

Growth and properties of InN/Al₂O₃ and InN/GaN/Al₂O₃ studied by in situ Spectroscopic Ellipsometry and different ex situ techniques

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1 Introduction

Growth of good quality epitaxial InN layers is a challenging issue due to the lack of suitable substrates and the very low enthalpy of formation. The InN growth is consequently characterised by extreme conditions with a V/III ratio in the order of 10⁴. The difficulty to achieve homogeneous InN layers plays a major role in the determination of the electronic band gap: a value of 0.9 eV has been recently proposed for the band gap of InN, highly contrasting with the commonly accepted values of 1.8–2.1 eV [1]. The use of Spectroscopic Ellipsometry (SE) as in-situ monitoring tool [2] offers the possibility to find appropriate growth conditions through displaying the InN electronic properties during growth.

2 Experimental

Samples were grown in a RF heated horizontal reactor equipped with optical windows for in-situ control, using TMI and NH₃ as precursors. To suppress indium memory effects from previous epitaxies and achieve reproducibility, the susceptor was thermally etched at 1050°C for 20 minutes under H₂ flow and the liner tube was cleaned in a HCl/HNO₃ 3:1 mixture prior to each epitaxy run. InN growth is performed in four main steps: 1. sapphire nitridation, 2. nucleation layer (NL) growth, 3. temperature increase, 4. epitaxy with increased TMI flux. Nitrogen was used as carrier gas and a minimum V/III ratio of 3x10⁴ was necessary to suppress In droplet formation. SEM images showed coalescence for a ~20 nm thick NL grown at 400°C. With such a NL we grew samples with the best crystal quality directly on sapphire. Those samples are black with specular surfaces.

3 Results and discussion

3.1 Growth on InN nucleation layer

First layers grown directly on sapphire have been studied. Here the large lattice mismatch with sapphire and the impossibility to anneal the NL leads to peeling off of parts of the InN layer. In Fig. 1 transients of the reflected light intensity and of the imaginary part of the effective dielectric function $\langle \epsilon_2 \rangle$ at 5 eV, recorded during growth at 500°C, are given. The energy of the transient was chosen since in this region higher interband transitions of InN occur [2,3]. The reflectivity shows initially a dependence from the layer thickness due to features originating from Fabry-Perot interferences and remains subsequently almost constant up to about 200 minutes growth duration. $\langle \epsilon_2 \rangle$ shows essentially the same behaviour. At t_1 , corresponding to a layer thickness of about 150 nm, a sudden decrease occurs. The reflectivity drops with no recover, while $\langle \epsilon_2 \rangle$ shows a drop and then recovers partially to the original value. Both indicate a deterioration of the layer. This form of the transient at t_1 occurs for each InN epitaxy, regardless of the growth parameters if the thickness of ~150 nm is exceeded. SEM images taken from a sample grown up to t_1 show that the surface partially bulges (Fig. 2a). This feature is not observed in thinner layers (i.e. at shorter growth times) and indicates an onset of a peeling off of parts of the layer. Hence, holes originating from the peeled off material are found in thicker layers with a longer time growth, t_2 as an example (Fig. 2b). Thus the decrease of the reflected light intensity (Fig. 1a) is a result of roughening on a micrometer scale due to the occurrence of holes in the layer, while the recovery of $\langle \epsilon_2 \rangle$ after t_1 is due to the growth of a new InN layer on the bare sapphire substrate in the holes.

The critical thickness for the onset of the peeling off depends on growth parameters like temperature and growth rate and may occur already at 100 nm. It should be noted that the peeling off was always observed for samples grown on InN NL. For all samples showing this optical behaviour (i.e. thicker than ~150 nm thickness) ellipsometry was crucial in determining the critical thickness. The adhesive strength of the low temperature InN

NLs (we investigated different thicknesses and different growth temperatures) is apparently too low to counteract the strain in the layer accumulated up to t_1 . We stress that the peeling off of the InN layer clearly occurs already during growth and not during cooling down, due to the thermal mismatch to substrate. Hence this is a critical issue for growth of close, defect-free, thick InN layers directly on sapphire.

The surface morphology displayed in Fig. 2b shows further features: flat hexagonal crystallites with a large diameter in the μm range and irregular smaller crystallites. The holes described above could be the seeds for the 3-dimensional growth of the flat hexagons (see Fig. 2a). In fact a large number of this species of crystallites can be found in samples grown beyond t_1 (the onset of the layer peeling off), with a density of $\sim 10^7 \text{ cm}^{-2}$, while for samples grown just below the peeling off edge (like the sample showed in Fig. 2a) they occur with a low area density, below 10^4 cm^{-2} , being completely absent in thinner samples.

The irregular crystallites are about 10 times smaller than the hexagonal ones and have a broad size distribution. SEM images of samples with various thicknesses show that some arise already at initial stages of the growth, others later due to parasitic nucleation. Here temperature plays an important role to control the appearance of such defects. A growth temperature increase of $\Delta T = 20^\circ \text{C}$ reduces the density of these defects by 2 orders of

magnitude, from $5 \times 10^7 / \text{cm}^2$ to $5 \times 10^5 / \text{cm}^2$. Effects of higher temperatures are presently investigated.

The growth at higher temperature allowed also for control and reduction of texturing. In Fig. 3 we show a polar ϕ

scan obtained through a rotation by the normal of the Bragg planes referring to the asymmetric (10.2) reflection at fixed ω and 2θ angles for 2 samples grown on sapphire at 500°C (top) and at 520°C (bottom). The thickness of

the samples was 150 nm. Sapphire shows three intense sharp peaks spaced 120° due to the three-fold symmetry. InN shows 6 peaks due to the wurtzite six-fold symmetry, shifted with respect to the sapphire peaks due to in-plane twist of InN with respect to sapphire. In Fig. 3 top each InN peak is split into two peaks and the angle between sapphire peaks and the InN double peaks is of 24° and 26° . This demonstrate a mosaic texture twist of the crystal. Slightly higher growth temperature (520° , Fig.3 bottom) reduce sensibly this phenomenon: the peak splitting is absent and the twist angle of InN to sapphire with respect to the growth (0001) direction is 30° , as mentioned also in ref. [4] for InN and widely reported for GaN [5].

3.2 Growth on GaN nucleation layer

The use of a GaN buffer layer further improves the crystalline quality considerably and allows for growth of thicker InN layers. 50 nm thick GaN buffer layers were grown directly on sapphire at low temperature after nitridation. Subsequent annealing was performed at 1050°C . Some samples were additionally prepared with a 300 nm thick GaN layer grown at 1050°C .

By this procedure InN layers with thickness up to 300 nm have been successfully grown on 50 and 350 nm thick GaN layers, showing good crystal quality. Ellipsometry transients at 5 eV showed only constant values for the ellipsometric parameters up to these thicknesses. The surface morphology of a 250 nm InN layer investigated by SEM clearly shows a close layer free from damages produced by the peeling off (Fig. 3c). Further optimisation of the growth conditions is still necessary for a close, defect free thick layer, but it is demonstrated that GaN buffer layers allow for growth of InN layers with thicknesses beyond 150 nm.

3.3 Dielectric function of InN

The effective dielectric function measured ex-situ from 0.5 to 3.5 eV and in-situ from 1.5 to 6.4 eV for InN/sapphire is shown in Fig. 4 (black curves). The small difference in the data obtained from the two different ellipsometry setups arise probably from a macroscopic inhomogeneity of the sample and from the effects of the exposure to air (oxidation) on the thin InN layer during the ex-situ measurements.

We assign the features at 4.9, 5.3, and 6.1 eV to bulk properties, interpreting them as InN higher inter-band transitions, in general accordance to theoretical predictions reported in ref. [3].

The double peak structure present in $\langle \epsilon_2 \rangle$ below 2 eV is due partially to bandgap adsorption and partially to

interference between layer and substrate. The latter occurs in this spectral range due to light penetrating the layer. Using a 4-layer model (1. semi infinite sapphire substrate, 2. 150 nm InN, measured by means of an SEM cleave edge image, 3. a roughness of 2 nm from AFM, and 4. air/vacuum as semi infinite environment) we determined the bandgap position to $E_g=1.0$ eV with a broadening of ~ 100 meV. This broadening may result from the layer defects which are still present (e.g. crystallites, inhomogeneity, strain, etc.). At 2 eV the calculated ϵ fits well with the measured ϵ where no more interference effects occur due to the lower penetration depth of the light.

4 Conclusions

InN is grown on sapphire by MOVPE using SE in-situ control. SE indicates a critical thickness at which the layer properties undergo a dramatic change. During growth parts of the layer peel off, probably because of the high lattice mismatch and an insufficient adhesion of the InN NL on sapphire. Thicker layer are achievable by the use of a GaN buffer layer. Higher growth temperatures allowed for the suppression of parasitic nucleation and crystal twist texture, indicating that growth parameters can be still further optimised. Finally, the effective dielectric function shows the bandgap at 1.0 eV and higher interband transition energies at 4.9, 5.3, and 6.1 eV, respectively. We gratefully acknowledge the financial support of the Deutsche Forschungsgemeinschaft via SFB 296.

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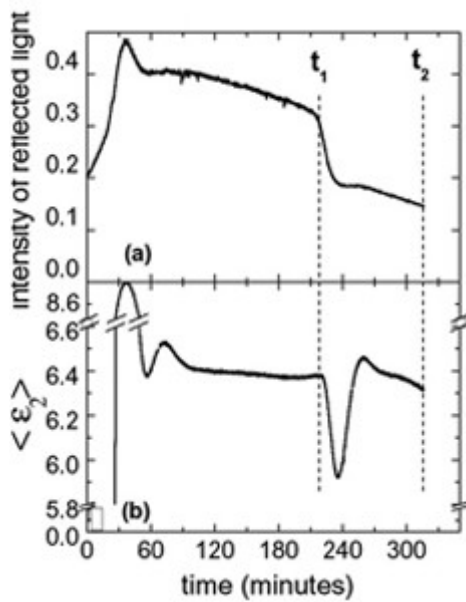


Fig. 1: Transients of the reflected light intensity (a) and of the effective dielectric function $\langle \epsilon_2 \rangle$ (b) recorded in-situ at fixed energy (5 eV) and 500°C growth temperature. Time t_1 and t_2 refer to surface morphologies shown in Fig. 2.

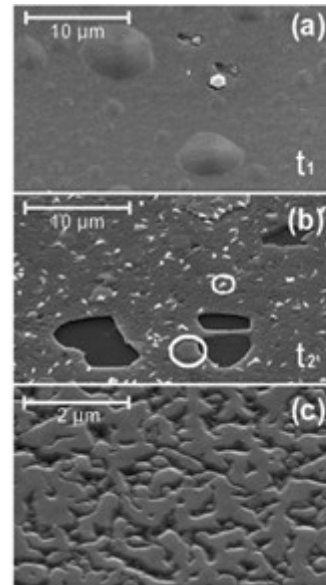


Fig. 2: SEM pictures showing InN surfaces. (a) and (b) are grown on sapphire for different growth times, t_1 and t_2 and slightly different growth temperature (520°C and 500°C, respectively). At t_1 (top) the surface partially bulges, some evidence of peeling off is present. At a later time t_2 (bottom) the layer is disrupted by holes. Crystallites of different size and shape (white circles) are clearly visible. (c) is grown on 50 nm GaN/sapphire

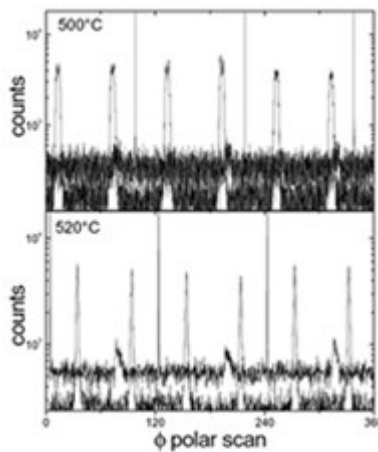


Fig. 3: XRD ϕ polar scan of the asymmetric (10.2) reflection for 2 InN layers 150 nm thick grown on sapphire at 500°C (top) and 520°C (bottom), respectively.

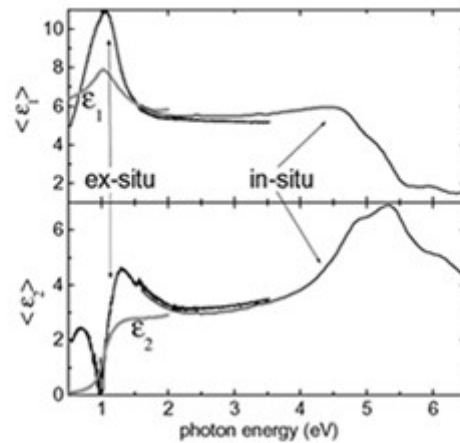


Fig. 4: Effective dielectric function $\langle \epsilon \rangle$ of a 150 nm thick InN layer in the range from 0.5 to 6.4 eV (black curves). The spectra were recorded in-situ at room temperature in the high energy range and ex-situ in the low energy range. Grey curves: evaluation of the dielectric function ϵ by means of a 4-layer optical model.