Radiation-induced alloy rearrangement in In$_{x}$Ga$_{1-x}$N

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The effect of radiation damage on the defect and alloy structure in In$_x$Ga$_{1-x}$N thin films grown on Si substrates was studied using positron annihilation spectroscopy. The samples were subjected to double He$^+$ implantation at 40 and 100 keV. The results show the presence of cation vacancy-like defects in high concentrations (> 10$^{18}$ cm$^{-3}$) already in the as-grown samples. The evolution of the annihilation characteristics after the implantation suggests strong alloy disorder rearrangement under irradiation.

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Following the breakthrough in manufacturing of efficient blue light-emitting diodes (LEDs), devices operating in the wavelength range 500 nm – 570 nm need to be optimized next. The most promising candidate for building a path across the green LED field is expected to be In$_x$Ga$_{1-x}$N. Alloying GaN with InN enables the development of a platform with combined blue and green LEDs based on a homogeneous system. However, the required indium content of at least 25 % in alloys$^1$ leads to defect formation$^2$ and subsequent deterioration of electrical properties and decrease of device efficiency. On the other hand, the adjustable direct band gap and exceptional resistance to irradiation damage enable the application of In$_x$Ga$_{1-x}$N in solar cells for outer space.$^3$–$^5$ Further integration with silicon promises even more: the band alignment at the In$_x$Ga$_{1-x}$N/Si heterointerface eliminates the need for heavy doping, and the energy conversion efficiencies were shown to reach 31% and 33% for two- and three-junction In$_x$Ga$_{1-x}$N/Si solar cells, respectively.$^6$–$^7$ Despite the lattice mismatch with Si and induced cracking and high dislocation density, several successful attempts to grow In$_x$Ga$_{1-x}$N/Si-based structures are reported.$^8$–$^{10}$

Leaving the expectations aside, surprisingly little is known about defect structure in In$_x$Ga$_{1-x}$N alloys. So far, inhomogeneous indium distribution, dislocations and surface-related defects have been reported.$^{11}$–$^{14}$ Cation vacancies have been predicted to play a crucial role in Shockley-Read-Hall recombination in wide-band-gap semiconductors.$^{15}$–$^{17}$ Experimental studies of vacancy-type defects in thin-film III-nitrides have been extensively performed by positron annihilation spectroscopy (see Ref. 16, 18 and references therein). The sensitivity of positions is not affected by conductivity of samples,$^{19}$ making them especially suitable for studying In$_x$Ga$_{1-x}$N-based structures.

In this work, we apply positron annihilation spectroscopy to study the effect of radiation damage on the defect and alloy structure in In$_x$Ga$_{1-x}$N thin films. The as-grown In$_x$Ga$_{1-x}$N films contain cation vacancies in the 10$^{18}$ cm$^{-3}$ range with characteristics reflecting the random site distribution of In and Ga atoms in the lattice. Upon He$^+$ implantation, the nature of the introduced cation vacancy defects gradually changes with increasing fluence towards that of the indium vacancy $V_{in}$ in InN, reflecting a change in the distribution of the metal atoms and indicating the generation of indium-rich regions in the lattice.

The In$_x$Ga$_{1-x}$N samples were grown by metal-organic chemical vapour deposition on 10-nm-thick In$_x$Al$_{1-x}$N buffer layers deposited on Si (111) substrates. The thicknesses of the samples with $x = 0.37$ and $x = 0.45$ are 463 nm and 446 nm, respectively. Samples 3 and 4 were superficially etched with nitric acid. The samples were doubly implanted at energies of 40 keV and 100 keV with He$^+$ fluences calculated to obtain a homogeneous damage profile over the whole layer thickness. Each pair of He$^+$ implantation fluences on the respective samples ranging from 10$^{12}$ cm$^{-2}$ to 10$^{15}$ cm$^{-2}$ are listed in Table I. The implantation-induced damage was estimated with Stopping and Range of Ions in Matter (SRIM) code.$^{20}$ He$^+$ implantation with similar fluence and damage level has been shown to produce single cation vacancy type defects in InN.$^{21}$

Positron annihilation spectroscopy is an efficient method for identification of negatively charged and neutral vacancy-type defects.$^{19}$ The momentum of the positron-electron pair is conserved in the annihilation event. The momentum distribution corresponds to the measured Doppler broadening of the annihilation photons. The shape of the Doppler broadened annihilation line (often characterized by $S$ and $W$ parameters) gives detailed information about the identity and concentration of the vacancy-type defects present. The $S$ ($W$) parameter reflects the annihilations with valence (core) electrons and is defined as a fraction of counts in the central region (wing areas) of the Doppler peak.
TABLE 1. Growth parameters and properties of In$_x$Ga$_{1-x}$N thin film samples. Samples 3 and 4 are as-grown samples chemically etched with HNO$_3$. Displacement damage dose parameter $D_d$ is defined as the product of the non-ionizing energy loss and the particle fluence. For the implanted samples, the implantation-induced damage was estimated with SRIM code. The vacancy concentration in the non-implanted samples was estimated from positron annihilation experiments.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$d$, nm</th>
<th>$x$</th>
<th>$\text{He}^+$ fluence at 40 keV, cm$^{-2}$</th>
<th>$\text{He}^+$ fluence at 100 keV, cm$^{-2}$</th>
<th>$D_d$, MeV/g</th>
<th>Vacancy concentration, cm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/2</td>
<td>463 / 446</td>
<td>0.37 / 0.45</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>&gt; 10$^{18}$</td>
</tr>
<tr>
<td>3/4</td>
<td>463 / 446</td>
<td>0.37 / 0.45</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>&gt; 10$^{18}$</td>
</tr>
<tr>
<td>A/B</td>
<td>463 / 446</td>
<td>0.37 / 0.45</td>
<td>1.4 x 10$^{12}$</td>
<td>3.7 x 10$^{12}$</td>
<td>8.0 x 10$^{14}$</td>
<td>9 x 10$^{18}$</td>
</tr>
<tr>
<td>C/D</td>
<td>463 / 446</td>
<td>0.37 / 0.45</td>
<td>8.9 x 10$^{12}$</td>
<td>2.3 x 10$^{13}$</td>
<td>5.0 x 10$^{16}$</td>
<td>6 x 10$^{19}$</td>
</tr>
<tr>
<td>E/F</td>
<td>463 / 446</td>
<td>0.37 / 0.45</td>
<td>5.7 x 10$^{13}$</td>
<td>1.5 x 10$^{14}$</td>
<td>3.2 x 10$^{15}$</td>
<td>3 x 10$^{20}$</td>
</tr>
<tr>
<td>G/H</td>
<td>463 / 446</td>
<td>0.37 / 0.45</td>
<td>3.6 x 10$^{14}$</td>
<td>9.3 x 10$^{14}$</td>
<td>2.0 x 10$^{16}$</td>
<td>2 x 10$^{21}$</td>
</tr>
</tbody>
</table>

The shaded region between the layers-related data changes, and the measured values reflects the scattering in the Si substrate for sample A in terms of the $(S, W)$ plane. At implantation energies above 10 keV (bottom right corner of the highlighted area) the slope of the layer-related data changes, and the measured values reflect the scattering in the Si substrate. The $S$ parameter in all the samples is higher than the characteristic values for GaN and InN lattices. The $(S, W)$ points for GaN and InN bulk are shown for comparison. The dash-dotted line connecting the GaN and InN extremes represents the $(S, W)$ parameters for defect-free In$_x$Ga$_{1-x}$N as a function of indium content as shown in Ref. 29. The region in the $(S, W)$ plane corresponding to defect-free alloys with 37% < x < 50% indium is highlighted. Further, three more anchor points, gallium vacancy $V_{Ga}$ in GaN, and indium vacancy $V_{In}$ in indium vacancy decorated with several nitrogen vacancies $V_{In}+nV_{N}$, $n \geq 2$, both in InN, are obtained by combining experiments and theoretical calculations. The shaded region between $V_{Ga}$ and $V_{In}$ reflects the scatter of the Doppler parameters in In$_x$Ga$_{1-x}$N systems containing a metal vacancy. The $(S, W)$ parameters for the InN bulk, $V_{In}$ and $V_{In}+nV_{N}$ have been as well normalized to the GaN reference sample. The inset shows the $S$ and $W$ parameters calculated in In$_x$Ga$_{1-x}$N systems containing one metal vacancy with different In contents and varying In/Ga distributions. Please note that the calculation results are provided for illustration and cannot be directly compared to the measurement results. Isolated nitrogen vacancies do not trap positrons due to decreased electron density on a vacancy site typically reflected as an increase of positron lifetime and the narrowing of the 511 keV photo-peak in the annihilation gamma spectrum, compared to a defect-free crystal. The Doppler broadening spectra were measured using a monoenergetic positron beam at room temperature. The measurements were performed with a high purity germanium detector, with an energy resolution of 1.3 keV at 511 keV. Each set of measurements consists of series of spectra with approximately $1 \times 10^6$ counts recorded, as a function of positron implantation energy in the range 0.5 – 35 keV.

The electronic structure calculations for bulk systems were performed using a 16-atom In$_x$Ga$_{1-x}$N wurtzite supercell. For systems containing a vacancy the supercell size was increased to 128 atoms. The structures were modelled using the local-density approximation (LDA) for exchange and correlation as implemented in the VASP code. Positron states are modelled assuming that the positron does not affect the average electron density and taking the zero-positron limit of the LDA correlation energy and enhancement factor. For localised positrons we take into account the repulsive forces on ions due to the localized positron. Momentum densities of annihilating electron-positron pairs are calculated using the projector augmented-wave (PAW) method.

The results of conventional Doppler measurements for selected samples are presented in Figure 1. The expected values for defect-free In$_x$Ga$_{1-x}$N with 37% and 45% In are found between the characteristic $(S, W)$ parameters for InN and GaN lattices. The reference $(S, W)$ parameters (for GaN $S_{ref} = 0.44(6)$ and $W_{ref} = 0.054(4)$) are obtained from samples where positrons annihilate in the delocalized state in the lattice. The significantly higher values of the $S$ parameter in the samples at low energies result from annihilations at the surface states. When the implantation energy $E$ reaches approximately 4 keV (corresponding mean implantation depth $\sim 60$ nm), the dominant fraction of positrons annihilates inside the In$_x$Ga$_{1-x}$N film. At 15 keV and higher energies the positrons reach the substrate, thus the high values of $S$ parameter are attributed to the annihilations in Si lattice. The inset in Figure 1 demonstrates positrons annihilating from the surface states, in the In$_{0.37}$Ga$_{0.63}$N layer and in the Si substrate for sample A in terms of the $(S, W)$ plane. At implantation energies above 10 keV (bottom right corner of the highlighted area) the slope of the layer-related data changes, and the measured values reflect the scattering in the Si substrate. The $S$ parameter in all the samples is higher than the characteristic values for GaN and InN lattices. The $(S, W)$ points for GaN and InN bulk are shown for comparison. The dash-dotted line connecting the GaN and InN extremes represents the $(S, W)$ parameters for defect-free In$_x$Ga$_{1-x}$N as a function of indium content as shown in Ref. 29. The region in the $(S, W)$ plane corresponding to defect-free alloys with 37% < x < 50% indium is highlighted. Further, three more anchor points, gallium vacancy $V_{Ga}$ in GaN, and indium vacancy $V_{In}$ in indium vacancy decorated with several nitrogen vacancies $V_{In}+nV_{N}$, $n \geq 2$, both in InN, are obtained by combining experiments and theoretical calculations. The shaded region between $V_{Ga}$ and $V_{In}$ reflects the scatter of the Doppler parameters in In$_x$Ga$_{1-x}$N systems containing a metal vacancy. The $(S, W)$ parameters for the InN bulk, $V_{In}$ and $V_{In}+nV_{N}$ have been as well normalized to the GaN reference sample. The inset shows the $S$ and $W$ parameters calculated in In$_x$Ga$_{1-x}$N systems containing one metal vacancy with different In contents and varying In/Ga distributions. Please note that the calculation results are provided for illustration and cannot be directly compared to the measurement results. Isolated nitrogen vacancies do not trap positrons due to
FIG. 1. The S parameter as a function of positron implantation energy and mean implantation depth in as-grown, the lowest and the highest fluence implanted samples. The highlighted region between the InN and the GaN lattice S values depicts the S parameter for defect-free In$_x$Ga$_{1-x}$N with 0.37 < x < 0.5 (Ref. 29). The skipped data in the range from 23 to 33 keV are consistent with the presented values at high implantation energies. Inset: the (S, W) plot for sample A. The surface, layer and substrate regions are marked. The data at the far extent of the In$_x$Ga$_{1-x}$N layer are not yet affected by the Si substrate.

their small size and positive charge state, but strongly modify the cation vacancy signal when cation vacancy – nitrogen vacancy complexes are formed.16,30

In the as-grown samples 1 – 4, the layer (S, W) values lie rather close to one of the extremes of the cation vacancy in In$_x$Ga$_{1-x}$N systems (the shaded region in Figure 2). In addition, the very short diffusion length seen in Figure 1 implies saturation trapping at group III cation vacancies or vacancy-related complexes, indicating a cation vacancy concentration of the order of 10$^{18}$ cm$^{-3}$ or higher. The right shift of data points for samples 1 – 4 obtained at higher implantation energies in (S, W) plane displayed in Figure 2 (larger symbols) can be attributed to cation vacancies complexed with nitrogen vacancies. Similar rightward shift was observed in MBE-grown In$_x$Ga$_{1-x}$N for V$_{III}$–nV$_{N}$ and in InN for V$_{In}$–nV$_{N}$ complexes.16,17 In fact, these In$_x$Ga$_{1-x}$N/Si interface values are very close to those of V$_{In}$–nV$_{N}$ calculated for InN indicating an increase in the number of V$_{N}$ associated with a cation vacancy as shown in Ref. 16 and suggesting a higher indium content in the near-interface region. It is unlikely that this observation would reflect preferential formation of cation vacancy defects in the regions of higher indium content in random alloys: the cation vacancy formation energy is higher in InN than in GaN.31–33

FIG. 2. The (S, W) values at 4/5 keV (smaller markers) and 9/10 keV (larger markers) normalized to the GaN reference. The dash-dotted line represents the (S, W) scattering for defect-free In$_x$Ga$_{1-x}$N. The highlighted region on the GaN – InN line corresponds to defect-free alloys with 37% – 50% indium. The shaded region of the Va - V$_{In}$ line shows scattering span of the (S, W) parameters in cation vacancy containing In$_x$Ga$_{1-x}$N corresponding to the values presented in the inset. Inset: calculated S and W parameters for In$_x$Ga$_{1-x}$N systems containing a metal vacancy with varying In/Ga distribution as a function of indium content.

Considering the In$_x$Ga$_{1-x}$N layers, after the lowest implantation dose the data resemble that of the as-grown samples, in line with the estimated concentrations of pre-existing vacancy defects and the SRIM estimate of implantation-induced damage. As the He$^+$ implantation fluence increases, the nature of the vacancy type defects in In$_x$Ga$_{1-x}$N layers clearly changes. For the highest He$^+$ fluence the data points in the layers essentially converge towards the V$_{In}$ characteristic value. Hence, either the vacancy defects are mostly created in In-rich regions, or formation of In-rich regions is enhanced by high-fluence implantation leading to increasing positron trapping at vacancies in those regions. Interestingly, despite the increasing implantation dose there is no observable change near the In$_x$Ga$_{1-x}$N/Si interface where the cation vacancies already exhibit V$_{In}$–nV$_{N}$-like character. It should be noted that in III-nitride alloys the cation shell has the most impact on the positron data, while the lattice parameters play a minor role. In addition, In vacancy formation in InN under irradiation has been shown to be much less efficient than the formation of Ga vacancies in GaN (Ref. 34) and irradiation damage has been shown to be more important in Ga-rich than in In-rich In$_x$Ga$_{1-x}$N (Ref. 3). Thus, as there is no reason for enhanced positron annihilation in the regions with higher indium composition naturally occurring in a random distribution, we interpret that either the indium content of the In-rich regions increases or the distribution of In-rich regions densifies in the implantation by a mechanism...
Acknowledgments

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References

