Damage formation and annealing at low temperatures in ion implanted ZnO

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N, Ar, and Er ions were implanted into ZnO at 15 K within a large fluence range. The Rutherford backscattering technique in the channeling mode was used to study in situ the damage built-up in the Zn sublattice at 15 K. Several stages in the damage formation were observed. From the linear increase of the damage for low implantation fluences, an upper limit of the Zn displacement energy of 65 eV could be estimated for [0001] oriented ZnO. Annealing measurements below room temperature show a significant recovery of the lattice starting at temperatures between 80 and 130 K for a sample implanted with low Er fluence. Samples with higher damage levels do not reveal any damage recovery up to room temperature, pointing to the formation of stable defect complexes.

ZnO with its wide and direct band gap (3.437 eV) is a promising and widely investigated material for electronic and optoelectronic devices (see recent reviews, Refs. 1–3). Besides the unique optical and electrical properties, it was shown by irradiations with electrons,\textsuperscript{4–7} protons,\textsuperscript{8,9} and heavier ions\textsuperscript{10,11} that ZnO is significantly more radiation resistant than other semiconductors including GaN (its major rival with regard to electronic and optoelectronic applications and a compound semiconductor with similar structural properties). Ion implantation was used to dope single crystalline ZnO with electrically,\textsuperscript{12,13} magnetically,\textsuperscript{7} or optically\textsuperscript{11} active ions. Ion implantation is a powerful tool to introduce controllable ion concentrations at precise depths below the surface with the facility of selective area doping; however, it creates lattice damage, and the processes of damage built-up and its removal need to be understood. Kucheyev et al.\textsuperscript{10} studied in detail the damage built-up in ZnO during implantation of Au and Si ions at RT and 77 K. Strong dynamic annealing effects were observed and even implantation with high fluences of heavy Au ions did not render ZnO amorphous. To get more insight into the mechanisms that are responsible for the outstanding radiation hardness and dynamic annealing, we performed implantations and Rutherford backscattering spectroscopy/channeling (RBS/C) measurements at 15 K, where no thermal diffusion of atoms and defects is expected. The implanted species were chosen due to their technological relevance and also to cover a large spectrum of masses. Erbium is known to be optically active in ZnO with emissions in the infrared and green spectral region\textsuperscript{11} and nitrogen is among the most promising dopants for p-type material.\textsuperscript{1} An important parameter, controlling the production of radiation damage in materials, is the threshold displacement energy $E_d$ for the different species. From the damage production curve a value for $E_d$ (Zn) could be estimated. Annealing experiments between 15 K and RT were performed to investigate the thermal stability of the produced defects.

Commercial (Eagle-Picher) O-face (0001) ZnO single crystals were used for this work. N, Ar, and Er ions were implanted with fluences between $1 \times 10^{11}$ and $7 \times 10^{16}$ at/cm$^2$ and energies of 80, 200, and 380 keV, respectively. The implantations were performed at 15 K in a special target chamber at the Institut für Festkörperphysik in Jena, where in situ RBS/C measurements were carried out without changing the target temperature.\textsuperscript{14} The sample is mounted on a four axis goniometer and cooled by a closed cycle He refrigerator. The implantations were performed with the surface normal tilted by 7° off the ion beam direction to prevent channeling effects. The RBS/C analysis was done with 1.4 MeV He$^+$ ions and a Si surface barrier detector at 170°.

In the case of Er, two samples were implanted, one up to a fluence of $2 \times 10^{12}$ at/cm$^2$ and the second starting at a fluence of $1.5 \times 10^{12}$ at/cm$^2$ up to $2 \times 10^{14}$ at/cm$^2$. Annealing experiments between 15 K and RT were performed by heating the sample holder to a certain temperature, holding it for 10 min and then cooling it down to 15 K for the RBS/C measurement.

Figure 1 shows selected RBS/C aligned spectra for three different N-ion fluences as well as the spectrum for an unimplanted (virgin) sample and a random spectrum. As a measure for the produced damage concentration, the difference in minimum yield $\Delta \chi_{\text{min}}$ is taken. It is given by $\Delta \chi_{\text{min}}=(Y_{\text{al}}-Y_{\text{al}}^{\text{vir}})/Y_{\text{al}}$ where $Y_{\text{al}}^{\text{vir}}$ and $Y_{\text{al}}$ are the RBS yields of the aligned spectra and $Y_{\text{al}}$ is the maximum yield measured in random direction. To calculate the damage level the yields were integrated within a window comprising the whole implanted layer leaving out the surface peak, as indicated in Fig. 1. Figure 2 shows $\Delta \chi_{\text{min}}$ as a function of the ion fluence $N_I$. Four stages of damage production can be distinguished, labeled stage I–IV. Similar damage built-up processes were observed for ion implantation into GaN.\textsuperscript{15} In stage I, an almost linear increase of the lattice damage with ion fluence is observed. In stage II the damage saturates which is attributed to the overlapping of the damage cas-

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cades 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. Stage IV shows a second plateau still being considerably lower than expected for amorphization. The last stage was only reached in the case of Ar implantation. In this work we will focus on the early stages (I and II) of damage production. A more detailed description of the Ar data will be given elsewhere.

The evolution of point defects and point defect clustering as described earlier can be represented by the differential equation

$$\frac{d\Delta x_{\text{min}}}{dN_I} = Pe^{-R^2N_I^2} + C\Delta x_{\text{min}}^{1.2} \left( 1 - \frac{\Delta x_{\text{min}}}{\Delta x_{\text{min}}^C} \right). \tag{1}$$

Herein $P$ and $R$ are the cross sections for production and recombination of point defects and $C$ the one for the formation of non-recombinable point defect clusters. The saturation with point defect clusters results in a maximum $\Delta x_{\text{min}}$ with a value of $\Delta x_{\text{min}}^C$ (only reached for Ar). Equation (1) was fitted to the experimental data (lines in Fig. 2) and the resulting parameters are summarized in Table I. Note that this model does not consider temperature effects and a more accurate kinetic model would require measurements at various temperatures.

$P$ describes the very first almost linear increase of the damage curve in stage I. From this value the number of Zn displacements per ion and unit depth can be calculated by $N_{\text{displ}} = PN_0$, where $N_0 = 4.1475 \times 10^{22}$ Zn/cm$^3$ is the density of Zn atoms. $N_{\text{displ}}$ was also obtained from SRIM2003 (Ref. 18) simulations assuming values for the displacement energies $E_d$ of the two atoms. The input of $E_d$ was varied until the value of $N_{\text{displ}}$ deduced from the $\Delta x_{\text{min}}(N_I)$ curves was obtained, thus giving an estimate for $E_d$. In the case of GaN this procedure gave values in good agreement with molecular dynamic calculations.15 It should be noted that with RBS/C the signal from O is not accessible because it is superimposed to the Zn signal. Assuming a displacement energy $E_d(O) = 41.4$ eV as in Ref. 4, the SRIM simulations could reproduce the experimental value for the displaced Zn atoms for all three implanted ions when using $E_d(Zn) = 65$ eV. One must note that the derived value for $E_d(Zn)$ is not very sensitive to the choice of $E_d(O)$. If in a first approximation we assume the O sublattice being similarly damaged as the Zn sublattice the displacement energy for Zn and O follows to be $E_d(Zn) = 65$ eV and $E_d(O) = 50$ eV.

As reviewed in Ref. 19, previous work on ZnO reported displacement energies of 40–70 eV for the Zn sublattice and 47–55 eV for the oxygen sublattice, in good agreement with our results. However, our value of $E_d(Zn) = 65$ eV is only an upper bound for the actual displacement energy as in-cascade recombination of point defects occurs even at 4 K.19 Such annihilation of point defects taking place within the lifetime of the collision cascades even at low temperatures could be possibly driven by electric forces. The recombination of positively charged Zn interstitials and negatively charged Zn vacancies can thus cause a higher effective displacement energy even at such low temperatures.

Several authors have argued that the radiation hardness of ZnO is due to effective diffusion and annihilation of point defects already at low temperatures. Gorelkin et al.5 found evidence for several annealing stages between 4.2 K and RT after 2.5 MeV electron irradiation, with the first annealing stage starting at 110 K. Coscun et al.7 argue that long term damage for electron irradiation of ZnO is limited by defect annihilations even at 130 K.

Figure 3 shows the damage removal for annealing the sample after the first Er-implantation series, i.e., at the end of the first stage after implantation of $2 \times 10^{12}$ Er/cm$^2$. Like for electron irradiation, a significant recovery of the crystal occurs between 80 and 130 K. Annealing at 180 and 230 K further reduces the damage level but no full recovery is seen. The second Er sample after implantation of

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**TABLE 1.** Resulting parameters of the fits to the experimental data based on the defect interaction and amorphisation model of Hecking et al. (see Ref. 16) [Eq. (1)].

<table>
<thead>
<tr>
<th></th>
<th>$P$ (cm$^2$)</th>
<th>$R$ (cm$^2$)</th>
<th>$C$ (cm$^2$)</th>
<th>$\Delta x_{\text{min}}^C$</th>
<th>$N_{\text{displ}}$ (Å$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>$2.3 \times 10^{-16}$</td>
<td>$1.2 \times 10^{-14}$</td>
<td>$4.0 \times 10^{-14}$</td>
<td>N/A</td>
<td>0.09</td>
</tr>
<tr>
<td>Ar</td>
<td>$8.4 \times 10^{-16}$</td>
<td>$4.5 \times 10^{-14}$</td>
<td>$1.1 \times 10^{-15}$</td>
<td>0.45</td>
<td>0.35</td>
</tr>
<tr>
<td>Er</td>
<td>$3.9 \times 10^{-15}$</td>
<td>$2.8 \times 10^{-13}$</td>
<td>$1.4 \times 10^{-14}$</td>
<td>N/A</td>
<td>1.62</td>
</tr>
</tbody>
</table>

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FIG. 1. Aligned and random RBS/C spectra before and after implantation with N ions. The window used for the integration of counts to determine $\Delta x_{\text{min}}$ is indicated.

FIG. 2. $\Delta x_{\text{min}}$ as a function of the ion fluence for N, Ar, and Er implantation. The plotted curves are fits based on the defect interaction and amorphisation model of Hecking et al. (See Ref. 16) [Eq. (1)].
2 × 10^{14} \text{ Er/cm}^2 \) (beginning of stage III) did not show any recovery of lattice damage at these temperatures. This confirms the assumption that in stage III stable point defect clusters are formed. Probably they are extended defects which are known to be stable and lead to a steep increase of lattice damage. Annealing studies of samples implanted with even higher fluences \((5 \times 10^{14} \text{ Er/cm}^2 \text{ and } 5 \times 10^{15} \text{ Er/cm}^2)\) showed that implantation damage could only be fully recovered after annealing at 1050 °C.\(^{11}\)

In summary, we have performed implantation and annealing studies in ZnO at low temperature. Several stages of damage built-up were observed, comparable to the ones reported for GaN. Although showing similar damage production processes as GaN, the absolute concentration of defects is much lower in ZnO and no amorphization is observed for the studied fluence ranges. Recombination of defects is observed when collision cascades start to overlap, being one reason for the outstanding radiation hardness. For the highest studied fluences a second stage occurs where defect production saturates. An upper bound of the Zn displacement energy of 65 eV for [0001] oriented ZnO was estimated. Possibly even at 15 K recombination of point defects takes place during the lifetime of the collision cascade leading to an overestimate of the actual displacement energy. After implantation with low fluences damage annealing starts between 80 and 130 K showing that point defects are becoming mobile. Higher ion fluences lead to thermally more stable point defect clusters or extended defects.

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\(^{12}\) T. S. Jeong, M. S. Han, C. J. Youn, and Y. S. Park, J. Appl. Phys. 96, 175 (2004).