

GaNPAs Solar Cells Lattice-Matched to GaP

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GaNPAs SOLAR CELLS LATTICE-MATCHED TO GaP

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ABSTRACT

III-V semiconductors grown on silicon substrates are very attractive for lower-cost, high-efficiency multi-junction solar cells, but lattice-mismatched alloys that result in high dislocation densities have been unable to achieve satisfactory performance. $\text{GaN}_x\text{P}_{1-x-y}\text{As}_y$ is a direct-gap III-V alloy that can be grown lattice-matched to Si when $y = 4.7x - 0.1$. We propose the use of lattice-matched GaNPAs on silicon for high-efficiency multijunction solar cells. We have grown $\text{GaN}_x\text{P}_{1-x-y}\text{As}_y$ on GaP (with a similar lattice constant to silicon) by metal-organic chemical vapor phase epitaxy with direct bandgaps in the range of 1.5 to 2.0 eV. We demonstrate the performance of single-junction $\text{GaN}_x\text{P}_{1-x-y}\text{As}_y$ solar cells grown on GaP substrates and discuss the prospects for the development of monolithic high-efficiency multijunction solar cells based on silicon substrates.

INTRODUCTION

State-of-the-art GaInP/GaAs/Ge and many proposed future generations of III-V high-efficiency solar cells are based on GaAs or Ge substrates [1]. In particular, much attention has been given to GaInNAs materials grown lattice-matched on GaAs over the past few years [2]. More recently, GaNP materials have been shown to become direct-gap with only a few % N [3]. GaNPAs alloys have been grown lattice-matched to GaP [4] and Si [5] with band gaps that could be useful for

solar cells. Growth on silicon substrates is very exciting because it would allow for significant cost savings of substrates and the potential for integration with existing Si technology. Lattice-mismatched III-V cells on Si substrates have been studied extensively, but the reduction of defect densities remains a significant challenge that typically requires complex graded buffer layers [6-8]. Nearly lattice-matched $\text{Al}_{0.01}\text{Ga}_{0.99}\text{N}_{0.01}\text{P}_{0.99}$ on Si solar cells has been proposed [9], but this composition limits the range of band gaps available. We propose a structure based on lattice-matched $\text{GaN}_x\text{P}_{1-x-y}\text{As}_y$, hereafter GaNPAs, alloys grown on silicon. The solar cell structure shown in Fig. 1 composed of a lattice-matched III-V cell grown on a Si cell could potentially rival the efficiencies of high-efficiency cells on GaAs or Ge, with significant cost savings and improvements in mechanical stability. Indeed, a two-junction cell composed of a 1.65-eV to 1.75-eV GaNPAs junction on a 1.1-eV silicon junction has a nearly optimal set of band gaps for high efficiency solar cells, as shown in Fig. 2.

GaP is only 0.36% lattice-mismatched with silicon, and growth on GaP substrates avoids some of the diffi-

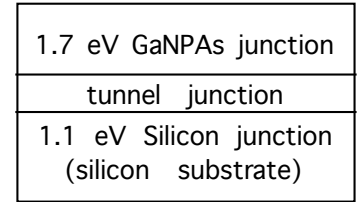


Fig. 1. Proposed lattice-matched GaNPAs on silicon tandem solar cell.

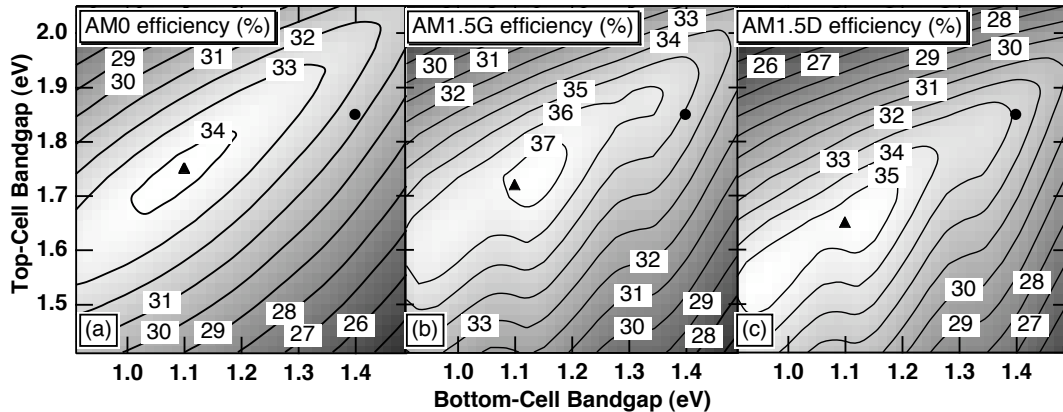


Fig. 2. Iso-efficiency contour plots of ideal series-connected, two-junction solar cell with an optimized top cell thickness [10], as a function of top-cell and bottom-cell direct band gap using standard spectra: (a) AM0 (space), (b) AM1.5 global (terrestrial), (c) AM1.5 direct (concentrator terrestrial). All efficiencies were calculated at 300 K and 1-sun conditions. The triangles show optimal GaNPAs/Si tandems and the circles show the standard GaInP/GaAs tandem cell.

culties associated with growth on silicon. Therefore, as a first step, we study here GaNPAs solar cells grown on GaP substrates.

MATERIAL PROPERTIES

GaNPAs layers were grown by atmospheric-pressure metal-organic vapor-phase epitaxy (MOVPE) on (001)-oriented, double-side-polished GaP wafers using trimethylgallium (TMG) or triethylgallium (TEG), unsymmetric-dimethylhydrazine (DMH), phosphine (PH₃), and t-butylarsine as sources. Growth was performed at 600°–700°C, with nominal growth rates (GR) of 2–4 μm/h, and PH₃ / Ga ratios of 6–52. Incorporation efficiencies of the group V elements follow the trend of As>P>N and are highly temperature dependent. While N incorporation drops off with increasing temperature, P incorporation increases relative to As. Thus, achieving the intended compositions required a sensitive balance between group V source flows and temperature. By carefully adjusting the group V flows, alloys nearly lattice-matched to GaP were grown.

A series of nominally GaNPAs layers were grown directly on double-side-polished, undoped GaP substrates to determine the absorption coefficient (α). Simultaneous reflectance (R) and transmittance (T) measurements of the layer were used to determine α(λ) below the band gap energy of the GaP substrate, and spectral ellipsometry (SE) measurements were used above the band gap of the substrate. Fig. 3 shows the absorption for several different compositions of GaNPAs. The strong direct-like absorption in this spectral range indicates that these alloys may be quite useful as solar cell absorber layers. The absorption edge indicated band gaps in the range of 1.5 to 2.0 eV for different compositions lattice-matched to GaP.

Double-crystal x-ray diffraction (DCXRD) was performed in the (004) reflection and, in some cases, (115)

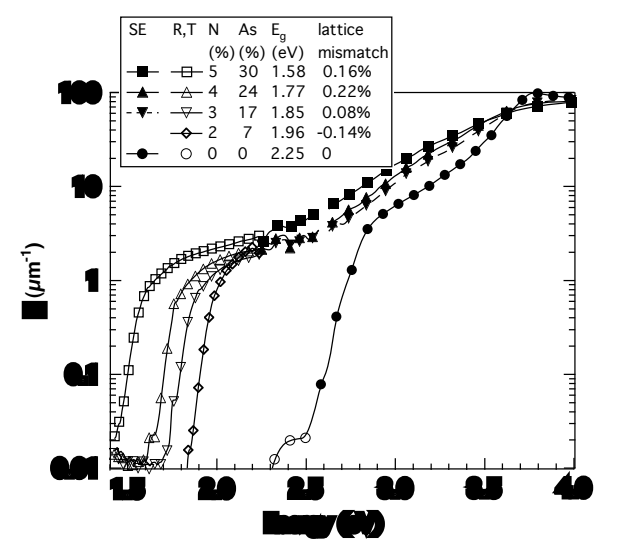


Fig. 3. Absorption coefficient of GaN_xP_{1-x-y}As_y layers grown on GaP substrates. The GaP substrate is shown as circles.

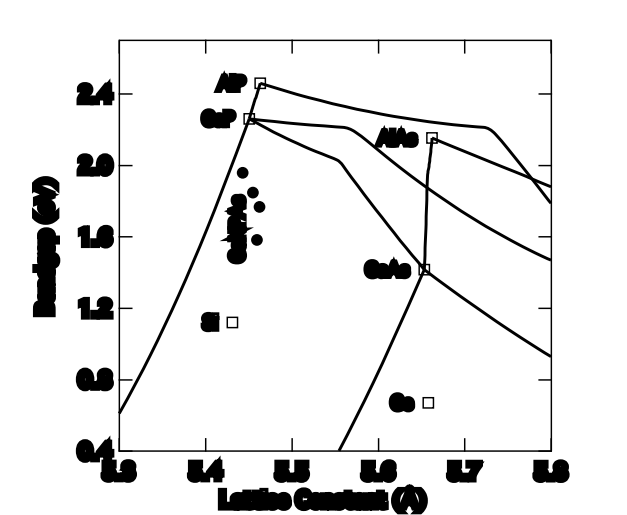


Fig. 4. Band gap vs. lattice constant of III-V semiconductors including data for GaNPAs alloys from Fig. 3.

reflections. Nitrogen composition in GaNP was estimated using Vegard's law. Although the nitrogen and arsenic composition in GaNPAs could not be unambiguously determined from these measurements, the peak splitting, □□, was used to determine the average lattice parameter of the material. The compositions were then estimated based on the measured lattice parameter and the pseudo-binary bowing parameters of GaNP (~15 eV), GaNAs (~15 eV), and GaPAs [11]. Fig. 4 shows how closely the GaNPAs layers were lattice-matched to GaP and Si.

SOLAR CELLS

The simple single heterojunction cell design shown in Fig. 5 was used to study these GaNPAs cells. The cells consisted of a Zn-doped GaP back surface field, an undoped GaNPAs base, a Se- or Si-doped GaP emitter, and a Se-doped GaAs contact layer. The cells were grown on Zn-doped (001) GaP substrates. The active GaNPAs base was grown at 700°C. Au/Zn/Au back-side contacts and Au/Sn/Au front-side contacts were deposited and annealed at 450°C. Devices were isolated with a KMnO₄/HF/H₂O mesa etch. The GaAs contact layer was selectively etched with a solution of NH₄OH/H₂O₂/H₂O.

The carrier concentration in the nominally undoped GaNPAs base and similar layers was measured by capacitance-voltage (CV) measurements. The layers were consistently found to be p-type (on the order of 1x10¹⁶ cm⁻³)

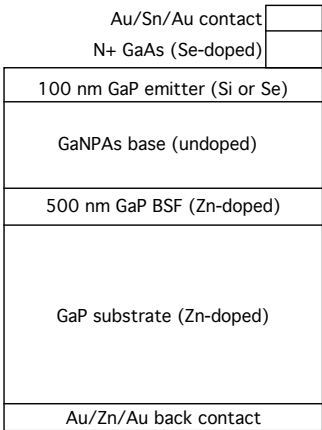


Fig. 5. Single-junction GaNPAs cell structure.

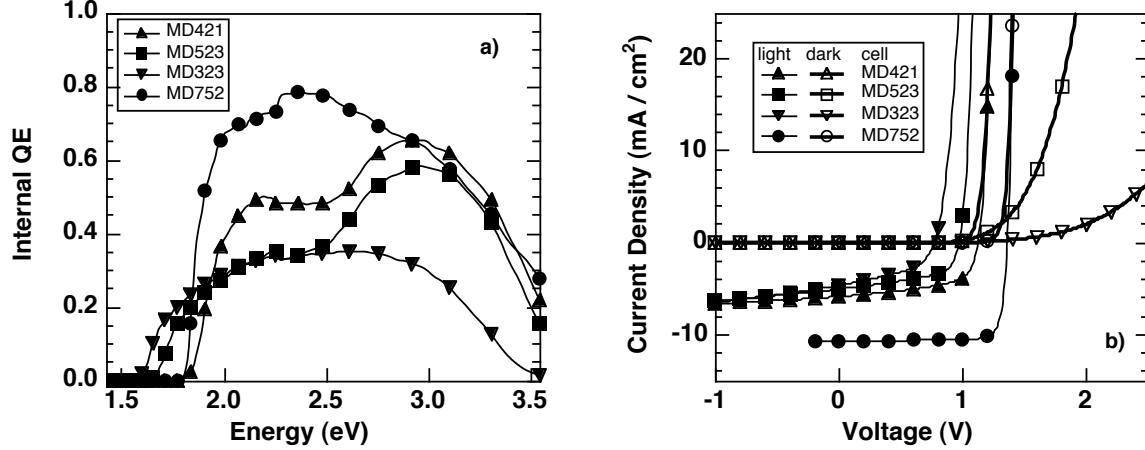


Fig. 6. (a) Internal quantum efficiency of three solar cells with different compositions of GaNPAs nearly lattice-matched to GaP and a GaInP cell for comparison, and (b) current-voltage curves of the same solar cells under AM1.5G conditions. A summary of these cells is listed in Table 1.

under normal measurement conditions, but were depleted when measured in the dark. Estimates of the base thickness determined from this depleted CV measurement are given in Table 1.

The external quantum efficiency (QE) and reflectance of the cells were measured to calculate the internal QE. The internal QE is shown in Fig. 6a for three solar cells with different compositions of GaNPAs along with a standard GaInP solar cell (MD752) with a similar band gap for comparison. The integrated current was calculated from the AM1.5 global spectrum and used to set the light level on an XT-10 solar simulator. The current-voltage (IV) curves were measured both in the light and dark. The IV curves corresponding to the cells from Fig. 6a are shown in Fig. 6b. A summary of the devices is given in Table 1.

The increased QE for cells MD421 and MD523 above 2.5 eV (the direct gap of GaP) probably comes from collection in the GaP emitter layer. The collection of blue light in these cells compares favorably with the AlInP-passivated GaInP cell, MD752, in spite of the lack of a passivating window layer in our design. An AlGaP window layer may further improve the blue response of these cells. The GaP emitter in MD323 was grown at 650° rather than 700°C using Se-doping rather than Si-doping. The lack of an increased QE above 2.5 eV indicates a lower quality of the GaP emitter in MD323.

The QE below 2.5 eV comes entirely from collection in the GaNPAs base layer, as this is the only layer of the structure with significant absorption in this region. A

0.64- μ m-thick base layer should absorb more than 60% of the light above the band gap of the layer based on the absorption coefficients presented in Fig. 3. The thicker layers should absorb more than 80%. The relatively low quantum efficiencies in this region indicate a problem with the material quality (diffusion length) of the GaNPAs. This problem is similar to the short diffusion lengths observed in GaInNAs [2]. The cells with lower nitrogen content (~3%) and higher band gap in general seem to be able to achieve slightly higher QE than the cells with more nitrogen (~5%), as represented by the data in Fig. 6a.

The performance of these GaNPAs cells is less than ideal. The short-circuit current (J_{sc}), open-circuit voltage (V_{oc}), and fill factor (FF) of the GaNPAs cells are all significantly less than the values of the GaInP cell (MD752) with a comparable band gap. The shunt in the light IV curves, but not the dark IV curves, indicates field-aided collection.

An additional problem can be observed in the dark IV of the cells. A shift in the dark IV relative to the light IV suggests important differences in the material properties in the light and dark. Again, this IV shift is more pronounced in cells with higher nitrogen content and lower band gap. To better understand this difference in the light and dark, CV measurements were performed under different levels of light: dark, ambient, and under an intense desk lamp. The capacitance was measured from 0 to 2 V reverse bias, and the resulting carrier concentration versus depletion width data is plotted in Fig. 7. The free carrier concentration in the GaNPAs

base of these two cells changed significantly under different light bias conditions. In the dark, both cells appear to be completely depleted,

Table 1. Solar Cell Device Parameters (AM1.5G).

sample	base material	E_g (eV)	J_{sc} (mA/cm ²)	V_{oc} (V)	FF (%)	Ga source	Emitter dopant	t_{Base} (μ m)	GR (μ m/h)
MD421	GaN _{0.03} P _{0.83} As _{0.14}	1.88	5.8	1.12	60	TEG	Si	0.64	2.5
MD523	GaN _{0.05} P _{0.69} As _{0.26}	1.69	5.0	0.97	56	TEG	Si	~1	4.0
MD323	GaN _{0.05} P _{0.68} As _{0.27}	1.62	4.6	0.77	46	TMG	Se	0.89	4.0
MD752	Ga _{0.5} In _{0.5} P	1.83	10.7	1.36	85	TEG	Se	0.5	4.4

but as the light bias was increased, the free hole concentration increased. The change in hole concentration was more dramatic in MD323 than MD421. The shifted dark-IV curves are probably the result of the resistive nature of the depleted GaNPAs base. Such photoconductive behavior is reminiscent of oxygen-contaminated AlInP and amorphous silicon.

As a result of the light bias-dependent carrier concentration, the QE is also dependent on light bias. The QE increases with reduced light level because of the increased depletion width. The QE should therefore be measured under a one-sun light bias. Since we measured the QE under less than a one-sun light bias, our values of J_{sc} are overestimated.

The light-dependent carrier concentration of the GaNPAs material suggests the presence of a deep trap state, which can be filled by photogenerated carriers. Such a deep trap may also explain the low quantum efficiencies of the devices.

Future work will focus on improving and understanding the electrical properties of GaNPAs materials and the growth of lattice-matched GaNPAs on silicon substrates. The growth of lattice-matched GaNPAs on silicon is challenging due to the polarity and thermal expansion mismatch between III-V and silicon. Fortunately, these problems seem to have been solved to some extent [5].

CONCLUSION

Lattice-matched GaNPAs solar cells on GaP substrates have been demonstrated with absorption characteristics appropriate for the top cell of an optimal lattice-matched III-V on silicon tandem solar cell. The performance of these cells was less than ideal, suggesting problems with the electrical quality of this novel material. Photoconductive behavior of this material has been identified as the cause of a shift in the dark-IV curve relative to the light-IV curve. Further study of the growth and properties of GaNPAs may allow for improvements that result in a lower-cost, high-efficiency tandem solar cell device.

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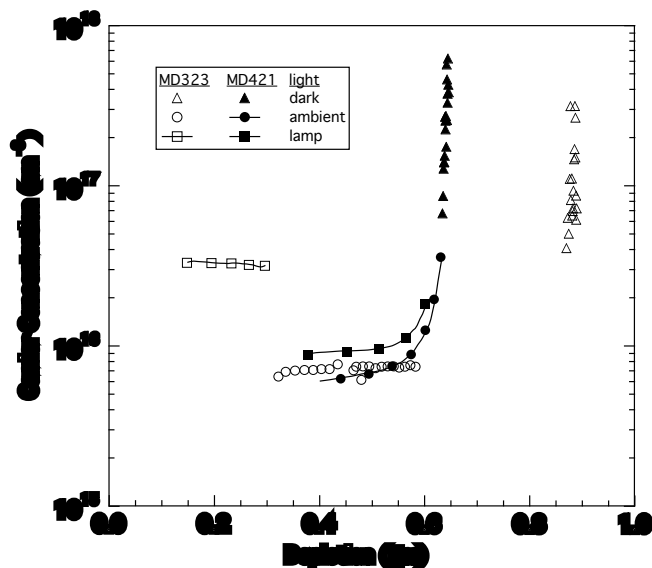


Fig. 7. Carrier concentration vs. depletion depth of two GaNPAs cells as measured by CV under different light conditions.

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