Growth and Development of GaInAsP for Use in High-Efficiency Solar Cells

Annual Subcontract Report 1 July 1991 – 30 June 1992

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Printed in the United States of America
Available from:
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

Price: Microfiche A01
Printed Copy A03

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1.0 Introduction and Summary of Phase II Accomplishments

1.1 Introduction

The purpose of this report is to review the progress that has been made during Phase II of Subcontract No. XM-0-19142-3. The report is a description of the work that was accomplished between July 1, 1991 and the end of June, 1992. The overall goals of the program are:

1. to develop the necessary technology to grow high-efficiency GaInAsP layers that are lattice-matched to GaAs,

2. to demonstrate high-efficiency GaInAsP single junction solar cells, and

3. to demonstrate GaInAsP/Ge cascade solar cells suitable for operation under concentrated (500x) sunlight.

Specific Phase II goals include the following:

1. optimization of the GaInAsP cell on GaAs, and the demonstration of a 500-sun (AM 1.5) efficiency of > 23 percent,

2. development of a window layer, including the evaluation of AlGaAs, GaInP, AlGaAsP, AlGaInP, and GaP,

3. development of a front-surface contact, with a grid designed for 500-sun concentration, and a goal of a contact resistivity of ~ 10^5 ohm-cm^2 , and

4. growth of GaInAsP cells on Ge, with a goal of a 1-sun (AM 1.5) efficiency of > 15 percent

1.2 Summary of Phase II Accomplishments

Many of the goals of Phase II have been achieved. The major accomplishments include:

1. fabrication of p-on-n and n-on-p GaInAsP cells on GaAs, with the n-on-p cell demonstrating a 10-sun (AM1.5) active area efficiency of 23.4%, as measured at NREL,

2. evaluation of $Al_xGa_{(1-x)}As$, $GaInP_2$, and $AlInP_2$ window layers, and

3. fabrication of GaInAsP cells on Ge, with the demonstration of a p-on-n GaInAsP cell grown on Ge with a 1-sun (AM1.5) active area efficiency of 14.4%.

    The above items will be discussed in further detail in the following pages.

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2.0 Technical Effort

2.1 Introduction

The focus of the technical effort for Phase II has been on the optimization of the GaInAsP cell on GaAs, as well as on the development of the GaInAsP cell on Ge.

2.2 System Modification

Due to the requirements of another contract, the OMVPE system was modified from a horizontal to a vertical atmospheric-pressure configuration. Also included in the modifications was the installation of a burn-box in the exhaust line. The advantage for the GaInAsP program is:

1. that much lower flow rates are required with the new configuration to achieve the same film thickness, i.e., there is a much higher utilization of the precursors, resulting in lower costs for growth of a cell, and

2. that there is a much lower generation of white phosphorus in the exhaust lines, leading to a safer growth process.

There was a need for re-calibration of both the composition and the doping levels of the GaInAsP, but this is no different than what would be normally required with a source change.

2.3 GaInAsP Cells Grown on GaAs

Both n-on-p and p-on-n cells have been grown on GaAs substrates. The basic details of the growth are included in last year's annual report. A schematic of the n-on-p cell is shown in Fig. 1. The p-on-n cell is similar, except for the dopant in each layer. A

ARC		
n^+-GaAs:Se	5×10^{18} cm^{-3}	0.2μm
n^+-GaInP$_2$:Se	1×10^{18} cm^{-3}	400 Å
n^+-GaInAsP:Se	1×10^{18} cm^{-3}	0.3 μm
p-GaInAsP:Zn	1×10^{17} cm^{-3}	2.5 μm
p-GaInP$_2$:Zn	1×10^{17} cm^{-3}	400 Å
p-GaAs:Zn	1×10^{17} cm^{-3}	0.2 μm
p^+-GaAs	substrate	

Figure 1. Schematic of the n-on-p GaInAsP cell grown on GaAs substrates.

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layer of GaInP$_2$ to develop a back surface field is incorporated to prevent carrier loss at the GaInAsP-GaAs interface. The GaInP$_2$ has a bandgap of 1.86 eV, as determined from PL measurements. GaInP$_2$ is also used as the window material for the comparison of the n-on-p structure with the p-on-n structure. Results for the two cell types, both with an active area of 0.136 cm^2, as measured under 1-sun AM1.5 direct illumination at RTI, are shown in Table I. Because the cells are eventually going to be used in concentrator applications, which will include a large grid obscuration, the efficiencies are reported for the active area of the cells. The results indicate that while the V$_{oc}$ and fill factor for both the cells are similar, the n-on-p structure gives better currents than the p-on-n structure. This is reflected as significantly higher efficiencies for the n-on-p structure. The higher currents are believed to be due to the longer minority carrier diffusion length of the electron in the p-type base as compared to the hole in the n-type base, for comparable dopant levels. The results of the GaInAsP cells grown on GaAs indicate that the n-on-p structure is preferable.

The n-on-p cell was sent to NREL and re-measured using their simulator. Fig. 2 gives the results for 1-sun (AM1.5) direct illumination, and Fig. 3 gives the results for 9.73-sun (AM1.5) illumination. The efficiencies are for the total area of the cell, and translate to active area values of 21.8% for 1-sun illumination and 23.4% for the 9.73 sun illumination. The NREL efficiency result for the 1-sun measurement differs from the RTI efficiency measurement by 1.4%, in absolute percentage. A spectral response measurement was made at NREL on the same cell, and the results are in Fig. 4. The longer wavelength cut-off corresponds well with the bandgap of GaInAsP (1.55 eV), and is fairly sharp, indicating a good minority carrier diffusion length. There is some loss in the shorter wavelengths, and this is believed to be due to the thickness of the emitter (0.3 μm). Because the cell is ultimately designed for concentrator applications, the emitter needs to be thick enough to keep the series resistance low, particularly under

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Table I

Results for n-on-p and p-on-n Cells Grown on GaAs

	n-on-p	p-on-n
V_{oc}, volts	1.04	1.05
J_{sc}, mA/cm^2	27.4	20.4
ff	0.814	0.790
η, active area	23.2%	17.0%

AM1.5 direct illumination

Sample: 6−402−4   Temperature = 25.0°C

Jun. 5, 1992 12:45 pm   Area = 0.174 cm²

NREL
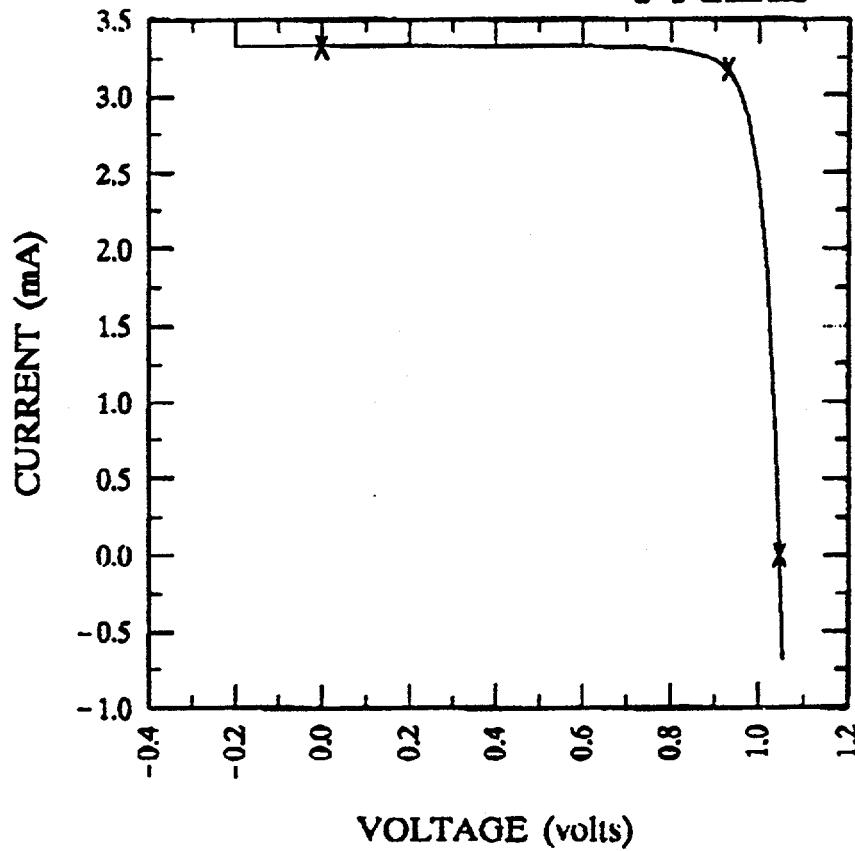
V_{oc} = 1.047 volts I_{sc} = 3.325 mA

J_{sc} = 19.11 mA/cm² P_{max} = 2.954 mW

Fill factor = 84.89 % I_{max} = 3.169 mA

Efficiency = 17.0 % V_{max} = 0.9322 V

Figure 2. I-V curve for n-on-p GaInAsP cell on GaAs, under AM 1.5 direct illumination

Sample: 6-402-4   Temperature = 25.0°C

Jun. 5, 1992 2:52 pm   Area = 0.174 cm²

NREL
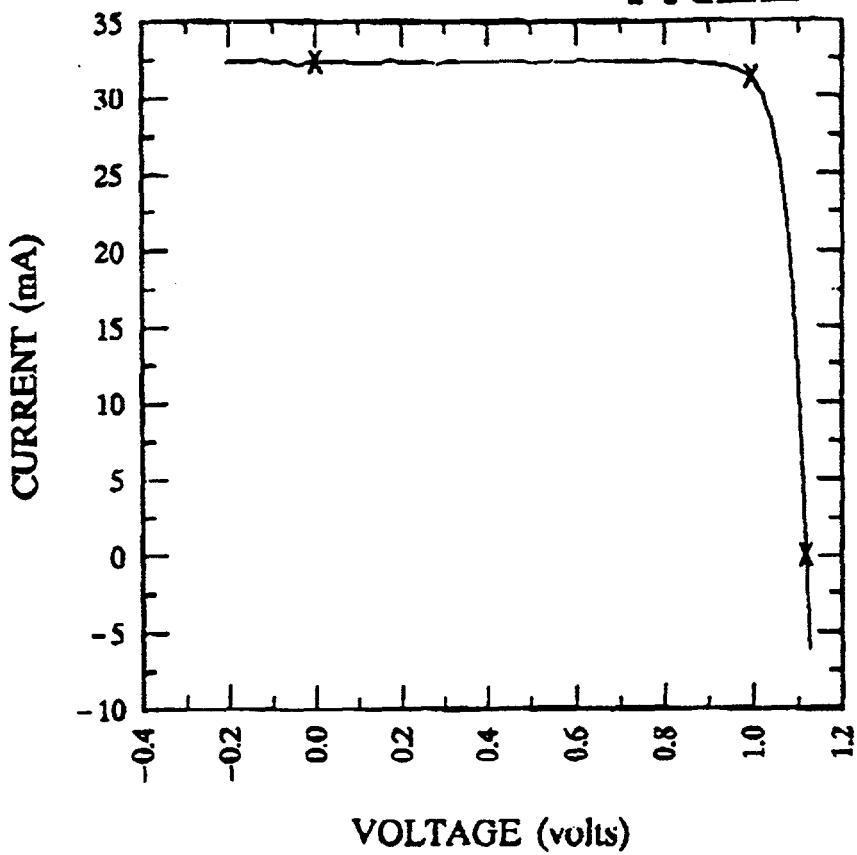
V_{oc} = 1.117 volts I_{sc} = 32.36 mA

J_{sc} = 186.0 mA/cm² P_{max} = 31.24 mW

Fill factor = 86.40 % I_{max} = 31.38 mA

Efficiency = 18.4 % V_{max} = 0.9955 V

Figure 3. I-V curve for n-on-p GaInAsP cell on GaAs, under 9.73 sun AM1.5 illumination.

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Sample: 6−402−4   Temperature = 25.0°C

Jun. 5, 1992 9:18 am   Area used = 0.174 cm²

NREL
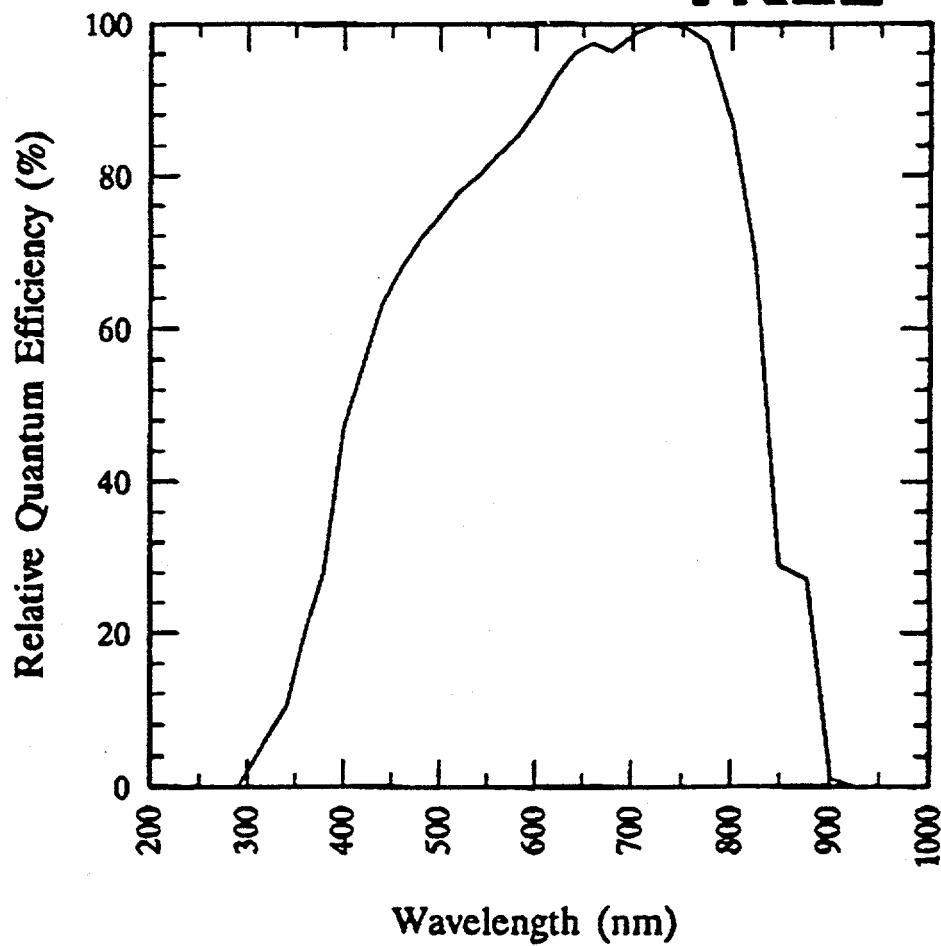
Light bias = 0.70 mA

Zero voltage bias

Figure 4. Spectral response curve for n-on-p GaInAsP cell on GaAs.

concentration. However, there is still some flexibility in the emitter thickness in optimizing the final cascade structure, so there may be some improvement in the collection of the shorter wavelength light with the use of a thinner emitter.

2.4 Window Material Comparison

Due to financial constraints, there was only sufficient time to evaluate $Al_{0.8}Ga_{0.2}As$, $GaInP_2$, and $AlInP_2$ as window materials. Since $AlInP_2$ is lattice-matched to GaAs, and has a bandgap of 2.36 eV, it is actually a better choice than either AlGaAsP, AlGaInP, or GaP, all of which either have smaller bandgaps or are not lattice-matched to GaAs. The only difficulty in utilizing $AlInP_2$ is that it is difficult to grow p-type material in our reactor at 675°C. Hence, the comparison of the three window materials was made with the n-on-p structure. The basic structure of the cells is similar to that of Fig.1, although no back surface field was incorporated. The results are shown in Table II. The $Al_{0.8} Ga_{0.2}As$ window gives the lowest J_{sc}, with the $GaInP_2$ and $AlInP_2$ windows giving J_{sc} values about 3.5 mA/cm^2 higher. The V_{oc}s and fill factors for the cells with the various windows are similar. The poor quality of the $Al_{0.8}Ga_{0.2}As$ layers is believed to be the reason for the lower J_{sc} for the cell with the $Al_{0.8}Ga_{0.2}As$ window. Although specular, SIMS measurements on the $Al_{0.8}Ga_{0.2}As$ indicate oxygen in the 10^{19} cm^{-3} range, leading to recombination centers both at the GaInAsP/AlGaAs interface and in the AlGaAs layer itself. The $AlInP_2$ window is slightly better than the $GaInP_2$ window, and this is believed to be due to the higher bandgap of $AlInP_2$ (2.36 eV) as compared to $GaInP_2$ (1.86 eV). The oxygen is not as critical an issue in the $AlInP_2$ as compared to the $Al_{0.8}Ga_{0.2}As$, mainly due to the higher bandgap and lower Al content of the $AlInP_2$.

Table II

Comparison of n-on-p Cells With Various Window Materials

Window	$Al_{0.8}Ga_{0.2}As$	$GaInP_2$	$AlInP_2$
V_{oc}, volts	1.090	1.093	1.094
J_{sc}, mA/cm^2	14.4	17.2	17.93
ff	0.75	0.80	0.82
η, active area	12.4%	16.8%	16.9%

AM1.5 direct illumination

2.5 GaInAsP Cells Grown on Ge

Both n-on-p and p-on-n GaInAsP cells have also been grown on Ge. The structure of the n-on-p cell is shown in Fig. 5. Again, the p-on-n cell is similar except for dopant type. Although specular films of GaInAsP have been nucleated directly on Ge at 675°C, the most consistent results to date are achieved using a thin GaAs nucleation layer. The GaAs nucleation layer is grown at 710°C for a brief time, followed by a decrease in temperature to 675°C and growth of a thicker buffer layer. Ultimately, the buffer layer will be GaInAsP, but to date the layer has been GaAs. Results for a cell with a p-on-n structure using GaAs as the buffer are shown in Table III. The overall cell performance is lower than that for the cell grown on GaAs. The V_{oc}, J_{sc}, and fill factor are all lower, probably due to Ge incorporation in the junction. A thicker buffer layer (6.0 μm) should help improve the overall quality of the cell. Cells were also grown with the n-on-p structure, but the I-V curves for the cells indicate the formation of a junction at the Ge/GaAs interface. Since the Ge substrates are heavily doped p-type (~5 x 10^{18} cm^{-3}), in all likelihood Ge is entering the p-GaAs layer and causing type conversion. Future plans for the growth of n-on-p cells on Ge involve heavily doping the initial GaAs nucleation layer such that type conversion does not occur. Other ideas for the improvement of the GaInAsP cells on Ge include using GaInAsP for the buffer layer, growing a thicker (6 μm) buffer layer, and obtaining consistent morphologies using GaInAsP as the nucleation layer. Because of the current loss that will be caused if a GaAs nucleation layer is used in the final cascade structure, the GaInAsP nucleation layer is preferable.

ARC		
n$^+$-GaAs:Se	5×10^{18} cm^{-3}	0.2μm
n$^+$-GaInP$_2$:Se	1×10^{18} cm^{-3}	400 Å
n$^+$-GaInAsP:Se	1×10^{18} cm^{-3}	0.3 μm
p-GaInAsP:Zn	1×10^{17} cm^{-3}	2.5 μm
p-GaInP$_2$:Zn	1×10^{17} cm^{-3}	400 Å
p- Buffer:Zn		3.5 μm
p-GaAs:Zn		500 Å
p-Ge	substrate	

Figure 5. Schematic of the n-on-p GaInAsP cell grown on Ge substrates.

Table III

Results for the p-on-n GaInAsP Cell Grown on Ge

V_{oc}, volts	1.01
J_{sc}, mA/cm^2	19.7
ff	0.72
η, active area	14.4%

AM1.5 direct illumination

3.0 Final Cascade Structure

Based on the results to date, a proposed structure for the GaInAsP/Ge cascade structure is shown in Fig. 6. The n-on-p configuration is preferred based on the results of the GaInAsP cell on GaAs. However, several key areas in the successful development of the n-on-p cascade structure include development of the n-on-p GaInAsP cell on Ge, as well as the development of a GaInAsP/Ge heterotunnel junction. The n-on-p GaInAsP cell on Ge seems within reach, the critical issue being the growth of the p-type buffer layer. Growth of a GaAs/Ge heterotunnel junction has already been demonstrated at RTI, so the development of a GaInAsP/Ge junction does not seem unreasonable.

ARC		
n^+-GaAs:Se	5×10^{18} cm^{-3}	0.2 μm
n^+-AlInP$_2$:Se	1×10^{18} cm^{-3}	400 Å
n^+-GaInAsP:Se	1×10^{18} cm^{-3}	0.3 μm
p-GaInAsP:Zn	1×10^{17} cm^{-3}	2.5 μm
p-GaInP$_2$:Zn	1×10^{17} cm^{-3}	400 Å
p-GaInAsP:Zn	1×10^{17} cm^{-3}	3-5 μm
p^+-GaInAsP:Zn	1×10^{19} cm^{-3}	500 Å
n^+-Ge:As	1×10^{20} cm^{-3}	500 Å
n-Ge:As	4×10^{18} cm^{-3}	3.0 μm
p-Ge:B	1×10^{17} cm^{-3}	10 μm
p-Ge	substrate	

Figure 6. Schematic of the suggested structure for the GaInAsP/Ge cascade cell.

4.0 Preview of Phase III

The work during Phase II has been very encouraging. The Phase II efficiency goal for the GaInAsP cell on GaAs has been achieved, several different window materials have been evaluated, and the Phase II efficiency goal for the GaInAsP cell on Ge is easily within reach. Unfortunately, due to budgetary constraints, little effort has been put forth in developing the front surface contacts to GaInAsP during Phase II, and this portion of the work has been moved to Phase III.

The focus of Phase III will be on developing the final cascade structure. Specifically, Phase III includes the following goals:

1. optimization of the GaInAsP cells grown on Ge, particularly for the n-on-p configuration,

2. optimization of the grids and front-surface contacts for 500x concentration solar cells,

3. development of a three-layer AR coating for the cascade cell, and

4. demonstration of a GaInAsP/Ge cascade cell with a 500x concentration efficiency of > 32 percent.

Based on the results to date, we are excited about the start of Phase III and expect significant results during the next year.

Document Control Page	1. NREL Report No. NREL/TP-451-5414	2. NTIS Accession No. DE93000098	3. Recipient's Accession No.
4. Title and Subtitle Growth and Development of GaInAsP for Use in High-Efficiency Solar Cells			**5. Publication Date** April 1993
			6.
7. Author(s) Paul R. Sharps			**8. Performing Organization Rept. No.**
9. Performing Organization Name and Address Research Triangle Institute P.O. Box 12194 Research Triangle Park, NC 27709			**10. Project/Task/Work Unit No.** PV321101
			11. Contract (C) or Grant (G) No. (C) XM-0-19142-3 (G)
12. Sponsoring Organization Name and Address National Renewable Energy Laboratory 1617 Cole Blvd. Golden, CO 80401-3393			**13. Type of Report & Period Covered** Technical Report 1 July 1991 - 30 June 1992
			14.

15. Supplementary Notes
NREL technical monitor: J. Benner

16. Abstract (Limit: 200 words)

This report describes work done during Phase II of the subcontract. Goals for Phase II include the following: (1) Optimize the GaInAsP cell on GaAs and demonstrate a 500-sun at air mass (AM) 1.5 efficiency of >23%. (2) Develop a window layer, including the evaluation of AlGaAs, GaInP, AlGaAsP, AlGaInP, and GaP. (3) Develop a front-surface contact, with a grid designed for 500-sun concentration, and a goal of a contact resistivity of ~10^5 ohm-cm^2. (4) Grow GaInAsP cells on Ge, with a goal of a 1-sun (AM 1.5) efficiency of >15%. Accomplishments reported herein include (1) the fabrication of p-on-n and n-on-p GaInAsP cells on GaAs, with the n-on-p cell demonstrating a 10-sun (AM 1.5) active-area efficiency of 23.4% as measured at NREL; (2) the evaluation of $Al_xGa_{(1-x)}As$, $GaInP_2$, and $AlInP_2$ window layers; and (3) the fabrication of GaInAsP cells on Ge, with the demonstration of a p-on-n GaInAsP cell grown on Ge with a 1-sun (AM 1.5) active-area efficiency of 14.4%.

17. Document Analysis
   a. Descriptors
      high efficiency ; gallium indium arsenide ; photovoltaics ; solar cells

   b. Identifiers/Open-Ended Terms

   c. UC Categories
      273

18. Availability Statement National Technical Information Service U.S. Department of Commerce 5285 Port Royal Road Springfield, VA 22161	**19. No. of Pages** 24
	20. Price A03

Form No. 0069E (6-30-87)