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

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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 area1–3. 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 conductivity4–7. 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 well8. 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 conduction9. Therefore, evidence of p-type conduction is mostly shown by electrolyte-based capacitance-voltage (ECV)10 and thermopower measurements11,12. 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 (RH = (n_e μ_n^2 + n_p μ_p^2)/e(n_e μ_e + n_p μ_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 \((\mu_n > \mu_p)^{11,13,14}\). 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\(^{11,12,15–18}\). 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 \(n_i \mu_i^2\) in the Hall coefficient and thus the relative contribution from the accumulated electrons would be greatly pushed down, whereas 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 \(E_F\) near the valence band is proposed to act as a scattering center under illumination\(^9\), 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 conduction band \((E_c)\) and donor states \((E_d)\) are excited to the conduction band \((E_c)\), and the corresponding quasi-Fermi levels for electrons \((E_{Fp})\) and holes \((E_{Fn})\) are formed. Some free holes will be trapped by the recombination centers \((E_b)\), making the latter positively charged \((\text{process 3})\) 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 \((\text{process 5})\) and thus the positively charged recombination centers return to neutral.

We would like to stress here that the role of the recombination center level \((E_b)\) 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 \(E_F < E_F\), 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 \([(\text{Mg})]\) 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:0.001Mg samples changes from negative to positive with increasing Mg cell temperature \((T_{\text{Mg}})\), just as we expected. To see more clearly, the saturation photocurrents \((\Delta I = I_{\text{light}} - I_{\text{dark}})\) are depicted in figure 3(b) as a function of \(T_{\text{Mg}}\) 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 \(T_{\text{Mg}}\): 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 transient response with above-bandgap excitation.
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 thermopower measurement\textsuperscript{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 $T_{\text{Mg}}$ 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.
n and \( \mu \) 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 (\( \sigma_{\text{total}} \)) is low since the much smaller hole mobility compared with electron which leads to the low bulk conductivity (\( q n_b \mu_b \)), 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-\( \mu \)m-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 (Agilent-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 \( \times \) 10^{15} cm^{-1}. For the electrical measurements, two electrodes in coplanar stripe with a length of 1 mm and apart of 7 mm were fabricated by evaporating Ta/Al/Ni/Au. Carrier concentration and mobility were investigated by Hall-Effect measurement system (ACCENT-HL5500).

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Author contributions

X.Q.W. supervised the project. L.G. and X.Q.W. designed the experiments. X.Q.W. and X.T.Z. performed the film growth. L.G., X.L.Y. and L.W.L. performed the photconductivity measurement. L.H.D. and T.S. performed thermopower measurement. L.G. and X.Q.W. wrote the paper. F.J.X., N.T., L.W.L., W.K.G. and B.S. gave scientific advices. All the authors contributed through scientific discussion and reviewed the manuscript.

Additional information

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