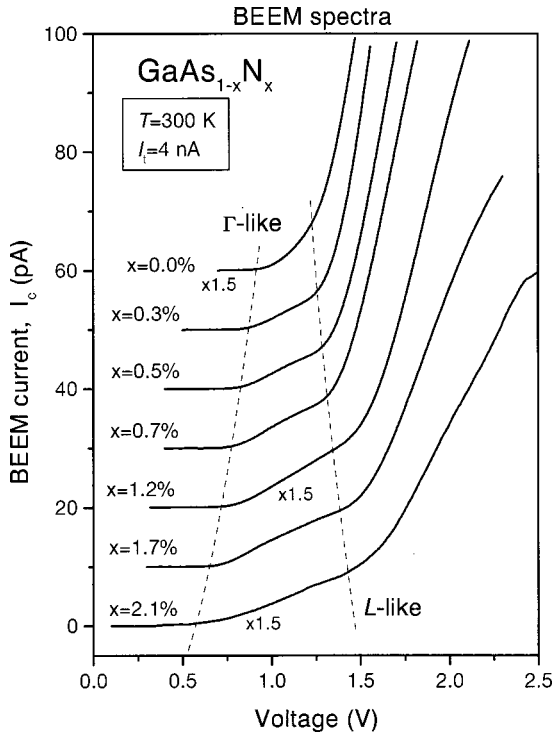

FIG. 1. Room-temperature BEEM spectra for seven different nitrogen compositions (from 0 to 0.021). For clarity, the BEEM spectra are shifted along the vertical axis. Thin dashed lines are eye guides for the peaks position development.

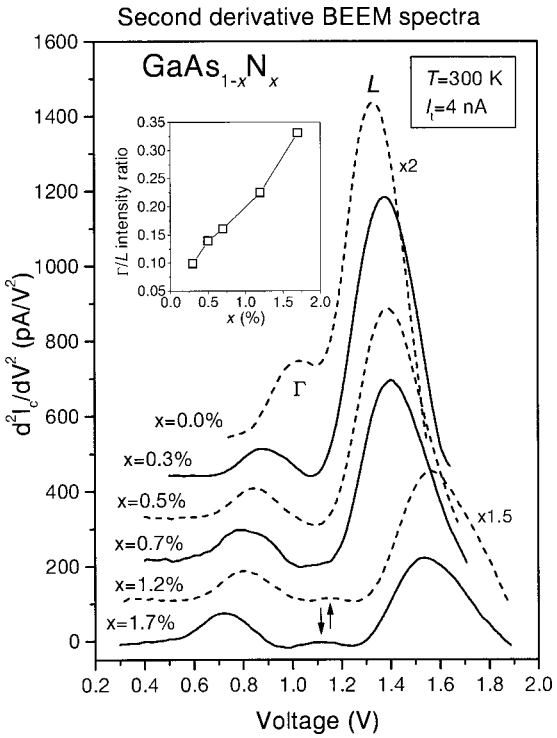

FIG. 2. Room-temperature SD-BEEM spectra (corresponding to the BEEM spectra in Fig. 1) for six different nitrogen compositions (from 0 to 0.017). For clarity, the SD-BEEM spectra are shifted along the vertical axis. The inset shows the ratio of the Γ-like peak to the *L*-like peak as a function of the nitrogen concentration. The arrows indicate the additional weaker peak that might represent the contribution from the $a_1(L_{1c})$ singlet state.

ies that have indicated the alloy formation already at $x > 0.1-0.25\,\%$.[17,18] To make the Schottky contacts, Au layers (65 Å thick) were deposited by thermal evaporation through a shadow mask at a background pressure of 2×10^{-7} torr. The details of the diode fabrication procedure were published elsewhere.[13] The BEEM measurements were performed with a Surface/Interface AIVTB-4 BEEM/STM (scanning tunneling microscopy) system using a Au tip. The tip-to-base voltage (V_t) was varied between 0.3 and 2.3 V to acquire the BEEM current (I_c), while keeping a constant tunneling current (I_t) of 4 nA.

Figure 1 shows the room-temperature BEEM spectra of $GaAs_{1-x}N_x$ for seven different nitrogen compositions. For all nitrogen compositions except $x=0$, one can distinguish two thresholds in BEEM spectra. As the nitrogen concentration increases, the low-energy threshold shifts toward lower voltages, whereas the high-energy threshold shifts toward higher voltages (the thresholds' development is shown by thin dashed lines in Fig. 1). This behavior is very different from our previously reported BEEM studies of $Al_xGa_{1-x}As$ (Ref. 14) and $Ga_xIn_{1-x}P$,[19] where only the first threshold (counting from low voltages) can be unambiguously seen from the original BEEM spectra (all additional thresholds are visible to the naked eye only in the SD-BEEM spectra).

The room-temperature SD-BEEM spectra extracted from the experimental BEEM spectra in Fig. 1 by numerical differentiation with a 10-meV window are shown in Fig. 2. The SD-BEEM current is approximately the heterostructure transmission coefficient,[20] and, therefore, allows an explicit energetic partitioning of the transport channels. We associate two main features (peaks) observed in the SD-BEEM spectra with the Γ- and *L*-like conduction minima in $GaAs_{1-x}N_x$. Indeed, it is apparent from Fig. 2 that these peaks originate from gradually moving apart the Γ and *L* peaks of GaAs (top spectrum in Fig. 2) identified in our previous study.[14] The alternative *L*-like band identification as a localized resonant N level is very unlikely because in this case one would expect a resonant N-level contribution to increase with the nitrogen concentration [larger density of-states (DOS)], whereas the experimentally observed high-energy peak amplitude decreases with the nitrogen concentration. The inset of Fig. 2 shows that the relative *L*-like band contribution to the BEEM current reduces by two-thirds as the nitrogen concentration increases from 0.3% to 2.1%. The absence of the *X* conduction minimum contribution in $GaAs_{1-x}N_x$ is due to the image potential-induced strong electron scattering in the space between the metallurgical *m-s* interface and the maximum of the barrier height,[21] similar to our previously reported results.[14]

The compositional dependencies of the thresholds observed in the SD-BEEM spectra are plotted in Fig. 3. While the Γ-like threshold decrease has a nearly linear compositional dependence up to $x=2.1\%$, the *L*-like threshold position initially increases at $x\leqslant1.2\%$ and then is almost constant. The energetic separation between Γ- and *L*-like transport channels as a function of the nitrogen composition is close to but slightly exceeds (<0.1 eV) the recently reported E_+-E_0 dependencies in optical experiments.[8,22] This difference between the *L*-like and E_+ energies above the conduction-band edge is most likely due to the difference in the experimental techniques. In both the BEEM and optical

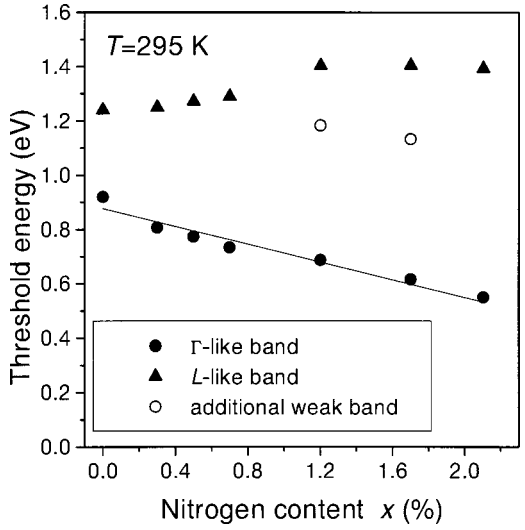

FIG. 3. The compositional dependencies of the thresholds observed in the SD-BEEM spectra of $GaAs_{1-x}N_x$. The solid line is the best linear fit to the Γ-like threshold, giving a slope of −16.4 eV.

techniques, the observed high-energy state is a weighted combination of the conduction states, but the BEEM weighting of the different bands is proportional to their DOS's,[15] while the optical transition probability is defined by their Γ character.[8,11] Since nitrogen substitution results in the splitting of the fourfold L valley into the $a_1(L_{1c})$ singlet and $t_2(L_{1c})$ triplet states,[10,11] the L-like band in the BEEM experiments is mostly weighted on the $t_2(L_{1c})$ triplet state, and the E_+ transition is mostly weighted on the $a_1(L_{1c})$ singlet state.

The SD-BEEM spectra of two $GaAs_{1-x}N_x$ samples, $x=1.2\%$ and 1.7% (see Fig. 2) reveal an additional weaker peak (indicated by the arrow), located ~0.40 and ~0.43 eV above the Γ-like state, respectively. (At lower nitrogen concentrations, this peak is probably masked due to the insufficient Γ- and L-like peak separations, whereas at higher nitrogen concentrations, due to the alloy-scattering-induced signal decrease, our sensitivity is too low to extract the SD-BEEM spectra reliably.) This peak might represent the contribution from the $a_1(L_{1c})$ singlet state. The weaker amplitude of this peak matches the expected small DOS due to the increasing Γ-character of the $a_1(L_{1c})$ state in the alloy limit.[11] It should be noted that the contributions of the different conduction bands to the BEEM current could also be selectively attenuated by the nitrogen-activated alloy and the intervalley electron scattering.

As the nitrogen concentration increases, the $Au/GaAs_{1-x}N_x$ Schottky barrier (Γ-like threshold) decreases considerably, as shown in Fig. 3. The solid line in Fig. 3 is the best linear fit to the experimental data (with a slope of −16.4 eV). Using $E_g(GaAs)=1.42$ eV and $E_g(GaN)=3.5$ eV at room temperature, the same slope of $E_g(GaAs_{1-x}N_x)$ would correspond to the bowing parameter of −18.9 eV. This value of the E_g bowing parameter is in a good agreement with the experimental estimates.[2,23,24] Thus we conclude that the nitrogen-induced Schottky barrier reduction accommodates most of the band-gap reduction in $GaAs_{1-x}N_x$. This result, which is very important for device applications, indicates that the effect of the nitrogen incorporation on the valence band is small, in agreement with other studies.[6,22]

In conclusion, the SD-BEEM spectra of $GaAs_{1-x}N_x$ show two main peaks, which we associate with the contribution of the Γ- and L-like bands of $GaAs_{1-x}N_x$. As the nitrogen concentration increases, the energetic separation between these peaks increases as well, with a relative decrease of the L-like band contribution to the BEEM current. Our results imply that the observed L-like band is mostly weighted on the $t_2(L_{1c})$ triplet state of $GaAs_{1-x}N_x$. In addition, the weaker structure observed in our experiments may result from the $a_1(L_{1c})$ singlet state. Another prominent effect of the nitrogen incorporation is a giant decrease of the $Au/GaAs_{1-x}N_x$ Schottky barrier. The observed Schottky barrier reduction approximately follows the band-gap reduction.

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