SAND99-2465C

THE GROWTH OF InGaAsN FOR HIGH EFFICIENCY SOLAR CELLS BY METALORGANIC CHEMICAL VAPOR DEPOSITION

A. A. Allerman, Steven R. Kurtz, E. D. Jones, J.M. Gee,
J. C. Banks and A. Climent-font[1]
Sandia National Laboratories
Albuquerque, NM 87185-0603

ABSTRACT

InGaAsN alloys are a promising material for increasing the efficiency of multi-junction solar cells now used for satellite power systems. However, the growth of these dilute N containing alloys has been challenging with further improvements in material quality needed before the solar cell higher efficiencies are realized. Nitrogen/V ratios exceeding 0.981 resulted in lower N incorporation and poor surface morphologies. The growth rate was found to depend on not only the total group III transport for a fixed N/V ratio but also on the N/V ratio. Carbon tetrachloride and dimethylzinc were effective for p-type doping. Disilane was not an effective n-type dopant while SiCl4 did result in n-type material but only a narrow range of electron concentrations (2-5e17cm^{-3}) were achieved.

INTRODUCTION

InGaAsN alloys are being developed for high efficiency multi-junction tandem solar cells for satellite power systems. Models indicate that record efficiencies (≈ 38-40%) would be obtained for tandem cells where a 1.05eV bandgap cell is added in series to proven InGaP-GaAs tandem structures.[1] The $In_xGa_{1-x}As_{1-y}N_y$ alloy system appears ideal for this application. Bandgaps less than 1.0eV are obtained for $In_xGa_{1-x}As_{1-y}N_y$ alloys with minimal N concentrations ($y \approx 0.02$).[2,3] However, the addition of N even at these low concentrations results in a serious degradation of minority carrier lifetime. It remains a challenge to grow $In_xGa_{1-x}As_{1-y}N_y$ alloys with sufficient quality to realize the projected improvements in solar cell efficiency.[4,5] In this paper we describe the growth and material properties of $In_xGa_{1-x}As_{1-y}N_y$ ($y < 0.03$) alloys grown by MOCVD.

---

1. Now at Universidad Autónoma de Madrid, Cantoblanco, E-28049 Madrid, Spain.

DISCLAIMER

EXPERIMENTAL

The material in this work was grown in a vertical flow, high speed rotating disk, Emcore GS/3200 MOCVD reactor. $In_xGa_{1-x}As_{1-y}N_y$ films were grown using trimethylindium (TMIn), trimethylgallium (TMG), 100% arsine and dimethylhydrazine (DMHy). N-type material was achieved using silicon tetrachloride ($SiCl_4$) and carbon tetrachloride (CCl_4) was used to dope films p-type. Disilane (Si_2H_6) was also investigated as an n-type dopant. The V/III ratio ranged between 50 to 150 and the growth rate between 6 and 20Å/sec. All samples were grown at 60torr and at 600°C or 610°C with hydrogen as the carrier gas. Room temperature Hall measurements were made to determine the carrier concentration and mobility. Photoluminescence (PL) at 300K was used to determine the bandgap.

Indium composition of the quaternary alloy was determined from using the Group III composition obtained from calibration growths of InGaAs. The nitrogen composition was then determined from double crystal x-ray diffraction measurements of the alloy. The indium and nitrogen compositions were also confirmed from Rutherford Backscattering Spectroscopy (RBS) and Elastic Recoil Detection (ERD) measurements respectively. RBS measurements of the In composition showed the it to be 1 to 2 atomic percent higher than that expected from the In/III gas phase ratio. The indium compositions reported in this work are based on In/III gas phase ratio.

RESULTS

A significant increase in photoluminescence intensity was observed from InGaAsN films following a post-growth anneal[6] (Fig. 1). Anneals were carried out in a rapid thermal anneal system under nitrogen using a sacrificial GaAs wafer in close proximity to the InGaAsN sample. The PL intensity was a maximum for samples annealed for either 700°C for 2 minutes or 650°C for 30 minutes. Longer times at higher temperatures resulted in lower PL intensities. Without annealing, little band edge luminescence was observed at 300K and only a broad, low energy band was present. After annealing, band edge luminescence was observed at 300K and the emission from the low energy band was noticeably reduced. All samples reported in this work were annealed at 650°C for 30 minutes. This thermal annealing process also increased the internal quantum efficiency of solar devices by a factor of 5.[5]

High DMHy/V ratios (0.90< N/V<0.98) were required to incorporate nitrogen (Fig. 2). In general, higher N/V ratios resulted in increased N incorporation as indicated by the shift in lattice mis-match and the longer PL emission wavelengths. However, for N/V ratios exceeding 0.981 the nitrogen incorporation decreased rapidly and surface morphology degraded. The low partial pressure of AsH_3 in the gas phase for the highest N/V ratios used results in the surface decomposing and roughening.

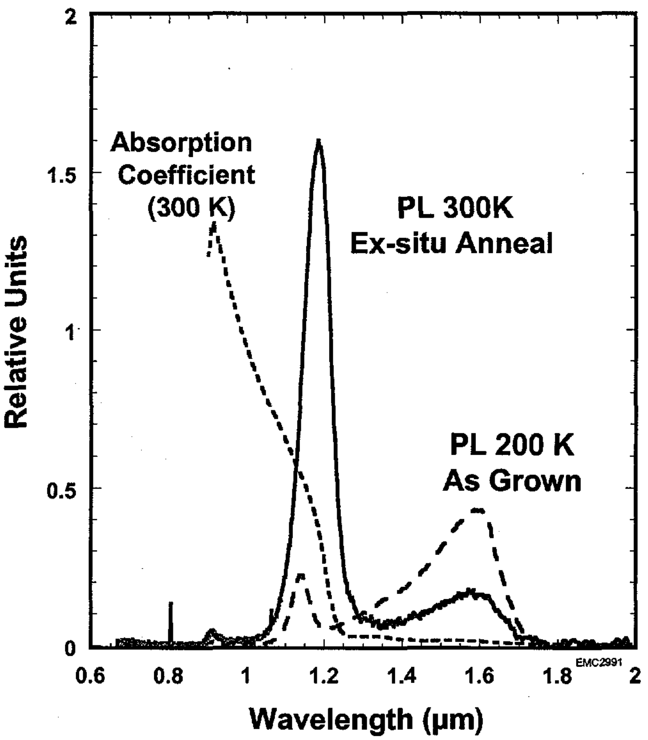

Figure 1. Post growth or "ex-situ" thermal annealing significantly increased the band edge photoluminescence and reduced the broad, low energy peak.

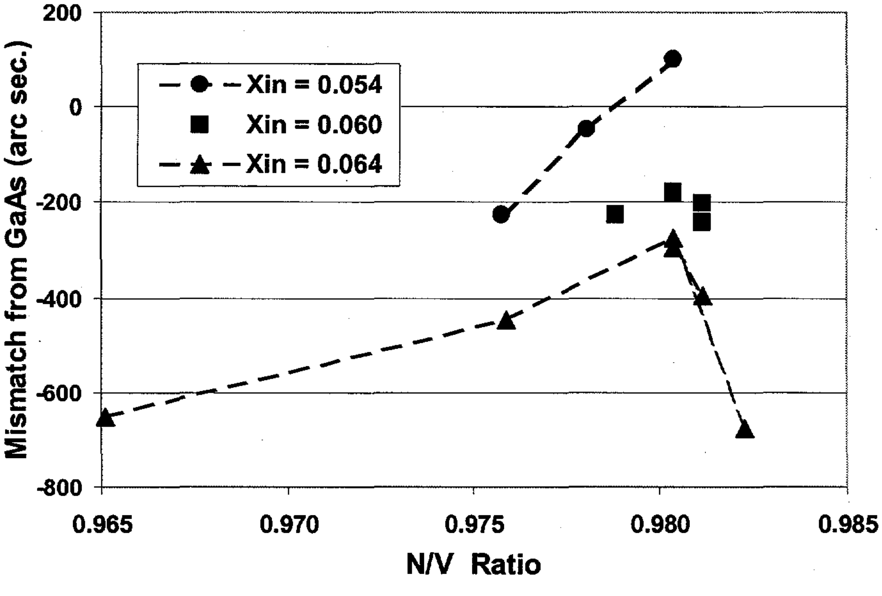

Figure 2. The lattice mismatch from GaAs measured by x-ray diffraction of InGaAsN alloys grown with different N/V ratios are shown. The Group III flux was held constant for each set of constant indium composition. The nitrogen composition of samples plotted ranged from <0.01 to 0.022 depending on the In composition.

All unintentionally doped films measured were p-type with hole concentrations from the 1 to 5e17cm^{-3} with mobility ranging from 55 to 80 cm^2/V/sec. No correlation in mobility with N/V ratio was observed in the "as grown" films. However, following the post-growth anneal, the hole concentration increased significantly and ranged from 9e17 to 1.3e18 cm^{-3} as the N/V ratio increased. The hole mobility was similar to that of the as grown samples. It is believed that the post-growth anneal is activating background carbon by driving off passivating hydrogen. Sufficiently high concentrations of carbon have been measured by Secondary Ion Mass Spectrometry (SIMS) to account for the hole concentration following annealing. The change in hole concentration suggests that carbon incorporation is enhanced at higher N/V ratios. Thus, growth conditions under lower N/V ratios would be desirable for photovoltaic devices as less carbon will be incorporated with higher AsH_3 flows.

As shown in Figure 3a, the growth rate depends on the total group III flux when the group V transport is fixed as is typical of III-V compound semiconductors. However, the growth rate has also been found to depend on the N/V ratio. (Fig. 3b) Lower N/V ratio's result in higher growth rates regardless of whether the AsH_3 flow is increased or the DMHy flux is decreased. Considering the large excess of DMHy, changes in this flow could be perturbing the gas flow in the chamber resulting in the observed change in growth rate. However, similar changes in growth rate are effected by small changes in the AsH_3 flow which would not be expected to alter gas flow. It is likely that some parasitic gas phase reaction with the DMHy is occurring though site blocking arguments can not be ruled out.

P-type doping was readily achieved with CCl_4 and DMZn. (Fig. 4) Hole concentrations to 9e17 cm^{-3} were achieved in C doped films before post growth annealing. Higher doping levels were not investigated since they would not be of interest for photovoltaic devices. Similar hole concentrations could be obtained using DMZn. Measurements of the Zn concentration by SIMS was consistent with the hole concentration. Following post growth anneals, the hole concentrations in both Zn and C doped material increased significantly as the passivated background carbon is activated. The carbon concentration as measured by SIMS was again sufficiently high enough to account for the increased hole concentration. As with the unintentionally doped alloys, hole mobility was low in both C and Zn doped films and ranged between 56 to 93 cm^2/V/s. Again, no significant change in mobility with post growth annealing was observed.

Alloy composition did not change with DMZn doping. However, both the lattice mis-match and bandgap changed with CCl_4 doping level. As the CCl_4 concentration increased, the x-ray diffraction peak moved in the $+\omega$ direction and the bandgap decreased. Though higher incorporation levels of nitrogen would have this same effect it is more plausible that the group III composition was altered by preferential etching of either In or Ga which would also in turn effect the nitrogen incorporation.

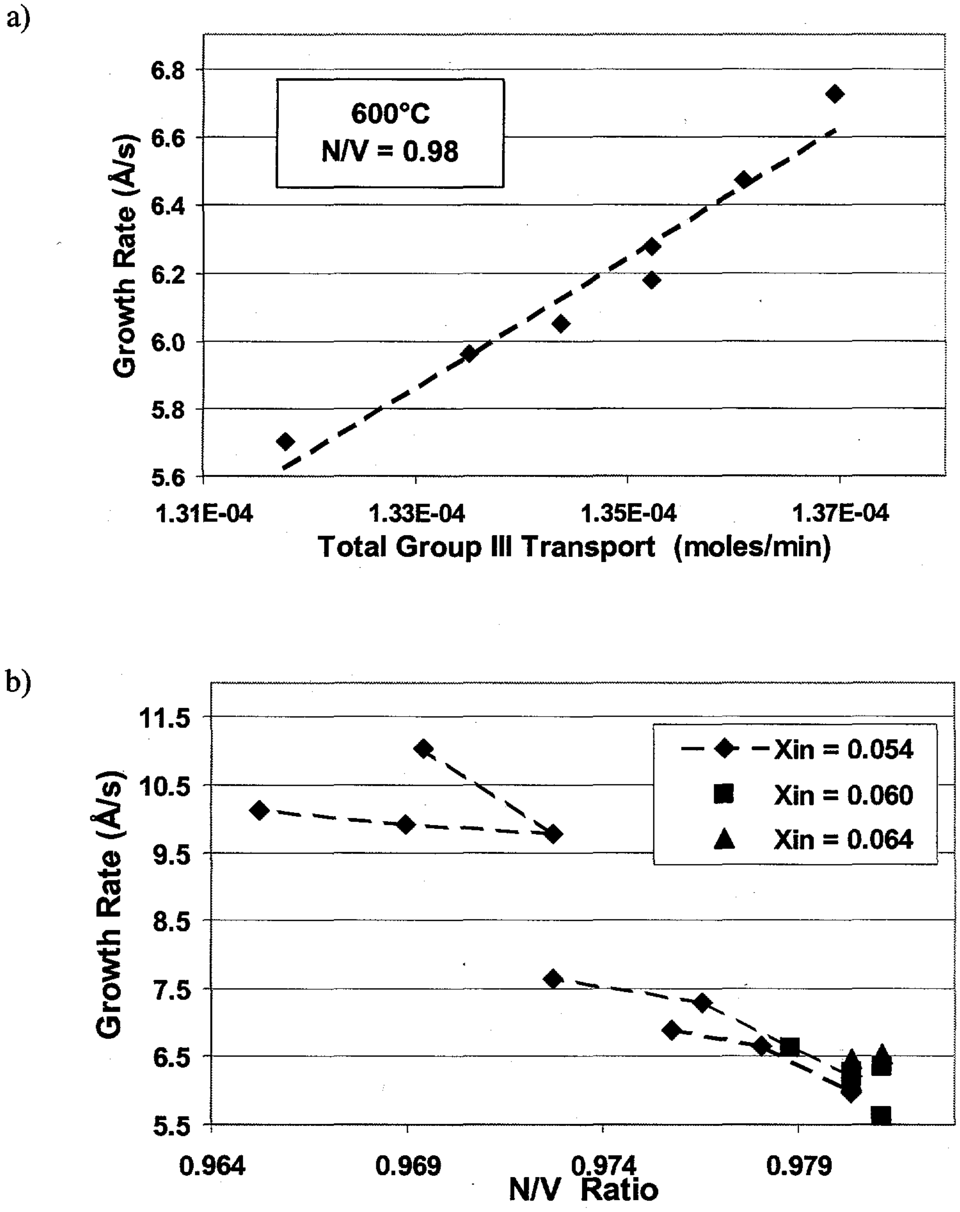

Figure 3. (a) The growth rate of InGaAsN alloys depend on the total group III transport for a fixed N/V ratio. (b) Unlike most III-V compound semiconductors, the growth rate also depends on mass transport of the either group V element.

N-type doping has been more difficult to control. For alloy compositions approximately 2% N and 7% In, only p-type or heavily compensated material was obtained using disilane (Si_2H_6). SIMS analysis of a such a sample showed a Si concentration of 2.4e18cm^{-3} even though the as grown material was p-type with a hole concentration of 3e17cm^{-3}. The C concentration measured by SIMS (8e17cm^{-3}) was clearly less than Si indicating that Si is either largely interstitial or self compensating under this growth condition. Also, poor surface morphologies typically resulted from attempts to use disilane for these conditions. Good surface morphology and n-type material was obtained for disilane doped alloys with approximately 1% N and 3% In. The effectiveness of disilane was found to be strongly dependent on growth conditions.

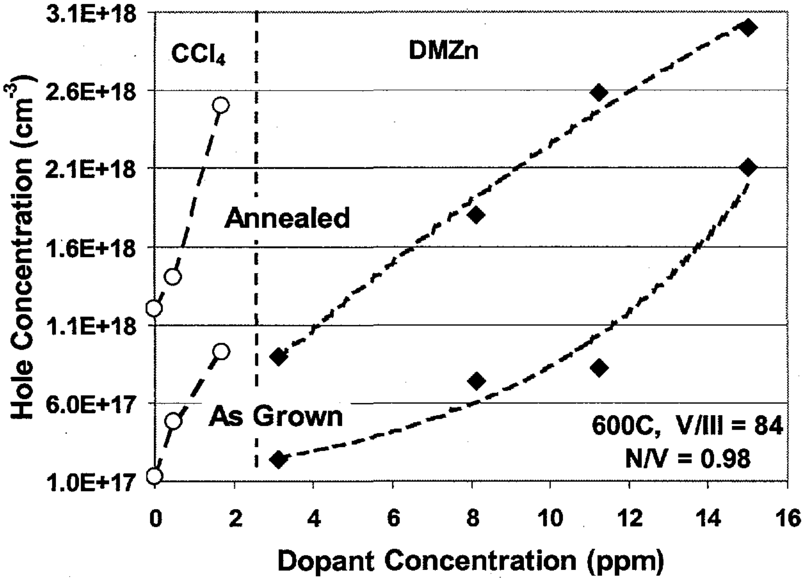

Figure 4. P-type doping was achieved with CCl_4 and DMZn. However, samples doped with increasing levels of CCl_4 shifted composition where as DMZn doped samples did not.

Silicon tertrachloride ($SiCl_4$) was successfully used to obtain n-type material with a 1.05eV bandgap. Electron concentrations from 2 to 5e17 cm^{-3} and hole mobilities between 150 to 250 cm^2/V/sec were measured in as grown material. Thermal annealing reduced the electron concentration to the 5 to 9e16cm^{-3} as the residual carbon was activated. Only a narrow range of electron concentration could be obtained as higher $SiCl_4$ flows resulted in lower carrier concentrations and poor surface morphology. The composition was also found to change with increasing $SiCl_4$ flows similar to that observed when doping with CCl_4. A SIMS measurement shows that Si (2.5e18cm^{-3}) is incorporating at a level similar to that measured for disilane. The low resulting electron concentration and C levels at 7e17cm^{-3} again suggest problems with Si incorporating as an n-type dopant under the growth conditions used in this work.

ACKNOWLEDGEMENTS

The authors thank T.W. Hargett and B.E. Hammons for technical support. Sandia is a multiprogram laboratory operated by Sandia Corporation, managed by Lockheed Martin Company, for the U.S. Dept. of Energy under contract DE-AC04-94AL85000. Additional funding was provided by Air Force Research Laboratory and Lockheed Martin Missile and Space.

REFERENCES

1. Sarah R. Kurtz, D. Myers, and J. M. Olsen, Proc. 26th IEEE Photovoltaics Spec. Conf., 875 (1997).
2. M. Weyers, M. Sato, and H. Ando, Jpn. J. Appl Phys. 31, 853 (1992).
3. S. Sato, Y. Osawa, and T. Saitoh, Jpn. J. Appl. Phys. 36, 2671 (1997).
4. J.F. Geisz, D.J. Friedman, J.M. Olson, S.R. Kurtz and B.M. Keys, J. Crys. Growth, 195 401 (1998)
5. Steven R. Kurtz, A.A. Allerman, E.D. Jones, J.M. Gee, J.J. Banas, and B.E. Hammons, appl. Phys. Lett. 74, 729 (1999).
6. E. V. K. Rao, A. Ougazzaden, Y. Le Bellego, and M. Juhel, Appl . Phys. Lett. 72, 1409 (1998).

KEY WORDS: InGaAsN, MOCVD, Metalorganic Chemical Vapor Deposition,
solar cells, photovoltaics