



Incorporation of hydrogen into MBE-grown dilute nitride GaInNAsSb layers in a MOCVD growth ambient

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ABSTRACT

In this work, lattice-matched 3-junction and 4-junction solar cells including the dilute nitride subcells were fabricated by a hybrid growth technique of metalorganic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE). It was found that photocarrier extraction in the MBE grown dilute nitride GaInNAsSb subcells degraded after the overgrowth of the upper subcells by MOCVD. Then, we focused on the effect of annealing for a set of MBE grown GaInNAsSb single junction solar cells annealed in the MOCVD reactor under an arsine flow ambient. It was found that degradation of the carrier extraction due to the MOCVD growth ambient is in a correlation with the selective hydrogen incorporation into the GaInNAsSb layers. We demonstrated that the subsequent annealing in nitrogen ambient promoted the outdiffusion of hydrogen which led to a recovery of the GaInNAsSb solar cell performances.

1. Introduction

In the category of ultra high efficiency multi-junction solar cells (MJSCs), more than 40% concentrator efficiencies have been achieved so far [1–6]. Especially, 44–46% efficiencies were realized in the MJSCs with the combination of different lattice-constant systems [4–6], where the integration of lattice-mismatching subcells was realized by a compositional graded buffer or wafer bonding technologies. On the other hand, the Ge-based GaInP/GaAs/Ge 3-junction (3J) cell is still regarded as an industrial standard. The growth method of this type of 3J cell has been well established, and needless of the above mentioned special integration technologies is one of the attractive advantages because the every subcell are consisted of the lattice-matched materials. However, there is a large mismatch in the photocurrent among the subcells, *i.e.*, Ge cell generate the current nearly double to the other subcells. This issue mainly limited the efficiency to be 41.6% [2]. Therefore, in order to achieve the increased efficiency, it is effective to insert a 1.0 eV subcell between the GaAs (1.4 eV) and Ge (0.66 eV) cells to make a 4J structure. The most conventional 1.0 eV materials cannot satisfy the constraint of lattice-matching to the Ge bottom cell except dilute nitrides, such as GaInNAs, GaNAsSb, and GaInNAsSb [7–12]. With changing N, In, and Sb compositions in the GaInNAs(Sb) or GaNAsSb, the bandgap energy can be varied below ~ 1.4 eV (*i.e.*, the bandgap of GaAs) while its lattice constant is controlled. However, it is well known

that incorporation of N atoms into the host matrices generally causes degradation of electrical and optical characteristics [7,13]. As for the solar cell material, poor minority carrier properties such as the carrier diffusion length and life time limit the photocurrent value. One of the effective approaches to deal with this issue is applying pin junction, where photocarriers can be collected through the drift process by electric field in the depletion region [14–16]. However, the width of depletion region is not always equalled to the i-layer (or undoped layer) thickness, because it depends on the level of carrier concentration. This issue can be severe when the i-layer thickness is increased, whereas optical thickness of the dilute nitride layer should be thicker than 2 μm in order to generate the photocurrent high enough to be matched with the other subcells in the MJSCs [16]. In the literatures for the growth using metalorganic chemical vapor deposition (MOCVD), dilute nitrides suffered from unintentional incorporation of carbon and hydrogen atoms, which originated from the precursors of the source gases in the MOCVD growth and could act as the unintentional dopants to increase the carrier concentration in the i-layer [17–19]. On the other hand, in solid source molecular beam epitaxy (MBE), dilute nitrides are usually incorporated with such impurities as low as the detection limit levels [18,19] and can be obtained the lower level of background carrier concentration (BGCC) [16].

Regarding the fabrication of multi-junction structure, it can be thought that it is worth choosing each subcell in the best growth

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method. As Solar Junction have demonstrated 44.0% concentrator efficiency, MBE-based MJSCs is one of the effective approach to integrate the subcells including the dilute nitrides [3,20]. However, difficulty to handle the phosphorous source in MBE system is a concern. Instead, in this work first we tried to complete the 3 and 4J solar cells (i.e., GaInP/GaAs/GaInNAsSb and GaInP/GaAs/GaInNAsSb/Ge) by the hybrid growth technique of MOCVD and MBE, and characterized the cell performances. Especially, we focus on the characteristics of the dilute nitride GaInNAsSb subcells. Next, the effect of annealing in an ambient simulating the MOCVD growth condition on the GaInNAsSb solar cells were investigated.

2. Experimental procedures

The 4J solar cell was grown as follows. First, the Ge bottom subcell was grown by MOCVD together with a first tunnel junction. Next, the sample was transferred to MBE chamber and the GaInNAsSb subcell was overgrown. Then, again the sample was shuttled back to the MOCVD and a second tunnel junction, a GaAs subcell, third tunnel junction, and a GaInP subcell were overgrown. During the transfer between MOCVD and MBE, the samples were kept in air ambient. Then, the samples were immersed in hydrochloric acid to remove the surface oxidation layer followed by deionized water rinse and drying with N₂, and immediately loaded to the growth systems. The 3J sample was fabricated in the same manner except the first MOCVD process as summarized in Table 1. The GaInNAsSb subcells in these MJSC samples consisted of the n-GaAs/i-GaInNAsSb/p-GaAs double heterostructure with 1 μm-thick GaInNAsSb absorber (nominally, In ~ 5%, N ~ 1.5%, and Sb ~ 1%). In terms of the other set of samples for the annealing experiments, the GaInNAsSb single junction cells consisted of the nip double heterostructure with 3 μm-thick GaInNAsSb (nominally, In ~ 7%, N ~ 2%, and Sb ~ 2%) on the p-type GaAs substrates. These layers were grown at around 570 °C except the GaInNAsSb whose temperature was in the range of 480–520 °C with growth rate of 1.0 μm/h. Further details can be found elsewhere [16,21]. On top of the junction n-AlGaAs window and n⁺-GaAs contact layers were formed. Anti-reflection coating was not employed in this work.

3. Results and discussion

3.1. Characterization of 3- and 4-junction cells

Fig. 1(a) and (b) show the external quantum efficiency (EQE) spectra of each subcell for the 3 and 4J devices which are plotted in colored lines. There also displays the EQEs for non-overgrown GaInNAsSb single junction and GaInNAsSb/Ge dual-junction cells in black lines as references. For the reference devices the measurements were performed under a long pass filter (LPF) whose cut-off wavelength is nearly matched to the GaAs absorption edge, and the magnitudes were corrected with the transmittance of the LPF. All MJSC devices show the individual subcells' EQE features, indicating that the connections of the

Table 1

Summary of the growth methods and orders for the 1–4J cells fabricated by the hybrid growth technique.

Growth order	1J-cell	2J-cell	3J-cell	4J-cell
Substrate	p-GaAs	p-Ge	p-GaAs	p-Ge
1	GaInNAsSb subcell by MBE	Ge subcell by MOCVD	GaInNAsSb subcell by MBE	Ge subcell by MOCVD
2	–	GaInNAsSb subcell by MBE	GaAs subcell by MOCVD	GaInNAsSb subcell by MBE
3	–	–	GaInP subcell by MOCVD	GaAs subcell by MOCVD
4	–	–	–	GaInP subcell by MOCVD

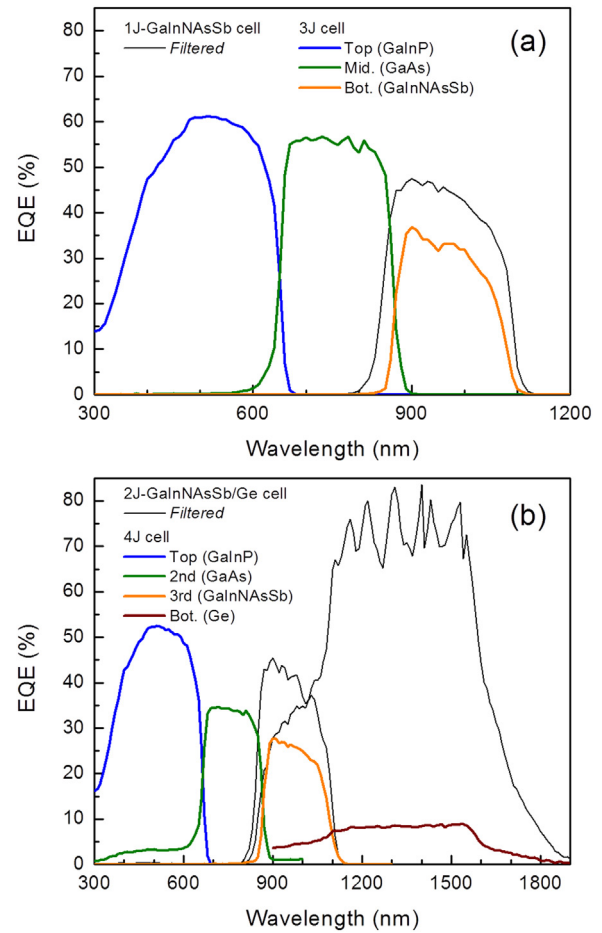


Fig. 1. EQE spectra for each subcell in the 1–4J cells. The 1J and 2J cells were characterized under a LPF.

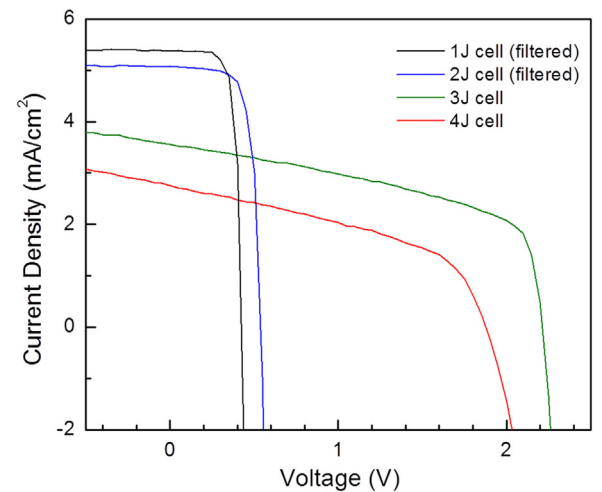


Fig. 2. Light J-V curves for the 1–4J cells. The 1J and 2J cells were characterized under a LPF.

subcells through the tunnel junctions were formed successfully through the hybrid growth. This can be confirmed in the light current density-voltage (J-V) characterization as shown in Fig. 2, which reveals that open-circuit voltages (V_{OC}) for the 3J and 4J cells are greater than those for 1J and 2J cells. Here, J-V measurements for the 1J and 2J cells were performed under the same LPF, and magnitudes of the current density were corrected. As compared to the 3J cell, smaller V_{OC} was observed in the 4J cell. This is because the overgrowth condition for the GaInP/

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