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Novel InGaAsN pn Junction for High-Efficiency Multiple-Junction Solar Cells

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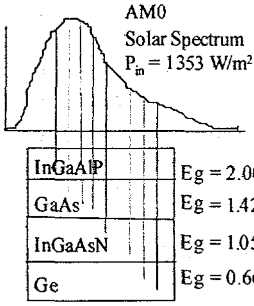
ABSTRACT

We report the application of a novel material, InGaAsN, with bandgap energy of 1.05 eV as a junction in an InGaP/GaAs/InGaAsN/Ge 4-junction design. Results of the growth and structural, optical, and electrical properties were demonstrated, showing the promising perspective of this material for ultra high efficiency solar cells. Photovoltaic properties of an as-grown pn diode structure and improvement through post growth annealing were also discussed.

INTRODUCTION

High efficiency solar cells are very important for use in space power systems. Increased solar cell efficiency results in reduced satellite mass and launch cost, and increased payload and satellite mission life. Current state-of-the-art design includes InGaP (bandgap energy Eg~1.85 eV) and GaAs (Eg=1.42 eV) junctions interconnected by a quantum tunnel junction grown on either GaAs or Ge substrates.[1] A proper epitaxial growth process can make the Ge (Eg=0.67 eV) junction active, yielding the third junction. It was demonstrated that the air mass 0 (AM0) efficiency from InGaP/GaAs tandem-junction solar cells is ~25-27% [2,3] in laboratories and ~22-24% in production.[4] However, there is a major loss mechanism inherent to the material combination of this tandem junction design. The large energy difference between the bandgaps of Ge and GaAs, ~0.75 eV, results in a significant amount of super-bandgap energy loss in the form of heat. Solar photons of energy hν absorbed in the solar cell layers with bandgap Eg result in an energy loss of hν-Eg. This loss can be minimized through the use of a material having a bandgap between those of Ge and GaAs. For example, a material with bandgap of ~1 eV and lattice-matched to GaAs would be suitable.[5] Attempts have been made to circumvent this super-bandgap loss in the Ge cell of the 3-junction InGaP/GaAs/Ge cell design or sub-bandgap loss in an InGaP/GaAs dual-junction design by introducing a material with bandgap energy of ~1.05 eV, such as strain-relaxed InGaAs,[6] $ZnGeAs_2$,[7] TI compound, and wafer bond InGaAsP junction grown on InP to GaAs substrates where the InGaP/GaAs junctions were grown.[8] However, all these efforts have failed to produce high enough quality materials for this application to date. We elected to use an $In_xGa_{1-x}As_yN_{1-y}$ compound for this application.[9] With this design, a four-junction InGaP/GaAs/InGaAsN/Ge cascade solar cell will give a theoretical AM0 efficiency of ~41%. If the top junction InGaP material is replaced with a Eg ~ 2 eV quaternary InGaAlP, lattice-matched to GaAs, the top junction can be made infinitely thick optically unlike the current design where the top junction has to be thinned to achieve current-matching.[10] Assuming infinite optical thickness for solar cell junctions and ideal characteristics for all the junctions, the AM0 efficiency could theoretically be as high as 42.3%. Projected values for individual solar cell junction open-circuit voltage (V_{oc}), short-circuit current (I_{sc}), fill factor (FF), and efficiency (EFF) are shown in Figure 1.



	Eg	Voc (V)	Isc (mA/cm^2)	FF	EFF
InGaAlP	Eg = 2.00eV	1.59	18.6	0.918	0.201
GaAs	Eg = 1.42eV	1.02	18.6	0.884	0.124
InGaAsN	Eg = 1.05eV	0.64	18.6	0.835	0.074
Ge	Eg = 0.66eV	0.25	18.6	0.689	0.024
					0.423

Fig. 1 Calculated photovoltaic properties of a 4-junction solar cell using InGaAsN materials

Material Growth

$In_xGa_{1-x}As_yN_{1-y}$ was first proposed by Kondow *et al.* for quantum well lasers at ~1.3 μm wavelength for fiber-optic communications.[11] Due to the large electronegativity of the N atom, the bandgap of the InGaAsN has a large bowing factor, leading to an energy in the range of 0 to 1.42 eV theoretically while still maintaining a lattice constant which is the same as that of GaAs. The large conduction band offset of InGaAsN/GaAs quantum wells provides a better carrier confinement for uncooled lasers for high-bandwidth local network access. For the multi-junction solar cell application, the N composition needed to achieve a bandgap energy of 1.05 eV is about 2.3%, and the lattice matching condition to GaAs requires the In composition of ~ 7%.

The growth was carried out in an Emcore metalorganic chemical vapor deposition (MOCVD) rotating disk reactor. The precursors used for InGaAsN are trimethylindium, trimethylgallium, arsine, and asymmetric dimethylhydrazine (DMHy) for In, Ga, As, and N, respectively. The DMHy bubbler was set at 18 °C and 300 torr. The growth temperature ranged from 500 to 650 °C, and growth pressure was 60 torr. The growth rate ranged from 0.5 to 1.5 nm/s. The N incorporation is difficult and depends strongly on the growth temperature, being much lower at a higher growth temperature. The molar ratio of N/(As+N) was from 0.8 to 0.95.[12] We were able to obtain nitrogen composition of up to 5% in $GaAs_{1-y}N_y$. However, the addition of indium reduces the N incorporation in the compound significantly.

Material and Device Characterizations

In the work published previously, this material was used as a thin quantum well active layer for lasers.[11,12] The lattice matching condition is not as critical as with solar cells where the total thickness for a junction is typically in the order of ~3 μm. When the compositions of $In_xGa_{1-x}As_{1-y}N_y$ are properly selected (x~3y), this material can be lattice-matched to GaAs or Ge substrates. The lattice-matching condition has to be excellent to keep the whole junction within the critical layer thickness. We have been able to reproducibly achieve lattice-matching growth of this material on GaAs substrates with a thickness adequate for a homojunction application in the solar cell. Figure 2 shows the x-ray rocking curve from a ~ 450-nm thick $In_{0.023}Ga_{0.977}As_{0.93}N_{0.07}$ epilayer grown on a GaAs substrate. Excellent lattice matching condition to the GaAs substrate is obtained. The clearly resolved Pendellosung fringes indicate good crystalline quality.

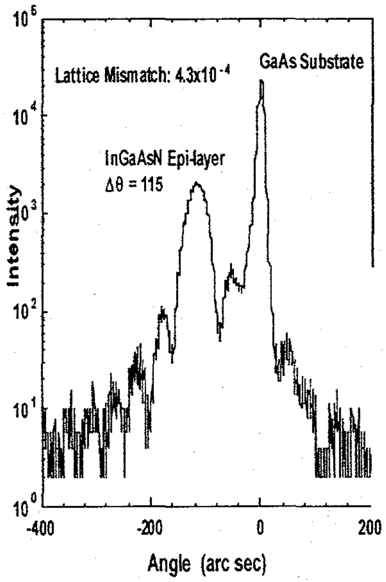


Fig. 2 X-ray rocking curve from a lattice-matched $In_{0.023}Ga_{0.977}As_{0.93}N_{0.07}$ epilayer on GaAs substrates

The lattice constant and bandgap energy for this quaternary can be adjusted independently. The composition combination has to be adjusted so that the material is lattice matched to GaAs and provides a bandgap as designed. In order to obtain a N composition for an appropriate bandgap energy, InGaAsN has to be grown at a lower temperature (<600

°C), but the optical quality as characterized by photoluminescence (PL) and time-resolved PL measurements is poor. We developed a two-step process, namely low-temperature growth (~550 °C) followed by an *in situ* anneal at high temperature (~750 °C). As a result, improvement of PL intensity by 2 orders of magnitude was achieved. Figure 3 shows absorption spectra from two InGaAsN epilayers grown with different conditions. A sharp absorption edge at 1.05 eV with no sub-bandgap impurity states was obtained with the *in situ* anneal MOCVD growth process.

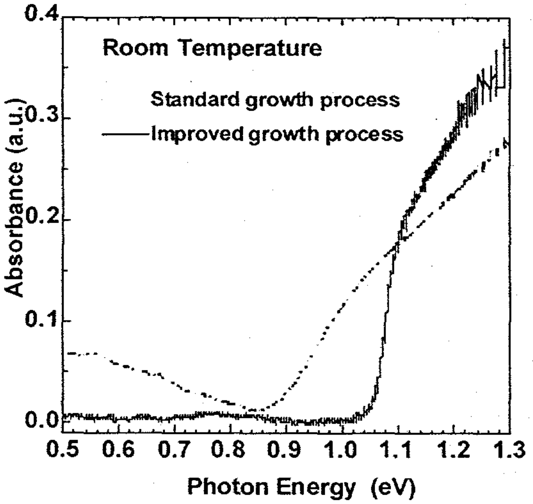


Fig. 3 Room temperature absorption spectra from InGaAsN layers. The layer grown at higher temperature and with an *in situ* annealing shows sharp absorption edge at 1.05 eV.

Both n- and p-doping are needed in the compound to form a p-n junction. We found that the disilane, a common n-type doping precursor, does not dope efficiently in InGaAsN at low growth temperatures (~550 °C), while the diethyltellurium was found to pre-react with dimethylhydrizine. An alternative dopant precursor is $SiCl_4$ which cracks very efficiently at a low temperature. Carbon from CCl_4 is found to be a good p-type dopant, and the free carrier concentration of up to 1×10^{19} cm^{-3} has been obtained. Figure 4 shows the forward I-V characteristics for an InGaAsN pn diode. Excellent characteristics were obtained with a low leakage current I_0 (~1 μA/cm^2) and a good ideality factor of 1.25.

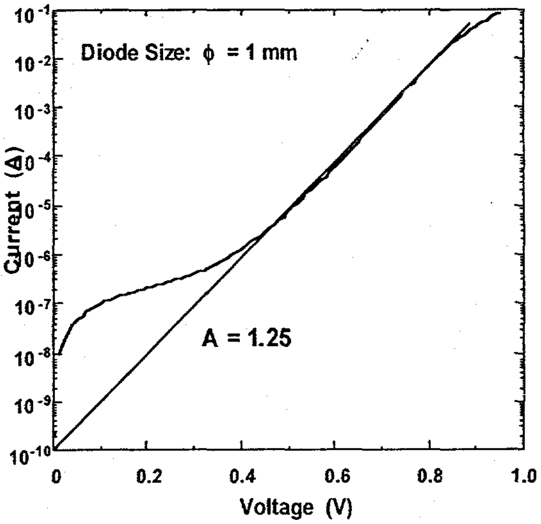


Fig. 4 Forward I-V characteristics of the InGaAsN pn junction. The diode ideality factor is 1.25.

The InGaAsN pn junction was examined for its photovoltaic properties using an X25 solar simulator. The 1.05-eV bandgap homojunction consists of a 300-nm thick $3x10^{18}cm^{-3}$ p-type layer doped with C and 800-nm thick $6x10^{16}cm^{-3}$ n-type layer doped with Si. The structure was capped with a 200-nm thick GaAs window layer. Figure 5 shows the IV curve of a 1x1 cm^2 solar cell under X25 illumination. The open-circuit voltage of is measured ~0.47 V. However the short-circuit current is low, being ~4.5 mA/cm^2. Furthermore, the photocurrent from this cell was found to be dependent on the reverse bias voltage applied to the diode significantly. This behavior was also observed by Freidman *et al.*,[13] and has attributed to the short diffusion length (< 0.4 μm). Only the carriers in the depletion region can be collected which results in a low internal quantum efficiency in the range of ~25%.

We have performed deep-level transient spectroscopy (DLTS) measurements for the p-n junction with 300 nm thick p-type doped (2×10^{18} cm^{-3}) and 3-?m thick n-type (1×10^{17} cm^{-3}). Four deep levels with energies of 60, 130, 290, and 370 meV below the conduction band were revealed. The trap density was as high as 7.5×10^{15} cm^{-3}.[14] The cause of these deep levels is currently under investigation. They may be related to the N-H bonds in the compound from incomplete cracking of DMHy or impurities in the DMHy precrsor. It was recently reported by Allerman *et al.*[15] that the deep level density was reduced by a factor of 40 through post growth annealing, either inside or outside the growth chamber. The thermally unstable level at 60 meV below conduction band disappeared. The internal quantum efficiency increased from 25% to 60%, and the minority carrier diffusion length increased from 0.4 to 1.1 μm. As a result, the photocurrent does not change with the reverse bias on the solar cell. The short-circuit current increased by a factor of 4 after annealing at 600 °C for 30 min in a N_2 ambient.

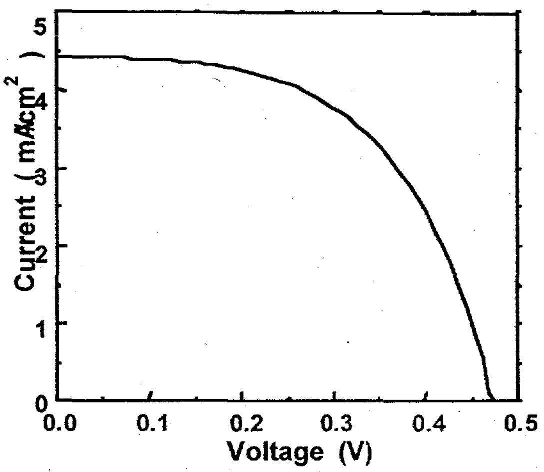


Fig. 5. The light I-V characteristics of an InGaAsN pn junction. The short-circuit current and open-circuit voltage for this 1x1 cm^2 device are 4.5 mA/cm^2 and 0.47 V, respectively.

Conclusion

In conclusion, we demonstrated that InGaAsN is a promising material for high-efficiency multi-junction solar cells. Lattice-matched InGaAsN with bandgap energy of ~1.05 eV can be reproducibly grown on GaAs substrates using dimethylhydrazine as N precursors by MOCVD. Structural, optical and electrical properties were characterized, and an open-circuit voltage of ~0.47 V was achieved. However, the short-circuit current was low due to the short carrier diffusion length. The material and device properties were improved by *in situ* and post-growth annealing, and yet, further improvement for the InGaAsN material is needed for achieving high efficiency four-junction solar cells. Work at Sandia is supported by the US DOE under contact No. DE-AC04-94AL85000 and by the US Air Force Research Laboratory.

References

[1]. J. M. Olson, S. R. Kurtz, A. E. Kibbler, and P. Faine, Conf. Rec. 21st IEEE Photovoltaic Specialists Conference -1990, p.24.

[2]. K. A. Bertness, S. R. Kurtz, D. J. Friedman, A. E. Kibbler, C. Kramer, and J. M. Olsen, *Appl. Phys. Lett.* **65**, 989 (1994).

[3]. T. Takamoto, E. Ikeda, H. Kurita, M. Ohmori, M. Yamaguchi, and M. J. Yang, *Jpn. J. Appl. Phys.* **36**, 6215 (1997).

[4]. P. K. Chiang et al., First World Conf. On Photovoltaic Energy Conversion, 1994, pp. 2120-2123.

[5]. S. R. Kurtz, D. Myers, J. M. Olson, Conf. Rec. 26th IEEE Photovoltaic Specialists Conference -1997, p. 875.

[6]. B. -C. Chung, G. F. Virshup, J. C. Shultz, Conf. Rec. 21st IEEE Photovoltaic Specialists Conference -1990, p. 179.

[7]. M. L. Timmons, private communications.

[8]. P. R. Sharps, M. L. Timmons, J. S. Hills, J. L. Gray, Conf. Rec. 26 IEEE Photovoltaic Specialists Conference -1997, p. 895.

[9]. H. Q. Hou and K. C. Reinhardt, US Patent Disclosure SD6087S89237, June, 1997.

[10]. S. R. Kurtz, P. Faine, and J. M. Olson, J. Appl. Phys., **68**, 1890 (1990).

[11]. M. Kondow, K. Uomi, A. Niwa, T. Kitatani, S. Watahiki, Y. Yazawa, *Jpn. J. Appl. Phys.* **35**, 1273 (1996).

[12]. S. Sato, Y. Osawa, T. Saitoh, *Jpn. J. Appl. Phys.* **36**, 2671 (1997).

[13]. D. J. Freidman, J. F. Geisz, S. R. Kurtz, and J. M. Olson, *J. Cryst. Growth*, (to be published).

[14]. R. J. Kapler, S. A. Ringel, H. Q. Hou and B. E. Hammons, *Proc. Electron. Mater. Conf.* June 1998, Charlesville, VA.

[15]. A. A. Allerman, S. R. Kurtz, J. M. Gee, H. Q. Hou, and B. E. Hammons, *Appl. Phys. Lett.* (submitted).

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