Lawrence Berkeley National Laboratory

Lawrence Berkeley National Laboratory

Title Taming transport in InN

Permalink https://escholarship.org/uc/item/85v3z98m

Author Ager III, Joel W.

Publication Date 2011-12-23

Taming transport in InN

Joel W. Ager III^{*, 1} and Nate R. Miller^{1, 2}

¹ Materials Sciences Division, Lawrence Berkeley National Lab, Berkeley, CA 94720 USA

² Emcore, Albuquerque, NM 87123 USA

Keywords Indium nitride, thermopower, doping, conductivity

The large electron affinity of InN, close to 6 eV and the largest of any III-V semiconductor, creates a strong driving force for native donor formation, both in the bulk and at surfaces and interfaces. Moreover, all InN surfaces, regardless of crystal orientation or doping, have been observed to have a surface accumulation layer of electrons, which interferes with standard electrical measurements. For these reasons, until recently, it was uncertain whether or not compensation by donor defects would prevent "real" p-type activity (i.e. existence of sufficiently shallow acceptors and mobile holes). A coordinated experimental approach using a combination of electrical (Hall effect) and electrothermal (Seebeck coefficient) measurements will be described that allows definitive evaluation of carrier transport in InN. In Mg-doped InN films, the sensitivity of thermopower to bulk hole conduction, combined with modeling of the parallel conducting layers (surface/bulk/interface), enables quantitative measurements, along with a considering of the scattering mechanisms, leads to a quantitative understanding of the crucial role of charged line defects in limiting electron transport.

1 Introduction Depending on the band offset values used, the electron affinity of InN is in the range of 5.5-5.8 eV [1-3]. This is the largest electron affinity of all group III-V semiconductors and has a number of important consequences for the study of electron and hole transport in this material. Based on considerations of both the charge neutrality level (also known as the branch point energy) [4,5] and of the amphoteric native defect (Fermi level stabilization) model [6,7], InN would be expected to have its surface Fermi level pinned high above the conduction band minimum. Indeed, surface pinning corresponding to a Fermi level position in the range of 0.7-0.9 eV above the CBM has been observed experimentally by a number of techniques including electron energy loss spectroscopy, x-ray photoelectron spectroscopy, angle-resolved photoemission, and electrolyte contacted capacitance voltage (CV) measurements [8-12].

The large electron affinity of InN also affects bulk conduction properties. Native point defects have a strong driving force to be donors. Energetic particle irradiation experiments have shown that their average energy is 0.9 eV above the CBM, similar to the position of the surface pinning energy [13,14]. Both hydrogen and also certain types of dislocations are also predicted to be donors in InN [15,16]. As a result, undoped InN thin films grown to date by molecular beam epitaxy have been degenerate n-type, with the lowest reported electron concentration in the low 10^{17} cm⁻³ range [17,18].

The presence of electron-rich surface layers and the strong propensity for the formation of native donors created challenges for producing p-type InN. While CV techniques were able to show that Mg forms acceptors, as in GaN [11], direct measurement of the transport properties had been prevented by the n-type surface inversion layer. Recently, thermopower [19-22] and Hall effect/conductivity studies [23-24] have shown that Mg doping produces mobile holes in InN, but there are only a few reports concerning the hole concentration and mobility.

In this work, we are "taming" the transport of InN in two ways. (1) We use the ability of an electrolyte to form an insulating surface layer to deplete InN's surface accumulation/inversion layers to reveal the bulk transport properties of InN epitaxial films [25]. (2) We take advantage of the sensitivity of thermopower measurements to bulk hole conduction to obtain the free hole concentration and mobility in p-type InN:Mg films grown by MBE. The additional use of thermopower yields a more precise assessment of hole conduction properties than with Hall/conductivity analysis alone.

2 Experimental Methods for the MBE growth of the films used in this study are described in the literature by our collaborators [17,26,27]. Hall effect measurements were measured using a 3000 Gauss magnet with contacts placed in the van der Pauw configuration. Thermopower measurements were performed using a system

^{*} Corresponding author: JWAger@lbl.gov

that has been described previously [19,28]. Undoped (n-type) films in this study have electron concentrations ranging from $4x10^{17}$ cm⁻³ to $5x10^{19}$ cm⁻³. Mg-doped films have Mg concentrations as measured by secondary ion mass spectrometry (SIMS) of between $3x10^{16}$ and $4x10^{19}$ cm⁻³.



Figure 1 Calculations within the relaxation time approximation of the Seebeck coefficient of n-type and p-type InN.

3 Results and Discussion

3.1 Mg-doped InN The surface inversion layer discussed above creates a short circuit path for topcontacted Hall effect measurements. Therefore, normal low field Hall measurements find n-type conductivity with relatively low mobility corresponding to transport in the surface layer only [11]. In contrast, thermopower (Seebeck coefficient) measurements have a number of characteristics that discriminate against the effects of this layer. First, the temperature gradient that creates the Seebeck effect cannot be screened; this is in contrast to the electrical fields used in the Hall measurements. Also, the Seebeck coefficient is larger for heavier effective masses and lower carrier concentrations, as illustrated in Fig. 1. Both these favor the detection of transport of holes in the bulk of the film, even in the presence of the electron-rich surface layer.

Observed Seebeck coefficients for undoped and lightly Mg-doped InN films are in the -10 to -100 μ V/K range, corresponding to bulk n-type conduction. For the lightly Mg-doped films, any acceptors which are formed are compensated by native donors or donor impurities. However, as shown in Fig. 2, for a "window" of Mg concentration in the 10¹⁸ range, positive Seebeck coefficients are observed, which is unmistakable evidence of mobile hole and p-type conduction [22]. A study of the room temperature Seebeck coefficient combined with Hall effect in a series of Mg-doped films in which electron conduction was considered both at the surface and at the heterointerface used in the MBE growth yield quantitative hole concentrations and mobilities. For the window shown in Fig. 2, these are in the range of 1-3x10¹⁸ cm⁻³ and 15-60 cm² V⁻¹ s⁻¹ [29].

We have obtained additional insights into the effect of the surface layer on the observed Seebeck coefficient by modulating the surface layer with an electron gate (electrolyte gated thermopower or ETP) [28]. The results of initial ETP measurements are shown in Fig. 3 for two p-type samples and one n-type sample, although gate biases near the open circuit potential (V_{OC}) were applied to only one of the p-type samples. Here the Seebeck coefficient is plotted as a function of gate bias. For the p-type sample plotted in green, applying a positive gate bias relative to the open circuit potential results in an increasing Seebeck coefficient, which quickly saturates. Biasing in this direction depletes electrons from the surface inversion layer. Applying a negative gate bias results in a decreasing Seebeck coefficient by accumulating even more electrons into the inversion layer. For the n-type sample, modulation of the gate bias around V_{OC} has little effect on the Seebeck coefficient since the surface makes little contribution in a thick n-type sample.



Figure 2 Summary of Seebeck coefficient measurements performed on Mg-doped InN films. A positive Seebeck coefficient indicates p-type behaviour. Adapted from [22].

Figure 3 Seebeck coefficient of two p-type samples (green and red) and one n-type sample (blue) as a function of gate bias. Here the open-circuit potential, V_{OC} , is marked indicating the near equilibrium state for these samples in a 1 M NaOH solution. Adapted from [28].

We have obtained additional insights into the effect of the surface layer on the observed Seebeck coefficient by modulating the surface layer with an electron gate (electrolyte gated thermopower or ETP) [28]. The results of initial ETP measurements are shown in Fig. 3 for two p-type samples and one n-type sample, although gate biases near the open circuit potential (V_{OC}) were applied to only one of the p-type samples. Here the Seebeck coefficient is plotted as a function of gate bias. For the p-type sample plotted in green, applying a positive gate bias relative to the open circuit potential results in an increasing Seebeck coefficient, which quickly saturates. Biasing in this direction depletes electrons from the surface inversion layer. Applying a negative gate bias results in a decreasing Seebeck coefficient since the n-type sample, modulation of the gate bias around V_{OC} has little effect on the Seebeck coefficient since the surface makes little contribution in a thick n-type sample.

3.2 Undoped InN The sensitivity of the magnitude of the Seebeck coefficient can be used to discern the nature of the majority carrier scattering. Charged dislocation scattering has been invoked to explain the temperature behaviour of the mobility in InN [30]. In contrast to the case in GaN, where they are believed to be acceptors [31], dislocations in InN are believed to be donor-like based on both *ab-initio* calculations [16] and experiments examining the relationship between their areal density and the electron concentration [32].

Here, we use thermopower measurements in combination with Hall effect to assess the contribution of ionized dislocation scattering to limiting mobility in InN; This has been done previously for GaN [33]. Extending the approach developed by Hsu *et al.* [34], we considered the effect on mobility of charged dislocation scattering. As shown in Fig. 4, charged dislocation scattering can be the dominant mobility limiting mechanism, particularly at low temperatures, even at the lower bound of reported dislocation densities.



Figure 4 Calculated mobility of InN as a function of temperature, both showing the individual contributions of dislocation scattering (disl) for $N_{dis} = 10^9 \text{ cm}^{-2}$, acoustic phonon scattering (ac), piezoelectric scattering (piezo), optical phonon scattering (LO), and ionized impurity scattering for $n = 10^{17} \text{ cm}^{-3}$. The solid black line is the total composite mobility, and the black dashed line is the composite mobility without dislocation scattering. Adapted from [28].

The magnitude of the Seebeck coefficient S depends both on the position of the Fermi level (i.e. the carrier concentration) but also on the electron energy dependence of the scattering processes. This can be seen by considering the form of S for the non-degenerate case in the relaxation time approximation:

$$S = -\frac{k_B}{T} \left(r + \frac{5}{2} - \frac{\zeta}{k_B T} \right) \tag{1}$$

where ζ is the position (negative for the non-degenerate case) of the Fermi level for electrons measured with respect to the CBM and *r* is defined

$$\tau = \tau_0 \left(\frac{\varepsilon}{k_B T}\right)^r \tag{2}$$

where τ is the electron scattering time and ε is the electron energy [35]. We have shown that under the degenerate conditions found in InN the effective value of *r* is greater for dislocation scattering compared to ionized impurity scattering [36]. Therefore, it is expected that |S| would increase at a given electron concentration if dislocation scattering plays an important role. Combined Hall and thermopower analyses are being employed to investigate this issue.

4 Conclusions We have shown that some of the interfering effects of the surface accumulation/inversion, which forms in InN due to its high electron affinity, can be "tamed" by modulating it or depleting it with an electrolyte gate. Electrolyte-gated thermopower measurements allow this modulation of the electron-conducting path to be observed directly. The sensitivity of the Seebeck coefficient can be used to elucidate the role of charged dislocation scattering in n-InN.

Acknowledgements This work was performed within LBNL's Electronic Materials Program which is supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Materials Sciences and

Engineering, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231. N. Miller acknowledges government support under and awarded by DoD, Air Force Office of Scientific Research, National Defense Science and Engineering Graduate (NDSEG) Fellowship, 32 CFR 168a. We thank Y. Nanishi (Ritsumeikan U.), W. J. Schaff (Cornell), and J. Speck (UC Santa Barbara) for providing the InN films used in this study and acknowledge many fruitful discussions with W. Walukiewicz, E. E. Haller, and K. M. Yu.

References

- [1] G. Martin, A. Botchkarev, A. Rockett, and H. Morkoç, Appl. Phys. Lett. 68, 2541 (1996).
- [2] Wu, C. L., Lee, H. M., Kuo, C. T., Gwo, S., and Hsu, C. H. Appl. Phys. Lett. 91, 042112 (2007).
- [3] P. D. C. King, T. D. Veal, C. E. Kendrick, L. R. Bailey, S. M. Durbin, and C. F. McConville, Phys. Rev. B 78, 033308 (2008).
- [4] J. Tersoff, Surf. Sci. 168 275 (1986).
- [5] W. Mönch, Semiconductor surfaces and interfaces. (Springer Verlag, Berlin, 2001).
- [6] W. Walukiewicz, Appl. Phys. Lett. 54, 2094 (1989).
- [7] W. Walukiewicz, Physica B 302, 123 (2001).
- [8] I. Mahboob, T. D. Veal, C. V. McConville, H. Lu and W. J. Schaff, Phys. Rev. Lett. 92 036804 (2004).
- [9] L. Colakerol, T. D. Veal, H.-K. Jeong, L. Plucinski, A. DeMasi, T. Learmonth, P.-A. Glans, S. Wang, Y. Zhang, L. F. J. Piper, P. H. Jefferson, A. Fedorov, T.-C. Chen, T. D. Moustakas, C. F. McConville, and K. E. Smith, Phys. Rev. Lett. 97 237601 (2006).
- [10] P. D. C. King, T. D. Veal, P. H. Jefferson, S. A Hatfield, L. F. J. Piper, C. F. McConville, F. Fuchs J. Furthmüller, F. Bechstedt, H. Lu, and W. J. Schaff, Phys. Rev. B 77 045316 (2008).
- [11] R. E. Jones, K. M. Yu, S. X. Li, W. Walukiewicz, J. W. Ager III, E. E. Haller, H Lu, and W. J. Schaff, Phys. Rev. Lett. 96 125505 (2006).
- [12] J. W. L. Yim, R. E. Jones, K. M. Yu, J. W. Ager III, W. Walukiewicz, W. J Schaff, and J Wu, Phys. Rev. B 76 41303 (2007).
- [13] S. X. Li, K. M. Yu, J. Wu, R. E. Jones, W. Walukiewicz, J. W. Ager III, W. Shan, E. E. Haller, H. Lu, and W. J. Schaff, Phys. Rev. B 71 R161201 (2005).
- [14] S. X. Li, R. E. Jones, E. E. Haller, K. M. Yu, W. Walukiewicz, J. W Ager III, Z., Liliental-Weber, H. Lu, and W. J. Schaff, Appl. Phys. Lett. 88, 151101 (2006).
- [15] A.Janotti and C. G. Van de Walle, Appl. Phys. Lett. 92 032104 (2008).
- [16] Y. Takei and T. Nakayama, J. Cryst. Growth **311** 2767 (2009).
- [17] C. S. Gallinat, G. Koblmüller, J. S. Brown, S. Bernardis, J. S. Speck, G. D. Chern, E. D. Readinger, H Shen, and M Wraback, Appl. Phys. Lett. 89 032109 (2006).
- [18] X Wang, S. B. Che, Y. Ishitani, and A. Yoshikawa, Appl. Phys. Lett. 90 151901 (2007).
- [19] J. W. Ager III, N. Miller, R. E. Jones, K. M. Yu, J. Wu, W. J. Schaff, and W. Walukiewicz, Phys. Status Solidi B 245, 873 (2008).
- [20] N. Miller, J. W. Ager III, R. E. Jones, H. M. Smith III, M. A. Mayer, K. M. Yu, M. E. Hawkridge, Z. Liliental-Weber, E. E. Haller, W. Walukiewicz, W. J. Schaff, C. Gallinat, G. Koblmüller, and J. S. Speck, Physica B 404, 4862 (2009).
- [21] L. H. Dmowski, M. Baj, T. Suski, J. Przybytek, R. Czernecki, X. Wang, A. Yoshikawa, H. Lu, W. J. Schaff, D. Muto, and Y. Nanishi, J. Appl. Phys. 105, 123713 (2009).
- [22] N. Miller, J. W. Ager III, H. M. Smith III, M. A. Mayer, K. M. Yu, E. E. Haller, W. Walukiewicz, W. J. Schaff, C. Gallinat, G. Koblmüller, and J. S. Speck, J. Appl. Phys. 107, 113712 (2010).
- [23] P. A. Anderson, C. H. Swartz, D. Carder, R. J. Reeves, S. M. Durbin, S. Chandril, and T. H. Myers, Appl. Phys. Lett. 89, 184104 (2006).
- [24] X Wang, S. B. Che, Y. Ishitani, and A. Yoshikawa, Appl. Phys. Lett. 92 132108 (2008).
- [25] G. F. Brown, J. W. Ager III, W. Walukiewicz, W. J. Schaff, and J.Wu, Appl. Phys. Lett. 93 262105 (2008).
- [26] H Lu, W. J. Schaff, J. Hwang, H. Wu, W. Yeo, A. Pharkya, and L. F. Eastman, Appl. Phys. Lett. 77 2548 (2000).
- [27] Y. Nanishi, Y Saito, and T Yamaguchi, Jap. J. Appl. Phys. 42 2549 (2003).
- [28] N. Miller, PhD thesis, "Electrical and Electrothermal Transport Properties of n- and p-type InN", University of California, Berkeley, (2010).
- [29] K. Wang, N. Miller, R. Iwamoto, T. Yamaguchi, M. A. Mayer, T. Araki, Y. Nanishi, K. M. Yu, E. E. Haller, W. Walukiewicz, and J. W. Ager III, Appl. Phys. Lett. 98, 042104 (2011).
- [30] X.-G Yu and X.-G. Liang, J. Appl. Phys. 103 043707 (2008].
- [31] D. C. Look and J. R. Sizelove, Phys. Rev. Lett. 82 1237 (1999)
- [32] X. Wang, S. B. Che, Y. Ishitani, and A. Yoshikawa, Appl. Phys. Lett. 90 151901 (2007).
- [33] M. S. Brandt, P. Herbst, H. Angerer, O. Ambacher, and M. Stutzmann, Phys. Rev. B 58 7786 (1998).
- [34] L. Hsu, R. E.; Jones, S. X. Li, K. M. Yu, and W. Walukiewicz, J. Appl. Phys. 102 073705 (2007).
- [35] K. Seeger, K. Semiconductor Physics, (Springer New York, 2002).
- [36] N. Miller et al., submitted.

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor The Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or The Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or The Regents of the University of California.