phys. stat. sol. (b) **245**, No. 5, 873–877 (2008) / **DOI** 10.1002/pssb.200778731

physica status solidi b
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Mg-doped InN and InGaN – Photoluminescence, capacitance–voltage and thermopower measurements

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Received 21 September 2007, revised 26 February 2008, accepted 26 February 2008
Published online 15 April 2008

PACS 61.72.uj, 61.82.Fk, 73.40.Kp, 73.50.Lw, 73.61.Ey, 78.55.Cr

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The bandgap range of InGaN extends from the near-IR (InN, 0.65 eV) to the ultraviolet. To exploit this wide tuning range in light generation and conversion applications, pn junctions are required. The large electron affinity of InN (5.8 eV) leads to preferential formation of native donor defects, resulting in excess electron concentration in the bulk and at surfaces and interfaces. This creates difficulties for p-type doping and/or measuring of the bulk p-type activity. Capacitance–voltage measurements, which deplete the n-type surface inversion layer, have been used to show that Mg is an active acceptor in InN and $In_xGa_{1-x}N$ for $0.2 < x < 1.0$, i.e. over the entire composition range. Mg acceptors can be compensated by irradiation-induced native donors. Thermopower measurements were used to provide definitive evidence that Mg-doped InN has mobile holes between 200 K and 300 K.

1 Introduction Metal-organic chemical vapour deposition (MOCVD) is used to grow $In_xGa_{1-x}N$ layers for blue and green LEDs and lasers and has been used successfully to grow InN [1]. However, phase separation is a frequent problem for In contents greater than about 20% [2–4]. Molecular beam epitaxy (MBE) has been used to grow $In_xGa_{1-x}N$ over the entire composition range and extensive structural and optical characterization has demonstrated that phase separation is not typically present in MBE-grown films [5]. The optical quality of MBE-grown films can be good, as evidenced by the correspondence between the absorption edge and the photoluminescence peak (absence of "Stokes shift") [6].

Based on the experimental measurement of the 1.05 ± 0.25 eV valence band offset between InN and GaN [7] and the known electron affinity of GaN, InN has an electron affinity of 5.8 eV, the largest of any known semiconductor. Using this value, absorption spectroscopy measurements of InGaN, and our recent evaluation of the Fermi-level position as a function of electron concentration in InN [8] and InGaN [9], the band offset diagram shown in Fig. 1 can be developed. In Fig. 1, the positions of the conduction and valence band edges as a function of x in $In_xGa_{1-x}N$ are depicted. Also shown is the Fermi stabilization energy, E_{FS} [10, 11]. The position of the Fermi level E_F in a semiconductor compared to E_{FS} affects the formation energy of charged native defects. Specifically, if $E_F < E_{FS}$, the formation energy of native donor defects is reduced compared to that of acceptors. Conversely, if $E_F > E_{FS}$ the formation energy of native acceptor defects is reduced compared to that of donors. Referring to Fig. 1, the conduction band edge of $In_xGa_{1-x}N$ lies below E_{FS} for $1 > x > 0.35$. Under these conditions, E_{FS} lies in the conduction band and native defects are expected to be donors except in films with very high n-type doping. This is observed experimentally: undoped InN and In-rich InGaN films are always n-type. It is also expected that the surface Fermi level in a semiconductor will be pinned at E_{FS} by surface defects; for InN this pinning is 0.9 eV above the conduction band edge, and surface electron accumulation is expected. Surface electron accumulation has been observed experimentally by high resolution electron energy

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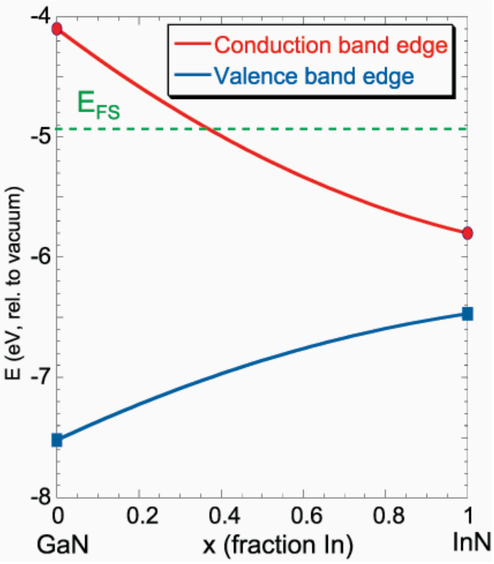

Figure 1 (online colour at: www.pss-b.com) Valence and conduction band edges for $In_xGa_{1-x}N$. The position of the Fermi stabilization energy (E_{FS}) at –4.9 eV is indicated with a dashed line. E_{FS} is above the conduction band edge for $0.35 < x < 1$.

loss spectroscopy [12, 13], angle-resolved photo-electron spectrosocopy [14], scanning tunnelling spectroscopy [15], and capacitance–voltage measurements [8].

Mg is a p-type dopant in GaN and Ga-rich InGaN; it would be expected to be an acceptor in InN, as well. However, the electron-rich surface layer in InN prevents direct measurement of the bulk electrical properties of InN doped with Mg. For example, Hall effect measurements using standard equipment indicate that InN:Mg films are n-type; that is, only the surface layer is measured and the electrically isolated Mg-doped bulk (Fig. 2) is not evaluated.

We have shown recently electrolyte-contacted capacitance–voltage ($C–V$) methods can be used to deplete the surface inversion layer in InN. By modelling the near-surface band bending and carrier concentrations using the Poisson equation, net acceptor concentrations in the 10^{19} cm^{-3} range are found in the bulk of InN:Mg, proving that Mg is an active acceptor in this material [16–18]. Additional evidence for hole conduction in InN:Mg has been reported recently using variable magnetic field Hall effect measurements with fields up to 12 T [19]. Also, photoluminescence measurements have suggested that the Mg activation energy is 60 meV in InN, substantially lower than in GaN [20].

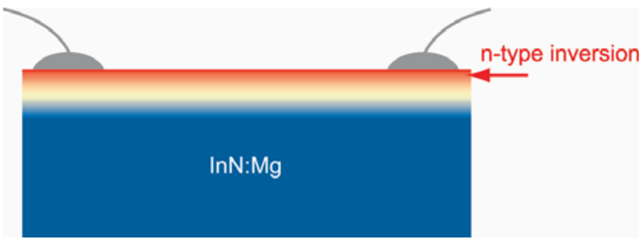

Figure 2 (online colour at: www.pss-b.com) Schematic drawing of InN:Mg (blue), showing the n-type inversion layer in red and the depletion region (light colour) below it.

Here, we report the results of CV experiments that show that Mg is an active acceptor over the entire InGaN composition range. We also show initial results demonstrating that thermopower measurements can be used to observe hole conductivity in the bulk of InN:Mg, in spite of the surface inversion layer.

2 Experimental Undoped and Mg-doped InN and InGaN films were grown by molecular beam epitaxy (MBE) on sapphire substrates. AlN nucleation and GaN buffer layers were used. The typical thicknesses of the InN and InGaN layers are 0.5 µm. Mg was introduced during growth and the incorporated concentration in InN ranged between 2×10^{20} cm^{-3} and 1×10^{21} cm^{-3} in InN as measured by SIMS. These values are much higher than the background electron concentration (mid 10^{18} cm^{-3}) of undoped films grown under similar conditions. The In content was determined with X-ray diffraction and Rutherford backscattering spectrometry. GaN films were grown in a Veeco Gen-200 MBE system on GaN templates.

As discussed above, Hall effect measurements indicated that the Mg-doped InN films were n-type, but with a reduced mobility compared to as-grown films of similar apparent electron concentration. Current–voltage ($I–V$) and $C–V$ measurements were performed with a Biorad ECV profiler using 0.2–1.0 M NaOH as the electrolyte. Capacitance values extracted from the complex admittance using the series, parallel, and 3-terminal models were in good agreement.

Thermopower measurements were performed with the apparatus shown in Fig. 3. Samples were suspended between two temperature-controlled Cu blocks. Voltage was measured between contacts at either end using a Keithley 2000-20 high impedance digital multimeter and the temperature at each contact measured by type-T thermocouples. In order to eliminate possible sources of error the voltage was measured for several small values of ΔT

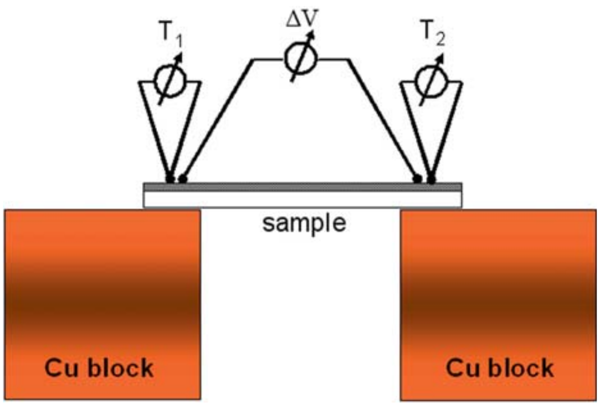

Figure 3 (online colour at: www.pss-b.com) Schematic drawing of the thermopower measurement system.

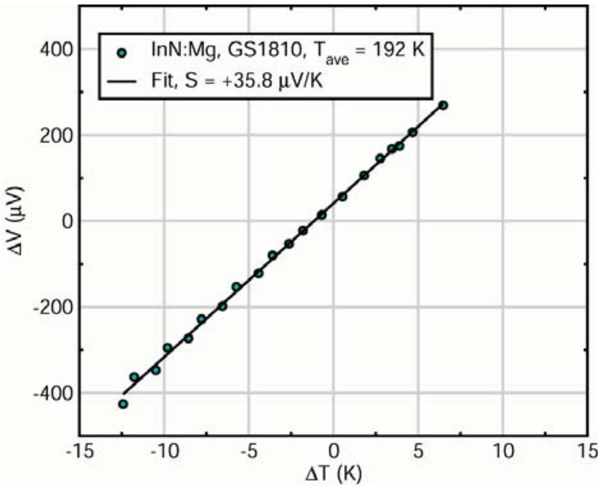

Figure 4 (online colour at: www.pss-b.com) Measured ΔV (in micro-volts) vs. ΔT ($T_2 - T_1$, see Fig. 3) for a InN:Mg film at 192 K. The positive thermopower is definitive evidence of mobile positive charge.

above and below a reference temperature keeping the average temperature of the system at the reference temperature. The slope of a line fit to this data (ΔV vs. ΔT) yields the Seebeck coefficient for the reference temperature, as shown in Fig. 4.

3 Results and discussion Capacitance–voltage data (Mott–Schottky plot, C^{-2} vs. V) for three Mg-doped InGaN films are shown in Fig. 5. For $x = 0.95$ and 0.67, the data are qualitatively similar to what we have reported previously for InN:Mg [17]. There is a region of shallow positive slope at low bias corresponding to space charge due to electrons from the surface donors. At increasing bias, the inversion layer is depleted and the slope of the Mott–Schottky plot changes and becomes negative. At higher applied biases, capacitance corresponding to the depletion edge of the p-type bulk is observed. While the depletion approximation [21] is not valid for the low-bias regions, our Poisson equation modelling has shown that an estimate of N_A–N_D (net acceptor concentration) can be obtained from a linear fit to the data in the negative slope region [18]. Using this method, net acceptor concentrations in the 10^{19} cm^{-3} range are obtained. Previously, we reported similar net acceptor concentrations in InN:Mg films which had Mg concentrations in the 10^{20}–10^{21} cm^{-3} range. It is possible that the measured acceptor concentrations in InN:Mg and InGaN:Mg indicate a substitutional limit for Mg in the 10^{19} cm^{-3} range. The third measured sample was of composition $In_{0.19}Ga_{0.81}N$. Referring to Fig. 1, the conduction band edge of $In_{0.19}Ga_{0.81}N$ lies above E_{FS}. Therefore, a surface inversion layer is not expected for this composition. This is consistent with the monotonic C^{-2} vs. V data shown in Fig. 5, which shows a net acceptor concentration throughout the measurement.

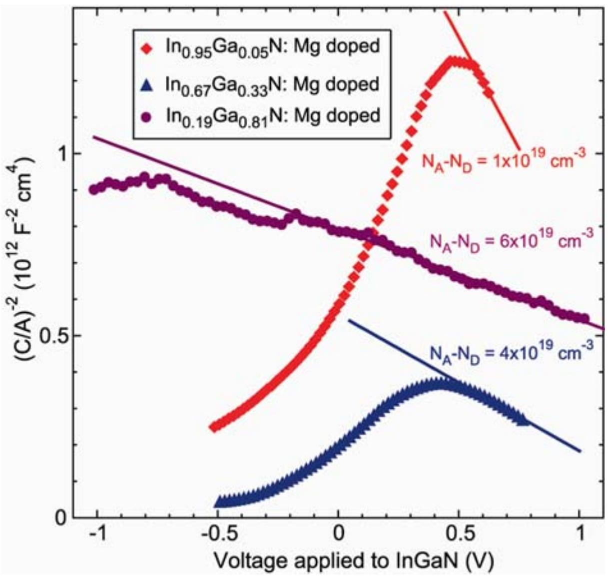

Figure 5 (online colour at: www.pss-b.com) Mott–Schottky plot of electrolyte-contacted capacitance data for three InGaN compositions. The net acceptor concentration was estimated using the depletion approximation in regions where the surface inversion layer (if present) had been depleted (see text).

InN:Mg films for which a bulk net acceptor concentration is detected by the CV method do not have observable photoluminescence (PL) [16]; this is in contrast to the strong and easily observable PL found in undoped InN. The threshold Mg concentration for PL quenching has been reported to be near 10^{19} cm^{-3} [19]. Irradiation of InN films by 2 MeV alpha particles creates a uniform density of point defects and can be used to control the electron concentration in undoped films, since these defects are donors [5, 8, 9]. Here, it is used to compensate the acceptors in InN:Mg. As shown in Fig. 6(a), irradiating InN:Mg produces films with observable PL near the band edge at 0.7 eV. At the irradiation dose where PL appears, the mobility (Fig. 6(b)), also increases. Both of these observations are consistent with full compensation of the Mg acceptors by irradiation-induced native donors, converting the films to n-type polarity. The mobility increase and eventual decrease at very high electron concentrations was quantitatively modelled using a methodology based on ionized impurity scattering that has been described previously [22].

Thermopower data for undoped InN, Mg-doped InN, and Mg-doped GaN are shown in Fig. 7. The measurement of Mg-doped GaN was performed to validate the experimental technique; the values observed for p-GaN are in excellent quantitative agreement with those reported by Brandt et al. [23] for p-GaN with similar hole concentrations. Undoped InN has a negative Seebeck coefficient, as expected for n-type material. A positive Seebeck coefficient is observed for InN:Mg, showing that holes are mobile in this material. No evidence of carrier "freeze-out" was observed for temperatures down to 200 K; this is consistent with degenerate conduction in the highly doped films.

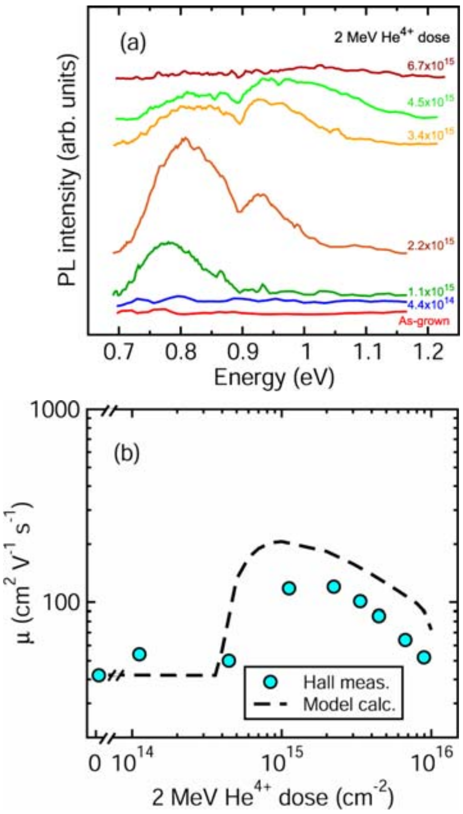

Figure 6 (online colour at: www.pss-b.com) PL (a) and mobility (b) data for irradiated InN:Mg. Irradiation creates native donors which compensate Mg acceptors, leading to observable PL and an increase in mobility (see text). The PL features near 0.9 eV are due to water absorption.

4 Conclusions The large electron affinity of InN creates a strong driving force for native n-type conduction and formation of an electron-rich surface layer. This latter effect prevents direct electrical measurements of hole properties in Mg-doped InN by standard methods such as Hall effect. However, electrolyte-contacted *CV* methods can be used to deplete the surface inversion layer, revealing space charge due to ionized acceptors in the bulk. *CV* measurements were used to show that Mg is an active acceptor over the entire InGaN composition range. Photoluminescence, which is absent in p-type InN, can be "restored" by fully compensating the Mg acceptors with native donors made by particle irradiation. Thermopower measurements provide direct and definitive evidence of mobile holes in InN:Mg under ambient conditions.

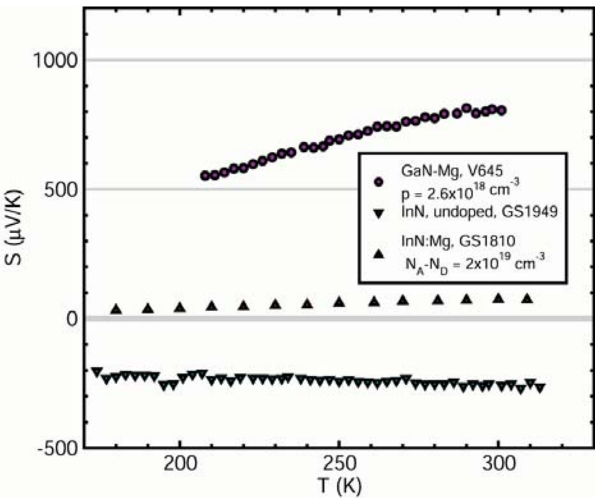

Figure 7 (online colour at: www.pss-b.com) Thermopower data for p-GaN, undoped InN, and Mg-doped InN. A positive thermopower, indicating hole conduction, is observed in Mg-doped GaN and InN.

Acknowledgements This work 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. The work at Cornell University is supported by ONR under Contract No. N000149910936. Growth of the GaN films was supported by Rose Street Energy Labs. N. Miller and R. E. Jones acknowledge support from National Defense Science and Engineering Graduate fellowships.

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