Nitrogen composition dependence of electron effective mass in $GaAs_{1-x}N_x$

T. Dannecker,[1,2,3] Y. Jin,[2,3] H. Cheng,[3] C. F. Gorman,[2] J. Buckeridge,[1] C. Uher,[3] S. Fahy,[1,3] C. Kurdak,[3] and R. S. Goldman[2,3,*]

[1]*Tyndall National Institute, University College Cork, Cork, Ireland*

[2]*Department of Materials Science and Engineering, University of Michigan, Ann Arbor, Michigan 48109-2136, USA*

[3]*Department of Physics, University of Michigan, Ann Arbor, Michigan 48109-1040, USA*

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We have investigated the N composition, x, and temperature, T, dependence of the electron effective mass, m^*, of $GaAs_{1-x}N_x$ films with sufficiently low carrier concentration that carriers are expected to be confined to near the bottom of the conduction-band edge (CBE). Using Seebeck and Hall measurements, in conjunction with assumptions of parabolic bands and Fermi-Dirac statistics, we find a nonmonotonic dependence of m^* on x and an increasing T dependence of m^* with x. These trends are not predicted by the two-state band anticrossing model but instead are consistent with the predictions of the linear combination of resonant nitrogen states model, which takes into account several N-related states and their interaction with the GaAs CBE.

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I. INTRODUCTION

Dilute nitride alloys such as GaAsN and InGaAsN are promising for a wide range of applications including laser diodes, high-efficiency solar cells, and high performance bipolar transistors. Earlier studies have shown that the electron mobility of (In)$GaAs_{1-x}N_x$ decreases significantly with N composition, x,[1–6] presumed to be partly due to the influence of N incorporation on the effective mass, m^*.[3,4,7,8] There have been conflicting experimental[3,7–9] and theoretical[8,10,11] reports on the x and temperature, T, dependences of m^*. For $x<0.005$, m^* was reported to either decrease[4] or rapidly increase[3,7,9] with increasing x. For $x>0.005$, m^* is predicted to either increase monotonically, according to the simple band anticrossing (BAC) model,[11] or to vary nonmonotonically with a minimum around $x=0.01$ and a maximum around $x=0.02$, according to the linear combination of resonant nitrogen states (LCINS) model.[10] However, experimentally, a x-dependent saturation in m^* was reported.[7] In terms of the T dependence, one group has reported measurements showing that m^* decreases monotonically with increasing T.[8] Here, we have determined the x dependence of m^*, using a combination of T-dependent Seebeck and Hall measurements, interpreted in the framework of parabolic conduction bands and Fermi-Dirac statistics. We find a nonmonotonic behavior of m^* with x. Our results are in contrast to the prediction of a simple BAC model[11] of a monotonic decrease in m^* with increasing x, but they are very similar to the predicted minimum at $x=0.01$ of the LCINS model[10] and to the experimental values for $x=0.016$ of Ibáñez *et al.*[3] In addition, our data suggest a more significant T dependence with m^* decreasing by ~30% from 150 to 300K.

II. EXPERIMENTS

For these studies, $GaAs_{1-x}N_x$ alloy films were grown on (001) GaAs substrates by molecular-beam epitaxy, using Ga, As, GaTe, and a N_2 radio-frequency plasma source with ultrahigh-purity N_2 gas, as described elsewhere.[5,12] For all samples, a 500-nm-thick buffer layer was grown at 580 °C on GaAs (001) substrates using a growth and annealing sequence described elsewhere.[13] Next, an electronically active layer of GaAs(N) was grown at 400 °C with targeted Te doping concentrations of $5-13\times10^{17}$ cm^{-3}. The buffer and active layers were grown with As to Ga incorporation rate ratios of 1.5.[14] In all cases, the surface reconstruction was monitored *in situ* with reflection high-energy electron diffraction.

Following growth, x in the $GaAs_{1-x}N_x$ films was determined using x-ray rocking curves, interpreted with an interstitial model, as discussed elsewhere.[15] For Hall and magnetotransport measurements, Hall bars (1050×150 μm^2) were prepared using standard lithography and lift-off processes. For thermoelectric measurements, 5 mm × 15 mm rectangles were cleaved and In-Sn contacts were applied, and subsequently annealed at 410 °C for 2 min in N_2 atmosphere.

To determine the carrier concentration, we measured the parallel resistivity, ρ_{xx}, and the transverse resistivity, ρ_{xy}, as a function of T (1.6 to 300 K) and magnetic field (−8 to 8 T). For measurements of the Seebeck coefficient, $S=\Delta V/\Delta T$, a current-driven heater and a copper block were attached to each end of the cleaved rectangles. The thermally induced T gradients were measured with thermocouples attached to the In-Sn contacts.

III. RESULTS AND DISCUSSION

Figure 1 shows a plot of S as function of T, from 2 to 300 K, for GaAs and GaAsN layers. At the lowest T, S decreases monotonically to a minimum (maximum absolute value) at 12 K, followed by a corresponding monotonic increase up to ~100 K. The significant enhancement of $|S|$ in the low-T regime is attributed to increased electron-phonon coupling, often termed the "phonon drag" component of S.[16] For $GaAs_{1-x}N_x$ with $x=0$, the maximum $|S|$ is 1000 $\mu V\ K^{-1}$, and increases with x, from 1800 to 3050 $\mu V\ K^{-1}$ for $x=0.01$ to $x=0.017$.

For $T>140$ K, for both GaAs and GaAsN, S decreases monotonically with T, due to electron diffusion driven by the

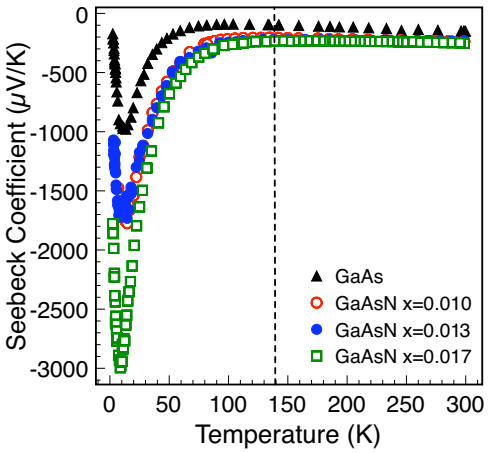

FIG. 1. (Color online) Seebeck coefficient, S, as a function of temperature, T, from 2 to 300 K. The significant enhancement in $|S|$ in the low-T regime is attributed to increased electron-phonon coupling, often termed phonon drag. For the T range from 140 to 300 K, $|S|$ decreases monotonically with T, due to electron diffusion driven by the T gradient.

T gradient. To consider the influence of x on S in this so-called "diffusion" regime, we examine S in the T range from 140 to 300 K, shown in Fig. 2(a). For GaAs, S is negative and decreases monotonically with increasing T, consistent with reported values for n-type GaAs.[17] In the GaAsN alloys, S is also negative and decreases monotonically with increasing T. However, the absolute values of S are larger than those of GaAs and the T dependence is less significant. In Fig. 2(a), linear least-squares fits to $S(T)$ are shown. For each value of x in $GaAs_{1-x}N_x$, the electron diffusion regime is identified within this T range. Interestingly, the low-T bound of the electron diffusion regime increases with x, from 140 K for GaAs to nearly 200 K for $GaAs_{1-x}N_x$ with $x=0.017$. Since S consists of a phonon drag, S_{Ph}, and a electron diffusion, S_{el}, component, the total is $S=S_{Ph}+S_{el}$. With increasing x, the phonon drag component, S_{Ph}, increases, and the S_{Ph} tail extends to higher T, presumably due to a shift of the electron diffusion regime to higher T.

As shown in Fig. 2(b), the GaAs free carrier concentration, n_s, is T independent. For GaAsN alloys grown with nominally identical doping concentration, n_s is approximately an order of magnitude lower than that of GaAs, presumably due to electron trapping at native N-related defect states, e.g., N interstitials.[12,18,19] In addition, for all the GaAsN alloys, n_s exhibits a gradual monotonic increase with temperature, suggesting the presence and thermal activation of deep-level donors related to N interstitials.[18] In all cases, n_s is sufficiently low that carriers are expected to be confined to near the bottom of the conduction-band edge (CBE). Indeed, the Fermi level, derived using Eq. (2) (below), is within ± 20 meV of the CBE, varying from +20 meV ($x=0.001$) to −20 meV ($x=0.019$). Therefore, any nonparabolicity of the CBE is expected to be negligible.

To determine the values of m^*, S is defined in terms of the reduced Fermi level, $\eta=E_F/k_BT$, where E_F is the Fermi level with respect to the CBE, and the electron momentum relaxation time τ_m, as follows:

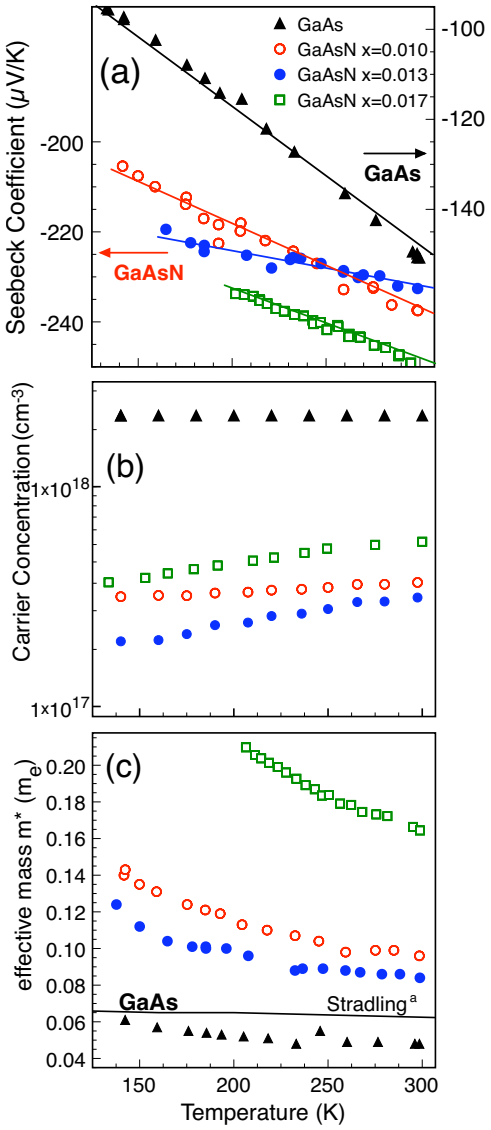

FIG. 2. (Color online) Electronic properties as a function of temperature, T, are shown from 135 to 300 K. (a) Seebeck coefficient, S, for $GaAs_{1-x}N_x$ (left axis) and GaAs (right axis). Linear least-square fits to the data are shown. The low-T bound of the electron diffusion regime increases with x, from 140 K for GaAs to nearly 200 K for $GaAs_{1-x}N_x$ with $x=0.017$. (b) Free carrier concentration, n_s, for $GaAs_{1-x}N_x$, and (c) m^* determined from S and n_s using assumptions of parabolic bands and Fermi-Dirac statistics. [a]See Ref. 33.

$$S = \frac{k_B}{e}\left(\frac{\langle \tau_m \eta \rangle}{\langle \tau_m \rangle} - \eta\right). \tag{1}$$

In general, τ_m is a function of the reduced Fermi level $\tau_m=\tau_0\eta^r$, where $r=3/2$ for ionized impurity scattering (GaAs) (Ref. 20) and $r=-1/2$ for localized N scattering (GaAsN).[5] We note that the introduction of N into GaAs has been reported to lead to an order of magnitude decrease in electron mobility.[2,3,5,8,18,21] Since the majority of N is incorporated substitutionally, it is thus assumed that electrons in GaAsN are primarily scattered by localized states associated

with N atoms. Furthermore, LO phonon scattering in GaAs has been reported to be insignificant at room temperature (RT) and to decrease with decreasing temperature;[22,23] therefore, it is not expected to be significant in GaAsN at low T. S is then simplified to

$$S = \frac{k_B}{e}\left[\frac{(r+5/2)\,F_{r+3/2}(\eta)}{(r+3/2)\,F_{r+1/2}(\eta)} - \eta\right], \tag{2}$$

where $F_j(\eta)$ is the jth Fermi integral given as

$$F_j(\eta) = \frac{1}{j!}\int_0^\infty \frac{E^j}{e^{(E-E_F)/k_BT}+1}dE. \tag{3}$$

Using Fermi-Dirac statistics, the free carrier concentration is written as

$$n = 2\left(\frac{m^* k_B T}{2\pi\hbar^2}\right)^{3/2} F_{1/2}(\eta) \tag{4}$$

and the effective mass becomes

$$m^* = \frac{2\pi\hbar^2}{k_B T}\left[\frac{n}{2F_{1/2}(\eta)}\right]^{2/3}. \tag{5}$$

For GaAs, using the values of S and n, shown in Figs. 2(a) and 2(b), and solving for η in Eqs. (2) and (5), we find a RT value of m^* of 0.048 ± 0.019 times the free-electron mass (m_e) and a monotonic decrease in m^* with increasing T (19% from 140 to 300 K), as shown in Fig. 2(c). Similar RT values of m^* were obtained by other groups using indirect experimental methods, including analysis of electric susceptibility and Shubnikov de Haas measurements.[24–26] However, a larger RT m^* value, $0.067m_e$, was observed via direct experimental methods, such as cyclotron resonance, Faraday rotation, and Faraday oscillation.[27–30] In addition, a significantly smaller gradient in the monotonic T-dependent decrease in m^* is typically observed,[27,30–32] consistent with the calculations of the dilatational change in the energy gap in GaAs by Stradling and Wood.[33] Overall, at room temperature, our GaAs m^* is within 20% of literature values, and the estimated error in m^*, $\pm 0.019m_e$, is negligible compared to the variations in the GaAsN m^* (from $0.084m_e$ to $0.164m_e$).

For GaAsN, m^* is larger than that of GaAs, and decreases monotonically with increasing T. Similar low-T values for m^* in GaAsN were reported in Refs. 7 and 9. The significant T dependence of m^* in GaAsN is likely due to a nonparabolic perturbation in the electron dispersion relation, leading to a local increase in m^*. In PbTeTl,[34] a similar temperature dependence of S and m^* were reported, and attributed to an isolated Tl energy level in close proximity to the PbTe CBE. In addition, a maximum of m^* was observed at 230 K and attributed to a resonance between the Tl state and the PbTe CBE.

In both GaAs and GaAsN, it appears that the phonon drag component of S (for $T<150$ K), shown in Fig. 1, contributes to a small artificial increase in m^*. Indeed, significant decreases in S are observed for $T<150$ K with the most significant decreases for $T<100$ K. The lower S value leads to an increase in E_f, and a subsequently smaller m^* [see Eqs. (2) and (5)].

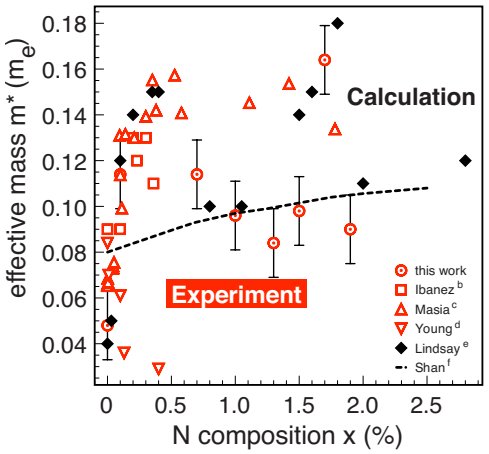

FIG. 3. (Color online) Effective mass, m^*, vs N composition, x, for as-grown bulk $GaAs_{1-x}N_x$. "This work" values are given at RT; Ibáñez *et al.* are extracted by Raman spectroscopy at 80 K; Masia *et al.* from magnetophotoluminescence at 20 K; Young *et al.* from magnetotransport at RT; Lindsay *et al.* from the LCINS model at low T; and Shan *et al.* (dashed line) from the two-state BAC model at low T. [b]See Ref. 3. [c]See Ref. 7. [d]See Ref. 4. [e]See Ref. 10. [f]See Ref. 11.

The influence of x on m^* is shown in Fig. 3. For $x<0.005$, an increase in the m^* with increasing x up to $x=0.04$,[3,7] and subsequent saturation beyond $x=0.005$ (Ref. 7) have been reported experimentally. The rapid increase up to $x=0.004$ is in good agreement with the predictions of the LCINS model.[7,10] For $x>0.005$, the LCINS model predicts nonmonotonic behavior of m^* with increasing x, with a minimum at $x=0.010$ and a maximum at $x=0.018$. The oscillatory dependence of m^* on x was explained by a strong hybridization of states arising from N clusters near the CBE of GaAs,[10] leading to a large locally increased m^* in GaAsN.

Our RT m^* values for $GaAs_{1-x}N_x$ films are in good agreement with low-temperature values predicted by the LCINS model[10] and those from other experimental reports.[3,7] For a limited composition range ($x=0.010-0.015$), our RT m^* values are also in agreement with those predicted by the BAC model.[11] Indeed, the temperature dependence of m^* is apparently negligible. As the temperature is reduced from 300 to 0 K, the relative energies of the nitrogen-induced localized states and the CBE are shifted by approximately 36 meV.[6] Since the x values investigated range from 0.001 to 0.019, a negligible temperature dependence of the x values at which the localized state-CBE resonance induced increase in effective mass is expected.

For the lowest x values, $x=0.001$ and $x=0.006$ ($m^*=0.114m_e$) is consistent with the maximum at $x=0.005$ ($m^*=0.15m_e$), predicted by the LCINS model. In addition, we find a local minimum at $x=0.013$ ($m^*=0.084m_e$), which agrees very well with the LCINS-predicted minimum at $x=0.010$ ($m^*=0.1m_e$). We also find a local maximum at $x=0.017$ ($m^*=0.164m_e$) which is in very good agreement with the LCINS-predicted maximum at $x=0.018$ ($m^*=0.18m_e$). Indeed, our observed nonmonotonic increase in m^* with x agrees very well with the x dependence (maxima at $x=0.004$ and $x=0.018$, minimum at $x=0.010$)

predicted by the LCINS model. Our m^* values are also in good agreement with experimental values from Masia *et al.*[7] for $x=0.014$ but are significantly lower for $x=0.011$. The discrepancy for $x=0.011$ can be resolved with corrections for x from the interstitial model by Reason *et al.*,[15] shifting m^* values by Masia *et al.* to higher x. In the very dilute limit, the decrease in m^*, reported by Young *et al.*,[4] is likely to be an artifact of the parabolic band-structure assumption for highly doped GaAsN.

IV. CONCLUSION

In summary, we have determined the T dependence of m^* for a set of $GaAs_{1-x}N_x$ alloy films with x values ranging from 0 to 0.018. We observe a nonmonotonic dependence of m^* *on* x and an increasing m^* T dependence with x, both of which cannot be explained by a simple two-state BAC model. Instead, the data is in good agreement with the LCINS model, which takes into account several N-related states and their interaction with the GaAs CBE.

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*Corresponding author; rsgold@umich.edu

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