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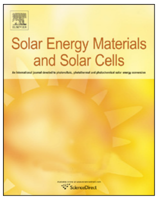

Composition dependent growth dynamics in molecular beam epitaxy of GaInNAs solar cells

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ABSTRACT

We have investigated the role of the nitrogen content, the growth parameters, and the annealing processes involved in molecular beam epitaxy of GaInNAs solar cells lattice-matched to GaAs. The nitrogen composition was varied between 1% and 5%. The influence of the growth temperature was assessed by performing photoluminescence, atomic force microscopy, X-ray diffraction, reflection high-energy electron diffraction, quantum efficiency and light-biased current–voltage measurements. The growth temperature ensuring the best cell parameters was found to be 440 °C. At this temperature we were able to incorporate up to 4% of nitrogen and achieve a good material quality. Further increase of the N composition to 5% led to phase separation. For the lattice matched samples grown within the optimal temperature range, we have identified a clear (1×3) surface reconstruction. Using the optimized growth we have demonstrated a GaInNAs p-i-n solar cell structure containing 4% nitrogen, that exhibited a short-circuit current density as high as 33.8 mA/cm^2 in respect to effective area illuminated. These measurements have been performed under real sun AM1.5 ($\sim$1000 W/m^2) illumination.

1. Introduction

Multi-junction III–V solar cells (MJSCs) with efficiencies above 40% are poised to make a strong impact on the development of concentrated photovoltaic (CPV) systems [1,2]. Solar cells (SC) with efficiency above this level would make CPV systems even more attractive and could accelerate the penetration and the development of more advanced solutions to the market. This goal can be achieved by using MJSCs with 4 or even 5 junctions collecting efficiently the solar energy spectrum down to 1 eV and below. However, the developments are daunted by a lack of high-quality 1 eV band gap materials that are lattice matched to GaAs and Ge and can ensure high current generation. The state-of-the-art commercial solar cells that are based on 3 junctions, i.e. GaInP/GaInAs/Ge, can reach efficiencies slightly above 41% under concentrated sunlight [3,4]. SCs making use of GaInAs with small band gaps need to be grown metamorphically which complicates the fabrication and increases the number of crystalline defects. A very promising alternative for the development of 1 eV compounds lattice-matched to GaAs is to use dilute nitrides, i.e. GaInNAs [5,6] with an N content of only a few percent. Replacing a small fraction of the As atoms with N induces a strong reduction of the band gap and reduces the lattice constant enabling lattice matching to GaAs [7]. Despite these prospects, achieving a sufficiently high material quality for SC applications of dilute nitrides has remained elusive, at least when it comes to the use of metal–organic chemical vapor deposition (MOCVD), which is currently adopted for the commercial fabrication of III–V SCs. Generally speaking, the synthesis of dilute nitride materials is rather challenging because these alloys are metastable and have a large miscibility gap [8,9]. Therefore, they have to be grown under non-equilibrium conditions to incorporate even small amounts of N. We note here that in order to achieve 1 eV GaInNAs material lattice-matched to GaAs, we would need to incorporate about 3% of N, which is already a high value and can lead to significant defect densities. In particular, the use of dilute nitrides has been hampered by the rather complex defects associated with N incorporation [10] and relatively low growth temperature used in the epitaxy of dilute nitrides [11]. Such defects decrease the carrier lifetimes and diffusion lengths. These effects get more severe when the amount of nitrogen is increased leading to reduced voltages and poor quantum efficiencies [10,12].

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Despite the complexity of GaInNAs material system, there are means to reduce the number of defects associated with N incorporation. First of all, when it comes to epitaxial techniques used for fabricating dilute nitrides, molecular beam epitaxy (MBE) offers clear advantages over MOCVD, as it avoids issues related to C doping and hydrogen related complexes [16]. MBE also allows operation at relatively low growth temperatures to avoid phase separation and clustering effects. The most common way of incorporating N in MBE uses a radio frequency (RF) plasma source to crack high purity N_2 molecules into N atoms. The down side of using RF plasma source is that it simultaneously generates N ions that cause additional defects within the epitaxial structure. Fortunately, in plasma assisted molecular beam epitaxy (PAMBE), the detrimental effect of the ions can be reduced by optimizing the design of the RF plasma source and using ion deflecting electric or magnetic fields [13–15]. The use of surfactants [15], post growth annealing [16,17], and the overall growth parameter optimization in MBE [12,18–20] have also a remarkable effect on the number and the type of defects.

The fundamental surface processes involved in dilute nitride growth by PAMBE are mainly controlled by thermal energy applied to the substrate [11,18,21–23]. The optimal growth temperature (T_g) window for the epitaxy of GaInNAs is defined by different processes limiting the crystal quality at high and low T_g. In the low T_g range (defined as $T_g < 420$ °C), high quality epitaxy is hindered by the formation of various point defects that appear due to lack of thermal energy. The point defects have been identified as group-III vacancies [24], arsenic anti-sites [24], interstitial nitrogen [18] and even arsenic dimers [25]. GaAs [26] and GaNAs [27] growth also evolves to an amorphous growth mode if the T_g is lowered below 300 °C, and thus similar effect can be predicted for GaInNAs. At the high T_g range (i.e. $T_g > 480$ °C) the high quality two-dimensional (2D) growth is mainly limited by the phase separation of the GaInNAs crystal to InAs and GaN rich phases [38]. It has also been proposed that the phase separation takes place because the N segregation to the surface leads to enhanced In segregation, which eventually leads to a three dimensional growth mode and poor interfaces [21–23]. After growth, the defect density can be reduced by annealing the crystal at high temperatures [16,17]. The main effects of annealing are related to a change of the neighboring configuration of atoms in the crystal lattice. Essentially, the amount of Ga–N bonds is reduced compared to In–N bonds [16,28] while there is also a substantial decrease of the point defects, leading to higher crystal quality [15,16].

The temperature related processes involved in the epitaxy of dilute nitride quantum wells (QW) have been thoroughly studied [11,21–23]. However, in most of the published reports, the GaInNAs layers have been compressively strained or the studies have been carried out only for a specific N composition. Much less is known about the composition dependent growth dynamics in thick GaInNAs layers lattice matched to GaAs or about the effect of the growth processes on the operation of solar cells using such GaInNAs heterostructures. In this paper, we report a study focused on improving the understanding of the relation between the MBE growth temperature and the quality of GaInNAs solar cells with various N contents in connection with annealing processes. Finally, we assess the performance of 1 eV GaInNAs solar cell containing 4% N and which was grown under optimized conditions. We have also incorporated the 1 eV absorbing region within a GaInP/GaAs/GaInNAs solar cell with an AlInP window to show that the growth conditions we have devised are suitable for the fabrication of multijunction solar cells.

2. Description of structures and the experiments

2.1. Growth and processing

The GaInNAs heterostructures were grown on n-GaAs(1 0 0) and p-GaAs(1 0 0) substrates using a Veeco GEN20 solid source MBE equipped with a Veeco Uni-Bulb RF plasma source for nitrogen activation. For all samples, we used a As/III beam equivalent pressure (BEP) ratio of 10; this ratio was shown to result in high optical quality GaInNAs [20]. For the GaInNAs experiments, the In compositions were calibrated using $Ga_{0.9}In_{0.10}As$/GaAs superlattice structures comprised of four periods of 6-nm-thick GaInAs and 10-nm-thick GaAs layers grown on n-GaAs (1 0 0) substrates. The In compositions of GaInAs were analyzed from high-resolution x-ray diffraction (XRD) rocking curves using dynamical diffraction theory and commercial fitting algorithms. The N composition was varied by changing the plasma power between 150 W and 300 W, and the N_2 flow between 0.15 sccm and 0.53 sccm. This parameter range corresponds to a variation of the N content from 1% to 5%. After the composition calibrations, we fabricated three sets of GaInNAs samples.

The first set of samples was grown on n-GaAs(1 0 0) and consisted of GaInNAs bulk layers without contact layers. This set was used for structural characterization and optimization of the growth temperature. The samples' structure is shown in Fig. 1. The N compositions were 3% and 5% while the In flux was fixed and corresponded to a composition of 8%. Therefore, for 3% N, the GaInNAs layers were lattice matched to GaAs and their thickness was 500 nm. Accordingly, for the 5% N, the GaInNAs layer was tensile-strained and had a thickness of 200 nm (below the critical thickness). For this set, the growth temperature was changed between 375 °C and 525 °C.

The second set of samples was grown on n-GaAs(1 0 0) and consisted of an undoped GaInNAs layer with a thickness of 320 nm, which was incorporated between Si- and Be-doped GaAs layers, as shown in Fig. 1. This set was used for optical and electrical characterization. The In and N compositions were 2.7%, 5.6% and 8.0%, and 1%, 2%, and 3%, respectively, as required for lattice matching to GaAs. The growth temperature for the GaInNAs region was changed between 395 °C and 495 °C, while the In and N fluxes were kept fixed for each lattice-matched compositions targeted. We should note here that the effective N composition

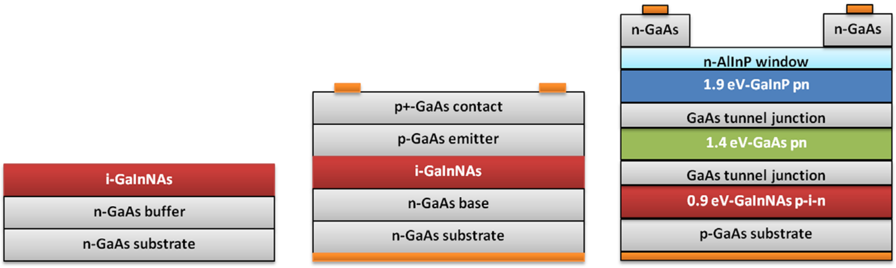

Fig. 1. Generic structure of the bulk sample for structural characterization, the p-i-n solar cell including a 320 nm thick InGaAsN absorber lattice matched to n-GaAs(1 0 0) substrate and GaInP/GaAs/GaInNAs MJSC.