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Effect of hydrostatic pressure on the fragmented conduction band structure of dilute Ga(AsN) alloys

J. Endicott,[1] A. Patanè,[1,*] D. Maude,[2] L. Eaves,[1] M. Hopkinson,[3] and G. Hill[3]
[1]*School of Physics and Astronomy, University of Nottingham, Nottingham NG7 2RD, United Kingdom*
[2]*Grenoble High Magnetic Field Laboratory, MPI-CNRS, F-38042 Grenoble, France*
[3]*Department of Electronic and Electrical Engineering, University of Sheffield, S3 3JD Sheffield, United Kingdom*
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We show that the combined use of magneto-tunneling spectroscopy and hydrostatic pressure P provides a powerful means of probing and strongly modifying the fragmented conduction band structure of dilute $GaAs_{1-y}N_y$ quantum well layers. We demonstrate the strong effect of pressure on the $GaAs_{1-y}N_y$ states over a wide range of energies and k vectors not accessible in previous optical investigations of interband transitions around $k=0$. Also, we report a large pressure coefficient for the effective mass, m, of the conduction electrons, $\partial m/\partial P \approx 3\times10^{-3} m_e$ kbar^{-1}, nearly an order of magnitude larger than that found in GaAs ($\partial m/\partial P = 4\times10^{-4} m_e$ kbar^{-1}, where m_e is the electron mass in vacuum).

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Hydrostatic pressure P is an important thermodynamic variable and provides the condensed matter physicist with a means of probing interatomic bonding in molecules and solids, and of understanding how this determines fundamental physical and chemical properties, such as band structure and structural and phase transitions.[1]

Pressure experiments have been extensively used to investigate the band structure of semiconductors and have played a useful role in the development of several important electronic devices, such as transferred electron devices and strained semiconductor quantum well lasers.[2] Of the semiconductor compounds, GaAs has been the most widely investigated. In GaAs, moderate hydrostatic pressures decrease the lattice parameter without changing the crystal symmetry, and modify electronic energy levels, carrier effective masses, and phonon frequencies. The variations with pressure of the energy gaps, E_g, between the Γ, X, and L conduction band minima and the valence band edge are described by the co efficients $\alpha_\Gamma = \partial E_{g\Gamma}/\partial P = 10.8$ meV/kbar $\alpha_X = -1.35$ meV/kbar, and $\alpha_L = 5.5$ meV/kbar.[3] Also the effective mass m of the Γ conduction electrons increases with P at a rate $\partial m/\partial P = 4\times10^{-4} m_e$ kbar^{-1}, where m_e is the free electron mass.[4]

In this paper, we show how the incorporation of a small amount of N (0.1–0.2 %) in GaAs leads to a fundamental change in the pressure dependence of the band structure. In $GaAs_{1-y}N_y$, isolated N atoms and N-N pairs introduce localized energy levels above the Γ conduction band minimum of GaAs.[5–7] These localized states admix and hybridize with the extended band states of GaAs and break up the conduction band into highly nonparabolic energy–wave-vector dispersions, $\varepsilon(k)$,[8–11] with states that have partial Γ character.[7,10,11] We use magneto-tunneling spectroscopy[9] and hydrostatic pressure to tune and probe this remarkable band structure. Our experiment reveals a large pressure coefficient for the effective mass of the conduction electrons, $\partial m/\partial P \approx 3\times10^{-3} m_e$ kbar^{-1}, which is almost an order of magnitude larger than that found in GaAs. Also, we demonstrate the strong effect of pressure on the $GaAs_{1-y}N_y$ states over a wide range of energies and k vectors not accessible in previous optical investigations of interband transitions around $k=0$.[5,6,12–15]

We use a series of n-i-n $GaAs/Al_{0.4}Ga_{0.6}As/GaAs_{1-y}N_y$ resonant tunneling diode (RTD) heterostructures grown by molecular beam epitaxy on (100)-oriented n-type GaAs substrates. The layer structure in order of growth on the substrate is as follows: 500 nm of GaAs doped with Si to 2×10^{18} cm^{-3}; 50 nm of GaAs doped with Si to 2×10^{17} cm^{-3}; 50-nm-thick undoped GaAs spacer layer; 6-nm-thick undoped $Al_{0.4}Ga_{0.6}As$ tunnel barrier; 10-nm-thick $GaAs_{1-y}N_y$ quantum well (QW) ($y=0.2\%$); 6-nm-thick undoped $Al_{0.4}Ga_{0.6}As$ tunnel barrier; 50 nm of undoped GaAs spacer layer; 500 nm of GaAs doped with Si to 2×10^{17} cm^{-3}; 50 nm of GaAs top layer doped with Si to 2×10^{18} cm^{-3}. We also investigated similar RTDs with $y=0$ and 0.08% in the QW and with different QW widths. Each sample was processed into a small free-standing piece of wafer to facilitate mounting in the bore of a liquid clamp pressure cell. Mesas with a diameter of 50 μm with ring-shaped metallic top contact layers were fabricated to provide optical access for current-voltage $I(V)$ measurements under illumination. These were performed at temperature $T=4.2$ K under hydrostatic pressure, P, up to 10 kbar ($\approx$1 GPa), and magnetic fields, B, up to 23 T.

Figure 1 shows a schematic band diagram for our RTDs. When a voltage, V, is applied to the device, tunneling of electrons through a particular subband in the $GaAs_{1-y}N_y$ QW gives rise to a peak in $I(V)$, whenever this is resonant with an adjacent filled state in the negatively biased emitter accumulation layer. We observe three main features in $I(V)$, labeled E_{0-}, E_{1-}, and E_{0+} (this notation will be explained later in the text), whose amplitude and voltage position are affected by pressure [see $I(V)$ plots at $B=0$ T in Fig. 2(a)]. The P dependence of the resonances can be seen more clearly in the differential conductance $G=dI/dV$ plots shown in Fig. 2(b). With increasing P, the amplitudes of all resonances decrease; also, resonances E_{0-} and E_{1-} shift to higher voltages, while the E_{0+} feature shifts to lower bias.

To examine further this pressure behavior, we apply a magnetic field B parallel to the QW plane. In this magneto-

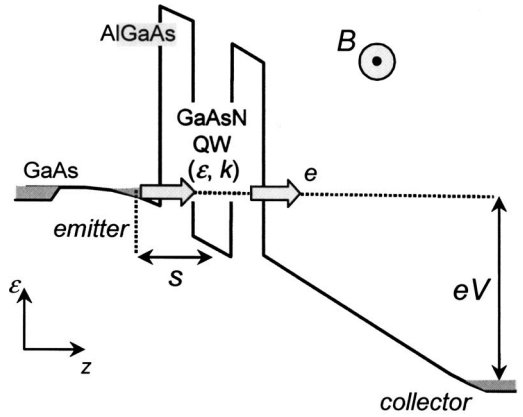

FIG. 1. Schematic band diagram of our RTDs and of the geometry of our magneto-tunneling experiment. The magnetic field B is applied perpendicular to the direction of current z. Varying the intensity of B allows us to tune an electron to tunnel into a k-vector state of the $GaAs_{1-y}N_y$ QW, while the applied voltage V tunes the energy ε.

tunneling experiment, varying the intensity of B allows us to tune an electron to tunnel into a QW state with a k vector given by $k=eBs/\hbar$, where s is the electron tunneling distance from the emitter accumulation layer to the center of the QW (see Fig. 1).[9] Since the applied voltage tunes the energy of the tunnelling electron ($V\sim\varepsilon$), we can map out the $\varepsilon(k)$ dispersion relations of the $GaAs_{1-y}N_y$ QW subbands by measuring the voltage position of the resonances in $I(V)$ or $G(V)$ as a function of B ($\sim k$). The measured voltage shift, ΔV, of a resonant feature in $I(V)$ is related to the energy shift, $\Delta\varepsilon$, along the $\varepsilon(k)$ curve according to the relation $f=e(\Delta V/\Delta\varepsilon)$, where f is the electrostatic leverage factor. Using a simple electrostatic and quantum mechanical model of our device, we estimate that $f=3.4\pm0.4$ and $s=(26\pm5)$ nm.[16] By constructing color plots of the intensity of the differential conductance as a function of ε and k, we can reveal in detail the form of the $\varepsilon(k)$ curves and their dependence on pressure (see Fig. 3). The uncertainty in the values of f and s limits the accuracy of our experiment in determining $\varepsilon(k)$ at a given pressure. However, relative changes of the $\varepsilon(k)$ curves due to pressure can be determined very accurately.

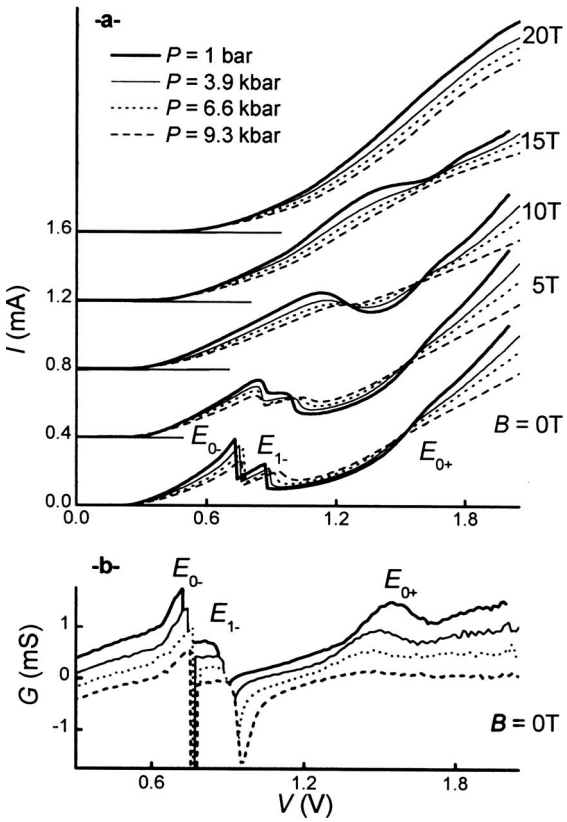

FIG. 2. (a) $I(V)$ at $T=4.2$ K for a $GaAs_{1-y}N_y$ RTD ($y=0.2\%$; $w=10$ nm) at different values of B and P. (b) Differential conductance, $G(V)=dI/dV$, plots at $B=0$ T and different P. For clarity, the curves are displaced along the vertical axis.

For ambient pressure, $P=1$ bar, the measured $\varepsilon(k)$ curves show two energy regions of anticrossing indicated by horizontal arrows in Fig. 3(a) and reveal the existence of three subbands, E_{0-}, E_{1-}, and E_{0+}. We attribute this break-up of the dispersion curve to the admixing and hybridization of the two lowest energy quantized subbands E_0 and E_1 of the GaAs QW, with the localized energy levels associated with isolated N-atoms (top horizontal arrow) and with second-neighbor [220] N-N pairs (bottom arrow).[11] The white stripelike regions in these plots correspond to the minima in G just beyond the resonant peak in $I(V)$. The brightness of these stripes is related to the Γ character of the $GaAs_{1-y}N_y$ states. The interaction between the Γ conduction band states of GaAs and the localized energy levels due to N incorporation gives to the hybridized subband states of the $GaAs_{1-y}N_y$ QW a partly Γ character over a wide energy range, and allows electrons to tunnel into them from the GaAs emitter accumulation layer, where the band states have a pure Γ character. At ε and k values for which the Γ character of the QW states is small, electron resonant tunneling from the emitter is negligible so that no negative differential conductance occurs; these regions appear as dark bands in the plots of Fig. 3(a). The weakening of all resonances at characteristic energies and k vectors indicate that the $GaAs_{1-y}N_y$ states become increasingly localized (i.e., low Γ character) as they approach the energy of isolated N-atoms and N-N pairs.

As shown in Fig. 3, the form of the $\varepsilon(k)$ curves and the amplitude of the resonances are modified significantly by pressure. The decrease of the tunnel current with increasing P was also observed in our control samples, i.e., $GaAs/Al_{0.4}Ga_{0.6}As$ RTDs with no N, and in other similar $GaAs/Al_xGa_{1-x}As$ RTDs reported in the literature.[17] This is likely to be caused by the increase with P of the Γ effective mass. A larger effective mass for the electrons decreases the transmission coefficient through the $Al_{0.4}Ga_{0.6}As$ tunnel barriers, thus reducing the current.[17] Tunneling of electrons through the X-related states in the $Al_{0.4}Ga_{0.6}As$ barriers can also decrease the negative differential conductance associated with electron tunneling into the Γ conduction band minimum. However, we believe that this effect is small in our sample as it can be observed only at high pressures (>10 kbar) and/or for an Al content in the tunnel barrier larger than that used in this work.[18]

The most striking feature of the $\varepsilon(k)$ curves in Fig. 3 is the strong pressure dependence of the $GaAs_{1-y}N_y$ states over

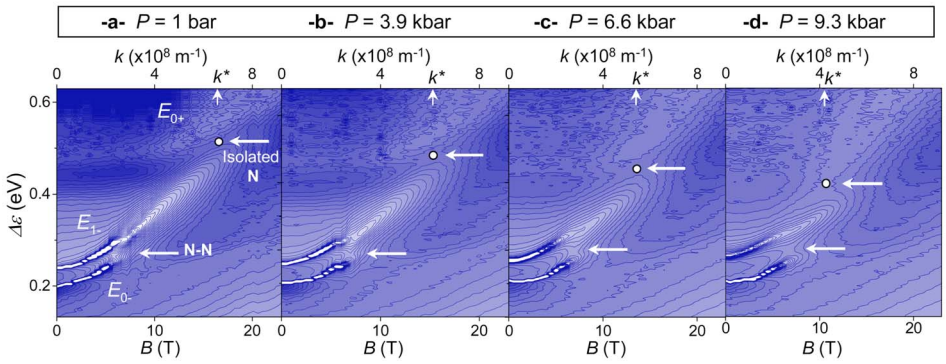

FIG. 3. (Color online) Color and contour line plots of $G(V)$ as a function of energy ε ($\sim V$) and k vector ($\sim B$) as derived from our magneto-tunneling experiment on a $GaAs_{1-y}N_y$ RTD ($y=0.2\%$; $w=10$ nm). The vertical scale does not correspond to an absolute energy scale. Plots (a)–(d) correspond to $P=1$ bar, 3.9 kbar, 6.4 kbar, and 9.3 kbar, respectively. The full dot and the arrows indicate energy and k vector k^* values of anticrossing in the $\varepsilon(k)$ curves. The value of k^* is considerably smaller than the size of the Brillouin zone k_{BZ}, i.e., $k^*/k_{BZ}\sim 0.1$.

a wide range of energies and k vectors. With increasing P, the high-energy region of anticrossing in $\varepsilon(k)$ shifts to a lower k vector and energy values (see point k^* in Fig. 3). Also, the decreasing dispersion of the lowest $\varepsilon(k)$ curve at $k=0$ indicates that the effective mass m of the conduction electrons increases rapidly with increasing P. By fitting the $\varepsilon(k)$ curve in the range of k between 0 and 2×10^{-8} m^{-1} to a parabola, we derive the value of m for each pressure. We find that m at $k=0$ increases with P with an unusually large pressure coefficient, $\partial m/\partial P=(3\pm1)\times10^{-3}m_e$ $kbar^{-1}$. The measured variation of the density of states effective mass, $m=\hbar^2k/(\partial\varepsilon/\partial k)$, is larger around $k=4\times10^8$ m^{-1}, where we measure a value $\partial m/\partial P=(4\pm1)\times10^{-3}m_e$ $kbar^{-1}$ (see Fig. 4). We measured similar values of $\partial m/\partial P$ in two other tunneling diodes with $GaAs_{1-y}N_y$ QWs, one with a $GaAs_{1-y}N_y$ layer thickness $w=7$ nm and $y=0.2\%$, the other with $w=8$ nm and $y=0.1\%$. The value of $\partial m/\partial P$ for $GaAs_{1-y}N_y$ is almost an order of magnitude larger than that measured in our $GaAs/Al_{0.4}Ga_{0.6}As$ RTDs with no N, and also that found in bulk GaAs ($\partial m/\partial P=4\times10^{-4}m_e$ $kbar^{-1}$) (Ref. 4) and is a clear manifestation of the effect of band anticrossing with the N levels.

The strong sensitivity of the $\varepsilon(k)$ curves to the relatively modest pressures used in our experiment indicates that relevant band properties, such as effective masses and electron velocity, can be tailored using a fundamentally new concept. Increasing pressure and/or quantum confinement raise the energy of the Γ conduction band minimum of GaAs, while leaving relatively unaffected the energy of the strongly localized isolated N atoms.[5] Thus, in our experiment the pressure provides a powerful means of continuously modifying the interaction between these two levels and hence the form of the $\varepsilon(k)$ curves.

Data shown in Fig. 3 represent a stringent test for the various theoretical models reported in the literature. These include band anticrossing (BAC) models, which describe the conduction band of $GaAs_{1-y}N_y$ alloys in terms of the admixing and hybridization of the extended GaAs conduction band states with the localized single N-impurity levels[8] and/or N clusters,[10] and detailed band structure calculations which consider multivalley coupling[7] and the formation of a N-impurity band.[19]

To explain our data, we first consider a two-level BAC model for bulk $GaAs_{1-y}N_y$, in which the GaAs Γ conduction band states are hybridized with the energy levels of isolated N atoms.[20] This model predicts that N incorporation in GaAs leads to a splitting of the conduction band into two subbands, E_- and E_+, whose energy separation Δ_G decreases with increasing P. This is in qualitative agreement with our observation of a decreasing energy separation between subbands E_{0-} and E_{0+} at $k=0$ (see Figs. 3 and 4). The model explains the shift of the characteristic k vector for anticrossing k^* to lower values that is also revealed by the measured $\varepsilon(k)$ curves [see the white circles in Figs. 3(a)–3(d) and Fig. 4]. Finally, we find that the density of states effective mass, $m=\hbar^2k/(\partial\varepsilon/\partial k)$, calculated at $k=0$ and $k=4\times10^8$ m^{-1} using

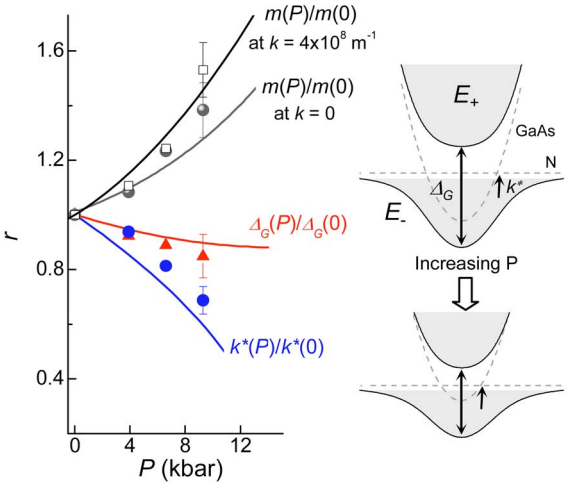

FIG. 4. (Color online) P dependence of the ratios $k^*(P)/k^*(0)$, $\Delta_G(P)/\Delta_G(0)$, and $m(P)/m(0)$ as derived from our magneto-tunneling measurements on a $GaAs_{1-y}N_y$ RTD ($y=0.2\%$; $w=10$ nm). The three ratios are labeled as r in the vertical axis. The curves represent the P dependence of the three ratios calculated using a two-level BAC model for bulk $GaAs_{1-y}N_y$. The P dependences of k^* and Δ_G are shown in the inset.

the $\varepsilon(k)$ dispersion of E_-, increases with P with pressure coefficients, which agree with those derived from the measured $\varepsilon(k)$ curves (see Fig. 4).

The two-level BAC model provides us with a simple quantitative explanation for the pressure dependence of m, Δ_G, and k^*. However, we also note that this model does not describe accurately the measured $\varepsilon(k)$ curves due to the additional effect of N-N pairs: note the form of the dispersion close to the lower horizontal arrow in Fig. 3. This effect is weaker for the N-N pairs than for isolated N atoms due to their low density. For a random incorporation of N and low $y \sim 0.1\%$, the density of N-N pairs is small ($\sim 10^{17}$ cm^{-3}) compared to that of isolated N atoms ($\sim 10^{19}$ cm^{-3}). The effect of the N-N pairs on the $\varepsilon(k)$ curves can be described by extending the two-level BAC model to include the interaction between the GaAs host conduction band Γ states and the full range of N-related levels in the alloy, with the N states described explicitly using a linear combination of isolated nitrogen states (LCINS) model.[10,11]

The color plots in Fig. 3 show that the hybridized states resulting from the interaction with the N-N pairs shift with pressure at a similar rate as that of the conduction band minimum of $GaAs_{1-y}N_y$ (see the bottom horizontal arrow in Fig. 3). This result is in contrast with the very weak pressure dependence of the N-N pair energy levels revealed in previous optical studies (see, for example, Refs. 6 and 14), but it can be explained in terms of the complementarity of the optical and magneto-tunneling techniques. Previous optical studies have revealed interband transitions associated with N-N pairs and higher order N clusters in the band gap of GaAs,[6,14,15,21–23] but they were not able to probe directly the energy levels of N-N pairs that are resonant with the conduction band states. It has been proposed that these states have a significant Γ character due to hybridization effects and that they can shift with pressure at a similar rate as the conduction band minimum.[24] In our experiment, we can probe directly these types of states as magneto-tunneling spectroscopy provides us with a means of probing the $GaAs_{1-y}N_y$ states over a wide range of energies.

In conclusion, we have shown that the incorporation of a small amount of N in GaAs gives rise to an unusual pressure dependence of the electronic properties. Isolated N-atoms and N-N pairs disrupt the extended Bloch states of the GaAs conduction band at characteristic resonant energies, thus breaking up the band into sections with strongly modified $\varepsilon(k)$ dispersion. Hydrostatic pressure provides a powerful means of tuning and probing this band structure. Our experiment reveals a large pressure coefficient for the effective mass of the Γ conduction electrons in $GaAs_{1-y}N_y$, $\partial m/\partial P \approx 3\times 10^{-3} m_e$ kbar^{-1} for $y=0.1-0.2\,\%$. Also we have revealed the existence of hybridized states resulting from the interaction with the N-N pairs that shift with pressure at a similar rate as the conduction band minimum.

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*Email address: Amalia.Patane@nottingham.ac.uk

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[16] We assume a uniform electric field across the device and define the electrostatic leverage factor f as the ratio d/s, where s is the electron tunneling distance from the emitter to the center of the QW and d is the separation between the free electrons in the emitter and collector sides of the device. The value of s is given by $s=\lambda+w/2+b$, where $b=6$ nm is the width of the collector $Al_{0.4}Ga_{0.6}As$ barrier, $w=10$ nm is the QW width and $\lambda=15\pm5$ nm is the mean standoff distance of the accumulation layer from the barrier interface estimated from the Fang-Howard model [F. F. Fang and W. E. Howard, Phys. Rev. Lett. **16**, 797 (1966)]. The value of d is given by $d=d_c+s$, where $d_c \sim b+w/2+u$ is the distance of the center of the well from the edge of the doped collector layer and $u=50$ nm is the thickness of the undoped GaAs layer. This model and analysis gives $f=3.4\pm0.4$ and $s=(26\pm5)$ nm.

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