

Thin Film CuIn_{1-x}Ga_xSe-Based Solar Cells Prepared From Solution-Based Precursors

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THIN FILM CuIn_{1-x}Ga_xSe₂-BASED SOLAR CELLS PREPARED FROM SOLUTION-BASED PRECURSORS

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ABSTRACT: We have fabricated high-efficiency thin-film CuIn_{1-x}Ga_xSe₂ (CIGS)-based photovoltaic devices from solution-based electroplated (EP) and auto-plated (AP) precursors. As-deposited precursors are Cu-rich CIGS. Compositions were adjusted to CuIn_{1-x}Ga_xSe₂ with additional In and Ga by physical vapor deposition (PVD) to the EP and AP precursor films. Auger analysis and grazing incident X-ray diffraction (GIXRD) were performed on devices prepared from EP and AP precursor films. We have also analyzed and compared EP, AP, and an PVD CIGS device by deep-level transient spectroscopy (DLTS).

Keywords: CuInGaSe₂ - 1: Electrodeposition - 2: Devices - 3

1. INTRODUCTION

Photovoltaic solar cells are a very attractive source of clean energy. At present, the photovoltaic industry primarily uses wafers of single-crystal and polycrystalline silicon, which generally have a wafer thickness in the range of 150–330 μm . The wafers must go through several processing steps and then be integrated into a module. The high material and processing costs make these modules relatively expensive. Thin-film solar cell technology is a promising alternative to silicon solar cell technology popular today in many applications. CuIn_{1-x}Ga_xSe₂ (CIGS) has become one of the leaders in this field. Its large optical absorption coefficient, due to a direct energy gap, permits the use of thin layers (1–2 μm) of active material. CIGS solar cells are also known for their long-term stability [1]. All these qualities have brought CIGS-based devices to the forefront in solar cell applications.

Currently, a great deal of effort is being made to develop low-cost technologies [2-7] for fabricating CIGS thin films. The recent record-breaking 18.8%-efficient [8] CIGS-based device fabricated in our research laboratory is based on a multistep process using physical vapor deposition (PVD). The PVD method is an excellent tool for understanding film growth and for developing models, but challenging to scale up. Sputtering techniques are suitable for large-area deposition; however, they require expensive vacuum equipment and sputtering targets. Electroplating (EP) and auto-plating (AP) are potentially suitable preparation methods to obtain low-cost precursor films. We have designated the standard electrochemical deposition process, which requires external voltage/current, as electroplating (EP); we designate the newly developed deposition process, where the electrochemical reactions are carried out without external voltage/current, as auto-plating (AP). The EP and AP process could provide: (a) very good-quality film with very low capital investment; (b) a low-cost, high-rate process; (c) use of very low-cost (low purity salts, solvents etc.) starting materials because of automatic purification of the deposited materials during plating; (d) a large-area, continuous, multi-component, low-temperature deposition method; (e) deposition of films on a variety of shapes and forms (wires, tapes, coils, and cylinders); (f) controlled deposition rates and effective material use (up to 95%); (g) minimum waste generation (solution can be recycled).

Devices fabricated using EP and AP CIGS precursors resulted in efficiencies of 15.4% and 13.4%, respectively. The quality of CIGS-based films and devices prepared from the solution-based EP and AP precursor film is very

promising. These completed cells have been examined and compared to an 18.5% PVD cell by deep-level transient spectroscopy (DLTS).

The device-quality EP and AP precursor films are Cu-rich CIGS films. Additional In and/or Ga, and Se are added to the precursor films by PVD to adjust the final composition to CuIn_{1-x}Ga_xSe₂. The solution-based precursor process (EP and AP) will be more attractive for CIGS solar cell fabrication if we can eliminate the PVD step. We are working toward this goal. Our near-term goal is to minimize the PVD step to only a few nanometer deposition and also to add only In or Ga in Se atmosphere. Previously, we added up to 50% material by PVD; at present, we add only 10%–20% of total materials by PVD to obtain high-efficiency devices.

2. EXPERIMENTAL

Both the EP and AP precursor films are deposited from an acidic bath (pH~2) containing 0.02–0.05M CuCl₂, 0.04–0.06M InCl₃, 0.01–0.03M H₂SeO₃, 0.08–0.1M GaCl₃, and 0.7–1M LiCl dissolved in deionized water. Cu, In, Ga, and Se are co-deposited from the solution at room temperature onto the substrate in a vertical cell in which the electrodes are suspended from the top of the cell. The EP precursors are prepared in a three-electrode cell in which the reference is a platinum pseudo-reference, the counter is platinum gauze, and the working electrode is the substrate. The substrates typically used are glass DC-sputtered with about 1 μm of Mo. A constant potential of –1.0 V is applied between the working and counter electrode with a Princeton Applied Research potentiostat/galvanostat Model 273A. The AP precursor films are prepared by shorting the substrate to an oxidizing counter electrode such as Fe, Al, or Zn. The precursors are subsequently rinsed in deionized water and dried in flowing nitrogen or air.

Compositions of the as-deposited precursors are determined by inductively coupled plasma (ICP) analysis. The as-deposited precursors are Cu-rich, and additional In, Ga, and Se are added by PVD to adjust their final composition to CuIn_{1-x}Ga_xSe₂. During this step, the substrate temperature is maintained at 560°±10°C. The photovoltaic devices are then completed with a 50 nm layer of chemically deposited CdS, 50-nm of RF-sputtered intrinsic ZnO, 350 nm of Al-doped ZnO, and bilayer Ni/Al top contacts deposited by e-beam. Finally, a 100-nm layer of MgF₂ is deposited to minimize reflection. The final configuration for all devices reported in this paper is MgF₂/ZnO/CdS/CuIn_{1-x}Ga_xSe₂/Mo/Glass.

3. RESULTS AND DISCUSSION

The morphology of the precursor films and devices were investigated by scanning electron microscopy (SEM). Figures 1 and 2 show the SEM image of the representative EP and AP precursor films. As the micrograph shows, the as-deposited precursor films are densely packed and have very small particle size. The AP precursor films are relatively less uniform compared with the EP precursor films. There is a strong indication of nucleation outgrowth for AP precursor film compared to EP precursor film.

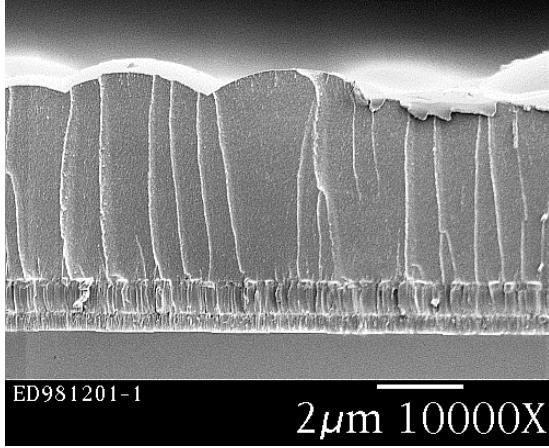


Figure 1: SEM image of an electroplated CIGS precursor film.

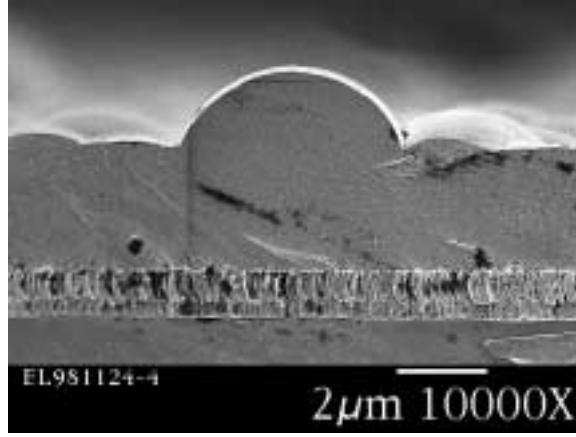


Figure 2: SEM image of an auto-plated CIGS precursor film.

Figures 3 and 4 are SEM micrographs of the representative EP and PVD devices. The processed devices from AP precursor films have similar morphologies to those of EP devices prepared from EP precursor films. The morphologies of the EP device and AP device differ significantly from the PVD-device. The PVD device has larger grain-size compared with EP and AP devices. We also noticed some significant lift-off at the Mo/CIGS interface for EP and AP devices prepared from Cu-rich precursor films.

Two devices prepared from EP and AP precursor films were examined by Auger analysis and grazing incident X-ray diffraction (GIXRD) analysis. The PVD addition of the In, Ga, and Se is observed to produce a non-uniform Ga/(In+Ga) distribution. Auger analyses of the cells are presented in Figs. 5 and 6. The Auger analysis shows non-uniform distribution of Ga in the absorber.

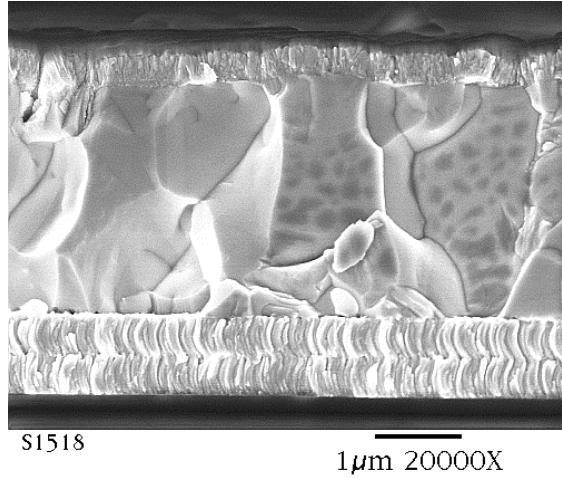


Figure 3: SEM image of a PVD-device.

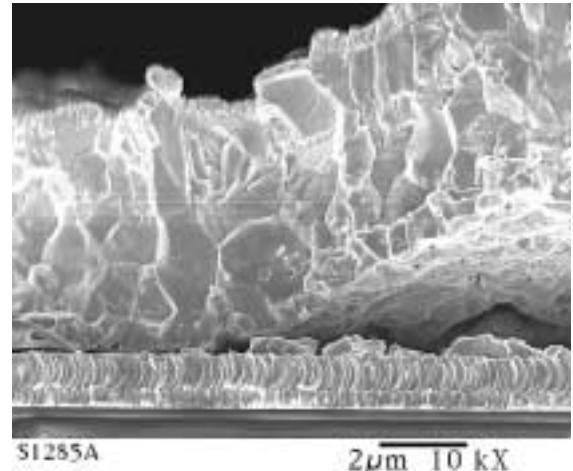


Figure 4: SEM image of a representative EP device (AP device has similar morphology).

These non-uniform distributions lead to two different phase formations, which are confirmed using GIXRD, presented in Figs. 7 and 8. Normal penetration depths for different incident angles, Ω , are indicated for each scan. X-ray diffraction of the AP device and EP device reveals a peak splitting in the (204/220) and (116/312) peaks of the CIGS. This indicates the existence of two phases of different compositions within the film when Ga is added by PVD. GIXRD has revealed a Ga-rich CIGS phase near the surface of these films [9], correlating with the Ga hump in the Auger analysis. This is due to a material of higher Ga composition existing on the surface from the second-stage PVD addition. The Ga hump is not helpful for the hole

collection. We expect to improve the device efficiencies by optimizing Ga distribution in the absorber layers. The optimized layers should have less Ga in the front and more Ga on the back, which facilitates hole collection.

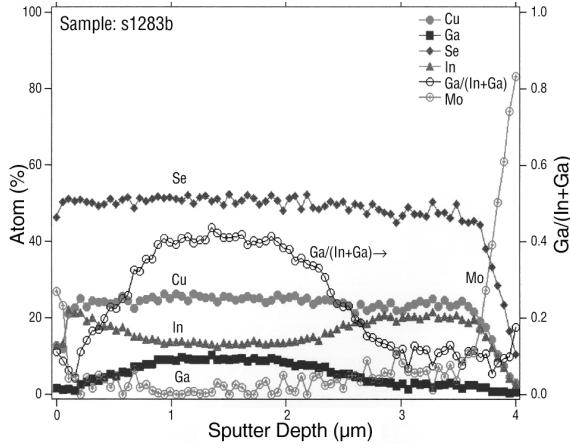


Figure 5: Auger analysis of AP device (12.4%).

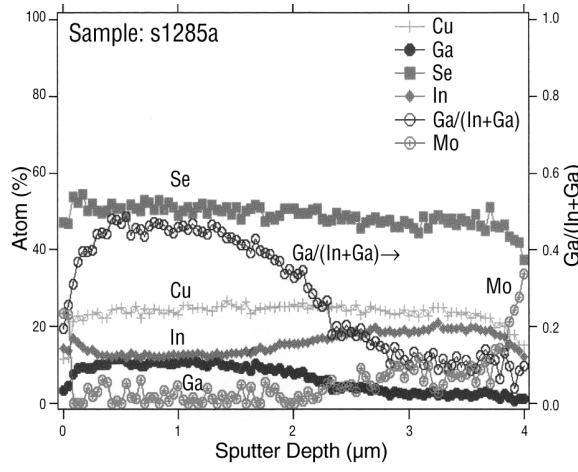


Figure 6: Auger analysis of EP device (15.4%).

We carried out DLTS measurements to estimate trap levels in CIGS thin-film solar cells. Deep-level impurities in CIGS solar cells grown by PVD, EP, and AP were investigated by using capacitance-voltage (C-V) and DLTS [10]. C-V profiling was used to determine the net carrier-concentration profile. The net carrier concentration was obtained at a frequency of 100 kHz and shown in Fig. 9. DLTS spectra were recorded at reverse and forward bias modes in the temperature range of 80–350 K. In the reverse bias mode, the devices were reverse biased from -1.2 V to -0.2 V, with a pulse width of 1 ms. Two hole (majority carrier) trap levels were found in all the devices. These levels are designated as H1 at $E_v+0.26$ and H2, for which its activation energy could not be resolved. Upon minority carrier injection (forward bias mode), DLTS showed two additional electron (minority carrier) traps that are labelled E1 ($E_c-0.1$ eV) and E2 ($E_c-0.83$ eV), as shown in Figure 10. The spectra were measured at an emission time of 465.2 sec $^{-1}$, and the width of the filling pulse was 1 ms. The trap concentration and activation energy of each

trap is summarized and tabulated in Table 1. The E1 trap level was detected in all of the devices, whereas, the E2 level was observed only in the AP device that had a lower efficiency of 12.4 %. We believe that the E2 trap level is an effective recombination center. The calculated Shockley-Hall-Read (SHR) lifetime of the E2 trap level, using the appropriate thermal velocity, capture cross-section, and trap density, is found to be about 0.5 ns. Previously, the H1 and E1 trap levels in CIS were reported by several groups [11-13], but not the E2 trap level.

Table 2 summarizes the device parameters of all the devices described in this paper. The device efficiencies were measured at the National Renewable Energy Laboratory under standard reporting conditions (1000 W/m 2 , 25°C, ASTM E 892 Global).

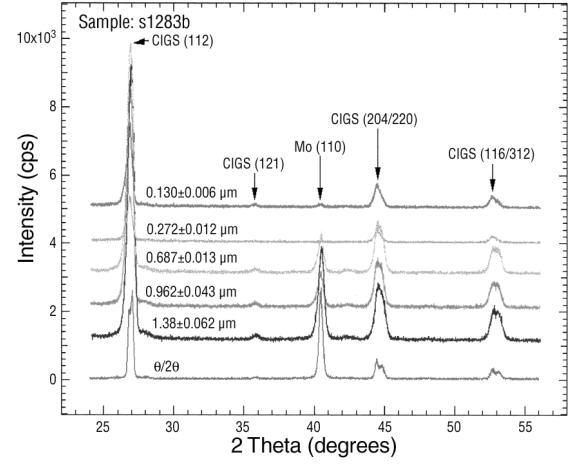


Figure 7: GIXRD and $\theta/2\theta$ of AP device (12.4%).

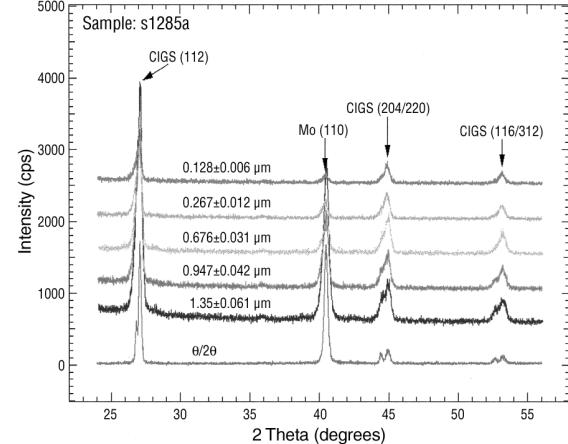


Figure 8: GIXRD and $\theta/2\theta$ of EP device (15.4%).

4. CONCLUSION

The EP and AP deposition processes are low-cost technologies. The device fabricated using EP precursor layers resulted in total-area conversion efficiencies up to 15.4%. The quality of CIGS-based films and devices prepared from EP and AP precursors is very promising. We are optimizing the processing conditions to eliminate or minimize the PVD stage.

Table I: Trap concentration and activation energy of each trap measured by DLTS.

Devices	Trap Level	Energy Level (eV)	Trap Concentration (cm^{-3})
PVD	E_1	$E_c - 0.1$	2.1×10^{14}
	H_1	$E_v + 0.26$	2.7×10^{14}
EP-15.4%	E_1	$E_c - 0.09$	8.4×10^{14}
	H_1	$E_v + 0.27$	1.2×10^{13}
EP-13.4%	E_1	$E_c - 0.09$	1.2×10^{15}
	H_1	$E_v + 0.26$	1.5×10^{14}
AP-12.4%	E_1	Not resolved	6.6×10^{14}
	H_1	$E_v + 0.26$	3.2×10^{14}
	E_2	$E_c - 0.83$	2.1×10^{14}

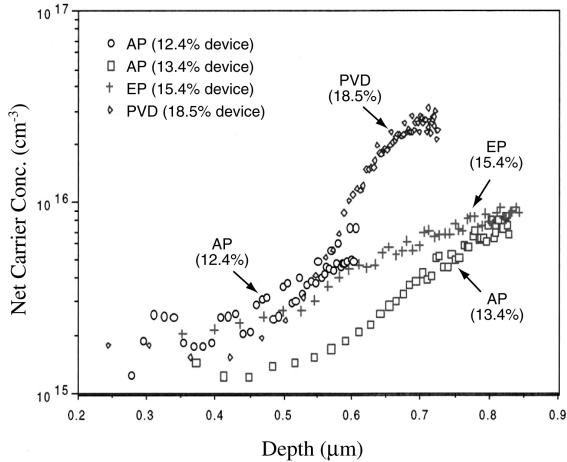


Figure 9: The net carrier concentration vs. depth for the devices measured by C-V.

Table 2: Parameters of the devices prepared from EP-precursors, AP-precursors, and also from PVD device.

Device	V_{oc} (V)	I_{sc} (mA/cm²)	FF(%)	Efficiency(%)
PVD	0.679	35.00	77.75	18.5
EP-15.4%	0.666	30.51	75.6	15.4
AP-13.4%	0.686	29.29	66.87	13.4
AP-12.4%	0.565	33.27	66.1	12.4

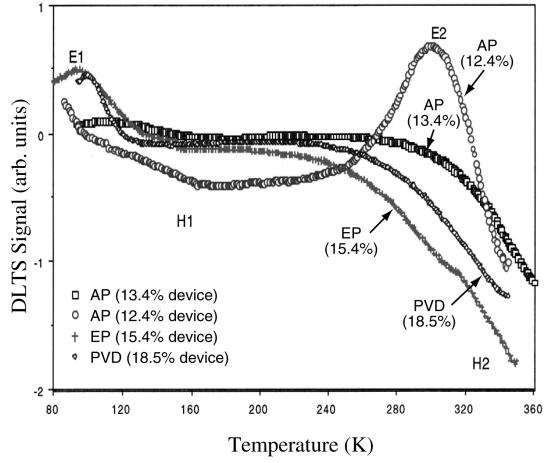


Figure 10: DLTS spectra of n^+ - p CIGS devices at a bias voltage of -0.8 V to $+0.2$ V (forward bias mode).

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