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Revealing of the transition from n- to p-type conduction of InN:Mg by photoconductivity effect measurement

L. Guo[1], X. Q. Wang[1,2], X. T. Zheng[1], X. L. Yang[1], F. J. Xu[1], N. Tang[1], L. W. Lu[1], W. K. Ge[1], B. Shen[1,2], L. H. Dmowski[3] & T. Suski[3]

[1]State Key Laboratory of Artificial Microstructure and Mesoscopic Physics, School of Physics, Peking University, Beijing 100871, China, [2]Collaborative Innovation Center of Quantum Matter, Beijing, China, [3]Institute of High Pressure Physics ''Unipress'', Polish Academy of Sciences, ul. Sokolowska 29/37, 01-142 Warsaw, Poland.

We report evidence of the transition from n- to p-type conduction of InN with increasing Mg dopant concentration by using photoconductivity (PC) measurement at room temperature. This transition is depicted as a conversion from negative to positive PC under above-bandgap optical excitation. The n- to p-type transition in InN:Mg is further confirmed by thermopower measurements. PC detection method is a bulk effect since the optical absorption of the surface electron accumulation is negligibly low due to its rather small thickness, and thus shows advantage to detect p-type conduction. This technique is certainly helpful to study p-type doping of InN, which is still a subject of discussions.

InN has rapidly emerged as a promising candidate for applications in high-speed electronic and optoelectronic devices. Observation of band gap energy of ∼0.64 eV at room temperature makes the coverage wavelength of III-nitrides (InN-GaN-AlN) extend to infrared region and thus greatly broaden the application area[1–3]. For application, high quality InN material with controllable conduction (either n or p-type) is necessary. Fortunately, recent progress in InN epitaxy has led to improved quality, low residual electron concentration, high electron mobility, and evidence of buried *p*-type conductivity[4–7]. However, InN is quite mysterious yet and many efforts are necessary to meet the requirement for applications. One of the key problems hindering the progress is the strong electron accumulation which exists on the surface and at the interface between the InN epitaxial layer and buffer layer as well[8]. These electron accumulation layers greatly hamper the direct measurement of the true transport properties of the bulk InN layer itself and thus it is not possible to reveal the p-type conduction by direct Hall-effect measurement, although temperature-dependent Hall-effect measurement did show buried p-type conduction[9]. Therefore, evidence of p-type conduction is mostly shown by electrolyte-based capacitance-voltage (ECV)[10] and thermopower measurements[11,12]. More evidences of p-type conduction by using other techniques are definitely of great importance at this moment.

Here, we report evidence of transition from n- to p-type conduction of InN by photoconductivity effect at room temperature. This transition is shown by the change from negative to positive photoconductivity effect under above-bandgap excitation. This method is basically a bulk effect since the optical absorption of the surface electron accumulation is negligible due to rather small thickness of the surface layer.

Results

Hall-effect measurements are the most popular method to determine carrier transport properties such as the carrier type, concentration and mobility. The measurement is performed together with resistivity measurement. In the measurement, the probed results are apparent ones and they are true when the sample contains only one kind of carrier, i.e. either electron or hole and the carrier transport takes place in one region of the sample. However, the measurement brings difficulty to precisely determine the transport properties in multi-layer cases such as InN layer in which surface and/or interface layers exist with large density/mobility of electrons. This is more serious in the case of p-type InN, where the p-type conduction might be compensated or covered by stronger n-type conductions so that the directly probed carrier type, concentration and mobility do not reveal the true situation. As a matter of fact, the Hall coefficient is the average of various carriers weighted by the square of mobility ($R_H = (n_n \mu_n^2 + n_p \mu_p^2)/e(n_n \mu_n + n_p \mu_p)^2$) and may always be negative (referring electrons being pre-

dominant) since the mobility of electrons are two orders in magnitude higher than that of holes ($\mu_n > \mu_p$)[6,13,14]. It leads to the situation when the square of the mobility of electrons are four orders higher in magnitude than that of holes ($\mu_n^2 \gg \mu_p^2$), even though the magnitude of the sheet hole concentration is higher than the electron concentration in the electron accumulation layer. That is the reason why all the reported Mg-doped InN samples showed apparently n-type conduction[9,11,12]. On the contrary, thermopower measurements have been confirmed to show buried p-type conduction[11,12,15–18]. The key difference of thermopower measurement over Hall-effect measurement is that the total Seebeck coefficient S is weighted by $n_i\mu_i$[13,14,17,19] ($S_{total} = (n_n\mu_n S_n + n_p\mu_p S_p)/(n_n\mu_n + n_p\mu_p)$) instead of $n_i\mu_i^2$ in the Hall coefficient and thus the relative contribution from the accumulated electrons would be greatly pushed down, where the Seebeck coefficient S is positive ($S > 0$) for holes and negative ($S < 0$) for electrons.

Based on the same idea, we here propose a new approach to study the conduction type of semiconductors like InN by using photoconductivity (PC) measurements at room temperature, where the total conductivity is a superposition of all conductive layers weighted by $n_i\mu_i$ rather than $n_i\mu_i^2$, very similar to the case of thermopower measurement.

Figure 1(a) shows the typical PC response of unintentionally doped InN, where a negative PC is observed. This negative PC has been studied previously. A recombination center at the energy level of E_R near the valence band is proposed to act as a scattering center under illumination[19], leading to negative PC at room temperature[20,21]. The typical processes to explain this negative PC is shown in Fig. 1(b): under illumination, large number of electrons in the valence band (process 1) and donor states (process 2) are excited to the conduction band (E_c), and the corresponding quasi-Fermi levels for electrons (E_{Fn}) and holes (E_{Fp}) are formed. Some free holes will be trapped by the recombination centers (E_R), making the latter positively charged (process 3) and act as scattering centers for electrons. The mobility of electrons is therefore reduced as having been confirmed by the Hall-effect measurement under laser illumination. Hence the photocurrent under laser irradiation shows a distinct drop till saturation with respect to the steady-state dark current as shown in Fig. 1(a), and then the current gradually recovers after the laser is off since the excited electrons recombine with the holes in the recombination center (process 5) and thus the positively charged recombination centers return to neutral.

We would like to stress here that the role of the recombination center level (E_R) in PC of InN is definitely influenced by the Fermi level position which determines the charge state of the centers. In theory, the recombination centers will be occupied by more and

more holes at the equilibrium situation as the Fermi level gradually moves down. Finally those centers will be mainly occupied by holes in p-type material, in particular when the Fermi level approaches to E_R. Consequently, there will be less number of free holes captured from the valence band under the same illumination, since the quasi-Fermi level for holes E_{Fp} would not significantly move away from the equilibrium Fermi level E_F. In other words, the concentration of the photo-generated scattering centers created by the above-bandgap laser illumination is quite low, and even negligible for p-type materials. Therefore, the negative photocurrent should become smaller as the Fermi level moves down and finally switches to positive one when $E_F < E_i$, i.e. in p-type material. That indicates that the reduction of the carrier mobility caused by the photo-generated metastable scattering centers will be gradually weakened with the Fermi level shifting towards valence band. As a result, the PC should normally be positive in p-type InN, as the recombination level does not play important role any more. This positive current will become stronger as the Fermi level further shifts towards the valence band.

The above prediction reveals that the conversion from n- to p-type conduction can be evidenced by that the negative photoconductivity of InN switches to positive one with increasing Mg concentration ([Mg]) and thus provide a novel method to determine n- to p-type conduction conversion with increasing Mg dopant concentration.

Then, figure 2 shows PC results of InN with increasing Mg dopant level. A significant feature is that the PC of InN:Mg samples changes from negative to positive with increasing Mg cell temperature (T_{Mg}), just as we expected. To see more clearly, the saturation photocurrents ($\Delta I = I_{light} - I_{dark}$) are depicted in figure 3(b) as a function of T_{Mg}. The PC keeps negative while ΔI changes from -0.018 to -0.008 mA with increasing T_{Mg} from 200 to 215°C. Further increasing T_{Mg} to 225°C leads to a conversion of PC from negative to positive which is kept till T_{Mg} of 300°C. Meanwhile ΔI increases from 0.001 to 0.0172 mA with increasing T_{Mg} from 225 to 300°C. As shown in Fig. 3(b), the transition from negative to positive PC happens at T_{Mg} between 215–225°C. It is interesting that this transition temperature is in agreement with that from n- to p-type conduction as shown in Fig. 3(a), which is determined by thermopower measurement. For the thermopower measurement, positive value of the Seebeck coefficient indicates p-type conduction whereas negative value means n-type conduction. As shown in Fig. 3(a), there are three regions with increasing T_{Mg}: region I refers to n-type material, where the sample is lightly doped and the doped acceptors cannot completely compensate the residual donors; region II refers to p-type material, where the concentration of the ionized Mg acceptors is higher than that of the ionized donors; region III refers to over-doped case in which the material becomes n-type again because the overdoping reduces the formation energy of donor-like defects and defect
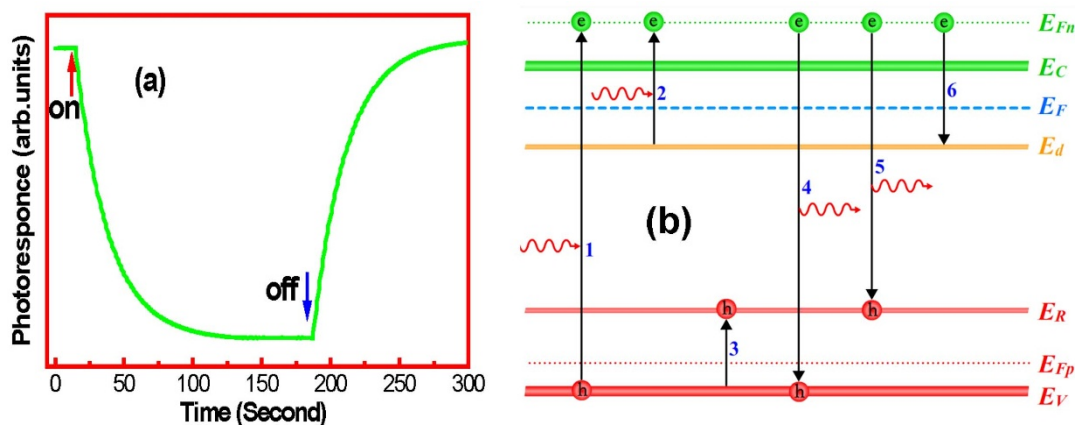

Figure 1 | (a) Photocurrent transient response of unintentionally doped InN, (b) Energy-level diagrams showing electron transitions responsible for the photocurrent trasient response with above-bandgap excitation.
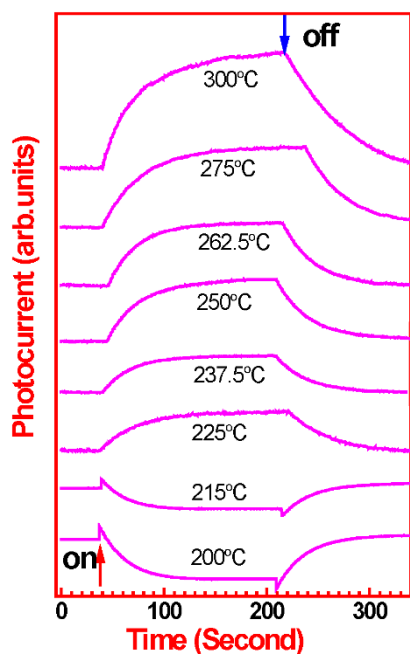
Figure 2 | Photocurrent transient response of the Mg-doped InN layers with different Mg cell temperatures under above-bandgap illumination measured at room temperature (300 K).
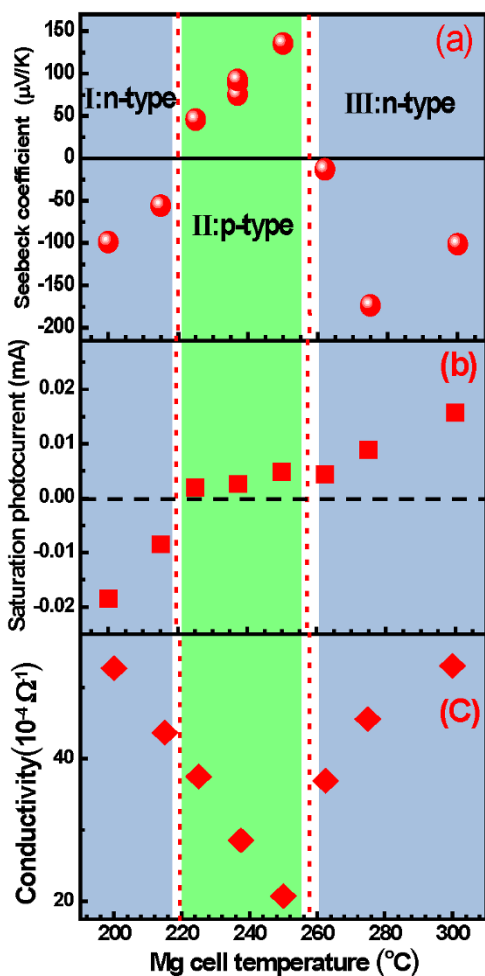

Figure 3 | (a) Seebeck coefficients, (b) Saturation photocurrents ($\Delta I = I_{light} - I_{dark}$) and (c) conductivities of the Mg-doped InN layers as a function of T_{Mg}.
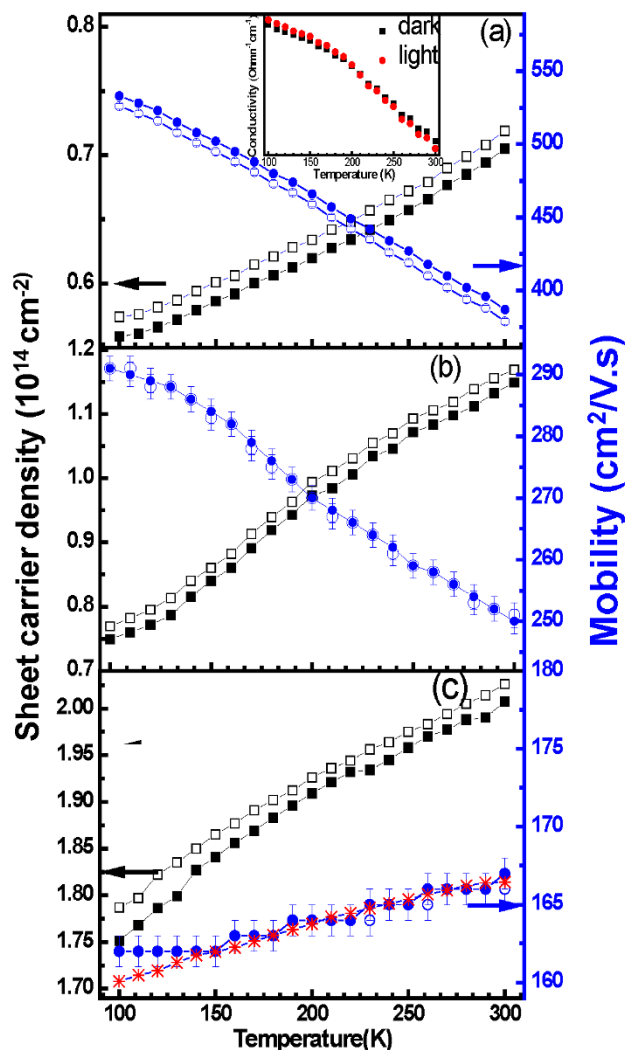

Figure 4 | Temperature-dependent sheet carrier density (solid square) and mobility (solid circle) in dark condition as well as sheet carrier density (open square) and mobility (open circle) under illumination at temperatures from 100 to 300 K of the Mg-doped InN layers with T_{Mg} of (a) 215°C (the conductivities with and without illumination are shown in the inset), (b) 225°C, and (c) 300°C [simulation curves (red stars) fitted to the experimental data] respectively, where error bars are also shown.

complexes but increases the formation energy of acceptor-like ones, leading to another conversion of the conduction type. This is similar to the previously reported investigations by both ECV and thermo-power measurement[11,15–17]. It is noted that the agreement between transition temperature from negative to positive PC and that from n- to p- conduction type confirms the above theoretical prediction.

Discussion

Fig. 3(b) shows that the PC is not negative as expected for n-type materials in the over-doped region (region III). To understand this, temperature-dependent Hall-effect measurements were performed for those samples in all of the three regions and the results are shown in figure 4. It is shown there that the mobility in the temperature range of 100–300 K is reduced upon light irradiation for the Mg-doped InN layers with $T_{Mg} = 215°C$ (Fig. 4(a)) while it almost does not change for $T_{Mg} = 225$ (Fig. 4(b)) and 300°C (Fig. 4(c)). One can tell that, in region I, $\Delta\mu$ ($\mu_{light} - \mu_{dark}$) is negative in the entire temperature range of 100–300 K as shown in Fig. 4(a), resulting in $|n\Delta\mu| > |\Delta n\mu|$, and thus leading to a negative photoconductivity ($\Delta\sigma$
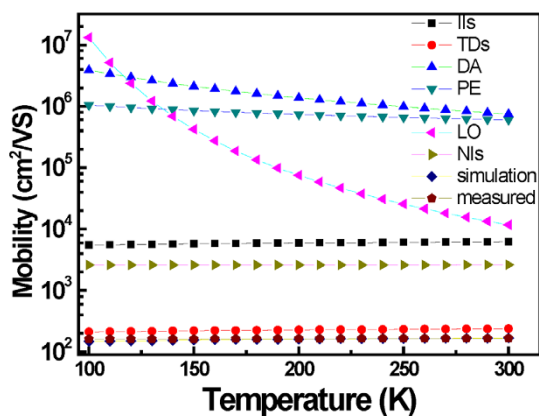
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Figure 5 | Relevant importance of the various scattering mechanisms, considering polar optical phonons (LO), acoustic phonons [including deformation potential (DA) and piezoelectric (PE) mode)], threading dislocations (TDs), ionized impurities (IIs), and neutral impurities (NIs), for the InN:Mg with T_{Mg} of 300°C. μ_e is quite high if only considering phonon scattering and decreases with increasing temperature, the mobility is greatly suppressed when large numbers of impurities and threading dislocation are taken into account and fits to the experimental data well.

$= \sigma_{light} - \sigma_{dark} \approx e(n + \Delta n)(\mu + \Delta\mu) - en\mu = en\Delta\mu + e\Delta n\mu$). This is shown by the smaller conductivity under illumination than that in dark at room temperature, as shown in the inset of Fig. 4(a). The former σ_{light} becomes larger than the latter σ_{dark} at temperatures lower than 200 K, which is the same as the unintentionally doped InN[21]. In region II, although the Hall-effect measurement is not sufficient to reliably reveal the variation of the hole mobility upon light irradiation, the directly probed mobility did not show detectable change upon light irradiation at 100–300 K as shown in Fig. 4(b). That coincides with our prediction that positive PC should be observed.

In region III, the sample actually returns to n-type. However, the photocurrent is still positive and ΔI keeps rising with increasing T_{Mg}. Hall-effect measurement shows that this region looks different from region I. As shown in Fig. 4 (c), the carrier mobility is less than 200 cm²/Vs and it does not show any difference with and without light irradiation. The mobility increases slightly from 162 to 166 cm²/Vs with increasing temperature from 100 to 300 K. This is quite different from that of lightly-doped InN whose carrier mobility decreases from 525 to 380 cm²/Vs with increasing temperature from 100 to 300 K. Quantitative simulations for the temperature-dependent mobility have been made for this sample and the simulated results are shown in figure 5. It shows that dislocations and impurities are dominant scatters. This is reasonable since the ionized or neutral impurities and dislocations in the over-doped InN layers (region III) are generally much higher than those in the light-doped InN layers (region I)[7,22,23]. The recombination centers thus do not play the same important role as it does in samples at region I anymore and the effect of photo-generated metastable scattering centers on electron mobility is negligible. Therefore, the positive PC is observed.

The positive PC observed in region-III implies a limitation for detecting conduction by using photoconductivity measurement itself. This shortage can be overcome by simply comparing the conductivity as shown in Fig. 3(c). It is obvious that the conductivity decreases with increasing T_{Mg} to 250°C and then greatly increases with further increasing T_{Mg}, which clearly show the overdoping effect and thus one can conclude the p- to n-type conduction easily. This is because the total conductivity is a superposition of the surface accumulation layer and the bulk weighted by $n_i\mu_i$, $\sigma_{total} = en_s\mu_s + qn_b\mu_b$,

n and μ are sheet carrier density and carrier mobility respectively, the subscript s and b represent surface electron accumulation layer and the bulk respectively. Therefore, the total conductivity for p-type material (σ_{total}) is low since the much smaller hole mobility compared with electron which leads to the low bulk conductivity ($qn_b\mu_b$), provided that the surface conductivity is almost constant. When the InN becomes overdoped, the bulk conductivity contribution becomes larger since the majority carrier changes to electron and thus the total conductivity jumps up as shown in Fig. 3(c). Further increasing Mg dopants leads to higher electron density and increased conductivity as well.

In conclusion, a method to detect the transition from n- to p-type conduction of Mg-doped InN has been proposed and practiced by using photoconductivity measurements. This transition was detected by the conversion of negative to positive photoconductivity, and has been further confirmed by thermo-power measurements. By comparing the conductivity, one can actually also detect the p- to n-type transition as well. It should be emphasized that this method is basically a bulk effect since the optical absorption of the surface electron accumulation is negligible due to rather small thickness of the surface layer. Therefore, it shows advantage to study materials with strong surface electron accumulation or surface states like InN.

Methods

Sample preparation. InN layers were grown by plasma-assisted molecular beam epitaxy. 4.5-μm-thick GaN layers grown by metal-organic vapor phase epitaxy were used as templates. After re-growth of a 200-nm-thick GaN layer on the GaN template, 800-nm-thick either undoped or Mg-doped InN films were directly grown. The InN growth was performed under slightly In-rich condition, which leads to a flat surface and efficient Mg incorporation.

Measurements. the photocurrent was measured by the semiconductor parameter analyzer (Aglient-4155) and the illumination was carried out by the semiconductor laser which was output by the coupling optical fiber. The estimated penetration depth of the incident laser beam is about 200 nm since the absorption coefficient at 808 nm is about 5×10^4 cm^{-1} [24]. For the electrical measurements, two electrodes in coplanar stripe with a length of 1 mm and apart of 7 mm were fabricated by evaporating Ti/Al/Ni/Au. Carrier concentration and mobility were investigated by Hall-Effect measurement system (ACCENT-HL5500).

1. Rinke, P. *et al.* Consistent set of band parameters for the group-III nitrides AlN, GaN, and InN. *Phys. Rev. B* **77**, 075202 (2008).
2. Wu, J. *et al.* Temperature dependence of the fundamental band gap of InN. *J. Appl. Phys.* **94**, 4457 (2003).
3. Jani, O. *et al.* Design and characterization of GaN/InGaN solar cells. *Appl. Phys. Lett.* **91**, 132117 (2007).
4. Lu, H. *et al.* Growth of a-plane InN on r-plane sapphire with a GaN buffer by molecular-beam epitaxy. *Appl. Phys. Lett.* **83**, 1136–1138 (2003).
5. Nanishi, Y. *et al.* RF-Molecular Beam Epitaxy growth and properties of InN and related alloys. *Jpn. J. Appl. Phys.* **42**, 2549–2559 (2003).
6. Wang, X. Q. *et al.* High-Electron-Mobility InN layers grown by Boundary-Temperature- Controlled epitaxy. *Appl. Phys. Exp.* **5**, 015502 (2012).
7. Wang, X. Q., Che, S. B., Ishitani, Y. & Yoshikawa, A. Growth and properties of Mg-doped In-polar InN films. *Appl. Phys. Lett.* **90**, 201913 (2007).
8. Mahboob, I. *et al.* Intrinsic Electron Accumulation at Clean InN Surfaces. *Phys. Rev. Lett.* **92**, 036804 (2004).
9. Ma, N. *et al.* Anomalous Hall mobility kink observed in Mg-doped InN: Demonstration of p-type conduction. *Appl. Phys. Lett.* **97**, 222114 (2010).
10. Wang, X. Q. *et al.* Systematic study on p-type doping control of InN with different Mg concentrations in both In and N polarities. *Appl. Phys. Lett.* **91**, 242111 (2007).
11. Dmowski, L. H. *et al.* Search for free holes in InN:Mg-interplay between surface layer and Mg-acceptor doped interior. *J. Appl. Phys.* **105**, 123713 (2009).
12. Bierwagen, O., Choi, S. & Speck, J. S. Hall and Seebeck profiling: Determining surface, interface, and bulk electron transport properties in unintentionally doped InN. *Phys. Rev. B* **84**, 235302 (2011).
13. Wang, X. Q. *et al.* Hole mobility in Mg-doped p-type InN films. *Appl. Phys. Lett.* **92**, 132108 (2008).
14. Ma, N. *et al.* Hole mobility in wurtzite InN. *Appl. Phys. Lett.* **98**, 192114 (2011).
15. Ager III, J. W. *et al.* Mg-doped InN and InGaN – Photoluminescence, capacitance–voltage and thermopower measurements. *Phys. Status Solidi B* **245**, 873–877 (2008).
16. Wang, K. *et al.* Mg doped InN and confirmation of free holes in InN. *Appl. Phys. Lett.* **98**, 042104 (2011).

17. Bierwagen, O., Choi, S. & Speck, J. S. Hall and Seebeck measurement of a p-n layer stack: Determining InN bulk hole transport properties in the presence of a strong surface electron accumulation layer. *Phys. Rev. B.* **85**, 165205 (2012).
18. Miller, N. *et al.* Hole transport and photoluminescence in Mg-doped InN. *J. Appl. Phys.* **107**, 113712 (2010).
19. Arnaudov, B. *et al.* Energy position of near-band-edge emission spectra of InN epitaxial layers with different doping levels. *Phys. Rev. B* **69**, 115216 (2004).
20. Wei, P. *et al.* Room-temperature negative photoconductivity in degenerate InN thin films with a supergap excitation. *Phys. Rev. B* **81**, 045306 (2010).
21. Guo, L. *et al.* Temperature sensitive photoconductivity observed in InN layers. *Appl. Phys. Lett.* **102**, 072103 (2013).
22. Wang, K. *et al.* Effect of dislocation scattering on the transport properties of InN grown on GaN substrates by molecular beam epitaxy. *App. Phys. Lett.* **89**, 162110 (2006).
23. Wang, X. *et al.* Polarity inversion in high Mg-doped In-polar InN epitaxial layers. *Appl. Phys. Lett.* **91**, 081912 (2007).
24. Wu, J. *et al.* Effects of electron concentration on the optical absorption edge of InN. *Appl. Phys. Lett.* **84**, 2805–2807 (2004).

Acknowledgments

Author contributions

Additional information