I. INTRODUCTION

Metamorphic triple-junction solar cells have recently reached efficiencies of 41.1% by combining lattice-mismatched light-absorbing materials, each efficiently collecting a different portion of the solar spectrum. Calculations show that four to six junction cells could approach efficiencies of 60%, but these cell designs will require top subcells with band gap ($E_g$) energies ranging from 2.0 to 2.2 eV. Most III-V materials available in this range possess indirect band gaps, necessitating thick absorber layers to fully collect the incoming sunlight. Furthermore, many of these materials contain Al, whose affinity for oxygen leads to efficiency-diminishing defects.

In$_y$Ga$_{1-y}$P ($y=0.27–0.40$), in contrast, has a direct band gap in the desired range and is Al-free. It is, however, lattice-mismatched to conventional substrates. In order to grow lattice-mismatched In$_y$Ga$_{1-y}$P films with low threading dislocation densities (TDDs) and long minority carrier lifetimes, we employ an intermediate GaAs$_x$P$_{1-x}$ graded buffer to engineer the lattice constant from that of GaAs to that of wide-$E_g$ In$_y$Ga$_{1-y}$P. GaAs$_x$P$_{1-x}$ graded buffers grown by both metalorganic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE) have recently been demonstrated. However, the unequal and temperature-dependent incorporation rates of the anionic species create challenges in achieving reproducible composition control.

In this work we first show that a kinetic growth model, previously used to describe anion incorporation in gas-source MBE of GaAs$_x$P$_{1-x}$, can be extended to solid source MBE (SSMBE) of GaAs$_x$P$_{1-x}$. We then discuss the growth of each component of a single junction wide-$E_g$ In$_y$Ga$_{1-y}$P solar cell individually, including the graded buffer, In$_y$Ga$_{1-y}$P active region, and InAlP window layer. Taken together, the growth techniques described in this paper have recently led to the demonstration of high open-circuit voltage ($V_{oc}$) metamorphic In$_y$Ga$_{1-y}$P solar cells.

II. EXPERIMENT

All samples were grown on GaAs (100) substrates in a Veeco GEN-II SSMBE chamber equipped with in situ reflection high energy electron diffraction (RHEED), allowing surface monitoring during growth. Our system contains elemental sources of Ga, In, Al, Be, Si, P, and As, with thermal cracking of the group-V species performed at 900 °C to produce dimer beam fluxes. All fluxes reported here are beam equivalent pressures (BEPs) while substrate temperatures ($T_{sub}$) refer to thermocouple readings; thermocouple temperatures of 650 and 700 °C were found to correspond to approximate pyrometer temperatures of 645 and 680 °C, respectively. After growth, we determined material composition and degree of relaxation using x-ray diffraction (XRD) measurements on a Bede-D1 system with a Cu $K_x$ source, while Nomarski optical microscopy allowed us to characterize surface morphologies. We carried out photoluminescence (PL) measurements using a 527 nm laser and an Ocean Optics USB 2000 spectrometer to estimate material band gaps and to confirm compositions acquired via XRD. We performed both cross-sectional-view (XV) and planar-view (PV) transmission electron microscopy (TEM) on a Tecnai...
T12 system operated at 120 kV to inspect interfaces and to determine TDDs, respectively. High angle annular dark field (HAADF) imaging, performed in a Tecnai Osiris scanning TEM operated at 200 kV, was used to complement the results from conventional TEM imaging. To calibrate the doping necessary for solar cell structures, we grew thick (≈1–2 μm) test samples with different dopant fluxes and measured carrier concentrations using a van der Pauw Hall effect system with a 0.51 T magnet. A 15–20 nm heavily doped GaAs cap layer was found to facilitate Ohmic contact formation, particularly for Al-containing samples. Using In solder contact points as a hard mask, the GaAs cap was selectively etched away to avoid errors resulting from parallel conduction in the GaAs cap layer. We fabricated single junction In$_x$Ga$_{1-x}$P solar cells and measured lighted current-voltage (L-IV) characteristics using a Newport solar simulator with a Keithley 2400 source meter.

III. RESULTS AND DISCUSSION

A. GaAs$_x$P$_{1-x}$ graded buffers on GaAs

We grew a series of GaAs$_x$P$_{1-x}$ buffers at $T_{sub}$=550–700 °C while keeping the $P_2/\{(As_2+P_2)\}$ flux constant in order to measure the kinetics of anion incorporation; the V/III BEP ratio was ≈20. XRD confirmed that $T_{sub}$-dependent composition variation can be minimized between 650 and 700 °C. The composition dependence of GaAs$_x$P$_{1-x}$ on $T_{sub}$ is minimized between 650 and 700 °C.

$$B = K \exp(-18000/T_{sub}).$$

By adjusting the pre-exponential terms (X, Y, Z, and K) in Eqs. (1)–(3) and using beam equivalent pressures to obtain $f_{As_2}/f_{P_2} = 7$, we fit our data using $X = 7.5 \times 10^{10}$, $Y = 2.5 \times 10^{15}$, $Z = 3.5 \times 10^6$, and $K = 4.4 \times 10^6$ (Fig. 1).

PL measurements, taken across a graded GaAs$_x$P$_{1-x}$ buffer grown at $T_{sub}=700$ °C on a 4 in. semi-insulating GaAs wafer, further confirmed the minimized $T_{sub}$-dependent composition variation predicted in the model of Liang and Tu. The results demonstrated a peak wavelength variation from center to edge of ±3 nm, yielding an As composition (assuming similar degrees of relaxation) variation of <1% (Fig. 2).

In addition to improved composition control, another advantage of using high $T_{sub}$ for GaAs$_x$P$_{1-x}$ growth is that the desorption rates of P and As become nearly equal for $T_{sub}$ ≥ 650 °C. Thus, P incorporation versus $P_2$ flux transitions from a superlinear dependence for $T_{sub}$ ≤ 580 °C to a simple linear dependence for $T_{sub}$ ≥ 650 °C. Employing a step-graded structure, we controlled the composition of each layer in the GaAs$_x$P$_{1-x}$ graded buffers by varying the $P_2$ flux in a stepwise fashion while keeping the $As_2$ flux constant [Fig. 3(a)], which led to uniform changes in phosphorous content from step to step. Figure 3(b) shows that P composition is linearly dependent on the $P_2/\{(As_2+P_2)\}$ flux ratio at $T_{sub}$=700 °C, again confirming the kinetic model of Liang and Tu.

The dislocation dynamics model of Fitzgerald et al. shows that a further benefit of growing at high $T_{sub}$ is improved kinetics for dislocation glide, which, in turn, should lead to lower TDD. In agreement with this model, our PVTEM measurements revealed that growing GaAs$_{0.8}$P$_{0.2}$ at $T_{sub}$=700 °C resulted in TDD=0.7–1.0×10^6 cm$^{-3}$, while growing at $T_{sub}$=650 °C resulted in TDD=2.0–3.0×10^6 cm$^{-3}$ (Fig. 4). Thus, lower TDD, a linear composition dependence on P flux, and minimized composition dependence on $T_{sub}$ are all enabled by growing at $T_{sub}$ ≥ 650 °C.

![Fig. 1. (Color online) P composition of GaAs$_x$P$_{1-x}$ samples grown under identical $P_2/\{(As_2+P_2)\}$ flux ratio at various values of $T_{sub}$. Fit (- - -) with model from Ref. 12. The composition dependence of GaAs$_x$P$_{1-x}$ on $T_{sub}$ is minimized between 650 and 700 °C.](image1)

![Fig. 2. (Color online) Room temperature PL spectra of a GaAs$_{0.8}$P$_{0.2}$ graded buffer collected from various positions on a 4 in. wafer. PL emission wavelength remains nearly constant from center to edge of the GaAs$_{0.8}$P$_{0.2}$ graded buffer, indicating minimal $T_{sub}$-dependent composition variation at $T_{sub}$=700 °C.](image2)
At $T_{sub} \geq 650$ °C, the Ga adatom sticking coefficient can no longer be assumed to be unity, and thus the growth rate will be decreased compared with growth at lower $T_{sub}$. We recalibrated the growth rate for elevated $T_{sub}$ by growing a GaAs film at $T_{sub}=700$ °C with a Ga flux known to provide a growth rate of 920 nm/h for $T_{sub}=580$ °C (where the Ga sticking coefficient is close to unity). By growing the GaAs film between two AlGaAs marker layers, we were able to measure the resulting GaAs thickness using cross-sectional scanning electron microscopy (XSEM). We then found the GaAs growth rate at $T_{sub}=700$ °C to be 700 nm/h, 25% lower than the growth rate at $T_{sub}=580$ °C. This growth rate reduction should thus be taken into account when growing graded buffers at high $T_{sub}$ in order to avoid an unintentional increase of the grading rate.

We observed that unoptimized GaAs$_{P_{1-x}}$ graded buffer structures suffered from a morphological defect propagating along the [011] direction, which we refer to as a faceted trench (FT). Using Nomarski microscopy we calculated FT densities (FTDs) by adding the lengths of each of the FTs and dividing by the measured area, yielding a value with units of cm$^{-1}$ [Fig. 5(a)]. A FTD exceeding 500 cm$^{-1}$ is observable in situ as a streaky chevron-like RHEED pattern along [011] [Fig. 5(b)]. The orientation of the FT planes can be determined from the angle the chevron makes with the vertical streak. In this way we obtained a facet angle of 24°$\pm$ 29° (verified by XSEM), which implies that the trenches form facets on the {113}A or {114}A planes. Using XSEM we also measured the depth of the FTs to be $\sim 100–300$ nm [Fig. 5(c)]. Similar morphologies, with facets only forming parallel to [011], have also been observed in other tensile-strained systems.

While FTs alone may not compromise device performance, PVTEM analysis of high-FTD GaAs$_{P_{1-x}}$ graded buffers revealed that FTs hinder dislocation glide and lead to threading dislocation (TD) pileups. The nucleation of additional TDs is then required to relieve any remaining strain, leading to higher global TDD. To investigate the effect of FTs on the electronic properties of the material, we inspected a 2.0 V forward-biased In$_{0.39}$Ga$_{0.61}$P solar cell (described in Sec. III D) containing a single FT [Fig. 6(a)] under an optical microscope. The electroluminescence image in Fig. 6(b) shows that FTs locally quench radiative recombination and suggests that FTs must be completely eliminated to attain high-efficiency solar cells.

In earlier work, we showed that the FTD was highly sensitive to the details of the graded buffer structure. For example, by reducing the grading rate from 0.53 to 0.29% µm$^{-1}$, we decreased the FTD from 120 to $<1$ cm$^{-1}$ for GaAs$_{0.3}$P$_{0.2}$ graded buffers. The resulting graded buffer...
yields a high degree of strain relaxation of ~90%, measured using (400) and (422) XRD reciprocal space maps. Figure 7 provides a schematic of the graded buffer structure used in this work, which consists of nine 250-nm-thick grading steps and a 1-μm-thick cap. The P content changes by 2% for each step and terminates in a GaAs0.8P0.2 cap, resulting in a grading rate of ~0.29% μm⁻¹. In comparison, MOCVD-grown GaAsP1−x graded buffers have used similar grading rates, ranging from 0.15 to 0.20% μm⁻¹,9,10 though FTDs were not reported. It should also be noted that conditions in the MBE chamber such as growth rate and V/III BEP ratio had little effect on FTD. Optimized GaAs0.8P0.2/GaAs graded buffers with low FTD and TDD were then used for the growth of metamorphic wide-Eg InyGa1−yP solar cells.

### B. Metamorphic InyGa1−yP growth

To determine the optimal value of Tsub for InyGa1−yP growth, we grew a series of In0.40Ga0.51P films, lattice-matched to GaAs, with Tsub = 450–490 °C. In0.40Ga0.51P grown at 460 °C exhibited the most intense PL spectra of all samples and was therefore chosen for subsequent device growth. Although the variation in PL intensity for samples grown between 450 and 460 °C was on the order of 5%, we note that the samples grown above 470 °C exhibited a ten times lower intensity than those at 460 °C.

We then grew metamorphic InyGa1−yP on the optimized GaAsP1−x graded buffers described above, lattice matched to the in-plane lattice constant of the GaAs0.8P0.2 cap as measured by XRD. We paused the growth after the graded buffer to allow strain relaxation of ~90%, measured using (400) and (422) reciprocal space maps. Figure 7 provides a schematic of the graded buffer structure used in this work, which consists of nine 250-nm-thick grading steps and a 1-μm-thick cap. The P content changes by 2% for each step and terminates in a GaAs0.8P0.2 cap, resulting in a grading rate of ~0.29% μm⁻¹. In comparison, MOCVD-grown GaAsP1−x graded buffers have used similar grading rates, ranging from 0.15 to 0.20% μm⁻¹,9,10 though FTDs were not reported. It should also be noted that conditions in the MBE chamber such as growth rate and V/III BEP ratio had little effect on FTD. Optimized GaAs0.8P0.2/GaAs graded buffers with low FTD and TDD were then used for the growth of metamorphic wide-Eg InyGa1−yP solar cells.

![Image](https://example.com/image.png)

**Fig. 6.** (Color online) InyGa1−yP solar cell under (a) zero bias with faceted trench running down image. (b) 2.0 V forward bias. Dark regions around the FT demonstrate the ability of these defects to quench radiative recombination.

![Image](https://example.com/image.png)

**Fig. 7.** Schematic of optimized GaAsP1−x graded buffer to allow metamorphic InyGa1−yP growth on GaAs.

![Image](https://example.com/image.png)

**Fig. 8.** (a) XVHAADF microscope image of InyGa1−yP. Dark regions correspond to Ga-rich domains, while light regions correspond to In-rich domains. (b) XVTEM image looking down the (011) zone reveals strong phase separation contrast when g=[022]. Insets show the (022) diffraction spots taken at the InyGa1−yP/GaAsP1−x/GaAs0.8P0.2 interface, and GaAsP1−x film. (c) XVTEM image shows muted phase separation contrast when g=[400].
also been observed in In0.28Ga0.72P (Ref. 20) and other III-V alloys,21,22 but its effect on solar cell performance remains unclear. We speculate that Voc will be degraded by the In-rich lower-Eg domains, and we intend to investigate strategies to minimize phase separation in the future.

C. InAlP growth

High efficiency In0.49Ga0.51P solar cells generally require the use of a thin In0.5Al0.5P window layer to attain high quantum efficiencies at photon energies much larger than the Eg.23 Typically, the window layer is grown with carrier concentration in the 10^{18} \text{cm}^{-3} range to maintain low series resistance and to minimize the extent of the depletion region resulting from the Fermi level pinning at the surface.24 While smooth In0.5Al0.5P layers lattice-matched to GaAs with streaky RHEED patterns could be readily grown under the same conditions used for In0.49Ga0.51P growth, we found it difficult to obtain In0.5Al0.5P with electron concentration (n) > 4 \times 10^{17} \text{cm}^{-3}. For example, Si/III flux ratios that would lead to n=1 \times 10^{18} \text{cm}^{-3} in In0.49Ga0.51P gave n=1 \times 10^{17} \text{cm}^{-3} for In0.5Al0.5P growth, indicating strong compensation. Significant compensation in Si-doped (Al0.5Ga0.5)0.52In0.48P grown by SSMBE was reported by Sun et al., though they were able to reach a peak electron concentration of n=2.1 \times 10^{18} \text{cm}^{-3}.25 In contrast, n=5 \times 10^{18} \text{cm}^{-3} has been reported for Si-doped In0.5Al0.5P grown by gas-source MBE.26,27

In order to gain further insight on the electron compensation mechanism, we annealed our Si-doped In0.5Al0.5P, capped with a thin GaAs layer, in the MBE chamber at 680 °C for 5 min with an As2 overpressure. Comparison with unannealed samples revealed a two to three times increase in electron concentration in the annealed In0.5Al0.5P with a peak of n~8 \times 10^{17} \text{cm}^{-3}. Several potential causes for autocompensation of group IV dopants in III-V (A-B) materials have been studied, including Si atoms on group-V sites (SiV) instead of group III sites, nearest neighbor pairs of an Si atom on a group III site and a Si atom on a group-V site (SiA–SiB), and Si atoms next to group III vacancies (Si−V_A).28–30 We hypothesize that one of the defect complexes present in our In0.5Al0.5P is Si−V_A and that thermal annealing gives Si atoms sufficient thermal energy to move and annihilate the group III vacancy.

D. Single junction In_xGa_{1-x}P solar cells

We grew metamorphic In0.39Ga0.61P solar cells on graded GaAs_{0.8}P_{0.2}/GaAs in order to investigate the photovoltaic properties of our material. The active region of each solar cell consisted of a 2 μm p-type base, Be doped with a hole concentration of 1 \times 10^{17} \text{cm}^{-3}, followed by a 100 nm emitter, Si doped to n=1 \times 10^{18} \text{cm}^{-3}. The InAlP window layer was grown while increasing the Si cell temperature from 1200 °C (for emitter growth) to 1250 °C (for contact layer growth). Based upon calibration data, the window doping should be graded from n=(1−4) \times 10^{17} \text{cm}^{-3}. To avoid a growth interruption between the emitter and window layers, the same In flux was maintained for both In0.49Ga0.51P and InAlP growth. Bertness et al. used an In0.53Al0.47P window layer with n=4 \times 10^{17} \text{cm}^{-3} in high efficiency dual junction In0.52Ga0.48P/GaAs tandem solar cells, motivating our decision to continue with a relatively low-doped window layer.31 For contact layer growth, we grew 2 nm of GaAs at T_{sub}=460 °C to protect the underlying InAlP during the subsequent growth interruption, then raised T_{sub} to 580 °C to grow the remaining 50 nm of the n=5 \times 10^{18} \text{cm}^{-3} Si-doped GaAs contact layer. A schematic of the final metamorphic In0.39Ga0.61P solar cell structure is given in Fig. 9a. In addition to the metamorphic In0.39Ga0.61P cell, we grew a control In0.49Ga0.51P cell lattice-matched to GaAs, with Ef (measured by PL) of 2.00 and 1.89 eV, respectively. The cells were processed “as grown” and were not subjected to the high-T annealing step described in Sec. III C.

We then fabricated 2.1×2.1 mm² cells which were free of FTs due to the optimized grading procedure described in Sec. III A. Under approximate AM1.5G illumination conditions, we measured an increase in Voc and a decrease in short circuit current for decreasing In content, consistent with expected trends for increasing Ef. The lattice-matched In0.49Ga0.51P cell with Ef=1.89 eV had Voc=1.31 V [Fig. 9b]. Increasing the band gap by 0.11 to 2.00 eV in the metamorphic In0.39Ga0.61P cell led to a proportional increase of Voc to 1.42 V [Fig. 9b]. Fill factors for both cells were nearly constant at ~0.8. The maximum practical value for Voc in a 2.00 eV solar cell is ~1.60 V (V_{oc,max}=E_f/q ~0.40 V).32 By adding a back surface field and antireflective
coating we aim to improve our cell performance and move closer to this maximum value of $V_{oc} = 1.60$ V.

IV. SUMMARY AND CONCLUSIONS

We have demonstrated the growth of graded GaAs$_{1-x}$P$_x$ buffers on GaAs by SSMBE. Buffer growth at $T_{sub} = 700$ °C was shown to simplify composition control and lead to low TDD. Despite the observation of significant phase separation within the In$_x$Ga$_{1-x}$P and difficulties in $n$-type doping of InAlP, we grew metamorphic In$_x$Ga$_{1-x}$P on the relaxed GaAs$_{1-x}$P$_x$ buffers and fabricated $E_g = 2.00$ eV solar cells with $V_{oc} = 1.42$ V. In future studies, the effects of phase separation and postgrowth thermal annealing will be further analyzed with the goal of identifying which defects ultimately limit $V_{oc}$ in these devices.

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