

Positron annihilation study of vacancies in GaInNAs

A. J. Ptak^{a)} and Sarah Kurtz

National Renewable Energy Laboratory, Golden, Colorado 80401

M. H. Weber and K. G. Lynn

Department of Physics and Center for Materials Research, Washington State University, Pullman, Washington 99164

(Received 27 October 2003; accepted 30 March 2004; published 9 June 2004)

GaInNAs is potentially useful in a wide variety of devices, including next-generation, high efficiency, multijunction solar cells. Unfortunately, a number of defects exist in this material that limit the overall device performance. Beam-based positron annihilation spectroscopy was used to examine vacancies in GaInNAs grown by both metal-organic chemical vapor deposition (MOCVD) and molecular-beam epitaxy (MBE). A significant concentration of vacancies exists only when hydrogen and nitrogen are both present during growth. This finding supports the theoretical prediction that gallium vacancies occur in complexes with nitrogen and hydrogen. Growing GaInNAs by solid-source MBE, a hydrogen-free growth method, minimizes the formation of the vacancy complexes. Because this complex is an acceptor, it may be a cause of the high background acceptor concentrations in MOCVD-grown GaInNAs. © 2004 American Vacuum Society.

[DOI: 10.1116/1.1752914]

The dilute-nitride semiconductor GaInNAs is potentially useful in next-generation solar cell applications,¹ heterojunction bipolar transistors,² and infrared laser diodes.³ Unfortunately, this material has not achieved ideal performance to date. The role of various defects in GaInNAs is only beginning to be resolved. The signatures of specific defects, including arsenic antisites,^{4,5} nitrogen split interstitials,^{6–8} and gallium vacancies (V_{Ga})^{7,9} are present in GaInNAs. The specific growth process may cause some of these defects, whereas others may be intrinsic to GaInNAs. Defects caused by the growth process may be avoidable, and understanding these defects may provide a pathway to improving material quality. Here, we study vacancies in GaInNAs and how their presence is affected by the growth process.

Recent theoretical calculations indicate that gallium vacancies are far more likely to form in GaInNAs in the presence of hydrogen.¹⁰ Indeed, the formation energy for V_{Ga} is more than 2 eV lower in GaInNAs with significant concentrations of hydrogen than in similar GaAs, increasing the expected concentration of vacancies by a significant amount.¹⁰ Therefore, V_{Ga} should be much more common in GaInNAs grown by metal-organic chemical vapor deposition (MOCVD) or gas-source molecular-beam epitaxy (MBE) than in solid-source MBE. We present experimental evidence that this is the case by comparing positron annihilation spectroscopy (PAS) beam measurements of GaInNAs grown by solid-source MBE, with and without an atomic hydrogen ($a\text{-H}$) flux, and MOCVD. PAS measurements of the low-momentum broadening parameter, S , indicate a lack of defects in GaInNAs samples grown without hydrogen present. We observe an increase in the S parameter when hydrogen is present in the growth environment, indicating that positrons are annihilating with low-momentum electrons in an open-

volume defect. We assume that the open-volume defects are related to gallium vacancies, implying that V_{Ga} are a much larger problem for MOCVD-grown GaInNAs than for that grown by MBE. The effect of the gallium vacancies on the background carrier concentration is also discussed.

GaAs and GaInNAs epilayers were grown by either solid-source MBE or atmospheric-pressure MOCVD. All samples were lattice-matched, deposited on Zn-doped GaAs substrates miscut 2° from (100), and had nominal bandgaps of 1 eV. The thickness of the active layer was 1 μm . Double heterostructures, with passivating layers on the front and back of the active layer, were employed to minimize the effects of positron trapping by surface and interface states. The MOCVD growths used a sample temperature of 550 °C with a nominal growth rate of 4 $\mu\text{m/h}$. Triethylgallium, trimethylindium, nitrogen trifluoride, and arsine were the precursors used for Ga, In, N, and As.

Elemental sources of Ga and In were used for MBE growth. Arsenic was thermally cracked to produce As_2 . Nitrogen incorporation was achieved using an HD25 RF-plasma source from Oxford Applied Research. Typical source parameters were ~ 400 W with a nitrogen (N_2) flow of 0.3 sccm. Atomic hydrogen was supplied by a commercial atomic hydrogen source (EPI-AHS-L) operating at 9.5 A with a hydrogen beam-equivalent pressure of about 2×10^{-5} Torr. Substrate temperatures during MBE growth were about 530 °C, with a nominal growth rate of 1.5 $\mu\text{m/h}$.

In the PAS experiments¹¹ a beam of monoenergetic positrons ranging from 0.02–0.63 keV is implanted into the MBE- and MOCVD-grown samples. The beam energy determines the mean implantation depth. Photons from the annihilation of electron–positron pairs are detected by a high-purity Ge detector with an energy resolution of 1.45 keV at 514 keV. The momentum component of the annihilating electron–positron pair parallel to the direction of the de-

^{a)}Electronic mail: aaron_ptak@nrel.gov

tected photon causes measurable Doppler shifts away from 511 keV, the rest mass energy of the particles, which over many annihilation detections average out to a broadening of the annihilation line.

At vacancies, the missing atom and the negative charge from conduction and valence electrons form an attractive potential well that traps (or localizes) positrons. Negatively-charged defects have a higher trapping cross section than neutral defects. Positively charged defects do not trap positrons at all. In a vacancy, the photon momentum distribution narrows because there are fewer annihilations with high-momentum core and valence electrons. This manifests itself as an increase of the low-momentum broadening parameter, S , defined as the ratio of the central peak region to the total peak area.¹²

Positrons thermalize very quickly (typically <10 ps), much faster than the average lifetime of positrons in vacancy-containing GaAs (~260 ps),¹³ so the broadening is almost exclusively due to the electron momentum. If all implanted positrons were to annihilate from vacancy sites, the S -parameter would increase by about 1.5% over the value for a defect free environment.¹¹ A larger increase in S could indicate the presence of di-vacancies or larger open-volume defects.

Typically, with knowledge of the defect trapping cross section the concentration of defects can be estimated within an order of magnitude. Absolute defect concentrations are much less reliable in thin layer structures or in samples with internal electric fields. However, the sample-to-sample trends of more (or less) defects can be determined.

PAS beam measurements showed no differences in open-volume defect densities between GaAs samples grown by MBE and MOCVD. These measurements assumed that defect-free GaAs has an S value of one. The small deviations from one in these data (shown below) are due to a minor systematic error in the PAS system. All of the GaAs samples indicate significant positron diffusion lengths, suggesting low vacancy concentrations.

The S broadening parameter measured by PAS is shown in Fig. 1 for MOCVD-grown GaAs and GaInNAs. The addition of nitrogen introduces a significant concentration of open-volume defects. Also shown in Fig. 1 is a similar MOCVD-grown GaInNAs sample that was annealed at 650 °C for 30 min in an arsine ambient. The concentration of open-volume defects is reduced during the anneal, but the signal is not completely removed.

Figure 2 shows a similar plot for the MBE-grown samples. The MOCVD-grown GaAs sample is included for reference. Importantly, there is no significant difference for the GaAs and GaInNAs samples grown by MBE. This observation is consistent with the expectation that GaInNAs grown in the absence of hydrogen will not form gallium vacancies. To test whether the addition of hydrogen to the MBE growth environment would add a measurable concentration of vacancies, a sample was grown under an a -H flux. This GaInNAs:H sample does show an increase in the S parameter, and hence defect concentration, in the upper half of

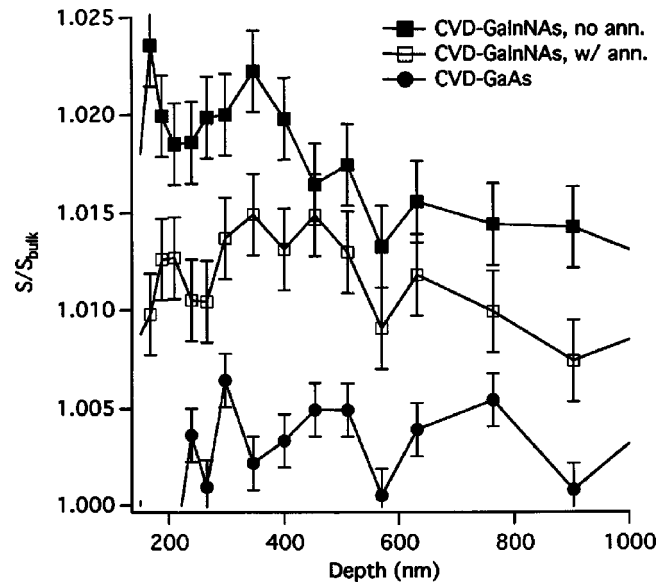


Fig. 1. Normalized S parameter (indicative of vacancy concentration) versus depth in MOCVD-grown samples. The as-grown GaInNAs sample (solid squares) has the highest concentration of vacancies, with a reduction visible due to annealing (open squares). The lines are guides to the eye.

the sample. This indicates that the addition of nitrogen and an atomic hydrogen flux to the growth atmosphere in the MBE system generates vacancies, but that these vacancies may be avoided by growing without hydrogen. Although not shown in Figs. 1 or 2, it is important to note that the magnitude of all of the positron beam measurements are similar in the bulk substrates. The data from the front passivation layer of the double heterostructure is hidden in the figures.

The first issue to address is the assignment of the observed open-volume defects to gallium vacancies. The recent

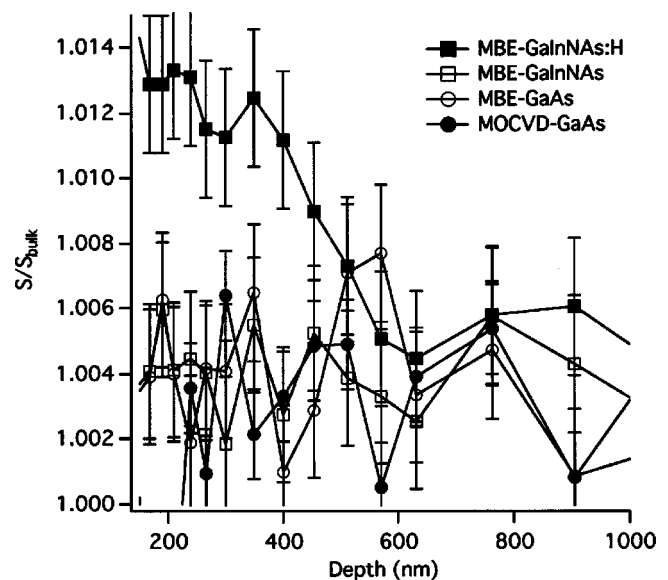


Fig. 2. Normalized S parameter (indicative of vacancy concentration) versus depth in MBE-grown samples. The hydrogen-free MBE growth technique avoids the formation of open-volume defects. The MOCVD-grown GaAs sample is included for reference. The lines are guides to the eye.

work by Toivonen *et al.*⁹ on MOCVD-grown GaNAs makes this assignment based on a comparison of their PAS data to the annihilation broadening parameters expected for V_{Ga} and the arsenic vacancy, V_{As} . The parameters deduced from their data agree more closely with those expected for V_{Ga} . Additionally, V_{As} are not expected to trap positrons in *p*-type material due to their positive charge. Toivonen *et al.* also found evidence for V_{Ga} in a complex.⁹ They rejected defects involving carbon, hydrogen, and nitrogen interstitials before settling on a complex of V_{Ga} with either N_{Ga} or As_{Ga} , due to the donor–acceptor nature of this pair.

The work of Janotti *et al.*, however, indicates that the $(V_{\text{Ga}}-\text{N}-x\text{H})^{x-3}$ complex, with $x=1, 2, 3$, or 4, can be a stable defect.¹⁰ This complex is more likely to form with $x=1$ or 2 for entropic reasons,¹⁰ and these forms of the complex are more likely to be observed by positrons due to their overall negative charge. Additionally, they found that nitrogen in GaAs lowers the formation energy of V_{Ga} by a small amount, but that hydrogen in GaNAs lowers the formation energy of V_{Ga} by more than 2 eV. This increases the concentration of vacancies well above what is expected in GaAs. As a result, there should be a noteworthy difference in the concentration of V_{Ga} observed in GaInNAs grown by MOCVD or gas-source MBE versus solid-source MBE. This trend is certainly present in our data and also explains the presence of V_{Ga} in the works of Toivonen *et al.*⁹ and Li *et al.*⁷ Li *et al.* used gas-source MBE to grow GaInNAs, where the necessary hydrogen is supplied by arsine. Given that the formation of the $(V_{\text{Ga}}-\text{N}-x\text{H})$ complex is energetically favorable, it is possible that this complex (with $x=1$ or 2) is the one observed in the PAS measurements.

From Fig. 1, it is clear that thermal annealing reduces the concentration of vacancies. Similarly, Li *et al.* indicated that most of their V_{Ga} were removed upon anneal.⁷ In our case, the vacancy signal for the annealed MOCVD-grown sample is intermediate between the as-grown sample and the GaAs reference. The difference in the vacancy reduction between the work of Li *et al.* and the present work could stem from the different annealing conditions. Li *et al.* performed a rapid thermal anneal at 750 °C for 30 seconds in a flowing N_2 ambient, whereas our anneal was under arsine for 30 min at 650 °C. It is unclear whether removing the vacancies is more dependent on the anneal temperature used, or the anneal ambient.

The MBE-grown GaInNAs sample with added hydrogen does not show a measurable concentration of V_{Ga} until after about 300 nm of growth. The S parameter then becomes distinguishable from the baseline and increases toward the surface of the sample. A likely cause of the ramp-up of defects during the growth of the layer is that the hydrogen concentration increases throughout the growth. Figure 3 compares the normalized S parameter from the MBE-grown GaInNAs:H sample with the hydrogen concentration measured by secondary-ion mass spectrometry (SIMS). The data in this figure have been numerically smoothed using a binomial algorithm to make the trends more apparent. The measurement background limits the hydrogen data on the right

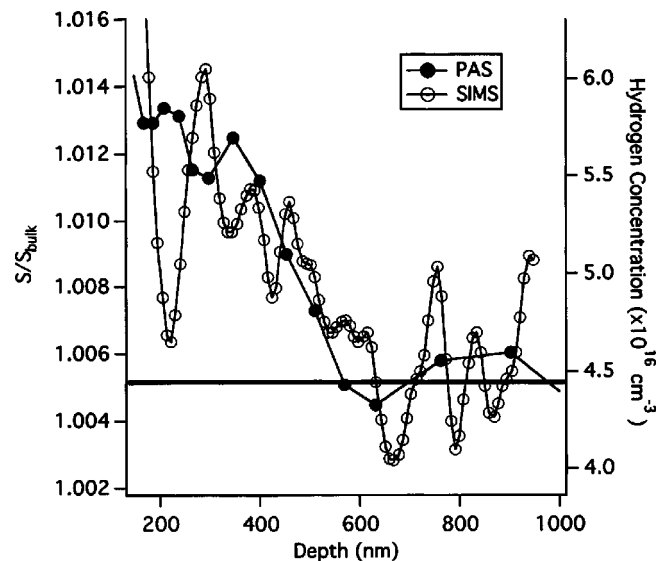


Fig. 3. A comparison of the hydrogen concentration measured by SIMS and the normalized S parameter (indicative of vacancy concentration) versus depth for the MBE-grown GaInNAs sample with intentional hydrogen doping. The data sets have been numerically smoothed to bring out the trends. The horizontal line is a guide to the eye.

hand side of the plot. Although the data sets are still noisy, the fact that both the S parameter and the hydrogen concentration begin to rise at the same depth is suggestive that there is a ramp-up of the hydrogen during growth. This trend of rising hydrogen incorporation has been observed in other GaInNAs samples grown under hydrogen that were not part of this study. If present, a gradual ramp-up of hydrogen toward the surface of the layer will manifest itself as a higher defect density at the surface, as seen in our data.

The magnitude of the change in hydrogen for the MBE- and MOCVD-grown samples qualitatively matches the trend observed in the PAS beam measurements. The MBE-grown GaInNAs:H sample shows a maximum hydrogen concentration in the 10^{16} cm^{-3} range, while the hydrogen concentration for the MOCVD-grown GaInNAs (not shown) is in the 10^{19} cm^{-3} range. This difference correlates with the larger percent change observed in the PAS measurements for the MOCVD-grown samples. These data lend further support to the role of hydrogen in the formation of the V_{Ga} complex, and the ability of solid-source MBE to avoid them.

A final question deals with the effect of this vacancy complex on the background acceptor concentration of the GaInNAs samples. Our MOCVD-grown GaInNAs samples often have a background acceptor concentration approaching 10^{17} cm^{-3} , whereas the MBE-grown material is typically at 10^{15} cm^{-3} or lower. The incorporation of carbon from the MOCVD precursors may account for much of this difference, but GaInNAs samples grown under similar MOCVD conditions have been reported to have carbon concentrations of about 10^{16} cm^{-3} , despite the higher acceptor concentrations.^{14,15} As $(V_{\text{Ga}}-\text{N}-x\text{H})^{x-3}$ complexes act as acceptors (with $x=1$ or 2), they could play a significant role in the background acceptor concentration.

We have identified a defect complex involving a gallium

vacancy that is consistent with the $(V_{\text{Ga}}\text{--N--}x\text{H})^{x-3}$ complex, in agreement with theory. Significant concentrations of these vacancies have been observed in GaInNAs grown by MOCVD. The $(V_{\text{Ga}}\text{--N--}x\text{H})$ complex, an acceptor, likely plays a role in the background acceptor concentration of GaInNAs samples grown in the presence of hydrogen. Importantly, however, these defects do not appear to form in large concentrations in solid-source, MBE-grown GaInNAs. This provides a way to avoid these defects during growth, and any deleterious effects that they may have.

The authors thank C. Kramer for the sample preparation. This work was supported by the U.S. Department of Energy under Contract No. DE-AC36-99GO10337 to NREL.

¹D. J. Friedman, J. F. Geisz, S. R. Kurtz, and J. M. Olson, *J. Cryst. Growth* **195**, 409 (1998).

²P. C. Chang, A. G. Baca, N. Y. Li, P. R. Sharps, H. Q. Hou, J. R. Laroche, and F. Ren, *Appl. Phys. Lett.* **76**, 2788 (2000).

³M. Fischer, D. Gollub, and A. Forchel, *Jpn. J. Appl. Phys., Part 1* **41**, 1162 (2002).

⁴N. Q. Thinh, I. A. Buyanova, W. M. Chen, H. P. Xin, and C. W. Tu, *Appl. Phys. Lett.* **79**, 3089 (2001).

⁵N. Q. Thinh, I. A. Buyanova, P. N. Hai, W. M. Chen, H. P. Xin, and C. W. Tu, *Phys. Rev. B* **63**, 033203/1 (2001).

⁶S. G. Spruytte, C. W. Coldren, J. S. Harris, W. Wampler, P. Krispin, K. Ploog, and M. C. Larson, *J. Appl. Phys.* **89**, 4401 (2001).

⁷W. Li, M. Pessa, T. Ahlgren, and J. Decker, *Appl. Phys. Lett.* **79**, 1094 (2001).

⁸T. Ahlgren, E. Vainonen, T. Ahlgren, J. Likonen, W. Li, and M. Pessa, *Appl. Phys. Lett.* **80**, 2314 (2002).

⁹J. Toivonen, T. Hakkarainen, M. Sopanen, H. Lipsanen, J. Oila, and K. Saarinen, *Appl. Phys. Lett.* **82**, 40 (2003).

¹⁰A. Janotti, S.-H. Wei, S. B. Zhang, S. Kurtz, and C. G. V. d. Walle, *Phys. Rev. B* **67**, 161201 (2003).

¹¹K. Saarinen, P. Hautajarvi, and C. Corbel, *Positron Annihilation Spectroscopy of Defects in Semiconductors* (Academic, New York, 1998), Vol. 51.

¹²A. Dupasquier and A. P. Mills, *Positron Spectroscopy of Solids* (IOS, Amsterdam, 1995).

¹³J. Gebauer, M. Lausmann, T. E. M. Staab, R. Krause-Rehberg, M. Hakala, and M. J. Puska, *Phys. Rev. B* **60**, 1464 (1999).

¹⁴S. Kurtz, R. Reedy, B. Keyes, G. D. Barber, J. F. Geisz, D. J. Friedman, W. E. McMahon, and J. M. Olson, *J. Cryst. Growth* **234**, 323 (2002).

¹⁵S. Kurtz, J. F. Geisz, B. M. Keyes, W. K. Metzger, D. J. Friedman, J. M. Olson, A. J. Ptak, R. R. King, and N. H. Karam, *Appl. Phys. Lett.* **82**, 2634 (2003).