AIP Applied Physics Letters

Nitrogen-induced decrease of the electron effective mass in GaAs 1−x N x thin films measured by thermomagnetic transport phenomena

D. L. Young, J. F. Geisz, and T. J. Coutts

Citation: Applied Physics Letters **82**, 1236 (2003); doi: 10.1063/1.1554777
View online: http://dx.doi.org/10.1063/1.1554777
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/82/8?ver=pdfcov
Published by the AIP Publishing

Nitrogen-induced decrease of the electron effective mass in $GaAs_{1-x}N_x$ thin films measured by thermomagnetic transport phenomena

D. L. Young,[a] J. F. Geisz, and T. J. Coutts
National Renewable Energy Laboratory, 1617 Cole Blvd., Golden, Colorado 80401

(Received 3 October 2002; accepted 2 January 2003)

Thin films of $GaAs_{1-x}N_x$ were grown on insulating GaAs substrates and subjected to temperature-dependent resistivity, Hall, Seebeck, and Nernst coefficient measurements. Density of states, effective-mass values, which are calculated from the transport data, decrease from $0.084m_e$ to $0.029m_e$ as x increases from 0 to 0.004. © *2003 American Institute of Physics.*
[DOI: 10.1063/1.1554777]

$GaAs_{1-x}N_x$ alloys have sparked a flurry of experimental[1–5] and theoretical[6–8] work based on their dramatic material property changes with dilute N concentrations. The decrease in optical band gap down from that of GaAs (1.45 eV) to ~1 eV with <3 at. % N make the alloys candidates for a middle cell in a high-efficiency multijunction solar cell[9] and for infrared diode lasers.[10] Unfortunately, this drop in band gap with increasing N concentration is also accompanied by decreasing mobility. Previous experiments[2,5] have identified an increasing electron effective mass as the culprit for the poor mobilities, but lack of agreement between experimental techniques has left the question open for debate.

Effective-mass measurements on low-mobility materials are notoriously difficult. Cyclotron resonance techniques require the product $\omega\tau \gg 1$ to be satisfied, whereas optical resonance techniques depend on model[11] and input parameters,[5] including numerous uncertain quantities such as GaAs/GaAsN band offset, alloy bowing, and alloy deformation potential.

Zhitinskaya *et al.*[12] showed that the density-of-states (DOS) effective mass, m_d^*, at the Fermi level could be calculated from solutions to the Boltzmann transport equation using the relaxation time approximation,

$$m_d^* = \left(\frac{3}{|R_H| q \pi}\right)^{2/3} \frac{q\hbar^2}{k_B^2 T}\left(\alpha - \frac{Q}{|R_H|\sigma}\right), \tag{1}$$

where σ is the conductivity, α is the Seebeck coefficient, Q is the Nernst coefficient, $|R_H|$ is the Hall coefficient, T is the absolute temperature, q is the elemental charge, $\hbar$ is Planck's constant divided by 2π, and k_B Boltzmann's constant. Equation (1) illustrates that the DOS effective mass may be experimentally determined by measuring the conductivity, Hall, Seebeck, and Nernst coefficients of a single sample. This technique has been called the *method of four coefficients* and was originally applied to p-type PbTe single crystals.[13] Equation (1) is valid in a weak-field regime ($\mu B \ll 1$) that is easily satisfied by low-mobility samples ($\mu < 1200\ cm^2/V\,s$) and typical laboratory magnets.

Our recent work using this technique on low-mobility ($\mu < 70\ cm^2/V\,s$) transparent conducting oxide (TCO) thin films[14,15] has revealed the nonparabolicity of the conduction band in several TCO materials. In this letter, we present temperature-dependent resistivity and Hall, Seebeck, and Nernst coefficient transport data for thin films of $GaAs_{1-x}N_x$. We note a decrease in the effective mass with increased nitrogen content, in contrast to other experimental and theoretical reports.

Epitaxial $GaAs_{1-x}N_x$ layers were grown on semi-insulating, Cr-doped GaAs substrates by atmospheric-pressure, metalorganic chemical vapor deposition using trimethylgallium, arsine, and dimethylhydrazine (DMH) as sources. The GaAs substrates were miscut 2° from the (001) toward the (110) direction. The layers were highly doped with Se from a hydrogen diselenide source for n-type conductivity. Nominally 2-μm-thick layers were grown at about 6 μm/h. The inlet As/Ga ratio was 4.2 for all samples. The nitrogen composition was varied by adjusting the DMH flow and the growth temperatures between 550 and 650 °C (See Table I). The nitrogen composition was determined from secondary-ion mass spectroscopy or double-crystal x-ray diffraction (XRD) measurements. The films were Se doped to a carrier concentration of $5-7.6\times10^{18}\ cm^{-3}$ while varying the N concentration from 0%–0.4% ($x=0.004$). The samples for this work were grown under similar conditions and in the same deposition chamber as the samples used by Refs. 1,3,4,17. Samples with higher N concentrations ($x > 0.004$) were grown and characterized, but sever misfit dislocations caused cracking in the films that affected the lateral electron transport making the measurements unreliable.

Films were etched to the mesa pattern, shown in the inset of Fig. 1, with 2:1:2 $NH_4OH:H_2O_2:H_2O$ using typical photolithography techniques. The four transport coefficients were measured using a specially designed instrument that measures resistivity, and Hall, Seebeck, and Nernst coefficients on a single, thin-film sample. The instrument and data collection sequence are described in Ref. 16.

Room-temperature transport coefficient data are shown in Table I. Carrier concentrations were calculated from the Hall coefficients using a Hall factor of 1, as suggested by Stillman *et al.*[18] Figure 1 shows how severely the room-temperature mobility values decrease with N incorporation. The effect of nitrogen incorporation with temperature on mobility, Seebeck coefficient and the Nernst coefficient are shown in Fig. 2.

DOS effective-mass values were calculated from Eq. (1) and data from Table I and are given in Table I and Fig. 1. The pure GaAs sample has a DOS m_d^* which is consistent with

[a]Electronic mail: david_young@nrel.gov

TABLE I. Room-temperature transport data and calculated values. Uncertainties are given in italics below each number. R_{Hall} is the Hall coefficient, ρ is the resistivity, α is the Seebeck coefficient, Q is the Nernst coefficient, n is the carrier concentration, and m^* is the electron effective mass.

Sample No.	Growth Temperature (°C)	H_2Se (sccm)	DMH (sccm)	Thickness (μm)	R_{Hall} (m^3/C)	ρ (cm ohm)	α (μV/K)	Q (μV/kT)	Mobility (cm^2/V s)	n (cm^{-3})	m^* (m/m_e)	Relaxation time (s 10^{-15})
GaAs-MC171	650	5	0	0.96	-1.25×10^{-6}	9.89×10^{-4}	−94.02	9.67×10^{-1}	1263.71	-4.99×10^{18}	0.084	60.55
0% N				*0.08*	*7.66×10^{-8}*	*6.06×10^{-5}*	*0.83*	*1.54×10^{-2}*	*109.52*	*3.06×10^{17}*	*0.004*	*5.87*
GaAsN-MC799	650	3	10	2.0	-8.26×10^{-7}	9.75×10^{-4}	−52.86	-8.46×10^{-2}	846.90	-7.56×10^{18}	0.070	33.77
0.01% N				*0.20*	*5.85×10^{-8}*	*6.90×10^{-5}*	*0.75*	*1.01×10^{-2}*	*84.81*	*5.36×10^{17}*	*0.004*	*3.78*
GaAsN-MC801	550	3	10	2.0	-1.23×10^{-6}	4.70×10^{-3}	−62.90	2.93×10^{-2}	262.15	-5.06×10^{18}	0.061	9.12
0.1% N				*0.20*	*8.74×10^{-8}*	*3.33×10^{-4}*	*0.79*	*1.01×10^{-2}*	*26.25*	*3.59×10^{17}*	*0.003*	*1.02*
GaAsN-MC507	650	3	100	2.0	-9.72×10^{-7}	5.35×10^{-3}	−17.82	-2.42×10^{-1}	181.87	-6.42×10^{18}	0.036	3.75
0.13% N				*0.25*	*1.04×10^{-7}*	*5.12×10^{-4}*	*0.70*	*9.71×10^{-3}*	*26.05*	*6.84×10^{17}*	*0.003*	*0.63*
GaAsN-MC467	650	3	200	2.0	-1.14×10^{-6}	6.08×10^{-3}	−16.35	-2.11×10^{-1}	187.13	-5.48×10^{18}	0.029	3.05
0.4% N				*0.50*	*2.01×10^{-7}*	*1.08×10^{-3}*	*0.69*	*4.49×10^{-3}*	*46.81*	*9.70×10^{17}*	*0.004*	*0.88*

literature values for carrier concentrations of 5×10^{18} cm^{-3}.[19] The most interesting feature of Fig. 1 is the *decreasing* DOS m_d^* with increasing nitrogen concentration. Also shown in Fig. 1 are the relaxation times as calculated from the effective-mass and mobility values. The relaxation times decrease by a factor of 20, following the trend in mobility, even though m_d^* decreases by about three to four times over the same range of N. The trend of decreasing effective mass with increasing nitrogen concentration differs significantly from previous reports[2,5] using $GaAs_{1-x}N_x$/GaAs quantum well samples with nitrogen concentrations greater than 0.9%. In each of the reports, the effective mass for $GaAs_{1-x}N_x$, measured by different techniques was higher than the effective mass for GaAs. However, the trends in the effective mass differ between the reports. Zhang *et al.*[5] report a sharp increase (with respect to GaAs) in the effective mass with increased nitrogen concentration, followed by a gradually decreasing trend. Hai *et al.*,[2] on the other hand, using cyclotron resonance, show an increasing effective mass with increased nitrogen on samples not meeting the $\omega\tau\gg1$ criterion. However, the two reports fail to agree on the effective-mass value for nominally the same sample ($x=2.0\%$), differing by almost $0.16m_e$.

Franceschetti *et al.*[20] showed that the effective mass of alloys could have contributions from two opposing physical effects. First, a reduction in bandgap due to alloying would reduce the effective mass.[21] The traditional $k\cdot p$ theory[20] predicts that the effective mass should decrease with decreasing band gap,[20–22] and accurately predicts the trend and the value of the effective mass for many III–V and II–VI semiconductors.[21] N addition to GaAs reduces its band gap enormously, so this effect alone may be expected to reduce the effective mass. Second, any effect that admixes L or K character into the Γ-like conduction band minimum will increase the electron mass (because non-Γ masses are usually heavier than the Γ mass). Admixture of non-Γ character into Γ states can occur due to alloy ordering[20] or alloy localization.[6,8] The latter effect was predicted to occur in GaAsN. Kent *et al.*[6] identified distinct nitrogen concentration regions within the GaAsN system using the local-density approximation theory. In the dilute alloy limit ($x\leqslant0.4\%$), they found the conduction band to consist of weakly nitrogen-perturbed host states and cluster states inside the band gap. Cluster states were previously well known from experimental evidence.[23] In the intermediate nitrogen concentration region ($x\approx2\%-4\%$), they found localized cluster states overlapping the conduction band. This region showed very strong X_{1c} and L_{1c} band mixing with the Γ_{1c} state.

Our samples lie in the dilute alloy limit where minor perturbations of the conduction band exist. The reduction of effective mass with decreasing band gap is then a result of the bowing-induced mass reduction being larger than the $\Gamma-L$ mixing-induced mass enhancement.

The nitrogen concentration levels of the samples of Zhang *et al.*[5] and Hai *et al.*,[2] on the other hand, lie within the intermediate region. Here, enhanced mixing of conduction band states (Γ_{1c}, L_{1c}, and X_{1c}) as the N concentration increases alters the character of the lowest-energy state.[6] As x

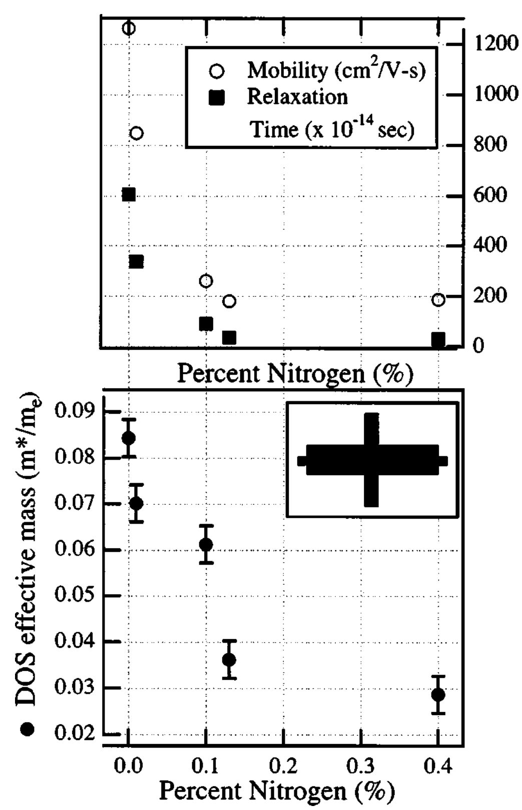

FIG. 1. DOS effective mass, mobility, and relaxation time as a function of nitrogen incorporation in $GaAs_{1-x}N_x$. Inset shows etched pattern in samples.

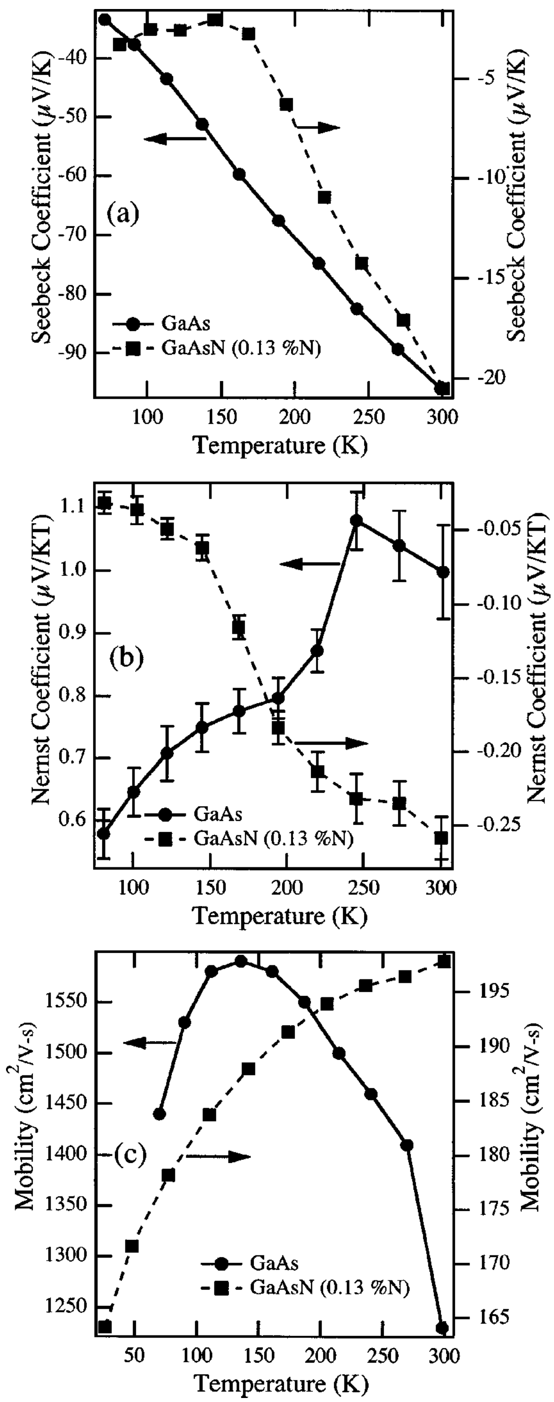

FIG. 2. Transport data for GaAs (circles) and $GaAs_{0.987}N_{0.013}$ (squares) as a function of temperature: (a) Seebeck coefficient, (b) Nernst coefficient, and (c) Mobility.

increases, X_{1c} and L_{1c} states mix with the Γ_{1c} state and strongly influence the character of the lowest-energy conduction band. X_{1c} and L_{1c} states have a much larger m_d^* than the Γ_{1c} state; hence, the DOS m_d^* value increases.[6,8]

We conclude that, in dilute $GaAs_{1-x}N_x$, the effective mass of the electrons decreases with increasing nitrogen concentration, in agreement with trends predicted by the $k\cdot p$ theory. The low mobilities in dilute $GaAs_{1-x}N_x$ are due to short relaxation times (Fig. 1) rather than large DOS m_d^* values. The *method of four coefficients* has been shown to be an excellent experimental technique for measuring the effective mass on low-mobility $GaAs_{1-x}N_x$ films. The technique is easily extended to higher x values provided continuous films can be grown.

The authors would like to thank Dr. Alex Zunger, Dr. Paul Kent, Dr. Yong Zhang, and Dr. Angelo Mascarenhas of the National Renewable Energy Laboratory and Dr. Victor Kaydanov of the Colorado School of Mines for useful discussions. This work was supported by the U.S. Department of Energy under Contract No. DE-AC36-99GO10337.

[1] C. Skierbiszewski, P. Perlin, P. Wisniewski, T. Suski, W. Walukiewicz, W. Shan, J. W. Ager, E. E. Haller, J. F. Geisz, D. J. Friedman, J. M. Olson, and S. R. Kurtz, Phys. Status Solidi B **216**, 135 (1999).
[2] P. N. Hai, W. M. Chen, I. A. Buyanova, H. P. Xin, and C. W. Tu, Appl. Phys. Lett. **77**, 1843 (2000).
[3] R. K. Ahrenkiel, S. W. Johnston, B. M. Keyes, and D. J. Friedman, Appl. Phys. Lett. **77**, 3794 (2000).
[4] J. D. Perkins, A. Mascarenhas, Y. Zhang, J. F. Geisz, D. J. Friedman, J. M. Olson, and S. R. Kurtz, Phys. Rev. Lett. **82**, 3312 (1999).
[5] Y. Zhang, A. Mascarenhas, H. P. Xin, and C. W. Tu, Phys. Rev. **61**, 7479 (2000).
[6] P. R. C. Kent and A. Zunger, Phys. Rev. B **64**, 115208 (2001).
[7] L. Bellaiche, S.-H. Wei, and A. Zunger, Appl. Phys. Lett. **70**, 3558 (1997).
[8] T. Mattila, S.-H. Wei, and A. Zunger, Phys. Rev. B **60**, R11 245 (1999).
[9] D. J. Friedman, J. F. Geisz, S. R. Kurtz, and J. M. Olson, J. Cryst. Growth **195**, 409 (1998).
[10] M. Kondow, S. Nakatsuka, T. Kitatani, Y. Yazawa, and M. Okai, Jpn. J. Appl. Phys., Part 1 **35**, 5711 (1996).
[11] C. Skierbiszewski, P. Perlin, P. Wisniewski, W. Knap, T. Suski, W. W. W. Shan, K. M. Yu, J. W. Ager, E. E. Haller, J. F. Geisz, and J. M. Oson, Appl. Phys. Lett. **76**, 2409 (2000).
[12] M. K. Zhitinskaya, V. I. Kaidanov, and I. A. Chernik, Sov. Phys. Solid State **8**, 295 (1966).
[13] I. A. Chernik, V. I. Kaidanov, N. V. Kolomoets, and M. I. Vinogradova, Sov. Phys. Semicond. **2**, 645 (1968).
[14] D. L. Young, T. J. Coutts, V. I. Kaydanov, A. S. Gilmore, and W. P. Mulligan, J. Vac. Sci. Technol. A **18**, 2978 (2000).
[15] D. L. Young, H. Moutinho, Y. Yan, and T. J. Coutts, J. Appl. Phys. **92**, 310 (2002).
[16] D. L. Young, T. J. Coutts, and V. I. Kaydanov, Rev. Sci. Instrum. **71**, 462 (2000).
[17] Y. Zhang, A. Mascarenhas, and J. F. Geisz, Phys. Rev. B **63**, 085205 (2001).
[18] G. E. Stillman, C. M. Wolfe, and J. O. Dimmock, J. Phys. Chem. Solids **31**, 1199 (1970).
[19] A. Raymond, J. L. Robert, and C. Bernard, J. Phys. C **12**, 2289 (1979).
[20] A. Franceschetti, S.-H. Wei, and A. Zunger, Phys. Rev. B **52**, 13992 (1995).
[21] P. Y. Yu and M. Cardona, *Fundamentals of Semiconductors Physics and Materials Properties*, 2nd ed. (Springer, Berlin, 1999).
[22] L. Malikova, F. H. Pollak, and R. Bhat, J. Electron. Mater. **27**, 484 (1998).
[23] H. Grüning, L. Chen, T. Hartmann, P. J. Klar, W. Heimbrodt, F. Höhnsdorf, J. Koch, and W. Stolz, Phys. Status Solidi B **215**, 39 (1999).