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Improvement of front-junction GaInP by point-defect injection and annealing

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Abstract— **Traditional front junction GaInP solar cells are radiation tolerant and can have good diffusion length, but have limited voltage and thus efficiency. Here, we investigate the impact of annealing on GaInP device performance. First, Zn-doped GaInP/AlGaInP double heterojunction structures are studied in order to investigate the impact of annealing in a simple structure. While standard anneals lower diffusion length and lifetime, annealing after injecting point-defects improves material quality, presumably by eliminating sources of non-radiative recombination. Atomic ordering is reduced by the anneal, which raises the device bandgap and requires consideration. These results can be used to improve front junction device performance while controlling the bandgap. Then, GaInP front-junction devices are created using anneals with and without point-defect injection. Voc and EQE trends follow the diffusion length and lifetime trends from the DH structures. Baseline devices have Woc of 0.484 V, raising to 0.504 V after a high temperature anneal. However, injecting point defects prior to the anneal results in a front junction device with Woc of 0.405 V and a diffusion length greater than 8 μm. Optimized front-junction GaInP devices with an ARC have ~20% efficiency without a rear reflector.**

Keywords—III-V multijunction, GaInP, anneal

I. INTRODUCTION

Although rear-heterojunction GaInP solar cells have excellent voltage,[1] they have limited carrier collection due to diffusion length limitations and have poor radiation hardness.[2] Record efficiency GaInP devices with rear-heterojunctions rely on a back reflector to achieve complete carrier collection, which is not present in a multijunction device. On the other hand, front junction GaInP devices are radiation hard and have longer diffusion length, but typically have lower efficiency. In addition, the performance of both types of solar cells can be negatively impacted by annealing. With improved voltage and long diffusion lengths, a traditional front junction GaInP device could outperform a rear-heterojunction device in a multijunction cell, and provide its well-known radiation hardness.[3] Here we investigate the impact of annealing on front junction GaInP performance with and without prior point-defect injection. The annealing behavior is complex, but can be controlled to result in excellent front junction devices.

II. EXPERIMENTAL

Front-junction GaInP devices, and GaInP/AlGaInP double heterostructures were grown using atmospheric pressure OMVPE and standard precursors on (001) GaAs substrates miscut 2° towards (111)B. Growth was in the inverted direction, and devices and double heterostructures were both followed by point-defect injection layers and GaAs annealing layers. Device layers were grown at 720 °C, point-defect injection layers were grown at 620 °C, and GaAs annealing layers were grown at either 620 °C or 725 °C. The point-defect injection layers were simply AlGaAs:C/GaAs:Se tunnel junctions (TJ), and so simulates a structure used in multijunction solar cells. The structures are shown in Fig. 1a and Fig. 2a and described later in the text. After growth, solar cell samples were electroplated with a Au back contact, inverted onto a Si handle, the substrate and GaInP stop etch were removed, front Au grids were electroplated, and devices were isolated with selective etchants. External quantum efficiency (EQE) and current-voltage (IV) curves were measured on solar cell devices using custom-built instruments. Double heterostructures were tested for diffusion length and emission energy using cathodoluminescence (CL), lifetime using time resolved photoluminescence (TRPL), and atomic ordering using X-ray diffraction (XRD).

III. : RESULTS

A. Annealing tests of GaInP/AlGaInP double heterostructures

Zn-doped $Al_{0.3}Ga_{0.2}In_{0.5}P/Ga_{0.5}In_{0.5}P/Al_{0.3}Ga_{0.2}In_{0.5}P$ (0.2 μm/1 μm/ 0.2 μm) double heterostructures are grown with varying annealing layers after the DH structure:

- No growth after DH (baseline structure)
- 1-μm-thick undoped GaAs annealing layer, grown for 30 min at 620 °C or 725 °C
- An AlGaAs:C/GaAs:Se TJ for point defect injection, followed by a 1-μm-thick undoped GaAs annealing layer, grown for 30 min at 725 °C.

Table I: Zn-doped GaInP/AlGaInP DH annealing. Including a thin layer to inject point defects into the structure prior to an anneal dramatically influences the material quality.

Point-defect injection layer	Annealing temp. (°C)	Lifetime (ns)	Diffusion length (µm)
none	none	40	11
none	620	30	8
none	725	13	5
standard TJ	725	40	11

After the growth, the TJ and annealing layers were selectively etched, and the remaining DH structure was characterized with CL to extract diffusion length (Fig. 1b), TRPL to measure lifetime, and XRD for observing changes to atomic ordering. The structures are shown in Fig. 1a.

The lifetime and diffusion length results are shown in Table I. The Zn-doped GaInP/AlGaInP DH structure initially has high material quality, but is quickly impacted by a low temperature anneal at 620 °C, and further impacted as the anneal temperature is raised to 725 °C. Lifetime decreases from 40 ns to 30 ns and 13 ns, respectively, and diffusion length decreases from 11 to 8 to 5 µm, respectively. However, implementing a TJ prior to annealing improves diffusion length and lifetime dramatically, back to their initial values prior to degradation. Speculation about possible point defect interactions leading to this result is included in the discussion section.

Annealing with a TJ reduces GaInP atomic ordering of the wrt annealing without a TJ, shown in XRD diffraction of the ½(113) peak in Fig. 1c. Controlling atomic ordering is necessary to control the bandgap in GaInP devices and optimize multijunction current balancing. In addition, the variation of atomic ordering gives some insight into the type of point defect interactions that occur upon annealing, discussed later.

B. *GaInP solar cell annealing*

Inverted, front-junction GaInP devices with 2-µm-thick GaInP:Zn bases and varying annealing layers are grown and compared. The device structures are identical until after the growth of the AlGaInP:Zn BSF, after which varying annealing layers are added:

- AlGaAs:C contact layer (baseline device)
- 1-µm-thick GaAs:C annealing layer, grown for 30 min at 620 °C or 725 °C, then an AlGaAs:C contact layer
- AlGaAs:C/GaAs:Se tunnel junction (point-defect injection layer), then 1-µm-thick GaAs:Se annealing layer, grown for 30 min 725 °C, then an GaAs:Se contact layer

The structure is shown in Fig. 2a. The baseline device has a Woc of 0.484 V. Notably, the EQE benefits from the Au contact, which acts as a rear-reflector, leading to interference fringes and an improved absorption near the bandedge. The high Woc indicates a low radiative efficiency, and so the voltage is not appreciably impacted by photon recycling. Adding annealing at 620 °C and 725 °C increasingly degrades the device performance, raising Woc to 0.501 and 0.504, respectively. Notably, these devices have a 1-µm-thick absorbing layer after the cell, lowering the EQE near the bandedge and absorbing any light that passes through the base. Including a tunnel junction prior to the anneal improves device performance above that of the baseline device, improving the EQE and lowering Woc to 0.405, which is very good for a device with an absorbing layer behind the base. The external radiative efficiency improves from 0.1% to 4% at 20 mA/cm^2 (not shown). The general trends in diffusion length and lifetime from the DH experiment are thus confirmed in solar cell devices.

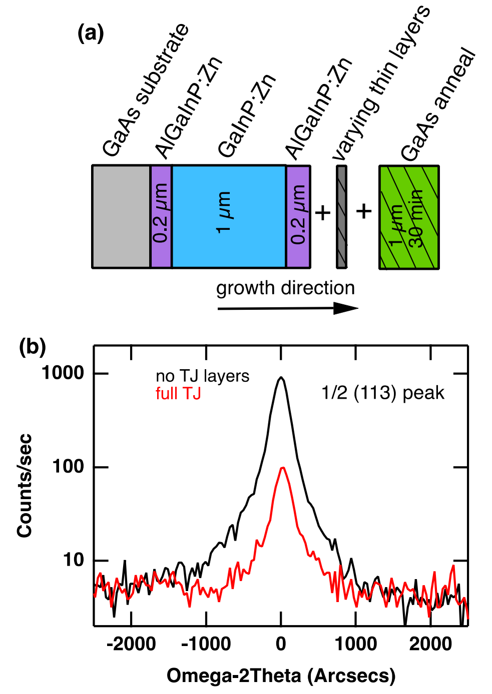

Figure 1: (a) Illustration of Zn-doped GaInP/AlGaInP double heterostructure experiment. Annealing is performed with and without various thin layers prior to the anneal. (b) XRD of the ½ (113) peak, which is used to observe changes in atomic ordering due to annealing.

To further test the diffusion length of annealed devices, we increased the thickness of the GaInP:Zn base from 2 µm to 4 µm. Even at a base thickness of 4 µm, no carrier loss is observed. EQE modeling predicts the diffusion length is 8-10 µm. When the diffusion length is longer than the base thickness, the error in diffusion length modeling from EQE is significant. However, the results quantitatively agree with the diffusion length measurement of the DH structures, and the near bandedge absorption is sharp.

Devices using optimized anneals including point-defect injection were measured after coating with a MgF$_2$/ZnS anti-reflective coating, shown in Fig. 3b. The device structure includes an absorbing GaAs layer (Fig 2a), and so the efficiency simulates performance in a multijunction device. Voc of 1.45 V and efficiency of 19.8% (not NREL-certified) are shown.

IV. DISCUSSION

The behavior of Zn-doped GaInP is clearly complex. Here, we speculate that the introduction of Zn into GaInP creates point defects (pX) that result in non-radiative recombination. Annealing the sample without a TJ either introduces more defects or increases the recombination associated with these defects. Including a TJ injects a complementary point defect (pY), which, upon anneal, passivates pX. This type of passivation could occur if pX is a group III vacancy and pY is a group III interstitial, or vise versa. In this case, we don't know what type of point defect interactions are occurring. However, we get some information from the difference in atomic ordering with and without a TJ. Highly doped layers such as TJs are known to inject point defects such as Ga interstitials into the previously grown material, which then enhances Zn diffusion through the kick-out mechanism.[4-6] The kick-out mechanism involves group III interstitials swapping place with an substitutional Zn atom, resulting in more mobile interstitial Zn. Rearrangement of the group III sublattice also occurs, which leads to the observed reduction in atomic ordering. Therefore, we have some confidence that group III interstitials are being injected by the TJ due to the reduction in atomic ordering. It is possible that group III interstitials also passivate pX. Alternatively, multiple types of point defects could be injected by the TJ. More investigation is needed to determine the type of point defect interaction occurring in these devices, which could be performed through a detailed study of DH structures or solar cells with varying point defect injection layers. Despite not fully understanding the underlying mechanisms, we have shown that GaInP:Zn is very sensitive to point defects, have shown some of the important parameters impacting performance, and have shown effective ways of improving devices. Final devices with optimized anneals have ~20% efficiency with an ARC, despite having an absorbing GaAs layer behind the cell.

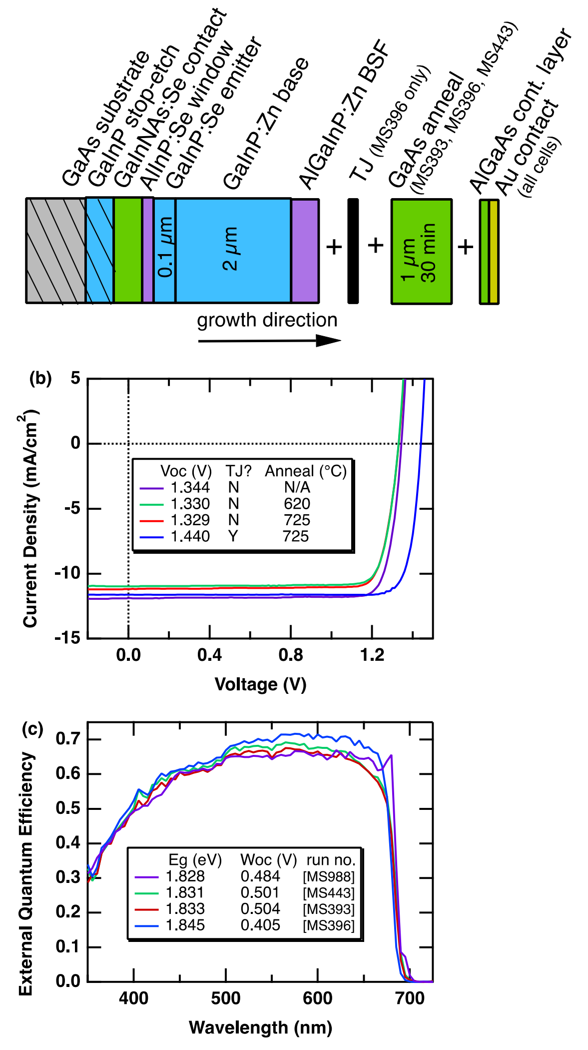

Figure 2: (a) Illustration of the front-junction GaInP devices investigated. Standard inverted GaInP cells are compared to devices with 30 min anneals at 620 °C and 725 °C. Then a device with point defects injected using a tunnel junction is annealed at 725 °C. (b) IV and (c) EQE of these devices.

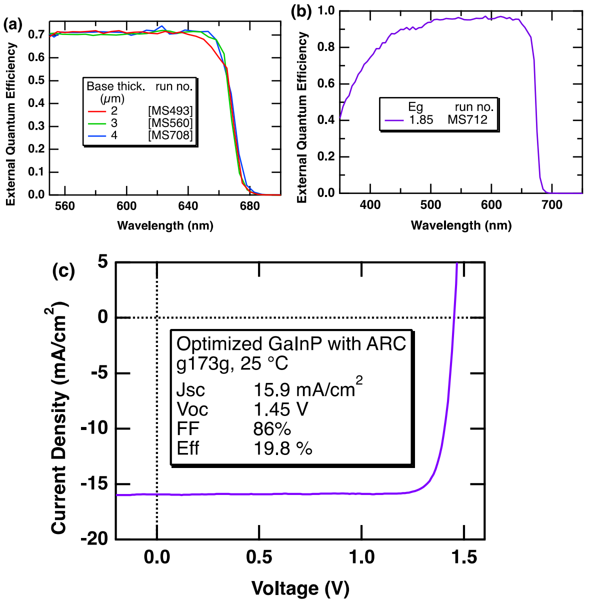

Figure 3: Front-junction GaInP cells with the structure shown in Fig. 1a, including a point defect injection and anneal at 725 °C. (a) The base thickness is varied from 2 – 4 μm as a test of diffusion length. (b) EQE and (c) IV results from 2-μm thick GaInP device including a GaAs absorbing annealing layer after ARC.

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