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Compensating point defects in $^4\text{He}^+$ -irradiated InN

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We use positron annihilation spectroscopy to study 2 MeV $^4\text{He}^+$ -irradiated InN grown by molecular-beam epitaxy and GaN grown by metal-organic chemical-vapor deposition. In GaN, the Ga vacancies act as important compensating centers in the irradiated material, introduced at a rate of 3600 cm^{-1} . The In vacancies are introduced at a significantly lower rate of 100 cm^{-1} , making them negligible in the compensation of the irradiation-induced additional n -type conductivity in InN. On the other hand, negative non-open volume defects are introduced at a rate higher than 2000 cm^{-1} . These defects are tentatively attributed to interstitial nitrogen and may ultimately limit the free-electron concentration at high irradiation fluences.

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Indium nitride has a rather narrow band gap of $\sim 0.7\text{ eV}$.^{1–5} This makes InN a suitable material for infrared applications such as light-emitting diodes and lasers that are used in optical communications industry. Additionally, its radiation hardness makes it a desirable material for multijunction solar cells.⁶ The material has been lately under intense research in order to determine the basic electronic and optical properties. Only few experimental results are available on irradiation-induced defects in InN. It has been shown that irradiation produces donorlike defects resulting in an increase of the free-electron concentration and a decrease of the electron mobility.⁷ The electron concentration saturates at high irradiation fluence due to the pinning of the Fermi level high in the conduction band.^{8,9} Also, the high tolerance against particle radiation of InN compared to other photovoltaic materials such as GaAs, GaInP, and GaN has been observed.⁶

Our goal is to study the compensating point defects introduced in InN irradiated with 2 MeV He^+ ions. In earlier studies,⁹ the electron concentration in initially n -type InN ($n_e = 1 \times 10^{18}\text{ cm}^{-3}$) has been observed to increase linearly with the irradiation fluence and to saturate to the value of $n_e = 4 \times 10^{20}\text{ cm}^{-3}$ at the fluence of $2 \times 10^{15}\text{ cm}^{-2}$. This behavior has been explained by the production of donorlike point defects that are preferable when the Fermi stabilization energy (E_{FS}) is above the Fermi level (E_F), which is the case in as-grown InN. Further, when the Fermi level reaches the E_{FS} , compensating acceptorlike defects are supposedly formed at the same rate as donorlike defects, resulting in the saturation of the electron concentration.⁹ The electron (donor) production rate in InN has been observed to be $\sim 4 \times 10^4\text{ cm}^{-1}$.⁷

We present results obtained in InN grown by molecular beam epitaxy (MBE). The samples were irradiated with 2 MeV $^4\text{He}^+$ particles to fluences ranging from $\phi = 5 \times 10^{13}\text{ cm}^{-2}$ to $\phi = 2 \times 10^{16}\text{ cm}^{-2}$. The InN samples were $0.6\text{--}2.7\text{ }\mu\text{m}$ thick. Hence, as the penetration depth of

the 2 MeV $^4\text{He}^+$ particles is about $7\text{ }\mu\text{m}$, the produced damage is relatively uniform throughout the layers. The residual electron concentration in as-grown InN was $1 \times 10^{18}\text{ cm}^{-3}$ and the electron mobility was $1560\text{ cm}^2/\text{V s}$ based on Hall effect measurements. The electron concentration increased with the irradiation fluence up to $\sim 4 \times 10^{20}\text{ cm}^{-3}$, while the mobility decreased all the way to $\sim 60\text{ cm}^2/\text{V s}$. For comparison, we studied also similarly irradiated GaN samples grown by metal-organic chemical-vapor deposition, which turn from slightly n -type to semi-insulating in the irradiation.

We used a variable-energy positron beam with high-purity Ge detectors to measure the Doppler broadening of the positron-electron annihilation radiation. Positrons are sensitive to negative and neutral vacancy defects, and they can also get trapped at negatively charged nonopen volume defects such as negative impurities.¹⁰ At a vacancy, the electron density is lower and electron momentum distribution narrower compared to the defect-free lattice. We use the conventional low-momentum (S) and high-momentum (W) parameters to analyze the data.

Figure 1 shows the S parameters measured at room temperature as a function of positron implantation energy in selected InN and GaN samples. The higher parameter values at low energy result from the positron annihilations at the surface of the samples. The plateau starting from energy of $\sim 4\text{ keV}$ is due to the positron annihilations in the InN and GaN layers. The effect of irradiation can be seen as a shift upwards in these parts of the curves. At higher energies, depending on the thickness of the sample, the S parameter decreases as positrons reach the substrate material (Al_2O_3).

The S (and W , not shown) parameters in the as-grown GaN sample coincide with those measured in high-quality GaN samples grown by hydride vapor phase epitaxy, where positrons are known to annihilate only in the free state.¹¹ The InN sample irradiated to the fluence of $5 \times 10^{13}\text{ cm}^{-2}$ exhibited a slightly lower S parameter than the previously used InN reference.^{12,13} We interpret this to originate from the

FIG. 1. S parameters as a function of positron implantation energy measured in selected InN and GaN samples.

greater thickness of the current sample ($2.7 \mu\text{m}$) since in the same work the quality of the MBE-grown InN is known to improve with increasing layer thickness. In addition, as shown below, the vacancy concentration produced in InN with this fluence should be below the detection limit of the positron method at room temperature. This sample is thus taken as a reference for the InN lattice in this work.

As can be seen in Fig. 1, the S parameter increases clearly less in InN than in GaN with the same irradiation fluence. In order to determine the possible effect of negative ions on the room temperature data, we measured four irradiated InN samples at temperatures ranging from 20 to 300 K (Fig. 2). The S parameter measured in the layer decreases with decreasing temperature, indicating that negative ions compete with vacancies in trapping positrons at low temperatures, as the negative ions produce the annihilation parameters of the defect-free lattice. At temperatures near 300 K, the S parameter changes only slightly, indicating that most of the posi-

FIG. 2. S parameters measured in the InN samples (fluences from 5.6×10^{14} to $1.8 \times 10^{16} \text{ cm}^{-2}$) as a function of temperature. The behavior is typical of negative-ion-type defects competing with vacancies in positron trapping.

FIG. 3. Relative W parameter as a function of the relative S parameter in He^+ -irradiated layers. The points fall on a straight line.

trons annihilate as trapped at vacancy defects. The plateau at low temperatures further indicates that the temperature dependences of the trapping rates of vacancies and negative ions are the same ($T^{-1/2}$, see Ref. 14), and thus the vacancy defects are negatively charged.

We identify the vacancy defects by plotting the S and W parameters measured in the layers in the (S, W) plot. When the vacancy concentration is below the detection limit, we obtain values S_b and W_b , representing bulk. Similarly, in a sample where all the positrons annihilate as trapped at vacancies (saturation trapping), we get S_d and W_d , characterizing the vacancy. All the samples containing the same type of vacancies at different concentrations fall on the line connecting (S_b, W_b) and (S_d, W_d) . The slope of the line gives the identity of the vacancy, and the position of a point of the line gives the vacancy concentration.

We use the In vacancy specific parameters determined in previous studies in InN, namely, $S_v = 1.049 \times S_b$ and $W_v = 0.79 \times W_b$.¹² These parameters are shown together with the measured parameters from the irradiated InN samples in Fig. 3. As all the points fall on the same straight line connecting the InN bulk and In vacancy-specific parameters, we identify the observed vacancy defect as the In vacancy. Interestingly, the In vacancy concentration seems to saturate at the fluence of $2 \times 10^{15} \text{ cm}^{-2}$.

In the GaN samples, the S (and W) parameters increase (decrease) with the irradiation fluence until they reach the values $S/S_b = 1.058(6)$ and $W/W_b = 0.76(3)$ at the fluence of $2 \times 10^{15} \text{ cm}^{-2}$. Above this fluence, no change in the S and W parameters was observed. The saturated parameters coincide with the values determined previously for the Ga vacancy,¹⁵ taking into account the present detector resolution of 1.24 keV at 511 keV. The points measured in the GaN samples irradiated to lower fluences fall on the line connecting the GaN bulk to the Ga vacancy parameters, indicating that Ga vacancies are produced in the irradiation, as expected from earlier studies on irradiated GaN.^{16,17}

The vacancy concentrations in the samples can be estimated from the layer-specific S parameters using the stan-

FIG. 4. Estimated In and Ga vacancy concentrations at different irradiation fluences. The vacancy production rates are 100 and 3600 cm^{-1} , respectively (fitted lines). The encircled point gives the lower limit for the Ga vacancy concentration in the GaN samples with the highest irradiation fluences.

dard positron trapping model with a positron trapping coefficient of $2 \times 10^{15} \text{ cm}^3 \text{ s}^{-1}$.¹⁰ Figure 4 shows the estimated vacancy concentrations as a function of irradiation fluence. $[V_{\text{In}}]$ saturates to $4 \times 10^{17} \text{ cm}^{-3}$ at the fluence of $2 \times 10^{15} \text{ cm}^{-2}$. This result clearly indicates that the saturation of the free-electron concentration⁹ cannot be due to the In vacancy production. The Ga vacancy concentration in GaN increases linearly as a function of irradiation fluence. All the positrons annihilate as trapped at Ga vacancies in the three most heavily irradiated samples, and hence only a lower limit of $\sim 1 \times 10^{19} \text{ cm}^{-3}$ can be given for those samples.

The introduction rates (defined as $\Sigma_V = [V]/\phi$) of the In and Ga vacancies can be estimated from the data in Fig. 4. The introduction rate of the In vacancies is $\Sigma_{V,\text{In}} = 100 \text{ cm}^{-1}$, and that of the Ga vacancies is $\Sigma_{V,\text{Ga}} = 3600 \text{ cm}^{-1}$. The introduction rate of the Ga vacancies in GaN is of the expected order of magnitude if compared to 2 MeV electron irradiation, in which the introduction rate is about 1 cm^{-1} , as the 2 MeV He^+ ions are about 2000 times heavier than the 2 MeV electrons. Hence, the Ga vacancies act as important compensating centers causing the material to become semi-insulating in the irradiation. On the other hand, the introduction rate of the In vacancies, which is over one order of magnitude lower than that of the Ga vacancies, suggests that the observed In vacancies are not primary defects produced in the irradiation. In addition, their final concentration and low introduction rate clearly indicate that the saturation of the free-electron concentration at $4 \times 10^{20} \text{ cm}^{-3}$ (the donor introduction rate is $4 \times 10^4 \text{ cm}^{-1}$)⁹ is not due to In vacancy production.

To find out if the negative ions could be the compensating defects giving rise to the saturation of free-electron concentration in InN, we estimate the negative-ion concentrations in the samples irradiated to the fluences of $6 \times 10^{14} - 2 \times 10^{16} \text{ cm}^{-2}$. The concentrations can be estimated using the temperature-dependent trapping model.¹⁰ The

trapping rate to the In vacancies at room temperature can be estimated from the measured S parameters from $\kappa_V(T=300 \text{ K}) = \lambda_b(S - S_b)/(S_d - S)$ when we know the lattice- and vacancy-specific parameters S_b and S_d . The trapping rate to the negative ions can be estimated in the same way as in Ref. 18 using $\kappa_V(T=50 \text{ K})$ obtained from the $T^{-1/2}$ temperature dependence of the trapping coefficient for negative defects. Based on this, we estimate the negative ion concentrations in all the four measured samples to be in the range of $(0.8 - 3) \times 10^{18} \text{ cm}^{-3}$ (Fig. 4), using the same positron trapping coefficient for negative ions as for negatively charged vacancies. As the concentration is not increasing significantly with the irradiation fluence, it seems that the negative ions could not explain the compensating effect obtained in InN irradiated to very high fluences.

From the sample with the two lowest He^+ fluences where the negative-ion concentration was measured, we can estimate that the introduction rate is about $\Sigma_{\text{ion}} = 2000 \text{ cm}^{-1}$, which is still an order of magnitude too low to explain the saturation of the electron concentration. However, the decrease in the apparent negative-ion concentration in the samples with the highest fluences suggests an explanation for this difference. As the donor concentration is high (above 10^{19} cm^{-3}) already after the irradiation fluence of $5 \times 10^{14} \text{ cm}^{-2}$, it is likely that the negative charge of the negative ions is screened due to the very high free-electron concentration. This screening becomes naturally even more efficient at higher fluences, finally causing the apparent negative-ion concentration to decrease with increasing fluence. Hence, the negative-ion concentrations may be severely underestimated. On the other hand, this screening of the negative charge would not have any significant effect on the estimation of the vacancy concentration, as the difference in the positron trapping coefficients between negative and neutral vacancies is only about a factor of 2 at room temperature. Based on the Hall mobility, the actual concentration of negatively charged defects is indeed likely to be higher than the apparent concentration of negative ions at high fluences. In a previous study,¹² the Hall mobility of $200 \text{ cm}^2/\text{V s}$ was correlated with a negative defect (In vacancy) concentration of about 10^{19} cm^{-3} . In the present work the mobility is $60 \text{ cm}^2/\text{V s}$ at its lowest, suggesting that the concentration of (negative) scattering centers could be an order of magnitude higher.

The amphoteric defect model, where the nature of vacancy-type defects is controlled by the position of the Fermi energy E_F relative to the Fermi level stabilization energy E_{FS} ,¹⁹ has been used to explain the excess production of donor defects in the irradiation of InN.⁹ Our results are in good agreement with this model: the introduction rates of the acceptor-type defects in InN, where $E_F < E_{\text{FS}}$, are at least an order of magnitude lower than that of the donor-type defects. On the other hand, in n -type GaN, where $E_F > E_{\text{FS}}$, the introduction rate of the negatively charged Ga vacancies is high enough to compensate the residual donors already at low irradiation fluence, again in good agreement with the amphoteric defect model. The very low introduction rate of the In vacancies suggests that the negatively charged In vacancies in the irradiated material are stabilized by forming complexes with the residual donors, while the isolated V_{In}

could undergo a similar acceptor-to-donor transition as the $V_{\text{Ga}} \rightleftharpoons (V_{\text{As}} + \text{As}_{\text{Ga}})$ transition in GaAs.¹⁹ The saturation of the In vacancy concentration is possibly related to the enhancement of the Frenkel pair recombination due to the decrease of the average distance between the irradiation-induced In interstitials and In vacancies at the highest irradiation fluences. Finally, as the cation antisite and interstitial defects tend to be of donor type for all Fermi energy positions in the III nitrides, it is likely that the negative-ion-type defects observed in our positron experiments originate from the damage in the N sublattice. As the N vacancies are likely to be donor defects, we suggest that the dominant compensating defect introduced in the irradiation is related to interstitial N.

In summary, we have studied the compensating point defects introduced in the 2 MeV He⁺ irradiation of InN and GaN. In GaN, the Ga vacancies act as important compensating centers in the irradiated material, introduced at a rate of 3600 cm⁻¹. Negative In vacancies are introduced at a significantly lower rate of 100 cm⁻¹, making them negligible in the compensation of the irradiation-induced additional *n*-type conductivity. On the other hand, negative non-open volume defects are introduced at a rate higher than 2000 cm⁻¹. We propose that these defects are related to N interstitials and may ultimately limit the free-electron concentration at the highest irradiation fluences. Our results are in good agreement with the amphoteric defect model.

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