Radiation damage formation and annealing in GaN and ZnO

K. Lorenz\textsuperscript{a,b}, M. Peres\textsuperscript{c}, N. Franco\textsuperscript{a,b}, J. G. Marques\textsuperscript{a,b}, S. M. C. Miranda\textsuperscript{a}, S. Magalhães\textsuperscript{a,c}, T. Monteiro\textsuperscript{c}, W. Wesch\textsuperscript{d}, E. Alves\textsuperscript{a,b}, E. Wendler\textsuperscript{d}

\textsuperscript{a}Instituto Tecnológico e Nuclear, EN10, 2686-953 Sacavém, Portugal
\textsuperscript{b}Centro de Física Nuclear da Universidade de Lisboa, Av. Prof. Gama Pinto 2, 1649-003 Lisboa, Portugal
\textsuperscript{c}Departamento de Física e i3N, Universidade de Aveiro, 3810-193 Aveiro, Portugal
\textsuperscript{d}Institut für Festkörperphysik, Friedrich-Schiller-Universität Jena, Max-Wien-Platz 1, 07743 Jena, Germany

ABSTRACT

The radiation damage formation upon low temperature ion implantation and neutron irradiation has been compared for GaN and ZnO. Both materials exhibit strong dynamic annealing effects during implantation, even at 15 K, leading to high amorphisation thresholds. The damage build-up with fluence was found to proceed in a similar way for GaN and ZnO, both showing two saturation regimes below the amorphisation level where, over wide fluence regions, the damage level increases only very slowly. For low fluences the damage accumulation rate is similar for both materials. For higher fluences, on the other hand, GaN shows considerably higher damage levels and finally collapses into an amorphous structure while ZnO remains single crystalline up to the highest fluence of $7 \times 10^{16}$ Ar/cm$^2$.

Neutron irradiation produces similar defects as ion implantation but within the entire sample while the defect density is much lower. The main effect of irradiation on the structural properties of GaN is an expansion of the $c$-lattice parameter. Optical properties are significantly deteriorated after irradiation and only recover partially after annealing. ZnO does not suffer such a pronounced change of the lattice parameters but reveals a strong deterioration of the surface, possibly due to blistering and exfoliation. At the same time the optical properties are less affected than for GaN. The near band edge emission is partly quenched but recovers to a large extend after annealing while broad defect bands are observed below the bandgap for irradiated samples, before and after annealing.

Keywords: ZnO, GaN, ion implantation, neutron irradiation, Rutherford Backscattering Spectrometry, X-ray diffraction, Photoluminescence

1. INTRODUCTION

GaN and ZnO are wide bandgap semiconductors suitable for the production of optoelectronic as well as high temperature, high frequency and high power electronic devices. While GaN based light emitting diodes and lasers are already realized on an industrial scale, ZnO still suffers from fundamental problems, in particular, the lack of efficient and reproducible p-type doping. Nevertheless, the two materials are considered competitors on the way to novel (opto)electronic applications and show several common characteristics\textsuperscript{1}. Both materials have a wide and direct band gap (3.437 eV in ZnO and 3.507 eV in GaN at low temperature), a similar valence band structure, and both crystallize in the wurtzite lattice structure. Another common feature of both semiconductors is their strong resistance to radiation damage.\textsuperscript{2} The latter is an important characteristic for device processing steps involving ion implantation, for example for doping or isolation and for the use in electronic circuits in radiation environments, such as in space or nuclear reactors.

In this paper we review similarities and differences of implantation damage build-up in GaN and ZnO at 15 K. The mobility of point defects at temperatures well below room temperature will be demonstrated. Finally, the effect of neutron irradiation on structural and optical properties of GaN and ZnO will be discussed.

\* Contact author. E-mail: lorenz@itn.pt; Phone: (+351) 219 946 052; Fax: (+351) 219 946 285; Website: www.itn.pt
2.  EXPERIMENTAL DETAILS

Ion implantation
Ion implantations were performed at 15 K in a special target chamber at the Institut für Festkörperphysik in Jena, where \textit{in situ} Rutherford Backscattering/Channeling (RBS/C) measurements along the \langle0001\rangle axis allow monitoring the defect accumulation without changing the target temperature.\textsuperscript{3} At this low temperature thermal diffusion of atoms and defects is minimized. The sample is mounted on a four axis goniometer and cooled by a closed cycle He refrigerator. The implantations were carried out with the surface normal tilted by 7° off the ion beam direction to prevent channeling effects. The RBS/C analysis was performed with 1.4 MeV He\textsuperscript{+} ions and a Si surface barrier detector at 170°.

Commercial (Eagle-Picher) O-face (0001) ZnO single crystals were used for implantation work. N, Ar, and Er ions were implanted with fluences from $1\times10^{11}$ to $7\times10^{16}$ at/cm\textsuperscript{2} and energies of 80, 200, and 380 keV, respectively. GaN layers grown, either by Metal Organic Chemical Vapor Deposition (MOCVD) or by Hydride Vapor Phase Epitaxy (HVPE), on (0001) sapphire substrates were implanted with 300 keV Ar ions to fluences from $3\times10^{12}$ to $3\times10^{16}$ at/cm\textsuperscript{2} as well as with 150 keV O, 780 keV Te, 800 keV Xe or 380 keV Au ions.

Neutron irradiation
Nominally undoped GaN (~7 µm thick) and ZnO (~3 µm thick) layers, both grown by MOCVD on (0001) sapphire substrate, were used for the neutron irradiation studies. The samples were irradiated in the 1 MW Portuguese Research Reactor (RPI) with a thermal neutron fluence rate of $2.8\times10^{13}$ n/cm\textsuperscript{2}/s (E<0.5 eV), a fast fluence rate of $0.6\times10^{13}$ n/cm\textsuperscript{2}/s (E>1 MeV), an epithermal fluence rate of $0.1\times10^{13}$ n/cm\textsuperscript{2}/s (at 1 eV) and a gamma dose rate of $2\times10^{6}$ Gy/h. The GaN samples were irradiated first for 240 h, measured and subsequently irradiated for another 240 h, as described in detail in ref. [4]. Some of the samples were shielded inside Cd boxes, in order to cut significantly the thermal neutron component while others were irradiated with the full spectrum. In the following, samples irradiated with fast and thermal neutrons will be labeled 240ft (for 240 h irradiation) and 480ft (for 480 h irradiation) and those which were irradiated with fast neutrons only will be labeled 240f and 480f. ZnO was irradiated for 240 h and shielded inside Cd boxes (240f). The fast neutron fluences reached after 240 h and 480 h were $0.5\times10^{19}$ n/cm\textsuperscript{2} and $1.0\times10^{19}$ n/cm\textsuperscript{2}, respectively. The temperature during the irradiations was less than 70 °C.

The 480 h irradiated GaN samples were annealed for 20 min at temperatures from 600 °C to 1000 °C in a nitrogen atmosphere. The ZnO sample was annealed for 20 min at 800 °C in air.

X-ray diffraction (XRD) characterization was performed on a high resolution diffractometer equipped with a Göbel mirror, a 2-bounce Ge(444) monochromator and a position sensitive detector using monochromated CuK\textsubscript{a1} radiation. Asymmetric (105) reciprocal space maps (RSM) were acquired in order to determine the \textit{a} and \textit{c} lattice parameter of the samples. Other measurements were carried out on a D8Discover system from Bruker-AXS using a Göbel mirror, an asymmetric 2-bounce Ge(220) monochromator and a scintillation detector. In this case, the lattice parameters were determined using the extended Bond method.\textsuperscript{5}

Steady state photoluminescence (PL) spectroscopy was carried out at 10 K using above band gap excitation with the 325 nm line of a HeCd laser. The visible luminescence was analyzed by a single grating spectrometer Spex 1704 monochromator (1 m, 1200 mm\textsuperscript{-1}) and detected by a thermoelectrically cooled Hamamatsu R928 photomultiplier tube.
3. LOW TEMPERATURE IMPLANTATION DAMAGE BUILD-UP AND ANNEALING

Damage build-up at 15 K in ZnO

Figure 1 shows selected RBS/C aligned spectra for N and Er implanted ZnO for two different fluences. The aligned spectra of as-grown samples are also shown for comparison. As a measure for the produced damage concentration, the difference in minimum yield $\Delta \chi_{\text{min}}$ is determined, where $\Delta \chi_{\text{min}}$ is given by $\Delta \chi_{\text{min}} = (Y_{\text{al}} - Y_{\text{al,virgin}})/Y_{\text{ra}}$. $Y_{\text{al,virgin}}$ and $Y_{\text{al}}$ are the RBS yields of the aligned spectra for the unimplanted and implanted sample, respectively, and $Y_{\text{ra}}$ is the maximum yield measured in random direction. To calculate the damage level the yields were integrated within windows comprising the entire implanted layer leaving out the surface peak, as indicated in Fig. 1. The fluences in Fig. 1 were chosen to give approximately the same values of $\Delta \chi_{\text{min}}$ for both Er and N implantation. As expected, the fluence to produce a certain damage level is lower for the heavier Er ion.

![Figure 1](image_url)

Figure 1. $<$0001$>$ aligned RBS/C spectra for ZnO implanted with N (a) and Er (b) to different fluences compared to the as-grown sample. The windows used for the determination of $\Delta \chi_{\text{min}}$ are indicated.

Figure 2a shows $\Delta \chi_{\text{min}}$ as a function of the ion fluence $N$. The curves for all implanted ions do not show a simple linear increase of damage with the fluence but two plateaus can be distinguished, where, within wide fluence ranges, the damage level saturates. Such behavior is common in materials with strong dynamic annealing effects, i.e. a large number of created vacancies and interstitials recombine during the implantation. Four stages of damage production can be distinguished, labeled stage I to IV in Fig. 2, and which are interpreted as follows: In stage I, an almost linear increase of the lattice damage with ion fluence is observed due to the formation of point defects in well separated collision cascades. In stage II the damage saturates, this is attributed to the overlapping of the damage cascades of single ions, allowing for an increased recombination of point defects. In stage III the damage increases steeply, pointing to the formation of stable defect clusters or extended defects like stacking faults or dislocation loops. Stage IV shows a second plateau, being still considerably below the amorphisation level. The last stage was only reached in the case of Ar implantation.

The lines in Fig. 2 are calculated using a simplified version of the Hecking model. From the fit of this model to the data, in particular from the first low fluence regime, the displacement energy for Zn could be determined to be 65 eV. Simulations with the Monte Carlo program SRIM 2008 were performed to determine the number of Zn displacements per ion and unit depth at the maximum of the damage profile, $N_{\text{dpa}}$, using values for the displacement energies of Zn and O of 65 and 50 eV, respectively. Subsequently, the number of displacements per Zn atom, $n_{\text{dpa}}$, was calculated for each fluence and ion using $n_{\text{dpa}} = N_{\text{dpa}}/N$, where $N$ is the ion fluence and $N_0 = 4.1475$ at/cm$^2$ the atomic density of Zn in ZnO. In Fig. 2b the damage build-up curve is re-plotted as a function of $n_{\text{dpa}}$. In this representation the curves for different ions almost overlap.
Figure 2. The difference in minimum yield $\Delta \chi_{\text{min}}$ in ZnO as a function of the ion fluence (a) and as a function of the number of displacements per Zn atom, $n_{\text{dpa}}$ (b) for 80 keV N, 200 keV Ar and 380 keV Er implantation into ZnO single crystals. The plotted curves are fits based on the defect interaction and amorphisation model of Hecking.6

The slight differences observed may be due to the different nature of defects created by ions with largely different masses. The collision cascades are denser in the case of Er implantation, favoring the formation of extended defects and defect clusters, which may be the reason why the steep damage increase in stage III sets in at lower $n_{\text{dpa}}$ values than it does for the lighter ions. In fact, Fig. 1 shows that the shape of the aligned spectra is very different for N and Er implantation even for samples showing similar $\Delta \chi_{\text{min}}$ values; the defect levels DL1 and DL2 corresponding to the selected spectra in Fig. 1 are marked in Fig. 2 (b). For N implantation, for both defect levels the expected approximately Gaussian defect distribution is clearly seen from the increased backscattering yield within the implanted region (channel 250 and higher) while the backscattering yield decreases again for deeper layers (below channel 250). For Er implantation, on the other hand, especially for DL2 the backscattering yield increases even for depths beyond the implanted region. It was shown previously that point defects and amorphous zones preferentially lead to direct backscattering at displaced atoms while stacking faults and dislocation loops rather contribute to the increasing minimum yield by dechanneling of the analyzing beam.8 Therefore, both the high dechanneling rates (Fig. 1b) and the early on-set of stage III in the damage build-up curve (Fig. 2b) for Er suggest that heavy ions facilitate the formation of extended defects like dislocation loops.

Figure 3. Defect profiles $n_{\text{dpa}}(z)$ for 200 keV Ar implanted ZnO for various ion fluences. In (a) the calculated distributions of primary displacements (solid line) and implanted ions (dashed line) derived from SRIM simulations are given in arbitrary units for comparison. For clarity in (b) only some fluence values are given in the legend.
Figure 4. Relative defect concentration $n_{da}$ at different depth regions versus the number of displacements per lattice atom $n_{dpa}$ for 200 keV Ar implanted ZnO. Part (a) represents stages I and II and part (b) stages III and IV. The maximum nuclear energy deposition is at 0.06-0.10 µm and the maximum ion concentration at 0.11-0.15 µm (see Fig. 3).

The occurrence of extended defects becomes especially obvious when analyzing the RBS/C spectra in more detail, which is done for Ar implanted ZnO. Figure 3 plots the relative concentration of displaced lattice atoms $n_{da}$ versus the depth $z$ (referred to as defect profiles). The profiles were calculated with the computer code DICADA assuming the occurrence of uncorrelated displaced atoms which follow when point defects, clusters of point defects or amorphous zones exist within the implanted layer. Behind the implanted layer, $n_{da}$ should reach zero if the correct type of defects is assumed in the calculation. Within the experimental error this is only the case for very small ion fluences ranging within stage I (see profile for $8 \times 10^{12}$ cm$^{-2}$ in Fig. 3 (a)). This supports the interpretation that stage I is mainly correlated with the production of point defects. Within stage II strong defect recombination results in a nearly constant defect concentration (see Fig. 2). Furthermore, the profiles in Fig. 3 (a) for $1.5 \times 10^{14}$ and $2 \times 10^{15}$ cm$^{-2}$ (both fluences belong to stage II) suggest that there is also an extension of the defect distribution towards deeper regions and the defect concentration appears to deviate from zero below the implanted layers. These findings indicate that, within stage II, point defects do not only recombine but extended defects may start to form. The processes within stages I and II are solely determined by the energy deposition into collision processes. This can be seen from Fig. 2 which compares results for various ion species and also from Fig. 4 (a) which compares the defect concentration for Ar implanted layers at various depths. The curves overlap for stages I and II. For stages III and IV, on the other hand, Fig. 2 shows that the curves $\Delta \chi_{\text{min}}$ versus $n_{dpa}$ start to split for the various ion species in stage III suggesting that the implanted ion species themselves become important for the damage formation. The same result can be deduced from the profiles of the Ar implanted ZnO layers in Fig. 3 (b). The rise of defect concentration within stage III is dominant at the depth of maximum ion concentration (compare profiles for $3 \times 10^{15}$ and $7 \times 10^{15}$ cm$^{-2}$ in Fig. 3 (b) with ion distribution in Fig. 3 (a)). The occurrence of secondary effects in the damage formation, being not solely determined by the nuclear energy deposition for stages III and IV, is also seen in Fig. 4 (b), which shows the defect concentration versus the number of displacements per lattice atom at various depths. In contrast to the results in Fig. 4 (a) no uniform dependence is found. From Fig. 3 (b) it is obvious that, for ion fluences within stages III and IV, the calculated profiles do not reach zero and long artificial tails extend far beyond the implanted layer (maximum range of primary displacements or ions is about 0.3 µm). This suggests that the dechanneling of the analyzing ions within the implanted layer is not correctly treated when assuming only uncorrelated displaced lattice atoms. Therefore the implanted layers must contain extended defects. Most probably they consist of a mixture of point defect clusters and dislocation loops.
Damage build-up at 15 K in GaN

In Fig. 5, a set of RBS/C spectra is plotted for Ar implanted GaN. For fluences between \(1.2\times10^{16}\) to \(2\times10^{16}\) Ar/cm\(^2\) the random level is reached which is commonly taken as an indication for amorphisation.

![Figure 5. <0001> aligned RBS/C spectra for GaN implanted with 300 keV Ar to different fluences: a) low ion fluences compared to the as-grown sample and b) high fluences with random spectrum as reference. The window used for the determination of \(\Delta \chi_{\text{min}}\) is indicated.](image)

To see this effect more clearly in the damage build-up curves, the window for the determination of the \(\Delta \chi_{\text{min}}\) does not contain the whole implanted layer (see Fig. 5). In order to compare the results for the various implanted ion species, Fig. 6 shows \(\Delta \chi_{\text{min}}\) versus the ion fluence which was converted into displacements per Ga atom. Herein a displacement energy of 41 eV was taken in the SRIM calculations, which was determined in the same way as for ZnO by fitting the Hecking model to the damage build-up curve.\(^{10}\) The curves in Fig. 6 exhibit five stages of damage formation with the first four being similar as discussed above for ZnO and stage V being the amorphisation which occurs for all ion species.\(^{11}\) Figure 6 suggests that stage I occurs at given numbers of \(n_{\text{dpa}}\) independent of the ion species.

![Figure 6. The difference in minimum yield \(\Delta \chi_{\text{min}}\) as a function of the number of displacements per Ga atom, \(n_{\text{dpa}}\) for 150 keV O, 300 keV Ar, 780 keV Te, 800 keV Xe and 350 keV Au implantation into single crystalline GaN.](image)

The first saturation value in stage II is similar for all ion species except for Au ions which may be connected with the fact that in this case the thickness of the implanted layer is only one third of that for the other ion species. Stages III, IV and V shift to larger \(n_{\text{dpa}}\) values with decreasing mass of the implanted ions, pointing to the role of the implanted ions.
themselves in these cases. More details about the defect evolution can be seen in the defect profiles plotted in Fig. 7 for Ar implanted GaN, which were calculated as described above for ZnO. Within stage II there is not only a recombination of defects causing the very weak increase of the defect concentration with rising ion fluence as seen in Fig. 6, but the defect profiles extend into larger depth (see Fig. 7 a) and b); stage II for Ar ranges up to about 1×10^{15} cm^{-2}). This indicates the occurrence of some defect mobility even at 15 K and suggests that the formation of more complex defect structures starts already at the end of stage II. At the onset of stage III, defect accumulation occurs preferentially at the depth of maximum nuclear energy deposition and within stage IV the defects again extend into larger depth (see Fig. 7 b) and c)). Amorphisation processes in GaN are complex and not well understood. For room temperature implantation it was believed to start at the surface. However, recent studies indicate that this highly damaged surface layer often consists of randomly oriented nanocrystals rather than an amorphous phase. At 15 K we assume that real amorphisation occurs since dynamic annealing is slowed down, however, from RBS/C measurements alone it is not possible to distinguish amorphous or poly/nanocrystalline material. For all ion species studied, amorphous seeds nucleate within a rather narrow layer at a depth below the surface but which is neither that of maximum nuclear energy deposition nor that of maximum ion concentration (see Fig. 7 d)). A further increase of the ion fluence renders the implanted layer amorphous similar to a process known for silicon called ion beam induced interfacial amorphisation (IBIIA).\textsuperscript{12} Within stage IV a complex defect structure of point defect clusters and extended defects is to be expected with the extended defects causing the artificial tails in the defect profiles at depths above 0.35 \(\mu\)m. The successive transformation into the amorphous state is also suggested by the successive disappearance of these tails in the defect profiles with increasing ion fluence (see Fig. 7 d)).

![Figure 7. Defect profiles \(n_{\text{da}}(z)\) for 300 keV Ar implanted GaN for various ion fluences (in cm\(^{-2}\)). The calculated distributions of primary displacements (solid lines) and implanted ions (dashed lines) are given in arbitrary units for comparison. Notice the different scale of the ordinate.](image)

**Comparison of damage build-up in ZnO and GaN**

Both ZnO and GaN are considered to exhibit strong resistance to implantation damage. Fig. 8 compares directly the damage build-up curves for 15 K Ar implantation in ZnO and GaN. As already mentioned, GaN exhibits a very similar damage accumulation behavior to ZnO for the first four stages. In contrast to ZnO, in GaN the damage level reaches the random level for the highest fluences (stage V), showing that the channeling effect is completely inhibited and indicating the amorphisation of the material for fluences of 2×10^{15} cm\(^{-2}\) (\(n_{\text{dpa}}=24\)) and higher. In ZnO, on the other hand, the damage level stays well below the random level up to the highest fluence of 7×10^{15} cm\(^{-2}\) (\(n_{\text{dpa}}=59\)).
For low fluences (up to \( n_{\text{dpa}} \approx 0.02 \)) very similar damage levels are observed for GaN and ZnO as expected, since the masses and displacement energies of the two materials are comparable. The second stage, however, starts at slightly higher values of \( n_{\text{dpa}} \) and the saturation damage level is considerably higher in the case of GaN. The second stage is interpreted as the fluence regime in which individual collision cascades start to overlap. The volume and lateral extension of collision cascades should be of the same order of magnitude for both materials due to their similar masses and displacement energies. GaN has a slightly higher density than ZnO which could account for a lower volume of the collision cascades in GaN and therefore, the overlap of independent collision cascades only occurs at higher fluences. This effect, however, is counteracted in part by the higher implantation energy used for GaN. On the other hand, the conversion of the fluence to \( n_{\text{dpa}} \) has some uncertainty as it depends on the knowledge of the correct value of the displacement energy. The values we determined from our data are only upper limits since in-cascade recombination of point defects can even occur at 4 K.\(^{13}\) Despite these uncertainties, it is clear that the saturation damage level in stage II is considerably higher in GaN than it is in ZnO. This may also be due to a lower diffusivity of point defects and therefore lower recombination rates. The steep increase of damage level in stage III for GaN sets in at slightly lower \( n_{\text{dpa}} \) values than for ZnO and suggests the increased formation of extended defects. For implantation at room temperature the dominant extended defects in ion-implanted GaN were shown to be stacking faults.\(^{14}\) Also for the second plateau region (stage IV) the damage level in ZnO stays well below than that observed for GaN showing its better radiation resistance. Furthermore, ZnO could not be rendered amorphous even for the highest fluence of \( 7 \times 10^{16} \text{ Ar/cm}^2 \).

**Low temperature annealing of implantation damage**

We previously showed that implantation defects in low-fluence implanted ZnO become mobile at temperatures as low as 130 K.\(^{7}\) Similar annealing experiments have been performed in GaN. Samples were first implanted at 15 K to a fluence corresponding to the end of stage I in the damage build-up curve. Then isochronous annealing steps were performed between 15 K and 250 K by heating the sample up to a certain temperature for 10 min and then cooling it back to 15 K in order to perform the RBS/C measurement. Fig. 9 shows \( \Delta \chi_{\text{min}} \) values as a function of the annealing temperature after 15 K implantation of \( 2 \times 10^{12} \text{ Er/cm}^2 \) into ZnO and \( 1.5 \times 10^{13} \text{ Ar/cm}^2 \) into GaN. Both materials show partial recovery of the lattice at low temperatures. In the case of ZnO the defect removal starts between 80 and 130 K while for GaN the first annealing step at 100 K already reveals a decrease of \( \Delta \chi_{\text{min}} \). The total lattice recovery in the measured temperature range was seen to be better in ZnO. The damage level in ZnO decreases by 60% while that in GaN only decreases by 30%. However, the initial damage level in GaN was higher which may also influence the subsequent annealing results.
4. NEUTRON IRRADIATION

Unlike in ion-implantation, neutrons do not interact with the electrons of the irradiated material and their range in a solid is very deep, resulting in homogeneous irradiation of the whole sample. Fast and thermal neutrons create lattice disorder due to direct knock-on atoms and recoil processes during neutron activation. The main contribution to the lattice damage in neutron irradiated materials is commonly assumed to be produced by fast neutrons that transfer kinetic energy through elastic collisions with the matrix atoms. In the case of GaN (ZnO), a fast neutron with 1 MeV energy can transfer up to 56 keV (59 keV) to a primary knock-on Ga (Zn) atom or 230 keV (221 keV) to a primary knock-on N (O) atom. Here the maximum energy transfer is given by $T_{\text{max}} = E \cdot 4A / (A+1)^2$, where $A$ is the target atom’s mass. These energies exceed by far the displacement energies for Ga and N in GaN and Zn and O in ZnO. These atoms will be knocked out and initiate collision cascades which are comparable to those produced by keV ion implantation. Just like in the case of ion implantation, large numbers of point defects like vacancies, interstitials, antisites as well as point defect clusters and extended defects can be produced but the larger distances between the single collision cascades will favor point defects to the formation of extended defects. In the case of thin films, one must emphasize that only a small fraction of the neutrons will interact. For GaN, only a fraction of $2.5 \times 10^{-4}$ of the fast neutrons will interact in a 10 μm layer.

Irradiation with thermal neutrons has been investigated due to the possibility of Ge n-type doping of GaN\textsuperscript{15} and Cu, Ga and F doping of ZnO\textsuperscript{16,17} through transmutation. Thermal neutrons can produce indirect atomic displacements as the result of radiative capture ($n,\gamma$) reactions. When a $\gamma$ photon is emitted by the excited compound nucleus formed by neutron capture, the residual atom may suffer recoil if the transferred energy exceeds its displacement energy. The nuclear reactions taking place during irradiation of GaN and the produced prompt $\gamma$ energies\textsuperscript{18} are:

\begin{align*}
14\text{N} (n,\gamma) & \rightarrow 15\text{N}, \text{ with prompt } \gamma \text{ up to 10.8 MeV} \\
60\text{Ga} (n,\gamma) & \rightarrow 70\text{Ga} \rightarrow 70\text{Ge}, \text{ with prompt } \gamma \text{ up to 7.6 MeV} \\
71\text{Ga} (n,\gamma) & \rightarrow 72\text{Ga} \rightarrow 72\text{Ge}, \text{ with prompt } \gamma \text{ up to 6.5 MeV}
\end{align*}

Following the equation $E_{\text{recoil}} = E_\gamma^2 / (2A \cdot c^2) = 5.4 \cdot 10^{-4}\frac{E_\gamma^2}{A}$, photons with energies higher than 2.4 MeV will displace activated Ga atoms, while for the displacement of activated N atoms the minimum photon energy is 1.7 MeV. Furthermore, it is possible that the photon produces Compton electrons. The Compton electrons can displace atoms themselves if they transfer energy above the displacement energy of the target atoms. Also, they can excite the electronic system of the material which can give rise to a change in the charge state of certain defects or impurities already present in the material and thus can significantly influence diffusion and defect annihilation processes in semiconductors.
In this study we investigated the effect of fast and thermal neutrons in the case of GaN while for ZnO the thermal neutrons were shielded in order to avoid radioactive activation of the samples through the $^{64}$Zn($n$,γ)$^{65}$Zn reaction; the resulting $^{65}$Zn isotope has a half-life of eight months. We showed previously that the RBS/C channeling quality of GaN after irradiation remains unchanged in the case of 240 h irradiation, and only for the sample irradiated with fast and thermal neutrons for 480 h a slight increase of the dechanneling rate along the tilted $<10\bar{1}1>$ axis was observed while the minimum yield along the $c$-axis was not affected by the irradiation. Also the widths of XRD rocking curves of the 0002, 0004 and 0006 reflections did not change after irradiation. On the other hand, a strong effect was observed on the lattice parameters. Fig. 10 a) and c) present the change of the $c$ and $a$ lattice parameters – derived from the XRD (10$ar{1}5$) RSM – as a function of the irradiation time for samples irradiated with fast and with fast+thermal neutrons. The $c$-lattice parameter is increasing strongly with the neutron fluence and a surprisingly strong role of thermal neutrons in the damage build-up is evidenced. For the sample with the highest neutron fluence (480ft) the expansion of the $c$-lattice parameter is as high as 0.012 Å or 0.2% of the original value while the $a$ lattice parameter remains unchanged within the error of the measurement. The samples irradiated for 480 h were subjected to isochronal annealing steps between 600 and 1000 ºC. The change of lattice parameters with annealing is shown in Fig. 10 b) and c). Already after annealing at 600 ºC the $c$- parameter decreases again and after annealing at 1000 ºC the expansion is completely reversed. At the same time, the $a$-parameter increases slightly from 3.185 Å to 3.188 Å for sample 480ft. This is probably due to the relaxation of residual compressive strain which is caused by the lattice mismatch and different thermal expansion coefficients of GaN and the sapphire substrate. Indeed, the measured lattice constant is very close to that of free standing or bulk GaN.$^{19}$ Note that an unirradiated sample does not relax during the same thermal treatment (see Fig. 10 d).

![Graph](attachment:graph.png)

Figure 10. $c$ and $a$ lattice constants of neutron irradiated GaN as a function of the irradiation time (a and c) and as a function of the annealing temperature after irradiation for 480 hours (b and d). The lattice parameters for an unirradiated but annealed sample are also shown.
ZnO shows a very different behavior upon neutron irradiation. The lattice parameters after irradiation only change slightly ($a=3.252$ Å, $c=5.204$ Å in the as-grown and $a=3.251$ Å, $c=5.206$ Å in the irradiated sample). However, the XRD intensity drops strongly in the irradiated and even more in the irradiated and annealed sample. At the same time the width of 002 and 004 rocking curves does not increase significantly. A strong degradation of the surface quality is observed in optical microscopy images (Fig. 11). The as-grown sample has a smooth surface which becomes inhomogeneous over wide regions of the sample after the irradiation. After annealing the irradiated sample, strong blistering occurs. This result is surprising since heavily damaged ion implanted samples of the same material which were annealed in similar conditions did not show such pronounced surface damage. Furthermore, blistering and exfoliation of ZnO upon hydrogen implantation was shown to occur at considerably higher fluences than for GaN. Defects in the ZnO-sapphire interface caused by the irradiation may be the reason for the observed strong effects on the sample’s quality.

Figure 11. Optical microscope images (300×400 μm) of the as-grown, as-irradiated, and irradiated and annealed ZnO samples.

Figure 12. PL spectra of neutron irradiated GaN. a) as grown and 240 h irradiated sample. b) 480 h irradiated and as-grown samples after annealing at 1000 ºC.
Figure 13. PL spectra of as-grown and neutron irradiated ZnO before and after annealing at 800 °C.

PL spectra upon excitation above the band gap are shown in Fig 12 for GaN and in Fig. 13 for ZnO, before and after irradiation and annealing. In GaN, 240 h irradiation with fast neutrons leads to an almost complete quenching of its intrinsic luminescence (yellow luminescence band (YL), ultra violet luminescence (UVL) and donor bound exciton (DBE) recombination). Surprisingly the sample irradiated with fast and thermal neutrons shows stronger luminescence than that irradiated with fast neutrons only. But also here the near band edge emission is quenched and the spectrum is dominated by broad defect bands. After annealing at 1000 °C the samples irradiated for 480 h show partial recovery of the optical activity. For the 480f GaN sample, near band edge emission and yellow luminescence is observed while for the 480f sample broad defect related emission bands are still dominant. Both samples show an additional broad band around 3 eV which is not present in the virgin sample.22 Deep defect levels were also reported for electrical measurements in neutron irradiated GaN.23,24

In the case of ZnO (Fig. 13) the irradiation caused a strong decrease of the intensity of the near band edge emission and introduced a strong defect related emission band in the red spectral region around 1.8 eV. After annealing the near band edge luminescence is partially recovered and the defect band shifts to higher energies (around 2 eV). The origin of the observed defect bands is not clear to date but it is worth noticing that similar broad emission bands are frequently observed in as-grown and annealed ZnO films and bulk crystals.25 Interestingly, the optical properties of ZnO seem to suffer less from the irradiation than GaN despite the severe structural deterioration of these samples.

5. CONCLUSIONS

The radiation damage formation upon low temperature ion implantation and neutron irradiation has been compared for GaN and ZnO. Ion implantation studies showed that both materials exhibit strong dynamic annealing effects even at 15 K. The damage build-up with fluence was found to proceed in a similar way for GaN and ZnO. For low ion fluences a linear increase of damage with the ion fluence is observed due to the formation of point defects. When the damage regions produced by single ions start to overlap, vacancies and interstitials can recombine resulting in a plateau-like slow increase of the damage level. For higher fluences more stable defect complexes form and the damage level increases steeply before reaching another plateau. For low fluences (\(n_{dpa}<0.02\)) the damage accumulation rate is similar for both materials. For higher fluences, on the other hand, GaN shows considerably higher damage levels and starts to amorphise for \(n_{dpa}\) values of 24. ZnO was not rendered amorphous up to the highest fluence corresponding to \(n_{dpa}=59\).

Neutron irradiation produces similar defects to ion implantation but within the entire sample while the defect density is much lower. The main effect of irradiation on the structural properties of GaN is an expansion of the c-lattice parameter while the in-plane parameter remains unchanged. Figures of merit quantifying the crystal quality, such as the RBS/C minimum yield and XRD rocking curve widths, are not altered significantly. Optical properties are strongly deteriorated after irradiation and only recover partially after annealing. ZnO does not suffer such a pronounced change of the lattice.
parameters but reveals a strong deterioration of the surface, possibly due to blistering and exfoliation. Rocking curve widths only increase slightly but their intensity is strongly reduced after irradiation and annealing. At the same time the optical properties are less affected than those of GaN. The near band edge emission is partly quenched but recovers to a large extent after annealing while broad defect bands are observed below the bandgap for irradiated samples before and after annealing.

6. ACKNOWLEDGEMENTS

We thank O. Briot and S. Ruffenach (University of Montpellier) for the MOCVD GaN samples and H. D. Sun (Nanyang Technological University) for the MOCVD ZnO samples. Funding by FCT Portugal (Ciência 2007, PTDC/CTM/100756/2008) and the bilateral collaboration program Acções Integradas Luso-Alemãs/DAAD-FCT is gratefully acknowledged. M. Peres and S. Magalhães thank FCT for their grants, SFRH/BD/45774/2008 and SFRH/BD/44635/2008, respectively.

REFERENCES