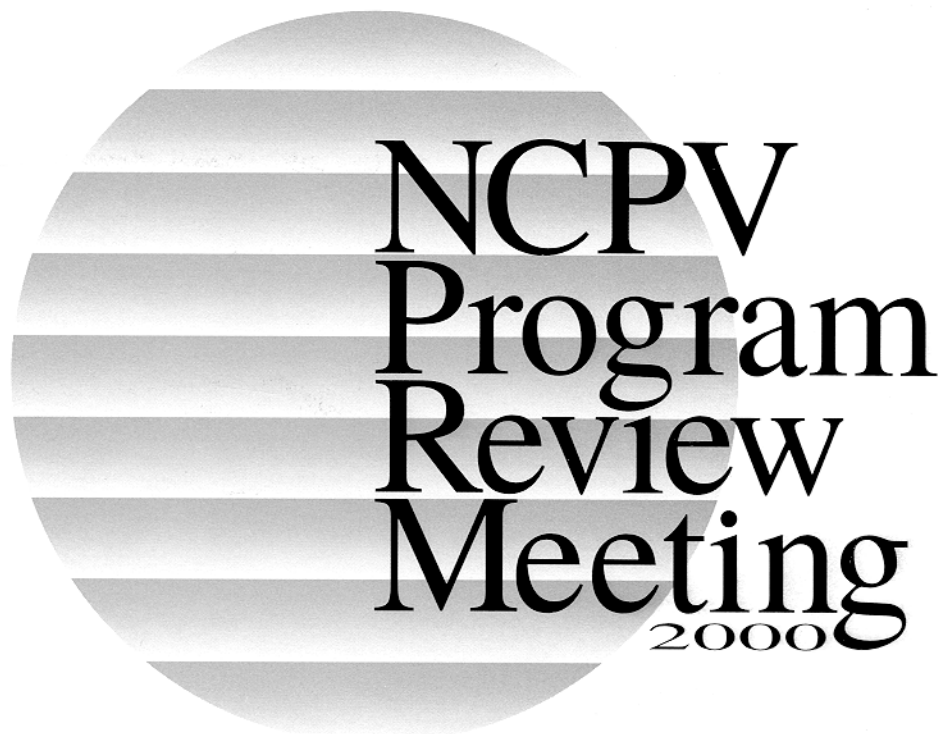


# ***PROGRAM AND PROCEEDINGS***



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# CuIn<sub>1-x</sub>Ga<sub>x</sub>Se-Based Solar Cells Prepared from Electrodeposited and Electroless-deposited Precursors

W. K. Batchelor<sup>a,b</sup> and R.N. Bhattacharya<sup>a</sup>

<sup>a</sup>National Renewable Energy Laboratory, 1617 Cole Blvd., Golden, CO 80401, USA

<sup>b</sup>Department of Physics, Colorado School of Mines, Golden, CO 80401, USA

## ABSTRACT

Three devices were fabricated from electrodeposited (ED) and electroless-deposited (EL) precursors. Compositions were adjusted with additional In and Ga by physical vapor deposition (PVD) for an ED and an EL device. A third, an ED device, was adjusted with only In. Auger analysis and grazing incidence X-ray diffraction (GIXRD) reveal a non-uniform Ga/(In+Ga) distribution when In and Ga are both added whereas a uniform distribution is observed when only In is added.

## 1. Introduction

Thin-film solar cell technology has proven to be a promising alternative to silicon solar cells popular today in many applications. CuIn<sub>1-x</sub>Ga<sub>x</sub>Se<sub>2</sub> (CIGS) has become one of the leaders in this field. Its large optical absorption coefficient, known long-term stability [1], and relatively good diffusion length has brought this material to the forefront. Electrodeposition (ED) and electroless deposition (EL) are two potential low-cost and scaleable techniques that have proven to yield high-quality CIGS thin-film solar cells. We have produced cells with efficiencies of 15.4% and 12.4%, respectively, from precursors deposited by ED and EL techniques. These completed cells have been examined and compared to 17.7% and 18.8% PVD cells by current voltage, capacitance voltage, and spectral response in previous articles [2,3].

## 2. Experimental

Both the ED and EL precursors are deposited from an acidic (pH~2) bath containing 0.02-0.05M CuCl<sub>2</sub>, 0.04-0.06M InCl<sub>3</sub>, 0.01-0.03M H<sub>2</sub>SeO<sub>3</sub>, 0.08-0.1M GaCl<sub>3</sub>, and 0.7-1M LiCl dissolved in deionized water. Cu, In, Ga, and Se are codeposited at room temperature onto the substrate in a vertical cell; i.e., the electrodes are suspended from the top of the cell. The ED 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 is the substrate. The substrate typically used is glass DC-sputtered with about 1 μm of Mo. A constant potential of -1.0 V is applied between the working and counter electrodes with a potentiostat. The EL precursor films are prepared by shorting the substrate to an oxidizing counter electrode such as Fe or Zn. Oxidation of the metal at the counter electrode causes a reduction of the Cu, In, Ga, and Se at the substrate. The precursors are subsequently rinsed in deionized water and dried in flowing nitrogen. The ED and EL films are nearly identical in precursor quality.

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<sub>1-x</sub>Ga<sub>x</sub>Se<sub>2</sub>. 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 radio-frequency sputtered intrinsic ZnO, 350 nm of Al-doped ZnO, and bilayer Ni/Al top contacts deposited by e-beam. Finally, 100 nm of a MgF<sub>2</sub> layer is deposited to minimize reflection.

## 3. Results and discussion

Three different devices were examined: an EL cell to which 2500Å Ga and 5800Å In were added (S1283b), an ED cell to which 3000Å Ga and 7200Å In were added (S1285a), and an ED cell to which only 2300Å In was added (S1482a). The electrical characteristics of the finished devices are described in Table 1.

Table 1: Electrical Characteristics of ED and EL Devices

Cell	EL device S1283b	ED device S1285a	ED device S1482a
V <sub>oc</sub> (V)	0.565	0.666	0.429
J <sub>sc</sub> (mA/cm <sup>2</sup> )	33.27	30.51	36.04
FF (%)	66.1	75.6	58.37
Efficiency (%)	12.4	15.4	9.0

The differences in device performance are likely due to the second-stage PVD addition. The addition of the In, Ga, and Se is observed to produce a non-uniform Ga/(In+Ga) distribution in cases where In and Ga are both added, whereas a uniform distribution is observed when only In is added. The gradient created in Ga composition can create a band-gap gradient, which can enhance the V<sub>oc</sub>, fill factor and, in turn, the efficiency. Auger analysis of the cells can be seen in Figs. 1, 2, and 3.

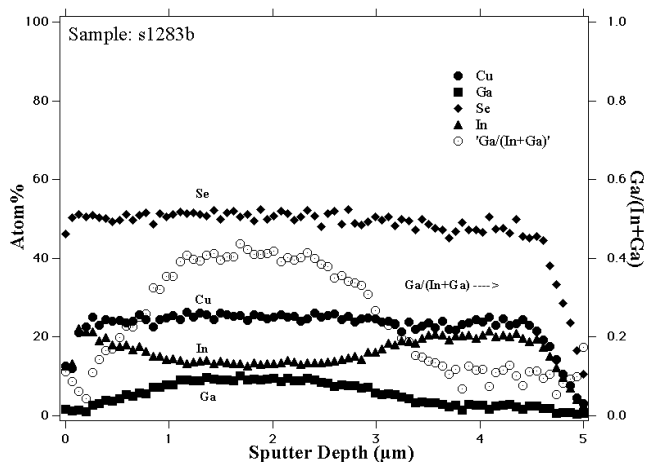


Fig. 1: Auger analysis of EL device S1283b

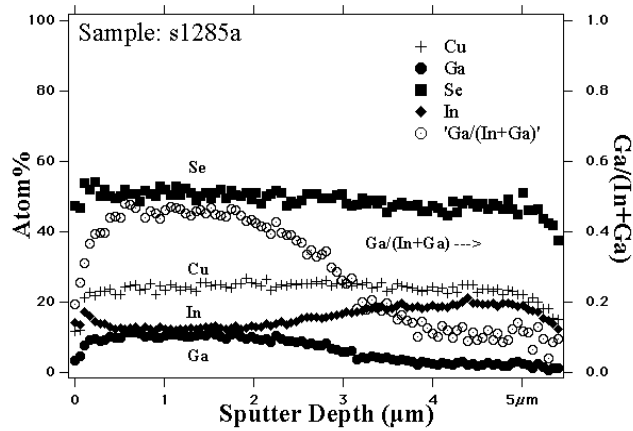


Fig. 2: Auger analysis of ED device S1285a

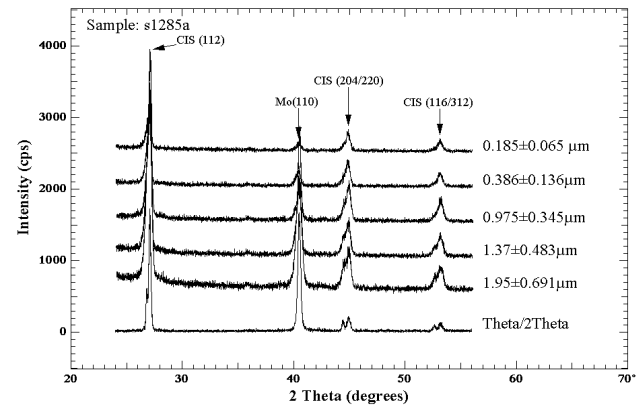


Fig. 5: GIXRD and Theta/2Theta of ED device S1285a

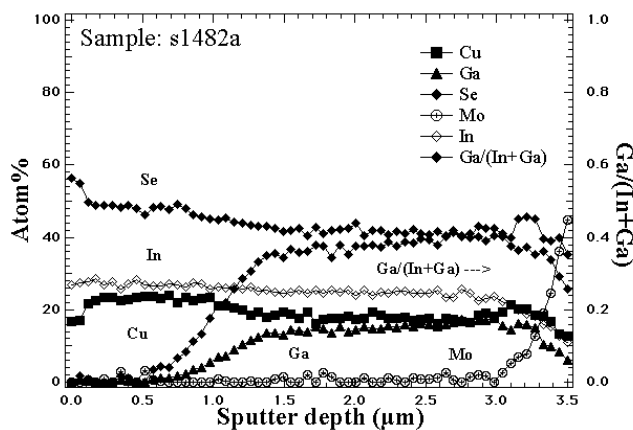


Fig. 3: Auger analysis of ED device S1482a

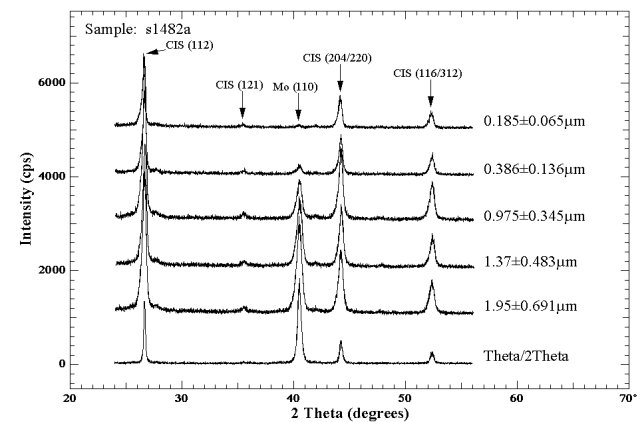


Fig. 6: GIXRD and Theta/2Theta of ED device S1482a

These observations were also confirmed using grazing incidence X-ray diffraction (GIXRD), observed in Figs. 4, 5, and 6. Normal penetration depths for different incident angles,  $\square$  are indicated for each scan. X-ray diffraction of S1283b and S1285a reveals a peak splitting in the (204/220) and (116/312) peaks of the CIGS that is not observed in S1482a. This indicates the existence of two phases of different compositions within the film when Ga is added by PVD. GIXRD has revealed only one phase on the surface of these films [4,5], 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.

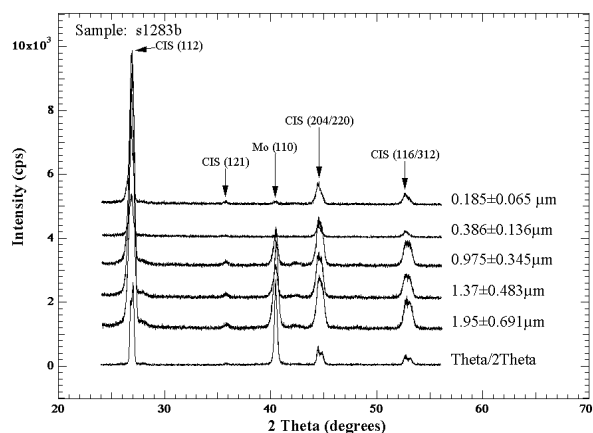


Fig. 4: GIXRD and Theta/2Theta of EL device S1283b

#### 4. Conclusion

ED and EL are able to produce high-quality CIGS precursors for solar cell production. Second-stage PVD additions of In are uniformly incorporated into the precursors, but Ga is not as easily incorporated into the final polycrystalline structure, yielding gradients in Ga composition throughout the films that alters the device performance.

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