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INSTITUTE OF ENERGY CONVERSION

UNITED STATES DEPARTMENT OF ENERGY
UNIVERSITY CENTER OF EXCELLENCE
FOR PHOTOVOLTAIC RESEARCH AND EDUCATION

October 18, 2006

Bolko von Roedern
National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, CO 80401

Re: NREL Subcontract #ADJ-1-30630-12
D.5.4

Dear Bolko:

This report covers research conducted at the Institute of Energy Conversion (IEC) for the period from May 16, 2006 to June 15, 2006, under the subject subcontract. The report highlights progress and results obtained under Task 2 (CIS based solar cells).

TASK 2: $CuInSe_2$-BASED SOLAR CELLS

In-Line Evaporation

A paper, "Design Strategy For Scale-Up of Physical Vapor Deposition of $Cu(InGa)Se_2$ On Flexible Substrates" by Kapil Mukati, Babatunde A. Ogunnaike, Erten Eser, Shannon Fields, Robert W. Birkmire, was presented at the 4th WCPEC. This paper addressed critical issues for the design and scale-up of evaporation sources used in $Cu(InGa)Se_2$ Physical Vapor Deposition (PVD) onto flexible substrates for use over long run times. Issues associated with the thermal characteristics of the source boats and the effects of melt level reduction over time can negatively impact film quality and reproducibility. Specifically, difficulties encountered with the design of the sources presently in operation are addressed, and new designs are proposed that resolve the problem of thickness and composition uniformity over wider substrates (~12 inches). Simulation results are presented comparing the old source design with the proposed new one for a 12-inch wide substrate. It is shown that improved film thickness uniformity and hence, composition uniformity, is achieved with the proposed designs, and material utilization can be improved by an appropriate choice of system design parameters such as nozzle-to-substrate distance.

$Cu(InGa)(SeS)_2$ Formation by H_2Se/H_2S Reaction

A paper, "Composition Control In The Growth Of $Cu(InGa)(SeS)_2$ By The Reaction Of Cu-In-Ga Precursors In H_2Se And H_2S" by Gregory M. Hanket, William N. Shafarman, and Robert W. Birkmire, was presented at the 4th WCPEC. The two-reaction selenization/sulfization of metallic Cu-In-Ga precursors is a commercially viable process for the manufacture of $Cu(InGa)(SeS)_2$ films. In this work, the reaction pathways in single-reaction selenization and sulfization processes are studied, as well as composition profile development in two-reaction processes. Sputter-deposited precursor films were annealed at 450ºC to characterize the starting intermetallic composition, or reacted in either H_2Se or H_2S at 450ºC to observe changes in phase composition as the reaction progressed. The key observation was the formation of an initial $Cu_9(In_{0.64}Ga_{0.36})_4$ intermetallic that is depleted incongruently to form Cu_9Ga_4 during selenization, and $Cu_{16}In_9$ during sulfization. In studying the two-reaction selenization/sulfization process, a 2 x 2 matrix of reaction times was examined. Samples were selenized for either 15 or 30 minutes at 450ºC, followed by sulfization at 550ºC for either 15 or 30 minutes. Samples selenized for 15 minutes exhibited uniform Ga through the depth of the film, while those selenized for 30 minutes exhibited the commonly observed back-contact Ga accumulation.

In other work, the effect of precursor heat treatment on improving the uniformity of reacted $Cu(InGa)(SeS)_2$ films has been studied. An ongoing difficulty in recent investigation of the H_2Se/H_2S reactions of Cu-Ga-In precursors has been the occurrence of lateral non-uniformities in reacted films. These non-uniformities are visible to the eye. Figure 1 shows two $Cu(InGa)(SeS)_2$ films fabricated by reacting $Cu_{0.8}Ga_{0.2}$/In precursor films sputtered onto Mo/soda lime glass substrates from a single reaction. These samples were reacted at 450ºC for 15 minutes in 0.35% H_2Se/0.0035% O_2, followed by reaction in 0.35% H_2S/0.0035% O_2 at 550ºC. This is the same process that has previously produced relatively uniform Ga incorporation and $V_{OC} \sim 0.64$ V. The compositions measured at the center and near the edge of a sample similar to the top sample from Figure 1 are listed in Table I. The edges are characteristically low in [Ga]/[In+Ga] relative to the center. The ratio [Ga]/[In+Ga] has been related to the extent of the reaction during the H_2Se step and fully selenized films have [Ga]/[In+Ga] ˜ 0 as measured by EDS with the Ga segregated to the back of the film.

A second typical non-uniformity, observable in the bottom sample of Figure 1 is a diffuse, speckled pattern, which appears in SEM micrographs. This is believed to be related to the agglomeration of In on the surface during reaction. Several potential causes for the non-uniformities have been identified. These include the formation of a convective flow pattern above the sample, temperature non-uniformities, and effects due to the edges of the substrate.

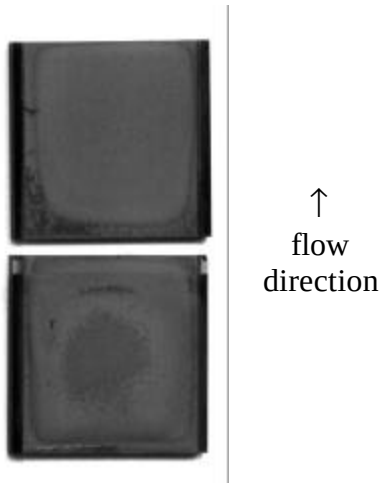

Figure 1. $Cu_{0.8}Ga_{0.2}$/In precursors reacted by 2-step process (15 min selenization @ 450ºC, followed by 30 min sulfization @ 550 ºC).

Table I. EDS composition measurements of a $Cu(InGa)(SeS)_2$ film exhibiting the characteristic center/edge pattern shown in the top sample of Figure 1.

Location	Cu at%	In at%	Ga at%	Se at%	S at%	$\frac{Cu}{In+Ga}$	$\frac{Ga}{In+Ga}$	$\frac{S}{Se+S}$
Center	24.3	21.1	5.3	31.8	17.5	0.92	0.20	0.35
Edge	24.7	25.2	1.6	30.7	17.9	0.92	0.06	0.37

During the standard reaction process, precursor samples reside in a cool end of the quartz tube while reaction temperature and hydride gas flows are established. The "start" of the reaction is the insertion of the samples into the 450ºC reaction zone. Thus, samples begin to anneal, resulting in the formation of a $Cu_9(InGa)_4$ intermetallic, and simultaneously begin to selenize, with the liquid In being the most rapidly reacting phase, as demonstrated previously. The use of a heat treatment before reaction was investigated to separate the mechanisms of intermetallic formation and H_2Se reaction and has been found to improve the uniformity.

As-sputtered $Cu_{0.8}Ga_{0.2}$/In precursor films were heat treated in flowing H_2(4%)/Ar for 2 hours during a slow ramp up to 250°C, an additional hour at 250°C, and finally a slow cool to ~60ºC over a period of ~5 hours. To examine the effect of the heat treatment on reacted film uniformity, three reactions were carried out with heat treated (HT) as as-sputtered (AS) samples in either upstream or downstream positions, as summarized in Table II.

Table II. Summary of two-step reaction runs investigating the effect of precursor heat treatment on reacted film uniformity. HT – heat treated, AS – as-sputtered.

Run	position	sample	Rxn. times (min) H_2Se/H_2S	Rxn. temps. (°C) H_2Se/H_2S
1	upstream downstream	HT AS	15/30	450/550
2	upstream downstream	AS HT	10/30	450/550
3	upstream downstream	HT HT	10/30	450/550

Visible uniformity results are shown in Figure 2. The heat-treated samples are all visibly more uniform, although there is a visible edge which has lower [Ga]/[In+Ga] around the heat treated sample in Run 1.

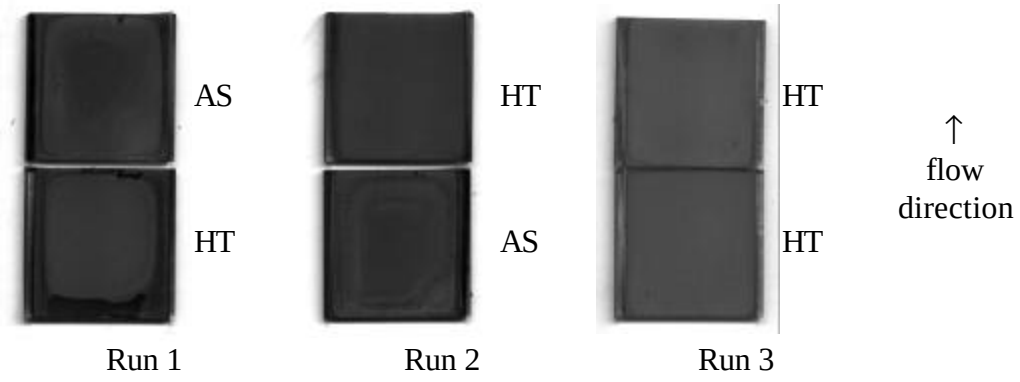

Figure 2. Samples reacted by 2-step selenization/sulfization reaction. Gas flow during reaction is from bottom to top, so lower samples are upstream and upper samples are downstream.

Thus, the heat treatment of as-sputtered precursors preceding the 2-step selenization/sulfization reaction clearly improves film uniformity but further investigation is necessary to determine whether edge effects are due to the substrate or the formation of convective flow or temperature non-uniformities.

Fundamental Materials and Interface Characterization

A paper, "Characterization Of Cu(InGa)Se_2 Solar Cells Using Etched Absorber Layers" William. N. Shafarman, Rongxue S. Huang, and Scott H. Stephens, was presented at the 4th WCPEC. In this work, an aqueous Br-etch to smooth the surface of Cu(InGa)Se_2 thin films and reduce their thickness is used to enhance characterization of Cu(InGa)Se_2 solar cells. Two

applications of this etch are presented. First, the etch is used to obtain the smooth surface necessary for precise optical characterization by spectroscopic ellipsometry. Optical constants of etched Cu(InGa)Se_2 match those of films peeled from the substrate, as has previously been used to provide the smooth surface for characterization. The optical properties of CdS grown on the etched Cu(InGa)Se_2 have been determined and are compared to those of single crystal CdS. Second, the etch is used to controllably reduce the Cu(InGa)Se_2 thickness for characterizing the effect of absorber layer thickness. Devices have been fabricated using Cu(InGa)Se_2 layers with thicknesses from 0.4 to 1.8 μm with fill factor greater than 74% over the entire range. The main loss in efficiency with absorber layers less than 1 μm is from lower short circuit current due partly to incomplete optical absorption. Solar cell losses with the thin specular absorber layers obtained by etching are compared to those with rougher deposited films.

Precise determination of the optical constants n and k using SE data requires a relatively smooth surface. A rule-of-thumb is that the roughness should be less than 10% of the wavelength. We previously compared the optical constants of Cu(InGa)Se_2 over the energy range 0.8 - 4.6 eV on peeled and etched films from the same run for the optical constants and showed good agreement, particularly in the critical optical transition energies. Small differences in magnitude might be due to different surface contamination in the two cases, with oxidation of the peeled surface and excess Se on the etched sample, or simply the result of sample-to-sample variation.

With the smooth Cu(InGa)Se_2 surface, the CdS emitter layer grown by chemical bath deposition (CBD) has been can be characterized as it is deposited in a device configuration. CdS films, with thickness ~50 nm, were deposited using the same procedure used for device fabrication on Br- and KCN-etched Cu(InGa)Se_2. These optical constants of the CdS on Cu(InGa)Se_2 were determined from measured SE data using a general oscillator model and incorporating an effective medium approximation to model the Cu(InGa)Se_2/CdS interface. The results shown in Figure 3 are compared to n and k for bulk single crystal CdS [1]. Although the films grown for this work are of the optically anisotropic wurtzite phase, confirmed by XRD measurements on separate films, they are polycrystalline with randomly orientated grains and assumed to be effectively isotropic. The crystal data shown is for the wurtzite phase with perpendicular orientation, although the difference between this and parallel orientation is small. The differences between the optical constants of the CBD CdS films and the crystal data are significant. The optical constants of the films are lower then those of the crystal and are less sharp. This suggests poorer crystallinity of the CBD grown films as opposed to the bulk single crystals. An apparent ~0.1 eV shift in bandgap suggested by the minimum in n may be due to lattice strain in the film.

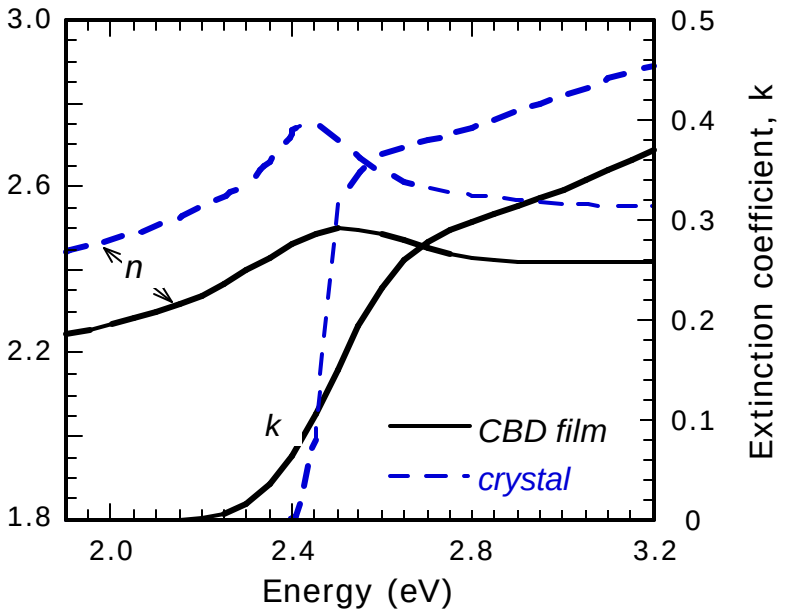

Figure 3. Optical constants of CBD CdS layers deposited on Cu(InGa)Se_2 compared wurtzite crystal, with E⊥c, from [1].

Collaborations

University of Nevada, Las Vegas

IEC has begun collaboration with Clemens Heske at UNLV in a project to study the absorber/back contact interface in terms of its chemical and electronic properties. Specifically, IEC provided 5 samples, including glass/Mo/Cu(InGa)Se_2 and glass/Mo/Cu(InGa)$(SeS)_2$. A procedure for packaging the samples with minimum air exposure was developed for shipping these samples. Initial studies will include photoemission and inverse photoemission measurements on the front surface and on both surfaces of the Mo/Cu(InGa)Se_2 interface after peeling the film from the substrate.

University of Syracuse

IEC has begun collaboration with Eric Schiff at Syracuse to characterize electronic transport properties of Cu(InGa)Se_2. A set of 3 Cu(InGa)Se_2 device samples was sent and will be characterized by drift-mobility measurements.

Reference:

1. S. Adachi, *Optical Constants of Crystalline and Amorphous Semiconductors*, Kluwer Academic Publishers, Boston, (1999).

Best regards,

Robert W. Birkmire
Director

RWB/eak

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