

Hydrazine N Source for Growth of GaInNAs for Solar Cells

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*Presented at the Electrochemical Society '99 Proceedings
Seattle, Washington
May 2-6, 1999*



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Contract No. DE-AC36-98-GO10337

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ABSTRACT

We evaluate hydrazine (Hy) as a nitrogen precursor source for the growth of GaNAs and GaInNAs for application in 1-eV solar cells lattice-matched to GaAs, and compare it to the more commonly used dimethylhydrazine (DMHy). The incorporation efficiency of N into the GaNAs alloy is found to be one to two orders of magnitude higher with Hy than with DMHy. This high N incorporation makes convenient the growth of GaNAs at higher growth temperatures, $T_g=650^\circ\text{C}$, and arsine flows, $\text{AsH}_3/\text{III}=44$, than are generally possible with the use of DMHy. GaInNAs and GaNAs solar cells are grown under these growth conditions and compared to a GaAs cell grown under the same conditions to determine the extent to which the poor minority-carrier properties routinely observed for the N-containing material can be attributed to the growth conditions. Finally, the background carrier concentrations for Hy- and DMHy-grown material are compared, and little difference is found between the two sources.

INTRODUCTION

Recently, there has been significant interest in the potential for improving upon the record 30% efficiency (1-3) (AM1.5 direct, 200 suns) of the GaInP/GaAs two-junction solar cell by adding a third junction with a 1-eV band gap and a fourth junction based on Ge at 0.7 eV band gap. Projected efficiencies (4) for such a four-junction structure are greater than 40%, if the third and fourth junctions can be made with near-ideal performance, as has been achieved with the GaInP and GaAs junctions (4). It has been shown that $\text{Ga}_{1-x}\text{In}_x\text{N}_y\text{As}_{1-y}$ can be grown with a 1-eV band gap and a lattice constant matched to GaAs for $y\approx 0.02$ and $x\approx 3y$ (5,6). Therefore, GaInNAs is a natural leading candidate for the third junction of the proposed three- and four-junction solar cell structures (7,8). However, GaInNAs with adequate minority-carrier properties has not been achieved. Low photocurrents and photovoltages, reflecting low minority-carrier diffusion lengths and high junction recombination, have limited the performance of GaInNAs-based cells grown thus far, so that they are not adequate for application in the multijunction structure (9). Furthermore, a high background doping on the order of 10^{17} holes/cm³ is typically observed for the as-grown material. This is usually attributed to the high carbon contamination observed with secondary-ion mass spectrometry (SIMS) (9). This background doping makes it difficult to generate low-doped layers for the p-i-n structures that are commonly used to improve photocarrier collection in low-diffusion-length material.

The precursors used in the growth of electronic materials can have an important effect on the electronic properties of the materials. For GaInNAs, dimethylhydrazine (DMHy) has typically been used as the nitrogen precursor for growth of this material by organometallic vapor-phase epitaxy (OMVPE). As an alternative to DMHy, hydrazine (Hy) has been shown to be an effective nitrogen precursor for the growth of GaN by molecular-beam epitaxy (10). Also, since the Hy

molecule contains no carbon in its structure while the DMHy molecule does, Hy might be expected to result in lower carbon incorporation into the GaInNAs epilayer than DMHy does. In this paper, we discuss the use of Hy for the OMVPE growth of GaInNAs. We contrast the composition of the GaInNAs, and its resulting electronic properties, with that of material grown using the more conventional DMHy nitrogen precursor.

EXPERIMENTAL

For simplicity, most of the work focused on the In-free ternary GaNAs, although some epilayers of lattice-matched GaInNAs were studied as well. Epilayers of these materials were grown by atmospheric-pressure OMVPE on GaAs substrates oriented 2° towards (111)_B from (100), at growth temperatures T_g ranging from 550°–650°C. Growth rates were nominally 5µm/hr (although the actual rate measured from the thickness was found to be significantly less for some of the high-N-content samples, as discussed below). Trimethylgallium (TMGa), trimethylindium (TMIn), and arsine (AsH₃) were used as precursors for Ga, In, and As. DMH and Hy were used as N precursors. The N precursors were used in bubblers, at room temperature, with hydrogen as a carrier gas.

The nitrogen content of the grown epilayers was determined from X-ray diffraction (9) and selectively cross-checked with SIMS. To measure the carrier concentration and band gap of each epilayer, a Schottky-barrier-like junction was formed between the epilayer and a liquid electrolyte. The carrier concentration was measured from the capacitance-voltage (CV) characteristic of the junction, and the band gap was determined from the band edge of the spectral photoresponse of the junction (11). For epilayers that did not have a measurable X-ray peak and band gap, the compositions were measured by Auger electron spectroscopy.

RESULTS

Epilayer Composition

Figure 1 summarizes the dependence of the nitrogen content of the grown GaNAs epilayers on the flow rates of the AsH₃ and nitrogen sources; the flows are normalized to the group-III flows. The figure shows that significant N incorporation (i.e. on the order of 1%, enough to reduce the bandgap below that of GaAs by 0.1 eV or more) can be achieved using the Hy precursor. Indeed, the Hy/III flow ratios which yield a given N incorporation are one to two orders of magnitude lower than the DMHy/III flow ratios required to give the same N incorporation using the DMHy precursor. Thus, the Hy source is a much more efficient N precursor for GaNAs growth than is DMHy. Unfortunately, under the growth conditions described here, it was not found to be possible to obtain N contents of greater than ~2% using Hy; as the Hy flow is increased, the composition of the resulting epilayer is found to make a sudden transition from crystalline GaN_yAs_{1-y} with $y \ll 1$ to nanocrystalline or amorphous material with $y \approx 1$. The Hy flow at which this transition occurs decreases with decreasing growth temperature T_g and AsH₃/III flow. This behavior is consistent with the general trend of increased N incorporation for decreased T_g and AsH₃/III flow. This trend is illustrated in Fig. 1, and has been reported by others previously (12,13).

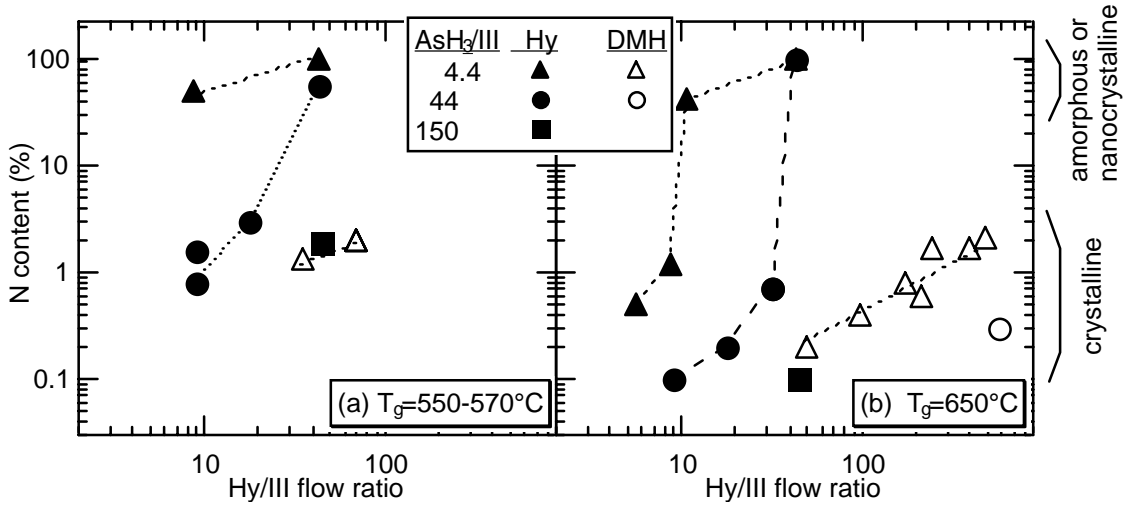


Fig. 1. Comparison of N content y in $\text{GaN}_y\text{As}_{1-y}$ grown with Hy and DMHy N precursors, as a function of N precursor flow, for several different AsH_3 flows. In panel (a) the epilayers grown using Hy were grown at $T_g=550^\circ\text{C}$ and the epilayers using DMHy were grown at $T_g=570^\circ\text{C}$; in panel (b), all epilayers were grown at $T_g=650^\circ\text{C}$. The dashed lines are a guide to the eye.

Solar Cells Grown at High T_g and AsH_3/III

A useful consequence of the high N incorporation using the Hy precursor is that it makes possible the incorporation of significant quantities of N into the Ga(In)NAs even at relatively high T_g and AsH_3/III flow. For instance, Fig. 1 shows that using Hy at $T_g=650^\circ\text{C}$ and $\text{AsH}_3/\text{III}=44$, an N incorporation of 0.7% is obtained at $\text{Hy}/\text{III}=32$. This composition has a corresponding band gap of 1.29 eV. In contrast, at the same T_g and AsH_3/III using DMHy, only 0.3% N incorporation was observed even with $\text{DMHy}/\text{III}=570$. To obtain increased N incorporation with DMHy without raising the DMHy flow, it is necessary to reduce either T_g or AsH_3/III . For instance, GaNAs growth using DMHy is frequently accomplished with $T_g < 600^\circ\text{C}$ and $\text{AsH}_3/\text{III} < 10$. These conditions can have an adverse effect on the electronic properties of the material even if the material being grown is simply GaAs . In contrast, at $T_g=650^\circ\text{C}$ and $\text{AsH}_3/\text{III}=44$, high-quality GaAs is readily obtained. Therefore, the ability to grow GaInNAs at $T_g=650^\circ\text{C}$ and $\text{AsH}_3/\text{III}=44$ makes it possible to determine whether the poor minority-carrier properties observed in GaInNAs can be improved simply by raising T_g and AsH_3/III .

To test this, two solar cells were grown. One cell with a GaNAs active layer was grown under the same conditions, $T_g=650^\circ\text{C}$ and $\text{AsH}_3/\text{III}=44$, as the $E_g=1.29$ eV epilayer discussed above. Another cell was grown almost identical except that In was added to give lattice-matched GaInNAs . The device structure for these cells consists of an 0.1- μm -thick n-type GaAs emitter on a 1- μm -thick p-type GaNAs or GaInNAs base, clad on both sides by GaInP passivating layers. The measured base band gaps for both cells were 1.26 eV. For comparison, a third cell was grown with a structure identical to that of the preceding two, except that the base is GaAs rather than GaNAs or GaInNAs .

The measured quantum efficiencies and illuminated current-voltage (IV) curves for these devices are shown in Fig. 2. Calculated IV curves for ideal GaAs and 1.26-eV Ga(In)NAs cells are also shown for comparison. The figure shows that the Ga(In)NAs cells have poor quantum efficiencies and voltages, as is observed consistently for cells made from Ga(In)NAs . In contrast, the GaAs cell grown under the same conditions of T_g and AsH_3/III has near-ideal characteristics. This comparison confirms that the poor characteristics of the nitrogen-containing material are not caused simply by the T_g and AsH_3/III growth conditions.

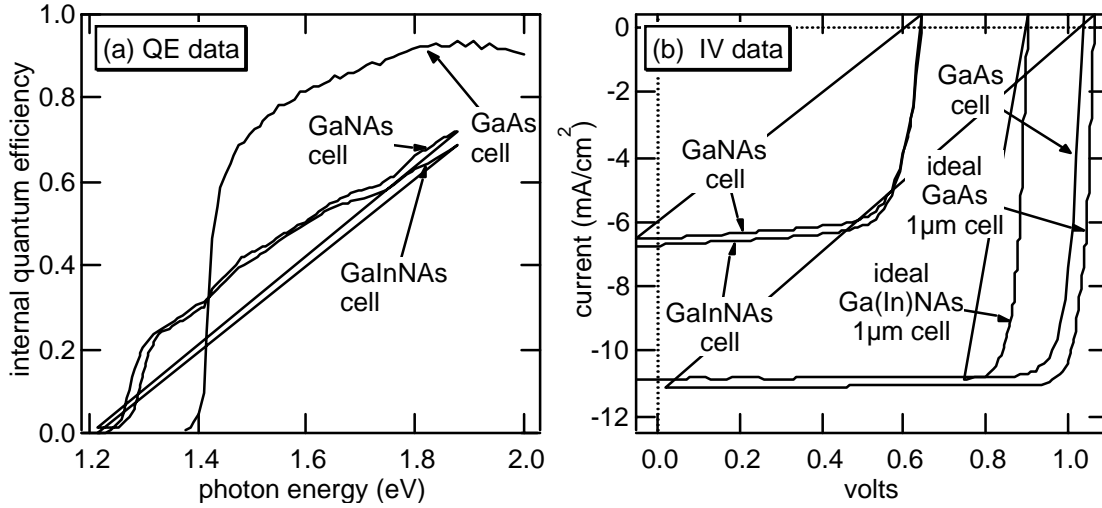


Fig. 2. (a) Internal quantum efficiencies for GaInNAs, GaNAs, and GaAs cells with 1- μ m-thick bases. Except for the composition of the active layers, the designs and growth conditions for these cells are virtually identical. The active layers were grown at $T_g=650^\circ\text{C}$ with $\text{AsH}_3/\text{III}=44$. (b) Current-voltage curves of the cells of panel (a), measured for the AM1.5 direct spectrum. The short-circuit current was set to the current obtained by integrating the external QE against the AM1.5 direct spectrum from the cell bandgap to 0.6 eV above the bandgap. Thus the currents shown are for devices without an antireflection coat. Calculated IV curves for ideal GaAs (1.41 eV) and GaInNAs (1.26 eV) cells are shown for comparison.

Background Carrier Concentration

Figure 3 compares the background carrier concentration for GaNAs epilayers grown with DMHy and Hy as a function of band gap / N concentration. The p-type background doping does not appear significantly lower than with DMHy, an unexpected result considering the presence of carbon in Hy and its absence in DMHy. (It should be noted that purification of the Hy source material, which was not performed for the present data set, could result in lower background concentrations).

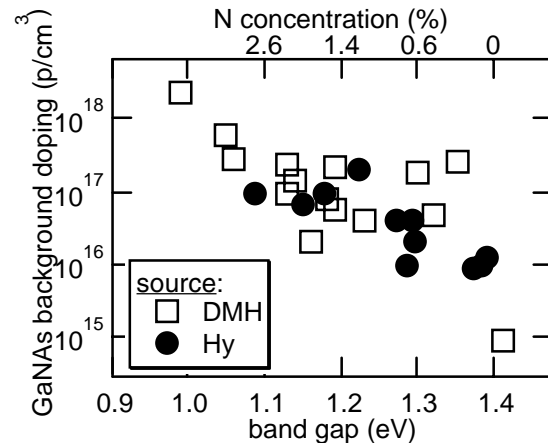


Fig. 3. Background carrier concentration for GaNAs and GaInNAs epilayers grown with DMHy and Hy, as a function of band gap (or N concentration). Carrier concentrations were measured by CV.

(sample ID)	source	
	DMHy	Hy
T_g	580°C	550°C
E_g (eV)	1.110	1.088
holes/ cm^3	2×10^{17}	8×10^{16}
carbon/ cm^3	1×10^{17}	2×10^{17}

Table I. Carbon concentration measured by SIMS vs hole concentration measured by CV for $\text{Ga}_{0.94}\text{In}_{0.06}\text{N}_{0.02}\text{As}_{0.98}$ epilayers grown with DMHy and Hy.

The metallurgical carbon concentrations for GaInNAs epilayers grown with DMHy and Hy are shown in Table I. The carbon concentration for the layer grown with Hy is comparable to that for the DMHy-grown layer. It is interesting to note that the carbon and hole concentrations are not proportional, suggesting that the carbon may not be directly responsible for the background

doping (although the uncertainties in the SIMS and CV measurements are too great for this conclusion to be drawn firmly).

CONCLUSIONS

Hy is a useful alternative to DMHy as an N precursor in the growth of GaNAs. The N incorporation is one to two orders of magnitude higher with Hy than with DMHy. In addition to the consequential advantage of better source utilization, the higher incorporation makes convenient the growth of GaNAs at the relatively high growth temperature of 650°C and AsH₃/III flow ratio of 44. Comparison of GaAs and GaNAs solar cells grown under these conditions confirmed that the poor minority-carrier properties of the GaNAs cannot be ascribed simply to the low T_g and AsH₃/III growth conditions frequently used for the growth of this material. Finally, even though DMHy has carbon in its structure while Hy does not, no significant differences in the p-type background doping for the as-grown material were observed for the Hy source compared to the DMHy source.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy under Contract No. DE-AC36-98-GO10337. Portions of the work were financially supported by TECSTAR Inc. under contract no. FIA-98-1442.

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1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE May 1999		3. REPORT TYPE AND DATES COVERED Conference Paper
4. TITLE AND SUBTITLE Hydrazine N Source for Growth of GaInNAs for Solar Cells				5. FUNDING NUMBERS C: TA: PV904401
6. AUTHOR(S) D.J. Friedman, J.F. Geisz, S.R. Kurtz, A.G. Norman, and Y.C.M. Yeh				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) National Renewable Energy Laboratory 1617 Cole Blvd. Golden, CO 80401-3393				8. PERFORMING ORGANIZATION REPORT NUMBER
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)				10. SPONSORING/MONITORING AGENCY REPORT NUMBER CP-520-26609
11. SUPPLEMENTARY NOTES				
12a. DISTRIBUTION/AVAILABILITY STATEMENT National Technical Information Service U.S. Department of Commerce 5285 Port Royal Road Springfield, VA 22161				12b. DISTRIBUTION CODE
13. ABSTRACT (<i>Maximum 200 words</i>) We evaluate hydrazine (Hy) as a nitrogen precursor source for the growth of GaNAs and GaInNAs for application in 1-eV solar cells lattice-matched to GaAs, and compare it to the more commonly used dimethylhydrazine (DMHy). The incorporation efficiency of N into the GaNAs alloy is found to be one to two orders of magnitude higher with Hy than with DMHy. This high N incorporation makes convenient the growth of GaNAs at higher growth temperatures, $T_g=650^\circ\text{C}$, and arsine flows, $\text{AsH}_3/\text{III}=44$, than are generally possible with the use of DMHy. GaInNAs and GaNAs solar cells are grown under these growth conditions and compared to a GaAs cell grown under the same conditions to determine the extent to which the poor minority-carrier properties routinely observed for the N-containing material can be attributed to the growth conditions. Finally, the background carrier concentrations for Hy- and DMHy-grown material are compared, and little difference is found between the two sources..				
14. SUBJECT TERMS photovoltaics ; solar cells ; hydrazine ; GaNAs ; GaInNAs ;				15. NUMBER OF PAGES
17. SECURITY CLASSIFICATION OF REPORT Unclassified		18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified		19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified
16. PRICE CODE				