

Optical properties of InN grown on templates with controlled surface polarities

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The structural and optical properties of InN layers grown on GaN/sapphire templates with controlled Ga-/N-polar surfaces are investigated. Raman spectroscopy and XRD reciprocal space map analysis suggest that the InN layers were grown strain free with a high crystal quality. A line shape analysis of the $A_1(\text{LO})$ Raman mode yields to a decreasing carrier concentration for the sample grown on Ga-polar substrate.

Low temperature photoluminescence measurements exhibit a shift to lower energies of the luminescence maximum for the sample grown on Ga-polar GaN probably due to a reduced carrier concentration and thus, a decreased Burstein–Moss shift. Following this, we demonstrate that the use of polarity controlled GaN/sapphire substrates leads to unstrained layers with good structural and optical properties.

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1 Introduction InN still receives much attention due to its possible implementation into the GaN system, which would allow the fabrication of tunable emitter from the infrared to the ultraviolet wavelength regime. Additional applications may include high efficiency solar cells and ultra-fast optoelectronic devices. But the growth of indium-rich $\text{In}_{1-x}\text{Ga}_x\text{N}$ at temperatures typically used for GaN remains a problem due to spinodal decomposition and compositional fluctuations in the ternary InGaN [1–8] system. A potential pathway to overcome the difficulties associated with the phase stability and the growth temperature gap between the group III–N binaries is to assess the pressure dependency of surface chemical reactions and growth surface stabilization – a pathway assessed in the growth of InN by high-pressure chemical vapor deposition (HPCVD) [9]. At present, a number of physical properties, such as the band structure or Raman shift of the fundamental phonon modes of relaxed InN system are still under discussion. Especially, the value of the InN bandgap varies upon growth method deployed – from 1.9 eV [10] down to 0.9–0.7 eV [11] to as low as 0.62 eV [12, 13], a shift commonly related to the free carrier density dependency and attributed to Moss–Burstein effect [14, 15]. However, a

verification of the band gap position is still outstanding and no excitons were so far observed. For InN layers grown by HPCVD, the IR-reflection and absorption measurements indicate band gap values between 0.8 and 1.4 eV, strongly depending on the carrier concentration [14]. In this paper, XRD, Raman, and photoluminescence studies are presented on such samples. An important parameter in the growth of thin layers is the choice of the substrate. Typical substrate templates for InN are sapphire, ZnO or GaN [13], with GaN/sapphire templates providing the best conditions for high quality InN layers due to a low lattice mismatch and availability. However, the influence of the substrate polarity and the polarity of the layer itself on the optical and structural properties is investigated only marginal, especially for high-pressure CVD grown samples [16]. We will demonstrate that the use of polarity controlled GaN/sapphire substrates leads to unstrained layers with good structural and optical properties. Additionally, a lower carrier concentration and less impurity incorporation can be achieved in the case of gallium polar instead of nitrogen polar substrates. This is well known from GaN, where Ga-polar grown samples exhibit increased quality [17], but was not shown for InN before.

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We present a study of two different samples of InN grown on a GaN/sapphire substrate with controlled surface polarity. The nominal thickness of the InN layers was 300 nm. Sample A was grown on N-polar GaN, while sample B was grown on Ga-polar GaN. Despite the polar substrates the InN layers are supposed to exhibit a mixed polarity. Both samples were grown with HPCVD at 15 bar reactor pressure and temperatures around 1080 K, while the NH₃/TMI ratio was 791. Details about the growth process can be found elsewhere [18]. XRD measurements revealed for these sample single phase InN(0002) with hexagonal symmetry [16].

2 Experimental procedure In order to get information about the strain in the layers the samples were investigated by high-resolution X-ray diffraction (HRXRD). The instrument was a commercial X-Pert Pro X-ray diffraction system by Philips. The X-ray source was an optimized copper tube with a long line focus. The beam dimensions are $0.4 \times 12.0 \text{ mm}^2$. A beryllium window with a thickness of 300 μm and a hybrid X-ray mirror setup is used for focusing the beam and selecting the Cu K α line. The generator tube is driven with a voltage of 45 kV and a current of 40 mA. Additionally, micro-Raman spectroscopy and low temperature photoluminescence (PL) was done. The Raman spectra were taken at room temperature with a DILOR XY 800 triple grating Raman spectrometer, whereby the excitation source was the 488 nm line from an argon-krypton ion laser. All spectra were calibrated with a neon light source. PL spectra were taken in backscattering geometry, with the incident light orientated parallel to the *c*-axis of the InN layers. For PL, the samples were cooled with an OXFORD continuous flow cryostat to temperatures around 10 K. Excitation source was a Ti/sapphire laser with an excitation wavelength of $\lambda = 714 \text{ nm}$. The PL signal was detected with an InGaAs diode. Using this setup temperature dependent measurements were carried out for temperatures from 10 to 300 K. For the InN layer grown on Ga-polar GaN time resolved measurements for the two main PL peaks were performed using a micro-channel plate with an attached Hamamatsu S1 photomultiplier.

3 Results and discussion Figure 1 shows the reciprocal space map (RSM) around the 10–12 reflexes of the GaN and the InN layers. As expected the reflex of the GaN is much sharper and has a much higher intensity than the reflex of the InN. Both effects are due to the large difference in layer thickness. In addition both reflexes feature asymmetric broadening in omega direction. This broadening can be explained by a macroscopic mosaic crystal structure due to a temperature gradient in the reactor as well as a lateral incoherence of the sample. Because of the dimensions of the X-ray beam and the fact that the sample shows visible color variations on the surface, it is most likely that the lateral incoherence of the layers have a greater influence on the broadening than the small angle grain boundaries.

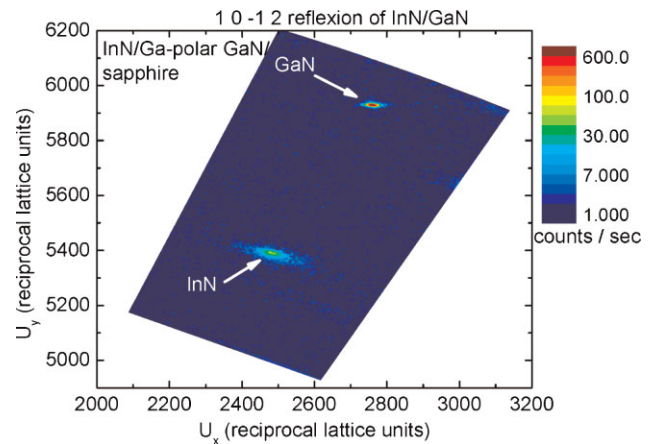


Figure 1 (online color at: www.pss-a.com) XRD reciprocal map scan for sample B (InN/Ga-polar GaN/sapphire) around the 10–12 reflex of InN/GaN.

Raman spectra from both samples taken in $z(yx)z$ geometry are shown in Fig. 2. Although only the non-polar $E_2(\text{high})$ mode is allowed, the $A_1(\text{TO})$ (442 cm^{-1}), $E_1(\text{TO})$ (472 cm^{-1}), and the $A_1(\text{LO})$ (587 cm^{-1}) are visible, too. The Raman shifts for these modes are in good agreement with phonon frequencies reported for InN before [19, 20]. This observation of symmetry forbidden modes for InN layers is well known. Possible explanations for this violation of the selection rules might be disorder in the samples, a tilt of the *c*-axis or multi-reflections from internal interfaces. The position of the non-polar $E_2(\text{high})$ for both samples is 488.8 cm^{-1} , whereby the error is below 0.3 cm^{-1} .

It should be mentioned that the full width at half maximum (FWHM) of the $E_2(\text{high})$ is 9.9 cm^{-1} for sample A and 8.6 cm^{-1} for sample B. These are very low values for CVD grown InN [21] but still high compared to MBE grown InN [22]. They indicate an increasing crystalline quality in the case of Ga-polar GaN/sapphire substrates. This is a well-known behavior for the hexagonal crystals GaN and ZnO were

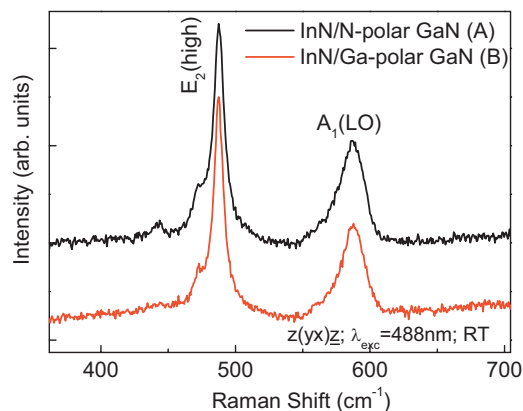


Figure 2 (online color at: www.pss-a.com) Raman spectra of InN grown on N-polar GaN (black) and Ga-polar GaN (red). $E_2(\text{high})$ and $A_1(\text{LO})$ mode are marked for better visibility. Spectra were shifted horizontal for clarity.

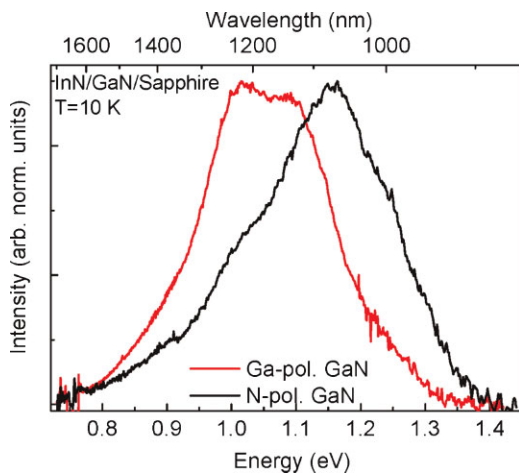


Figure 3 (online color at: www.pss-a.com) Low temperature PL spectra of InN grown on polarity controlled GaN. Spectra were normalized to their maximum.

the cation polar side exhibits an increased crystal quality and decreased impurity incorporation [23–25]. Thus, since we grow on polarity controlled GaN, the differences could be related to the different quality of the GaN layers, leading to a decreased impurity incorporation for the InN layer in the case of Ga-polar GaN substrate. Additionally, for sample B the FWHM of the $A_1(\text{LO})$ decreases. Line shape calculations reveal a decrease of the carrier concentration from 4.2×10^{18} to $2.5 \times 10^{18} \text{ cm}^{-3}$, respectively [16]. This also indicates lower impurity incorporation due to the Ga-polar substrate.

Figure 3 shows PL spectra of both samples taken at 10 K. On the one hand sample A exhibits a broad spectrum from 0.8 up to 1.42 eV. The spectrum can be deconvoluted to a number of Gaussians, whereby a peak around 1.17 eV dominates the spectrum. On the other hand the sample grown on a Ga-polar GaN template shows a much narrower spectrum starting around 0.8 eV with PL signal up to only 1.35 eV. The spectrum is dominated by two transitions around 1.01 and 1.11 eV. Thus, the use of Ga-polar GaN leads to a decreased PL maximum compared to N-polar GaN. This is probably due to decreased impurity incorporation and carrier concentration as confirmed by XRD and Raman measurements. On the low energy side the intensity decreases drastically, no transition can be observed for energies below 0.8 eV. Thus the effective band gap of our samples lies around 0.8 eV. This value is only slightly above the actual stated band gap value of 0.7 eV. The shift of the band gap value is attributed to the Burstein–Moss shift due to the high carrier concentration in the samples [26] and the excitation with a pulsed Ti/sapphire laser, which leads to high excitation density. While the low energy peaks are attributed to the band gap emission of InN, the higher energy peaks may be explained by a two or more layer model with a lower carrier concentration (10^{18} cm^{-3}) in the bulk InN and a thin (10–50 Å) surface accumulation layer with higher carrier concentration (10^{19} cm^{-3} and above). Recently,

Moret et al. [27] calculated the FWHM of a typical InN PL signal and correlated it to the residual doping. If a simple model of one transition is used, the FWHM of the Ga-polar sample is estimated to 230 meV, the FWHM of the N-polar sample to 260 meV, respectively. This would lead to an electron density of $1.5 \times 10^{19} \text{ cm}^{-3}$, whereby the carrier concentration in the N-polar sample would be slightly higher. If only the main transition is taken into account, the FWHMs are estimated to 110 meV (Ga-polar) and 180 meV (N-polar), which would lead to an electron density of 7×10^{18} and $9 \times 10^{18} \text{ cm}^{-3}$. These values are above the values estimated from Raman spectroscopy, which might be due to the fitting procedure. However, in both cases the quantitative behavior (lower electron density in Ga-polar vs. N-polar) is reproduced. Temperature dependent measurements were made in order to identify possible exciton related transition and observe thermalization effects (not shown). A decreasing intensity with increasing temperature was observed indicating strong non-radiative recombination channels. Despite that, the shape of the PL signal did not change with increasing temperature neither any new peak appeared. It should be mentioned that even at room temperature a PL spectrum for both samples was obtained.

Time resolved measurements for the peaks at 1.01 and 1.11 eV for sample B have been performed (not shown). The data indicate that for both peaks the shape of the transients is within the instrumental response to the laser system, suggesting that the involved radiative and/or non-radiative processes have a lifetime shorter than 30 ps. This value is much lower than typical lifetimes reported for InN before [28]. A reason could be the high electron concentration, In clustering or high defect density. It is well known that in such degenerated materials the radiative and non-radiative lifetimes are very short due to electron–electron interaction and impurity scattering.

4 Conclusion In conclusion, we compared results from XRD, Raman spectroscopy, and PL for two InN layers grown on polarity controlled GaN/sapphire substrates. InN grown on a Ga-polar template exhibits an increased crystal quality, lower free carrier concentrations, and a band gap of around 0.8 eV. Consequently, the growth of InN on Ga-polar substrates should be preferred to N-polar GaN substrates.

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