Preliminary analysis of annealing impact on 1 eV GaNAsSb Solar Cells

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Abstract—Impact of annealing temperature, time and process gas on 1 eV GaNAsSb solar cells is assessed. In situ and ex situ annealings are carried out in order to analyze their effect on the solar cell performance. Ex situ annealings on as grown samples using N₂ as process gas increase the external quantum efficiency while using H₂ as process gas degrades the solar cell performance. Best performance is obtained by in situ annealing in a molecular beam epitaxy reactor. External quantum efficiency increases in the short wavelength range (≤ 700 nm) and decreases in the long wavelength range (≥ 700 nm) after ex situ annealing using N₂ as process gas on in situ annealed samples (in a molecular beam epitaxy reactor).

Keywords—annealing; dilute nitride; solar cell;

I. INTRODUCTION

Compounds of the Ga(In)AsN(Sb) system with minute amounts of N ($N < 3\%$) are of high interest in photovoltaics due to their potential use as 1 eV subcells in multijunction solar cells. Being at least quaternary materials, their bandgap and lattice constant can be independently adjusted in a broad range (for instance to Ge or GaAs substrates). A triple junction solar cell with a GaInNAsSb subcell achieved the world record efficiency under concentration (44.0%) in 2012. A road map for the implementation of four, five and six junction solar cells was also proposed [1]. Alternative dilute nitrides such as GaInNAs, GaNAsSb, etc. are also candidates for 1 eV subcells in high efficient multijunction solar cells [2][3]. However, several growth issues such as high background doping, C or H impurities, non-homogeneous composition and nitrogen related defects have been reported for MOVPE (Metal Organic Vapour Phase Epitaxy) and MBE (Molecular Beam Epitaxy) growth techniques in all the aforementioned materials [4][5] as limiting factors for their photovoltaic performance. Dilute nitride materials need to be annealed after the epitaxial growth process to improve their material quality [6][7][8] even though the reasons of this improvement are still not clear. Within the frame of a collaboration among UPM, IQE and the Nanyang

Technological University of Singapore (NTU), a 1 eV GaNAsSb dilute nitride solar cell has been developed in the quest for a four junction solar cell. Since a deep understanding of the phenomena taking place during the annealing process is necessary to obtain the best solar cell performance, we preliminary analyze in this work the impact of in situ and ex situ annealing on GaNAsSb single junction solar cells (Fig. 1) grown by MBE [9].

GaAs Cap $5 \cdot 10^{18} \text{ cm}^{-3} (\text{n}^{++})$	50-500nm
AlGaAs Window $5 \cdot 10^{17} \text{ cm}^{-3} (\text{n})$	50nm
GaAs Emitter $5 \cdot 10^{17} \text{ cm}^{-3} (\text{n})$	100nm
GaNAsSb Emitter $10^{17} \text{ cm}^{-3} (\text{n})$	100nm
GaNAsSb Base $10^{15} \text{ cm}^{-3} (\text{p - NID})$	2 μm
GaAs Buffer $10^{18} \text{ cm}^{-3} (\text{p}^{+})$	300 nm
GaAs Substrate $5 \cdot 10^{18} \text{ cm}^{-3} (\text{p}^{++})$	300 μm

Fig. 1. Schematic structure of MBE grown GaNAsSb single junction solar cell. NID refers to “non-intentionally doped”.

II. EXPERIMENTAL

A. Solar cell manufacture

The solar cell baseline structure is shown in (Fig. 1). The most relevant layers from top to bottom are:

- Highly doped GaAs ($5 \cdot 10^{18} \text{ cm}^{-3}$, n doped) cap layer in order to be able to form ohmic contacts. Two thicknesses were grown, 500 nm for samples A and B, and 50 nm for samples C and D.

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- 100 nm thick GaAs ($5 \cdot 10^{17} \text{ cm}^{-3}$, n doped) layer as a second emitter in order to take advantage of the field-aided photocarrier collection.
- 100 nm thick GaNAsSb (10^{17} cm^{-3} , n doped) emitter layer of the pn junction.
- 2 μm thick GaNAsSb (10^{15} cm^{-3} , p non-intentionally doped) base layer of the pn junction.

After annealing treatment, samples were manufactured into 0.1 cm^2 solar cells to test them. No antireflection coating was deposited. GaAs cap layer thickness and its related optical absorption must be taken into account in order to understand different EQEs for wavelengths shorter than 750 nm.

B. Annealing Processes

In order to assess the impact of the annealing treatments, four kind of samples are defined (related to three annealing processes) (Fig. 2):

- Sample A: Sample as grown by MBE (non-annealed)
- Sample B: Sample after annealing 1A
- Sample C: Sample after annealing 2A
- Sample D: Sample after annealing 2A and 2B

The following annealings are applied:

- Annealing 1A: ex situ annealing in a rapid thermal process (RTP) oven, using N_2 or H_2 as process gases, at 700 or 750 $^\circ\text{C}$ for 5 minutes.
- Annealing 2A: in situ MBE reactor annealing under As overpressure at 700 $^\circ\text{C}$ for 5 minutes.
- Annealing 2B: ex situ RTP oven annealing at 700, 800 or 850 $^\circ\text{C}$ for 10 minutes using N_2 as process gas.

Fig. 2. Different samples from the point of view of annealing treatments. Moreover, different cap thicknesses were used for each sample (see previous section A “Solar cell manufacture”)

Ex-situ annealings were carried out in an RTP oven with gas flows between 3 and 5 standard liters per minute (slpm) for N_2 and H_2 . A GaAs wafer was used to cover the sample surface and prevent As evaporation, which would degrade the contact layer surface. However, for extremely high temperatures (850 $^\circ\text{C}$), deterioration of the contact layer could not be avoided. A typical RTP temperature profile of annealing 2B at

different temperatures is shown in Fig. 3. Similar profiles were used for annealing 1A.

Fig. 3. Experimental temperature profile inside the RTP of three typical annealings 2B with plateau values of 10 minutes and temperatures of 700, 800 and 850 $^\circ\text{C}$.

C. Device and Material Characterization

External quantum efficiency (EQE) measurements were carried out in order to analyze the annealing effects. Energy-dispersive X-ray spectroscopy on scanning electron microscope (EDX-SEM) was also performed on samples A and B in order to detect composition variations.

III. RESULTS AND DISCUSSION

A. Annealing 1A

Typical EQEs for samples A and B are shown in Fig. 4. Improvement for almost all wavelengths is achieved when N_2 is used as process gas (disregarding wavelengths around 825 nm where samples A have an EQE peak). When H_2 is used as process gas, lower EQE is obtained. Moreover, for wavelengths longer than 970 nm the EQE is even lower than that one of samples A.

Fig. 4. EQE measurements of solar cells manufactured on sample A and B (700 and 750 $^\circ\text{C}$ using N_2 and H_2 as process gases).

Detrimental impact of H in diluted nitrides has been previously reported [10], although beneficial impact has been published as well [9][11]. Higher EQEs are obtained when using 700 °C instead of 750 °C for both, N₂ and H₂ process gases.

B. Annealing 2A

EQE of solar cells manufactured on samples C is shown in Fig. 5 and Fig. 6, for comparison with ex situ annealings. Best EQEs after first annealing (i.e. samples B and C) are shown in Fig. 5 together with sample A for comparison. The best EQE is achieved by in situ MBE annealing. As already pointed out, different EQEs in Fig. 5 for wavelengths shorter than 750 nm are due to different GaAs cap layer thicknesses.

Fig. 5. EQE measurements of best solar cells on samples A, B (annealed at 700 °C with N₂ as process gas), and C.

Although the EQE peaks are similar for samples B and C, sample C exhibits a higher EQE for wavelengths longer than 900 nm together with a bandgap red-shift. Further experiments need to be carried out in order to determine the origin of these differences. This could be a key in order to understand what is happening inside the dilute nitride as there seems to be different kind of effects due to annealing (higher photocurrent and bandgap red-shift variation) but they are not always observed together. Although blue-shift is the usual effect reported in diluted nitrides after annealing [5], red-shift has also been reported [6].

C. Annealing 2B

EQEs of solar cells manufactured on samples C and D (with different heat loads) are shown in Fig. 6. It can be seen that as the heat load increases, the EQE starts to decrease in the long wavelength range, whereas increases in the short one. EQE peak keeps almost constant, but the shape changes significantly. GaNAsSb and mainly GaAs emitter layers increase their contribution to the EQE while the base one decreases. This suggests changes in the pn junction because as shown in [12] the EQE is strongly dependent on the electric field inside the solar cell reported in this work. The EQE response at wavelengths shorter than 400 nm of sample D annealed at 850°C, was due to evaporation of GaAs contact layer (as aforementioned said) during ex situ annealing

treatment. This is in agreement with simulation results and SEM measurements (not shown for the sake of simplicity).

Fig. 6. EQE measurements of solar cells manufactured on samples C and D (750, 800 and 850°C for 10 minutes).

D. Simulation and Data Fitting

Simulations of the EQE of solar cells on samples C and D try to shine light on the effects of annealing (Fig. 7). EQE solar cell performance simulations are carried out with the ATLAS software from Silvaco. Similar EQEs to the ones achieved for largely annealed samples are achieved through decreasing emitter doping level simulation parameter (or increasing the base one). This hypothesis is supported by a similar EQE shape in an intentionally doped ($5 \cdot 10^{17} \text{ cm}^{-3}$, p doped) 1.5 μm thick base sample, indicating that a possible modification of the pn junction doping levels is taking place during the annealing (Fig. 7). Different base thicknesses (2 μm for sample D against 1.5 μm in the case of the intentionally doped base one) could explain [12] the gap between sample D and the intentionally doped base sample EQEs. In order to achieve a better fit of the sample D annealed at 850 °C EQE, it is also necessary to decrease the GaAs cap layer thickness and to adjust the carrier life time parameters of the sample C simulation.

Fig. 7. Experimental and simulated EQEs of solar cells on samples C and D (850°C for 10 min) and intentionally doped base sample EQE measurement.

E. SEM-EDX

In order to understand the reason of the EQE performance improvement after annealing 1A (using N_2 as process gas), SEM-EDX measurements have been carried out in samples A and B for Ga, As, N, Sb and Al elements. The only effect observed was an increase in the measurement noise for Al and Sb. Ga and As seems to suffer no effect during the annealing, while N composition could not be properly measured. Sb composition decreases before the GaNAsSb/GaAs interface (Fig. 8). This could be related to the bandgap difference between samples A/B and C (Fig. 5) as Sb decrease the bandgap in dilute nitrides [13]. However, SEM-EDX in samples C need to be carried out in order to explore this hypothesis.

Fig. 8. SEM-EDX measurement of Sb composition for samples A and B. Measurement begins at the top of the cap layer surface.

IV. CONCLUSIONS

Impact of in situ MBE and ex situ RTP annealing on GaNAsSb single junction solar cells has been assessed. Best performance for wavelengths longer than 800 nm has been achieved by means of MBE in situ annealing which also produces bandgap red shift. Ex situ RTP annealing with H_2 as process gas degrades the EQE compared to N_2 . For subsequent ex situ annealings after the in situ MBE ones only changes in EQE shape were detected for large heat loads. Preliminary results suggest variations in the pn junction doping levels. Simulation and EQE data fittings suggest a decrease of the emitter doping level (or an increase in the base one). Similar EQEs are obtained for samples with an intentionally doped base, which supports the hypothesis. This work constitute a preliminary analysis in the quest of a deeper understanding of the physical mechanisms behind annealing. Further annealings

need to be carried out in order to determine optimum annealing conditions and more measurements (such as ECV/CV or TEM-EDX) will be carried out in order to confirm variations in the doping levels under large heat loads.

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