

Improved Performance in CuInSe₂ and Surface-Modified CuGaSe₂ Solar Cells

J. AbuShama, R. Noufi, S. Johnston, S. Ward,
and X. Wu

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



NREL

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

NOTICE

The submitted manuscript has been offered by an employee of the Midwest Research Institute (MRI), a contractor of the US Government under Contract No. DE-AC36-99GO10337. Accordingly, the US Government and MRI retain a nonexclusive royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for US Government purposes.

This report was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or any agency thereof.

Available electronically at <http://www.osti.gov/bridge>

Available for a processing fee to U.S. Department of Energy and its contractors, in paper, from:

U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831-0062
phone: 865.576.8401
fax: 865.576.5728
email: <mailto:reports@adonis.osti.gov>

Available for sale to the public, in paper, from:

U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
phone: 800.553.6847
fax: 703.605.6900
email: orders@ntis.fedworld.gov
online ordering: <http://www.ntis.gov/ordering.htm>



IMPROVED PERFORMANCE IN CuInSe_2 AND SURFACE-MODIFIED CuGaSe_2 SOLAR CELLS

Jehad AbuShama*, Rommel Noufi, Steve Johnston, Scott Ward, and X. Wu
National Renewable Energy Laboratory, Golden, Co 80401, U.S.A.

*Physics Department, Colorado School of Mines, Golden, CO 80401, U.S.A.

ABSTRACT

In this paper, we present an update and review on the progress made in the development of low-bandgap CuInSe_2 (CIS) and wide-bandgap CuGaSe_2 (CGS) solar cells. Our research project is primarily concerned with the optimization of the bottom and top cells of the tandem solar cell. This past year, we established new record total-area efficiencies of 15.0% and 10.2% for CIS and surface-modified CGS solar cells, respectively. These achievements were possible by modifying the growth process for CIS and CGS absorbers. We attempt to modify the surface region of the CGS absorber to be CIGS-like in composition. We also have designed a mechanical-stacked tandem solar cell where the 15% CIS cell serves as the bottom cell and transparent CdTe cell serves as the top cell. The NREL-confirmed total-area efficiency for this CdTe/CIS tandem device is 15.31%.

INTRODUCTION

Polycrystalline thin-film solar cells based on $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ (CIGS) (where $0 \leq x \leq 1$) have great potential for photovoltaic applications. Total-area efficiencies exceeding 19% have been established for CIGS solar cells [1,4]. In this contribution, we report new record total-area efficiencies of 15.0% and 10.2% for CIS and surface-modified CGS solar cells, respectively. These improved efficiencies were possible by modifying the growth process for CIS and CGS absorbers. CIS and CGS are important candidates for bottom- and top-cell absorber materials for thin-film tandem devices. We designed a 4-terminal polycrystalline thin-film mechanical-stacked tandem cell where our 15% CIS cell serves as the bottom cell and a newly developed transparent CdTe cell serves as the top cell. The NREL-confirmed efficiency for this tandem cell is 15.3%. In this paper, we present material and device properties for the new CIS and surface-modified CGS films and devices.

EXPERIMENTAL

Our technical approach is based on the following:

Growth: We investigated the dependence of the device performance of CIS and CGS solar cells on the growth conditions of the respective absorber layers. We deposited CIS and CGS absorbers on Mo-coated soda-lime glass substrates using the three-stage process. We deposited the new CIS absorber (S2279) at temperatures about 15 °C higher than those used during the growth of the

previous one (S2044) [2]. We deposited the new CGS film (S2194) under more Cu-rich conditions and with the addition of a very small amount of In at the end of the growth (with $\text{In}/(\text{In}+\text{Ga}) \leq 0.8\%$). Therefore, S2194 will be referred to as surface-modified CGS.

Device Fabrication: We deposited 500-600 Å of CdS using chemical-bath deposition (CBD) at a bath temperature of about 65 °C. We deposited the ZnO layer using sputtering in Ar/O_2 working gas. An undoped ZnO layer 90 nm thick was deposited from a pure ZnO target, followed by an Al-doped ZnO layer about 120 nm thick deposited from an Al_2O_3 -doped ZnO target. The ZnO bilayer has a sheet resistance of about 65–70Ω/square. We deposited the Ni/Al grids by electron-beam evaporation. We defined the cell area of our CIS cells by photolithographic procedure and by chemical etching, whereas for the modified CGS cells, the cell area was defined using mechanical scribing. We then deposited a 100-nm-thick MgF_2 antireflection coating using sputtering.

Characterization: We analyzed our devices using a number of device characterization techniques. We used deep-level transient spectroscopy (DLTS) and admittance spectroscopy (AS) techniques to study the defects in our solar cells. We also used a number of materials characterization techniques (e.g. X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning Kelvin probe microscopy (SKPM), photoluminescence (PL), cathodoluminescence (CL)) to examine our absorbers. Due to lack of space here, we will not include all data.

In this paper, we present a comparison in device performance between the previous and new record CIS and CGS cells.

RESULTS AND DISCUSSION

We demonstrated improved efficiency of 10.2% for surface-modified CGS solar cells. The NREL-confirmed device operating parameters for this cell are given in Table 1. For comparison, the device parameters for the previous CGS cell (S2087) [3] are also given. Figure 1 shows the current-voltage (I-V) data for the new modified CGS cell. CGS is a candidate top cell absorber material for thin-film tandem devices. Its bandgap is ideal at 1.67 eV. This particular device had a bandgap of 1.64 eV. Improving CGS device efficiency has proven to be a challenge over the past several years. The recent understanding of the differences in structural and electronic properties between CIGS and CGS thin films and devices has led to varying the growth process in a way that is likely to make the CGS surface region similar to that of CuIn(Ga)Se_2 and to minimize

defects in the material. This change led to a gain in the current density of about 3.7 mA/cm² versus the previous record cell.

We also demonstrated an improved total-area efficiency of 15.0% for CIS solar cells. The NREL-confirmed device parameters for this cell (S2279) are given in Table 1. Figure 2 shows the I-V data for this cell. For comparison, device parameters for the previous CIS cell (S2044) [2] and record CIGS [4] cell are also given in Table 1.

Figure 3 shows the absolute external quantum efficiency (QE) curves for the previous (S2087) and new (S2194) CGS cells. It also shows the absolute external QE for the new CIS cell (S2279). The better QE gain and the higher currents for sample S2194 resulted from a modified deposition scheme and a modified surface of the CGS absorber. This figure reveals higher overall collection for the 10.2% cell compared to the 9.53% one. About 30% of the increase in current comes from a slight decrease in the energy bandgap, whereas the remaining current (~70%) comes from better overall collection. In sample S2194, the V_{oc} and the fill factor decreased compared to sample S2087, which indicates that the recombination mechanisms are different in the two devices.

Table 1. Device parameters for previous (S2044 and S2087) and improved (S2279 and S2194) CIS and CGS cells, respectively. Device parameters for record CIGS cell are also included [4].

Sample Number	V _{oc} (V)	J _{sc} (mA/cm ²)	Fill factor (%)	Total-area efficiency (%)
S2194-B23	0.823	18.61	66.77	10.2
S2087-B33 [3]	0.905	14.88	70.79	9.53
S2279-B31	0.491	40.58	75.15	15.0
S2044-A35 [2]	0.491	41.1	71.9	14.5
CIGS [4]	0.692	35.22	79.87	19.5

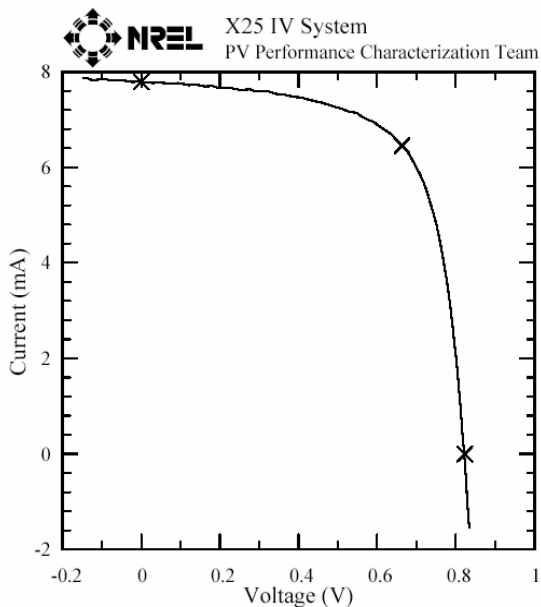


Fig. 1. Total-area current-voltage characteristics of the 10.2% surface-modified CuGaSe₂ solar cell. Cell measured under standard reporting conditions (1000 W/m², AM1.5 Global spectrum at 25°C). Total area of the cell is 0.419 cm².

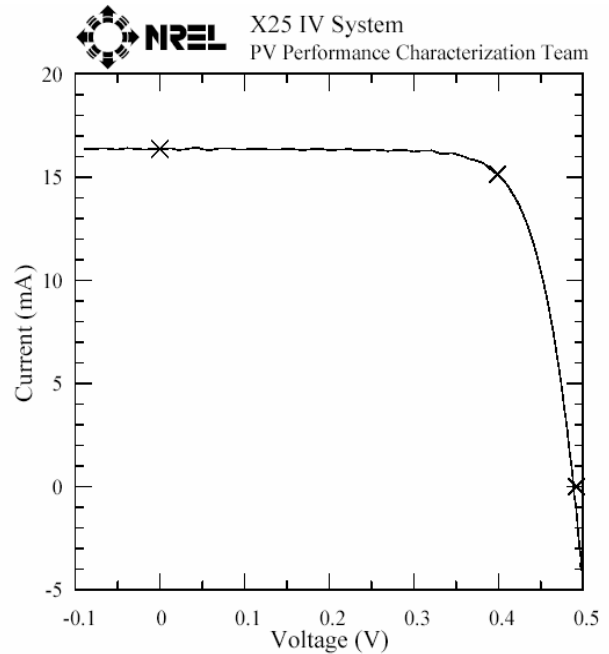


Fig. 2. Total-area current-voltage characteristics of the 15.0% ZnO/CdS/CuInSe₂ solar cell. Cell measured under standard reporting conditions (1000 W/m², AM1.5 Global spectrum at 25 °C. Total area of the cell is 0.403 cm²).

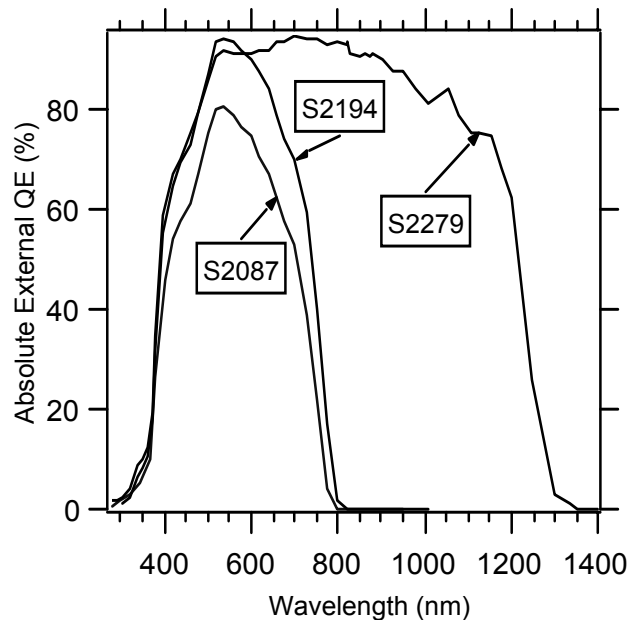


Fig. 3. Absolute external quantum efficiency (QE) for surface-modified CGS cell, S2194-B2#3. For comparison, absolute external QEs for new CIS cell [2] and our previous [3] CGS cell are also included.

For the new record CIS cell (S2279), the absolute external QE is almost identical to that of the previous one (S2044) [2]. The major improvement in device performance comes from the fill factor. The increase in fill factor is 4.4% (70.79% for S2044, compared to 75.15% for S2279). The series and shunt resistance for sample S2044-A35 are ~ 1.2 and $\sim 1893 \Omega\text{-cm}$, and those for sample S2279-B31 are ~ 1.1 and $\sim 3000 \Omega\text{-cm}$, respectively. This higher shunt resistance for sample S2279-B31 may be responsible for the higher fill factor. The V_{oc} and J_{sc} for samples S2044-A35 and S2279-B31 are almost the same.

We designed a 4-terminal polycrystalline thin-film mechanical-stacked tandem cell where our 15% CIS cell serves as the bottom cell and a newly developed transparent CdTe with an NREL-confirmed total-area efficiency of 13.8% [5] serves as the top cell. This mechanical-stacked tandem has an NREL-confirmed new record efficiency of 15.31%, which exceeds a U.S. Department of Energy program milestone of 15%. The newly designed mechanical-stacked tandem will be the subject of another publication.

Our group is also focusing on developing CGS/TCO as the top cell for the tandem device. Given the CIS and CGS bandgaps of 1.0 and 1.67 eV, respectively, we expect the photovoltaic performance of the CIS bottom cell under a CGS top cell to be better than if it is under a CdTe cell. We designed a mechanical-stacked tandem where CIS serves as the bottom cell and CGS serves as the top cell. The NREL-confirmed efficiency for this tandem is 9.7%.

Figure 4(a) shows the cross-sectional scanning electron microscopy (SEM) images for the surface-modified CGS film (S2194), previous CGS film (S2171), and a thicker CGS film (S1820). The thickness of these films are 2.3, 1.8, and 3.0 μm , respectively. Figure 4(a) shows large columnar grains of the surface-modified CGS film. This image also shows distinct surface structure, as compared to the cross-sectional SEM image of the previous CGS film shown in Fig. 4(b). We believe that this different surface structure of the surface-modified CGS film is due to a modified growth process and the addition of a small amount of In at the end of the growth. Figure 4(c) shows the cross-section SEM image of a CGS film grown using the three-stage process, but with a thickness of 3.0 μm , which is comparable to that of CIGS [1]. This figure shows a different grain structure compared to the structures shown in Fig. 4(a) and Fig. 4(b). The grains for sample S1820 are smaller in size, and the image shows a layer of smaller grains toward the back of the film (close to the Mo layer). Therefore, reducing the thickness of the CGS film caused better grain growth, which resulted in better device performance.

Figure 5 shows the cross-sectional SEM image for the CIS film used in the 15.0% new record CIS device. This image shows larger grains compared to those we reported or the CIS film used in our previous CIS record device [2]. It also shows better grain growth compared to our pervious film [2]. This better grain growth and larger grain size in the new CIS film may be due to the elevated substrate temperature we used during the growth of the new CIS film, as compared to our previous film [2].

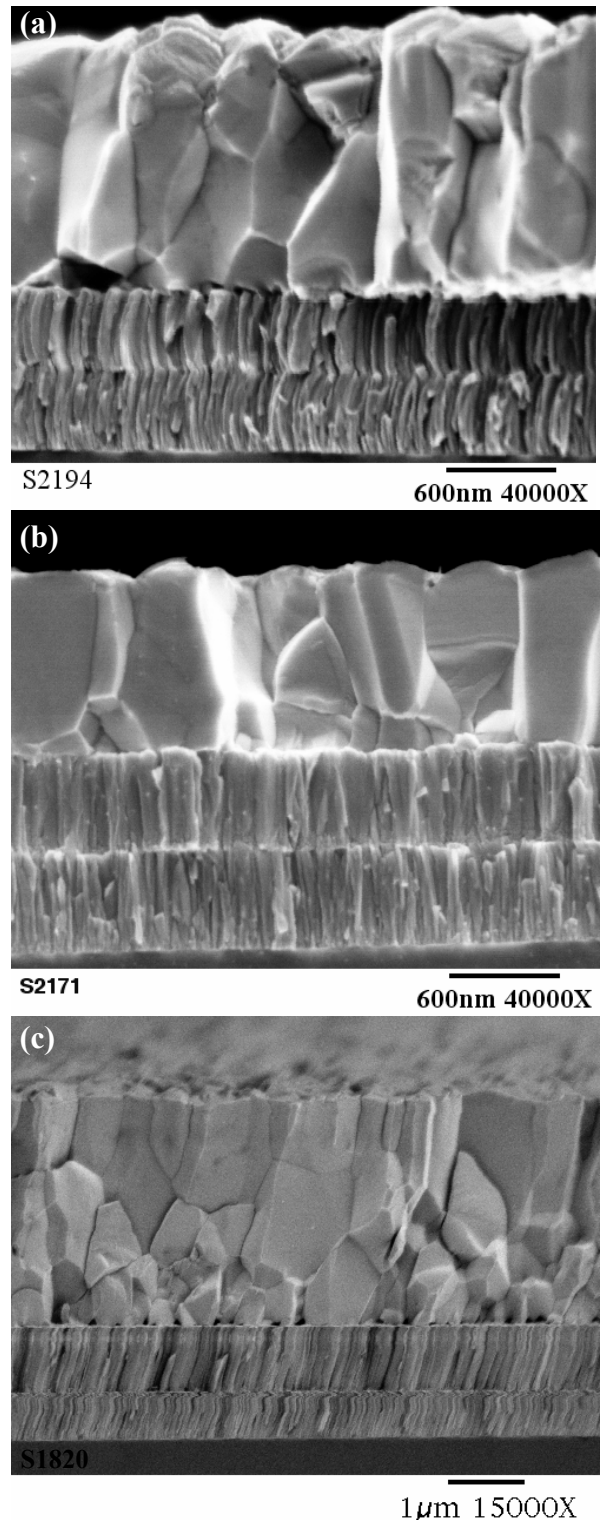


Fig. 4. Cross-sectional scanning electron microscopy images for (a) modified CGS film used in 10.2% device (S2194), (b) CGS film used in previous CGS device (S2171) [3], and (c) a CGS film (with $\sim 8\%$ efficiency) (S1820).

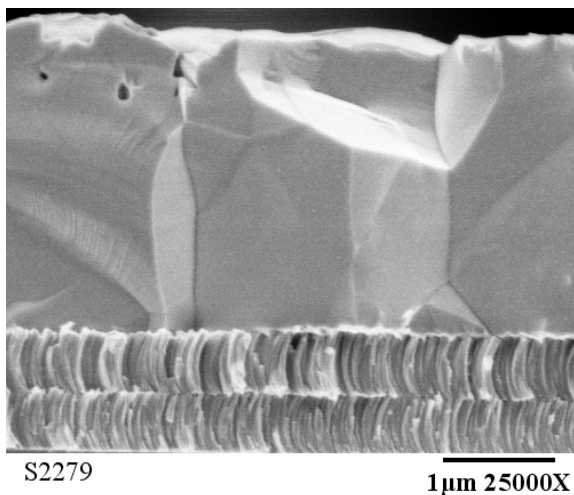


Fig. 5. Cross-sectional scanning electron microscopy image for CIS film used in 15% new record CIS device.

We examined our modified and previous CGS cells using deep level transient spectroscopy (DLTS). The DLTS data for the modified CGS sample exhibit deeper minority traps compared to our previous CGS. Figure 6 shows the trap density versus filling pulse width for improved CGS cell and our previous one. As the pulse duration varies from 10 μ s-10 s, the activation energy changes from E_c -0.3 to E_c -0.6 eV (where E_c is the energy of electrons at the conduction band minimum) in the modified CGS cell and from E_c -0.06 to E_c -0.1 eV in the previous CGS cell. We also observed the gradual increase in the amplitude of the DLTS signal until it apparently saturates at pulse durations of \sim 1s in the modified CGS and \sim 0.5s in the previous CGS (as shown in figure 6). This gradual increase is due to partial filling of the states with short pulse durations. Figure 6 shows lower defect density in the new modified CGS cell compared to the previous one. This decrease in defect density in the modified CGS cell is due to improved quality of the surface region of the modified CGS absorber layer as a result of a modified deposition scheme and a modified surface of the CGS absorber layer.

SUMMARY

We modified the growth process for CIS and CGS thin films. This modification resulted in new record total-area efficiencies of 15.0% and 10.2%, respectively, for these cells. The improved device performance in the new record CGS cell resulted, in part, from varying the growth process in a way that is likely to make the CGS surface region similar to that of Cl(G)S and to minimize defects in the material. The new CIS record efficiency may have resulted from a modified temperature profile, in which we used elevated temperatures during the three stages of the three-stage growth process.

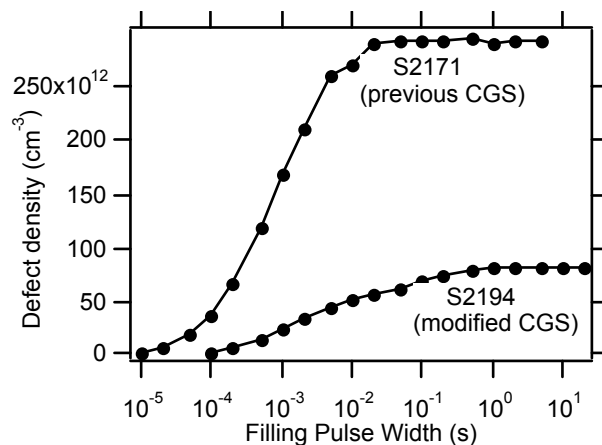


Fig. 6. Defect density vs. pulse width for improved modified CGS cell (S2194) and for previous CGS cell (S2171).

ACKNOWLEDGEMENTS

The authors acknowledge the technical support of J. Dolan and J. Keane. The authors thank T. Moriarty for the I-V and QE measurements and K. Ramanathan for his support. The authors thank M. Young for the QE measurements. The authors also thank B. To for the scanning electron microscopy analysis. This work is supported by DOE Contract No. DE-AC36-99GO10337. J. AbuShama was supported by NREL subcontract No. KXEA-3-33607-03 to the Colorado School of Mines.

REFERENCES

- [1] K. Ramanathan, M. Contreras, C. Perkins, S. Asher, F. Hasoon, J. Keane, D. Young, M. Romero, W. Metzger, R. Noufi, J. Ward, and A. Duda, "Properties of 19.2% Efficiency ZnO/CdS/CuInGaSe₂ Thin-film Solar Cells", *Prog. Photovolt. Res. Appl.* **11**, 225 (2003).
- [2] J. A. M. AbuShama, S. Johnston, T. Moriarty, G. Teeter, K. Ramanathan, and R. Noufi, "Properties of ZnO/CdS/CuInSe₂ Solar Cells with Improved Performance", *Prog. Photovolt: Res. Appl.* **12**, 39 (2004).
- [3] D. Young, J. Keane, A. Duda, J. AbuShama, C. Perkins, M. Romero, and R. Noufi, "Improved Performance in ZnO/CdS/CuGaSe₂ Thin-Film Solar Cells", *Prog. Photo volt: Res. Appl.* **11**: 535 (2003).
- [4] M. Contreras and J. AbuShama (private communication).
- [5] X. Wu and J. AbuShama (private communication).

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Department of Defense, Executive Services and Communications Directorate (0704-0188). Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ORGANIZATION.

1. REPORT DATE (DD-MM-YYYY) February 2005			2. REPORT TYPE Conference Paper		3. DATES COVERED (From - To) 3-7 January 2005	
4. TITLE AND SUBTITLE Improved Performance in CuInSe ₂ and Surface-Modified CuGaSe ₂ Solar Cells				5a. CONTRACT NUMBER DE-AC36-99-GO10337		
				5b. GRANT NUMBER		
				5c. PROGRAM ELEMENT NUMBER		
6. AUTHOR(S) J. AbuShama, R. Noufi, S. Johnston, S. Ward, and X. Wu				5d. PROJECT NUMBER NREL/CP-520-37411		
				5e. TASK NUMBER PVA54201		
				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-520-37411		
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) In this paper, we present an update and review on the progress made in the development of low-bandgap CuInSe ₂ (CIS) and wide-bandgap CuGaSe ₂ (CGS) solar cells. Our research project is primarily concerned with the optimization of the bottom and top cells of the tandem solar cell. This past year, we established new record total-area efficiencies of 15.0% and 10.2% for CIS and surface-modified CGS solar cells, respectively. These achievements were possible by modifying the growth process for CIS and CGS absorbers. We attempt to modify the surface region of the CGS absorber to be CIGS-like in composition. We also have designed a mechanical-stacked tandem solar cell where the 15% CIS cell serves as the bottom cell. The NREL-confirmed total-area efficiency for this tandem device is 15.31%.						
15. SUBJECT TERMS PV; CuInSe ₂ (CIS); CuGaSe ₂ (CGS); tandem solar cell; device; low-band gap; wide-band gap; surface-modified; absorbers; total-area efficiency;						
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UL	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON	
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (Include area code)	