

MOVPE growth and characterization of indium nitride on C-, A-, M-, and R-plane sapphire

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We have investigated the heteroepitaxial growth of indium nitride on sapphire substrates having different orientations. Growths were performed on C-, A-, M-, and R-plane-oriented sapphire in order to analyze the substrate orientation effect on the structural, optical, and electronic properties of InN. The orientation relationship between InN and sapphire was deduced by $\theta/2\theta$ High-resolution X-ray diffraction (HRXRD) measurements. These experiments show the ability to grow InN along nonpolar (11<u>2</u>0) orientation and the semipolar (11<u>2</u>2) orientation, depending of the orientations of the sapphire substrate. The

1 Introduction Indium nitride has recently received much substantial consideration, after the identification of its small band gap around 0.7 eV [1, 2] has been made. It is a very promising material for realizing optoelectronic devices susceptible of operation in the near infrared region of the electromagnetic spectrum. It will permit the nitride semiconductors to cover the optical range from 6.3 eV for aluminum nitride down to 0.7 eV for indium nitride.

Today, III/V nitrides are commonly grown on (0001) oriented sapphire substrate. A spontaneous polarization exists along the (0001) direction in wurtzitic (C_{6V}) crystals. This field and the stress-induced piezoelectric field if any, may be very deleterious for light generation: absorption in low dimensional systems due to quantum confined stark effect. The field-induced separation of electrons and holes, at different heterointerface, reduces the overlap of the electron hole wave functions, which reduces the light matter coupling efficiency, and in addition red shifts the luminescence. A useful approach for arm twisting (or reducing) the effects of these electric fields is to grow nitrides along nonpolar or semipolar directions, trying to encountered situation where both spontaneous polarization fields and piezoelectric one may compensate each other.

crystalline quality was assessed by XRD symmetric and asymmetric rocking curve measurements. We observed no drastic disparity between our samples, all exhibiting a reasonable crystalline quality. Atomic force microscopy imaging on these layers revealed different surface morphologies with a roughness varying between 30 and 60 nm. Electrical properties of the InN samples were investigated by room temperature Hall effect measurements and a line shape fitting of the photoluminescence was performed in order to get optically the values of the residual carrier density in the nitride layers.

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The growth of III–V nitrides semiconductors along nonpolar and semipolar directions have been already studied in fairly extensive details and it is now a well-documented topic in case of AlN, GaN, and Ga-rich InGaN alloys [3]. Fewer researchers have reported growth of InN along nonpolar direction. A-plane (1100) InN, for instance, has been grown on nitridated R-plane sapphire [4-6], on low temperature InN nucleation layers using a double-step growth process [7], and on A-plane GaN template initially deposited on R-plane sapphire [8-10]. M-plane InN was also recently grown on freestanding M-plane GaN [11]. To the best of our knowledge no report of growth of InN along semipolar direction has been reported to date. The aim of this work is to compare and to analyze the effect of sapphire substrate orientation on structural, optical, and electronic properties of InN.

2 Experiments To allow direct comparison of our samples, four quarters of 2 in. C-, R-, A-, and M-plane sapphire substrates were simultaneously inserted into the growth chamber of our Aixtron 200/4 RF-S MOCVD system. Substrates were first thermally cleaned in an H₂ atmosphere at a temperature of 1200 $^{\circ}$ C during 10 min. Then



the substrates were submitted to a nitridation in H_2/NH_3 atmosphere at 1150 °C during 10 min. Substrates were then cooled down to the InN growth temperature at 550 °C. InN layer was grown using N₂ as gas vector. Precursors used for getting atomic In and N elements were trimethylindium and ammonia, respectively. To prevent the formation of indium droplets on the surface, we used a V/III molar ratio of 15 000 during the growth. It is important to notice that, this MOCVD process is not an optimized one. It is just a base which can be easily modified for future process optimizations.

For measuring the crystal quality of the deposited InN films and for the determination of the epitaxial relationships, we used a Bruker D8 Discover high-resolution X-ray diffractometer (HRXRD). This setup allows us to collect diffraction features in the grazing incidence diffraction (GID) mode. Morphologies of the layer were imaged with an NT-MDT Solver Pro atomic force microscope (AFM). Finally, electronic properties of as-grown indium nitride films were studied using a photoluminescence (PL) line shape analysis and room temperature Hall effect measurement. The PL spectra were taken using as excitation source, a 10 mW HeNe laser, and an extended InGaAs photodiode for excitation and detection, respectively, together with a 600 grooves/mm grating blazed at 2 μ m.

3 Results and discussion

3.1 Epitaxial relationship and crystalline quality Figures 1a and b indicate that growth on C- and A-plane sapphire substrates lead to highly (0001) oriented polar InN. XRD shows also a weak contribution of (1100) oriented InN if using the A-plane sapphire as substrate. For determining the sign of the polarity of our polar layers, we have performed wet chemical etchings of InN in a 10 M KOH aqueous solution [12]. This characterization method, indicates that the polar InN layers grown on C- and A-plane sapphire always have N-polarity. Figure 1c, indicates that InN grown on M-plane sapphire, leads to pure (1122) oriented material. Such a surface is semipolar. To the best of our knowledge this is the first report of pure semipolaroriented InN in the literature.

Figure 1d shows HRXRD $\theta/2\theta$ scan of pure nonpolar InN deposited on R-plane sapphire substrate. Only (1120) oriented InN is observed. In contrast with previous report of InN growth on nitridated R-plane sapphire [4]: the mixed hexagonal/cubic phase InN, obtained in some MBE samples, is not present in our samples. The absence of the metastable cubic phase can be attributed to our nitridation conditions



Figure 1 (online color at: www.pss-a.com) $\theta/2\theta$ HRXRD scans: (a) InN on C-plane sapphire, (b) InN on A-plane sapphire, (c) InN on M-plane sapphire, and (d) InN on R-plane sapphire.

combined with the utilisation of a relatively high growth temperature for InN.

Figure 2 shows ϕ -scan X-ray diffraction data in the grazing incidence mode for InN layers grown on the A-, M-, and R-plane sapphire substrates, it allows us to measure the diffraction signature of the plane perpendicular to the sample surface. We can thus easily deduce the in-plane epitaxial relationship between the layer and the substrate.

For InN grown on A-plane sapphire the GID mode indicates the existence of two different contributions. As can be seen in Fig. 2a these two contributions can be attributed to two twisted orientations of C-plane InN. At this time, our GID experiments do not allow us to evidence any signature of the A-plane-oriented InN detected in the standard HRXRD configuration (Fig. 1b).

For C-plane InN grown on A-plane sapphire (Figs. 1b and 2a), the epitaxial relationship is $(0001)_{InN}//(1120)_{sapphire}$. Two twisted orientations are detected for the in-plane relation: the $[1120]_{InN}//[1100]_{sapphire}$ relation is the dominant grain orientation, together with another contribution for which $[1100]_{InN}//[1100]_{sapphire}$.

In the case of growth on M- and R-plane sapphire, indium nitride layers have a unique in-plane orientation relation with respect to the substrate. In these two layers, the



Figure 2 (online color at: www.pss-a.com) Grazing incidence XRD ϕ -scan of InN and Al₂O₃: (a) InN on A-plane sapphire, (b) InN on M-plane sapphire, and (c) InN on R-plane sapphire.

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Table 1	FWHM of XRE	orocking curves in	n large angles	standard configuration m	ode and in grazing incidence	e diffraction (GID) mode
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	(0001)-InN on C-plane	(0001)-InN on A-plane	(1122)-InN	(11 <u>2</u> 0)-InN
(<i>hkil</i>) standard FWHM (arcmin)	(0002): 37.4	(0002): 47.6	(1122): 51.2	(11 <u>2</u> 0): 61.8
(<i>hkil</i>) GID FWHM (arcmin)	(1 <u>1</u> 00): 56.2	(1 <u>1</u> 00): 57.8	(1100): 79.1	(0002): 48.7

in-plane M-direction of InN is parallel to the in-plane Adirection of the sapphire substrate.

In the case of the InN layer grown on nitridated M-plane sapphire with a semipolar surface, we face a unique epitaxial relation: $(1122)_{InN}//(1100)_{sapphire}$ for the growth plane and $[1100]_{InN}//[1120]_{sapphire}$ directions in the growth plane.

Concerning A-plane InN grown on R-plane sapphire, we also are in the situation of measuring a unique epitaxial relationship. These relations are $(1120)_{InN}//(1102)_{sapphire}$ and $[1100]_{InN}//[1120]_{sapphire}$, according with similar results which were previously reported in the literature [6, 8].

Table 1 summarizes the values of the full-width at halfmaximum (FWHM) of the XRD rocking curves of InN. The first row of the table correspond to the standard configuration for studying the tilt disorientation feature, the second one correspond to the grazing incidence condition for the twist.

We do not report observation of a drastic disparity among our samples. They all exhibit a similar reasonable crystalline quality. We, however, notice a slight degradation of the crystalline quality when growth occurs along orientations that lead to a reduction of the polarity along the growth direction of the epilayer.

It is worthwhile noticing that, in case of InN-grown nonpolar, on R-plane sapphire, the FWHM of the rocking curve (62 arcmin) indicates an enhancement of crystalline quality in comparison with results previously reported for direct epitaxy on sapphire (values of 128 down to 80 arcmin were reported by Kumagai et al. [4] and value of 106 arcmin was reported by Zhu et al. [6]). We attribute this little improvement of the crystalline quality to the conditions of our nitridation process. Note that for this layer, the tilt disorientation is larger than the twist one.

3.2 Morphologies AFM images taken in case of the two polar orientations displayed in Fig. 3a, indicate the standard morphologies of C-plane InN grown by MOCVD on nitridated sapphire. There is a partial coalescence of hexagonal grains. This amount of coalescence seems to be quasi-identical for the two substrate orientations, as an indication of the hexagonal step flow growth mode in the coalesced regions.

The AFM picture taken in the case of the (1122) oriented sample (Fig. 3b) reveals a 3D growth mode. The picture top in the figure reveals the (1122) oriented uncoalesced crystallites, with shapes similar to those sketched bottom in Fig. 3b representing the hexagonal lattice in the same orientation. Beneath them, one distinguishes larger anisotropic stripes, their larger dimension being generally oriented along [1100] InN direction, made from coalesced grains. The A-plane InN data given in Fig. 3c shows preferentially oriented grain features. We can also see some kind of stripe formation, like in the MBE grown A-plane InN on R-plane sapphire. In summary, we have here evidenced three different morphologies corresponding with three growth kinetics.

3.3 Electronic properties Low energy PL features have been measured for all the samples. In Fig. 4 are plotted PL spectra taken at a temperature of 10 K. We observe a blue shift of the PL features with increasing InN surface polarity as it is shown in Fig. 5a where is plotted the PL energy *versus* the angle between the (0001) direction of the InN crystal and the direction normal to the InN growth plane. This blue shift is associated with a simultaneous decrease of the PL intensity and with a broadening of the PL line shape. The FWHM of the PL features vary between typically 66 meV for the nonpolar orientations and typically 101 meV for the polar orientations, at 10 K, for these samples.



Figure 3 (online color at: www.pss-a.com) AFM images of the InN surfaces (a) both InN on C-plane and A-plane sapphire (left and right hand pictures, respectively), (b) (1122) oriented InN and the sketch of his hexagonal lattice representation, and (c) A-plane InN and a sketch of his hexagonal lattice representation.



Figure 4 (online color at: www.pss-a.com) Unpolarized photoluminescence spectra of InN epilayers grown on C-, A-, M-, and R-plane sapphire substrates taken at a temperature of 10 K.



Figure 5 (online color at: www.pss-a.com) Photoluminescence energies and band gap energies used for the line shape fitting *versus*: (a) polarity of the layer represented by the angle between growth plane and (0001)-InN, (b) FWHM of XRD rocking curves indicative of tilt disorientation.

To tentitatively interpret these phenomena in a more quantitative way; we have performed complementary room temperature Hall effect measurements. Measured values of residual dopings and mobilities are given in Table 2.

We observe that the best electron mobility is measured when growth occurs along the polar direction and that smaller values are measured for semipolar and nonpolar orientations. We attribute these phenomena to the decrease of crystalline quality and to the more grainy morphologies of these layers. The trend obtained concerning the residual dopings measured by Hall effect follows the trend in measured mobility values. To get rid of the influence of spatially extended topological defects that may alter electron

Table 2 Residual doping and mobility obtained by Hall effect measurement, and residual doping and band gap energy using for the line shape fitting of the photoluminescence.

	(0001)-InN ^a	(11 <u>2</u> 2)-InN	(11 <u>2</u> 0)-InN
Hall effect measu	urements		
$N ({\rm cm}^{-3})$	1.3×10^{19}	6×10^{18}	$5.5 imes 10^{18}$
$\mu (\text{cm}^2/\text{V s})$	429	302	283
PL line shape fitt	ing		
$N ({\rm cm}^{-3})$	3.3×10^{18}	2.3×10^{18}	1.2×10^{18}
$E_{\rm g}~({\rm meV})$	797	766	743

^aOn C-plane sapphire.

drift and correlate the measurement of mobility to sample dimensions, we have alternatively determined the bulk doping of our layers via a line shape fitting of the PL. We used a home-made program [13] based on the work of Arnaudov et al. [14]. This routine leads, after the line shape fitting has been successfully achieved, to the values of the bulk residual doping and to the value of the band gap at 2 K. We note that the low temperature broadening of the PL is correlated to the square root power of the doping as shown in Ref. [13]. It is also worthwhile telling here that this routine also correlates the decrease of the PL intensity with the residual doping, a well-known doped semiconductors textbook effect not recalled in Ref. [13]. Results extracted from this fitting are given in Table 2. We note the decreasing of the value of $E_{\rm g}$ extracted from the PL line shape fitting reported in Fig. 5a which indicates that the doping decrease cannot itself explain the blue shift of the PL.

The shift of the PL must be attributed to more complex processes than a simple doping effect one. Some groups have already reported a low value for nonpolar InN PL peak energy. They have made some assumptions to explain this phenomenon. Koblmuller et al. [11] have credited the lower PL peak energy of their M-plane grown InN to band tailing effects related to stacking faults. Their sample was grown on M-plane GaN. Shitaka et al. [10] have attributed the red shift, observed in case of the A-plane-oriented InN, grown onto R-plane sapphire, to Franz–Keldysh effect and consider that the hypothesis invoking contribution of the basal stacking faults has to be disregarded.

Figure 5b correlates the reduction of the PL energy with the broadening of the X-ray data that probes the grain tilt. Increasing the grain tilt reduces the PL energy. This seems to cautiously give some credit to a correlation between PL energy and the density stacking faults and does not plead in favor of Franz–Keldysh effect. Further investigations are obviously necessary to clarify the physical origin of the PL shift in our samples.

4 Conclusion Using sapphire flakes of various crystallographic orientations as substrates, we have grown reasonable quality indium nitride layers along polar, semipolar, and nonpolar orientations. The epitaxial relationships of the layers have been deduced from XRD measurements. We report the first growth of InN with (1122) semipolar orientation. Our InN layers exhibit different surface morphologies in correlation with growth orientations, due to different growth kinetics. The global correlation between the electron mobility, PL energy, structural properties, residual dopings is quite untrivial and can be, we believe it from bonafide, explained by the presence of a huge density of stacking faults.

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