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# Alternative Window Schemes for $CuInSe_2$-Based Solar Cells

## Annual Report
## 1 November 1995 - 31 October 1996

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# ABSTRACT

The objectives of this program are to develop alternate heterojunction partner layers (buffer layers) for high efficiency $CuInSe_2$-based thin-film solar cells, and improve the understanding of how these layers and the details of processing affect cell performance. Investigations have primarily involved three tasks: (1) MOCVD growth of non-cadmium containing buffer layers; (2) optimized processing of buffer layers for high efficiency solar cells; and (3) electrical and physical characterization of layers and devices. Investigations of alternative buffer layers emphasized studies of ZnO grown by MOCVD. Using CIS substrates obtained from Siemens for process development, it was determined that growth procedures that resulted in good results with Siemens CIS (non-sulfur containing material) substrates also worked well with NREL CIGS material. A two step process was developed for growing highly resistive ZnO buffer layers (i-ZnO). In particular, after growing 100 to 150 Å of ZnO at 250°C, an additional 600 Å to 800 Å were grown at 100 °C. Collaboration with NREL resulted in a n-ZnO/i-ZnO/CIGS cell which was determined to have a total area efficiency of 12.7 %, and an active area efficiency greater than 13 %. After growing i-ZnO with the two-step process onto NREL CIGS material, the i-ZnO/CIGS film structure was sent to NREL for deposition of a TCO, namely, conducting ZnO (n-ZnO). Collector grids and a $MgF_2$ AR coating were also deposited at NREL. Low level efforts were devoted to studies of ZnSe and InSe buffer layers. A total area efficiency of 9.5 % was achieved for a completed ZnSe/CIS cell making use of a RF sputtered ZnO for a TCO. Investigations of $In_xSe_y$ (InSe) buffer layers were also initiated this past year. InSe films were grown by reacting $H_2Se$ and ethyldimethylindium with substrate temperatures in the range of 300 to 400 °C. Test cells showed promise suggesting further work is warranted if time permits. Spectroscopic ellipsometry was utilized to investigate the surface layer of CIS substrates and ZnO buffer layers. Measurements and analyses indicated that a surface layer approximately 250 Å thick and characterized by interband transitions of 1.15 eV and 1.26 eV exists on Siemens surfaces. Finally, simulation studies carried out for ZnO/CIS cells with PC-1D indicate that the low efficiencies experienced for structures with low resistivity ZnO buffer layers may be a result of enhanced depletion region recombination caused by the ZnO deposition process.

# 1. INTRODUCTION AND BACKGROUND MATERIAL

This report concerns work carried out during the period 11/1/95 through 10/31/96 to investigate $CuInSe_2$ (CIS) and CIS alloy solar cells based on non-cadmium buffer layers. Background information, program objectives and the technical approach are discussed in the remainder of this section, and technical progress made during this reporting period is discussed in subsequent sections.

## 1.1 Background Material

Previous work conducted by the WSU group [1] involved investigations of the potential of ZnSe and ZnO buffer layers for application to solar cells based on $CuInSe_2$ and related alloys. Experimental studies were carried out with CIS and CIGSS substrates provided by Siemens Solar. ZnSe films were deposited by a CVD process which involved the reaction of a zinc adduct and $H_2Se$. Using Al/ZnSe/CIS test cells for process development, the optimum thickness for a ZnSe buffer layer was determined to be in the range of 150Å to 200Å for Siemens CIS material, and between 80Å and 120Å for the graded absorber material. If ZnSe buffer layers exceeded these values significantly, the short-circuit current would be reduced to zero. This effect is consistent with results reported in the literature indicating that there is a 0.9 eV band offset at the ZnSe-CIS interface [2, 3]. Completed cells were fabricated by utilizing a low resistance ZnO top contact layer deposited by Siemens, and then depositing an Al/Ag collector grid at WSU. The best efficiency achieved for a ZnSe/CIS cell was an active area value of 9.2 %. In general, deposition of a conductive ZnO film on top of a ZnSe/CIS structure resulted in either shunted or inflected I-V characteristics.

Two approaches were investigated for depositing ZnO buffer layers, namely, chemical bath deposition and chemical vapor deposition. CVD ZnO buffer layers were grown by reacting a zinc adduct with tetrahydrofuran. Best results were obtained for ZnO buffer layers grown with a substrate temperature ($T_{sub}$) $\approx$ 225°C to 250°C. These studies concentrated on cell fabrication with Siemens graded absorber material (CIGSS). ZnO/CIS solar cells have been fabricated by first depositing a ZnO buffer layer, followed by deposition of a low resistivity ZnO top contact layer (by

Siemens) and an Al/Ag collector grid. Several cells were fabricated with an area of 0.44 $cm^2$ that have total area efficiencies greater than 11 %. To date, the best performing ZnO/CIS cell was measured by NREL to have a total area, AM1.5G efficiency of 11.3 %. The active area efficiency of the device was approximately 12 %, which appeared to be the best result for a ZnO buffer layer at that time. In general, it was determined that ZnO buffer layers should have a resistivity > 1000 ohm-cm and have a thickness of several hundred Å. The requirement for a large ZnO resistivity appeared to be more related to processing than to effects on junction parameters. CIS cell studies with ZnO buffer layers grown by CBD also gave promising results. Finally, simulation studies were carried out using the one-dimensional code, PC-1D.

## 1.2 Program Objectives

The objectives of this program are to develop alternate heterojunction partner layers (buffer layers) for high efficiency $CuInSe_2$-based thin-film solar cells, and improve the understanding how these layers and the details of processing affect cell performance. A discussion of the technical approach being used to meet these objectives follows.

## 1.3 Technical Approach

Investigations have primarily involved three tasks: (1) MOCVD growth of non-cadmium containing buffer layers; (2) optimized processing of buffer layers for high efficiency solar cells; and (3) electrical and physical characterization of layers and devices. This past year's work focused on studies of ZnO buffer layers and their application to CIS and CIGS solar cells. Low-level efforts were also devoted to investigations of ZnSe and InSe buffer layers. Ellipsometric studies of ZnO were carried out in an effort to correlate optical properties of films with growth processes. Device studies were supported with simulation studies with PC-1D. Results of these investigations are discussed in the remaining sections according to buffer layer material, ellipsometric analyses and modeling studies.

# 2. CELLS BASED ON ZnO BUFFER LAYERS

ZnO buffer layers continue to be grown by MOCVD. As previously reported, deposition of ZnO is accomplished by reacting a zinc adduct with tetrahydrofuran [1]. A significant part of this effort involved studies with NREL CIGS substrates and collaboration with NREL to fabricate n-ZnO/i-ZnO/CIGS cells. Details regarding these investigations follow.

## 2.1 CVD ZnO Buffer Layers On NREL CIGS

Investigations of CVD ZnO buffer layers during this reporting period included studies with CIGS material provided by NREL. In particular, these investigations were part of a broader effort being conducted by the CIS Junction Team coordinated by Kannan Ramanathan. A 2 in. x 2 in. CIGS /Mo/Glass specimen was provided by NREL for use with CVD ZnO buffer layers. The objectives of the effort were to deposit CVD ZnO buffer layers on two 1 in. x 1 in. squares and supply them to NREL for deposition of a TCO, collector grid and AR coating. Prior to growth of CVD ZnO, one of the 1x1 inch substrates was to be cleaned according to WSU procedures and the other 1x1 inch substrate was to be subjected to the so-called background solution (BS). Since we had very little experience working the NREL material, some of the NREL CIGS specimen was utilized for process development before ZnO buffer layers were deposited onto the two 1x1 inch substrates.

### 2.1.1 Utilization Of The NREL Specimen

Figure 1 describes how the NREL specimen was utilized. The structure was scribed and broken to give two 1x1 inch substrates for cell fabrication and eight 0.5 in. x 0.5 in. substrates for process development.

### 2.1.2 Process Development

Process development involved two key aspects: (1) selection of a surface preparation process prior to deposition of a ZnO buffer layer; (2) identification of a ZnO

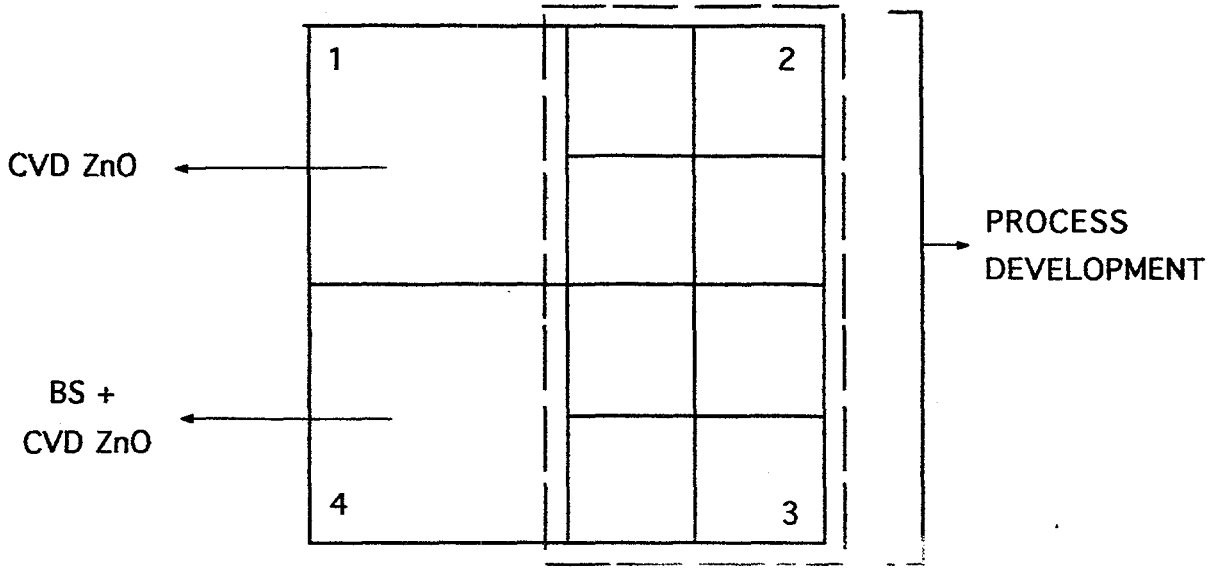


**Figure 1.** Description of how the 2 in. x 2 in., NREL CIGS specimen (when viewed from the back) was sectioned and utilized in these studies. The numbers 1,2,3 and 4 were placed on the back of the sample by NREL The NREL batch number was M1455.

growth process that results in an efficient, completed solar cell. Since most CIS research groups utilize CBD CdS buffer layers, the need for a surface preparation step may not be clear since the CBD process essentially involves chemical treatment of the CIS surface prior to CdS deposition. In addition, we have found that CIS /Mo/Glass parts or specimens which have been mailed to us need to be cleaned before processing. The CIS surface may have dust particles or even plasticizers which evolve from sample holders.

Early in our work with Siemens CIS and CIGSS material, we decided to prepare substrates by going through degreasing steps followed by an etching step with KCN. To determine a baseline surface preparation process for NREL material, two of the 0.5 x 0.5 in. substrates were subjected to the following steps:

| | |
|---|---|
| Sample 1 (Referred To 96NREL03) -- | Degreasing only |
| Sample 2 (Referred To 96NREL04) -- | Degreasing followed by KCN etch |

Transparent aluminum contacts were then deposited onto these substrates and I-V characteristics measured as illustrated in Figure 2A. Al/CIGS contact formed on 96NREL03 exhibited superior properties (See Table 1). Due to the limited amount of material, the surface cleaning process without a KCN etching step was selected as a result of these studies. The WSU procedure used for cleaning substrates and the approach for preparing the BS solution (as prescribed by NREL) are given in Table 2.

After selecting a cleaning process, efforts were devoted to determining a procedure for CVD growth of ZnO appropriate for the NREL material. After growing a ZnO buffer layer on a substrate, transparent Al contacts were then deposited onto the ZnO/CIGS structure and I-V characteristics measured (See Figure 2B). Since the ZnO buffer layers were always in the range of 400 to 600 Å thick, interaction of Al with the ZnO/CIGS interface should be negligible. Thus, Al contacts on such structures should effectively simulate a TCO layer, since the work function of Al is relatively low. Results obtained for Al/ZnO/CIGS test cells are summarized in Table 1. Growth parameters tabulated for CVD ZnO buffer layers refer to the deposition schedule defined in Figure 3.

Consider the results tabulated in Table 1. Properties are given for NREL samples 1 through 10. Substrates 3 and 4 were used for determining the preferred surface

**Table 1 -- Properties Of Al/ZnO/CIGS Test Cells**

| Samples | Run | Substrate | Zn Flow | Growth | ZnO | Test Cells * | | | |
|---|---|---|---|---|---|---|---|---|---|
| (Relatives) | | Temperature | ( sccm ) | Time | Thick | Jsc | Voc | FF | Eff |
| | | (°C) | | (sec) | (Å) | mA/cm^2 | (mV) | | (%) |
| 96NREL01 | A60412 | 250/225 | 20/30 | 100/500 | 632 | 36 | 434 | 0.533 | 8.33 |
| | HT In Eti@200 For 800 sec | | | | | | | | |
| 96NREL02 | B60412 | 225 | 30 | 500 | 446 | 36 | 437 | 0.54 | 8.5 |
| | HT In Eti@200 For 800 sec | | | | | | | | |
| 96NREL03 | - | SB Device Using Degeasing Only | | | | 36 | 336 | 0.502 | 6.07 |
| 96NREL04 | - | SB Device Using Degeasing & KCN | | | | 36 | 284 | 0.438 | 4.48 |
| | | | | | | | | | |
| 96NREL05 | A60415 | 225 | 30 | 500 | 406 | 36 | 459 | 0.546 | 9.02 |
| | | | | | | | | | |
| 96NREL06 | B60415 | 250/100 | 20/150 | 100/1000 | 635 | 36 | 567 | 0.719 | 14.7 |
| | | | | | | | | | |
| 96NREL07 | C60415 | 250/100 | 20/150 | 100/1000 | 570 | 36 | 547 | 0.726 | 14.3 |
| | | | | | | | | | |
| 96NREL8 | B60422 | 250/100 | 20/150 | 100/684 | 604 | | Test Cell NREL09: | | |
| & --9, -10 | | | | | | 36 | 523 | 0.682 | 12.8 |
| | | | | | | | | | |
| | | | | | | | | | |
| * Test Cell Illuminated I-V Measured With ELH Lamps And Jsc = 36 mA/cm^2. | | | | | | | | | |

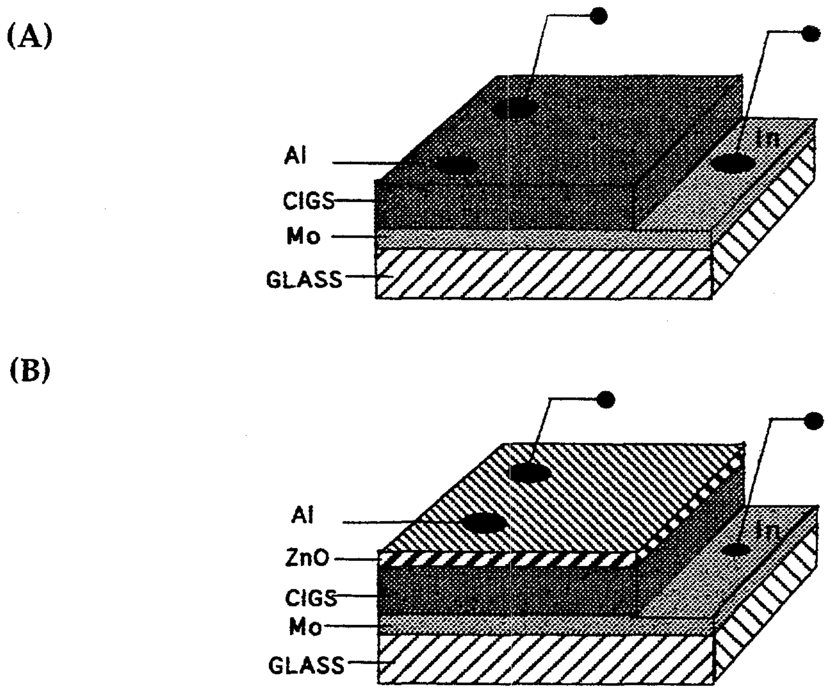


**Figure 2.** (A) Al/CIGS test cell structure used for determining surface preparation; (B) Al/ZnO/CIGS test cell structure for evaluating ZnO buffer layers.

preparation process. A KCN etching step was used on Substrates 1 and 2 before the experiment with Samples 3 and 4 had been completed. Substrates 8 and 10 were sent to NREL to be used for cell fabrication. The remaining substrates were used to determine a process for depositing ZnO buffer layers. The ZnO deposition approach used for Substrates 1, 2 and 5 are similar to procedures used successively with Siemens CIGSS substrates. The results obtained for Substrate 5 were disappointing, since better performance had been obtained with Siemens CIGSS material using the single step deposition schedule involving growth of ZnO at 225°C for 500 seconds. At this point, it was decided to use processes developed for Siemens CIS material as a guide, since that material does not have sulfur at the surface.

Prior to carrying out studies with the NREL material, we had found that a two step procedure as described by Figure 3 gave good results for the Siemens CIS material. Thus, CVD ZnO buffer layers were grown on Substrates 6 and 7 with this two step process. Test cell I-V characteristics were measured by forcing the short-circuit current to be 36 mA/cm2 . As indicated, very good values of Voc and FF were exhibited by these test cells. CVD ZnO buffer layers were then grown on Substrates 8, 9 and 10 with the

## Table 2. Surface Preparation

**WSU Process**

(1) Soak in TCA at ≈ 80°C
(2) Rinse In Acetone
(3) Rinse In Methanol
(4) Rinse In DI Water

**BS Process**

Total solution volume = 220 ml
Temperature 70°C
Composition of Bath: 0.0015 M $CdSO_4$, 27.5 ml $NH_4OH$, 192.5 ml DI water

(1) Weigh out amount of $CdSO_4$ needed to make 0.0015 in 220 ml. The molecular weight of the $CdSO_4$, you have may vary depending on the type of chemical (anhydrous or hydrated).

(2) Add the $CdSO_4$, to 192.5 ml water.

(3) Heat solution to 70°C on a hot plate. Stir. Cover beaker.

(4) Add 27.5 ml $NH_4OH$. Allow few minutes for temperature to recover to 70°C.

(5) Soak CIGS film in the solution for 4.5 minutes.

(6) Remove sample, rinse in DI water and dry in $N_2$.

(7) Process dipped sample as soon as possible.

same process. Substrate 9 was utilized for fabrication of a test cell, and Substrates 8 and 10 were sent to NREL to be used for cell fabrication. Substrate 8 was degreased prior to deposition of ZnO and Substrate 10 was subjected to the BS solution.

Although good test cell results had been obtained, one could not assume that the ZnO(CVD)/CIGS(NREL) junction would tolerate deposition of a n-ZnO TCO without degradation of performance. For example, although ZnSe/CIGSS test cells can be routinely fabricated with test cell efficiencies of approximately 14 %, these cell structures have not yet survived the Siemens TCO deposition process without significant degradation. It should be noted that NREL uses a sputtering process while Siemens ZnO TCO layers are deposited by CVD.

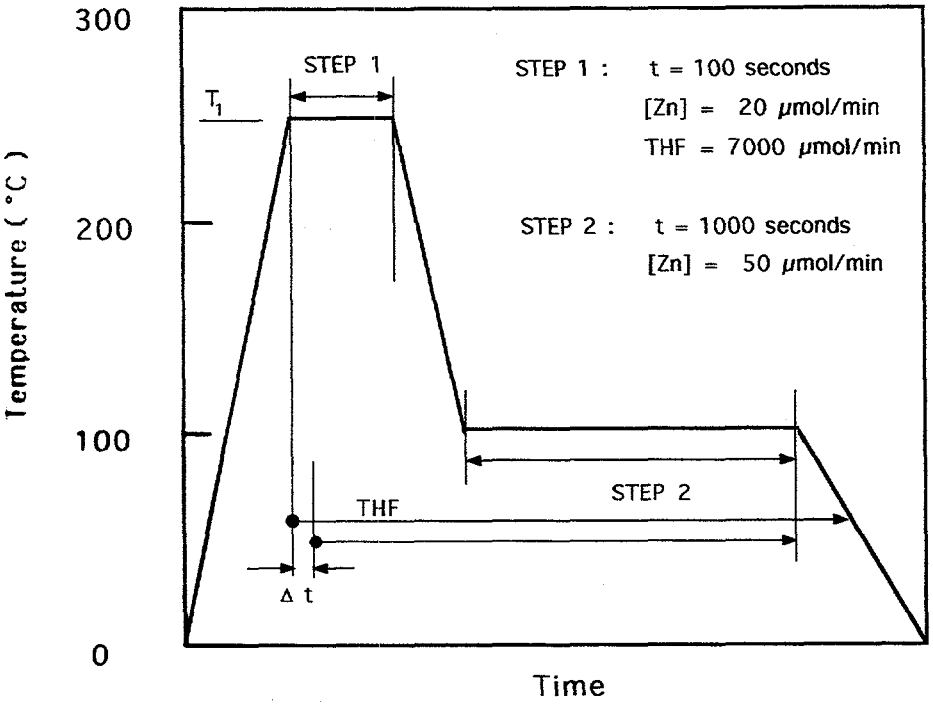


**Figure 3.** Deposition Schedule for a 2 step growth process for CVD ZnO buffer layers.

Clearly, it is desirable to understand why this particular two step process has resulted in test cells on the NREL CIGS material that exhibit good performance. Consider the two regions of the ZnO buffer layer resulting from two steps:

Step 1: ZnO is grown for 100 seconds at approximately 1 Å/sec at 250°C. The relatively high temperature required either to promote some reaction or to establish larger grains of ZnO at the interface. The ZnO layer must have a very high resistivity. If growth of ZnO continues much longer than 100 seconds at 250°C, inferior test cells result.

Step 2: 500 Å to 1000 Å of ZnO are grown at 100°C to provide protection of the first 100 Å and interface. This layer should also have a high resistivity.

The "high-resistivity" requirement is probably equivalent to requiring the ZnO buffer be stochiometric. This two step process is most likely not the optimum process for a ZnO/CIGS(NREL) structure but represents a good initial step towards that objective.

### 2.1.3 Performance Of Completed CIGS Solar Cells

After using the small samples for process development, the two-step approach was selected and utilized to grow buffer layers on the 1 in. x 1 in. substrates. One 1 in. x 1 in. substrate (NREL 1455-1, also designated as 96NREL08) was cleaned with degreasing steps and the other 1 in. x 1 in. substrate (NREL 1455-4, also designated as 96NREL10) was subjected to the so-called BS solution prior to the deposition of the ZnO buffer layer. A ZnO buffer layer was also grown on a small NREL substrate (96NREL09) in the same run. An Al/ZnO/CIGS test cell formed on 96NREL09 exhibited the following properties when Jsc was set equal to 36 $mA/cm^2$: Voc = 523 mV, FF = 0.682, and Efficiency = 12.8 %. Assuming that 36 $mA/cm^2$ represents a reasonable value for the active area current density, the 12.8 % is an estimate of the expected active area efficiency.

Substrates 96NREL08 and 96NREL10 were sent to NREL, for deposition of ZnO TCOs, collector grids and $MgF_2$ AR coatings. The efficiency of 96NREL10 which had been subjected to the BS solution exhibited an efficiency of approximately 6 %, while 96NREL08 performed with a total-area efficiency of 12.7 %. NREL measured I-V characteristics are given in Figure 4.

## 2.2 Other ZnO Buffer Layer Studies

Other ZnO studies were concerned with process optimization. Investigations of the effects of varying process parameters was conducted by growing films on Siemens CIS substrates, that is, the non-sulfur containing Siemens material. We have found that processes that are beneficial to these CIS substrates are usually appropriate for NREL CIGS. Our current baseline process is described by Figure 3. It is desirable to understand the effect of many of the process variables. For example, studies have been conducted or are planned to understand the effect of varying the following process parameters: the temperature $T_1$; the time lag between the initial flow of THF and the zinc adduct ($\Delta t$); the time for the first step ($t_1$); the Zn flow during the first step ($[Zn]_1$); the time for the second step ($t_2$); the Zn flow for the second step ($[Zn]_2$). Another important subject concerning ZnO buffer layers relates to the light-induced (LI) current losses that are observed when the ZnO buffer layer resistivity is too low. Understanding the LI effect is of general interest for CIS cells.

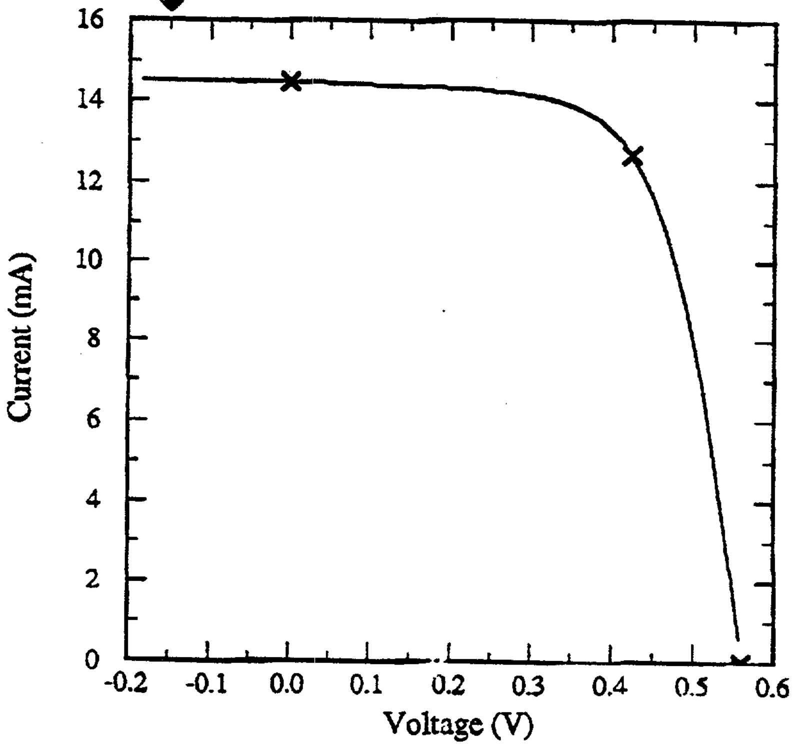
Some relevant studies concerning process parameters were conducted this past

# WSU/NREL CIGS

Sample: M1455-1#1
May 30, 1996 5:18 PM
ASTM E 892-87 Global

Temperature = 25.0°C
Area = 0.4245 cm$^2$
Irradiance: 1000.0 Wm$^{-2}$

NREL X-25 IV System



$V_{oc}$ = 0.5602 V
$I_{sc}$ = 14.46 mA
$J_{sc}$ = 34.06 mAcm$^{-2}$
Fill Factor = 66.43 %

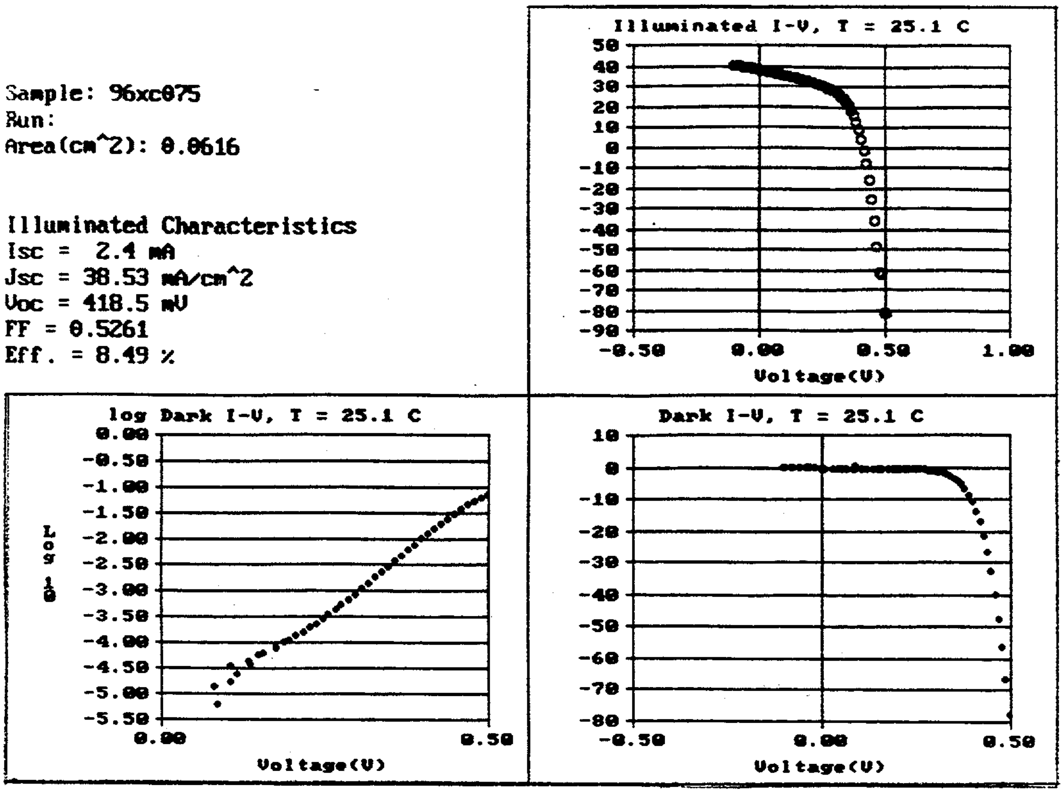
$V_{max}$ = 0.4247 V
$I_{max}$ = 12.67 mA
$P_{max}$ = 5.382 mW
Efficiency = 12.7 %

Immediately following 15 minutes near $P_{max}$ state.
Device uses ZnO instead of CdS

**Figure 4.** NREL measurement of ZnO/CIGS solar cell characteristics.

year. Some tentative conclusions are : (1) Δt can be varied between 0 and approximately 60 seconds without any problems; (2) values Δt on the order of 300 seconds definitely lead to decreased cell performance; (3) $[Zn]_1$ should be relatively low, say 20 sccm; (4) $t_1$ should not exceed 100 seconds. Longer times for Step 1 ($t_1$) probably result in interdiffusion effects at the interface. These studies are continuing.

Light-induced effects observed under certain circumstances present an interesting and important topic of study. Siemens CIS substrates were primarily utilized for process development during this past year -- as opposed to Siemens CIGSS material. Consider the dark and illuminated I-V characteristics for Test Cell 96XC075 given in Figure 5. Clearly, there are significant light-induced current losses in this device. These effects are observed if the as-deposited sheet resistance is less than $10^7$ ohms/sq. for a 1000 Å ZnO film. The sheet resistance value is approximate and refers to a value measured on a film deposited onto a glass witness. However, LI effects are not evident if the as-deposited sheet resistance is greater than $10^8$ ohms/sq.. I-V characteristics for a Test cell

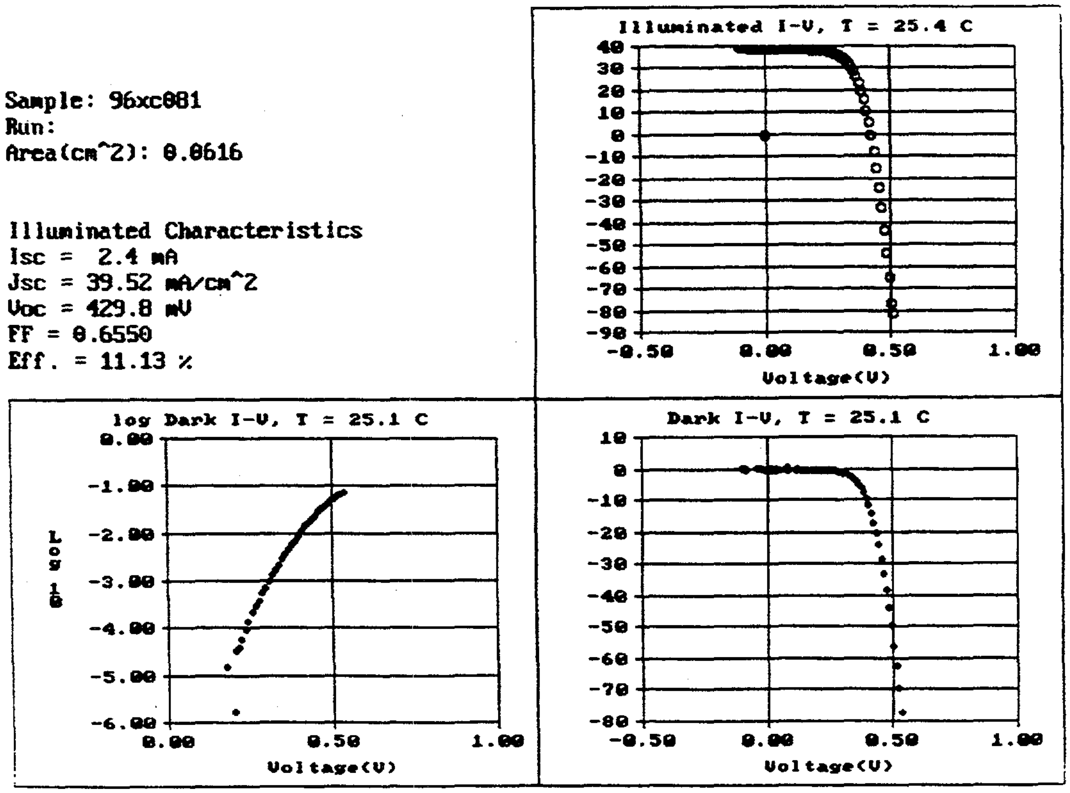

Sample: 96xc075
Run:
Area(cm^2): 0.0616

Illuminated Characteristics
Isc = 2.4 mA
Jsc = 38.53 mA/cm^2
Voc = 418.5 mV
FF = 0.5261
Eff. = 8.49 %

**Figure 5.** Dark and Illuminated I-V characteristics of Test Cell 96XC075 formed on a Siemens CIS substrate. The cell performance is greatly affected by induced current-loss mechanisms.

(96XC081) that did not exhibit LI effects are shown in Figure 6. The I-V characteristics translate extremely well. The estimated active area efficiencies for the two cases are 8.5 % and 11.1 %.

Preliminary studies indicate that if a ZnO/CIS structure such as Device 96XC075 is allowed to "age" in air for several days, the magnitude of the LI effect exhibited by test cells formed on the structure decreases. Future efforts will examine this effect. The possibility of defining a process that produces efficient cells appears very good. In particular, it may be necessary to heat structures in air (at relatively low temperatures) to accelerate the aging process.



Sample: 96xc081
Run:
Area(cm^2): 0.0616

Illuminated Characteristics
Isc = 2.4 mA
Jsc = 39.52 mA/cm^2
Voc = 429.8 mV
FF = 0.6550
Eff. = 11.13 %

Illuminated I-V, T = 25.4 C

log Dark I-V, T = 25.1 C

Dark I-V, T = 25.1 C

**Figure 6.** Dark and Illuminated I-V characteristics of Test Cell 96XC081 formed on a Siemens CIS substrate. The characteristics translate very well.

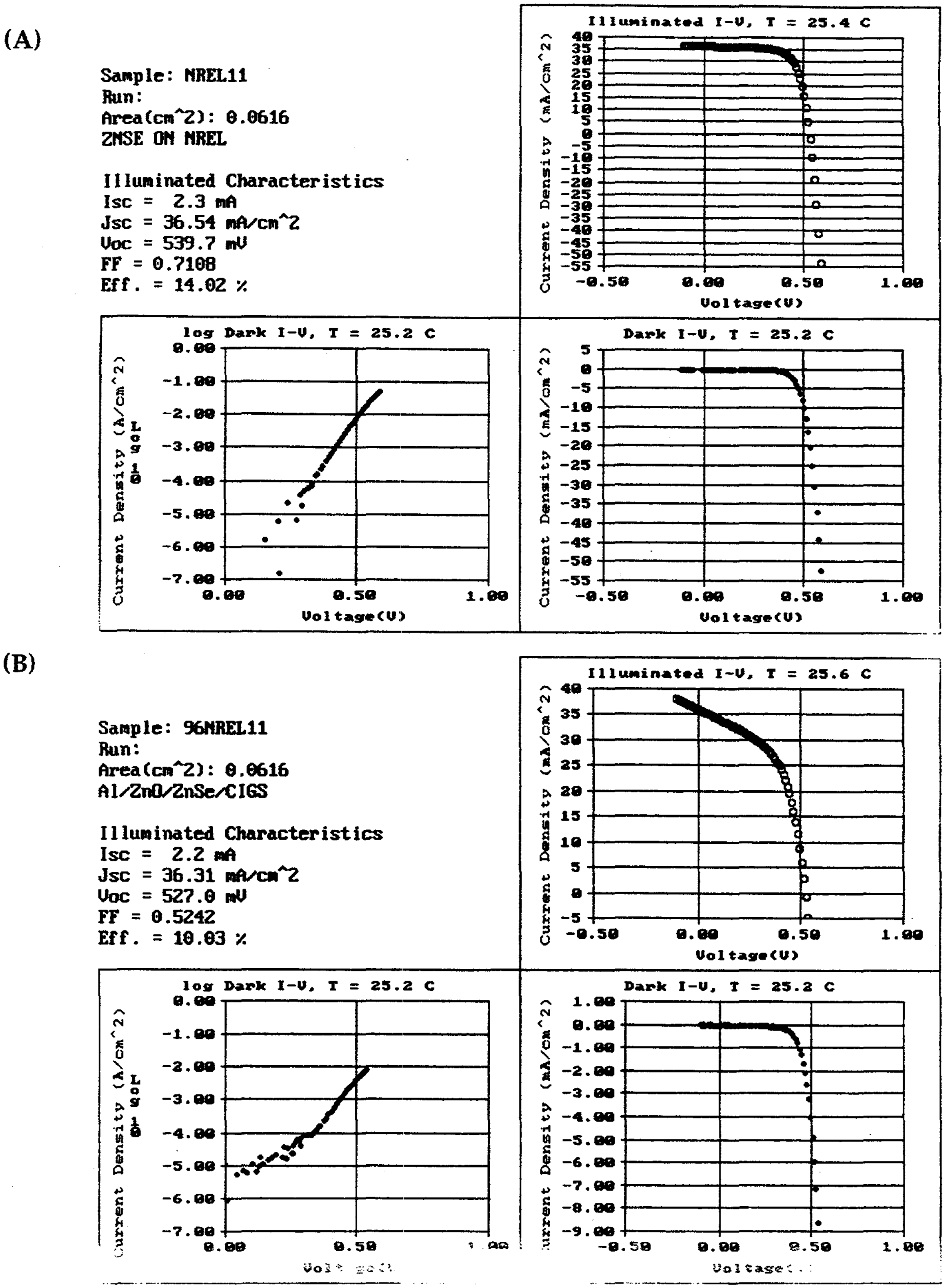
## 3. CELLS BASED ON ZnSe BUFFER LAYERS

Investigations of CIS cells based on ZnSe buffer layers continued, but at a lower level than the studies of ZnO layers. Test cells fabricated using ZnSe buffer layers exhibit exceptional properties. In particular, Test cells based on Siemens CIS and CIGSS substrates, and NREL CIGS substrates all exhibit fill factors $\geq 0.7$, and relatively large values of open circuit voltage. To date, a process for depositing a top contact layer that allows one to complete a cell with properties approaching those of test cells has not been developed. In particular, deposition of conductive ZnO TCOs by CVD at Siemens and deposition of ZnO by CVD has resulted in devices with degraded performance. A ZnSe/CIS structure sent to NREL for a sputtered ZnO TCO gave encouraging results, however. Further discussion of ZnSe studies conducted this past year follow.

### 3.1 ZnSe Buffer Layers Grown On NREL CIGS Substrates

One of the 0.5 in x 0.5 in NREL substrates (see Section 2.1.1) was utilized for testing the potential of a ZnSe buffer layer on CIGS. Figure 7A gives I-V characteristics for test cell 96NREL11 which had a 180 Å layer of ZnSe for a buffer layer. Note how well the I-V curve translates in Figure 7A. As shown, the estimated active area efficiency for this structure was 14 %. After setting Jsc = 36 mA/cm$^2$ , Voc and FF were 539.7 mV and 0.71, respectively.

Figure 7B shows I-V characteristics for a test cell formed on 96NREL11 after 1000 Å of ZnO were deposited by CVD at WSU onto the ZnSe/CIGS substrate. The original transparent Al contacts (used to acquire I-V characteristics shown in Figure 7A) were removed prior to deposition of ZnO. The CVD ZnO resulted in a light-induced effect, thus significantly reducing the fill factor and efficiency. One possible explanation of the problems experienced with ZnSe buffer layers is that growth of ZnO on top of ZnSe with a CVD process which utilizes hydrogen as a carrier gas, leads to a change in the ZnSe buffer layer. That is, the hydrogen and possibly the oxygen precursor react with the ZnSe.



(A)

Sample: NREL11
Run:
Area(cm^2): 0.0616
ZNSE ON NREL

Illuminated Characteristics
Isc = 2.3 mA
Jsc = 36.54 mA/cm^2
Voc = 539.7 mV
FF = 0.7108
Eff. = 14.02 %

(B)

Sample: 96NREL11
Run:
Area(cm^2): 0.0616
Al/ZnO/ZnSe/CIGS

Illuminated Characteristics
Isc = 2.2 mA
Jsc = 36.31 mA/cm^2
Voc = 527.0 mV
FF = 0.5242
Eff. = 10.03 %

Figure 7. (A) ZnSe/CIGS test cell I-V characteristics. (B) ZnO/ZnSe/CIGS test cell after deposition of 1000Å of ZnO at 100°C by CVD.

## 3.2 Results For Completed n-ZnO/ZnSe/CIS Solar Cells

In order to examine if a ZnSe/CIS structure could tolerate a sputtered ZnO TCO, a ZnSe/CIS(Siemens) structure was sent to NREL for deposition of a conducting ZnO top contact layer. Their deposition approach is based on RF sputtering. After the ZnO TCO was deposited by NREL. it was returned to WSU for deposition of collector grids and $MgF_2$. Illuminated characteristics measured at WSU for a <u>completed cell</u> are shown in Figure 8. Although the resulting cell performance is significantly less than the 12 to 13 % suggested by test cell studies, the completed cell exhibited improved properties over those previously obtained with other ZnO TCO deposition processes. The measurement was achieved by first setting the lamp intensity such that a cell previously characterized by NREL produced the same short circuit value as measured by NREL. In order to achieve this performance, however, the cell had to be light soaked. The light soaking was accomplished by setting the cell outside for 3 hours. The cell efficiency increased from 6.5 % to 9.5 % as a result of the light soaking.

**Siemens CIS**
**WSU ZnSe Buffer Layer**
**NREL RF Sputtered ZnO TCO**
**AREA = 0.464 sq. cm**

**Isc = 16.5 mA**
**Jsc = 36.44 mA/sq.cm**
**Fill Factor = 62.15 %**
**Voc = 0.420 Volts**
**Efficiency = 9.51 %**

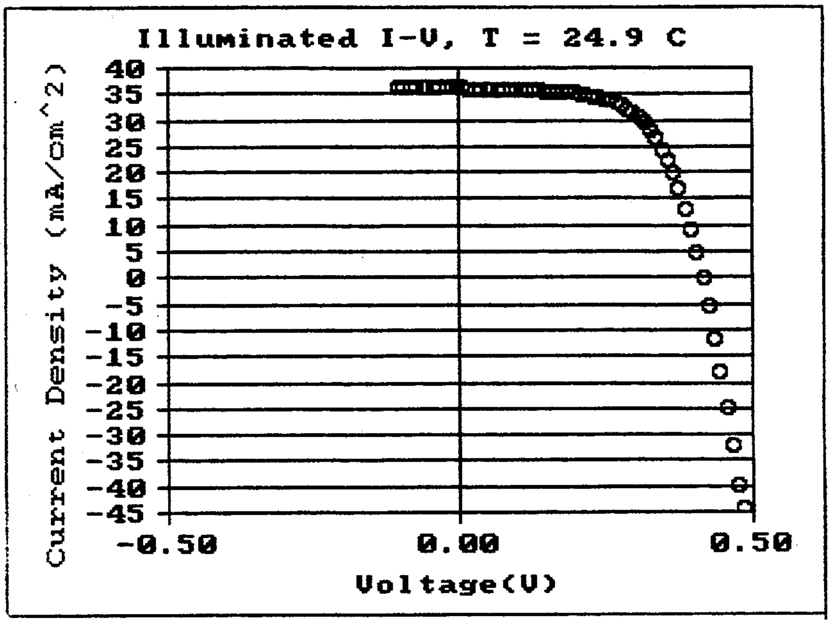


Figure 8. Illuminated I-V characteristics measured by WSU for a <u>completed</u> ZnSe/CIS solar cell.

## 4. InSe BUFFER LAYER STUDIES

Studies of $In_xSe_y$ (InSe) buffer layers were also initiated this past year. InSe films were grown by reacting $H_2Se$ and ethyldimethylindium with substrate temperatures in the range of 300 to 400 °C. It appears that no film growth occurs at 250 °C, whereas growth does definitely occur in the 300°C to 450°C range. Test cell studies have shown promise. Raman spectroscopic analyses indicate that the crystallinity of the films improves as $T_{sub}$ is increased from 300°C to 400°C. Raman studies also suggest that the amount of the $\gamma$-$In_2Se_3$ phase increases with $T_{sub}$. This phase has a bandgap of approximately 2.0 eV. Since the films must be deposited at relatively high temperatures, the desirability of further studies of these buffer layers is questionable. However, since deposition of InSe may be compatible with processes used for growth of CIS, additional studies may be considered.

# 5. PHYSICAL CHARACTERIZATION WITH SPECTROSCOPIC ELLIPSOMETRY

Ellipsometric studies were initiated that involved collaboration with the Pacific Northwest Laboratories in an effort to determine if spectroscopic measurements could be useful for characterizing buffer layers. One study conducted involved characterization of CIS surfaces under two conditions: (1) after cleaning with the WSU procedure described in Table 2; (2) after first cleaning with the WSU process followed by etching with a polishing etchant (KBr,Br) to remove approximately 500 Å of the surface. The substrates treated in this manner are referred to as Type A (Process 1) and Type B (Process 2).

Figures 9A and 9B show plots of the pseudoindex of refraction and pseudoextinction coefficient vs wavelength determined for Type A and Type B CIS substrates (Siemens). There is a clear difference between the two surfaces. These results are in general agreement with the work reported at the May PV conference by Abulfotah, et al.[4]. Figure 5C depicts the model utilized to fit the optical constants for the Type A substrate. In addition to allowing acquisition of continuous wavelength data, the computer software available with the PNL spectrometer is the best currently available. There are many possible models that will allow the fitting of ellipsometric data. Thus, it is imperative that one incorporate as much information as possible in the proposed model. In this particular case, information from photoluminescence data for the ODC layer was utilized. In particular, it was assumed that two interband transitions occur for the surface phase at 1.15 and 1.26 eV. An excellent fit to the data for the Type A material was achieved by assuming that it consisted of a surface layer with the 1.15 and 1.26 eV transitions and that the optical constants of the region below the surface layer were given by the experimental values determined for the Type B substrate. As shown in Figure 9C the surface layer was determined to have a thickness of 250 Å.

These studies will continue by characterizing structures involving buffer layers grown on Type A and Type B substrates. One goal of this effort is to understand in more detail the role of the ODC layer. These investigations will be supplemented by XPS, grazing angle XRD and other measurements NREL.

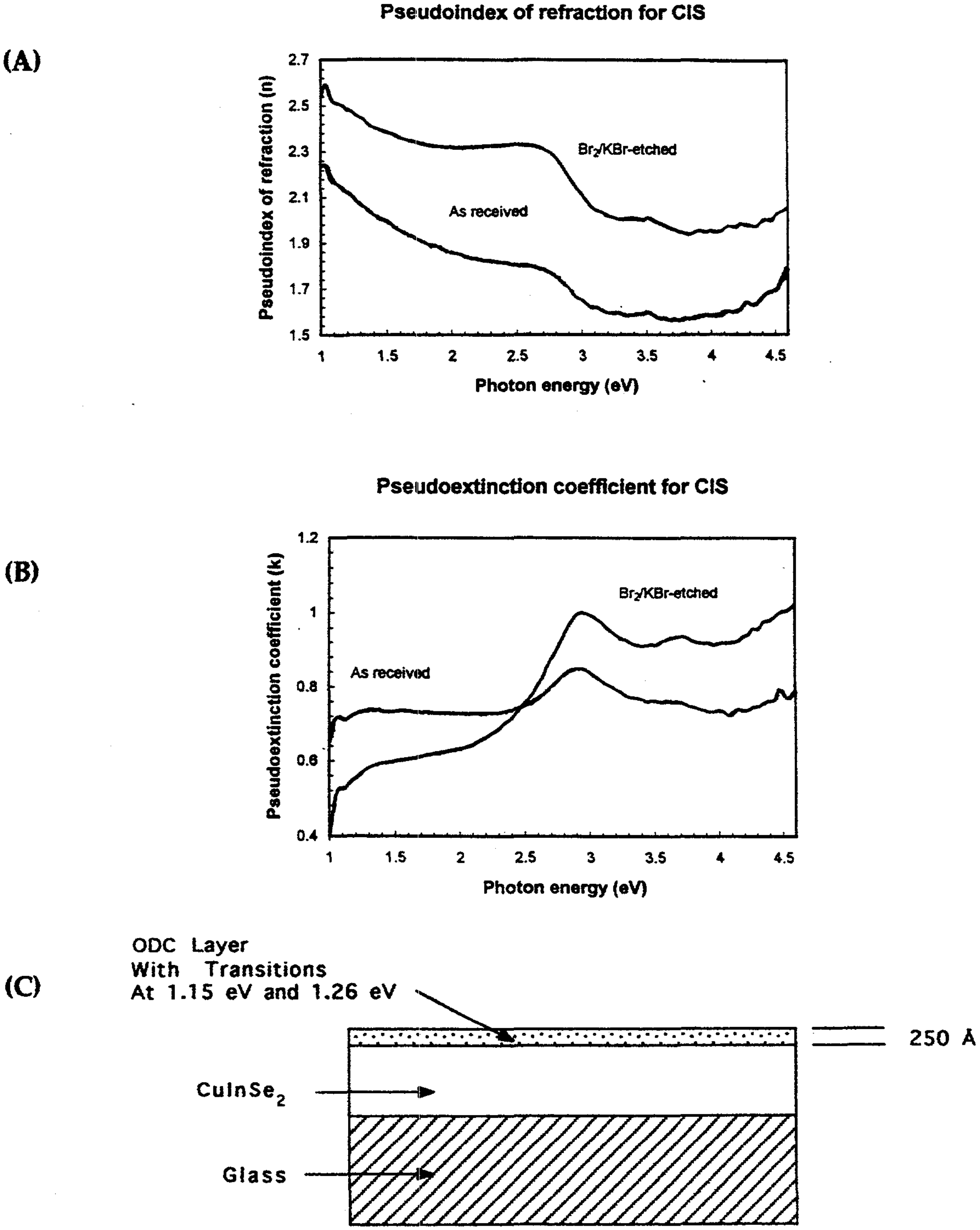


Figure 9. Results of Ellipsometric studies of Siemens CIS substrates.

(A) Pseudoindex of Refraction vs hv for as-received CIS substrates and CIS substrates with 500 Å removed with a KBr,$Br_2$ etch;

(B) Pseudoextinction Coefficient vs hv for the two types of substrates;

(C) Model utilized to fit data for as received Siemens substrates.

## 6. MODELING STUDIES

Simulation studies using PC-1D indicate that a resistive buffer layer combined with a CIS substrate should yield a higher efficiency compared to a structure with a low resistivity buffer layer -- or with the TCO in direct contact with CIS. This prediction is in general agreement with experimental results. In particular, one predicts that a ZnO/CIS cell with the ZnO layer having a resistivity of 0.01 ohm-cm should produce power with an efficiency of 8 % , whereas 11 % should be obtained with a ZnO buffer layer characterized by a resistivity of $10^4$ ohm-cm. These calculations assume the excess carrier lifetime is 40 psec within the CIS material. Experimentally. one finds cell efficiencies are typically 4 % when a conductive ZnO is in direct contact with CIS. Additional studies were carried out in an effort to understand the cause of this discrepancy.

Modeling calculations were conducted to examine the effects of interface recombination velocity and excess carrier lifetime. Figures 10 and 11 describe results of these studies. The solid lines describe results of simulations and the data points refer to experimental results for test cells made with ZnO buffer layers having a range of as-deposited resistivities. Figure 10 clearly indicates that we can not explain experimental results by simply assuming the deposition of low resistivity ZnO onto CIS leads to a high value for the interface recombination velocity. Referring to Figure 11, we conclude that one possible explanation of the low efficiencies for low buffer layer resistivities is that the deposition process results in reduced values of excess carrier lifetimes -- that is, increased densities of recombination centers. In our case, the low resistivity ZnO is grown by using a relatively high flow of Zn when growing ZnO. Thus, the presence of excess zinc may result in an increased density of recombination sites. Deposition of low resistivity ZnO usually involves the incorporation of dopants, which may also provide recombination sites. In conclusion, we postulate that a possible explanation of the apparent requirement for a high resistivity buffer layer for CIS-based cells is that deposition of low resistivity films directly on CIS and related alloys leads to enhanced recombination within the CIS material.

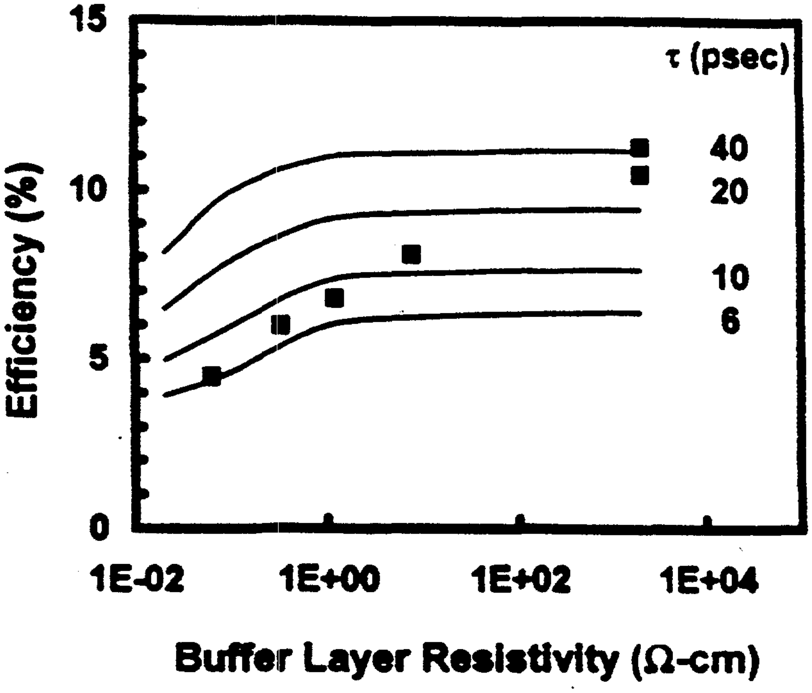


Figure 10. Calculated efficiency vs ZnO buffer layer resistivity for a CIS cell with varied values of surface recombination velocity and a ZnO buffer layer thickness of 300 Å. The data points are experimental results for test cells with CVD ZnO buffer layers.

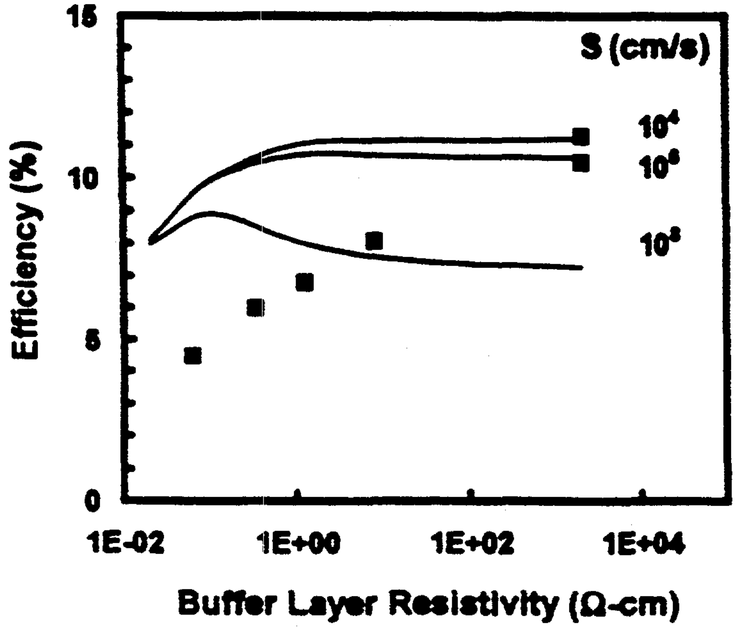


Figure 11. Calculated efficiency vs ZnO buffer layer resistivity for a CIS cell with varied values of excess carrier lifetime and a ZnO buffer layer thickness of 300 Å and S=1E4 cm/s. The data points are experimental results for test cells with CVD ZnO buffer layers.

## 7. KEY RESULTS AND FUTURE WORK

Investigations of alternative buffer layers emphasized studies of ZnO grown by MOCVD. CIS substrates obtained from Siemens were used for process development. It was determined that growth procedures that resulted in good results with Siemens CIS (non-sulfur containing material) substrates also worked well with NREL CIGS material. A two step process was developed for growing highly resistive ZnO buffer layers (i-ZnO). In particular, after growing 100 to 150 Å of ZnO at 250°C, an additional 600 Å to 800 Å were grown at 100 Å. Collaboration with NREL resulted in a n-ZnO/i-ZnO/CIGS cell which was determined to have a total area efficiency of 12.7 %, and an active area efficiency greater than 13 %. After growing i-ZnO with the two-step process onto NREL CIGS material, the i-ZnO/CIGS film structure was sent to NREL for deposition of a TCO, namely, conducting ZnO (n-ZnO). Collector grids and a $MgF_2$ AR coating was also deposited at NREL.

Low level efforts were devoted to studies of ZnSe and InSe buffer layers. ZnSe growth procedures had been developed in a previous program. Although very good properties had been achieved with Al/ZnSe/CIS test cells, an approach to grow a TCO on top of the ZnSe buffer layer had not been achieved. Previous attempts at depositing a conductive ZnO layer onto a ZnSe/CIS structure were done using a CVD process with a hydrogen carrier gas. An encouraging result was achieved this past year when NREL deposited a ZnO TCO by RF sputtering onto a ZnSe/CIS device. After completing the cell at WSU, and after a period of light soaking, a total area efficiency of 9.5 % was achieved. Further improvements are expected with ZnSe buffer layers. Investigation of $In_xSe_y$ (InSe) buffer layers was initiated this past year. InSe films were grown by reacting $H_2Se$ and ethyldimethylindium with substrate temperatures in the range of 300 to 400 °C. Test cells showed promise suggesting further work is warranted if time permits.

Spectroscopic ellipsometry was utilized to investigate the surface layer of CIS substrates and ZnO buffer layers. Measurements on as-received Siemen substrates and samples with 500 Å removed indicated that a surface layer approximately 250 Å thick and characterized by interband transitions of 1.15 eV and 1.26 eVexists on the Siemens substrate surfaces. Optical properties of ZnO buffer layers are also being investigated with ellipsometry.

Finally, further modeling studies were carried out using PC-1D. Simulation of

CIS cells suggest that low efficiencies observed for devices fabricated with low resistivity ZnO buffer layers may be a result of recombination centers being introduced into the depletion region as a result of the ZnO deposition process.

Future work will emphasize further development of i-ZnO buffer layers grown by CVD. These investigations will continue to utilize Siemens CIS and CIGSS material as well as NREL CIGS material. As time permits, ZnSe buffer layers will be further developed.

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13. ABSTRACT *(Maximum 200 words)*

The objectives of this program are to develop alternate heterojunction partner layers (buffer layers) for high-efficiency CuInSe$_2$-based thin-film solar cells, and improve the understanding of how these layers and the details of processing affect cell performance. Investigations have primarily involved three tasks: (1) metal-organic chemical vapor deposition (MOCVD) growth of noncadmium-containing buffer layers, (2) optimized processing of buffer layers for high-efficiency solar cells, and (3) electrical and physical characterization of layers and devices. Investigations of alternate buffer layers emphasized studies of ZnO grown by MOCVD. Using CIS substrates obtained from Siemens for process development, researchers determined that growth procedures yielding good results with Siemens CIS (nonsulfur-containing material) substrates also worked well with NREL CIGS material. A two-step process was developed for growing highly resistive ZnO buffer layers (i-ZnO). In particular, after growing 100 Å to 150 Å of ZnO at 250°C, an additional 600 Å to 800 Å were grown at 100°C. Collaboration with NREL resulted in a n-ZnO/i-ZnO/CIGS cell with a total-area efficiency of 12.7%, and an active-area efficiency greater than 13%. After growing i-ZnO with the two-step process on NREL CIGS material, the i-ZnO/CIGS film structure was sent to NREL for deposition of a transparent conducting oxide (TCO), namely, conducting ZnO (n-ZnO). Collector grids and a MgF$_2$ antireflective coating were also deposited at NREL. Low-level efforts were devoted to studies of ZnSe and InSe buffer layers. A total-area efficiency of 9.5% was achieved for a completed ZnSe/CIS cell making use of a RF-sputtered ZnO for a TCO. Investigations of In$_x$Se$_y$ (InSe) buffer layers also began this past year. InSe films were grown by reacting H$_2$Se and ethyldimethylindium with substrate temperatures in the range of 300° to 400°C. Test cells showed promise, suggesting further work is warranted if time permits. Spectroscopic ellipsometry was used to investigate the surface layer of CIS substrates and ZnO buffer layers. Measurements and analyses indicated that a surface layer about 250 Å thick and characterized by interband transitions of 1.15 eV and 1.26 eV exists on Siemens surfaces. Finally, simulation studies carried out for ZnO/CIS cells with PC-1D indicate that the low efficiencies experienced for structures with low-resistivity ZnO buffer layers may be a result of enhanced depletion-region recombination caused by the ZnO deposition process.

14. SUBJECT TERMS

photovoltaics ; CuInSe$_2$-based solar cells ; CIS ; buffer layers

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