Subcontractor Report

Alternative Heterojunction Partners for CIS-Based Solar Cells

Annual Subcontract Report
29 December 1997 — 28 December 1998

L.C. Olsen
Washington State University at Tri-Cities
Richland, Washington

NREL

National Renewable Energy Laboratory

February 2000   •   NREL/SR-520-27930

Alternative Heterojunction Partners for CIS-Based Solar Cells

Annual Subcontract Report
29 December 1997 — 28 December 1998

L.C. Olsen
Washington State University at Tri-Cities
Richland, Washington

NREL Technical Monitor: B. von Roedern

NREL

National Renewable Energy Laboratory

Available electronically at http://www.doe.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: 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

TABLE OF CONTENTS

ABSTRACT

The focus of the Phase I effort concerned further development of ZnO buffer layers. This work included further optimization of the MOCVD growth process and investigations of the interaction of zinc and oxygen with the absorber layers. Whereas much of our work had been carried out with Siemens CIS material prior to this reporting period, a process for growing ZnO buffer layers on Siemens CIGSS absorber had not been developed. It was determined that a two-step procedure involving raising the substrate temperature to 250°C in nitrogen and then growing the buffer layer at 100°C works well with CIGSS material. Through collaboration with IEC, completed cells with efficiencies in the 11 % to 12 % range were fabricated with the following structure: RF n-ZnO/i-ZnO/CIGSS. Cells with this structure were included as part of the Transient team studies. Cells were subjected to dark storage at 80°C followed by a light soak at 40°C at IEC. Illuminated I-V curves taken at each stage of the study determined that these cells do not degrade under dark storage conditions, which had been observed for Siemens cells with CdS buffer layers. In an effort to understand the reaction of zinc and oxygen with the absorber layers, SIMS depth concentration profiles were obtained for i-ZnO/CIS structures through collaboration with Angus Rockett at the University of Illinois. SIMS profiles were obtained for ZnO films grown on polycrystalline CIS and epitaxial CIS films grown on GaAs. Comparison of the profiles strongly suggests that zinc and oxygen diffuse into the CIS along grain boundaries during the MOCVD growth process. It is also proposed that excess zinc along grain boundaries may result in the grain boundaries being n-type, which can result in enhanced loss currents. This model is consistent with the apparent requirement that cell structures with MOCVD buffer layers must undergo an aging process in air before efficient cells can be obtained. Future studies will investigate processes that allow the aging step to be eliminated.

1.   INTRODUCTION

This report concerns work carried out during the time period 12/29/97 through 12/28/98 to investigate alternative heterojunction partner layers (buffer layers) for high efficiency CIS-based thin film solar cells. In particular, ZnO, ZnSe and ZnS are being examined as alternatives (to CdS) buffer layers for CIS cells. Background information, program objectives and the technical approach are discussed in the remainder of this section, and technical progress made during the program is discussed in subsequent sections.

1.1   Background

Prior to this program WSU investigated resistive ZnO layers as an alternative buffer layers to CdS in CIS and CIS-alloy solar cells. The general approach to these studies consisted of utilizing substrates provided by industry and NREL for cell fabrication with ZnO buffer layers. Specifically, Siemens CIS and CIGSS substrates and NREL CIGS substrates were used for the work. ZnO films were grown by MOCVD with the WSU reactor. CVD ZnO films are grown by reacting a zinc adduct with tetrahydrofuran. Completed cells were fabricated with efficiencies in the 12 to 14 % range. Limited studies were also devoted to investigating ZnSe buffer layers. The focus of the current program is to investigate ZnO, ZnSe and ZnS as alternative heterojunction partners in CIS-based cells. Efforts this first year have continued to concentrate on ZnO buffer layers.

1.2   Program Objectives

The objectives of this program are: to develop alternate heterojunction partner layers for high efficiency $CuInSe_2$-based thin film solar cells; and, to improve the understanding regarding the effects of these buffer layers and related processing upon cell performance.

1.3 Technical Approach

The general approach to these studies has consisted of utilizing substrates provided by industry and NREL, so that efforts could focus on buffer layer investigations. MOCVD growth of buffer layers is accomplished with a SPIRE 500XT reactor with added gas handling capabilities. Optimum processing parameters for candidate buffer layers are determined by characterizing Al/X/CIS test cell structures, where X refers to a heterojunction partner. Semitransparent Al films with thicknesses in the range of 100 to 150 Å are utilized so that illuminated I-V characteristics can be obtained for the test structure. After the buffer-layer growth parameters are determined, completed solar cell structures are fabricated and evaluated. Layers and devices are characterized at WSU and with the help of collaboration with NREL. Efforts this past year concentrated on studies of highly resistive ZnO buffer layers grown by MOCVD.

Substrates provided by Siemens and NREL consist of a CIS-based absorber layer grown on Mo-coated glass. Two Siemens substrates have been utilized. The Siemens absorber referred to as CIS is of the form $Cu(In,Ga)Se_2$ with the Ga concentrated at the back of the absorber structure [1]. The other Siemens substrate referred to as CIGSS (also graded absorber) has sulfur incorporated in the surface region such that the surface concentration is approximately CuInSeS [1]. The NREL absorber layers were grown with a 3-stage process and are referred to as CIGS [2]. TCO deposition, contact formation and cell testing were carried out by NREL and IEC. A sputtering system acquired near the end of this first year will allow deposition of n-ZnO TCO layers, and thus fabrication of complete cells at WSU in future work.

2. PROCESS DEVELOPMENT

2.1 Characterization Of The Two-Step Process

The baseline two-step process that has been utilized successively for MOCVD growth of ZnO buffer layers is described in Figure 1. Substrates are heated to 250°C in hydrogen where approximately 100Å of ZnO is grown, followed by further growth at 100°C. Since hydrogen is used as a carrier gas, hydrogen is flowing throughout the run. One objective of the current effort is to determine possible processing pathways that result in efficient cells with ZnO buffer layers. Three key points have been addressed: (1) the run temperature profile; (2) whether or not growth must occur at 250°C; (3) the role of hydrogen.
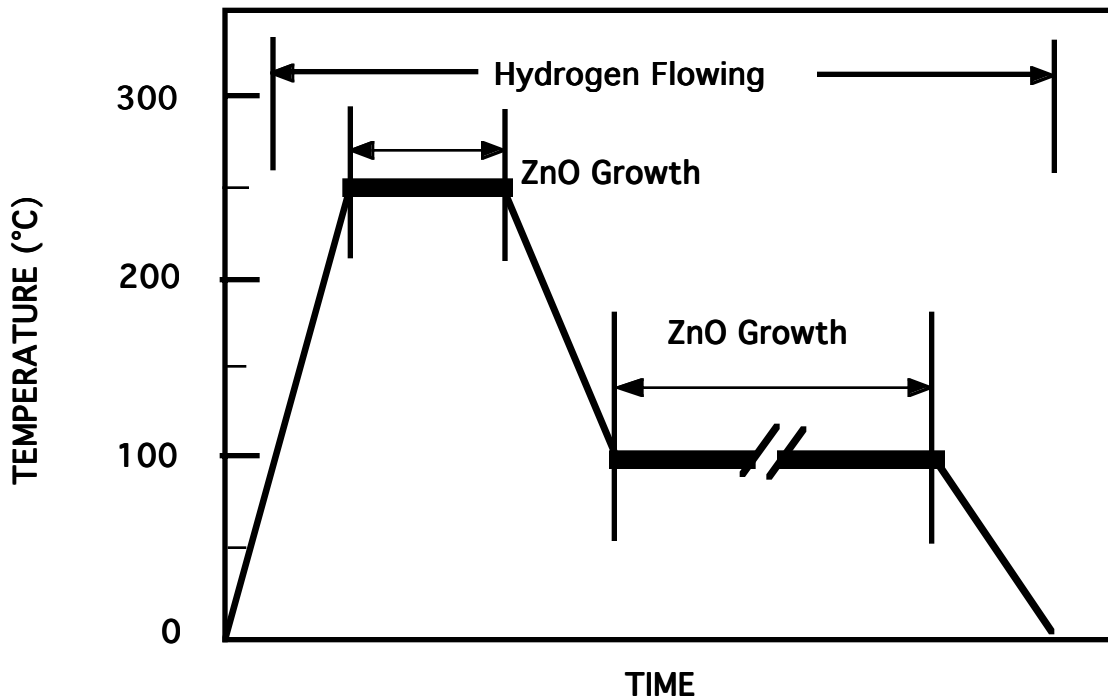
Figure 1. Baseline, two-step process used for growing ZnO buffer layers by MOCVD.

Three growth procedures used to address these questions are described in Figure 2. Test cells were fabricated with Siemens CIS material with the ZnO buffer layers grown by these three processes. Representative current voltage curves are shown in Figure 3. Results for the baseline process and a modified process are essentially the same, whereas devices made with buffer layers grown with a single step procedure always exhibit very poor performance. Structures with i-ZnO buffer layers were also sent to IEC for deposition of n-ZnO TCOs and collector grids. Results for two completed cells are given in Table 1 for cells with
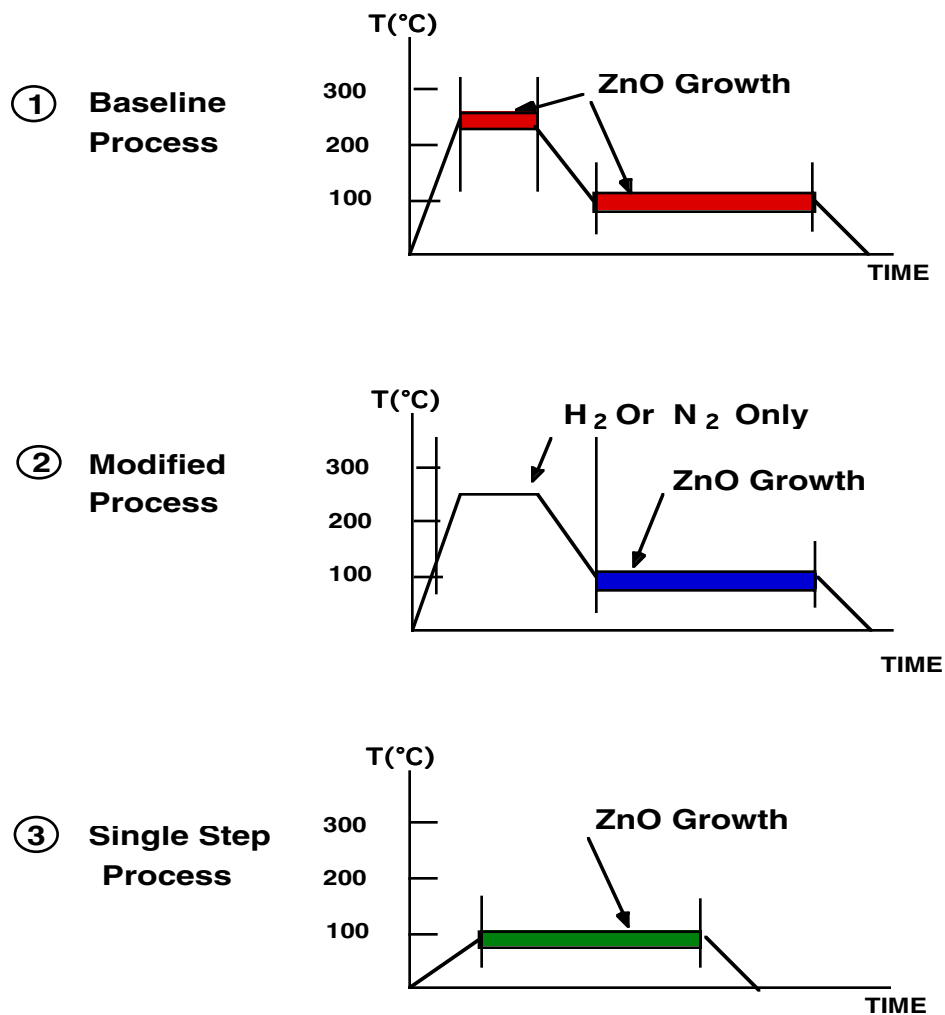
Figure 2. Three growth processes: (1) Baseline two-step; (2) Modified with hydrogen or nitrogen during heat-up; (3) Single step.
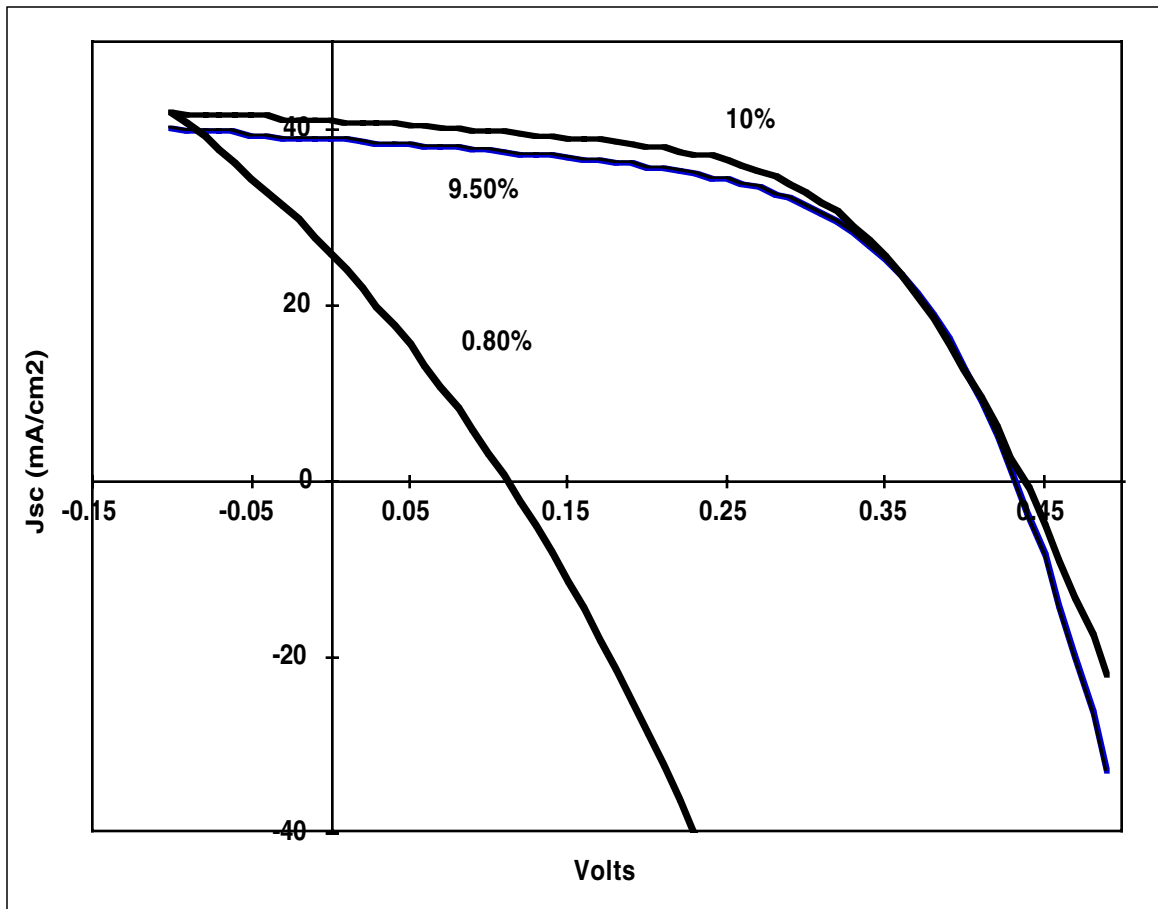
Figure 3. Current-voltage characteristics of test cells with ZnO buffer layers grown with processes described in Figure 2: Baseline (10 %); Modified with hydrogen (9.5 %); Single step (0.8 %).

Table 1. Completed Cell Performance Comparing Baseline And Modified/Nitrogen Processes

Cell	Process	J_{sc} (mA/cm^2)	V_{oc} (Volts)	FF	Eff (%)
98XC008	Baseline	30.6	.480	66.3	9.72
98XC010	Modified With N_2	34.6	.462	62.9	10.1

5

buffer layers grown with a baseline procedure and modified approach using nitrogen. The current densities and cell efficiencies are total area values.

Several conclusions can be made from these studies. First, growth of a buffer layer at 100°C without first heating the substrate to 250°C leads to poor cell performance. Secondly, it does not appear necessary to grow a nucleation layer at 250°C. Finally, it is not necessary to flow hydrogen during the high temperature step. Based on these conclusions, it appears that the main effect of the 250°C step is to thermally clean or modify the substrate surface. The I-V characteristics of test cells made with ZnO buffer layers grown with a single step process (see Figure 3) have suppressed short-circuit current densities, low values of FF and open circuit voltage. Thus it appears that without the thermal cleaning, a blocking interface layer exists between CIS and the ZnO buffer layer. It should be noted that the substrates had been cleaned prior to insertion into the reactor. However, exposure of CIS substrates to air occurs before the insertion step. Apparently, there is a need to remove carbon or other contaminants with the thermal step. Cell fabrication with CdS buffer layers deposited by CBD may not need such a cleaning step since any contaminant acquired from air is probably removed in the CBD procedure.

2.2   Process For CIGSS Substrates

Prior to this years effort most of our ZnO buffer layer development has been conducted with Siemens CIS material. Since Siemens discontinued growing the CIS material, and because higher efficiencies are possible with CIGSS absorbers, an increased emphasis was placed on the use of the graded absorber material. This material has sulfur incorporated in the surface region such that the surface concentration is approximately CuInSeS. Initial studies that led to the two-step process determined that the growth procedure was not compatible with the CIGSS material. Thus, the development of a process for ZnO buffer layer growth on the CIGSS absorbers was necessary. Using test cell structures for process development, it was determined that the modified procedure with nitrogen yielded good results. With this process, only nitrogen gas flows as the temperature is raised to 250°C and is then reduced to 100°C. Once ZnO growth is initiated, hydrogen is flowing in the system since it is used as the carrier gas. Using the modified process with nitrogen,

test cells were fabricated with CIGSS that were characterized by efficiencies of 11 to 12 %, and open circuit voltages on the order of 490 mV.

After developing a process for growing ZnO buffer layers on the CIGSS substrates, several completed cells were fabricated. After growing buffer layers, i-ZnO/CIGSS structures were sent to IEC where n-ZnO TCOs and collector grids were deposited. Current-voltage characteristics of one of the cells are given in Figure 4. Although this is a reasonable result, further optimization of the ZnO buffer layer growth process and subsequent cell fabrication steps should result in improved cell performance.
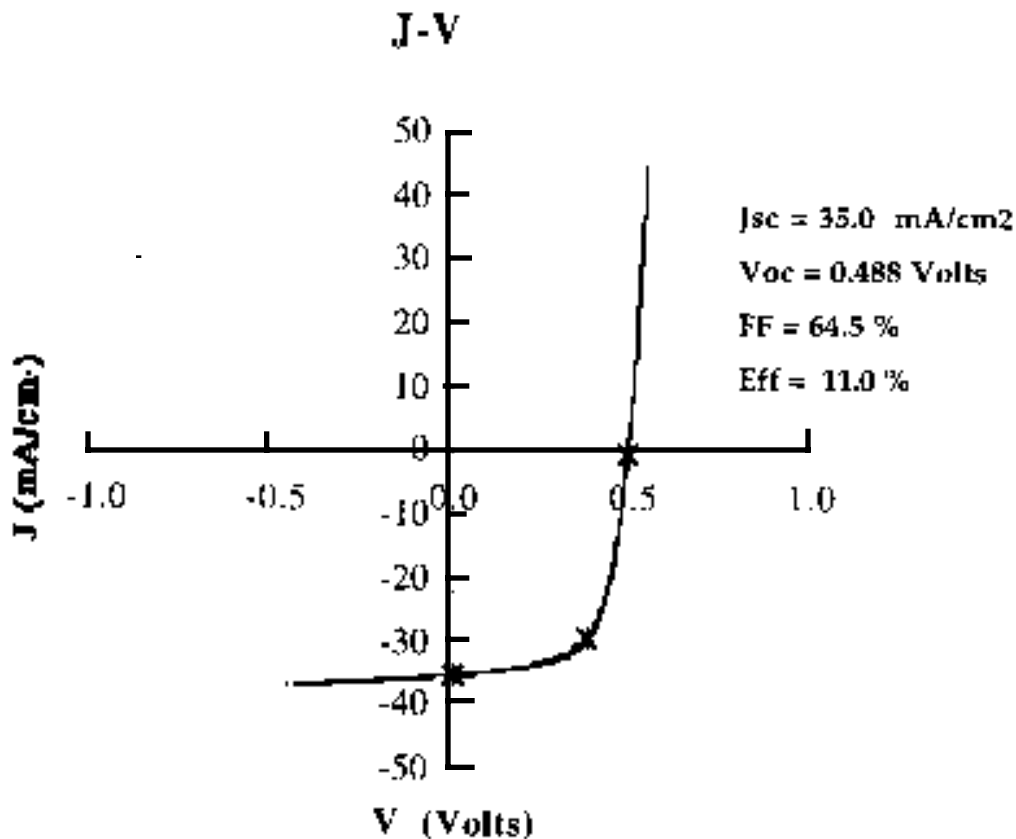
Figure 4. Illuminated I-V Characteristics for completed CIGSS cell with i-ZnO buffer layer.

2.3   Modification of MOCVD System

We have used a palladium purifier for purifying hydrogen gas in the WSU MOCVD system. During the last quarter of this past year a power outage caused damage to the purifier.   Due to the cost of repairing the unit, we decided to purchase a different type of purifier that would allow the use of nitrogen as well as hydrogen, and would not be vulnerable to power outages.   This approach will allow us to utilize nitrogen as a carrier gas.   This change was partly motivated by the results of our process development activities which indicated that hydrogen was not necessary in the growth of effective ZnO buffer layers.   Modification of the MOCVD system will be completed early in the 2nd phase of this program.

3.   TRANSIENT EFFECTS

3.1   Transient Team Activities

   As part of the Transient team activity within the National CIS R&D Team activities, WSU planned and assisted in implementing a study of Siemens cells with and without CdS buffer layers.   The study included two subtasks, which are described below and by Figure 5.

(1) Planned Study With Siemens Samples

   - Siemens Supplied Two Kinds Of 10 cm x 10 cm Parts:
     Type A: n-ZnO / CIGSS   Type B: n-ZnO / CdS / CIGSS

   - WSU Diced Into 2 cm x 2 cm Substrates And Sent 6 Each
      Of Type A and Type B Substrates To IEC For
      Collector Grid Deposition (Three 0.5 cm^2 Cells / Substrate)

   - IEC Characterized Cells And Then Carried Out Light Soak
       And Dark Storage Tests, And Sent Several Substrates
       To CSU For Testing

   - WSU Also Sent One Each Of Type A and Type B Substrate To
       Angus Rockett, Univ. Illinois, For SIMS Depth Concentration Profiles

(2) i-ZnO Buffer Layers Were Deposited Onto CIGSS Substrates By WSU For
      Characterization

   - i-ZnO / CIGSS 2 cm x 2 cm Substrates Sent
      To IEC For Sputtered n-ZnO TCO And Collector Grids

   - IEC Carried Out Light Soaking And Dark Storage Tests And
      Supplied Cells To CSU

   Results reported by IEC for the most efficient cells of each type, namely, Type A, Type B and cells with a WSU i-ZnO buffer layer are given in Table 2.   Dark storage refers to 16 hours @ 85°C under dark and open circuit conditions, and Light Soak refers to 16 hours at 40°C under illuminated and open circuit conditions. The SSI cells with CdS (Type B) and without CdS (Type A) behaved similarly to encapsulated cells that IEC and CSU tested earlier as part of the Transient Team

studies.   In particular, FF, V_{oc} and efficiency all decreased under dark storage, and then increased as a result of light soaking.

The cell with a WSU buffer layer exhibited different characteristics, however. The open circuit voltage and efficiency improved slightly under dark storage conditions, and improved further under light soaking.   It is particularly significant that the fill factor and open circuit voltage values did not decrease during dark storage.   Further dark and light stress studies of cells with WSU buffer layers will be carried out during Phase II of this program as part of the Transient Team effort.

Table 2. Transient Results for Best Cells

Cell And Condition	Eff (%)	FF (%)	V_{oc} (Volts)
SSI ZnO/CdS/CIGSS			
Initial	12.65	70.2	0.506
Dark Storage	10.99	63.8	0.485
Light Soak	11.66	67.0	0.494
SSI ZnO/CIGSS			
Initial	10.65	64.1	0.484
Dark Storage	9.82	60.4	0.477
Light Soak	10.97	65.0	0.494
RF ZnO/i-ZnO/CIGSS			
Initial	11.33	65.3	0.492
Dark Storage	11.44	65.2	0.496
Light Soak	11.87	66.5	0.507

3.2   Stability Of Cells With i-ZnO Buffer Layers

Much more data are needed before the stability or lack thereof of CIS cells with i-ZnO buffer layers can be understood.   However, two encouraging results have been attained during this last year. First, the results given in Table 2 for the cell with a WSU buffer layer indicate that it is possible to fabricate a cell with a CVD ZnO buffer layer that is quite stable.   Note that the TCO was deposited by IEC using RF magnetron sputtering.

Test results for a cell based on SSI CIS also exhibited very stable behavior. Several i-ZnO/CIS structures were sent to IEC in April, 1997 for deposition of n-ZnO and collector grids.   Efficiencies of these cells were in the 11 to 12 % range.   One of the cells was tested at WSU every few months to establish lifetime data.   After approximately one year, illuminated data was acquired with approximate AM1 conditions.   Results are summarized in Table 3.   As indicated, the CIS cell properties were essentially unchanged after one year being stored in the laboratory. Results for the CIGSS cell (Table 2) and the CIS cell (Table 3) are very encouraging, and suggest that processing approaches can be defined that will lead to stable cells based on ZnO buffer layers.

Table 3.   Performance Of Cell 97XC019

Measurement	Date	J_{sc} (mA/cm^2)	Eff (%)	FF (%)	V_{oc} (Volts)
IEC AM1 @ 30°C)	4/97	40.7	12.0	66.9	0.439
WSU Est AM1	4/9/98	39.6	11.7	64.5	0.460
WSU After Dark Storage 24 Hrs	4/10/98	39.9	11.6	63.7	0.458
WSU After 6 Hrs Light Soaking	4/10/98	39.8	11.7	64.3	0.457

4. INTERDIFFUSION IN ZnO/CIS STRUCTURES

In an effort to improve our understanding of the relationship between processing and cell performance, and to assist in the development of models for CVD grown ZnO buffer layers, we collaborated with Angus Rockett to acquire SIMS depth concentration profiles. ZnO buffer layers were grown on Siemens CIS substrates and on epi-CIS films grown on GaAs by Rockett, and supplied to Rockett for SIMS profiles.

4.1 SIMS Depth Concentration Profiles For ZnO On Epitaxial CIS Films

Angus Rockett provided epitaxial CIS substrates (CIS grown on GaAs) for growth of ZnO. Specifically, ZnO layers were grown on the substrates using a two-step approach involving growth of 100 Å at 250°C followed by growth of approximately 700 Å at 100°C. Figure 5 shows data taken for depth concentration profiles of zinc, oxygen, copper and selenium on a ZnO/Epi-CIS structure within a few days after ZnO film deposition. The profiles are presented as semilog plots so that changes at the interface are emphasized. There are two particularly interesting features, the sharp interface between ZnO and CIS, and the 'bump' in the Zn profile at the interface. Clearly, very little interdiffusion of elements has occurred for this ZnO/CIS structure in which the CIS region is essentially a single crystal layer. The apparent excess of Zn at the interface could be consistent with the Wessel model for growth of ZnO from reaction of DMZn and THF [3]. He proposed that DMZn first reacts with the substrate surface and then THF (the oxygen precursor) reacts with the DMZn/Surface system to produce ZnO. Thus, if the ZnO film nucleation process first involves zinc attaching to the surface followed by addition of oxygen through the reaction with THF, the 'bump' may indicate that the first few monolayers of the buffer layer are zinc-rich. These results are still considered preliminary.
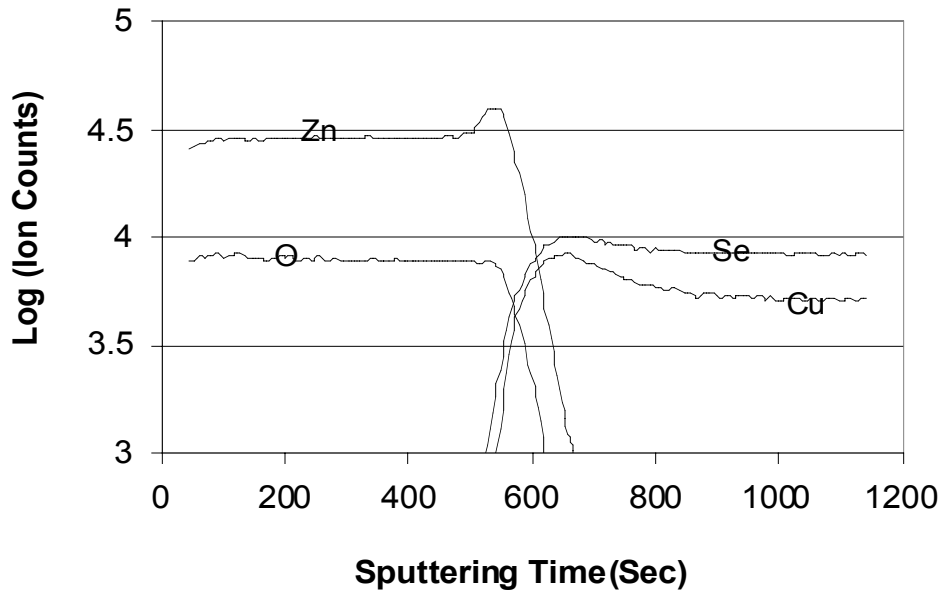
Figure 5.   Depth concentration profiles for a ZnO/Epi-CIS Structure presented on a semilog plot.

4.2   SIMS Depth Concentration Profiles For ZnO On Polycrystalline CIS

At the same time ZnO was grown on the epi-CIS substrates, ZnO was grown on a SSI polycrystalline CIS substrate.   Figure 6 shows depth concentration profiles presented as semilog plots.   The interface region is, of course, greatly affected by surface roughness, but it appears that one can conclude that both zinc and oxygen diffuse a significant distance into the polycrystalline CIS substrate.   It is interesting to compare the profiles for the epi-CIS sample with those for the polycrystalline CIS structure.   It is particularly useful to compare the semilog plots. The difference between the two structures is striking, and appears to establish that zinc and oxygen diffuse along grain boundaries in the polycrystalline material. In particular, it appears that zinc may penetrate further than oxygen.
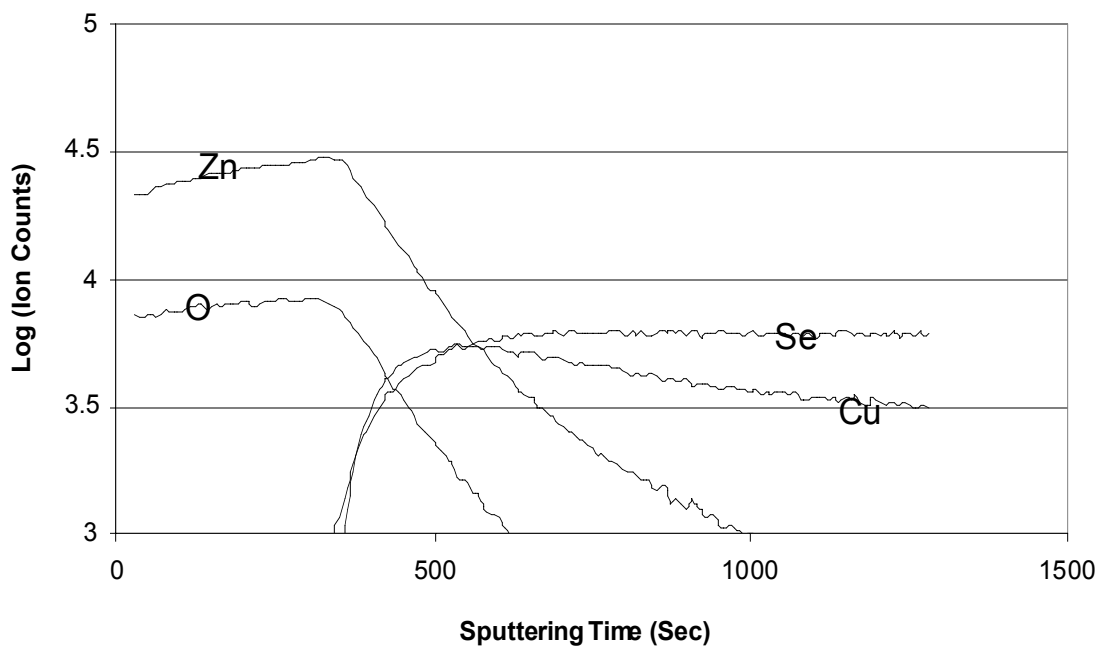
Figure 6. Depth concentration profiles for a ZnO/Poly-CIS Structure ZCIS26 presented on a semilog plot.

5.   MODEL FOR CELLS WITH CVD i-ZnO BUFFER LAYERS

5.1   Effect Of Air Exposure On ZnO/CIS Cells

Although 12 % to 14 % cells have been fabricated with highly resistive ZnO buffer layers grown by MOCVD, an improved understanding of processing required to achieve high efficiency is still desirable.   For example, it is found that it is beneficial to "age" i-ZnO/CIS cell structures in air for several weeks before completing the cell with a TCO and collector grid. Various aspects of these studies are discussed in the following sections.   All discussions pertaining to ZnO buffer layers concern films grown by the WSU reactor using THF and a zinc adduct as precursors.

5.1.1   Resistivity Of MOCVD ZnO Films

Figure 7 describes our general experience with MOCVD ZnO films grown on glass and CIS substrates. The results apply to films with nominal thicknesses of 700 Å to 800 Å. The time needed for films to acquire a resistivity of 10^4 ohm-cm is in the range of 10 to 30 hours. The initial conductivity is apparently due to the films being oxygen-deficient. It is expected that oxygen molecules are physisorbed on the ZnO surface and in grain boundaries, and then chemisorbed to provide two oxygen atoms to occupy two oxygen vacancies, and thereby neutralize two donor states. This process has been proposed for ZnO gas sensors [4].   The film probably becomes resistive due to barriers formed at the grain boundaries, and possibly due to changes within grains as well since the grain sizes are only on the order of 500 to 1000 Å.

5.1.2   Behavior Of ZnO/CIS Cells

As described in Figure 7, experience with MOCVD ZnO buffer layers indicates that exposure of i-ZnO/CIS structures to air beyond a 30 hour period is beneficial to
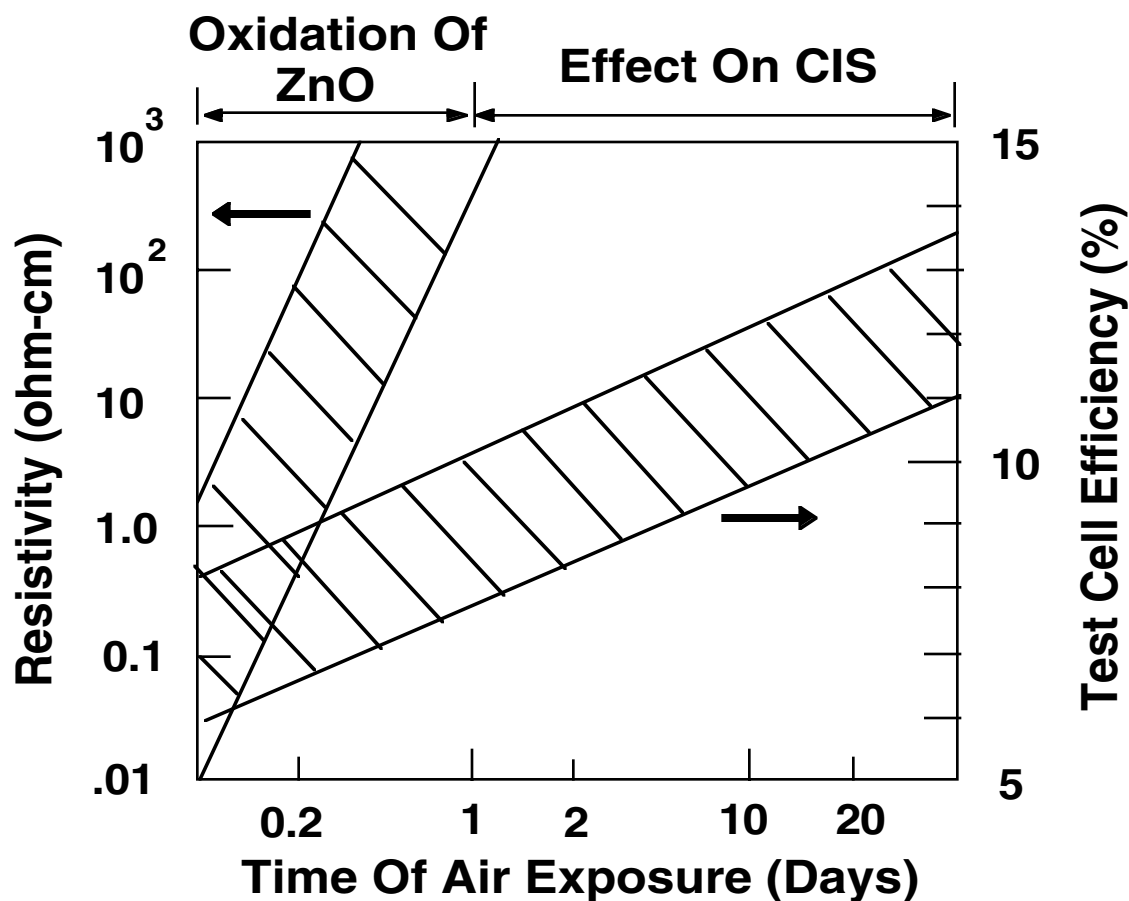
Figure 7.   Resistivity for ZnO films on glass witnesses and cell efficiency versus time of air exposure.

ultimate cell performance.   Therefore, adjustment of buffer layer resistivity alone is not sufficient to attain high efficiencies. The term test cell efficiency refers to estimated values obtained for devices fabricated with semitransparent Al contacts replacing a TCO layer.   The band shown in Figure 7 that refers to efficiency is also representative of completed cell results.   The effect of aging by exposure to air is further illustrated by Figure 8.   Current-voltage characteristics are shown for a test cell and for a completed cell, designated as 97XC022 and 97XC021, respectively. The MOCVD i-ZnO buffer layers were grown on these structures simultaneously.   Test cells were formed on 97XC022 within a few days after i-ZnO growth, while completed cells were formed on 97XC021 three   weeks   after   buffer   layer deposition.   Exposure of 97XC021 to air for several weeks allowed the fabrication

of cells with efficiencies greater than 11%. Cell fabrication involved: growth of a 800 Å i-ZnO buffer layer; deposition of 0.5 to 1.0 μm of n-ZnO by RF sputtering and deposition of Ni/Ag collector grid at IEC. Cells fabricated from ZnO/CIS structures immediately after buffer layer deposition and those completed after a structure has been exposed to air for several weeks (aging process) differ in two significant ways. First, efficiencies differ as illustrated by cells 97XC021 and 97XC022. Secondly, dark curves translate fairly well for cells based on aged structures, whereas, cells fabricated from non-aged structures exhibit enhanced current losses under illumination. In an effort to understand these differences, J-V analyses were conducted using PC-1D to determine the behavior of device parameters.
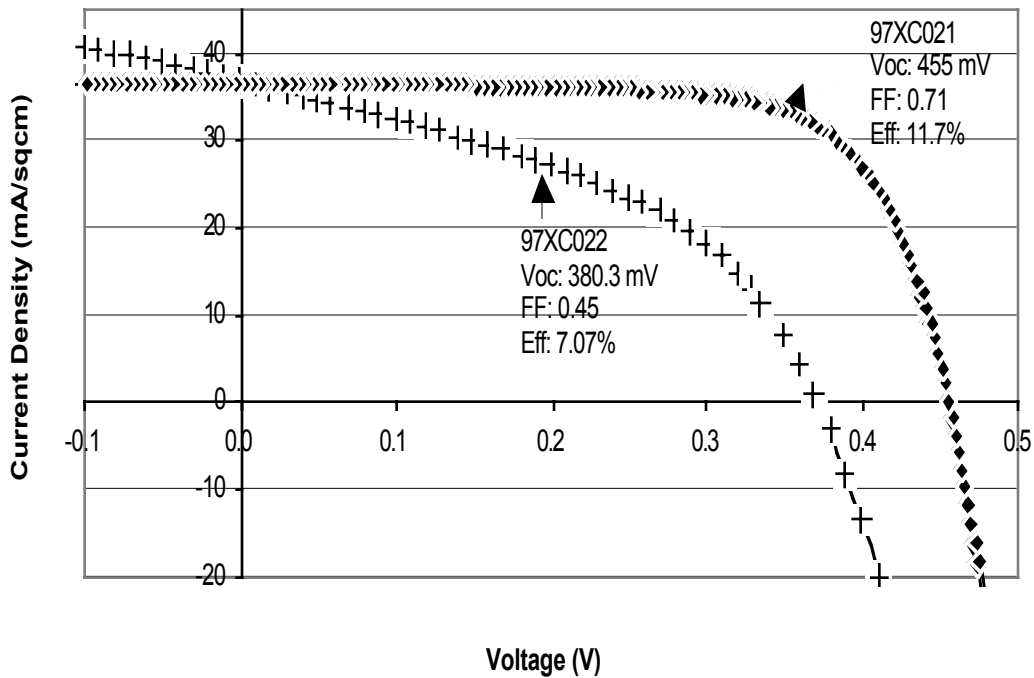

Figure 8.   Estimated active area characteristics for a test cell immediately after growth of ZnO buffer layer on device structure 97XC022, and active area characteristics of a completed cell for which the ZnO buffer layer was exposed to air for three weeks prior to deposition of a TCO and collector grid.

17

5.2   J-V Analyses Using PC-1D

The one dimensional code PC-1D was utilized to fit dark and illuminated data for both cells discussed above.   Four parameters were varied in the fitting process, the dopant concentration in CIS (p_{CIS}), surface recombination velocity (S_n), electron lifetime in CIS (τ_n), and the effective shunt resistance (R_{sh}).   Values of parameters for dark and illuminated curves are given in Table 4.   The experimental and simulated curves for the illuminated characteristics for Cell 97XC021 are given in Figure 9. Experimental and simulated curves are presented for Cell 97XC022 in Figure 10.   In this case we include the dark and illuminated characteristics to illustrate the light enhanced current-loss effect.   The surface recombination velocity is essentially the same for the two cells, whereas other parameters differ significantly.   It is interesting that τ_n and p_{CIS} are CIS bulk properties, and even though R_{sh} involves conducting paths intersecting the ZnO-CIS interface, the conducting paths penetrate into the CIS substrate.

The results for J-V analyses are typical for non-aged and aged cells with WSU MOCVD buffer layers.   There are several key features that can be identified.   First, consider the illuminated characteristics of non-aged and aged cells.   The model suggests that as aging occurs, electron lifetime increases from 80 to 330 picoseconds, indicating some change in the bulk of CIS.   Secondly, the hole density increases as

Table 4.   J-V Parameters Determined With PC-1D   (ohm-cm^2)

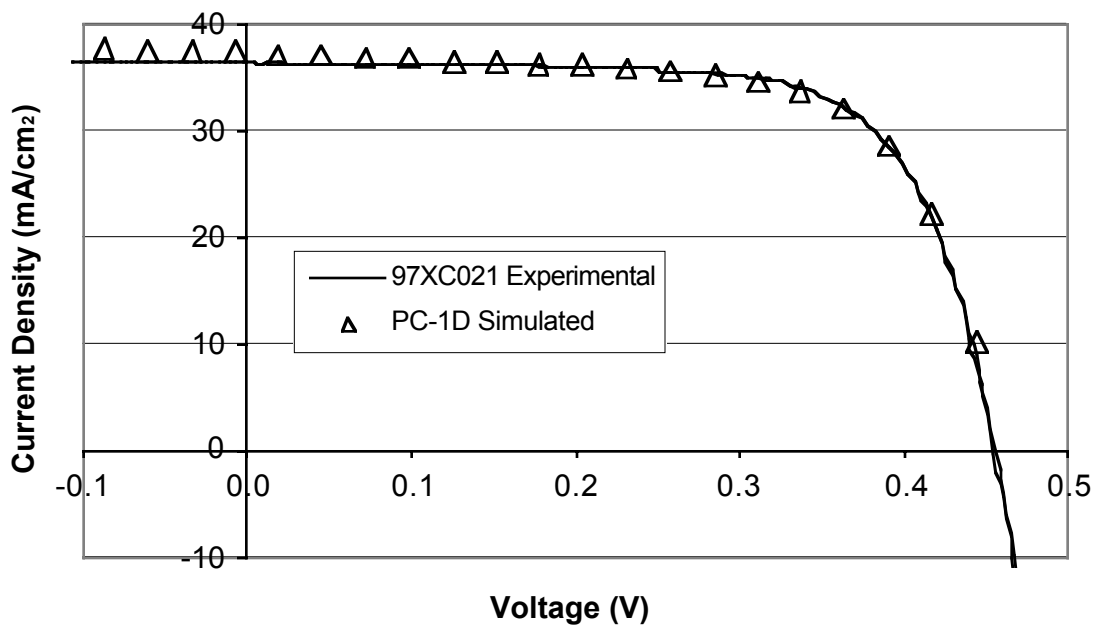|		τ_n (picosec)	S_n (cm/s)	R_{sh} (ohm-cm^2)	p_{CIS} (cm^{-3})
97XC021	Dark & Illuminated	330	5E6	500	9E16
97XC022	Dark	80	7E6	500	1E16
	Illuminated	80	7E6	40	1E16

18

Figure 9.   Experimental and simulated J-V characteristics for aged Cell 97XC021.
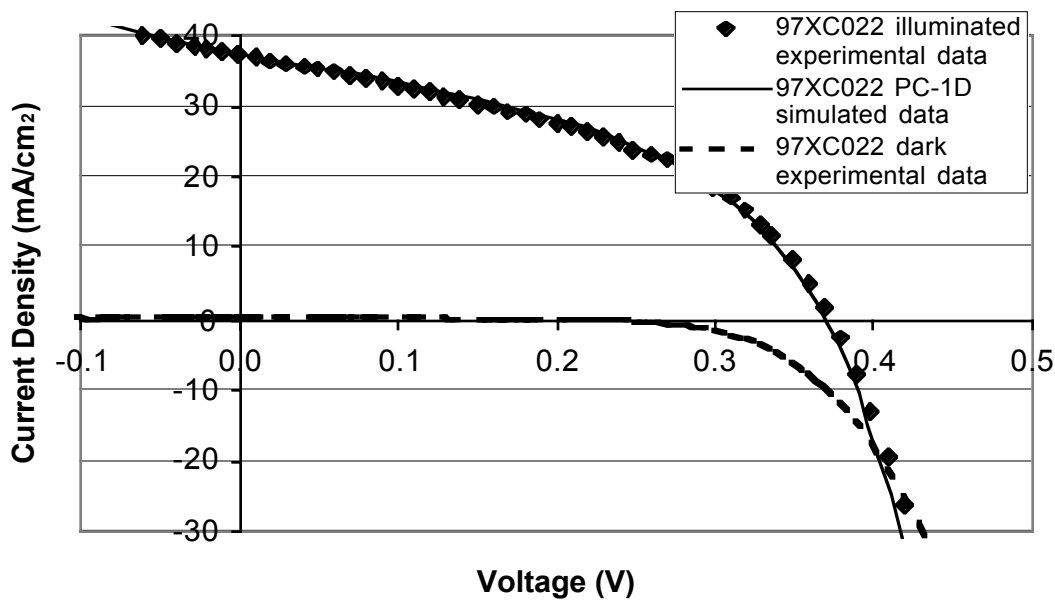

Figure 10.   Experimental and simulated characteristics for non-aged cell 97XC022.

cells age, which again suggests a change occurring in bulk CIS. A third feature is that the effective shunt resistance under illumination increases as a cell ages. Finally, the light enhanced current losses in non-aged cells can usually be attributed to light-induced reduction of cell shunt resistance.

5.3   Sensitivity Of ZnO And CdS To Oxygen

As noted above, Mitra, et al. have reported recently on electrical and gas sensing properties of chemically deposited zinc oxide films [4]. It was reported that in the range of 300°K to 400°K, the activation energy for chemisorption of O_2^- was determined to be 0.25 eV. Thus, the increase in resistance of chemically deposited ZnO films was attributed to physisorbed O_2, followed by ionization of the oxygen molecule by a conduction electron, and then chemisorption of the ionized molecule to provide two oxygen atoms in O-vacancy sites. The chemisorption of O_2^- occurred on the film surface and in grain boundaries, resulting in the neutralization of two donors (the O-vacancies). Mitra, et al. observed that adsorption of oxygen by ZnO films resulted in highly resistive films.

Sensitivity of CdS films to oxygen has also been observed. Since CdS is a II-VI compound with n-type conductivity due to Cd interstitials and/or S-vacancies, results for CdS films may be relevant to understanding ZnO films. Fahrenbruch and Bube discuss this subject in their book on solar cells [5]. They note that exposure to air at temperatures in the 300°K to 400°K range results in significant increases in resistivity of CdS films. Specific experiments were referred to for which the air exposure was done for 18 hours at 100°C. Explanation of the effect is based on O_2 being physisorbed on the film surface and in grain boundaries followed by establishment of chemical bonds. It is postulated that after physisorbtion the oxygen molecule acquires electrons from the CdS conduction band, and then dissociates with oxygen atoms residing in sulfur sites. Since oxygen residing in a S-vacancy eliminates a donor level, grain boundaries become depleted of donors resulting in potential barriers being established at the boundaries. Thus, the

explanation for the oxidized CdS films becoming resistive is that barriers to electron flow are established at the grain boundaries. It was also noted that the effect can easily be reversed by placing a film in vacuum in the same temperature range.

5.4   Background Information On Defect Models In CIS

In an effort to develop an understanding of our ZnO buffer layers, some time was devoted to reviewing work concerning defect models in CIS. Most CIS cell research has involved cells with structures based on a 500 Å CdS buffer layer and a sputtered n-ZnO TCO. It is common for these cells to be heat treated in air at 200°C for 2 minutes after deposition of the CdS buffer layer (usually by solution growth). Cell efficiencies are improved significantly as a result of this post-deposition heat treatment. As a result, there has been considerable interest in developing a defect model to explain the effect of oxygen on this cell structure. Cahen and Noufi published one of the first key papers on this subject [6]. XPS studies of air annealed CdS/CIS structures had previously shown that In-O bonding occurred after the anneal. Cahen and Noufi proposed that oxygen atoms neutralized (or passivated) V_{se} sites at grain boundary surfaces according to the following steps: (1) O_2 is physisorbed near two vacant Se sites; (2) the oxygen molecule is then dissociated with each oxygen atom acquiring two electrons from the valence band of CIS and bonding to In atoms in the vacant Se sites. Since the V_{se} site is a donor, the filling of the vacancy by oxygen neutralizes the donor state - that is, eliminates it. This model was consistent with observed increases in the hole concentration in CIS after air anneal, and the XPS results showing In-O bonding.

The defect model concerning the interaction of oxygen with CIS cells has also involved considerations of the role of Na. CIS cells are typically based on CIS films formed on Mo coated soda lime glass. It has been found that growth of CIS films on soda lime glass leads to the incorporation of Na impurities to levels of ≈ 0.1 at.% in the bulk of the film [7]. In fact, it has been determined that incorporation of Na in the film improves solar cell performance. Kronik, et al. recently proposed that the effects of Na and oxygen are related [8]. Based on previously published studies

of catalytic effects of alkali metals on surface oxidation of semiconductors, they proposed that Na catalyzes the oxidation process, that is, the passivation of the Se-vacancy donor states. The process consists of Na polarizing the O-O bond of a physisorbed O_2 molecule, enhanced tunneling of electrons from CIS to the oxygen molecule as a result of a lowered work function caused by Na on the CIS surface, and finally, the dissociation of molecular oxygen into two oxygen atoms. The dissociation process is made easier when the oxygen molecule is negatively charged. If no passivation of the Se-vacancies takes place, the positively charged grain boundaries will cause enhanced current losses. Kronik, et al. therefore argued that Na catalyzes the oxidation process involving oxygen atoms replacing Se-vacancies.

Kronik and coworkers assumed that Na and oxygen resided on CIS grain boundaries because of information provided by Niles that is in the process of being published [6]. The focus of the work reported by Niles and coworkers concerns the location of Na and O impurities in thin films of photovoltaic-grade CIS thin films. High-spatial resolution Auger electron spectra were taken on a Physical Electronics 670I equipped with a field emission tip. A beam diameter size of 23 nm was utilized for the study. Their studies determined that concentrations of Na and oxygen at CIS grain boundaries are typically 2.5 ± 0.6 at. % and 14.3 ± 6.7 at. %, respectively. Measurements of concentrations of Na and O in the grain interiors were below the detection limit, namely, 0.15 at. %.

Work regarding the effects of oxygen and Na in CIS solar cells were briefly reviewed for two reasons. First, this discussion provides background information for the model proposed below for ZnO/CIS devices. Secondly, the work of Niles, et al., clearly establishes that oxygen tends to migrate along grain boundaries as a result of a low temperature anneal in air. It should be emphasized that the air anneals in these studies were carried out at 200°C for only two minutes. Thus, although CIS is a polycrystalline material utilizing defect doping, oxygen did not diffuse into the interior regions of CIS grains in the samples of Niles, et al.. This result adds credibility to our contention that oxygen and zinc diffuse along grain boundaries during deposition of ZnO.

5.5   Model For MOCVD ZnO Buffer Layers

The results presented in this report combined with information from literature have led to the formulation of a model that can explain slow transient effects in ZnO/CIS cells, and light-induced current losses in cells on non-aged ZnO/CIS structures. J-V analyses indicated that beginning-of-life cell properties can be understood in terms of a light enhanced shunt conductance, and by assuming the electron lifetime is on the order of 80 picoseconds.   After 20 to 30 days of exposure to air at room temperature, analysis of cell J-V characteristics indicated that the light-induced shunt conductance was greatly reduced and the electron lifetime increased significantly.   A brief description of the proposed model that can explain these effects follows.

5.5.1   Possible Model For ZnO/CIS Cells

State Of CIS Right After ZnO Growth

(1)   Zinc atoms that have diffused along CIS grain boundaries reside primarily in vacant copper sites and provide shallow donors ;

(2)   Oxygen atoms along the grain boundaries reside in several possible sites, namely, bonded to Zn_{Cu} , vacant selenium sites (V_{se}), complexed with Na^+ or in some interstitial site (Oi).   The Zn_{Cu} and V_{se} sites are donors and, thus, when an oxygen atom occupies either site the donor is neutralized (or passivated).   Since the Siemens material is formed by selenization of metallic layers, the concentration of V_{Se} sites will be relatively small.

(3)   The Zn_{Cu} donors cause grain boundaries to be n-type, and thus, to have inverted electron band structures.   When illuminated, the electron concentration near the grain boundaries increases which in turn increases the shunting conductance associated with grain boundaries (assuming they intersect the ZnO-CIS interface) . The electron lifetime is also reduced by the inverted grain boundaries under both dark and illuminated conditions.

After Aging

(4)   As time evolves, additional oxygen atoms migrate from the ZnO buffer layer into CIS grain boundaries. The donor states associated with Zn_{Cu} sites are significantly reduced in number as oxygen atoms enter the CIS substrate and complex with Zn atoms on the Zn_{Cu} sites. This change leads to a band characterized by flatter bands, which will result in a greatly reduced light-induced effect on the shunt conductance. The electron lifetime will also be significantly increased.

5.5.2   Zinc Doping Of Grain Boundaries And Oxygen Passivation

The proposed model as outlined above assumes that both zinc and oxygen diffuse along grain boundaries during growth of ZnO by MOCVD. It is assumed that a significant fraction of the Zn atoms reside in Cu vacancies and thus provide a high concentration of donor states along grain boundaries that intersect the CIS-ZnO interface. The main acceptor in CIS that makes it p-type is the copper vacancy. Since CIS films are grown so that they are copper deficient near the surface, there will be a high concentration of V_{CU} sites along the grain boundaries near the CIS-ZnO interface. As indicated above there are several possible sites for an oxygen atom to reside along grain boundaries. Occupation of a Se-vacancy site by oxygen or complexing of oxygen with Zn leads to the neutralization of a donor state. The model assumes that immediately after growth of ZnO, the net doping along grain boundaries is n-type due to the Zn_{Cu} donors. As the ZnO/CIS structure is aged, it is assumed that oxygen gradually migrates from the ZnO film (due to ZnO continually reacting with oxygen) into CIS grain boundaries and significantly reduces the n-type doping along the CIS grain boundaries. It is assumed that the migration of oxygen correlates with the time required for cell properties to improve, namely, on the order of 30 days.

The plausibility of oxygen migrating along CIS grain boundaries depends on two key factors, namely, that a source of oxygen is available at the surface of CIS, and that the activation energy for oxygen diffusion along CIS grain boundaries is low enough for the adequate diffusion to occur over 30 days. Experimental results for the transient behavior of resistivity of ZnO films and results cited above for oxidation of CdS films are consistent with the supposition that oxygen molecules are dissociated at ZnO grain boundaries, followed by diffusion along ZnO grain boundaries to the ZnO-CIS interface. Since ZnO film resistivities increase to very large values within 20 to 30 hours, oxygen would be available at the ZnO/CIS interface after a day had passed.

As discussed above, air anneal of CdS/CIS cells at 200°C is done for 2 minutes, or 120 seconds. The time period for oxygen migration in the proposed model is 30 days, or 2.59E6 seconds. We are not aware of diffusion coefficients being reported for oxygen in CIS, but an approximate value for the activation energy associated with grain boundary diffusion of oxygen can be obtained if we assume that the air anneal of CdS/CIS cells and assumed migration of oxygen in ZnO/CIS structures result in oxygen penetrating to the same depth. Writing the diffusion coefficient as $D = D_o \exp(- \Delta E/kT)$, the depth of oxygen penetration is estimated for the two cases by

$$x^2 = (120) D_o \exp(- \Delta E/kT_1) , \qquad T_1 = 500°K \quad (CdS/CIS)$$

and
$$x^2 = (2.59E6) D_o \exp(-\Delta E/kT_2) \qquad T_2 = 300°K \quad (ZnO/CIS)$$

Setting these two expressions equal one finds $\Delta E = 0.64$ eV, a reasonable value for an activation energy for grain boundary diffusion.

5.5.3   Light Induced Shunt Conductance

Assuming that the proposed model is correct, let us consider the effect on the electron band structure near a grain boundary.   Figure 11 shows a possible diagram across a grain boundary that has a large concentration of Zinc donors. Figure 12 describes in a qualitative manner the effect of the system being illuminated.   Thus the total number of conduction band electrons available for conduction is significantly increased. Figure 13 describes the effect on the electron band structure near a grain boundary that intersects the interface between the ZnO buffer layer and p-type CIS. The diagram is drawn for short-circuit conditions, that is, with the structure being illuminated and current is being supplied to a load of zero resistance. As indicated in the figure, several phenomena are occurring within the CIS region. Electron-hole pairs are being generated by photon absorption, electrons are being driven into ZnO by the built-in electric field within the depletion region, and electrons are recombining via interband states along the grain boundaries.   In addition, an electron that has been swept by the field into ZnO is shown moving towards the grain boundary region.   Since there is no barrier in the region of the grain boundary, the electron can easily flow back into CIS. This
current loss is negligible under short circuit conditions, but when the load resistance becomes finite, and a potential develops across the junction with a negative polarity on the ZnO side and positive on the CIS side, electrons flow back into CIS through this "trough" in the band structure leading to a current loss.   Since the electron concentration is so large in the "trough" region, this current loss mechanism can be approximated by a shunt resistance.
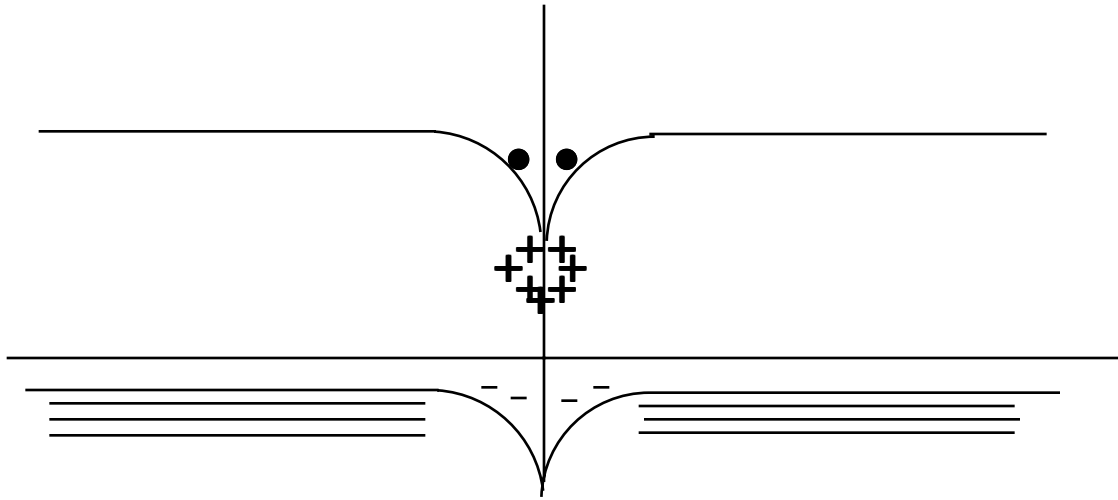
Figure 11.   Electron band structure at a grain boundary with donor states caused by zinc occupying Cu vacancies.
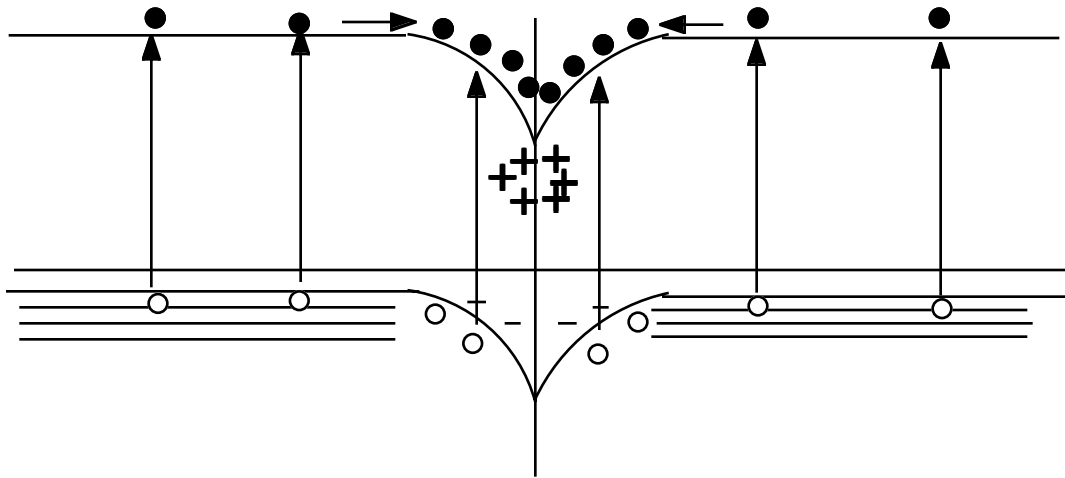

Figure 12.   The effect of light absorption on electron concentration near grain boundary.
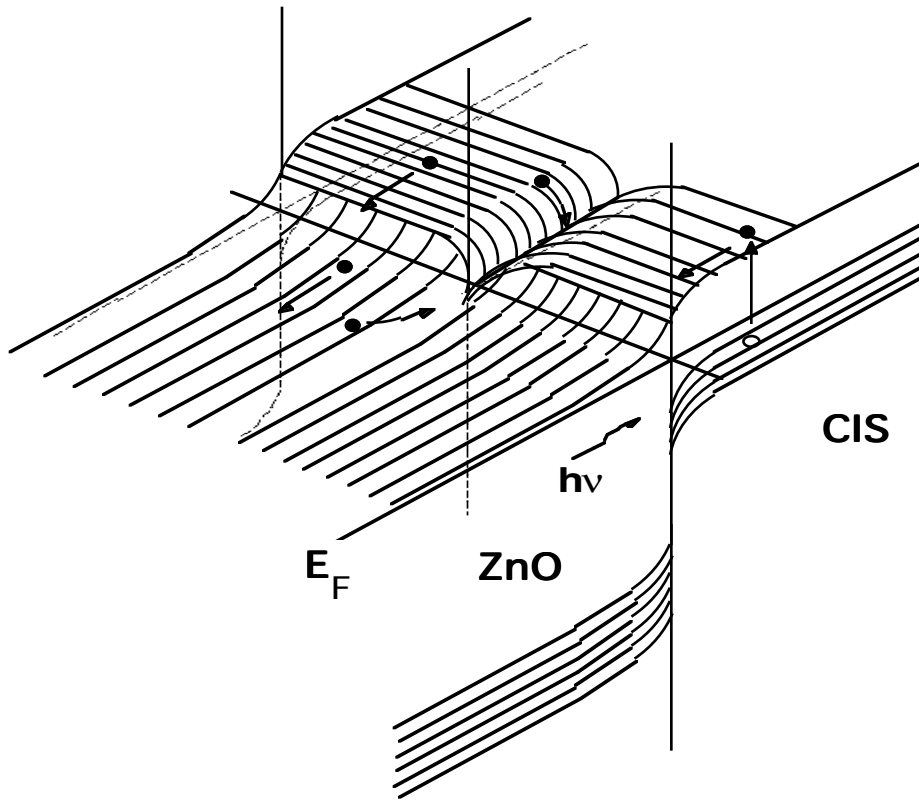
Figure 13. Electron band structure for a grain boundary intersecting ZnO-CIS interface.

As discussed above, it is found that the effective shunt resistance of ZnO/CIS cells based on non-aged structures typically decreases by a factor of 10 when going from dark to illuminated conditions. Modeling calculations were conducted to determine if it is reasonable to expect the conductance associated with grain boundaries as depicted in Figure 13 to change by a factor of 10 between dark and under illuminated conditions. Figure 14 describes the problem considered. A surface region 10 Å wide on a grain of p-CIS is assumed to be n-type with a donor concentration of 10^{17} cm^{-3}. The 10 Å region is to simulate a grain boundary and the donors are assumed to be due to Zn atoms residing on vacant Cu sites. The equivalent surface zinc concentration would be 10^{10} cm^{-2}, which is quite reasonable.

Calculations were carried out with PC-1D for this structure in the dark and under AM1.5 illumination. The electron concentration is plotted in Figure 15 for
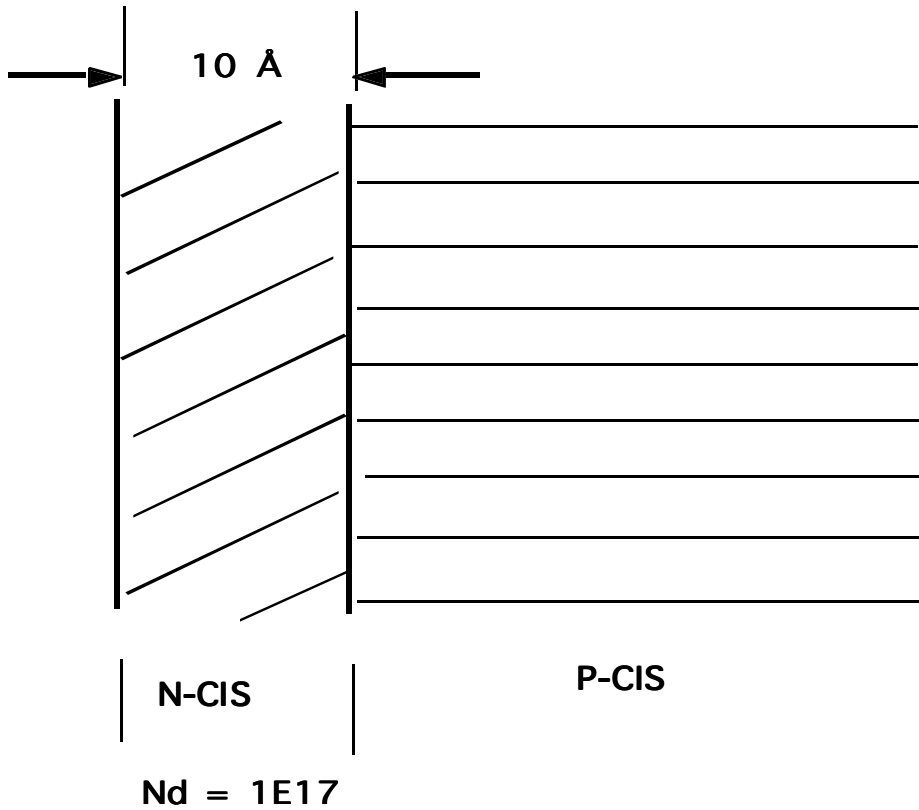
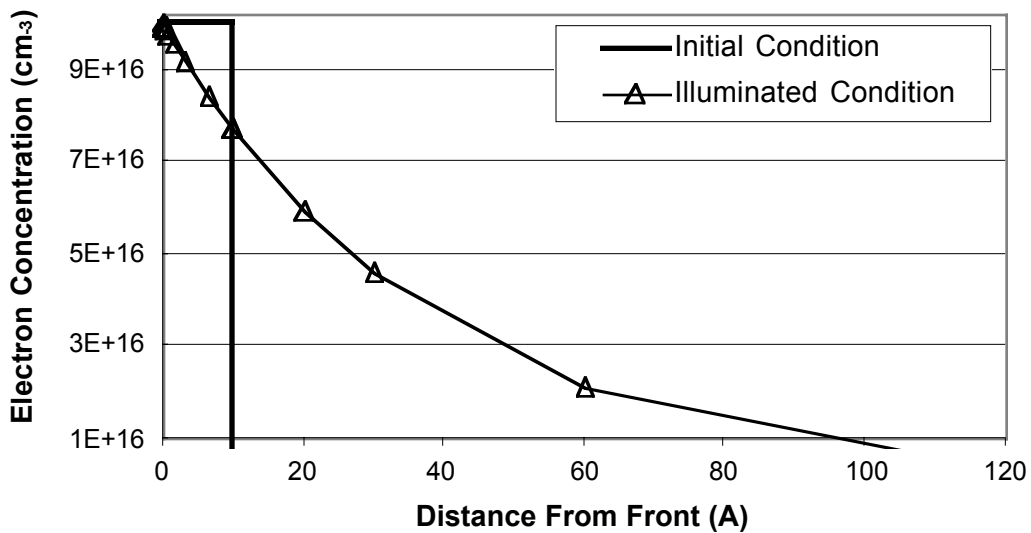**Figure 14.** Assumed configuration for simulation studies.

Figure 16. Calculated electron concentration for grain boundary region under dark and illuminated conditions.

each of these conditions.   Integrating the total electron concentration near the grain surface, we find that the total concentration increases by more than a factor of five between dark and illuminated conditions.   An additional gain in conductance would probably occur because a large percentage of the electrons move in regions 10 to 100 Å away from the grain boundary, and therefore would exhibit a higher mobility.   This calculation was for a specific condition but it supports the contention that illuminated n-type grain boundaries can lead to a light-induced shunt conductance.

5.5.4   Effect Of Aging On CIS Properties And Cell Performance

The proposed model assumes long term air exposure (aging) on ZnO/CIS cells leads to additional oxygen being provided along the CIS grain boundaries that can complex with the Zn_{Cu} sites and thus neutralize these donor levels.   Two important properties would change as a result of the passivated grain boundaries. The light-induced effect on shunt conductance would be greatly reduced allowing cells to have larger fill factors, and the average electron lifetime would increase resulting in larger values of short circuit current.   The net effect would of course be that the aged cell would exhibit a higher efficiency.   The phenomena involved in the transient effects discussed in this report may be related to those at work in "light soaking" effects.   For example, the open circuit condition that a cell is under during light soaking would reduce the built-in field making it easier for oxygen ions to diffuse inward along CIS grains.   On the other hand, light absorption could cause oxygen atoms to change sites such that additional passivation of Zn_{Cu} sites occurs.

6.   OTHER STUDIES

6.1   Raman Spectroscopy Of CuInSe$_2$: Effect Of KCN Etch

We routinely use a KCN etch of CIS and CIGSS absorbers before processing devices.   It is well known that CuSe and Cu$_2$Se precipitates are removed from CIS by soluble cyanide salts such as KCN.   To confirm that our etching procedure removes these precipitates, Raman spectra of as received CIS and KCN etched CIS substrates were acquired through collaboration with Dr. Exarhos at PNNL.   Figure 16 shows a Raman spectrum of an as-received sample of Siemens CIS material.   The spectrum exhibited a fairly broad peak at 173 cm^{-1}, which is consistent with reports for stoichiometric single crystal CIS, that is associated with the A1 mode from the ordered chalcopyrite lattice vibration [10].   Two other peaks at 250 cm^{-1}and 269 cm^{-1} observed for the as-received Siemens CIS film agree with peaks reported for Cu-rich CIS [11].   These peaks were assumed to be associated with Cu-Se compounds.

Figure 17 shows the Raman spectrum of a KCN etched CIS film surface.   Only one sharp intense peak at 173 cm^{-1} was observed.   Thus, it appears that the KCN etch removes Cu-Se precipitates .   Since Cu$_2$Se is known to be conductive, precipitates of this material could provide shunting paths across the heterojunction. The KCN etch process usually provides cells with improved values of FF and V$_{oc}$.

6.2   ZnSe And ZnS Buffer Layer Studies

Very little effort was devoted to investigations of ZnSe and ZnSe buffer layers.   The capability for depositing ZnSe already exists.   Preparations for ZnS deposition were initiated but are not yet complete.   Current plans for Phase II activity include investigations of both ZnSe and ZnS buffer layers combined with Siemens CIGSS absorbers.
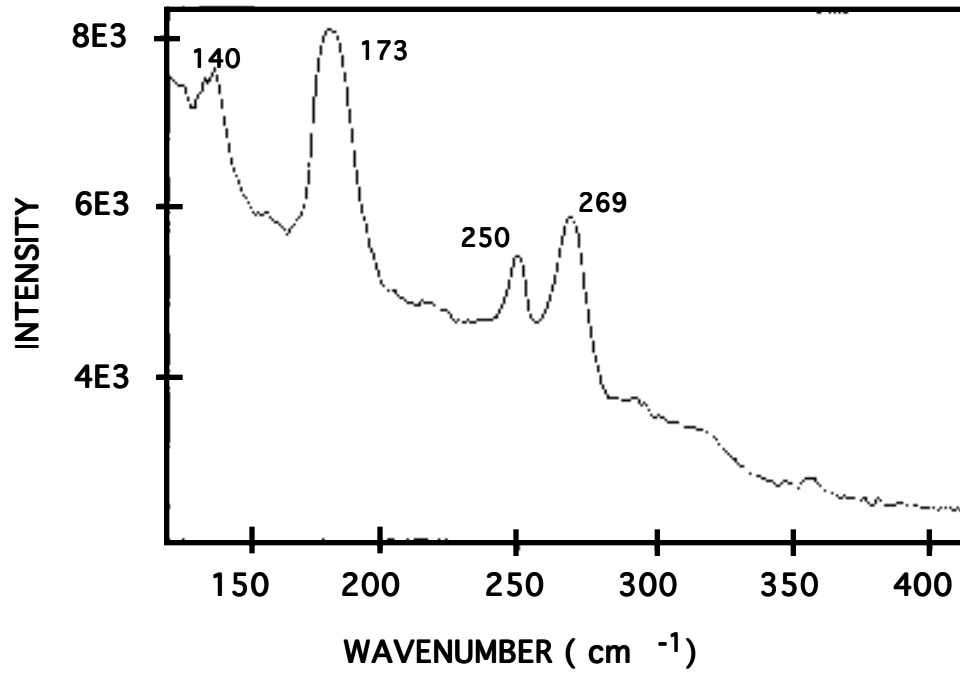
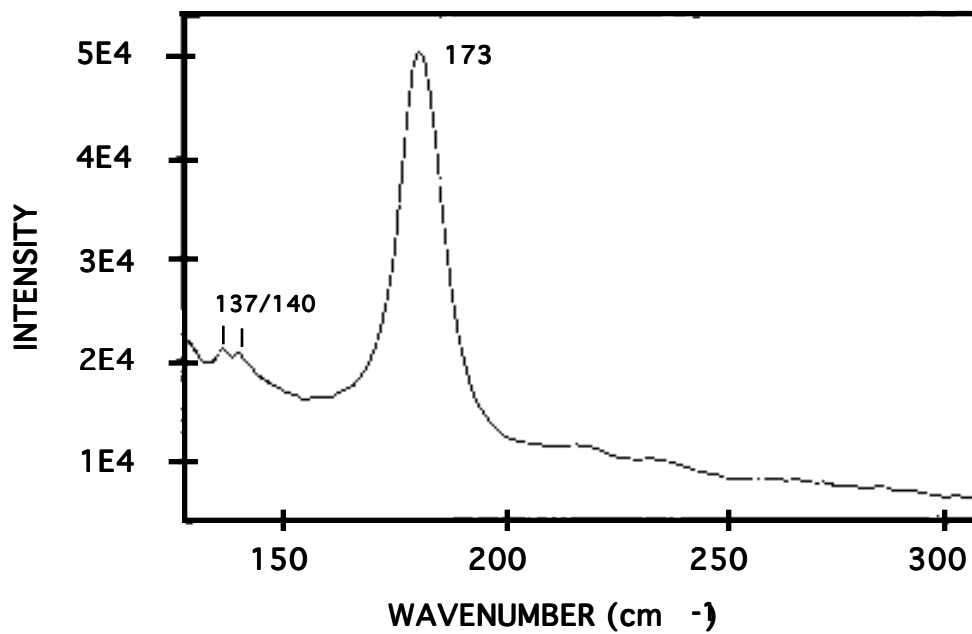**Figure 16.** Raman spectrum of as-received Siemens CIS surface.

Figure 17. Raman spectrum of KCN etched CIS surface.

7. SUMMARY AND FUTURE WORK

The various tasks carried out this past year all had a common element, namely, focus on understanding ZnO buffer layers grown by MOCVD. It was determined that hydrogen was not required for the heat-up step in the two-step process for depositing ZnO. In addition, it appears that it is not necessary to grow a nucleation layer at 250°C. Whereas much of our work had been carried out with Siemens CIS material prior to this reporting period, a process for growing effective ZnO buffer layers on Siemens CIGSS absorbers had not been developed. It was determined that a two-step procedure involving raising the substrate temperature to 250°C in nitrogen and then growing the buffer layer at 100°C works well with CIGSS material. Through collaboration with IEC, completed cells with efficiencies in the 11 % to 12 % range were fabricated with a structure defined by RF n-ZnO/i-ZnO/CIGSS. Cells with this structure were included as part of the Transient team studies. Cells were subjected to dark storage at 80°C followed by a light soak at 40°C at IEC. Illuminated I-V curves taken at each stage of the study determined that these cells do not degrade under dark storage conditions, which had been observed for Siemens cells with CdS buffer layers.

A significant effort was devoted to improving our understanding of ZnO buffer layers grown by MOCVD. In particular, although the resistivity of ZnO layers grown on glass witnesses increased to values greater than 10^4 ohm-cm within 24 hours, cell structures with ZnO buffer layers required a longer aging process. We find that higher efficiencies for cells with i-ZnO buffer layers appear to require exposure to air for 20 to 30 days prior to cell completion. It was assumed that oxygen entered the i-ZnO/CIS structure during this aging process to possibly combine with excess zinc within the CIS surface region. In an effort to provide further information concerning this subject, SIMS depth concentration profiles were obtained for i-ZnO/CIS structures through collaboration with Angus Rockett at the University of Illinois. SIMS profiles were obtained for ZnO films grown on polycrystalline CIS and epitaxial CIS films grown GaAs. Comparison of the profiles strongly suggests that Zn and oxygen diffuse into the CIS along grain boundaries

during the MOCVD growth process. It is also proposed that excess zinc along grain boundaries may result in the grain boundaries being n-type, which can result in enhanced loss currents. The beneficial effect of air exposure in the aging process could be a result of additional oxygen diffusing along grain surfaces and combining with excess zinc such leading to passivated grain boundaries.

The Phase II effort will include further work with ZnO buffer layers, as well as studies of ZnSe and ZnS buffer layers. Efforts to eliminate the need for the long aging process will be carried out. Approaches will consist of increasing the VI-II ratio in the growth process and to investigate air anneal procedures.

REFERENCES

1.   D. Tarrant and J. Ermer, "I-III-VI2 Multinary Solar Cells Based On CuInSe$_2$," Twenty Third IEEE PVSC, 1993, pp. 372 - 378.

2.   Miguel A. Contreras, et al., "High Efficiency Cu(In,Ga)Se$_2$-Based Solar Cells," First WCPEC, 1994, pp. 68 - 75.

3.   P. Souletie and B.W. Wessels, "Growth Kinetics of ZnO Prepared By Organometallic Chemical Vapor Deposition," J. Mater. Res. 3, 740 (19988).

4.   P. Mitra, A. Chatterjee and H. Maiti, "ZnO Thin Film Sensor," Materials Letters 35 (1998) p.33.

5.   Alan L. Fahrenbruch and Richard H. Bube, "Fundamentals Of Solar Cells," page 380, Academic Press, 1983.

6.   David Cahen and Rommel Noufi," Surface Passivation of Polycrystalline, Chalcogenide Based Photovoltaic Cells," Solar Cells 30 (1991) p. 53.

7.   David W. Niles, Kannan Ramanathan, Falah Hasoon, Rommel Noufi, Brian J. Tiesch and Julia E. Fulghum, Na Impurity Chemistry In Photovoltaic CIGS Thin Films: Investigation With X-Ray Photoelectron Spectroscopy," J. Vac. Sci. Technol. A 15(6), Nov/Dec 1997.

8.   Leeor Kronik, et al., "Oxidation, Sodium And Annealing Effects On Cu(In,Ga)Se2 Films And Solar Cells," 2nd World Conference On Photovoltaic Solar Energy Conversion, Vienna, Austria, July 1998.

9.   David W. Niles, Mowafak Al-Jassim and Kannan Ramanathan, "Direct Observation Of Na And O Impurities At Grain Surfaces Of CuInSe2 Thin Films, J. Vac. Sci. Technol. A, Vol. 17, No. 1, Jan/Feb 1999.

10.   Satoshi Yamanaka, et al., " Characterization of Copper Indium Diselenide Thin Films By Raman Scattering Spectroscopy For Solar cell Application," Japanese Journal of Applied Physics 28(8), L1337(1989).

11.   Satoshi Yamanaka, et al., "Study of CuInSe$_2$ Formation Kinetics In The Selenization Process By Raman Spectroscopy," Japanese Journal of Applied Physics 30(3), 442(1991).

REPORT DOCUMENTATION PAGE

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 this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	February 2000	Annual Subcontract Report, 29 December 1997–28 December 1998

4. TITLE AND SUBTITLE
Alternative Heterojunction Partners for CIS-Based Solar Cells; Annual Subcontract Report, 29 December 1997–28 December 1998

6. AUTHOR(S)
L.C. Olsen

5. FUNDING NUMBERS
C: XAF-8-17619-06
TA: PV005001

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Washington State University at Tri-Cities
2710 University Drive
Richland, WA 99352

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
National Renewable Energy Laboratory
1617 Cole Blvd.
Golden, CO 80401-3393

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
NREL/SR-520-27930

11. SUPPLEMENTARY NOTES
NREL Technical Monitor: B. von Roedern

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

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)
The focus of the Phase I effort concerned further development of ZnO buffer layers. This work included further optimization of the metal-organic chemical vapor deposition (MOCVD) growth process and investigations of the interaction of zinc and oxygen with the absorber layers. Although much of our work had been done with Siemens' CIS material prior to this reporting period, a process for growing ZnO buffer layers on Siemens' CIGSS absorber had not been developed. We determined that a two-step procedure involving raising the substrate temperature to 250°C in nitrogen and then growing the buffer layer at 100°C works well with CIGSS material. Through collaboration with the Institute of Energy Conversion (IEC), completed cells with efficiencies in the 11% to 12% range were fabricated with the following structure: RF n-ZnO/i-ZnO/CIGSS. Cells with this structure were included as part of the Transient team studies. Cells were subjected to dark storage at 80°C, followed by a light soak at 40°C at IEC. Illuminated I-V curves taken at each stage of the study determined that these cells do not degrade under dark-storage conditions, which had been observed for Siemens cells with CdS buffer layers. To understand the reaction of zinc and oxygen with the absorber layers, secondary ion mass spectroscopy (SIMS) depth concentration profiles were obtained for i-ZnO/CIS structures through collaboration with Angus Rockett at the University of Illinois. SIMS profiles were obtained for ZnO films grown on polycrystalline CIS and epitaxial CIS films grown on GaAs. Comparison of the profiles strongly suggests that zinc and oxygen diffuse into the CIS along grain boundaries during the MOCVD growth process. It is also proposed that excess zinc along grain boundaries may result in the grain boundaries being n-type, which can result in enhanced loss currents. This model is consistent with the apparent requirement that cell structures with MOCVD buffer layers must undergo an aging process in air before efficient cells can be obtained. Future studies will investigate processes that allow the aging step to be eliminated.

14. SUBJECT TERMS
photovoltaics ; heterojunctions ; CIS-based solar cells ; process development ; transient effects ; interdiffusion ; buffer layers ; MOCVD ; grain boundaries

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	UL