

# **15.4% $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ -Based Photovoltaic Cells from Solution-Based Precursor Films**

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# 15.4% $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ -BASED PHOTOVOLTAIC CELLS FROM SOLUTION-BASED PRECURSOR FILMS

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## Abstract

We have fabricated 15.4%- and 12.4%-efficient  $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$  (CIGS)-based photovoltaic devices from solution-based electrodeposition (ED) and electroless-deposition (EL) precursors. As-deposited precursors are Cu-rich CIGS. Additional In, Ga, and Se are added to the ED and EL precursor films by physical vapor deposition (PVD) to adjust the final film composition to  $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ . The ED and EL device parameters are compared with those of a recent world record, an 18.8%-efficient PVD device. The tools used for comparison are current voltage, capacitance voltage, and spectral response characteristics.

## Keywords

Electrodeposited, Electroless deposited,  $\text{CuIn}_{1-x}\text{Ga}_x\text{Se}_2$ , Physical vapor deposition.

## Introduction

Currently, a great deal of effort is being made to develop low-cost technologies for fabricating CIGS thin films.<sup>1, 2</sup> Several research groups<sup>3-6</sup> have demonstrated high-efficiency CIGS solar cells using physical vapor deposition (PVD) and sputtering techniques. The recent record-breaking 18.8% efficient  $\text{Cu}(\text{In,Ga})\text{Se}_2$ -based device fabricated in our research laboratory is based on a multistep

process using PVD.<sup>3</sup> The PVD method is an excellent tool for understanding film growth and for developing models. The PVD technique is challenging to scale up. Electrodeposition (ED) and electroless-deposition (EL) are potentially suitable preparation methods to obtain the low-cost precursor films. The ED and EL processes could provide: (a) a low-cost, high-rate process; (b) a large-area, continuous, multi-component, low-temperature deposition method; (c) deposition of films on a variety of shapes and forms (wires, tapes, coils, and cylinders); (d) freedom from the requirement or need to use expensive equipment; (e) controlled deposition rates and effective material use; and (f) minimum waste generation (solution can be recycled).

The devices fabricated using ED and EL CIGS precursors resulted in efficiencies of 15.4 % and 12.4%, respectively. The quality of CIGS-based films and devices prepared from the solution-based ED and EL precursor films is very promising. The ED and EL device parameters are compared with those of an 18.8%-efficient PVD device.

## Experimental

Codepositions of Cu-In-Ga-Se by the ED and EL processes were performed from a bath containing 0.02–0.05 M CuCl<sub>2</sub>, 0.04–0.06 M InCl<sub>3</sub>, 0.01–0.03 M H<sub>2</sub>SeO<sub>3</sub>, 0.08–0.1 M GaCl<sub>3</sub> and 0.7–1 M LiCl dissolved in deionized water. The films were deposited in a vertical cell in which the electrodes (both working and counter) were suspended vertically from the top of the cell. The ED precursors were prepared by using a three-electrode cell in which the reference electrode was Pt (pseudo-reference), the counter electrode was a Pt gauze, and the substrate was Mo/glass. The films were electroplated by applying a constant potential of –1.0 V. A Princeton Applied Research potentiostat/galvanostat Model 273 A with an IBM PC AT computer interface was used for the preparation of ED precursor films. The EL precursor films were prepared using Fe as an oxidizing counter electrode. The Mo film on glass substrate was about 1 μm thick and was deposited by DC sputtering. The ED and EL deposition experiments were performed at room temperature (24°C) and without stirring. The deposited films were rinsed with deionized water and dried in flowing N<sub>2</sub>.

The as-deposited precursors are Cu-rich CIGS films. Additional In, Ga, and Se were added to the precursor films by PVD to adjust the final composition to CuIn<sub>1-x</sub>Ga<sub>x</sub>Se<sub>2</sub>. The substrate (precursor film) temperature during the PVD step was 560° ± 10°C. The films were also selenized by exposure to selenium vapor during the cool-down time (~40°C/min). At present, addition of In and Ga and also selenization at high temperature are very crucial to obtain high-efficiency devices from ED and EL precursor films.

The PVD CIGS absorber is deposited in several stages.<sup>7</sup> First, (In<sub>1-x</sub>Ga<sub>x</sub>)<sub>2</sub>Se<sub>3</sub> [In/(In+Ga) = 0.30] is deposited at a substrate temperature of 350 ± 10°C. In the second stage, Cu-Se is deposited at a substrate temperature of 550° ± 10°C to form a Cu-rich CIGS layer. In the third stage, the Cu-rich CIGS precursor is converted to photovoltaic-quality material by exposure to (In<sub>1-x</sub>Ga<sub>x</sub>)<sub>2</sub>Se<sub>3</sub> [In/(In+Ga) = 0.25] at 550° ± 10 °C, which enhances the formation of a (In, Ga)-rich surface phase. The final absorber composition is about 0.86 ≤ Cu/(In+Ga) ≤ 0.96.

Photovoltaic devices were completed by chemical-bath deposition of about 50 nm CdS, followed by radio-frequency (RF) sputtering of 50 nm of intrinsic ZnO, and 350 nm of Al<sub>2</sub>O<sub>3</sub>-doped conducting

ZnO. Bilayer Ni/Al top contacts were deposited in an e-beam system. The final step in the fabrication sequence is the deposition of an antireflection coating (100 nm MgF<sub>2</sub>). The final device configuration for all devices is MgF<sub>2</sub>/ZnO/CdS/CuIn<sub>1-x</sub>Ga<sub>x</sub>Se<sub>2</sub>/Mo.

## Results and Discussions

The electrodeposition of CIGS films (pH ~ 2) on cathodes is most likely caused by the combination of electrochemical and chemical reactions as follows:



The electroless process for preparing CIGS precursor films is accomplished by the combination of electrochemical and chemical reactions. The counter-electrode (Fe) initiates the electrochemical reaction. The electroless deposition of CIGS is most likely caused as follows:

### E° vs SHE

Fe $\rightleftharpoons$ Fe <sup>2+</sup> + 2e	-0.447	(4)
Cu <sup>+</sup> + e $\rightleftharpoons$ Cu	0.521	(5)
Cu <sup>2+</sup> + 2e $\rightleftharpoons$ Cu	0.342	(6)
In <sup>3+</sup> + 3e $\rightleftharpoons$ In	-0.338	(7)
Ga <sup>3+</sup> + 3e $\rightleftharpoons$ Ga	-0.549	(8)
SeO <sub>3</sub> <sup>2-</sup> + 3H <sub>2</sub> O + 4e $\rightleftharpoons$ Se + 6 OH <sup>-</sup>	-0.366	(9)
Cu, In, Ga, Se $\rightleftharpoons$ Cu <sub>x</sub> In <sub>y</sub> Ga <sub>z</sub> Se <sub>n</sub>	Chemical reaction	(10)

The required reduction potential of Ga is higher than the oxidation potential of an Fe electrode. The deposition potential is composed of the equilibrium reduction potentials (E<sub>eq</sub>), the overpotential, and the ohmic potential drop (iR<sub>s</sub>) in the solution. The rest potential of the deposition bath solution is about 0.3 V. The applied potential (E) during codeposition of Cu-In-Ga-Se using Fe electrode is (0.447 + rest potential), which probably make the Ga deposition possible.

The composition of the as-deposited ED and EL precursors precursor as analyzed by inductively coupled plasma analysis (ICP) was CuIn<sub>0.32</sub>Ga<sub>0.01</sub>Se<sub>0.93</sub> and CuIn<sub>0.35</sub>Ga<sub>0.01</sub>Se<sub>0.99</sub>, respectively. The thickness of the ED and EL precursor films was about 2.2 and 1.5 μm, respectively. The composition of the ED precursor film was adjusted by adding about 3000 Å Ga and 7200 Å In by PVD step. The composition of the EL precursor film was adjusted by adding about 2500 Å Ga and 5800 Å In by PVD step. The final compositions of the CIGS absorber films prepared from ED and

EL precursors, as determined by ICP and electron-probe microanalysis, are  $\text{CuIn}_{0.72}\text{Ga}_{0.47}\text{Se}_{2.05}$  and  $\text{CuIn}_{0.83}\text{Ga}_{0.22}\text{Se}_{1.93}$ , respectively.

The Ga/(In+Ga) ratios, as determined by inductively coupled plasma and electron-probe microanalysis, are 0.40, 0.20, and 0.28 for the ED, EL, and PVD cells that will be compared, resulting in band gaps,  $E_g$ , of 1.20 eV, 1.09 eV, and 1.12 eV, respectively. Figure 1a shows the current density-vs.-voltage (J-V) curves of the devices. The device prepared from ED precursor film seems to compare well with the 18.8%-efficient PVD device in open-circuit voltage ( $V_{oc}$ ), and less well in short-circuit current ( $J_{sc}$ ), however, because of the band gap energy difference of 80 mV, one would expect a higher voltage in the ED device if all other qualities of the junction were equal. Quantum efficiency (QE) results are shown in Figure 1b. The ED cell shows comparable collection with the PVD device in the 500–1000-nm range, while the EL cell shows less collection in the same range for its band gap. This indicates an improvement in the carrier diffusion length in the ED cell in comparison with the EL cell. The different QE cutoffs in the red indicate the different band gaps, which are assumed to be due to variations in Ga content. The capacitance-voltage (C-V) results, Figure 1c, show a fairly uniform dopant density of  $10^{16} \text{ cm}^{-3}$  for the ED cell and  $1.5 \times 10^{16} \text{ cm}^{-3}$  for the EL cell. These are both within the typical range for high-quality CIGS cells.

**Table 1. Parameters of the Devices Prepared from Electrodeposition Precursor (ED device), Electroless-Deposition Precursor (EL device) and also from Physical Vapor Deposition (PVD device)**

Cell	ED device	El device	PVD device
Ga/(In+Ga)	0.4	0.20	0.28
Area [ $\text{cm}^2$ ]	0.418	0.418	0.432
$V_{oc}$ [V]	0.666	0.565	0.678
$J_{sc}$ [ $\text{mA}/\text{cm}^2$ ]	30.51	33.27	35.2
$V_{max}$ [V]	0.554	0.434	0.567
$J_{max}$ [ $\text{mA}/\text{cm}^2$ ]	27.8	28.6	34.5
FF [%]	75.6	66.1	78.6
$r_{shunt}$ [ $\Omega\text{-cm}^2$ ]	2000	1000	10000
$R_{series}$ [ $\Omega\text{-cm}^2$ ]	0.3	0.1	0.2
Ideality Factor [A]	1.8	2.5	1.5
Depletion Width [ $\mu\text{m}$ ]	0.2	0.25	0.5
Hole Density [ $\text{cm}^{-3}$ ]	$1 \times 10^{16}$	$1.5 \times 10^{16}$	$1 \times 10^{16}$
Band Gap [eV]	1.20	1.09	1.12
Efficiency [%]	15.4	12.4	18.8

Electrical characterization data of the devices prepared from ED precursors are listed in Table 1. Electrical characterization of the devices included current-voltage in the dark and under AM 1.5, 100-mW/ $\text{cm}^2$  illuminated conditions, QE, and C-V measurements. Resistance and diode-quality parameters were extracted from the J-V data. The shunt resistance ( $r_{shunt}$ ) is a measure of leakage

and is indicated by the slope of the J-V curve in reverse bias. The devices prepared from ED and EL precursors demonstrate slight leakage in the light, with shunt resistances of 1000–2000 ohm-cm<sup>2</sup>, as compared to the PVD device, with a higher value of 10000 ohm-cm<sup>2</sup>. Series resistance ( $R_{\text{series}}$ ) is indicative of the quality of the bulk material, whereas the diode-quality factor (A) indicates whether there is significant excess forward current through recombination states and hopping paths. Both of these quantities are extracted from the region of the curve between the maximum power point and open-circuit voltage.<sup>8</sup> As with shunting, the series resistance is not a significant factor for any of the cells. The quality factor of the EL device, however, is much greater than the other two. This is illustrated in Figure 1d, showing logarithmic forward-current comparisons with resistive losses removed. The more shallow slope for the EL device corresponds to a higher quality factor. The more ideal quality factor for the ED device, along with its higher  $V_{\text{oc}}$  and improved diffusion length, indicates that the ED process yields an improved material quality compared with the EL process.

**Table 2. Comparison of Primary ED and EL Parameters with the Record 18.8%-Efficient PVD Cell**

	ED vs. PVD (adjusted for $E_g$ )	EL vs. PVD (adjusted for $E_g$ )
Efficiency Difference [%]	3.4 (3.4)	6.4 (6.4)
Difference from $V_{\text{oc}}$ [%]	0.3 (1.4)	2.5 (2.1)
Difference from $J_{\text{sc}}$ [%]	2.3 (1.2)	0.8 (1.2)
Difference from FF [%]	0.8 (0.8)	3.1 (3.1)

Table 2 shows the relative contributions of the primary solar-cell parameters to the lower performance seen in ED and EL cells. The differences in voltage and current can be misleading if cells of different band gap are compared, and hence the second values in parenthesis, which are the performance differences for a common band gap. The second values show, in comparison with the PVD device, (a) somewhat smaller voltages attributed to the excess forward current, with a larger difference for the EL cells, (b) somewhat smaller currents primarily due to lower collection of carriers created by the more penetrating infrared photons, and (c) a small fill-factor (FF) difference for the ED cell, but a major one for the EL cell, due to the increased diode quality factor.

## Conclusion

The ED and EL processes are simple and fast, and they can synthesize binary or multinary precursors for subsequent processing into high-quality CIGS thin-film absorbers for solar cells. The device fabricated using ED precursor layers resulted in efficiencies as high as 15.4%, and none of the individual parameters showed significant deterioration from those of the PVD CIGS cells. The quality of CIGS-based films and devices prepared from ED precursors is very promising. This may lead to novel, fast, and low-cost methods for solar-cell absorber fabrication.

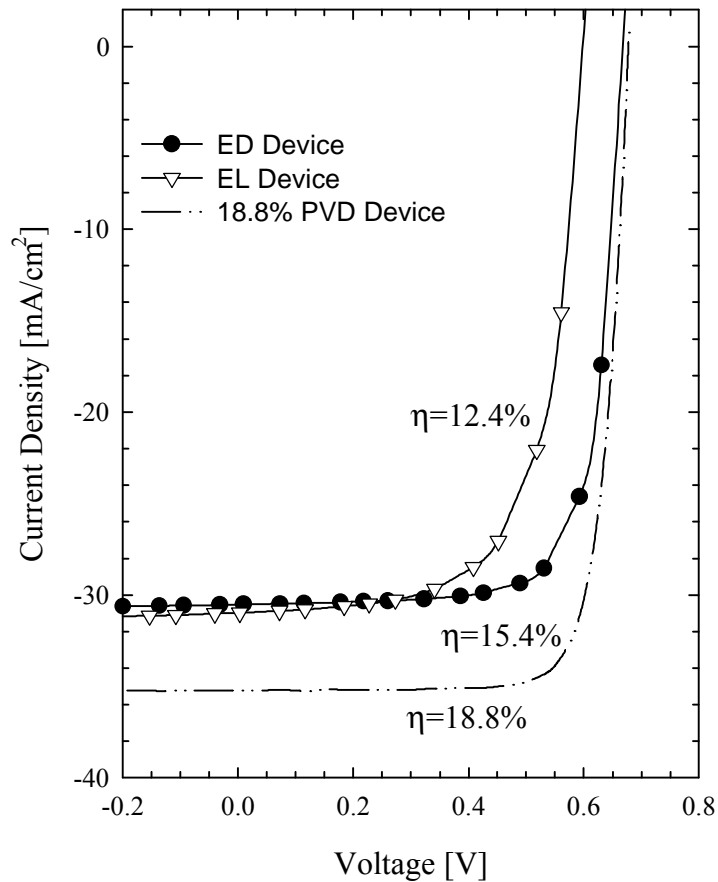


Fig. 1a. Current-voltage (I-V) characteristics of ED, EL, and PVD devices

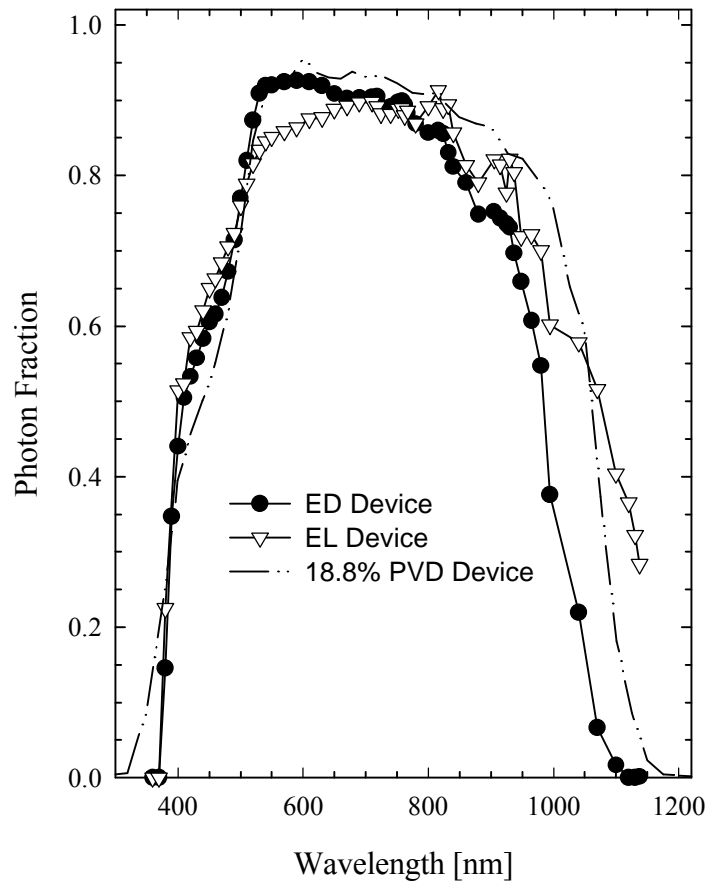


Fig. 1b. Quantum efficiency data

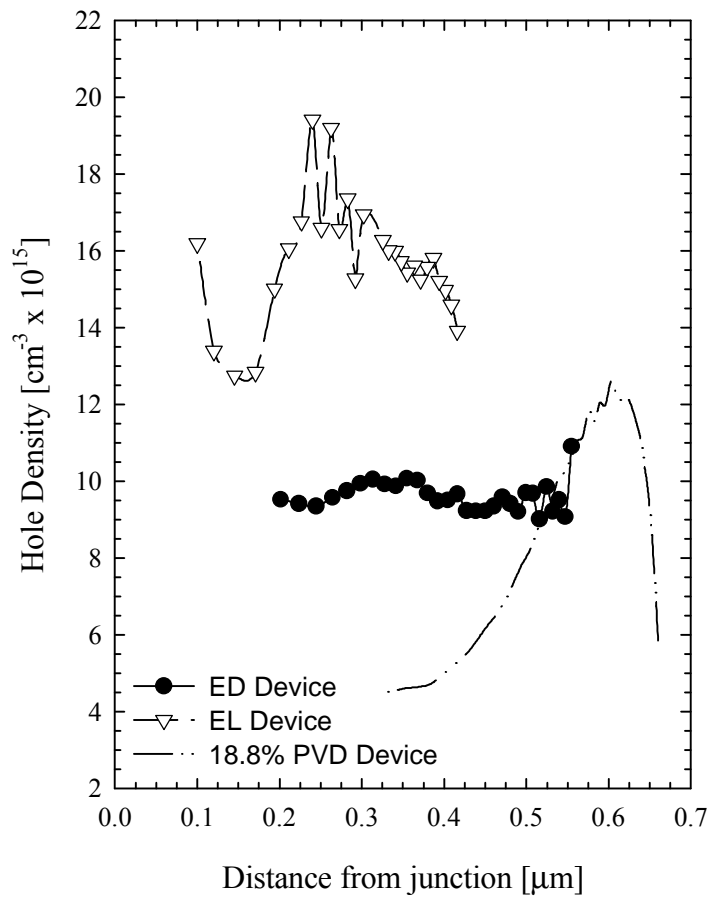
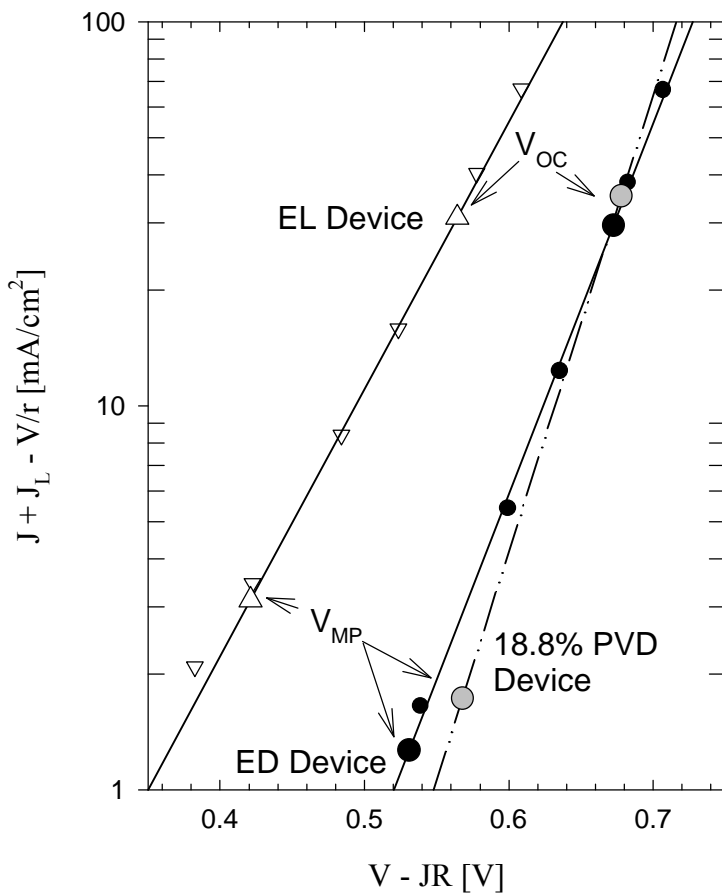


Fig. 1c. Hole density vs. distance curves



6 Fig. 1d. Logarithmic I-V characteristics with resistive losses removed



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