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Defect redistribution in postirradiation rapid-thermal-annealed InN

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We have applied positron annihilation to study point defects in 2 MeV $^4He^+$-irradiated and subsequently rapid-thermal-annealed (RTA) InN grown by molecular-beam epitaxy. The irradiation fluences ranged from 5×10^{14} to 2×10^{16} cm^{-2}. The irradiation primarily produces donor defects but the subjects of this work are the acceptor-type defects produced in lower concentrations: V_{In}, in addition to negative-ion-type defects. The heat treatment results in a redistribution of the irradiation-induced point defects. The In vacancies near the film-substrate interface appear restructured after the RTA process, possibly influenced by growth defects near the interface, while deeper in the InN layer, the defects produced in the irradiation are partially removed in the annealing. This could be responsible for the improved transport properties of the annealed films.

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Indium nitride, with a direct band gap of 0.7 eV,[1–3] is a promising material for long-wavelength optoelectronic devices, high-speed electronics, and multijunction solar cells.[4–6] The material has therefore lately attracted increasing attention. Potential device applications, however, have been hindered by the propensity of the material for *n*-type conductivity and by difficulties in the characterization of *p*-type samples.[7,8] The dominant donors causing the high residual electron concentrations in unintentionally doped InN remain debated. Of the native donor defects, nitrogen vacancies (V_N) have the lowest calculated formation energy[9,10] but their equilibrium concentration is still too low to account for the background carrier concentrations typically observed in high-quality InN ($\sim10^{17}-10^{18}$ cm^{-3}). The common unintentional impurities O, Si, and H, on the other hand, behave as shallow donors with low formation energies in InN,[9,11] and have been found to coexist with high electron concentrations.[12–14] Compensating In vacancies have also been identified by positron annihilation in InN grown by both molecular-beam epitaxy (MBE) and metal-organic chemical vapor deposition (MOCVD).[15,16]

High-energy particle irradiation has been demonstrated as an effective way to control the conductivity of undoped InN by creating donor defects.[17] The electron concentration has been reported to grow linearly with increasing 2 MeV He irradiation fluence up to a saturation level in the mid-10^{20} cm^{-3}. The electron mobility drops in the irradiation but can be nearly fully restored by subsequent rapid thermal annealing (RTA).[18] In this work, we have used positron Doppler-broadening and lifetime spectroscopy (see, e.g., Ref. 19 for an introduction to the techniques) to study acceptor-type defects in 2 MeV $^4He^+$-irradiated and subsequently rapid-thermal-annealed InN films. The samples were grown by MBE on *c*-sapphire (Al_2O_3) using AlN and/or GaN buffer layers. The irradiation fluences ranged from $\phi=5.6\times10^{14}$ to $\phi=1.8\times10^{16}$ cm^{-2}. The samples were 0.6–2.7 μm thick so the radiation damage was roughly uniform throughout the layers.[17] The sample annealing at temperatures ranging from 425 to 475 °C is described in more detail in Ref. 18. Based on Hall-effect measurements, the residual electron concentration and electron mobility in as-grown InN were 1×10^{18} cm^{-3} and ~1500 cm^2 V^{-1} s^{-1}, respectively. The electron concentration increased with irradiation fluence up to $\sim4\times10^{20}$ cm^{-3} while the mobility decreased all the way to ~60 cm^2 V^{-1} s^{-1}. The RTA treatment restores the mobility nearly fully with only minor decrease in carrier concentration.[18] For comparison, we also studied similarly irradiated and annealed GaN films (2.7 μm thick) grown by MOCVD on sapphire.

It has been shown in a previous work that He irradiation introduces compensating In vacancies at a rate of 100 cm^{-1}, which is much lower than the electron introduction rate.[20] Also, the concentration of V_{In} saturates in the mid-10^{17} cm^{-3} range for irradiation fluences above $\phi=2\times10^{15}$ cm^{-2}. However, negative-ion-type defects were also observed that were produced at a much higher rate of 2000 cm^{-1}, possibly acting as compensation centers ultimately limiting the *n*-type conductivity of the irradiated films. In similarly irradiated GaN, V_{Ga} were produced at a higher rate of 3600 cm^{-1}, without observable saturation.

We used variable-energy slow-positron beams to investigate the defect properties of the irradiated and annealed InN and GaN films. Positrons implanted in a solid can get trapped and localized at open-volume defects, especially vacancy-type defects, due to the missing ion core repulsion. This results in observable changes in the characteristics of the gamma photons emitted in the eventual electron-positron annihilation. Measurable quantities include the positron lifetime in the sample and the momentum of the electron-positron pair, which is preserved in the annihilation and reflected in the Doppler broadening of the annihilation photons. The lifetime is very sensitive to the open volume of the trapping vacancy up to a few missing atoms whereas the momentum distribution reflects the chemical environment of the trapping defect. The annihilation data can thus be used to determine vacancy concentrations as well as to distinguish between different types of vacancies. In addition to vacancy defects, negatively charged nonopen-volume defects, also termed negative-ion-type defects, can act as shallow traps for

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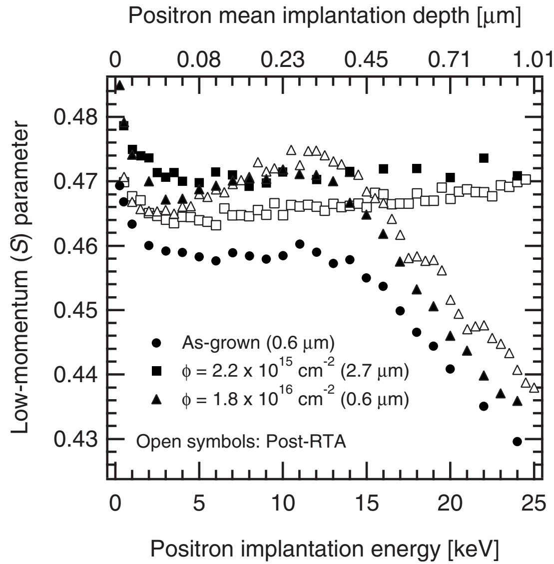

FIG. 1. Low-momentum S parameter (at room temperature) as a function of positron implantation energy in selected irradiated InN samples before and after RTA. The thermal annealing is seen to result in an inhomogeneous defect profile in the InN layers.

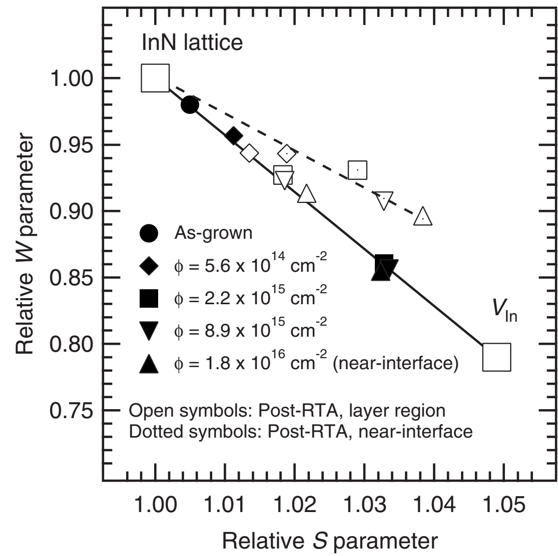

FIG. 2. (S, W) plot [normalized to the InN bulk value (S_B, W_B)] in the InN films. The heat treatment introduces a new In vacancy defect near the interface. This is seen as the deviation of the points from the line connecting the bulk and V_{In}. In the layer region, the In vacancy concentration decreases in the RTA, as the points are closer to the bulk value than in the as-irradiated samples (with the exception of the point for the lowest irradiation fluence).

positrons and can also be detected in some cases. We used high-purity Ge detectors to determine the Doppler broadening of the 511 keV annihilation line. The conventional line-shape parameters S and W were used, reflecting the low- and high-momentum states of the electron-positron pair, respectively.[19]

Figure 1 shows the S parameter at room temperature as a function of positron implantation energy/depth in selected irradiated InN samples before and after the RTA treatment. The high values of the S parameter at low energies result from annihilations at the surface of the film. At implantation energies above roughly 4 keV, the positrons are annihilated in the InN layer. At higher energies, depending on the thickness of the film, the positrons begin to reach the substrate, causing the S parameter to approach the low characteristic value of the substrate. The increase in the S parameter value in the InN layer after irradiation is due to the presence of V_{In}.[20] The heat treatment can be seen to introduce a depth profile in the defect distribution—in the annealed samples, the S parameter increases heavily toward the film-substrate interface. There also appears to be a correlation between the strength of the effect and the irradiation fluence. In fact, a similar profile is weakly visible in the sample irradiated at the highest fluence already before the RTA process.

To identify the defects in the annealed samples, we plotted the (S, W) points (Fig. 2), averaged over two different implantation energy ranges—one corresponding to the region of the InN films far from the film-substrate interface where the S parameter is smallest, termed "layer region" henceforth, and another to the region close to the interface, where S reaches maximum. For comparison, the data from the as-irradiated samples are also shown in Fig. 2. The (S, W) points are weighted superpositions of characteristic values of different annihilation states in the material. Consequently, in the presence of only a single type of positron-trapping defect, they fall on a straight line connecting the points corresponding to the defect in question and the delocalized, or bulk, state in the perfect (defect-free) lattice. The position on the line depends on the defect concentration. We see that in the layer regions of the films, the points fall on the same line as before the heat treatment, indicating that V_{In} are still present. Their concentration, however, is lower in the annealed films, as the points are closer to the bulk value. Near the interface, however, we find that a different vacancy is present since the points fall on a different line. Positron lifetime experiments showed a strong second lifetime component of roughly 260 ps, equal to the lifetime in V_{In}, throughout the depth of the InN layer, with increasing intensity toward the growth interface.[21] This indicates that the open volume of the near-interface defects is similar to the In monovacancy.

We also performed Doppler-broadening measurements as a function of sample temperature to examine the negative-ion-type defects observed in the irradiated films. Figure 3 shows the S parameter in one of the InN films measured at temperatures between 30 and 300 K. The general behavior is similar to that before the RTA treatment, indicating that negative ions are still present. Such defects compete with vacancies in trapping positrons only at low temperatures since their positron binding energy is generally much smaller than that of negative or neutral vacancies. This causes the line-shape parameters to converge with decreasing temperature toward their bulk values.

The defect concentrations can be estimated from the data using the temperature-dependent positron trapping model. We used a typical room-temperature trapping coefficient of $3\times10^{15}\ \mathrm{s}^{-1}$ for both V_{In} and the shallow traps. The fits to the data are included in Fig. 3. In the near-interface region, it

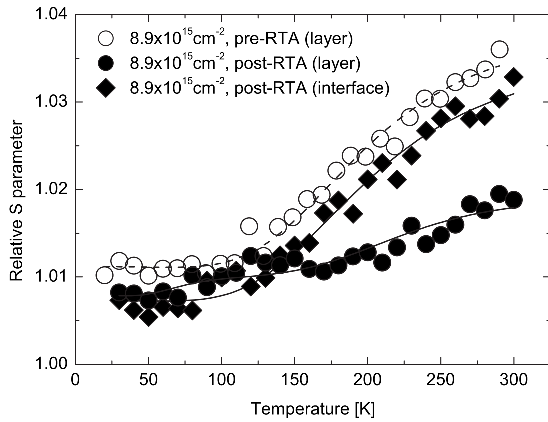

FIG. 3. Doppler-broadening S parameter at different temperatures from one of the InN samples ($\phi=8.9\times10^{15}$ cm^{-2}). The fits are based on the temperature-dependent trapping model.

was assumed that the unidentified vacancies have the same characteristic S parameter as V_{In}. This approximation is sufficient to show that the negative-ion defects are also present near the interface. More detailed information on the applied model and fitting procedure will be published elsewhere.[22] Figure 4 illustrates the estimated V_{In} and shallow-trap concentrations in the layer region at different irradiation fluences. The RTA is seen to result in a partial recovery of both defect types. The V_{In} concentrations were also estimated from the room-temperature data using the conventional trapping model, and were found to be consistent with the temperature-dependent data.

The behavior of the GaN films after the RTA was different. At lower irradiation fluences of $5.6\times10^{14}-2.2\times10^{15}$ cm^{-2} the Doppler-broadening data (not shown) indicated a partial recovery of the irradiation-induced V_{Ga} in the heat treatment, as expected from earlier studies on electron-irradiated GaN.[23] Especially, no depth profile was observed

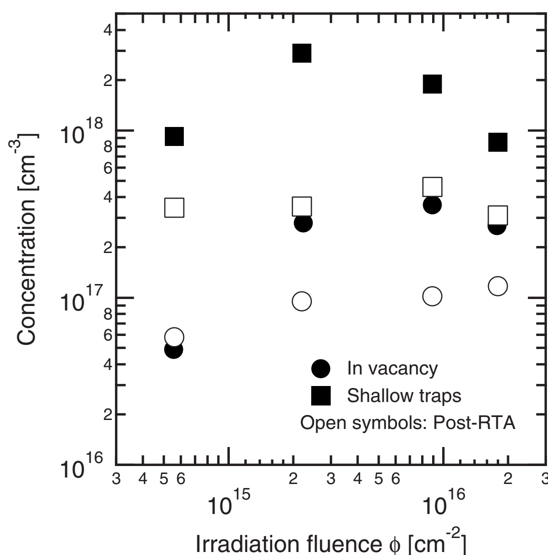

FIG. 4. Concentration of In vacancies and shallow positron traps (nonopen-volume defects) in the layer regions of the irradiated InN films before and after the RTA treatment.

in the GaN films. In more heavily irradiated samples, the V_{Ga} concentrations remained above the upper detection limit[20] even after the RTA, which is expectable based on the high V_{Ga} introduction rate in the irradiation.

The above results show that the RTA treatment results in a reorganization of the irradiation-induced defects in the InN films. The heat-treated InN layers are found to contain decreased concentrations of V_{In} and negative ion defects while on the other hand, different In-vacancy defects not observed in the as-irradiated samples appear to form toward the growth interface in the annealing. It is worth noting that similar depth profiles in the positron Doppler-broadening line shape have also been observed in Si-doped InN (Refs. 22 and 24) and in InN grown by MOCVD with low V/III molar ratios,[16] where the possibility of vacancy clustering near the interface was suggested. To fully identify the near-interface defects, further work is needed. On the other hand, transmission electron microscopy (TEM) has shown that the RTA causes structural changes in the irradiated InN films.[25] In as-grown material, elevated dislocation densities were recorded near the interface with the GaN buffer layer in TEM studies while the irradiation was found to produce small dislocation loops. After the thermal treatment, increased densities of dislocation loops were observed, possibly resulting from the agglomeration of irradiation-induced vacancies, and large voids were found at the InN/GaN interface.

It has been proposed that the improved electron mobility in the annealed InN samples could be due to the partial recovery and spatial reordering of triply charged defects acting as scattering centers.[18] Here, we observe a decrease in roughly half to one order of magnitude in the irradiation-induced V_{In} and negative-ion concentrations in the annealing (Fig. 4). However, as proposed in Ref. 20, because the irradiated films are heavily n-type, the negative ion concentrations might be underestimated due to screening by free electrons. Since the RTA treatment has little effect on the carrier concentrations, the screening effect in the annealed films should be similar to the as-irradiated samples. Hence, also the drop in absolute negative-ion concentrations might be larger than observed. It is thus possible that these defects ultimately limit the electron mobility in the irradiated films. Tentatively, the negative ions found in the as-irradiated material were ascribed to N interstitials (N_i) (Ref. 20) but it seems unlikely that the remaining shallow traps in the annealed films could be associated with nitrogen interstitials, as N_i are expected to be very unstable and easily form N_2 molecules.[9] Instead, it should be noted that while the N vacancy cannot be detected with positrons due to its small open volume, the findings of this work, on the other hand, do not rule out the presence of also nitrogen vacancies in the samples. On the contrary, the irradiation is expected to produce a large number of V_N, hence retaining the position of the N vacancy as a candidate for the dominant native donor in InN.[9]

The behavior of the InN samples is altogether quite different compared to the GaN films. Based on growth studies, the formation of In vacancies in InN is considered to be dominated by the structural properties of the material, such

as extended defects that form especially near the growth interface.[15,16,26] It is therefore interesting that the growth interface seems to play an important role in the behavior of the irradiation-induced point defects during the RTA, suggesting that their behavior is influenced by the local material structure. The unidentified near-interface vacancies might hence be associated with extended lattice defects, such as dislocations.[14]

In summary, we have performed positron annihilation experiments on He-irradiated and subsequently RTA-treated InN grown by MBE. The In vacancies near the film-substrate interface appear restructured after the RTA process, possibly influenced by growth defects near the interface, while deeper in the InN layer, the defects produced in the irradiation are partially removed in the annealing. This could be responsible for the improved transport properties of the annealed films.

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[1] V. Yu. Davydov, A. A. Klochikhin, R. P. Seisyan, V. V. Emtsev, S. V. Ivanov, F. Bechstedt, J. Furthmüller, H. Harima, A. V. Mudryi, J. Aderhold, O. Semchinova, and J. Graul, Phys. Status Solidi B **229**, r1 (2002).

[2] T. Matsuoka, H. Okamoto, M. Nakao, H. Harima, and E. Kurimoto, Appl. Phys. Lett. **81**, 1246 (2002).

[3] J. Wu, W. Walukiewicz, K. M. Yu, J. W. Ager III, E. E. Haller, H. Lu, W. J. Schaff, Y. Saito, and Y. Nanishi, Appl. Phys. Lett. **80**, 3967 (2002).

[4] J. Wu, W. Walukiewicz, K. M. Yu, W. Shan, J. W. Ager III, E. E. Haller, H. Lu, W. J. Schaff, W. K. Metzger, and S. Kurtz, J. Appl. Phys. **94**, 6477 (2003).

[5] E. Bellotti, B. K. Doshi, K. F. Brennan, J. D. Albrecht, and P. Paul Ruden, J. Appl. Phys. **85**, 916 (1999).

[6] B. E. Foutz, S. K. O'Leary, M. S. Shur, and L. F. Eastman, J. Appl. Phys. **85**, 7727 (1999).

[7] R. E. Jones, K. M. Yu, S. X. Li, W. Walukiewicz, J. W. Ager, E. E. Haller, H. Lu, and W. J. Schaff, Phys. Rev. Lett. **96**, 125505 (2006).

[8] J. W. L. Yim, R. E. Jones, K. M. Yu, J. W. Ager, W. Walukiewicz, W. J. Schaff, and J. Wu, Phys. Rev. B **76**, 041303 (2007).

[9] C. Stampfl, C. G. Van de Walle, D. Vogel, P. Krüger, and J. Pollmann, Phys. Rev. B **61**, R7846 (2000).

[10] A. Janotti and C. G. Van de Walle, Appl. Phys. Lett. **92**, 032104 (2008).

[11] X. M. Duan and C. Stampfl, Phys. Rev. B **79**, 035207 (2009).

[12] C. S. Gallinat, G. Koblmuller, J. S. Brown, S. Bernardis, J. S. Speck, G. D. Chern, E. D. Readinger, H. Shen, and M. Wraback, Appl. Phys. Lett. **89**, 032109 (2006).

[13] P. D. C. King, T. D. Veal, P. H. Jefferson, S. A. Hatfield, L. F. J. Piper, C. F. McConville, F. Fuchs, J. Furthmüller, F. Bechstedt, H. Lu, and W. J. Schaff, Phys. Rev. B **77**, 045316 (2008).

[14] C. S. Gallinat, G. Koblmuller, and J. S. Speck, Appl. Phys. Lett. **95**, 022103 (2009).

[15] J. Oila, A. Kemppinen, A. Laakso, K. Saarinen, W. Egger, L. Liszkay, P. Sperr, H. Lu, and W. J. Schaff, Appl. Phys. Lett. **84**, 1486 (2004).

[16] A. Pelli, K. Saarinen, F. Tuomisto, S. Ruffenach, and O. Briot, Appl. Phys. Lett. **89**, 011911 (2006).

[17] R. E. Jones, S. X. Li, L. Hsu, K. M. Yu, W. Walukiewicz, Z. Liliental-Weber, J. W. Ager III, E. E. Haller, H. Lu, and W. J. Schaff, Physica B **376-377**, 436 (2006).

[18] R. E. Jones, S. X. Li, E. E. Haller, H. C. M. van Genuchten, K. M. Yu, J. W. Ager III, Z. Liliental-Weber, W. Walukiewicz, H. Lu, and W. J. Schaff, Appl. Phys. Lett. **90**, 162103 (2007).

[19] K. Saarinen, P. Hautojärvi, and C. Corbel, *Identification of Defects in Semiconductors*, Semiconductors and Semimetals Vol. 51A (Academic Press, New York, 1998), Chap. 5.

[20] F. Tuomisto, A. Pelli, K. M. Yu, W. Walukiewicz, and W. J. Schaff, Phys. Rev. B **75**, 193201 (2007).

[21] F. Reurings, F. Tuomisto, W. Egger, B. Löwe, L. Ravelli, S. Sojak, Z. Liliental-Weber, R. E. Jones, K. M. Yu, W. Walukiewicz, and W. J. Schaff, Phys. Status Solidi A **207**, 1087 (2010).

[22] C. Rauch *et al.* (unpublished).

[23] F. Tuomisto, V. Ranki, D. C. Look, and G. C. Farlow, Phys. Rev. B **76**, 165207 (2007).

[24] C. Rauch, F. Reurings, F. Tuomisto, T. D. Veal, C. F. McConville, H. Lu, W. J. Schaff, C. S. Gallinat, G. Koblmüller, J. S. Speck, W. Egger, B. Löwe, L. Ravelli, and S. Sojak, Phys. Status Solidi A **207**, 1083 (2010).

[25] Z. Liliental-Weber, R. E. Jones, H. C. M. van Genuchten, K. M. Yu, W. Walukiewicz, J. W. Ager III, E. E. Haller, H. Lu, and W. J. Schaff, Physica B **401**, 646 (2007).

[26] F. Reurings, F. Tuomisto, C. S. Gallinat, G. Koblmüller, and J. S. Speck, Phys. Status Solidi C **6**, S401 (2009).