

DEVELOPMENT AND OPTIMIZATION OF A 1 eV (GaIn)(NAs) SOLAR CELL

K. Volz*, A. Szesney, C. Jurecka, I. Nemeth, O. Rubel, W. Stolz

Material Sciences Center and Faculty of Physics, Philipps University, Hans Meerwein Str, 35032 Marburg, Germany

E. Welser, E. Oliva, F. Dimroth, A.W. Bett

Fraunhofer Institute for Solar Energy Systems, 79110 Freiburg, Germany

*kerstin.volz@physik.uni-marburg.de

ABSTRACT

(GaIn)(NAs) lattice matched to GaAs and Ge and having a 1 eV bandgap is a promising candidate for future space and terrestrial multi-junction solar cell structures. The present paper summarizes results of structural and optical characteristics of this metastable material system. It is shown, that photoluminescence (PL) intensity can be taken as a measure of improving minority carrier characteristics in solar cell devices. A direct correlation between PL intensity and quantum efficiency in the (GaIn)(NAs) material system is observed. Thermal annealing in this material can be used to initiate the site change of the Nitrogen atom from a Ga-rich environment upon growth to an In-rich one after annealing. In addition, the dissolution of chain-like N-ordering in [001] direction is detected. The greatly enhanced optical performance leads to an improved quantum efficiencies of the (GaIn)(NAs) solar cell material.

INTRODUCTION

Single-junction III/V solar cells have a low theoretical efficiency limit (33% under 1 sun illumination) due to the inability to properly match the sun's spectrum with a semiconductor material having a single bandgap. Stacking semiconductor materials, which have different bandgaps, one on top of each other one can increase efficiency tremendously as thermalisation and transmission losses become less important. Maximum efficiencies increase with the number of junctions, however there is a reasonable compromise between the maximum possible efficiency and the cost-intensive and complex manufacturing process. Realistic calculations, also taking losses into account, predict a maximum efficiency under an AM1.5 spectrum in the range of 40%

for a three junction stack (Ge, (InGa)As, (GaIn)P) and of 52% for a stack, where a material, having a 1eV bandgap would be introduced between the substrate and the (InGa)As [1-4].

The novel, metastable compound semiconductor system (GaIn)(NAs) would be an optimal candidate as the 1eV solar cell material [5] in these multi-junction solar cell concepts, as it can be grown lattice matched to GaAs or Ge-substrates. The composition for lattice-matched growth on GaAs is 8% Indium and 2.8% Nitrogen, respectively. Up to now, however, the short minority carrier diffusion in the devices limit the performance of such cells. Minority carrier diffusion lengths as low as 10 –20 nm have been observed [6-9]. With minority carrier diffusion lengths shorter than the depletion widths, the carrier collection in such a device is dominated by field-aided collection rather than by diffusion collection, which is common for other III/V materials [10]. This results in low short circuit currents and low quantum efficiencies of the devices. It is crucial to determine whether these short diffusion lengths are due to extrinsic, growth related defects or are an intrinsic property of this material system.

EXPERIMENTAL

All (GaIn)(NAs) double hetero bulk and solar cell structures used for this study have been grown on (001) GaAs substrates in a commercially available horizontal reactor system (AIX200) by MOVPE (metal organic vapour phase epitaxy) using hydrogen carrier gas at a low reactor pressure of 50 mbar. Due to the large difference in covalent radius between Nitrogen and Arsenic, the material system under investigation is metastable, low substrate temperatures have to be chosen in order to achieve significant N incorporation. Substrate temperatures are usually fixed to 550°C. The substrate temperatures are calibrated to the Al/Si eutectic formation

occurring at 577 °C. As a consequence of the low growth temperatures, MO sources efficiently decomposing at lower temperatures like the group V sources tertiarybutylarsine (TBAs) and the unsymmetric dimethylhydrazine (UDMH) have to be used. As group III sources, trimethylgallium (TMGa) as well as triethylgallium (TEGa) and trimethylindium (TMIn) are applied. For solar cell device structures Te (from diethyltellurium (DETe)) was used as n-type dopant and Mg (from dicyclopentadienylmagnesium (Cp_2Mg)) as p-dopant, respectively.

To reduce the defect density in the as-grown quaternary, metastable material, which dramatically influences minority carrier properties, it needs to be thermally treated at elevated temperatures after growth. These annealing procedures were varied systematically. We applied annealing steps consisting of a 5 - 120 min TBAs stabilized anneal at 700°C - 800°C and a subsequent unstabilized annealing step in H_2 -ambient at 625 - 800°C for 25 min in the MOVPE reactor.

The structural characteristics of the quaternary material in dependence on growth and annealing conditions are determined by transmission electron microscopy (TEM) and high resolution X-ray diffraction (HRXRD), the optoelectronic ones by photoluminescence (PL) spectroscopy of $(\text{GaIn})(\text{NAs})$ double hetero structures. These properties are correlated to each other as well as to solar cell performance.

For the correlation of optical and structural properties with device performance, $(\text{GaIn})(\text{NAs})$ solar cells with an area of 0.25 cm^2 and 1 cm^2 were processed. Photolithography was used to define the front grid structure of the solar cells. Ti/Pd/Ag (30/30/100 nm) contacts were evaporated sequentially and annealed at 360°C for 2 min. The backside contact was made of Ni/AuGe/Ni (12 % Ge) (10/130/10 nm). The contacts were reinforced by electroplated Au. For simplicity no anti-reflection coating was applied during processing, but the EQE results were corrected for surface reflectivity, which had been measured.

RESULTS AND DISCUSSION

$(\text{GaIn})(\text{NAs})$ composition

Dealing with a metastable quaternary system, the first thing that has to be done, is to establish the lattice matching of the bulk films to the GaAs substrate, while keeping the fundamental bandgap at 1eV as required for optimum efficiency of the solar cells. Figure 1 gives the range of In and N compositions, for which lattice matching of the quaternary alloy to GaAs is obtained (squares). These points are calculated assuming Vegards law for both, GaInAs and GaNAs , resulting in the well-known $3y \approx x$ ($y=\text{N}$, $x=\text{In}$) rule for the composition to achieve lattice matching. The other curve in this plot (dots) is received from experimental data points on a wide range of MQW and bulk samples, which all exhibit a fundamental band gap of 1eV, but at different compositions. The intersection point of these curves gives us the composition to fulfill both requirements. The growth conditions have in the

following been chosen to yield this composition of about 8% Indium and 2.8 – 3% Nitrogen; nevertheless, PL and HRXRD have been always applied to confirm that the samples are lattice matched and that the emission is centered at 1eV.

Later growth on Germanium substrates will require a slightly increased In-content in the material due to Ge's larger lattice constant than GaAs.

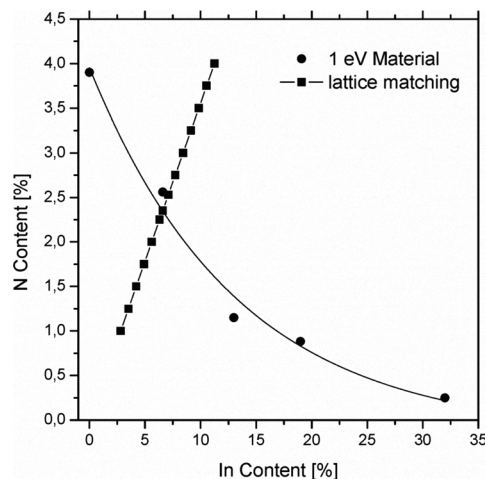


Fig. 1. Range of In and N compositions, for which lattice matching (squares) occurs and for which the samples have a fundamental band gap of 1eV (dots).

$(\text{GaIn})(\text{NAs})$ structural characteristics

From detailed considerations of strain energy as well as chemical binding energy on the surface of the growing $(\text{GaIn})(\text{NAs})$ layer as well as in the $(\text{GaIn})(\text{NAs})$ bulk after growth, inhomogeneous strain fluctuations, which are present in quaternary $(\text{GaIn})(\text{NAs})$ are attributed to chain-like Nitrogen ordering in [001]-direction as also described in [11-13]. This columnar N-ordering is an intrinsic property of dilute nitrides upon growth. The dissolution of the N-chains upon annealing is caused by the change in N-nearest-neighbour environment from a Ga-rich to an In-rich one, which is driven by a significant energy gain due to low strain energy of the In-rich configurations. This transition is mediated during the annealing by the introduction of As vacancies into the crystal. This nearest neighbour change in the N-environment is also responsible for the well-known blueshift of the fundamental bandgap of $(\text{GaIn})(\text{NAs})$, which amounts to 20 meV per one additional In nearest neighbour (i.e. 40 meV blueshift for a $2\text{In}2\text{Ga}$ configuration of N as compared to a 4Ga one). In fig. 2 several of the calculated N-nearest neighbour configurations are depicted schematically.

Tables 1 and 2 summarize the energies calculated by the valence force field method, when putting N in different configurations in $\text{Ga}(\text{NAs})$ (Table 1) and $(\text{GaIn})(\text{NAs})$ (Table 2). One finds that [011] oriented N-pairs have an even higher strain energy than two separated N-atoms in GaAs. Therefore, this configuration should not be adopted

from the crystal upon growth. In contrast to that, we find that N-ordering in [001] reduces the strain energy of the crystal by 0.10 eV as compared to putting two isolated N-atoms in GaAs. This strain energy is even further reduced, when longer [001] oriented N-chains in GaAs are formed. On the free growth surface, N will exclusively bond to Ga, as the GaN bond strength is larger than the InN bond strength. The situation however changes, when the quaternary material is embedded into GaAs as then strain arguments with respect to the substrate material start to play a more important role. The strain energies together with the differences in chemical energy and the total energy balance is summarized in Table 2. As expected, it can be seen that the strain energy of the crystal considerably decreases when putting N from a four Ga to a four In-environment. The energy gain when doing so is about 0.5 eV per additional one In-environment. The energy one loses when adopting the weaker In-N bonds compared to the Ga-N bonds is about 0.25 eV per additional one In-environment. In summary, if the proposed place-change happens, one gains 0.2 - 0.3 eV per one In-environment. Thus, one can gain a maximum of almost 1eV in total energy, when moving a Nitrogen atom from a four Ga-environment to a four In-environment, strongly supporting the above explained model.

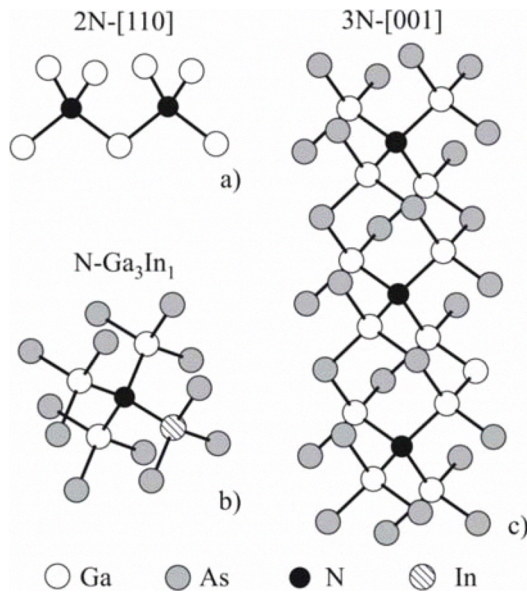


Fig. 2: Ball and stick models of different N configurations in Ga(NAs) and (GaIn)(NAs).

- (a) N nearest neighbour in [110] direction
- (b) N in a 3Ga 1 In configuration
- (c) N chain, oriented in [001] direction

Local configuration	E_{strain} [eV]	ΔE_{strain} [eV]
Isolated N in GaAs	1.69	
2 N in [110]	3.75	0.37
2 N in [001]	3.28	-0.1
3 N in [001]	4.85	-0.22

Table 1: Strain energies of various Nitrogen arrangements in GaAs.

Local configuration	E_{strain} [eV]	ΔE_{strain} [eV]	ΔE_{chem} [eV]	ΔE [eV]
N-Ga ₄ In ₀	1.69			
N-Ga ₃ In ₁	1.28	-0.55	0.23	-0.32
N-Ga ₂ In ₂	0.92	-1.05	0.46	-0.59
N-Ga ₁ In ₃	0.61	-1.5	0.69	-0.81
N-Ga ₀ In ₄	0.39	-1.86	0.92	-0.94

Table 2: Strain energies, chemical energies and resulting interaction energies of various N-III nearest-neighbour configurations.

Following this model, it becomes also evident that the dissolution of the intrinsic Nitrogen ordering in quaternary (GaIn)(NAs) should be the easier the higher the In-content of the material. Therefore, the annealing conditions, through which the place change is mediated, have to be adjusted for the solar cell material to allow for a long diffusion of the N. As the chain-like N-ordering might be a non-radiative center in (GaIn)(NAs) laser material [14], it might play an important role in solar cell devices acting as an electronic defect and hence limiting the minority carrier diffusion length. Carriers might scatter efficiently at those strain fluctuations and hence deteriorate solar cell performance. In how far homogenization of the solar cell material is also possible, will be elucidated in the following.

(GaIn)(NAs) optical characteristics

As a chain-like ordering of N can act as a non-radiative center in the dilute nitride material [14], photoluminescence spectroscopy is a technique one could use to judge on the amount of dissolution of the N-ordering. That PL intensity actually also correlates to solar cell device performance can be seen from Fig. 3. Here, the results of quantum efficiency measurements of processed solar cells, all having an absorber thickness of 1 μm are compared to the PL intensity measured from (GaIn)(NAs) double hetero (DH) structures, which were grown under identical conditions as the solar cells. To enable the comparison, the DH structures were excited using a 980 nm laser. From this clear correlation it becomes obvious, that processes which limit PL performance are also the ones to hinder optimum device performance. This graph can of course also be used to optimize devices using simple (GaIn)(NAs) DH test structures and measure PL properties under always identical conditions. To optimize PL efficiency, different annealing routines were applied and the conditions were varied systematically [15]. Annealing steps consisted of a 5 - 120 min TBAs stabilized anneal at 700°C - 800°C and a subsequent unstabilized annealing step in H₂-ambient at

625 - 800°C for 25 min in the MOVPE reactor. Selected annealings were also applied to complete solar cell devices.

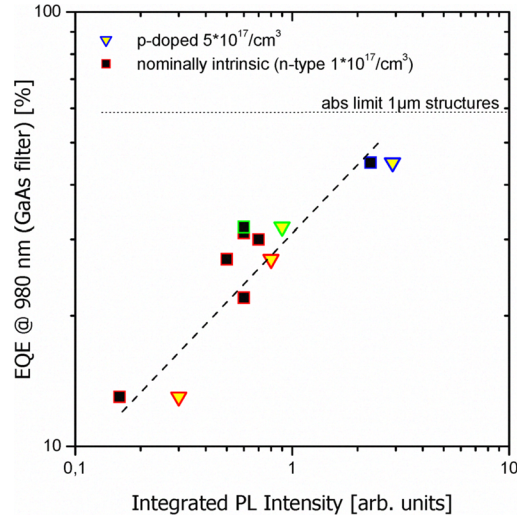


Fig. 3: Correlation of the quantum efficiency of (GaIn)(NAs) solar cell devices with the PL intensity of DH structures grown under identical conditions as the solar cells and measured using direct (980 nm) excitation.

(GaIn)(NAs) solar cell characteristics

Open circuit voltages (V_{oc}) measured from identical solar cell structures, which were annealed in different ways are plotted in Fig. 4. In addition, data from literature [16] is shown. As was reported, upon adding already small amounts of nitrogen to GaAs, V_{oc} drops about 250 meV below the value, which one would expect according to its bandgap. Unannealed (GaIn)(NAs) samples, which still show the chain-like N-ordering and hence the non-radiative recombination introduced by this defect, also exhibit this comparatively low V_{oc} (red datapoint). Annealing and successively dissolving the N-ordering results however in increased V_{oc} s.

This behaviour is also reflected in the internal quantum efficiency measured from these samples. Different annealing of identical structures can results in significantly different efficiencies, again suggesting that one removes an optoelectronic defect from the material when one thermally treats the structures.

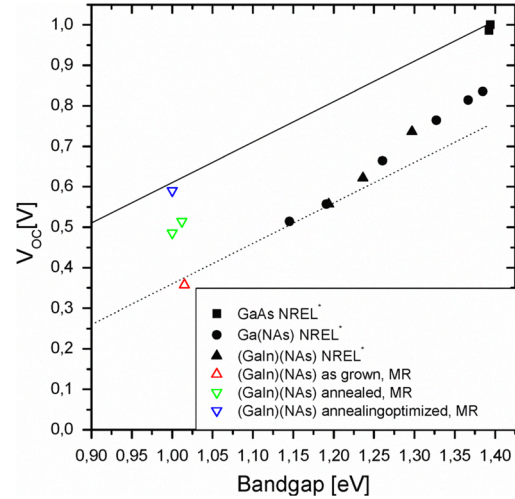


Fig. 4: Open circuit voltages of n-on-p (GaIn)(NAs) solar cells, which have been annealed under different conditions. The solar cell consists of a 50 nm thick Mg-doped back surface field region underneath the 100 nm thick Mg-doped base region, which is separated from the 300 nm thick Te-doped emitter by a 500 nm thick, nominally intrinsic ($10^{17}/\text{cm}^3$ p-type) region. To simulate the above-lying (Ga(In))As cell, a 700 nm thick GaAs cap was grown on top of the complete structure.

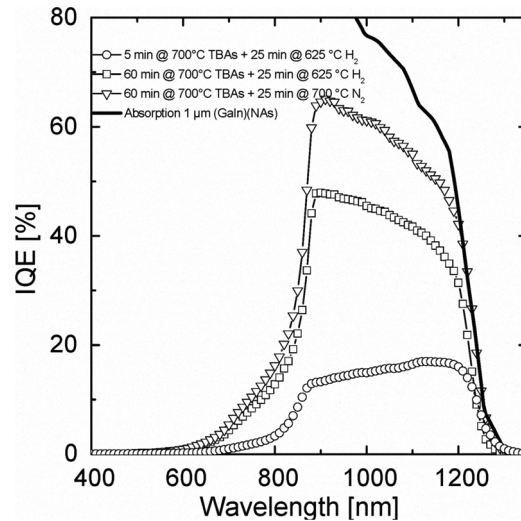


Fig. 5: Internal quantum efficiencies of n-on-p (GaIn)(NAs) solar cells, which have been annealed under different conditions. The solar cell design is identical to the one described in Fig. 4.

SUMMARY

(GaIn)(NAs) lattice matched to GaAs and Ge and having a 1 eV bandgap will be used for future space and terrestrial multi-junction solar cell structures, if the basic challenges of this material system will be solved. Among these challenges is a greatly reduced minority carrier diffusion length in the order of only several ten nanometers. The present paper summarizes results of an annealing study of the metastable quaternary alloy having an In content of 8% and a N content of 2.8%. It is shown, that photoluminescence intensity can be taken as a measure of improving minority carrier characteristics in solar cell devices. There is a direct correlation between PL intensity excited at 980 nm and quantum efficiency in the (GaIn)(NAs) material system. Anneal temperature, time and As-stabilization, have to be adapted to the particular In content of the material in order to initiate the site change of the Nitrogen atom from a Ga-rich environment upon growth to an In-rich one upon annealing. This goes along with the dissolution of chain-like N-ordering in [001] direction and finally with a greatly enhanced optical performance as well as with improved quantum efficiencies of the solar cells.

ACKNOWLEDGEMENT

We acknowledge support from the German science foundation (DFG) in the framework of the Topical Research Group on "Compound Semiconductors and Heterostructures" as well as in the framework of the European Graduate College on "Electron Electron Interactions in Solids". This project has also been funded by the European Community in the 6th program (IP "FULLSPECTRUM" SES6-CT-2003-502620).

REFERENCES

- [1] R. R. King, C. M. Fetzer, P. C. Colter, K. M. Edmondson, J. H. Ermer, H. L. Cotal, H. Yoon, A. P. Stavrides, G. Kinsey, D. D. Krut, and N. H. Karam, Proc. of 29th IEEE Photovoltaic Specialists Conference, New Orleans, USA (2002), 776
- [2] D. J. Friedman, J. F. Geisz, S. R. Kurtz, and J. M. Olson, Proc. of 2nd World Conference and Exhibition on Photovoltaic Solar Energy Conversion, Vienna, Austria (1998) 3
- [3] H. Q. Hou, K. C. Reinhardt, S. R. Kurtz, J. M. Gee, A. A. Allerman, B. E. Hammons, P. C. Chang, and E. D. Jones, Proc. of 2nd World Conference and Exhibition on Photovoltaic Solar Energy Conversion, Vienna, Austria (1998) 3600
- [4] G. Létay, A.W. Bett, Proc. of 17th European Photovoltaic Solar Energy Conference and Exhibition, Munich, Germany (2001) 178
- [5] K. Volz, J. Koch, B. Kunert, W. Stolz, J. Cryst. Growth 248 (2003) 451
- [6] D.J. Friedman, J.F. Geisz, S.R. Kurtz, J.M. Olson; J. Cryst. Growth 195 (1998), p. 409.
- [7] S.R. Kurtz, A.A. Allerman, E.D. Jones, J.M. Gee, J.J.

Banas, B.E. Hammons; Appl. Phys. Lett 74(5) (1999), p. 729.

- [8] C. Baur, A. W. Bett, F. Dimroth, S. v. Riesen, B. Kunert, M. Traversa, K. Volz, and W. Stolz, Proc. of WCPEC-3, Osaka, Japan, pp. 677-670, 2003.
- [9] D.J. Friedman, S.R. Kurtz ; Prog. Photovolt. Res. Appl.10 (2002), 331.
- [10] D.J. Friedman, J.F. Geisz, S.R. Kurtz, J.M. Olson; Presented at the 2nd World Conference and Exhibition on Photovoltaic Solar Energy Conversion, Vienna, Austria (1998).
- [11] K. Volz, T. Torunski, W. Stolz, J. Appl. Phys. 97 (2005) 014306
- [12] O. Rubel, K. Volz, T. Torunski, S.D. Baranovskii, F. Grosse, W. Stolz, Appl. Phys. Lett. 85 (2004) 5908
- [13] K. Volz, T. Torunski, B. Kunert, O. Rubel, S. Nau, S. Reinhard, W. Stolz, J. Cryst Growth 272 (2004) 739
- [14] K. Volz, J. Koch, B. Kunert, I. Nemeth, W. Stolz, J. Cryst. Growth (2007) 126
- [15] K. Volz, D. Lackner, I. Németh, B. Kunert, W. Stolz, C.Baur, F. Dimroth, A. W. Bett
J. Cryst. Growth 310 (7-9) (2008) 2222
- [16] S. Kurtz et al., Appl. Phys. Lett. 86 (2005) 113506