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Point defect evolution in low-temperature MOCVD growth of InN

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We present a systematic study of the influence of the growth temperature on the point defect landscape in metal-organic chemical vapor deposition (MOCVD) InN. State-of-the-art InN layers were grown at temperatures from 500 to 550 °C and positron annihilation spectroscopy has been used to investigate the incorporation of vacancy defects during the growth process. We find that a decrease of the growth temperature below 550 °C leads to increasing free carrier concentrations and lower mobilities. At the same time, positron measurements observe an enhanced introduction of mixed In-N vacancy complexes which gather preferentially at the interface between the InN layer and the GaN template. As the measured In vacancy concentration seems too low to promote efficient defect complexing, it suggests an increased formation of N vacancies at low temperature growth through insufficient cracking of NH_3, which may be responsible for the observed increase in the free carrier concentration.

1 Introduction III-Nitrides are an important semiconductor material system for a variety of applications in electronic and opto-electronic devices [1]. During the last years InN has emerged into a promising material on its own right, *e.g.*, for the realization of high-efficiency multijunction solar cells or in high-frequency/high-power applications [2]. While highest purity material can be deposited by plasma-assisted (PA) molecular beam epitaxy (MBE) [3], the development of a growth process utilizing metal-organic chemical vapor deposition (MOCVD) is strongly desirable for industrial application due to the good scalability of the latter. Although strong improvements in this area could be achieved during recent years [4, 5] the quality of MOCVD grown material remains still somewhat inferior with electron concentrations in the mid-10^{18} cm^{-3}, about one magnitude larger than in state-of-the-art PA-MBE grown InN layers [3]. Both, point defects such as nitrogen vacancies (V_N) and interstitials (N_I), as well as hydrogen impurities introduced in MOCVD growth through the use of NH_3 as the nitrogen source have been proposed as the responsible donors behind the increased electron concentrations in as-grown MOCVD InN [6–9]. The growth temperature in MOCVD growth of InN is an especially delicate parameter with large impact on the material quality. It is limited on the low-temperature end by insufficient decomposition of NH_3, and on the high-temperature end by nitrogen out-diffusion.

Positron annihilation annihilation spectroscopy is a powerful method for the investigation of point defects in semiconductors. After implantation in the material, positrons can get trapped and annihilate at neutral and negatively charged open-volume defects. This narrows the Doppler-broadening of the annihilating electron-positron (e–p) pairs and increases the positron lifetime, both of which can be measured by recording the 0.511 MeV annihilation γ-radiation. Selected results from previous positron studies in InN can be found in Refs. [10–16]. In this contribution, we present a systematic study of the point defect landscape in MOCVD growth of InN with varying growth parameters. Doppler broadening measurements are performed for a set of representative InN samples, and the interplay between growth temperature, vacancy defect incorporation, and free carrier concentration is investigated.

2 Methods All InN layers were grown by MOCVD in an AIXTRON close coupled showerhead (CCS) reactor on MOCVD GaN-on-sapphire templates. Trimethylindium

(TMIn) and ammonia (NH_3) are employed as precursors for In and N, and N_2 is used as carrier gas. Reactor pressure was kept at 800 mbar, except for sample No. 2 (600 mbar), and a V/III ratio of 146 k was chosen. The growth temperature was varied from 500 to 550 °C. For more details on the sample growth and properties please see Ref. [4].

Positron annihilation measurements were performed using a variable energy (0.5–38 keV) slow positron beam. The 0.511 MeV e–p annihilation γ-radiation was recorded with two Ge detectors with a Gaussian resolution function of 1.24 keV. The lineshape of the Doppler broadened annihilation peak was analyzed using the conventional valence (S) and core (W) annihilation parameters, with acceptance windows of $|p_L(S)| < 0.4$ a.u. and 1.5 a.u. $< |p_L(W)| < 3.9$ a.u. for S and W, respectively. More information about the experimental setup can be found elsewhere [17].

3 Results and discussion Results from Doppler broadening measurements at room temperature of the investigated set of samples (see Table 1) are displayed in Fig. 1 as a function of the positron implantation energy. At low implantation energies, *i.e.*, low mean implantation depth, most positrons annihilate at the surface of the material, which is characterized by a surface specific annihilation parameter. At around 3 keV, positrons penetrate deeper into the sample and the surface effects become negligible. The S-parameter decreases rapidly toward the value specific for the InN layer. As visible, these are in all samples close to the characteristic value for InN bulk and hence no vacancy trapping is observed. The InN reference value has been determined by measuring a reference sample in which all positrons annihilate in the delocalized state of the InN lattice. With higher implantation energies the spectrum shows for all samples except sample No. 1 a strong profile with increasing S-parameter and a maximum at around 7.5 keV, *i.e.*, a mean positron implantation depth of ~150 nm. This indicates an increase in positron trapping at vacancy-type defects. The turning point at about half of the layer thickness [18] is caused by positrons annihilating in the GaN template and confirms well the layer thickness determined by cross-sectional SEM, *i.e.*, 300 ± 30 nm [4]. In sample No.1 no such profile is visible and the S-parameter approaches with higher implantation energies directly the GaN bulk value in the GaN template. While in the near-surface region all samples are characterized by comparable lineshape parameters close to the InN lattice, clear differences between the different samples are visible closer to the interface. The characteristic S-parameters in this region are determined from Fig. 1 and plotted for each sample as a function of the growth temperature in Fig. 2. A clear trend is visible, and the S-parameter increases from 0.459 to 0.467 while the growth temperature decreases from 550 to 500 °C. Below 550 °C all measured S-parameters are higher than the characteristic value for the InN lattice and vacancy trapping is hence observed. Based on our data we can make two tentative observations so far. When investigating the region close to the interface with the GaN template, increased trapping of positrons at vacancies is visible in all samples except the sample grown at the highest temperature of 550 °C. For growth temperature below 550 °C we observe in the near-interface area an increase in vacancy trapping with decreasing temperature.

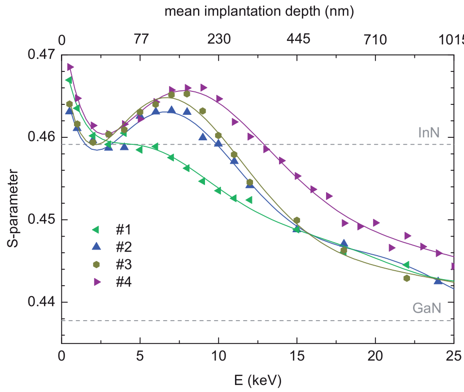

Figure 1 (online color at: www.pss-a.com) S-parameter of different InN layers as a function of the positron implantation energy/mean implantation depth. Characteristic values of the InN and GaN lattices are displayed for comparison. Solid lines are guides to the eye.

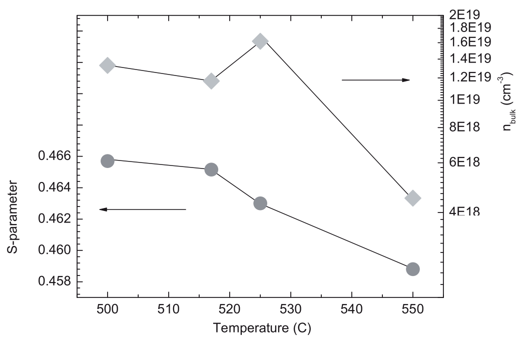

Figure 2 Effect of growth temperature on bulk electron concentration (light squares) and the near-interface S-parameter (dark circles).

Table 1 Growth parameters, electrical properties, and S-parameters of investigated set of InN layers.

ID	1	2	3	4
T_{growth} (°C)	550	525	517	500
pressure (mbar)	800	600	800	800
n_{sheet} ($\times 10^{14}$ cm^{-2})	1.43	3.92	3.24	4.61
n_{bulk} ($\times 10^{18}$ cm^{-3})	4.5	16.2	11.7	13.3
μ (cm^{-2}/Vs)	1070	647	779	536
S-parameter	0.459	0.463	0.465	0.466

Figure 2 also shows results from Hall measurements of the investigated set of samples. With decreasing temperature an increase in the bulk carrier concentration from mid-$10^{18}\,cm^{-3}$ to low-$10^{19}\,cm^{-3}$ is observed. The bulk electron concentration has been determined by averaging the measured sheet electron concentrations over the layer thickness. This method neglects the electron accumulation layer at InN surfaces and interfaces [19]. Due to the constant layer thickness in our samples, however, these contributions should be constant and hence only lead to a constant shift of the determined values. The electron mobility decreases with increasing electron concentration by around one half from $\sim$1100 to 550 cm^{-2}/Vs, for a temperature drop from 550 to 500 °C (see Table 1). This goes in hand with a degrading of the optical and structural properties, as reported in an earlier work [4]. With decreasing growth temperature below 550 °C, the intensity of the photoluminescence signal was found to decrease and In-droplet formation promoted.

In order to investigate the identity of the vacancy defects observed in the positron annihilation measurements, we take a look at the *SW*-plot in Fig. 3 in which the measured *W*-parameters of each sample are plotted as a function of the *S*-parameters. The characteristic values for the InN and GaN lattice, and the V_{In} [16], are displayed for comparison.

In Doppler broadening measurements the measured lineshape parameter is a weighted sum of the characteristic values of the present positron annihilation states, each multiplied with the annihilation fraction in the respective state. Therefore, if one dominant vacancy defect is present all measured lineshape parameter fall on a line connecting the defect-free lattice and the characteristic vacancy value. This is the case for the measured characteristic lineshape parameters in the near-interface area of the InN samples (see dotted line, Fig. 3). This line clearly shows a different slope than the one determined for the In vacancy (dashed line [16]), with faster increasing *S*-parameters. When comparing our experimental data to theoretical values calculated in earlier work [16], we find that our observed trends coincide with the effect of a decoration of In vacancies by one or more N vacancies. Judging from the amount of deviation from the In vacancy line a complex with an average of 2–3 N vacancies seems most likely.

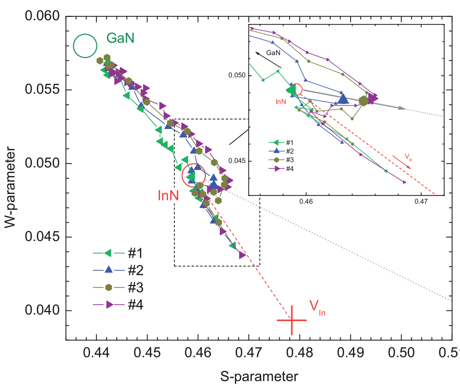

Figure 3 (online color at: www.pss-a.com) Lineshape analysis of the recorded *S* and *W* parameters of the investigated set of samples. A magnification of the most relevant area is included as inset, in which the characteristic SW point of the near-interface region of each sample is displayed enlarged. Reference values for GaN, InN, and V_{In} are shown for comparison.

The determined near-interface *S*-parameters are still comparably close to the InN lattice value and the concentration of the detected vacancy complexes should not exceed low-$10^{17}\,cm^{-3}$, even for the sample grown at 500 °C. The observation of V_{In}–nV_N vacancy complexes near the interface speaks for a close proximity of V_{In} and V_N prior to complexing, and therefore for highly elevated concentrations of N vacancies in this area. Isolated nitrogen vacancies do not trap positrons in InN [15, 16] and hence escape detection with positron annihilation spectroscopy. Single V_N are triply charged donors [20] and act as efficient donors in InN. The observed increase in electron concentrations with decreasing growth temperature might therefore be explained by an increased incorporation of nitrogen vacancies, indicated by an increasing *S*-parameter and the deviation of the measured points from the V_{In}-line. This is in good agreement with earlier reports on insufficient NH_3 decomposition at low growth temperatures [4, 6] which should promote the formation of V_N due to a lack of active nitrogen during growth. However, the applied experimental methods do not allow to rule out influences from N_I or H.

It is interesting to note that earlier positron studies in MOVPE grown InN [11] showed an enhancement of the vacancy signal for increasing growth temperatures from 550 to 625 °C, which has been attributed to beginning decomposition of the material. Assuming a direct comparability of the results, this speaks for 550 °C as the optimal growth temperature in terms of vacancy suppression. An observed maximum in electron mobility at this temperature [4] supports this statement.

4 Conclusions

We report on a systematic investigation of the role of vacancy defects in low-temperature MOCVD growth of InN using positron annihilation spectroscopy. A set of state-of-the-art InN layers is grown on GaN templates at growth temperatures from 550 to 500 °C. With decreasing growth temperature a degrading of the structural, electrical, and optical properties is visible. Positron measurements find that low growth temperatures promote the formation of V_{In}–nV_N vacancy complexes near the interface. This indicates the introduction of high concentrations of V_N donors in that area, which might be the reason behind the observed increase in free carrier concentration with decreasing growth temperature.

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