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Investigation on the structural origin of n-type conductivity in InN films

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Abstract
This work presents a study of the correlation between the electrical properties and the structural defects in nominally undoped InN films. It is found that the density of edge-type threading dislocations (TDs) considerably affects the electron concentration and mobility in InN films. The Hall-effect measured electron concentration increases, while the Hall mobility decreases with the increase in the edge-type TD density. With the combination of secondary ion mass spectrometry and positron annihilation analysis, we suggest that donor-type point defects at the edge-type TD lines may serve as dominant donors in InN films and affect the carrier mobility.

1. Introduction

InN has been an important issue for its newly discovered small band gap value (~0.7 eV) [1, 2] since 2002. Based on this finding, In(Ga,Al)N alloys cover the spectral range continuously from near-infrared to ultraviolet and make it possible to fabricate high-efficiency tandem solar cells based solely on nitrides [3]. However, the challenge in controlling the electrical properties of InN remains one of the major obstacles in the progress of device development. So far, nearly all nominally undoped InN films were found to be n-type conductive with an electron concentration of 10^{17}–10^{21} cm^{-3}, and it is very difficult to achieve effective p-type doping because of the strong compensation effect of background electrons.

Despite recent progress, the origin of the high electron concentration in nominally undoped InN is still an open question, and the contribution of various donor-type defects and impurities to the properties of this material awaits a detailed evaluation. Impurity atoms (e.g. O and H) [4, 5] and surface electron accumulation [6], which were once suggested to be the source of the measured n-type conductivity in InN, cannot account for the measured electron concentration. Other mechanisms of electron generation, such as native donor defects or other structure defects, may play a dominant role in determining the electrical properties of InN. Recently published results highlighted the contribution of dislocations to the electron concentration in InN epilayers [7, 8]. By taking both constant background electron density (due to donor impurities and surface accumulated electron density) and donor-type nitrogen vacancies (V_N) confined in the core of edge-type threading dislocations (TDs) into account, the variation of the apparent electron concentration with the film thickness characterized by Hall measurements can be well modelled [7]. However, more experimental works are still needed to further identify the structural origin of n-type conductivity in InN films.

Thus, in this work, we have conducted a variety of experimental techniques to characterize metalorganic chemical vapour deposition (MOCVD) grown InN films and aimed at revealing the relevance between n-type conductivity and specific structural defects of InN films. The combined results further suggest that the electrical properties of InN films are strongly influenced by the density of edge-type TDs.

2. Experimental

In-polar InN films with a nominal thickness of 200–400 nm were grown by MOCVD. These InN samples with various dislocation densities were prepared under different growth conditions [9]. The 4 μm thick Ga-face GaN layers grown on the *c*-plane sapphire substrate by MOCVD served as

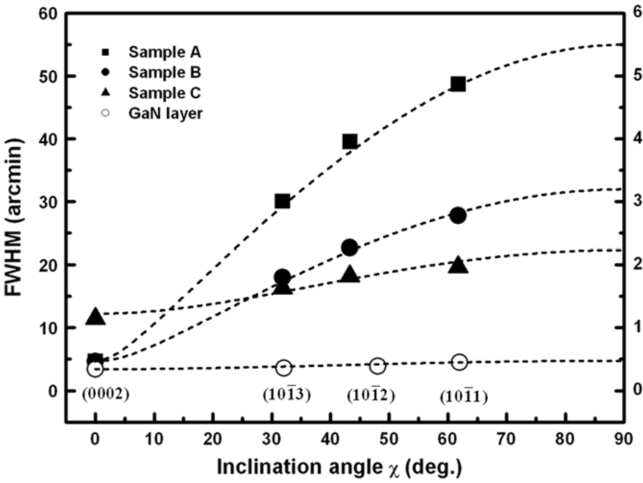

Figure 1. FWHM of x-ray rocking curves measured in a skew symmetric geometry as a function of the lattice plane inclination angle with respect to (0 0 0 2). The dashed lines are fitting curves.

templates for the InN growth. Prior to the growth, the as-grown GaN templates were thermally cleaned at 700 °C in NH_3 atmosphere. Trimethyl indium and NH_3 were used as precursors for In and N, respectively. The van der Pauw method was employed in the Hall measurements to obtain room-temperature electron concentration and mobility. Hall measurements revealed an n-type carrier concentration of $\sim 4 \times 10^{18}$–$5 \times 10^{19}\,\mathrm{cm}^{-3}$ for nominally undoped materials with an electron mobility of 1310–300 $\mathrm{cm}^2\,\mathrm{V\,s}^{-1}$.

In order to quantify the TD density in InN films, the full widths at half maximum (FWHMs) of the ω-scan rocking curves of InN films were measured by double crystal x-ray diffraction (DC-XRD). The measured FWHMs of symmetric (0 0 0 2) and skew (1 0 $\bar{1}$ l) reflection rocking curves of InN films and the as-grown GaN template are plotted (in figure 1, three InN samples with varying grain diameters are selected for illustration) as a function of the inclination angle (χ) between (0 0 0 2) and (1 0 $\bar{1}$ l) planes of the InN films, where l equals 3, 2 or 1 [10]. The dashed lines in the figure are fitting curves using the formula proposed in [11]. From these fitting curves, the FWHM of the (1 0 $\bar{1}$ 0) rocking curves can be extrapolated to $\chi = 90°$. The FWHMs of (0 0 0 2) and (1 0 $\bar{1}$ 0) rocking curves reflect the mean tilt and twist, respectively. Assuming localized edge-type TDs at grain boundaries and a random distribution of screw-type TDs in the films while taking the finite size broadening into account, the extracted tilt and twist angles of InN films can be used to calculate the TD density with screw and edge components, respectively [12]. In table 1, we have listed some growth parameters, the calculated TD density and other characteristic results of samples A, B and C.

3. Results and discussion

As shown in figure 1, the FWHM monotonically increases with the inclination angle (χ) between (0 0 0 2) and (1 0 $\bar{1}$ l) planes for these three InN samples. This indicates, compared with the GaN template we used, that there is a much larger twist than tilt in InN films, i.e. edge-type TDs are the dominant dislocation type in our samples. It is known that either edge- or screw-type TD density in our InN samples is affected by the lateral grain size [9]. The high edge-type TD density in InN films can be attributed to the large in-plane lattice mismatch (∼10%) between InN and GaN and island growth mode of InN on GaN.

Figure 2(*a*) shows the measured free-electron concentration as a function of the edge-type TD density of all investigated InN samples. In a statistical study, it is found that the electron concentration of InN films is nearly uninfluenced by the screw-type TDs (not shown here), but is strongly dependent on the edge-type TD density. Typically, the electron concentration obtained by Hall measurements is considerably affected by electron accumulation existing near the surface, especially for thinner films. However, the electrical charge associated with the surface accumulation, i.e. the two-dimensional sheet free electron, is of the order of $2.5 \times 10^{13}\,\mathrm{cm}^{-2}$ and located within a few nanometres of the surface [7, 13]. It has only a limited influence on the data of the electron concentration obtained by Hall measurements on the investigated InN films. Therefore, the obtained Hall data can well reflect the main feature of the bulk electron concentration in our samples. In fact, it can be seen from figure 2(*a*) that the edge-type TD density has a strong influence on the electron concentration in InN films. The electron concentration really increases with increasing edge-type TD density. Meanwhile, with the increase in the edge-type TD density, the electron mobility decreases rapidly, as shown in figure 2(*b*). The variation in electron transport properties of these films can be explained by the interaction between electrons and TDs. Electric active TDs can decrease the mobility either by distortion of the crystal lattice or by charged Coulombic scattering centres in and near the dislocation lines [14, 15].

There is a spread in the electrical data for the films with similar edge-type TD density. This fact suggests that there exist other mechanisms acting on the electrical properties of InN films. For example, comparatively, the films grown under a higher V/III ratio have improved electrical properties. By using a V/III ratio above 10^5, an InN film with an electron concentration of $\sim 5 \times 10^{18}\,\mathrm{cm}^{-3}$ and a Hall mobility up to 1310 $\mathrm{cm}^2\,\mathrm{V}^{-1}\,\mathrm{s}^{-1}$ has been achieved on GaN (0 0 0 1) by MOCVD. However, it is found that when edge-type TD density is higher than $10^{10}\,\mathrm{cm}^{-2}$, the effect of a high V/III ratio on both carrier density reduction and mobility increase becomes very small in comparison with the influence of the TD concentration, as indicated by the open data points in figure 2. Therefore, it is believed that the edge-type TD density should be the dominant factor in determining the electrical properties of InN films.

It is known that the effect of dislocation lines on the electronic behaviour of semiconductor material originates from two regions, i.e. the core region and the surrounding region around the core with a local strain field and possible point defect decorations. The energy levels can be induced by broken bonds, impurities and other point defects in and near the core of dislocations [16]. So, it is necessary to compare the content of typical donor-type impurities in the investigated heavily n-type-doped InN films with different edge-type TD densities.

Table 1. The growth parameters and characterized results of samples A, B, and C. The edge- and screw-type TD densities were estimated by XRD measurement, and the average grain diameter is determined by an atomic force microscope (AFM)

Samples	Growth temperature (°C)	Input V/III ratio ($\times 10^3$)	Average grain diameter (nm)	Electron concentration ($\times 10^{18}$ cm^{-3})	RT mobility (cm^2 V^{-1} s^{-1})	TD density (cm^{-2}) Edge-type ($\times 10^9$)	TD density (cm^{-2}) Screw-type ($\times 10^7$)
A	400	22.3	120	47.6	302	160.5	3.1
B	450	4.4	250	18.6	626	17.6	3.2
C	500	17.9	1000	5.5	1310	1.2	14.3

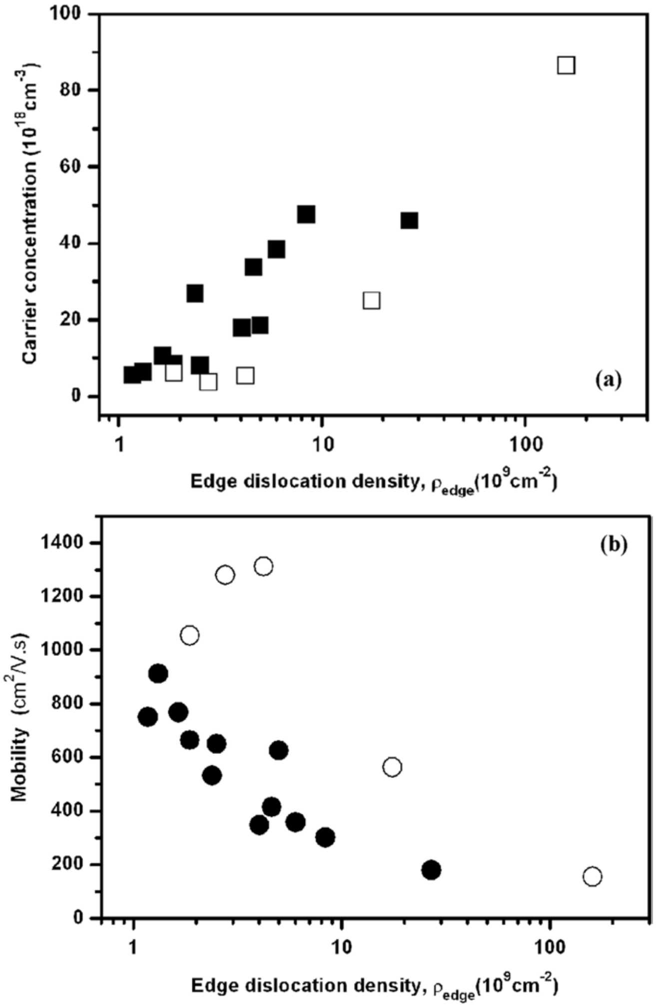

Figure 2. Free-electron concentration (*a*) and electron Hall mobility (*b*) as a function of edge-type TD density in MOCVD-grown InN samples. The solid data points are obtained from the samples grown under different conditions. The open squares and circles represent the data obtained from several selected samples which are grown with a V/III ratio above 10^5.

We have performed secondary ion mass spectrometry (SIMS) experiments on the three samples listed in table 1. SIMS experiments were conducted using a Cameca IMS 6*f* magnetic sector instrument with a caesium primary beam. The relative content of impurities in InN can be evaluated by normalization with respect to the matrix ion In$^+$ [17]. It means that the measurement error is related to surface morphology, and after normalization we can directly compare the impurity content for the investigated InN films. In figures 3(*a*) and (*b*), SIMS impurity profiles showed a relatively higher O and H level near the surface of InN films and at the InN/GaN interface in these samples. Very recently, the role of H-atom doping in the electrical property of InN has been theoretically and experimentally investigated [18,19]. The results suggested that monatomic hydrogen was an important cause of unintentional n-type conductivity, and it was shown that the donor density in the InN layer increased significantly after H ion irradiation. But, in our study, it seems that the electrical properties of the investigated samples have less dependence on the detected impurity contents because the average relative H and O contents in sample C, which has the best electrical properties among the three samples, are higher than those of samples A and B. Considering that the carrier density (as shown in table 1) of InN samples in this study is much higher than that of the reported hydrogenated samples [18], we suggest that the impurity donors, such as O and H, incorporated during growth are not the dominant source of unintentional donors of the InN films which have a very high edge-type TD density.

On the other hand, it was reported that negatively charged Ga vacancies (V_{Ga}) present along the core of edge-type TDs in GaN [20] might provide acceptor-type traps and form negatively charged scattering centres in n-type GaN [15, 21]. So, the next question is whether the edge-type TDs in InN are also negatively charged and the related indium vacancy (V_{In}) exists around the dislocations just like in other III-group nitride semiconductors. Positron annihilation measurement is known as a powerful tool for characterizing the concentration of point defects in materials [22]. We carried out positron annihilation experiments on the three InN films (as described in table 1) to gain further insight about the relationship between edge-type TD density and point defects in InN. In these experiments, the Doppler broadening spectrum of the annihilation line is recorded with a high-purity Ge detector. The broadening is described by the conventional low momentum parameter S [22].

Figure 4 shows the S parameter as a function of positron incident energy for the three InN/GaN samples, providing a depth profile of the S parameter. The high S parameter at low energies ($E < 3$ keV) results from the annihilation at the sample surface [16] and the S parameter in the energy range from 3 to 9 keV corresponds to the annihilation in the InN layer, and at even higher energies the S parameter decreases as fewer positrons can reach the underlying GaN layers. It is known that V_{In} in InN are negatively charged [23] and when positrons meet V_{In}, the low momentum parameter S increases due to the increased probability of annihilation with low momentum electrons. In other words, the concentration of V_{In} in InN can

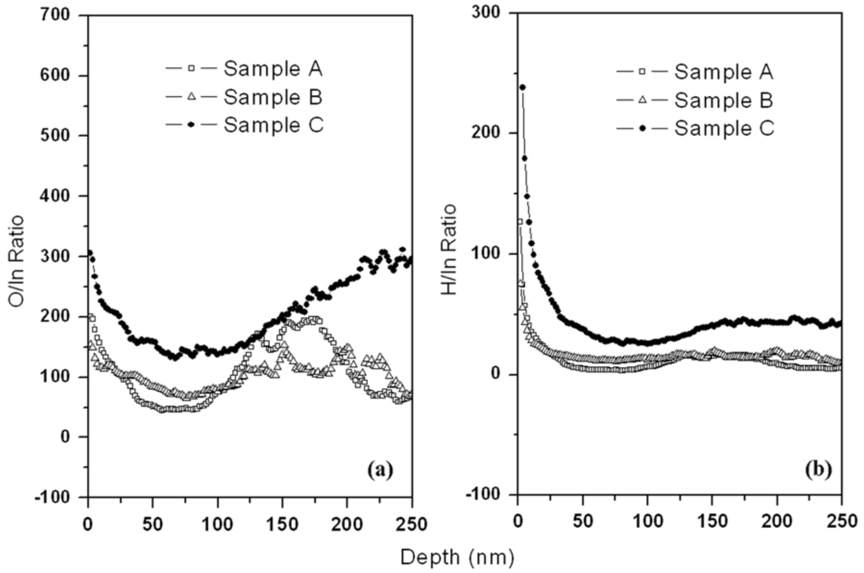

Figure 3. SIMS depth profile for O (*a*) and H (*b*) elements, respectively. The related concentration has been normalized by In signal of InN samples.

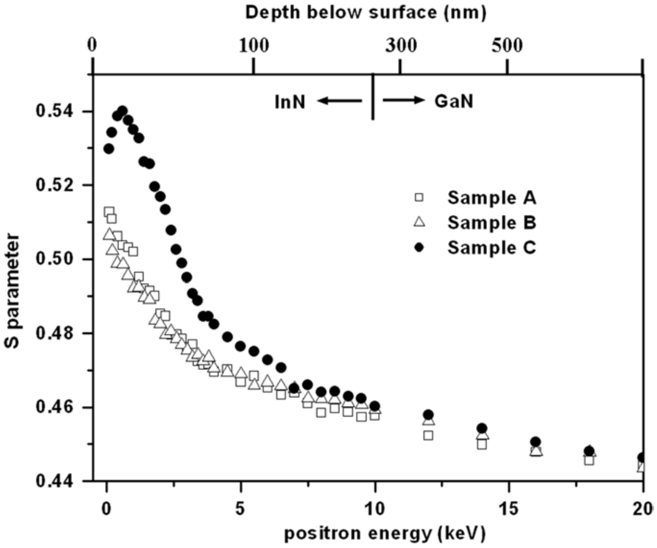

Figure 4. The dependence of the low momentum parameter S on the positron incident energy (or the depth below surface) in InN samples A, B and C.

be reflected by the S parameter. A larger S parameter implies a higher V_{In} concentration [24]. In our case, the S parameter value of the sample C is higher than those of other two InN samples, as shown in figure 4. It suggests that there are more V_{In} in sample C, although it has fewer edge-type TDs. We attribute the difference in the V_{In} concentration among the three samples to their different growth temperatures. When the growth is carried out at a temperature close to InN decomposition, more In lattice sites may be left empty [25]. But the important finding from figure 4 is that the formation of V_{In} in InN films is not spatially related to the edge-type TD lines, i.e. the edge-type TDs in InN films are apparently not V_{In} related.

Theoretical calculations show that the characteristics of preferably generated point defects in III-nitride semiconductors are determined by the position of the Fermi energy E_F level relative to the Fermi level stabilization energy E_{FS} [26]. In the case of InN, where $E_F < E_{FS}$, donor-type V_N defects are more likely to form than other point defects. Thus, with all the above-mentioned facts taken into account, it is reasonable to propose that it is the donor-type point defects at the edge-type TD lines that serve as the dominant donors in InN epilayers and affect the carrier mobility. In addition, as shown in figure 2, we found that the V/III molar ratio has a significant effect on the electrical property of InN films, indicating that some kinetic parameters such as stoichiometric N-to-In ratio on the growth surface can influence the concentration of bulk native defects and also the core structure of TDs.

4. Conclusions

In summary, we have studied the effects of TD density on the electrical properties of InN films grown by MOCVD. It is found that the edge-type TDs have strong effects on the electron concentration and mobility in InN films, i.e. the electron concentration increases, while the Hall mobility decreases with the increase in edge-type TD density. Our data from SIMS and positron annihilation measurements suggest that the edge-type TDs in InN films are neither H or O impurity related or V_{In} related. It is thus more reasonable to attribute the observed higher electron concentration and lower Hall mobility in InN films with a higher edge-type TD concentration to positively charged point defects around edge-type TDs in InN films.

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