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Defects in GaInNAs: What We've Learned So Far

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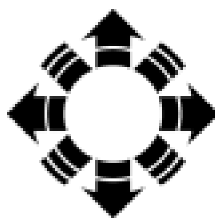

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ABSTRACT

We show results from a number of experimental and theoretical investigations on GaInNAs in an attempt to provide a more complete picture of defects in this material than is currently available. Much has been learned in recent years, including the effects of impurities such as hydrogen and carbon, the behavior of GaInNAs on annealing, and the defects that cause a degradation of material properties, including photoluminescence intensity and, especially important for solar cells, minority-carrier lifetimes.

Much of our current understanding stems from a comparison of GaInNAs grown by both MOCVD and MBE. This comparison, along with the use of several characterization techniques and theoretical modeling, has allowed us to understand the roles of various defects and to identify a signature for the defect that reduces the minority-carrier lifetime.

1. Introduction

Monolithic, three-junction $GaInP_2$/GaAs/Ge solar cells are currently in production. This device, however, cannot make efficient use of all of the light that reaches the Ge junction. A four-junction device that splits the sub-GaAs light between the Ge cell and a cell with a bandgap near 1 eV has an ideal, theoretical efficiency of 52% under 500-suns concentration and the AM1.5D spectrum. This should lead to a practical efficiency of greater than 40%.

The material used as the active layer for this new cell must be lattice-matched to GaAs and have a bandgap of approximately 1 eV. $Ga_{1-x}In_xN_yAs_{1-y}$, hereafter GaInNAs, has both of these properties when y~2.5% and x~7%, but suffers from low minority-carrier diffusion lengths. Insertion of this material into the three-junction cell would fall short of the "breakeven" efficiency of currently available technology [1].

The literature on GaInNAs shows that this material is replete with defects that cause a number of serious problems. For example, studies using deep-level transient spectroscopy (DLTS) measurements often show as many as five or six deep states in the bandgap. This makes the task of identifying the roles of these defects nearly impossible. Even something as seemingly straightforward as the background carrier concentration is not very well understood. As grown, unintentionally doped GaInNAs is usually p-type, although it can sometimes be n-type. Further confusing matters is the fact that annealing GaInNAs can take p-type material and cause it to become more p-type, or change it to n-type [2,3].

Among the serious issues in this material is the extremely low minority-carrier lifetime, typically less than 1 ns. This lifetime in GaInNAs is 50–100 times lower than in comparable GaAs. In addition, there are also drastic decreases in both the electron mobility and the photoluminescence intensity when compared to similarly grown GaAs. Clearly, the reduced lifetimes are due to some point defect in the crystal, owing to the overall lack of extended defects. However, almost nothing is known for certain of the nature of this defect.

In this work, we use a number of experimental studies and theoretical calculations to attempt to clarify the roles of the various defects, including hydrogen, carbon, and gallium vacancies. We also identify a signature of the defect that limits the minority-carrier lifetimes.

2. Procedures

GaInNAs epilayers are grown on GaAs substrates by both metalorganic chemical vapor deposition (MOCVD) and molecular-beam epitaxy (MBE). The growth conditions for each method are given explicitly in each published work referenced in this paper. Briefly, MOCVD uses metalorganic and hydride precursors that react on the heated substrate. In contrast, MBE uses elemental sources and an ultrahigh vacuum environment. Substrate temperatures in MOCVD growth are somewhat higher than in MBE: in the range of 550°–650°C for MOCVD and 450°–530°C for MBE.

Samples with specific structures are often necessary for certain characterizations to be performed. These are described in detail, along with a more complete description of the growth details, in the appropriate referenced publications.

3. Results

a. DLTS measurements

Deep-level transient spectroscopy (DLTS) measurements have provided a great deal of insight into the defect structure of GaInNAs. There are always at least two deep levels observed in our GaInNAs epilayers, and often there are only these two deep levels, compared with the five or six observed in the literature. Additional levels are seen in certain samples, but since these are not ubiquitous,

they cannot be the major cause of the poor properties of this material [4]. Of the two universal deep traps, one is a relatively shallow electron trap, and the other is a mid-gap state that traps both holes and electrons, forming a recombination center [5].

The activation energies of these two defect states change with changing nitrogen concentration, [N], as shown in Fig. 1. The electron trap appears at about 1.0 eV above the valence-band maximum (VBM) for samples with a small amount of nitrogen, and this activation energy decreases only slightly (about 0.1 eV) for samples with a bandgap near 1 eV. As the amount of nitrogen in GaInNAs increases, there is a corresponding decrease in the bandgap of the sample [6]. Because most of the motion of the bandgap is due to the lowering of the conduction-band minimum (CBM), the electron trap quickly approaches the CBM as [N] is increased. This motion makes the activation energy of the electron trap quite shallow for 1 eV GaInNAs, on the order of 0.1 eV. The recombination center, however, mirrors the motion of the CBM. This defect has an activation energy of ~0.9 eV for low [N] that drops to ~0.5 eV for high [N]. In this way, the recombination center maintains a position near the middle of the bandgap [5].

It is known that deep traps typically have a stronger influence on the minority-carrier lifetimes than do shallow traps. The recombination rate for traps near midgap is several orders of magnitude higher than for traps closer to the bands [7]. In addition, a defect that traps both holes and electrons provides a pathway for recombination that is not directly band-to-band. This allows us to conclude that the deep recombination center observed in the DLTS

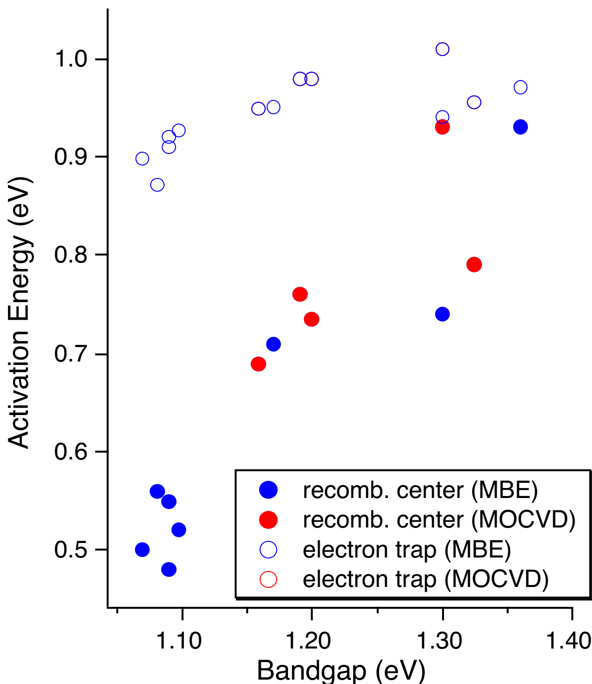

Figure 1. The activation energy of the electron trap (open circles) and the recombination center (filled circles) as measured from the VBM for samples with different amounts of nitrogen.

measurements is a signature of the defect limiting the minority-carrier lifetimes. Further work is necessary to identify the origin of this defect and to eliminate it.

b. Comparison of MBE- and MOCVD-grown GaInNAs

A material grown by disparate growth methods will often show differences in properties such as defect structure and background impurity levels. It was hoped that by comparing MBE- and MOCVD-grown GaInNAs that some differences would be observed that would shed light on the difficulties with GaInNAs. Studies of the mobility, minority-carrier lifetime, and deep-level defect structure yielded no major distinctions. Only two important differences were found in material from the two growth methods: photoluminescence (PL) intensity of the as-grown material and residual background impurity concentrations [4]. The different impurity levels also led to differences in the acceptor concentrations. The as-grown material from the MBE system was found to show significant room-temperature luminescence, whereas the PL from MOCVD-grown samples was very weak, if present at all. In addition, the MBE-grown material exhibited much lower concentrations of both hydrogen and carbon.

It is well known from the literature that annealing improves the PL efficiency of GaInNAs [8]. This is certainly the case for our MOCVD-grown material, where very low PL is observed before annealing, and significant luminescence, although far less than comparable GaAs, is observed after annealing. The MBE-grown material, in contrast, does show as-grown PL and a relatively small increase on annealing, although the PL intensity of this material is also far lower than that of GaAs. This discussion will become important in a later section.

The differences in hydrogen and carbon impurities are expected from the nature of the growth methods. MOCVD uses organic and hydride precursors, and carbon and hydrogen contamination is expected and extremely difficult to mitigate under the growth conditions that allow incorporation of nitrogen. MBE, however, uses elemental sources in an ultrahigh vacuum environment that drastically reduces the background impurities incorporated during growth. Typical hydrogen and carbon concentrations from MOCVD material are in the range of $1x10^{18}$–$1x10^{20}$ cm^{-3} and $5x10^{16}$–$1x10^{18}$ cm^{-3}, respectively. The background of the secondary-ion mass spectrometry measurements limited the detection of impurity concentrations in MBE-grown GaInNAs. The levels were no higher than $6x10^{16}$ cm^{-3} for hydrogen and $4x10^{14}$ cm^{-3} for carbon [4].

Because material with such drastically different impurity concentrations had such similar mobilities, lifetimes, and deep-level defect structures, it is clear that neither hydrogen nor carbon are a major factor in these properties. However, carbon contamination appears to contribute to the high background acceptor concentration observed in MOCVD GaInNAs [9]. In addition, there is evidence that carbon, in sufficient concentrations, can form a deep level when paired with nitrogen [10]. Hydrogen

almost certainly contributes to the carrier concentration in its own way, as seen in the next section.

c. The role of hydrogen

Theoretical calculations have helped to illuminate some additional effects of hydrogen in GaNAs. Nitrogen and hydrogen are expected to form a strong bond in this material, and this was verified by both theoretical calculations and experimental studies [11,12]. Indeed, the N-H defect was shown to act as a donor. This result is surprising because H is amphoteric in both GaAs and GaN, causing passivation rather than doping. These calculations indicate that the change of p-type GaInNAs to n-type on annealing under AsH_3 is, at least in part, related to hydrogen in the sample.

In addition, nitrogen and hydrogen were both found to bond very strongly with gallium vacancies (V_{Ga}), significantly reducing the formation energy of this intrinsic defect [13]. The resulting N-H-V_{Ga} complex has a formation energy that is about 2 eV lower than for the isolated V_{Ga} in GaAs, as seen in Fig. 2. This raises the expected concentration of V_{Ga} in GaNAs well beyond the levels expected in GaAs when hydrogen is present. This result allows us to infer that material grown by MBE will have a far lower concentration of V_{Ga}, due to the lack of hydrogen, than layers from the MOCVD system. This potentially has two consequences: the V_{Ga} complex acts as an acceptor and may be a significant contributor to the elevated background acceptor concentrations observed in MOCVD-grown GaInNAs, and the removal of V_{Ga} on annealing may be responsible for the improvement seen in PL intensity.

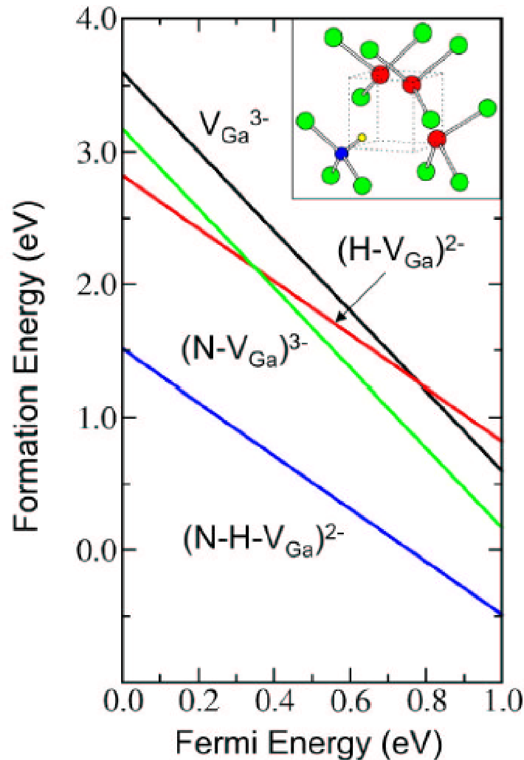

Figure 2. Formation energy vs. Fermi energy for V_{Ga}^{3-} and $(H-V_{Ga})^{2-}$ in GaAs, and for the same defects bonded to N, $(N-V_{Ga})^{3-}$ and $(N-H-V_{Ga})^{2-}$, in dilute GaAsN alloys under Ga-rich and H-rich conditions. In the inset we show the local atomic configuration for the $(N-H-V_{Ga})^{2-}$complex.

Recall that very weak room-temperature PL is observed from our as-grown MOCVD GaInNAs, whereas the MBE-grown samples do show significant luminescence. On annealing, the PL from the MOCVD-grown material increases dramatically, and a small increase in PL intensity is seen from the MBE-grown samples. For V_{Ga} to be involved in this phenomenon, two things must occur: there must be fewer V_{Ga} in as-grown MBE samples, and annealing must reduce the concentration of V_{Ga} in the MOCVD-grown material. This is the focus of the next section.

d. Positron annihilation spectroscopy

Positron annihilation spectroscopy (PAS) is a technique that is used to determine the concentration of open volume defects (OVD) in a crystal. OVDs are typically assumed to be related to vacancies. In collaboration with researchers at Washington State University, PAS was performed on a number of our MOCVD- and MBE-grown GaInNAs samples, as well as GaAs reference samples. Figure 3 shows the ratio of the S parameter in these samples to the S parameter of a bulk GaAs substrate versus the implantation depth of positrons into the samples. The S parameter is related to the concentration of vacancies. Neither the MBE- nor MOCVD-grown GaAs samples showed any OVD signal above that of the bulk GaAs reference sample. Figure 3a indicates that the MBE-grown GaInNAs sample did not show any OVD signal above background, but GaInNAs grown in the MBE system under an intentional flux of atomic hydrogen did show OVDs. The as-grown MOCVD

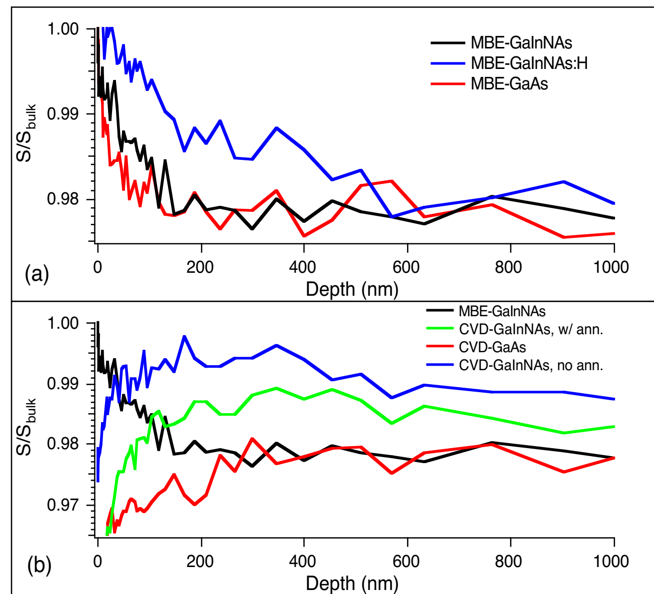

Figure 3. PAS measurements showing (a) the increase in V_{Ga} for MBE growth under H, and (b) the large concentration of V_{Ga} in MOCVD material that is somewhat reduced by annealing.

Table I. Summary of the defects in GaInNAs, including cause, signature, and possibility of removal.

Defect	*Cause*	*Signature*	*Can we remove?*
carbon	MOCVD growth	acceptors, reduced lifetime	by using MBE (acceptors)
hydrogen	MOCVD growth	donor	by using MBE
gallium vacancies, V_{Ga}	presence of H and N	acceptors, reduced PL, PAS	probably, by using MBE
shallow electron trap	N(?)	DLTS	??
deep recomb. center	N(?)	DLTS, reduced lifetime	??

GaInNAs sample shown in Fig. 3b (blue curve), however, showed the largest concentration of OVDs, and this level was reduced in a similar sample that was annealed at 650°C for 30 minutes. It should be noted that the topmost 100–200 nm of each measurement is within the passivating cap layer. Differences in the OVD signal from the different cap layers are fully expected. These data fit perfectly with the theoretical calculations described above, and indicate that there are, indeed, fewer V_{Ga} in MBE-grown GaInNAs and that their concentration in MOCVD-grown material is reduced with an anneal. These findings lend support to the idea that the V_{Ga} defect may well be involved in the suppression of the PL intensity.

4. Conclusion

We have attempted to describe the roles of various defects in GaInNAs, and our findings are summarized in Table I. By comparing material grown by both MBE and MOCVD, we have shown that hydrogen, carbon, and V_{Ga} cannot be the major cause of degradation in this material, although each has its own effect. Carbon contributes to the background hole concentration, and may form a deep level when combined with nitrogen whereas hydrogen acts as a donor. The incorporation of hydrogen in GaInNAs increases the concentration of V_{Ga} to very high levels. These V_{Ga} are likely responsible for at least some of the suppression of the PL intensity and may also act as acceptors that affect the background carrier concentration.

In addition, we have identified a peak in DLTS measurements that represents the defect limiting the minority-carrier lifetimes. The structure of this defect is still not known, and much work remains to see if it can be removed. However, this represents a large step forward as this signature can now be used as a figure of merit for future studies of GaInNAs.

Acknowledgements

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References

1. D.J. Friedman and Sarah Kurtz, “Breakeven criteria for the GaInNAs junction in GaInP/GaAs/GaInNAs/Ge four-junction solar cells.” Progress in Photovoltaics: Research and Applications **10**, 331 (2002).
2. J.F. Geisz, D.J. Friedman, J.M. Olson, S.R. Kurtz, and B.M. Keyes, “Photocurrent of 1 eV GaInNAs lattice-matched to GaAs.” J. Cryst. Growth **195**, 401 (1998).
3. Sarah Kurtz, J.F. Geisz, D.J. Friedman, J.M. Olson, A. Duda, N.H. Karam, R.R. King, J.H. Ermer, and D.E. Joslin, “Modeling of electron diffusion length in GaInAsN solar cells.” IEEE Photovoltaic Specialists Conference **28**, 1210 (2000).
4. A.J. Ptak, S.W. Johnston, Sarah Kurtz, D.J. Friedman, and W.K. Metzger, “A comparison of MBE- and MOCVD-grown GaInNAs.” J. Cryst. Growth, in press.
5. A.J. Ptak, S.W. Johnston, and Sarah Kurtz, “Signature of the defect limiting the minority-carrier lifetime in GaInNAs.” Submitted to Appl. Phys. Lett.
6. M. Weyers, M. Sato, and H. Ando, “Red shift of photoluminescence and absorption in dilute GaAsN alloy layers.” Jpn. J. Appl. Phys. **31**, L853 (1992).
7. R.K. Ahrenkiel, in “Minority-carrier lifetime in III-V semiconductors,” in Semiconductors and Semimetals, Vol. **39**, (Academic Press, 1993) p. 48-49.
8. M. Kondow, K. Uomi, K. Hosomi, and T. Mozume, “Gas-source molecular beam epitaxy of GaN_xAs_{1-x} using a N radical as the N source.” Jpn. J. Appl. Phys. Part 2, **33**, L1056 (1994).
9. Sarah Kurtz, R. Reedy, B. Keyes, G. D. Barber, J.F. Geisz, D.J. Friedman, W.E. McMahon, and J.M. Olson, “Evaluation of NF_3 versus dimethylhydrazine as N sources for GaAsN.” J. Cryst. Growth **234**, 323 (2002).
10. Sarah 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, “The effect of growth rate and gallium source on GaAsN.” Appl. Phys. Lett., in press.
11. A. Janotti, S.B. Zhang, Su-Huai Wei, and C.G. Van de Walle, “Effects of hydrogen on the electronic properties of dilute GaAsN alloys.” Phys. Rev. Lett. **89**, 6403 (2002).
12. S. Kurtz, J. Webb, L. Gedvilas, D. Friedman, J. Geisz, J. Olson, R. King, D. Joslin, and N. Karam, “Structural changes during annealing of GaInAsN.” Appl. Phys. Lett. **78**, 748 (2001).
13. A. Janotti, S.H. Wei, S.B. Zhang, Sarah Kurtz, and C.G. Van de Walle, “Nitrogen-hydrogen-V_{Ga} interactions in GaAsN alloys.” Submitted to Phys. Rev. Lett.

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