Component Integration Effects in 4-junction Solar Cells with Dilute Nitride 1eV Subcell

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Abstract — A GaInP/Ga(In)As/GaNAsSb/Ge 4-junction solar cell grown using combined MOVPE+MBE growth is used to analyze the effects during the integration of the subcell components into the full 4J structure. In this preliminary study, the Ge subcell is observed to suffer about 15% J_{sc} drop and ~50 mV V_{oc} loss at 1-sun, while the V_{oc} of the GaNAsSb subcell drops by as much as ~140 mV. The degradation of the Ge and GaNAsSb subcells in the current-matched 4J structure can hinder its efficiency potential to a higher extent than in the GaInP/Ga(In)As/Ge 3J. Besides, high quality GaNAsSb and Ge subcells would still limit the current and require redesigning the top subcells to achieve optimum efficiencies.

I. INTRODUCTION

Monolithic and lattice-matched multijunction solar cells are attractive for fabrication simplicity and, hence, lower cost. Using dilute-nitride subcells is promising and has already shown high efficiencies in 3J solar cells grown by MBE [1], and combined MOVPE + MBE [2]. A GaInP/Ga(In)As/GaNAsSb/Ge 4J solar cell, using the Ge substrate as an active subcell, conceptually consists on just adding the dilute nitride junction to the GaInP/Ga(In)As/Ge 3J solar cell. Currently, attaining a dilute-nitride subcell with longer minority carrier diffusion length so as not to limit the performance of the whole 4J structure is the main limitation to achieving high efficiencies. Therefore, a high fraction of the work to do consists on further developing the semiconductor deposition technique. Ideally, MOVPE would be used to grow the full 4J structure, given its advantages with respect to other growth techniques concerning high volume fabrication cost. However, attaining high quality dilute-nitride subcells by MOVPE has been elusive, although a recent publication has shown positive steps towards achieving this [3]. Conversely, better carrier diffusion lengths have been achieved by MBE, so as to obtain high efficiency 3J solar cells [1]. Thus, the combined MOVPE + MBE method makes sense at this stage of development and should allow the attainment of high efficiencies in the short term.

The 4J structure is complex and involves growing a large number of layers of different materials, growth temperatures and times. It is important to assess the integration of all these components to detect and take care of problems in advance, and facilitate the development of a high efficiency 4J solar cell. The focus has to be put in identifying and quantifying the effects that put in risk the efficiency potential of this 4J solar

cell and redesigning, if possible, the growth process to minimize their impact.

In this work we first present our 4J solar cell, based on a prototype structure achieved by the combined MOVPE + MBE method, and using a GaNAsSb junction. This solar cell exhibits a low performance due to the limiting behavior of the dilute nitride subcell, but represents a success in the implementation of the 4J structure. However, this structure is used to analyze the integration of subcells into the full 4J structure as the main point of this work. In this preliminary work, we focus on the GaNAsSb and, mostly, the Ge bottom subcell, which are subjected to long annealing times during the growth of the upper structures. It is found that significant losses are at stake, mainly in the Ge and GaNAsSb subcells, which can limit the potential of this 4J solar cell structure to compete in efficiency with other architectures.

Fig. 1. Structure of the 4J solar cell presented, with indication of the parts grown by MOVPE and MBE, and the annealing times that each component subcell and tunnel junction suffer during the rest of the structure.

Fig. 2. Symbols: measured EQE of the 4J solar cell implemented; dashed line: modeled GaNAsSb and Ge subcells using minority carrier collection efficiencies of 1 and optically thick GaNAsSb. The table on the right shows the J_{sc} obtained using these EQE and the AM1.5D G173 solar spectrum.

II. MOVPE+MBE 4J SOLAR CELL

The structure consists on a GaInP/Ga(In)As/GaNAsSb/Ge structure grown lattice-matched to a Ge substrate, which is also the 4th junction, as shown in Figure 1. The growth process comprises a sequence of MOVPE (GaInP nucleation on Ge and tunnel junction) + MBE (GaNAsSb subcell) + MOVPE (GaInP/Ga(In)As top junctions, including tunnel junctions). Given the low minority carrier diffusion length in the dilute nitride material, the GaNAsSb subcell absorber was made as thin as 1 μm [4], [5]. These structures were processed into solar cell devices using gold-based metal and standard photolithography techniques. No anti-reflection coating has been applied to these solar cells for this study.

A. External Quantum Efficiency (EQE).

The measured external quantum efficiency (EQE) of this solar cell is shown in Figure 2, with the corresponding J_{sc} calculated using the AM1.5D G173 solar spectrum detailed in the table on the right. The top subcells exhibit the usual EQE with good J_{sc} values, while the low EQE of the nitride subcell limits the J_{sc} of the whole device. The J_{sc} of the Ge bottom junction is also low considering the fact that the light absorption in the GaNAsSb junction is incomplete and the Ge bottom cell has an unrealistic extended response in the short wavelength range. As a first assessment of the potential and loss sources in this EQE, the modeled EQE of improved GaNAsSb and Ge subcell was calculated. The Generalized

Matrix Method was used to compute the absorption in each layer [6] and the EQE was obtained applying a carrier collection efficiency to the absorber layers to fit the experimental EQE. Then, the improved EQE was calculated using an optically thick GaNAsSb subcell and a minority carrier collection efficiency of 1 in both subcells. The resulting EQEs are also shown in Figure 2. A strong effect on the GaNAsSb subcell EQE and J_{sc} is observed, as expected, but, the Ge subcell carrier collection efficiency can also be improved to achieve a higher J_{sc} . This can be observed as a higher average value of the EQE. Note that the J_{sc} of the Ge subcell in the “improved bottoms” case is lower than the measured because the GaNAsSb subcell in this case is optically thick. The cause of the low EQE in this Ge subcell is discussed in Section III. Finally, according to the table on the right, the bottom subcells still limit the J_{sc} of the 4J even improving their carrier collection efficiency. This means that realizing the full efficiency potential of this 4J solar cell will involve making the top cells more transparent by changing their thickness or, optimally, their bandgap.

B. Open Circuit Voltage (V_{oc}).

Light I-V curves were measured on these 4J solar cells. We have published previous work about the performance and particularities in the shape of the I-V curve of the 4J, predicted using simulations with inputs from the characterization results of GaNAsSb 1J and GaNAsSb/Ge 2J cells [4], [5]. As for this work, we are mostly interested in the open circuit voltage (V_{oc}), which we showed to be around 420 mV for the

Fig. 3. Carrier concentration profiles of Ge subcells before and after growth of the full 4J structure.

GaNAsSb solar cell as an independent device [4]. The 4J solar cell presented here was measured under a calibrated solar simulator at NREL, and exhibited a V_{oc} at 1-sun of 2.44 V and 2.48 V for the AM1.5d and AM0 solar spectra, respectively. This V_{oc} is rather low, as compared to state-of-the-art GaInP/Ga(In)As/Ge 3J solar cells developed in our lab, which exhibit an V_{oc} of around the same value [7]. This means that the V_{oc} increase in the 4J expected with the insertion of the GaNAsSb subcell does not occur, which eliminates any performance advantage with respect to the 3J solar cell. Part of this voltage loss is due to degradation of the Ge and GaNAsSb subcells, as discussed in next section.

III. COMPONENT INTEGRATION ANALYSIS

In order to elucidate the origin of the voltage loss, and to assess the degradation of other possible solar cell performance parameters such as the EQE, an analysis of the possible sources of subcell degradation when integrating them into a 4J solar cell was carried out. The first suspect in the list of possible causes is the thermal loads applied to the subcells. In Figure 1 we show a list of the annealing times to which each subcell of the 4J structure is subjected to. The growth temperatures range from 550 °C for the tunnel junctions to 675 °C for the subcell growth. The GaNAsSb subcell growth includes a 700 °C annealing step for 5 minutes to improve its properties, similarly as with other dilute-nitride materials [8]–[11]. The insertion of the dilute nitride subcell increases the thermal load to the Ge bottom subcell, as compared to the 3J case. Considering the different growth times and temperatures used for each component in the 4J structure, it is not obvious to predict the real impact of this added thermal load, and we assessed it empirically by examining samples at different stages of the MOVPE + MBE + MOVPE process.

Fig. 4. IQE of the Ge subcell after being grown as a 1-junction, and in the 4-junction solar cell (measured after etching the top layers)

A first test was to measure the dopant diffusion in the Ge junction, which we did by taking electro-chemical capacitance-voltage (ECV) profiles of Ge junctions, shown in Figure 3. The profiles show the n-type and p-type carrier concentration corresponding to the emitter and base, respectively. The base carrier concentration corresponds to the Ge substrate nominal doping, around $3 \cdot 10^{17} \text{ cm}^{-3}$. The emitter doping is achieved by diffusion of group-V elements (phosphorus) during the growth of the GaInP nucleation layer. Group-III elements also diffuse and give rise to a lower effective doping at the surface of the emitter. Preliminary SIMS measurements appear to indicate that this is caused mainly by indium diffusion.

The dopant diffusion at the emitter during the growth of the 4J structure is evident in Figure 3: the average carrier concentration level and thickness of the emitter changes substantially. Not less importantly, a strongly compensated region appears at the surface of the emitter, due to further indiffusion of group-III elements. The carrier concentration level rises sharply to achieve its peak value at a depth of around 100 nm. The electric field created in this region can be expected to act as a sink for minority carriers which are lost by recombination.

IQE measurements were taken on these Ge subcells to assess this, as shown in Figure 4. Firstly, the IQE of the Ge subcell obtained right after the growth of the GaInP nucleation layer shows a value near 1 for all the wavelength range between the Ge and GaInP nucleation layer absorption edges. As for the Ge subcell after the growth of the 4J, an important degradation of the carrier collection efficiency in the lower wavelength region can be observed. The degraded Ge junction can be accurately modeled including the compensated layer ($\sim 40 \text{ nm}$) with 0 collection efficiency, and a degraded carrier collection in the emitter bulk.

It is important to point out that the apparent severity of the IQE degradation shown in Figure 4 is lessened by realizing the fact that, in the 4J, the Ge subcell absorption range falls in the higher photon wavelength region, where the degradation is not so severe. However, for the range of Ge subcell absorption in the 4J, the J_{sc} drop due to the degraded IQE is as high as $\sim 15\%$ calculated for the AM1.5D-G173 solar spectrum.

As expected, the V_{oc} of the Ge subcell exhibits changes too. The study of the degradation of the V_{oc} in the subcells is complicated in these 4J devices: the electroluminescence technique [12] cannot be used due to the undetectable emission of light from the dilute nitride subcell. In this work, the Ge subcell voltages were accessed by etching the upper layers. A drop of ~ 50 mV after the growth of the 4J structure can be observed. We are currently carrying out experiments to elucidate the evolution of the V_{oc} during the growth of the different 4J structure components.

All in all, an important degradation in the Ge junction when integrating it in the 4J structure is observed, which can limit the performance potential of this solar cell architecture. However, measures to minimize this degradation can be taken, such as redesigning the critical steps that determine the phosphorous and indium in-diffusion into the Ge to form the emitter during growth.

As for the GaNAsSb subcell, it is submitted to an intentional annealing in order to improve its material properties, as commented before. Additionally, the growth of the GaInP/Ga(In)As top subcells involves an extra annealing of this subcell, of about 2 hours at $\sim 675^\circ\text{C}$. However, no significant changes have been observed in its IQE, in the range of photon energies that it absorbs. However, the V_{oc} of GaNAsSb single-junction solar cells drop by as much as ~ 140 mV at 1-sun. The intentional annealing used to improve the GaNAsSb subcell is normally designed concerning the temperature and time used, so that there exists an optimum combination of these parameters. The additional annealing of our GaNAsSb subcell appears to deviate the total thermal load from the optimum required. This means that the optimization of the intentional annealing will need to take into account the subsequent, unwanted annealing that the GaNAsSb subcell suffers during the growth of the 4J structure.

IV. CONCLUSIONS

We have presented a GaInP/Ga(In)As/GaNAsSb/Ge 4J solar cell grown using MOVPE+MBE combined method. The GaNAsSb subcell quality is not enough to allow a high performance 4J solar cell, yet. However, this 4J structure was used for a preliminary assessment of effects during the integration of the subcell components. The Ge subcell has been found to degrade significantly during the growth of the 4J structure: its emitter carrier concentration profile changes substantially and this is correlated with a significant drop in the IQE (and J_{sc}) and V_{oc} . Moreover, the GaNAsSb subcell

shows a large V_{oc} drop, but no significant change in its IQE. Additional work to complete this analysis and extend it to the other subcells and tunnel junctions is underway. However, we can conclude that the efficiency potential of this 4J architecture can be significantly lowered if the observed degradation of the Ge and GaNAsSb subcells is not minimized by a proper design of the semiconductor structure growth routine. An important remark is that, even in the case of achieving high quality GaNAsSb and Ge subcells, they would still limit the current in the 4J and further optimization would require bandgap/thickness changes in the GaInP and Ga(In)As top junctions. Finally, the conclusions of this paper should be generalizable to other structures using dilute-nitride subcells, since the growth conditions used in our case are not harsher than commonly used.

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