February 2005 • NREL/CP-520-37157

Conference Paper

Collection of Photocarriers in $Ga_xIn_{1-x}N_yAs_{1-y}$ Solar Cells

S. Kurtz, J.F. Geisz, D.J. Friedman, and A.J. Ptak
National Renewable Energy Laboratory

R.R. King, D.C. Law, and N.H. Karam
Spectrolab, Inc.

Prepared for the 31st IEEE Photovoltaics Specialists Conference and Exhibition
Lake Buena Vista, Florida
January 3–7, 2005

National Renewable Energy Laboratory
1617 Cole Boulevard, Golden, Colorado 80401-3393
303-275-3000 • www.nrel.gov

Operated for the U.S. Department of Energy
Office of Energy Efficiency and Renewable Energy
by Midwest Research Institute • Battelle

Contract No. DE-AC36-99-GO10337

COLLECTION OF PHOTOCARRIERS IN $Ga_xIn_{1-x}N_yAs_{1-y}$ SOLAR CELLS

Sarah Kurtz, J.F. Geisz, D.J. Friedman, A.J. Ptak, R.R. King,[1] D.C. Law,[1] and N.H. Karam[1]
National Renewable Energy Laboratory, 1617 Cole Blvd., Golden, CO 80401
[1]Spectrolab, Inc., 12500 Gladstone Avenue, Sylmar, CA 91342

ABSTRACT

Collection of photocarriers in $Ga_xIn_{1-x}N_yAs_{1-y}$ solar cells is limited by the poor quality of the $Ga_xIn_{1-x}N_yAs_{1-y}$. Some reports have shown collection of photocarriers outside of the depleted layer in annealed $Ga_xIn_{1-x}N_yAs_{1-y}$, but the key to achieving the higher collection has been unclear. In this paper, we attempt to quantify the diffusion and collection lengths that contribute to the photocurrent in $Ga_xIn_{1-x}N_yAs_{1-y}$ solar cells. The data imply that the effective $\mu\tau$ product for the lightly doped $Ga_xIn_{1-x}N_yAs_{1-y}$ material may vary when a field is applied. We conclude that the fields present in most of our best $Ga_xIn_{1-x}N_yAs_{1-y}$ cells are large enough to aid collection of photocarriers.

BACKGROUND

A four-junction solar cell using GaInP/GaAs/X/Ge, where X is a 1-eV material, has the potential for a 40% efficiency [1]. The addition of nitrogen to GaAs dramatically reduces the bandgap. A $Ga_xIn_{1-x}N_yAs_{1-y}$ alloy (hereafter, GaInNAs) has been demonstrated with a 1-eV bandgap and with a lattice constant matched to that of GaAs, implying that it is a possible candidate for the desired 1-eV material. Unfortunately, attempts to use the GaInNAs in a solar cell show that its material quality is poor, resulting in inferior performance [2,3]. However, low-current GaInNAs cells can be used effectively in a 5- or 6-junction solar cell [4].

The optimization of solar-cell performance usually requires optimization of both the material quality and the device structure. Measurements of GaInNAs have shown reduced electron mobility, minority-carrier lifetime, and minority-carrier diffusion lengths relative to those of GaAs. Annealing GaInNAs has improved its photoluminescence and device performance, but the mechanism for the improvement is not completely understood. There is a large body of evidence showing that defects are removed from GaInNAs by certain types of anneals [5-7]. There is also clear evidence that annealing changes the net carrier concentration [8-10]. In a previous study, we showed that improved performance in our GaInNAs solar cells was correlated with type conversion of the top part of the active GaInNAs layer [10]. We have also shown that a GaInNAs layer grown without any intentional doping can show ~10^{17} cm^{-3} acceptors as grown, but ~10^{17} cm^{-3} donors after annealing [9]. The observed acceptors and donors are, apparently, related to point defects associated with the nitrogen and unintentionally added impurities. Lower background carrier concentrations can be achieved by reducing the carbon and hydrogen, as is described in this proceedings [11].

The intentional addition of dopants to GaInNAs can lead to the intended p- or n-type behavior of GaInNAs, but it is our experience that GaInNAs is sometimes highly compensated. For one set of growth conditions, we added more than 10^{18} cm^{-3} of Se to convert the as-grown GaInNAs to n-type, despite that the background acceptor concentration without Se was only ~10^{17} cm^{-3}. This result is not unexpected because the formation energy of acceptors is usually reduced in n-type material and *vice versa*. Thus, in many cases, GaInNAs is highly compensated and the net acceptor or donor concentration is difficult to predict.

Other researchers have also described compensated GaInNAs for which the background carrier concentration changes after annealing. For example, researchers at Sandia National Laboratories described a GaInNAs solar cell with an n-type (2 X 10^{17} cm^{-3}, Si doped) emitter and a p-type (4 X 10^{16} cm^{-3}, unintentionally doped) base made from layers with residual carbon contamination of 6-8 X 10^{17} cm^{-3} [3]. Given that the carbon concentration was higher than both the net acceptor and donor concentrations, their GaInNAs was compensated in both the base and the emitter. They reported that the GaInNAs cell had a depletion width of 0.15 μm before annealing and 0.26 μm after annealing, implying that the net acceptor and/or net donor concentrations changed after the anneal, affecting the device structure as well as the material quality.

Thus, the normal process of first optimizing the material quality, then the device design, becomes confused when GaInNAs cells are studied. In this paper, we seek to determine how the presence of an electric field affects the performance of the solar cell. We model the solar cells and determine the observed minority-carrier diffusion length depending on the estimated junction depth. Assuming that the minority-carrier mobility and lifetime are independent of field, we then compare the probable diffusion and collection lengths and propose that fields in the emitter and/or base layers enhance photocarrier collection.

EXPERIMENTAL METHOD

The fabrication and measurement of the GaInNAs solar cells and materials have been described elsewhere [9,10]. Briefly, the GaInNAs is grown by atmospheric-

pressure metal-organic chemical-vapor deposition in a hydrogen carrier gas. No intentional doping was added to the GaInNAs layers reported here; the background acceptor concentrations varied depending on the growth conditions and the annealing conditions. A 2-μm-thick GaInNAs layer was grown between p-type and n-type GaInP layers. Thus, the structure is nominally a p-i-n structure with the n-type layer (emitter) on top. However, the junction depth moved as the background doping of the GaInNAs varied. A 1-μm-thick GaAs layer was added on top to confine the cell's response to the approximate spectral region of interest.

GaInNAs CELL PERFORMANCE AND STRUCTURE

A first question asked in optimizing performance of a new material is whether a change in growth conditions can give improved results. We selected a range of growth conditions (e.g., growth rate, V/III ratio) that were known to give differing levels of carbon and hydrogen contamination. Using these, we fabricated GaInNAs solar cells, reoptimizing the anneal conditions for each. (In the undoped structure, the optimal anneal has been shown to cause formation of an n-type emitter of optimal thickness [10].) The resulting quantum efficiency curves are shown in Fig. 1. The compositions of the samples varied slightly, but in each case an internal quantum efficiency of ~0.8 was obtained near the GaAs bandedge. The similarity of the results implies that the growth conditions and background impurity levels are unimportant relative to the importance of defining the optimal structure of the background-doped cell by using an optimal anneal.

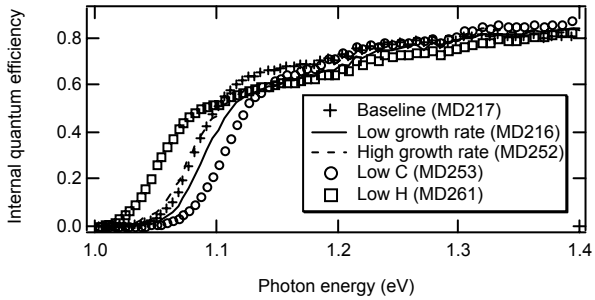

Fig. 1. Internal quantum efficiency curves for GaInNAs cells grown under a variety of growth conditions and annealed for an empirically optimized time.

A second way of studying the importance of the device structure is to compare the doping profiles of high- and low-performing cells. Starting with measurements for about one thousand GaInNAs solar cells, we selected those with high (> 8 mA/cm^2) and low (< 5 mA/cm^2) current densities. The absolute current densities for these cells are meaningless because the GaAs window allowed transmission of some light with energy above the GaAs band. The data were screened, removing data for samples that were shorted, resistive, or irrelevant for some other reason. For example, some of the samples had junctions located toward the back of the devices, resulting in poor photocurrent collection. Capacitance-voltage data for all of the rest of the samples are summarized in Fig. 2. The data are clumped in two groups: those with low photocurrents show narrow depletion widths; those with higher photocurrents show wider depletion widths. This result is not surprising because it has been reported that GaInNAs has poor minority-carrier properties. However, excellent GaAs cells can be grown with 10^{17} cm^{-3} doping (narrow depleted layer). Of greater importance to this study, we note that most of the better cells show a trend toward increasing carrier concentration with depth, implying the presence of an electric field that could aid the collection of photocarriers. This field is caused when the p-type, as-grown GaInNAs converts to n-type from the top down. The details of why the top surface converts first are unknown, but there is evidence that injection of hydrogen from the ambient contributes.

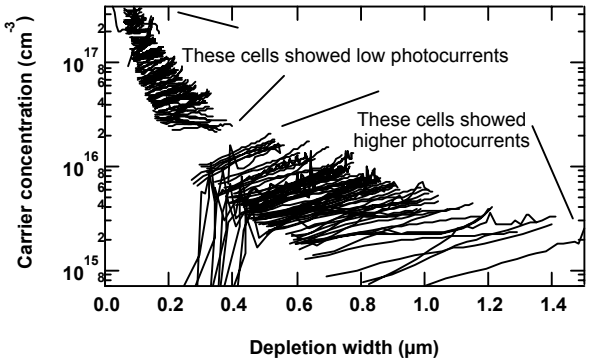

Fig. 2. Comparison of capacitance-voltage profiling for samples with relatively small (< 5 mA/cm^2) and large photocurrent densities (> 8 mA/cm^2).

DIFFUSION AND COLLECTION LENGTH

The minority-carrier diffusion, L_d, and collection, L_c, lengths are usually related to the mobility, μ, and lifetime, τ, by

$$L_d = (\mu\tau \mathrm{kT/e})^{0.5}; \quad L_c = \mu\tau E \qquad (1)$$

where k is Boltzmann's constant, T is the temperature, e is the electric charge, and E is the electric field. These equations assume that μ and τ are independent of E and Fermi level. The addition of a small amount of nitrogen to GaAs introduces states that are localized on the nitrogen [12]. Addition of more nitrogen lowers the conduction band dramatically, but the conduction band retains some localized character, implying that GaInNAs will not behave like a traditional semiconductor material [12]. Thus, μ and τ may not be independent of electric field; we will reexamine this question later in the paper.

Electron mobilities as high as 500 cm^2/Vs have been reported for GaInNAs [9], but more commonly the electron and hole mobilities have been reported near 300 cm^2/Vs [13]. It is not clear that the majority-carrier mobility measured by Hall is relevant to the minority-carrier mobility. Nevertheless, if the carrier mobility is ~300 cm^2/Vs and the lifetime is about 0.3 ns, then the $\mu\tau$ product is ~10^{-7} cm^2/V. The collection and diffusion lengths were calculated using Eq. 1 and $\mu\tau$ products within a factor of 10 of 10^{-7} cm^2/V. (See Fig. 3.)

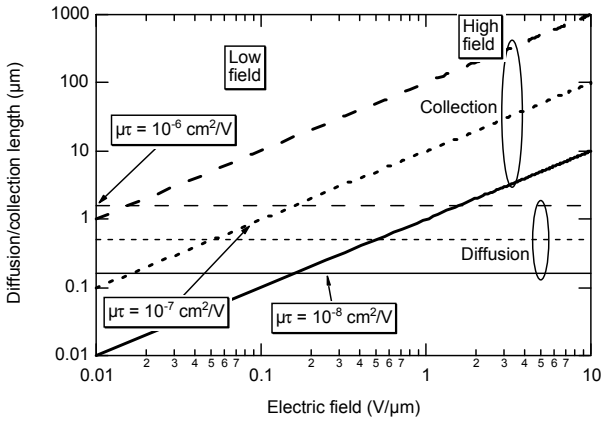

Fig. 3. Collection length expected from diffusion (thin lines) or collection (bold lines) as a function of electric field and $\mu\tau$ product calculated using Eq. 1 ($\mu\tau$ = 10^{-8} cm^2/V solid lines; 10^{-7} cm^2/V dotted lines; 10^{-8} cm^2/V dashed lines).

MODELED SOLAR-CELL PERFORMANCE

The absorption coefficient of GaInNAs is similar to that of GaAs except that the bandedge is shifted and shows an exponential tail [10]. We have assumed that the solar cells can be modeled as three layers: emitter (top), depleted layer, and base [10] with all photocarriers collected in the depleted layer, and the collection in the other two layers determined by an effective minority-carrier diffusion length and surface-recombination velocity. The equations are given in ref. [10]. The assumption that the emitter and base are uniform layers is an approximation, and leads to an effective diffusion length, L_{eff}, that reflects both diffusion and field-aided collection.

Modeling of these devices is complicated because the junction depth is unknown. In a standard solar cell, the emitter thickness can be estimated by measuring the emitter sheet resistance and electron concentration. Thus, we might estimate the junction depth from the sheet resistance of the type-converted, n-type emitter layer after removal of the n-type GaInP layer. Before removal of the GaInP layer, the sheet resistance is dominated by conduction in the GaInP layer. After removal, the cells with optimal performance show a sheet resistance on the order of MΩ/square. Depth profiling (capacitance-voltage profiling), as shown in Fig. 2, implies that the donor concentration is < 10^{16} cm^{-3}. The data in Fig. 2 reflect widening of the depleted layer both toward the front and toward the back of the device. Thus, it is not clear whether the carrier concentration measured in Fig. 2 reflects the net donor concentration, acceptor concentration, or a combination of both. Modeling of reverse-biased cells implies that the reverse-bias data in Fig. 2 include depletion of the emitter, giving confidence that the donor concentration is < 10^{16} cm^{-3}. For an electron mobility of 300 cm^2/Vs, an electron concentration of 3 X 10^{15} cm^{-3}, and a sheet resistance of ~1 MΩ/square, we expect a thickness of ~0.07 μm for the conducting layer. However, the free surface is known to pin the Fermi level in the middle of the gap of a GaAs-like material. This causes a second depleted layer that may be comparable to the first: ~0.4 μm wide. A measurement of the sheet resistance of the bare layer will be increased because carriers are found only in the part of the emitter that isn't depleted by the free surface. Thus, we anticipate that the probable junction depth is ~0.07 μm plus the probable width of the depleted layer, or 0.4 μm ± 0.4 μm.

Given the uncertainty of the junction depth, we treat the junction depth as a fit parameter. The width of the depleted layer is measured by capacitance-voltage profiling. If photocarriers are collected only in the depleted layer, a low response is expected, as shown for an illustrative example by the lowest curve in Fig. 4. The poor fit of the low curve implies that additional holes are collected from the emitter and/or electrons are collected from the base. Two additional fits are shown in Fig. 4. One assumes that the junction is at the front of the cell and that all added collection is from the base. The other assumes that there is no collection from the base and varies the thickness of the emitter and effective diffusion length in the emitter to give an optimal fit. These two fits are both excellent, as shown in Fig. 4, implying that the data can be explained either by collection of holes or electrons.

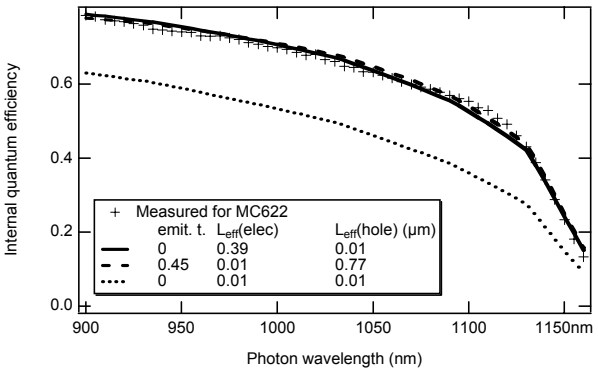

Fig. 4. Internal quantum efficiency of GaInNAs cell, measured and modeled using a depletion width of 0.465 μm and the indicated values for the emitter thickness and L_{eff} for electrons and holes.

Fundamentally, there are four possible mechanisms for collection outside of the depleted layer: 1) diffusion of holes from the emitter, 2) field-aided collection of holes from the emitter, 3) diffusion of electrons from the base, and 4) field-aided collection of electrons from the base. From the modeling shown in Fig. 4, it is impossible to differentiate these. From the observation that the formation of the n-type emitter increases the photocurrent [10], we are confident that holes from the emitter contribute to the photocurrent, but we can't be certain that electrons from the base don't also contribute.

In the depleted layer, field-aided collection of both holes and electrons occurs. If the $\mu\tau$ product of either the holes or electrons were insufficient for collection in this field, then those carriers would build up in the depleted layer, causing the field to change. For the samples described in Figs. 2 and 4, the depletion width is on the order of 0.5 μm. The built-in field is less than the bandgap

of the GaInNAs (~1.1 eV), yet greater than the open-circuit voltage observed for the cells (~0.4 V). Thus, if the built-in field is ~0.8 V, the strength of the field in the depleted layer is on the order of 1 V/μm. We observe that the photocarriers are efficiently collected for a depleted layer thickness of ~0.5 μm, implying that the collection length for both electrons and holes is at least 0.5 μm for a field of ~1 V/μm. Then, from Eq. 1, the $\mu\tau$ product for both holes and electrons is at least 5 X 10^{-9} cm^2/V. Assuming that $\mu\tau$ is independent of field, then the diffusion length for both carriers is at least ~0.1 μm. This is comparable to what we measure for holes in ~10^{17} cm^{-3}, n-type GaInNAs (data not shown), but longer than what we have measured for electrons (too small to be measured, or < 0.05 μm). This discrepancy for the electron transport might be resolved if the addition of a field facilitates the emission of an electron from a localized state, increasing its mobility or lifetime in the presence of an electric field. An alternative explanation is that the transport is degraded by doping at the ~10^{17} cm^{-3} level.

The lower lines in Fig. 2 show a change of about a factor of 2 to 4 in carrier concentration over a distance of about 0.5 μm. The change in Fermi level expected for a factor of 4 change in doping is kT ln(4) or 36 mV. Thus, we estimate that the low field outside of the depleted layer is ~0.04 V/ 0.5 μm, or ~0.1 V/μm. For this field, we model (Fig. 4) L_{eff} = ~0.4 μm outside of the depleted layer. For $\mu\tau$= 5 X 10^{-8} cm^2/V, the diffusion and collection lengths are both ~0.4 μm. Thus, the $\mu\tau$ product that provides an adequate diffusion length to explain the data also implies that field-aided collection is important in that same region.

The diffusion lengths observed for a GaInNAs/aqueous junction imply lower $\mu\tau$ either because these layers were more highly doped, or because the $\mu\tau$ is field dependent.

The observed $\mu\tau$ values are summarized in Table 1. Although these are very rough estimates, it is clear that 1) the observed $\mu\tau$ product varies with field, and 2) the ~0.1 V/μm fields observed in the best GaInNAs samples are expected to lead to field-aided collection. Evidence of field-aided minority-carrier transport in transistors has been reported by Welser, et al. [14].

Table 1. Estimates of observations of $\mu\tau$. The aqueous junction measurements were completed on uniform layers with donor concentrations of ~10^{17} cm^{-3}.

Carrier	Field (V/μm)	$\mu\tau$ (cm^2/V)	Collection from:
Electrons	~ 1	> 5 X 10^{-9}	Depleted layer
Electrons	~ 0.1	< 5 X 10^{-8}	Base
Electrons	~ 0	< 1 X 10^{-9}	Aqueous junction
Holes	~ 1	> 5 X 10^{-9}	Depleted layer
Holes	~ 0.1	~ 5 X 10^{-8}	Emitter
Holes	~ 0	~ 5 X 10^{-9}	Aqueous junction

In summary, we have observed that the device structure is more important than the growth conditions for high-performance GaInNAs cells. The high-performing devices show wide depletion widths and an electric field outside of the depleted layer. Modeling of the GaInNAs solar cells shows collection outside of the depleted layer, but is ambiguous about whether the added collection is from the emitter or base. Various estimates of the $\mu\tau$ product show that the $\mu\tau$ product may be field dependent or dependent on doping. The relevant $\mu\tau$ products are close to 10^{-8} cm^2/V. The analysis shows that field-aided collection in the emitter and/or base enhances the photocurrent of the solar cells.

ACKNOWLEDGMENTS

We thank C. Kramer and M. Young for the sample preparation. This work was funded, in part, under the Dual Use Science and Technology (DUS&T) program by the Air Force Research Laboratory, Space Vehicles Directorate (AFRL/VS), and, in part, by Spectrolab, Inc. This work was completed at the National Renewable Energy Laboratory under DOE Contract No. DE-AC36-99GO10337.

REFERENCES

[1] S.R. Kurtz, et al., "Projected performance of three- and four-junction devices using GaAs and GaInP," *26th IEEE PVSC*, 1997, pp. 875-878.
[2] D.J. Friedman, et al., "1-eV solar cells with GaInNAs active layer," *J. Cryst. Growth* **195**, 1998, pp. 409-415.
[3] S.R. Kurtz, et al., "InGaAsN solar cells with 1.0 eV band gap, lattice matched to GaAs," *Appl. Phys. Lett.* **74**, 1999, pp. 729-731.
[4] R.R. King, et al., "Metamorphic III-V materials, sublattice disorder, and multijunction solar cell approaches with over 37% efficiency," *19th European PVSEC*, 2004.
[5] D. Kwon, et al., "Deep levels in p-type InGaAsN lattice matched to GaAs," *Appl. Phys. Lett.* **74**, 1999, pp. 2830-2832.
[6] R.J. Kaplar, et al., "Deep levels and their impact on generation current in Sn-doped InGaAsN," *J. Appl. Phys.* **90**, 2001, pp. 3405-3408.
[7] P. Krispin, et al., "Nitrogen-related electron traps in Ga(As,N) layers (<=3% N)," *J. Appl. Phys.* **93**, 2003, pp. 6095-6099.
[8] J.F. Geisz, et al., "Photocurrent of 1 eV GaInNAs lattice-matched to GaAs," *J. Cryst. Growth* **195**, 1998, pp. 401-408.
[9] S. Kurtz, et al., "Annealing-induced-type conversion of GaInNAs," *J. Appl. Phys.* **95**, 2004, pp. 2505-2508.
[10] S. Kurtz, et al., "Modeling of electron diffusion length in GaInAsN solar cells," *28th IEEE PVSC*, 2000, p. 1210.
[11] A.J. Ptak, et al., "Enhanced-depletion-width GaInNAs solar cells grown by molecular-beam epitaxy," *31st IEEE PVSC*, 2005.
[12] P.R.C. Kent and A. Zunger, "Evolution of III-V nitride alloy electronic structure: The localized to delocalized transition," *Phys. Rev. Lett.* **86**, 2001, pp. 2613-2616.
[13] S.R. Kurtz, et al., "Minority carrier diffusion and defects in InGaAsN grown by molecular beam epitaxy," *Appl. Phys. Lett.* **80**, 2002, pp. 1379-1381.
[14] R.E. Welser, et al., "Minority carrier properties of carbon-doped GaInAsN bipolar transistors," *J. Phys.: Condens. Matter* **16**, 2004, pp. 53373-53385.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ORGANIZATION.

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
February 2005	Conference Paper	3-7 January 2005

4. TITLE AND SUBTITLE
Collection of Photocarriers in $Ga_xIn_{1-x}N_yAs_{1-y}$ Solar Cells

5a. CONTRACT NUMBER
DE-AC36-99-GO10337

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
S. Kurtz, J.F. Geisz, D.J. Friedman, A.J. Ptak, R.R. King, D.C. Law, and N.H. Karam

5d. PROJECT NUMBER
NREL/CP-520-37157

5e. TASK NUMBER
WR

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
National Renewable Energy Laboratory
1617 Cole Blvd.
Golden, CO 80401-3393

8. PERFORMING ORGANIZATION REPORT NUMBER
NREL/CP-520-37157

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR'S ACRONYM(S)
NREL

11. SPONSORING/MONITORING AGENCY REPORT NUMBER

12. DISTRIBUTION AVAILABILITY STATEMENT
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

13. SUPPLEMENTARY NOTES

14. ABSTRACT *(Maximum 200 Words)*

Collection of photocarriers in $Ga_xIn_{1-x}N_yAs_{1-y}$ solar cells is limited by the poor quality of the $Ga_xIn_{1-x}N_yAs_{1-y}$. Some reports have shown collection of photocarriers outside of the depleted layer in annealed $Ga_xIn_{1-x}N_yAs_{1-y}$, but the key to achieving the higher collection has been unclear. In this paper, we attempt to quantify the diffusion and collection lengths that contribute to the photocurrent in $Ga_xIn_{1-x}N_yAs_{1-y}$ solar cells. The data imply that the effective $\mu\tau$ product for the lightly doped $Ga_xIn_{1-x}N_yAs_{1-y}$ material may vary when a field is applied. We conclude that the fields present in most of our best $Ga_xIn_{1-x}N_yAs_{1-y}$ cells are large enough to aid collection of photocarriers.

15. SUBJECT TERMS
PV; photocarriers; solar cells; photocurrent; capacitance-voltage; electron mobilities; field-aided collection;

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER *(Include area code)*
Unclassified	Unclassified	Unclassified	UL		