Novel Thin-Film CuInSe$_2$ Fabrication

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PREFACE

This is an annual report of research carried out from May, 1992 to Oct., 1993 under subcontract No. XC-0-10012-1 to the University of Colorado, Boulder. The principal investigator is Allen Hermann, and Andrew Gabor is the co-investigator. The work carried out under this subcontract originally focused on using rapid thermal processing of various precursor layers to form $CuInSe_2$. It was then discovered at NREL that other precursor reaction schemes held the promise to obtain layers for high-efficiency devices. Thus, it was decided to align the objective with that of the NREL CIS task. The work was integrated in the deposition schemes pursued at NREL, as described below. The thin film fabrication, characterization, and device delineation were carried out at the NREL facilities, and were integrated into the operating plan as part of the NREL CIS team research effort (R. Noufi principal investigator) that resulted in world-record breaking $Cu(In,Ga)Se_2$ solar cells.

SUMMARY

A new technique for the formation of $CuIn_xGa_{1-x}Se_2$ thin films was explored. The Cu deposition was separated from the Ga+In deposition such that precursor films with composition of either a) Cu_xSe, or b) $(In_x,Ga_{1-x})_2Se_3$ were formed. These precursors were exposed to either a) In+Ga+Se or b) Cu+Se at substrate temperatures > 500 °C to form $CuIn_xGa_{1-x}Se_2$. Films made from the Cu_xSe precursors were unexceptional, but films made from the $(In_x,Ga_{1-x})_2Se_3$ precursors were of exceptional smoothness and density. During the work period, a device made from one of these films resulted in what at the time was the highest total-area efficiency measured for any non-single-crystal, thin-film solar cell, at 15.9%.

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INTRODUCTION

The goal of this subcontract is to explore novel methods of CIS thin-film formation. Simply put, we wish to discover better ways of depositing and reacting Cu, In, and Se on the substrate to form quality films of CIS for photovoltaics. Potential sources for the material are the CIS compound, Cu-In, Cu-Se and In-Se compounds, and elemental Cu, In, and Se. The material can be deposited over multiple stages, and the substrate temperature can be controlled to react the films when desired. With these variables of source material, substrate temperature, and order and rate of deposition, we have an infinite number of ways at our disposal to form the material.

Manufacturing limitations provide a framework for our explorations. Glass substrate temperatures cannot be held above ~575°C for a significant length of time. In addition, uniform codeposition from two or more separate sources is difficult to achieve. Therefore it is desirable to deposit from only one source at a time.

The selenization of Cu-In precursor films is one of the most explored pathways toward CIS formation and is consistent with these manufacturing constraints. The precursor can be formed by depositing separate layers of Cu and In, and the selenization step can occur via reaction with Se vapor or H_2Se gas. Problems such as adhesion and phase separation across the plane of the substrate have been seen by several researchers exploring this pathway, but recent results suggest that one can successfully engineer around these obstacles.[1] As attractive as this process may be, manufacturers have yet to use it to bring a product to the market. Therefore, exploration of other pathways is warranted.

The deposition of Cu, In, and Se at low substrate temperatures, followed by a post deposition anneal at higher temperatures is another attractive process. The "not fully reacted" precursor film may be deposited by many methods such as physical vapor deposition or sputtering of elemental layers or Cu-Se and In-Se compounds, or by electrodeposition. We have explored this route in past years using physical vapor deposition to form the precursor and rapid thermal annealing to react it.[2,3] Other groups have explored similar

pathways[4,5] and although high efficiency devices have yet to be formed by such processes, we feel they are very promising. An important consideration for such processes is to include some additional Se exposure at high temperatures during the anneal and when cooling down to retain good electrical properties. In addition, such techniques can be cheap ways to deposit and form the majority of the film. Such a film can then be used itself as a precursor to a final high-temperature deposition wherein a high-quality surface is formed.

While uniform codeposition of Cu and In over a large substrate is very difficult to achieve, the uniform codeposition of Cu and Se or In and Se over large areas is much simpler. At substrate temperatures >250°C, Se will not stick to a bare substrate, but instead can react with species on or being delivered to the substrate. The Se incorporation into the film is thus self-regulating. As long as a sufficient Se flux is maintained, moderate nonuniformities in the Se flux over the substrate will have little effect on the film growth. Thus codeposition of Cu+Se or of In+Se is a reasonable manufacturing technique. The use of compound Cu-Se and In-Se sources is also reasonable. Despite their attractions, pathways toward CIS formation commencing from In-Se or Cu-Se precursor films have not been well explored. Thus we chose to focus on these routes for the last year of this contract. In addition, we have incorporated Ga into the films to obtain a better match of the band gap to the solar spectrum and to construct graded-band-gap structures.

EXPERIMENTAL

The Appendix consists of a paper presented at the 12th NREL PV Program Review Meeting in Denver, Oct. 13-15, 1993. This paper contains the results of this report. Further information is presented elsewhere.[6,7] Provided here is some additional clarification concerning the formation process.

Figure 1 shows a time-temperature plot of a typical deposition. In the 1st stage an In2Se3 or (In,Ga)2Se3 precursor is formed by coevaporation of In+Se or In+Ga+Se. In the second stage the precursor is reacted with Cu+Se. Enough Cu is added during this second stage to cause the average film composition to become Cu-rich, such that Cu/(In+Ga) > 1. The excess Cu is believed to exist in a liquid Cu_xSe phase which can recrystallize the film. The excess Cu_xSe is then consumed in a third stage deposition of In+Se or In+Ga+Se.
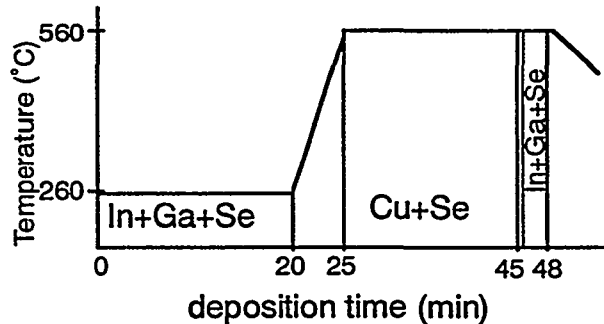
Fig. 1. Time-temperature profile for the three-stage (In,Ga)2Se3 precursor method

The Ga-free deposition adheres well to the manufacturing limitations discussed above. However, the Ga-containing case violates the limitations since it involves a codeposition of In+Ga in the 1st and 3rd stages. Such codeposition may be avoided in a variety of ways. In addition the process may be made friendlier for manufacturing by lowering the deposition temperatures. One possible scenario is shown in Fig. 2. Studies of these processes are suggested for future work.
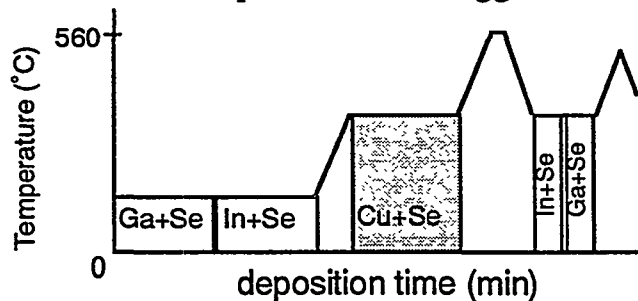
Fig. 2. Time-temperature profile for a simplified process.

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High Efficiency Polycrystalline Cu(In,Ga)Se$_2$-Based Solar Cells

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ABSTRACT

Thin films of Cu(In,Ga)Se$_2$ were formed from precursor films of
(In,Ga)$_2$Se$_3$. The films are smooth, with large, tightly packed grains.
Photovoltaic devices made from these films show great tolerance in the
efficiency to variations in film composition, and scalability of the process
appears promising. A device made from one of these films resulted in
the highest total-area efficiency measured for any non-single-crystal,
thin-film solar cell, at 15.9%.

INTRODUCTION

Thin films of CuInSe$_2$ (CIS) and alloys of CIS with the higher band-
gap CuGaSe$_2$ have been used to form photovoltaic (PV) solar cells with
total area efficiencies >14%.[1] Two of the most successful methods for the
formation of Cu(In,Ga)Se$_2$ (C(IG)S) thin films are 1) the selenization of
Cu-(In,Ga) alloys by Se vapor or H$_2$Se, and 2) various ways of
codepositing Cu and (In,Ga) with Se. It appears that both of these
methods involve reactions with Cu-Se and/or (In,Ga)-Se compounds.[2]
Variations on the latter method[3,4] utilize "Cu-rich" starting material,
where the excess Cu can exist as the Cu$_2$Se phase as is indicated in Fig. 1
by the Cu$_2$Se-In$_2$Se$_3$ pseudobinary phase diagram.[5] The Cu-Se binary
phase diagram[6] in Fig. 2 indicates that more Se-rich Cu(Se) phases can
exist as a liquid at high temperatures. Thus, by increasing the Se activity
during growth, the excess Cu$_2$Se can be converted to a liquid flux to aid
in mass transport to produce films with large grain structures. The
Cu(Se) can then be consumed through reaction with In and Se during
later stages of film growth in order to reach the Cu-poor stoichiometry
necessary for efficient solar cell operation.

A less-explored approach to forming C(IG)S is to start with Cu-poor
precursors. In so doing, one loses the benefits of a large-grain precursor
and risks crossing through the several In-rich phases shown on the
Cu$_2$Se-In$_2$Se$_3$ pseudobinary phase diagram. We have chosen to
investigate this route in detail. We have also chosen to simplify the

deposition process by separating the deposition of the Cu and the In(Ga) into different stages. Such separation may be advantageous in manufacturing.
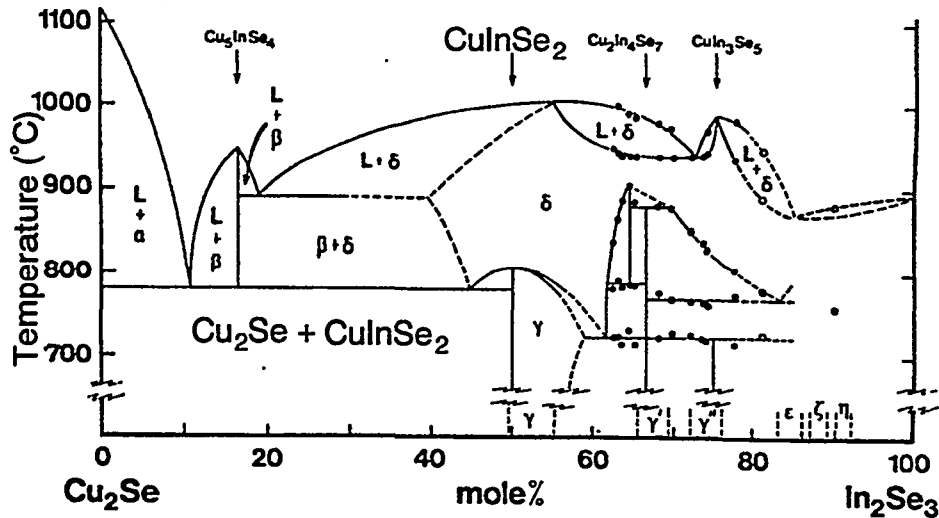

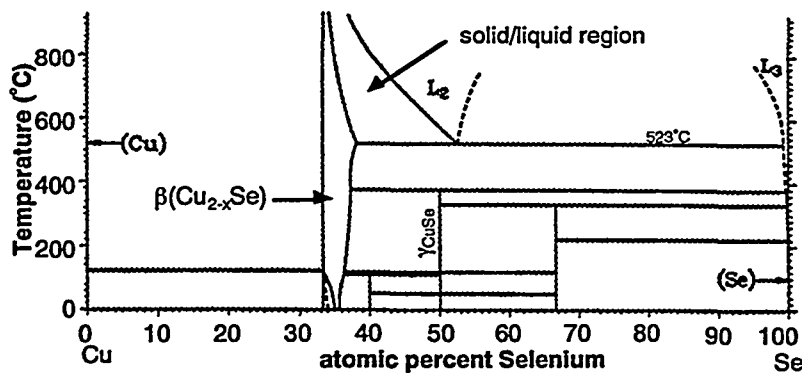Fig. 1. The Cu₂Se-In₂Se₃ pseudobinary phase diagram

Fig. 2. The Cu-Se binary phase diagram.

ABSORBER FORMATION AND CHARACTERIZATION

The thin-film absorbers were grown on soda-lime silica glass coated with 1 μm of Mo. CIS and CIGS films were formed using physical vapor deposition from resistively heated boats, each containing a separate element. The same process was used for both films, where Ga replaced part of the In for CIGS. The sources were oriented relative to the substrate to induce an intentional compositional gradient across the film surface.

C(IG)S thin films were formed by first forming $(In,Ga)_2Se_3$ precursor films and then exposing them to Cu_xSe_y activity at temperatures above

500 °C. The resulting films were smooth and had a densely packed grain structure with grains between 1 and 3 μm in size (see Fig. 3).
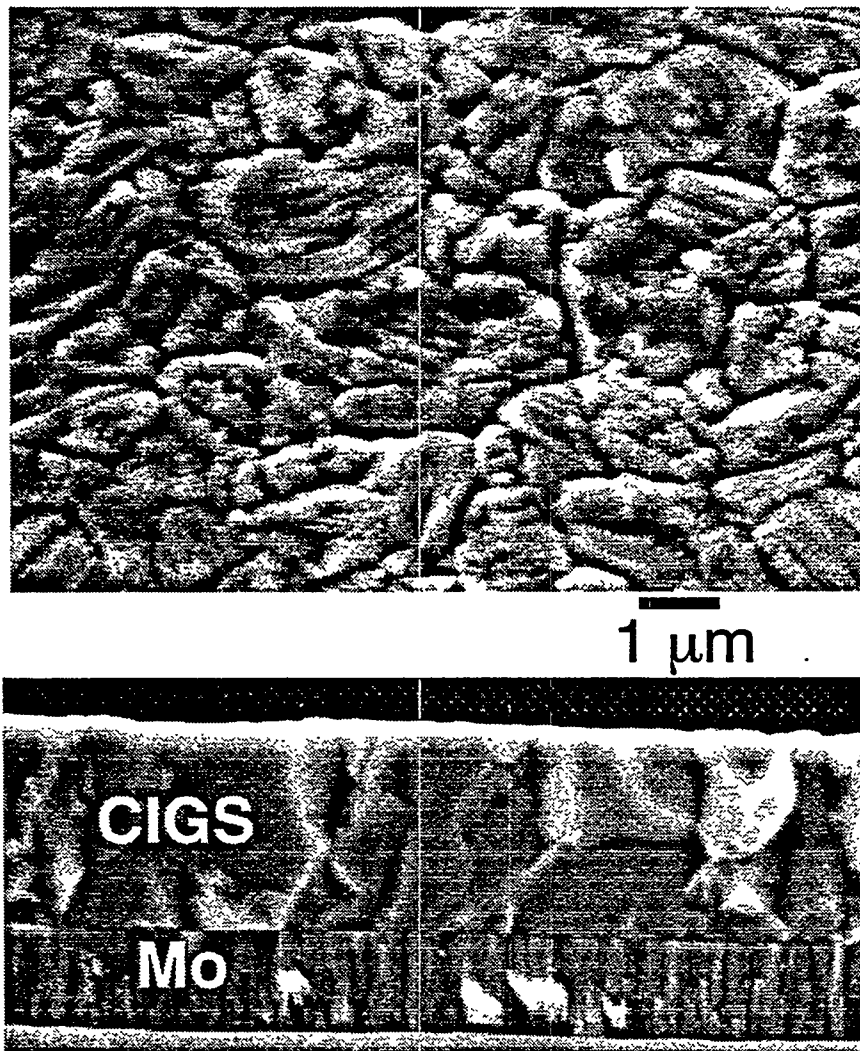

Fig. 3. SEM micrographs of the surface and cross-section of a CIGS film

The surface roughness was quantified by scanning over a 25-μm^2 projected area with an atomic force microscope. The calculated mean roughness and the ratio of surface area to projected area are shown in Fig. 4 for the best CIGS film formed by this technique as well as for the best CIGS films made at the National Renewable Energy Laboratory (NREL) using two other processes: a) selenization of a precursor containing Cu, In, and Ga; and b) growth from a Cu-rich precursor. A typical line scan taken from the area scan is shown in Fig. 4 for each of

these films. The CIGS film made from the $(In,Ga)_2Se_3$ precursor is far smoother than the others and has a significantly smaller surface area. Because this area is effectively the junction area, reducing it may contribute to a lowering of dark current in the device and to a reduction in the number of interface states between the CIGS and the window layer per unit projected area.
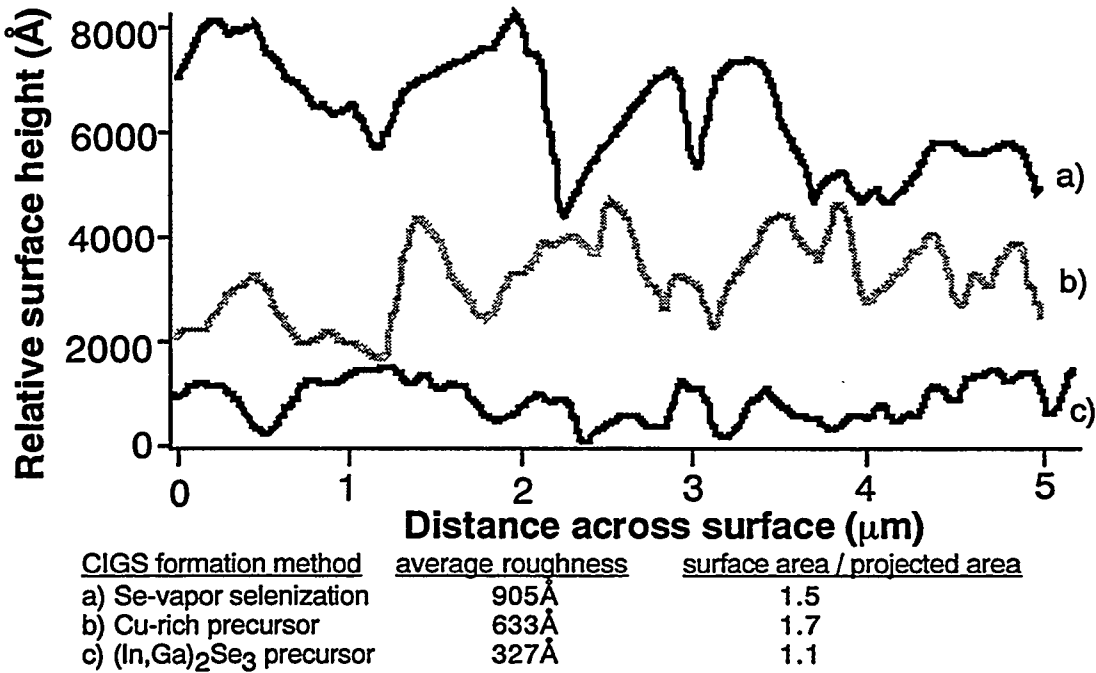

CIGS formation method	average roughness	surface area / projected area
a) Se-vapor selenization	905Å	1.5
b) Cu-rich precursor	633Å	1.7
c) $(In,Ga)_2Se_3$ precursor	327Å	1.1

Fig. 4. The ratio of surface area to a projected area of 25 μm^2, the average roughness over this area, and typical atomic force microscope line scans for CIGS films made by a) a Se-vapor selenization process (η=12.6%); b) a Cu-rich precursor process (η=15.1%); and c) the $(In,Ga)_2Se_3$ precursor process.

Another factor that may contribute to cell efficiency is the gradient in the Ga content as a function of depth in the CIGS films. Figure 5 shows an Auger depth profile obtained by sputtering through the film. The Ga content increases from front to back in the film. As the band gap increases with higher Ga contents, the gradient in Ga corresponds to a grading of the band gap. Such a grading[7] can aid in carrier transport outside the depletion region and can further reduce the dark current. In addition, the dip in the Ga content near the front of the film is qualitatively similar to the "notch structure" recently recommended for application to CIS-based materials.[8]
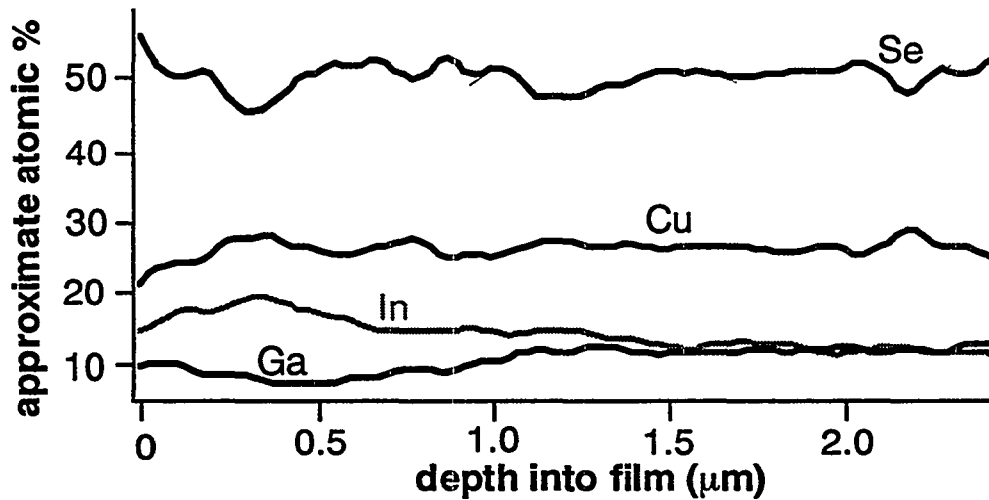
Fig. 5. An Auger depth profile of a CIGS film

CELL RESULTS

Devices were fabricated from the p-type absorber films by depositing 500 Å of CdS, 500 Å of resistive ZnO, 3500 Å of conductive n-type ZnO:Al, 500 Å of Ni and 3 μm of Al for top contacts, and ~1250 Å of MgF$_2$ for an antireflective coating. The CdS was grown from solution; the ZnO was deposited by ion-beam sputtering1; and the Ni, Al, and MgF$_2$ were deposited by physical vapor deposition. Figure 6 shows the J-V curves and total-area cell parameters for the best CIS and CIGS devices. The total-area efficiency for the CIS device is the highest ever officially measured at NREL for non-alloyed CIS, and the total-area efficiency for the CIGS device is highest measured at NREL for any non-single-crystal thin-film device.

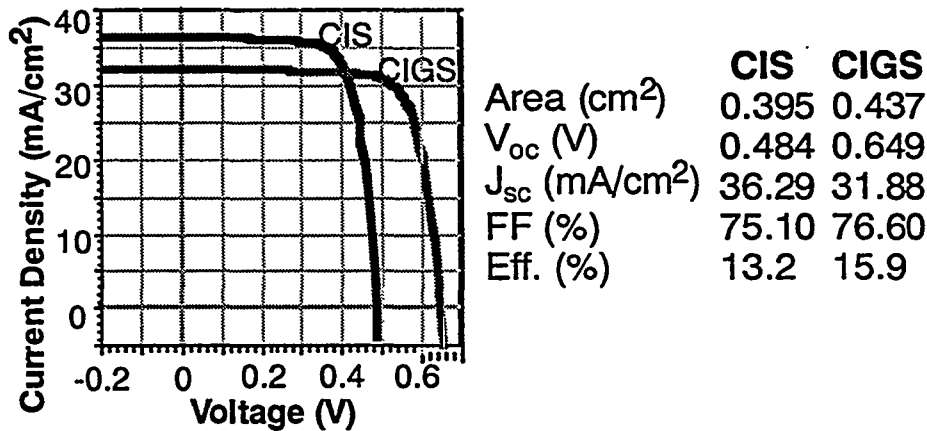|	CIS	CIGS
Area (cm^2)	0.395	0.437
V$_{oc}$ (V)	0.484	0.649
J$_{sc}$ (mA/cm^2)	36.29	31.88
FF (%)	75.10	76.60
Eff. (%)	13.2	15.9

Fig. 6. J-V curves for the best CIS and CIGS devices

From the compositional gradient across the substrate, one can see that the device efficiencies remain high across a significant variation in [Cu]/([In]+[Ga]), as is shown in Fig. 7. Such tolerance to compositional variations is significant from a manufacturing perspective.
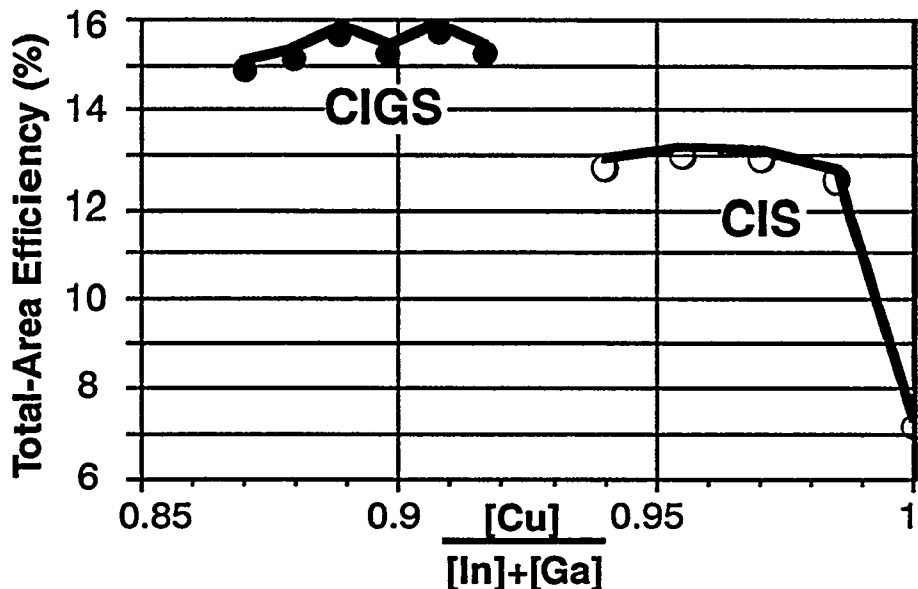
Fig. 7. Efficiency of devices vs. composition for CIGS and CIS

This compositional tolerance allowed us to make larger high-efficiency devices on our compositionally graded films. Figure 8 shows the compositional variations across a device with a total area > 6 cm^2. Despite a non-optimized grid, a poor antireflection coat, and excessive series resistance in the back Mo contact, a 13.9% efficiency was still achieved. Again, this implies that with this process, composition can vary significantly across a large module without disastrous effect on the efficiency.

Area   6.64 cm^2
V_{oc} 0.644 V
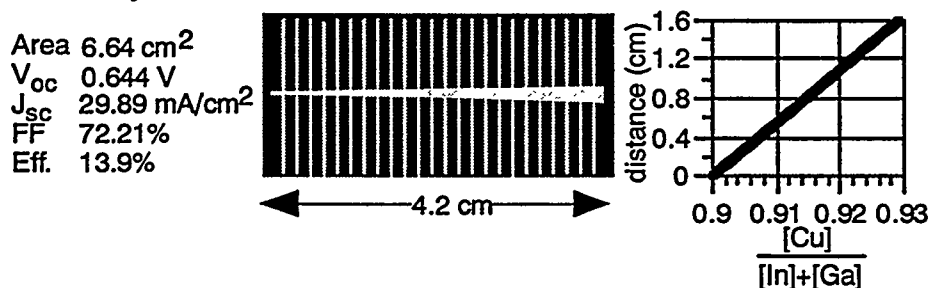J_{sc} 29.89 mA/cm^2
FF   72.21%
Eff.   13.9%

Fig. 8. Device parameters and compositional variation for a large-area device

Finally, an analysis of the device spectral response suggests that even better device performance can be realized with further improvements in

our window layers. Figure 9 compares the spectral response of our best CIGS device to that of the best CIGS cell (η=14.6%) made by the Boeing Corporation.[9] As seen in the figure, Boeing's device appears to be more responsive in both the near-infrared and blue regions of the spectrum. The improved behavior at shorter wavelengths is due to less light absorption in their CdZnS layer than in our CdS layer. The higher response at longer wavelengths may be due to less free-carrier absorption in their ZnO. If these losses were eliminated from the NREL cell, the efficiency would climb from 15.9% to 17.6%.
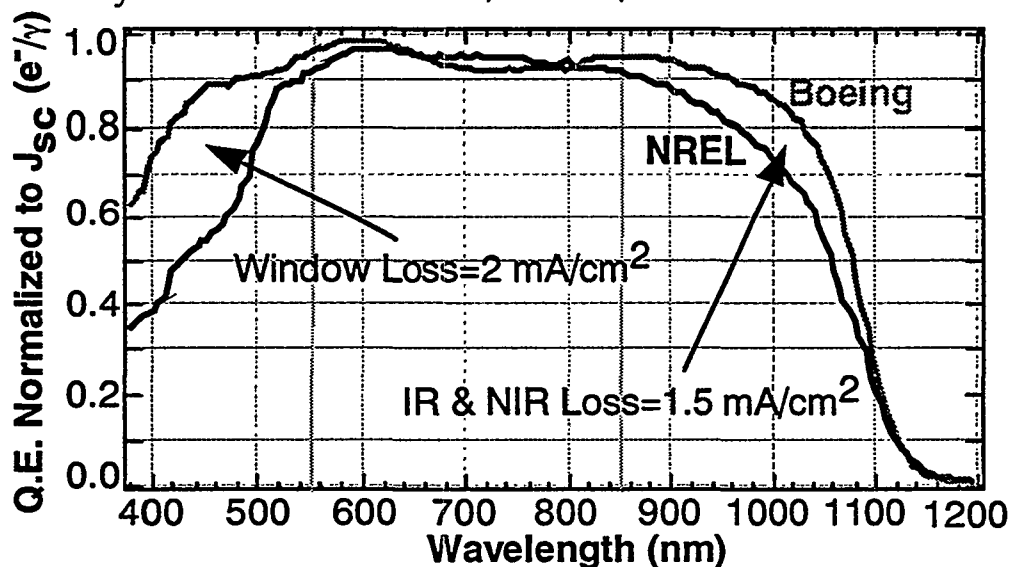
Fig. 9. Spectral responses of the best CIGS device from this study and the best CIGS device made by the Boeing Corporation

CONCLUSIONS

We have demonstrated the highest total-area efficiency confirmed by NREL for a thin-film solar cell using a new process for C(IG)S formation. The process yields smooth films and can result in compositional profiles conducive to current collection. Optimization of window material, back contacts, band-gap grading, and further alloying of CIS with other compounds should push CIS-based solar cell efficiencies toward 20% in the foreseeable future. From the standpoint of sensitivity to compositional variations, scalability of the process appears promising. Future work will focus on further identifying the characteristics specific to these films that contribute to the high cell performance, and on identifying both the growth mechanisms and chemical pathways leading to C(IG)S formation by this technique.

ACKNOWLEDGMENTS

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13. ABSTRACT *(Maximum 200 words)*

This report describes work exploring a new technique for the formation of $CuIn_xGa_{1-x}Se_2$ thin films. The Cu deposition was separated from the Ga+In deposition such that precursor films with compositions of either Cu_xSe or $(In_xGa_{1-x})_2Se_3$ were formed. These precursors were exposed to either (a) In+Ga+Se or (b) Cu+Se at substrate temperatures > 500°C to form $GaIn_xGa_{1-x}Se_2$. Films made from the Cu_xSe precursors were unexceptional, but films made from the $(In_xGa_{1-x})_2Se_3$ precursors were of exceptional smoothness and density. During the period covered in this report, a device made from one of these films resulted in what, at the time, was the highest total-area efficiency measured for any non-single-crystal, thin-film solar cell, at 15.9%.

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