Phys. Status Solidi C **8**, No. 7–8, 2059–2062 (2011) / **DOI** 10.1002/pssc.201001067

physica status solidi c
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current topics in solid state physics

Growth temperature and growth rate dependency on reactor pressure for InN epilayers grown by HPCVD

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Received 17 September 2010, revised 8 January 2011, accepted 10 January 2011
Published online 19 May 2011

Keywords InN, HPCVD, high-pressure, InN, epitaxy, growth temperature, growth rate

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This contribution presents results on achievable growth temperatures and growth rates as a function of reactor pressure for the growth of InN by high-pressure chemical vapour deposition (HPCVD). The InN epilayers were grown at reactor pressures ranging from atmospheric pressure to 19 bar. The results show that the InN growth temperature increased linearly with the reactor pressure from 759 °C to 876 °C. The growth rate decreases from 127 nm/h to 20 nm/h as the reactor pressure is increased from 1 bar to 19 bar. The structural, optical, and electrical properties of the epitaxial layers were analyzed by X-ray diffraction, Raman spectroscopy, IR reflection spectroscopy, and optical transmission spectroscopy.

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1 Introduction In recent years significant progress has been made on the growth of epitaxial InN and indium-rich group III-nitride alloys. Nonetheless, a serious challenge remains in the integration of indium-rich InGaN epilayers into wide band gap group III-nitrides heterostructures due to the significantly lower growth temperatures at which indium-rich InGaN layers have to be grown by MOCVD [1] and MBE [2] compared to wide band gap group III-nitrides such as GaN (1080 °C [3]) or InGaN with low indium contents (750 °C - 1000 °C, depending on the composition [4]).

The use of high reactor pressures was proposed by MacChesney et al. [5] as a potential pathway to stabilize group III-nitrides at higher growth temperatures. The thermodynamic equilibrium calculations indicated that the gaps in the growth temperatures within ternary or quaternary alloys can be reduced or even eliminated at higher reactor pressures. This contribution analyzes the effect of the reactor pressure on the growth temperature and the growth rate of InN epilayers by exploring the growth and stabilization of these layers at elevated growth temperatures that might be more compatible with the growth of wide band gap alloys.

2 Experiment

2.1 HPCVD growth The InN layers have been grown in a custom built high-pressure CVD system at pressures ranging from atmospheric pressure up to 19 bar with growth temperatures between 759 °C and 876 °C. All of the layers have been grown on GaN/Sapphire templates, except for the sample grown at 19 bar which was deposited directly on sapphire. The group-III precursor, tri-methyl-indium, and the group-V precursor, ammonia, are embedded into a nitrogen carrier gas stream. In order to avoid gas phase reactions during the growth process they are injected separately by pulsed injection which is temporally controlled, maintaining a constant reactor pressure at all times. The carrier gas flow has been adjusted so that the gas flow velocity above the sample surface was kept constant. The

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layers were grown with a V/III precursor flow ratio of 7500, except the ones grown at 15 bar and 19 bar where the V/III precursor ratio has been reduced to 3000. The reduced V/III precursor ratio was chosen due to the increased cracking efficiency of the ammonia precursor and the reduced loss rate of nitrogen above the hot growth surface. Integrated real time optical characterization tools such as Principle Angle Reflection Spectroscopy (PARS), Laser Light Scattering measurements (LLS), and UV Absorption Spectroscopy (UVAS) were used to monitor the growth process as well as potential gas phase chemistry processes in the HPCVD reactor system. These techniques allow for analysis of changes in the dielectric function, the films thickness, the evolution of the surface roughness, and the arrival as well as the decomposition of the precursors respectively. Further details on the growth system can be found elsewhere [6-10].

2.2 Layer characterization The structural properties of the InN epilayers have been analyzed by X-ray diffraction (XRD) and Raman spectroscopy. The thickness and electrical properties have been investigated by IR reflection spectroscopy and optical transmission spectroscopy.

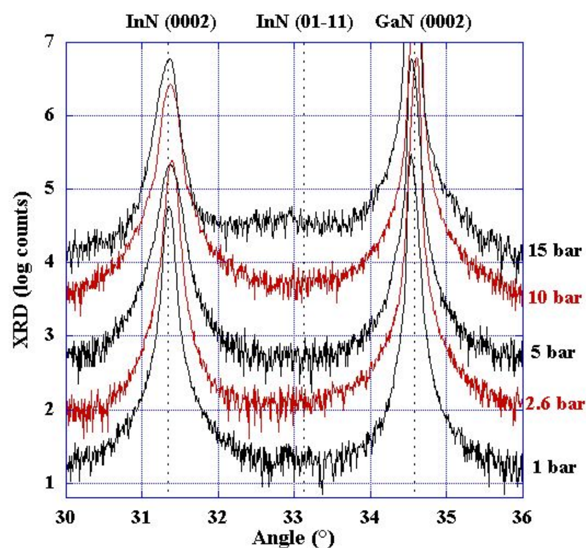

Figure 1 XRD 2Θ-ω scans of InN epilayers grown on GaN templates showing the (0002) Bragg reflexes of InN at 31.31° and of GaN at 34.54°.

The XRD spectra have been recorded utilizing a X`Pert PRO MPD (Philips) four-circle diffractometer, which is equipped with a monochromatic X-ray (CuKα) source. The Raman data has been collected using a custom built setup with a 20 cm double spectrometer to suppress the excitation wavelength and a 1.5 m single monochromator as a dispersive element equipped with a liquid nitrogen cooled CCD camera. The Raman spectra were taken in unpolarized backscattering geometry in the range from 450 cm^{-1} to 650 cm^{-1}. The IR reflection measurements were performed at room temperature on a Perkin-Elmer Fourier-transform infrared spectrometer with an HgCdTe (MCT) detector and a KBr beamsplitter for the range of 400-7000 cm^{-1} under near-normal incidence geometry (less than 8° incidence angle). The transmission spectra were measured utilizing a halogen light source and a 24 cm double spectrometer equipped with a Hamamatsu R928-21 photomultiplier and a EMM InGaAs photodiode, which are sensitive to the visible and the IR region, respectively.

3 Results and discussion The epitaxial InN layers grown on GaN templates show in the 2Θ-ω scans one InN (0002) Bragg reflex, which is in addition to the template's GaN (0002) reflex. The InN layer directly grown on sapphire showed an additional weak InN (01-11) Bragg reflex, which is assumed to be from islands with tilted facets along the nucleation layer. The FWHM's of the (0002) InN Bragg reflexes varied between 390 arcsec and 680 arcsec except for the sample grown at 5 bar, which showed a slightly higher FWHM of 800 arcsec (Fig. 1).

All epilayers showed the Raman modes E_2(high) and A_1(LO) at 488 cm^{-1} and 593 cm^{-1} respectively, which are to be expected for that particular geometry. The FWHM's of the E_2(high) Raman mode were all in the range of 8.6 cm^{-1} to 14.5 cm^{-1}. The InN layer directly deposited on sapphire in addition showed a weak contribution from A_1(TO) and E_1(TO) Raman modes at 449 cm^{-1} and 472 cm^{-1} respectively which is assumed to originate also from the nucleation layer.

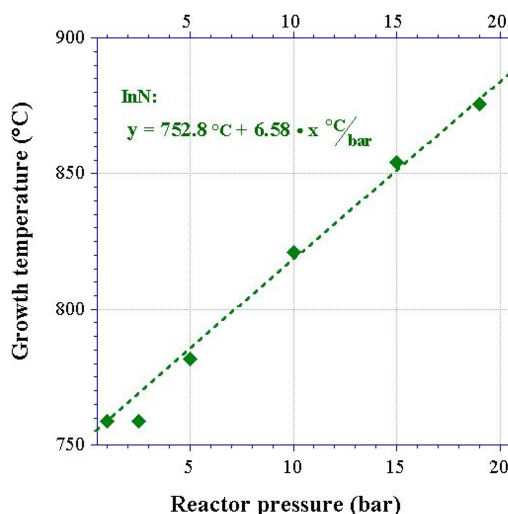

Figure 2 InN growth temperature as function of reactor pressure between 1 bar and 19 bar.

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The growth temperature has been varied for the different reactor pressures. As depicted in Fig. 2, the optimum growth temperature for InN - as established via the crystalline layer properties - rises linearly with increasing reactor pressure from 752 °C to 876 °C with a slope of 6.6 °C/bar. This demonstrates that the reactor pressure can be utilized to efficiently stabilize InN at significantly higher growth temperatures compared to commonly utilized low-pressure MOCVD. This avenue may therefore provide a pathway to integrate indium-rich InGaN or InN into wide band gap layers.

The growth rate and free carrier concentrations in the InN epilayers were analyzed by IR-reflectance spectroscopy. A typical experimental and simulated IR spectrum is shown in Fig. 3 for the InN layer grown at 10 bar reactor pressure and at 820 °C. The epilayers' reflection has been fitted using a multilayer stack model to accommodate for the GaN template and the sapphire substrate. Details of the simulation can be found elsewhere [11]. By employing an electron mass of 0.09 m_e the simulation of that exemplary layer showed a plasma frequency of 3684 cm^{-1} which can be attributed to a free carrier concentration of 7.8 × 10^{19} cm^{-3}, a high frequency dielectric function ε_∞ of 5.78. The phonon oscillators for the LO and TO modes have been found to be at 590.3 cm^{-1} and 477.5 cm^{-1} respectively. The comparatively low high frequency dielectric constant can be understood due to average media theory, the relatively big spot size of 2.5 mm in diameter leads to an average over potential holes and voids in the film, reducing the effective dielectric constant.

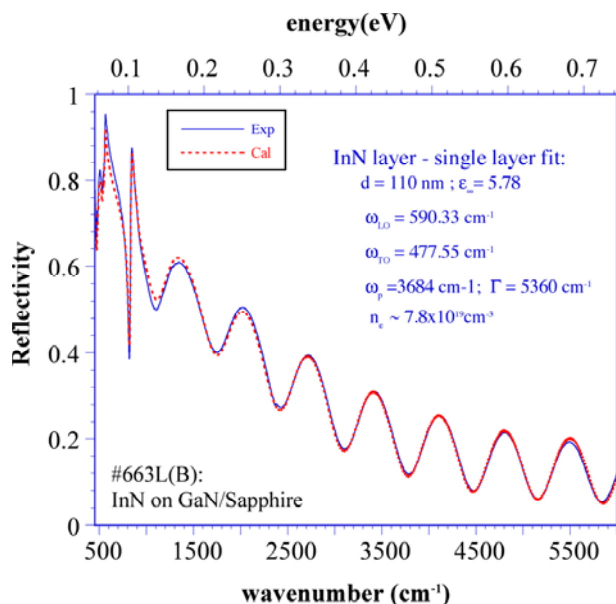

Figure 3 Experimental and simulated IR-reflection spectra for a InN epilayer grown at 10 bar reactor pressure at a temperature of 820 °C.

The free carrier concentrations varied between 4.8 × 10^{19} cm^{-3} and 8.4 × 10^{19} cm^{-3} with a trend to lower values for films with smaller XRD FWHM's and for thicker films. Optical absorption measurements show absorption edges ranging from 0.87 eV to 1.23 eV, following a similar trend to the free carrier concentrations. The origin of free carrier concentration and variation in band gap values as well as their functional dependencies on reactor pressure are under investigation and to be published elsewhere.

In addition, a decrease of the growth rate with increasing reactor pressure has been observed (see Fig. 4). The growth rate decreased from 128 nm/h at atmospheric pressure to 20 nm/h at 19 bar. This can be understood by considering the reduction in the mean free path of the precursor fragments in the gas phase leading to a significantly reduced thickness of the reaction layer, thus less of the injected material reaches the growth surface and contributes to the layer formation. From ideal gas theory the diffusion constant D should be proportional to 1/n, with the molecules number density n; thus it is expected to be as well proportional to 1/P, with the reactor pressure P. With the diffusion length L_D being proportional to $D^{1/2}$, a proportional decrease of the diffusion length and the growth rate with $1/P^{1/2}$ is expected.

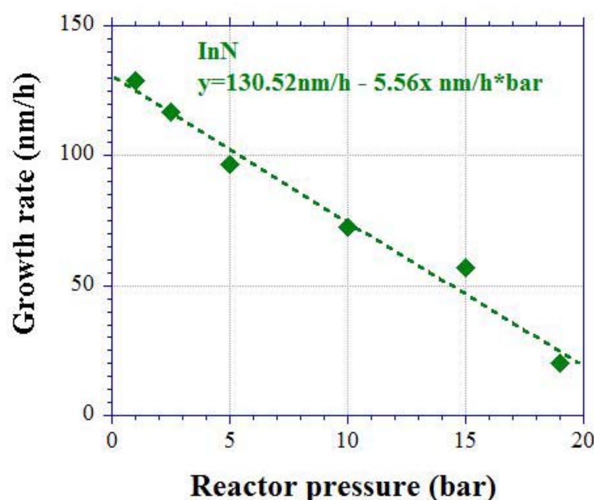

Figure 4 Growth rate as function of reactor pressure, thicknesses were extracted from fitting IR reflection measurements.

From the simulation of IR reflection spectra the thickness of the epilayers has been extracted. The analysis shows a linear decrease of the growth rate with reactor pressure, with a slope of -5.6 nm/h per bar. The deviation from the expected $1/P^{1/2}$ dependency is under ongoing investigation and might be linked to the limited pressure range analyzed and/or to the chemical growth kinetics at elevated temperatures, affecting the growth rate at elevated pressures.

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4 Summary A series of InN epilayers grown at reactor pressures ranging from 1 bar to 19 bar has been studied. The analysis showed that the growth temperature can be increased linearly as a function of rector pressure with a slope of 6.6° C/bar from 752 °C to 876 °C. At the same time, the growth rate decreases from 128 nm/h at open tube conditions to 20 nm/h at 19 bar, a slope of approximately -5.6 nm/h per bar reactor pressure. The increase in InN growth temperature at elevated reactor pressures shows that high-pressure CVD is a viable approach for the integration of indium-rich InGaN alloys and InN epilayers into wide band gap group III-nitrides heterostructures.

Acknowledgements This work has been supported by AFOSR under award #FA9550-10-1-0097 and GSU RPE. Parts of this work were supported by DFG within SFB 787.

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