Ion implantation of Cd and Ag into AlN and GaN

Miranda, Sérgio M C (ITN, Sacavem) ; Kessler, Patrick (Bonn U., HISKP) ; Correia, João Guilherme (ITN, Sacavem ; Lisbon U., CFNUL) ; Vianden, Reiner (Bonn U., HISKP) ; Johnston, Karl (Saarland U.) ; Alves, Eduardo (ITN, Sacavem ; Lisbon U., CFNUL) ; Lorenz, Katharina (ITN, Sacavem ; Lisbon U., CFNUL)

Published in: Phys. Status Solidi C 9 (2012) 1060-1064

The final publication is available at

<http://onlinelibrary.wiley.com/doi/10.1002/pssc.201100203/abstract>

Ion implantation of Cd and Ag into AlN and GaN

S. M. C. Miranda¹, P. Kessler², J.G. Correia^{1,3}, R. Vianden², K. Johnston⁴, E. Alves^{1,3}, K. Lorenz^{*,1,3}

¹ Instituto Tecnológico e Nuclear, Estrada Nacional 10, 2686-953 Sacavém, Portugal

² Helmholtz – Institut für Strahlen- und Kernphysik, Universität Bonn, 53115 Bonn, Germany

³ Centro de Física Nuclear da Universidade de Lisboa, Av. Prof. Gama Pinto 2, 1649-003 Lisboa, Portugal

⁴ Technische Physik, Universität des Saarlandes, 66041 Saarbrücken, Germany

Keywords (III-nitrides, ion implantation, perturbed angular correlation, Rutherford backscattering/channelling, X-ray diffraction)

* Corresponding author: e-mail: Lorenz@itn.pt, Phone: +351 21994 6052, Fax: +351 21994 6285

GaN and AlN thin films were implanted with cadmium (Cd) or silver (Ag), to fluences ranging from 1×10^{13} to 1.7×10^{15} at/cm². The implanted samples were annealed at 950 °C under flowing nitrogen. While implantation damage could be fully removed for the lowest fluences, for higher fluences the crystal quality was only partially recovered. For the high fluence samples the lattice site location of the ions was studied by Rutherford Backscat-

tering/channelling (RBS/C). Cd ions are found to be incorporated in substitutional cation sites (Al or Ga) while Ag is slightly displaced from this position. To further investigate the incorporation sites, Perturbed Angular Correlation (PAC) measurements were performed and the electric field gradients at the site of the probe nuclei were determined.

1 Introduction Despite the successful commercialization of InGaN based light emitting diodes and laser diodes many basic questions on the mechanisms of light emission remain unanswered. A subject of intensive scientific discussion is the fact that the intense luminescence of these devices is relatively insensitive to the large density of defects, mainly threading dislocations [1]. A widely accepted explanation for this behaviour is the localization of excitons at regions with potential minima. The microscopic origin of this localization remains highly disputed but seems to be especially effective in In-containing III-nitride alloys (InGaN and InAlN) [2].

Perturbed Angular Correlation (PAC) is a valuable technique to probe the immediate lattice neighbourhood of a radioactive probe at the atomic scale. PAC measures the hyperfine interaction of the electric field gradient (EFG) at the site of a radioactive probe with the quadrupole moment Q of the intermediate state of a γ - γ cascade in the daughter nucleus. This interaction causes a perturbation of the anisotropic emission pattern of the second γ ray with respect to the emission direction of the first. From the time dependence of this perturbation, the parameters of the quadrupole interaction can be derived. It is usually characterized by the quadrupole interaction frequency ν_Q and by the asymmetry parameter η . ν_Q is proportional to the product of the principal component of the EFG, V_{zz} ,

and the quadrupole moment Q of the intermediate state of the cascade. The EFG is characteristic for the charge distribution in the microscopic lattice surrounding of the probe nucleus. In the case of the III-nitrides, a substitutional probe experiences an axially symmetric EFG ($\eta=0$) pointing along the c-axis, caused by the wurtzite lattice structure itself and defects may cause additional EFGs.

The ¹¹¹In probe is perfectly suited to shed light on the role of In in III-nitride samples [3]. Recent PAC studies suggest that Indium in GaN and AlN tends to trap a nitrogen vacancy, which may strongly influence the properties of InGaN and AlInN alloys and may play a role in the above mentioned mechanisms of exciton localisation [4]. PAC measurements using the probes ¹¹⁷Cd, ^{111m}Cd and ¹⁸¹Hf show that this probe-vacancy complex does not form at other heavy impurities and is a peculiarity of In in III-nitrides [5]. In these studies the radioactive probes were introduced by ion implantation. For the interpretation of these measurements the location of the probes in the lattice as well as the ability to remove implantation damage during annealing are of major importance. This work presents Rutherford Backscattering Spectrometry/Channelling (RBS/C) and X-ray Diffraction (XRD) studies on Cd and Ag implanted and annealed samples to get a deeper insight into these processes.

2 Experimental details AlN and GaN thin films, 3 μm thick, grown on sapphire by hydride vapour phase epitaxy were ion implanted, to fluences from 1×10^{13} at/cm^2 to 1.7×10^{15} at/cm^2 , with stable Cadmium (Cd), or Silver (Ag) at 150 keV. The ion implantations were performed at room temperature (RT) with the sample's surface normal tilted about 10° away from the incident beam to prevent channelling effects during the implantation. The samples were annealed in a tube furnace at 950°C for 10 (Cd) or 20 (Ag) minutes under flowing nitrogen. An as-grown sample was placed front-to-front as a proximity cap to prevent N loss during the thermal treatment.

RBS/C studies were performed with a 1 mm diameter collimated beam of 2 MeV He^+ ions from a Van de Graaff accelerator. The backscattered particles were detected by a silicon surface barrier detector at a backscattering angle of 140° . RBS/C aligned spectra were acquired by orienting the crystal c-axis parallel to the beam direction and for random spectra the sample was tilted away from the aligned position by 5° and rotated during the measurement. Full angular scans in the $\langle 0001 \rangle$ and $\langle -2113 \rangle$ directions were performed to determine the lattice site location of the implanted ions using a two axes goniometer.

High resolution XRD experiments were carried out using monochromated $\text{CuK}\alpha_1$ radiation in a Bruker D8 Discover system equipped with a Göbel mirror, a Ge(220) double reflection asymmetric monochromator and a scintillation detector. 2θ - ω scans served to study the changes of the c lattice parameter induced by the large strains caused by the implantation defects.

For PAC measurements, the GaN and AlN samples were implanted at ISOLDE-CERN at RT with the shortlived ^{117}Ag (fast decaying to the PAC probe $^{117}\text{Cd}/^{117}\text{In}$) or the metastable $^{111\text{m}}\text{Cd}/^{111}\text{Cd}$ to typical fluences between 10^{11} and 10^{12} at/cm^2 at 30 keV. These samples were annealed under similar conditions as described above. The measurements were performed at RT with the probes ^{117}Cd and $^{111\text{m}}\text{Cd}$ in standard BaF_2 6-detector and 4-detector setups, respectively. Results are compared to those previously published employing the probe $^{111}\text{In}/^{111}\text{Cd}$ [3, 4]. Fig. 1 shows the decay schemes of all PAC probes used in this study. Both ^{111}In and $^{111\text{m}}\text{Cd}$ decay via the same intermediate state and therefore the PAC spectra should be similar if the probes have the same lattice environment. The probes ^{111}In and ^{117}Cd are in a way complementary since ^{111}In is decaying to ^{111}Cd and ^{117}Cd is decaying to ^{117}In . The actual PAC measurement is done in the daughter nucleus while the incorporation behaviour is mainly influenced by the implanted species.

Figure 1 Decay schemes for the three PAC probes ^{111}In , $^{111\text{m}}\text{Cd}$ and ^{117}Cd used in this study.

3 Results and discussion Figure 2 shows XRD $0002\ 2\theta$ - ω scans of GaN and AlN samples implanted with Ag to two different fluences before (as-implanted, ai) and after annealing. The curves for a virgin sample and that for the sample implanted with 1×10^{13} Cd/cm^2 and annealed are also shown.

The implantation introduces point defects into the lattice. In c-plane GaN and AlN epitaxial films these defects are known to create large hydrostatic strains leading to an expansion of the c-lattice parameter [6, 7].

This expansion is clearly seen in Fig. 2 causing a pronounced shoulder at the left side of the main diffraction peak; the former arises from the implanted layer close to the surface and the latter from the undamaged film underneath the implanted region. As expected, more damage (a larger shift of the secondary peak to lower angles) is observed in the higher fluence samples. This expansion is partly or fully reversed after annealing. In particular for the high fluence samples residual damage is still retained. Both AlN and GaN show full recovery for the lowest fluence (1×10^{13} Cd/cm^2) as shown by the XRD scans that completely overlap with those of the as-grown samples (Fig. 2).

In RBS/C measurements the implantation damage is seen in the aligned spectra when compared with that of the virgin sample since the backscattering yield is increased by the defects in the implanted layer. The minimum yield ($\chi_{\min}$) is a measure of the crystal quality and is given by the yield in the aligned spectrum divided by the yield in the random spectrum. $\chi_{\min}$ was determined for all samples in a depth window comprising the entire implanted region and the values are summarised in Table 1. For the high fluence samples also $\chi_{\min}$ for the implanted ion is given. The as-grown GaN and AlN samples present a $\chi_{\min}$ of about 2 %, evidence of high structural quality.

RBS/C spectra for Ag implantation are presented in Fig. 3, and similar results are found for Cd implantation. In the case of GaN, $\chi_{\min}$ increases to 5.4 % for the lower fluence, and to 33 % for the higher fluence.

After annealing the backscattering yield decreases, indicating that recovery of the crystal quality has occurred.

For the lower fluence the channelling quality of the as-grown sample is almost restored in good agreement with the XRD measurements showing close to complete recovery of the crystal. In the case of AlN, the aligned spectra after low fluence implantation (not shown for clarity) coincide with that of the as-grown sample. At the same time XRD clearly reveals an expansion of the c-lattice parameter (Fig. 2). This shows the high sensitivity of XRD to very low levels of radiation damage in III-nitrides. For the higher fluence the RBS/C spectra reveal an increase in minimum yield and an increased dechannelling rate. The minimum yield for AlN stays well below the values for GaN showing the superior radiation resistance of AlN. However, annealing does not significantly alter the RBS spectra indicating that implantation damage once formed is very stable. The extreme difficulty in removing implantation defects in AlN has been reported previously even for annealing temperatures as high as 1450 °C [8].

The decreased backscattering from Ag and Cd in the aligned spectra (see minimum yields in Table 1) indicates that the implanted ions are incorporated on substitutional sites in the wurtzite lattice. The substitutional fraction (F_S) is calculated by $F_S = (1 - \chi_{\min}(D)) / (1 - \chi_{\min}(M))$, where $\chi_{\min}(D/M)$ are the D/M minimum yields obtained from the random and <0001> aligned RBS/C spectra given in Table 1; D stands for dopant and M for the matrix elements (Ga or Al). The experimental data summarized in Table 1 reveal that Cd implanted samples have high F_S , (90 % for AlN and 99 % for GaN) directly after the implantation. After annealing in GaN, F_S decreases slightly to 96 % probably due to the interaction of Cd with implantation defects.

Figure 2 0002 2θ-ω XRD curves of Ag and Cd implanted in GaN and AlN.

Table 1 Minimum yields, $\chi_{\min}$, and substitutional fractions, F_S .

Sample	Element	$\chi_{\min}$ (%)	F_S (%)
AlN:Cd as-implanted 0.8×10^{15} at/cm ²	Al	4.6	90
	Cd	14	
AlN:Cd annealed 0.8×10^{15} at/cm ²	Al	4.3	70
	Cd	33	
GaN:Cd as-implanted 0.8×10^{15} at/cm ²	Ga	6.2	99
	Cd	7.2	
GaN:Cd annealed 0.8×10^{15} at/cm ²	Ga	4.7	96
	Cd	8.1	
AlN:Ag as-implanted 1.7×10^{15} at/cm ²	Al	7.4	53
	Ag	50	
AlN:Ag annealed 1.7×10^{15} at/cm ²	Al	6.1	69
	Ag	35	
GaN:Ag as-implanted 1.7×10^{15} at/cm ²	Ga	33	75
	Ag	50	
GaN:Ag annealed 1.7×10^{15} at/cm ²	Ga	21	51
	Ag	59	
AlN:Cd as-implanted 1×10^{13} at/cm ²	Al	2.4	
	Cd	-	
AlN:Cd annealed 1×10^{13} at/cm ²	Al	3.1	
	Cd	-	
GaN:Cd as-implanted 1×10^{13} at/cm ²	Ga	3.2	
	Cd	-	
GaN:Cd annealed 1×10^{13} at/cm ²	Ga	2.8	
	Cd	-	
AlN:Ag as-implanted 2×10^{13} at/cm ²	Al	4.2	
	Ag	-	
AlN:Ag annealed 2×10^{13} at/cm ²	Al	4.0	
	Ag	-	
GaN:Ag as-implanted 2×10^{13} at/cm ²	Ga	5.4	
	Ag	-	
GaN:Ag annealed 2×10^{13} at/cm ²	Ga	2.9	
	Ag	-	
AlN as-grown	Al	2.1	
	-	-	
GaN as-grown	Ga	1.7	
	-	-	

For AlN a considerable decrease to $F_S=70$ % is observed suggesting a low solubility of Cd in AlN.

For Ag implantation, in the as-implanted samples F_S is about 75 % and 53 %, for GaN and AlN, respectively. After annealing, F_S in GaN decreases significantly to around 51 %. A very interesting case is that of Ag implanted AlN where, unlike in the other samples, annealing promotes the incorporation of Ag into substitutional sites in the crystal as there is an increase in F_S to around 69 %.

Full angular RBS/C scans were performed and are shown in Fig. 4 for the <0001> direction for the as-

implanted samples. The scans indicate that Cd occupies substitutional positions in the crystal as the widths of the scans for Cd and the matrix elements (Ga or Al) are similar.

Figure 3 RBS spectra of Ag implanted AlN (top) and GaN (down), R. for random spectra and A. for <0001> aligned spectra. Stars for the random level and thin black line for the virgin samples aligned spectra.

Figure 4 Full angular RBS/C scans in the <0001> axis for all high fluence as-implanted samples.

Figure 5 RT PAC measurements in GaN and AlN using the probes ^{111}In , $^{111\text{m}}\text{Cd}$ and ^{117}Cd , dots for data and line for the fit.

Along the <0001> direction the atomic rows are mixed rows containing the cation element and N; therefore it is not possible to distinguish between the Ga/Al-site and the N-site. Angular scans across the <-2113> direction (not shown) confirm that Cd is incorporated on substitutional cation sites.

Ag occupies a position slightly displaced from the substitutional site in the crystal as the width of the Ag scans are narrower than for the matrix elements Al or Ga (Fig. 4). Since the fluence for the Ag samples was higher than for the Cd implanted samples this displacement is possibly due to the interaction of Ag with lattice defects. A strong correlation of the displacement of implanted ions with implantation damage was also shown to exist for rare earth implanted AlN. Er was found on substitutional sites when implantation damage was reduced by performing the implantation along the c-axis while a significant displacement was found for random implantation as performed in this study [9]. Therefore we can assume that Ag is incorporated on substitutional sites if the implantation damage is reduced. The fact that the Ag substitutional fraction increases after annealing in the case of AlN indicates that the solubility of Ag in AlN is high.

Fig. 5 shows RT PAC spectra and their fits using the probes ^{111}In , $^{111\text{m}}\text{Cd}$ and ^{117}Cd in GaN and AlN after annealing at 950 °C (1000 °C in the case of ^{111}In [3, 4]). The RBS/C and XRD measurements suggest that the probe ions are incorporated on substitutional cation sites and that the crystal is completely recovered after annealing. Note that the typical implantation fluences for PAC measurements are one order of magnitude lower than for the low fluence samples characterized by RBS/C and XRD. Each spectrum shows a typical quadrupole interaction frequency (V_Q) caused by the EFG of the wurtzite lattice at the site of the probe nucleus. The values for V_Q and V_{ZZ} (the main

component of the EFG) are given in Fig. 5. The uncertain-uncertainties in the obtained v_Q values of around 1% are mainly determined by the error in the time calibration of the spectrometers. V_{zz} depends on the quadrupole moment Q which is not known with high accuracy (we used a value of $Q = 0.83(13)$ barn) [10]. We further point out that the EFG can vary for layers with different strain states or doping levels. As expected, the values of the main lattice EFG measured with ^{111}mCd match those measured using the probe ^{111}In since both probes occupy the same substitutional site and use the same intermediate state for the PAC measurement. The slight discrepancy of v_Q in GaN measured using ^{111}In or ^{111}mCd is attributed to different strain states of the different GaN materials used.

In the spectra measured with ^{111}In a second frequency, faster than that corresponding to the lattice EFG, is visible; this is clearly seen for the case of AlN while for GaN it causes a shoulder at around 50 ns. This additional frequency was attributed to the formation of an In-defect complex, most probably a nitrogen vacancy trapped at the site of the In probe [11]. No second frequency is observed in the spectra measured with ^{111}Cd and ^{117}Cd , confirming that no defects are trapped at the site of these probe atoms.

4 Conclusions In this work GaN and AlN thin films were implanted with Cd or Ag to fluences ranging from 10^{13} to 1.7×10^{15} at/cm². Annealing of the samples is carried out in order to recover lattice damage induced during implantation. The samples are then compared to the as-implanted and as-grown samples using XRD and RBS/C measurements. It is found that a large percentage of dopants occupy substitutional or near-substitutional positions in the lattice and that annealing promotes structural recovery of the samples. In particular for low fluences, typically used for PAC measurements, a complete recovery of the lattice is found and results point to a complete incorporation of Ag and Cd on substitutional Ga/Al-sites in GaN/AlN.

PAC studies were performed in samples implanted with the radioactive probes ^{111}mCd and ^{117}Cd to fluences from 10^{11} to 10^{12} at/cm² at 30 keV and compared to similar measurements using the ^{111}In probe. The EFGs were determined and it was shown that in the case of ^{111}mCd and ^{117}Cd the majority of probe atoms occupy undisturbed substitutional sites and do not trap point defects as it is the case of ^{111}In in GaN and AlN. Although vacancies and other defects are created during ion implantation, the fact that the observed In-defect complex is very stable at high temperatures suggests that such complex may also be formed during the growth of InGaN and AlInN compound semiconductors. In fact, recent calculations in the framework of density functional theory (DFT) suggest a high concentration of nitrogen vacancies in GaN [12]. It is presently unclear what would be the impact of In- V_N complexes on the optical and electrical properties of the material. Further DFT calculations would be desirable to establish the formation energies of such In- V_N complexes

(as well as Cd- V_N for comparison) and to determine if they would introduce additional energy levels into the band gap which may be involved in the light emission processes in InGaN and AlInN.

Acknowledgements We acknowledge support by FCT, Portugal (Ciência 2007, PTDC/CTM/100756/2008 and CERN-FP-116320-2010), and by the European Union seventh framework project ENSAR (contract no. 262010).

References

- [1] R. A. Oliver, S. E. Bennett, T. Zhu, D. J. Beesley, M. J. Kappers, D. W. Saxey, A. Cerezo, C. J. Humphreys, *J. Phys. D: Appl. Phys.* 43, 354003 (2010).
- [2] S. F. Chichibu, A. Uedono, T. Onuma, B. A. Haskell, A. Chakraborty, T. Koyama, P. T. Fini, S. Keller, S. P. Denbaars, J. S. Speck, U. K. Mishra, S. Nakamura, S. Yamaguchi, S. Kamiyama, H. Amano, I. Akasaki, J. Han, T. Sota, *nature materials* 5, 810 (2006).
- [3] K. Lorenz, F. Ruske, R. Vianden, *Appl. Phys. Lett.* 80, 4531 (2002).
- [4] J. Schmitz, J. Niederhausen, J. Penner, K. Lorenz, E. Alves, R. Vianden, *Physica B* 404, 4866 (2009).
- [5] P. Keßler, K. Lorenz, R. Vianden, *Defect and Diffusion Forum* 311, 167 (2011).
- [6] C. Liu, B. Mensching, K. Volz, B. Rauschenbach, *Appl. Phys. Lett.* 71, 2313 (1997).
- [7] S. Magalhães, M. Peres, V. Fellmann, B. Daudin, A. J. Neves, E. Alves, T. Monteiro, K. Lorenz, *J. Appl. Phys.* 108, 084306 (2010).
- [8] K. Lorenz, S. Magalhães, E. Alves, M. Peres, T. Monteiro, A. J. Neves, M. Boćkowski, *Nucl. Instr. Meth. Phys. Res. B* 268, 2907 (2010).
- [9] M. J. Soares, J. P. Leitão, M. I. N. da Silva, J. C. González, F. M. Matinaga, K. Lorenz, E. Alves, M. Peres, T. Monteiro, *Optical Materials* 33, 1055 (2011).
- [10] P. Herzog, K. Freitag, M. Reuschenbach and H. Walitzki *Zeitschrift für Physik A Hadrons and Nuclei* 294, 13 (1980).
- [11] P. Kessler, K. Lorenz, S. M. C. Miranda, J. G. Correia, K. Johnston, R. Vianden, the ISOLDE collaboration, *Hyperfine Interact.* 197, 187 (2010).
- [12] M.G.Ganchenkova, R.M.Niemininen, *Phys. Rev. Lett.* 96, 196402 (2006).