

## Efficient CuInSe<sub>2</sub> Solar Cells Fabricated by a Novel Ink Coating Approach

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A novel technique is developed for the deposition of CuInSe<sub>2</sub> (CIS) thin films for solar cell applications. The technique uses an ink formulation that contains Cu-In metallic pigments. A precursor layer is first formed coating this ink onto the selected substrate. The precursor film is then reacted with Se to form the CIS compound. Solar cells were fabricated on CIS absorber layers prepared by this low cost ink coating approach and devices with a conversion efficiency of over 9.0% were demonstrated.  
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Group I-III-VI materials are considered to be highly promising as absorber layers in high-efficiency thin film solar cell structures. In fact, the highest efficiency thin film device to date was produced on a Cu(In,Ga)Se<sub>2</sub> (CIGS) absorber film grown by a vacuum evaporation technique. The demonstrated conversion efficiency of 17.7% confirmed the capability of this material to yield highly efficient active devices when employed in thin film solar cell structures.<sup>1</sup>

Conversion efficiency is just one of the factors to consider when commercialization potential of a thin film photovoltaic (PV) technology is evaluated. Another factor that is equally important is the cost of the PV product. To make a thin film solar cell technology competitive, first with the existing Si-based PV modules, and then with the traditional methods of electric power generation, one has to develop film growth techniques that can deposit high quality absorber materials and other components of the solar cells on large area substrates, using cost-effective approaches with high yield and high materials utilization.

High-efficiency solar cells have commonly been fabricated on CuInSe<sub>2</sub> (CIS) or CIGS absorbers deposited by costly vacuum deposition techniques such as coevaporation<sup>1</sup> and two-stage processes utilizing evaporation or sputtering.<sup>2</sup> There is presently great interest in the development of new lower cost processing methods for the growth of high quality CIS-type absorbers for thin film solar cell applications.

Slurry or ink deposition by large area nonvacuum coating methods such as screen printing, spraying, curtain coating, roll coating, or doctor blading are attractive low-cost approaches for the growth of thin film solar cell absorbers, provided that the precursor layers obtained by these deposition techniques can be converted into high quality semiconductor films that are required for solar cell fabrication.

There have been several attempts to deposit CIS absorbers using the screen printing technique. For example, Arita et al. described a method that involved (i) mixing pure Cu, In, and Se powders in the compositional ratio of 1:1:2, (ii) milling these powders in a ball mill and forming a screen printable paste, (iii) screen printing the paste on a substrate, and (iv) sintering this precursor film to form the compound layer.<sup>3</sup> Milling of the powder mix was done in a medium such as water or ethylene glycol monophenyl ether to reduce the particle size, and the paste was formed using a propylene glycol binding agent. A precursor film was formed on a high temperature borosilicate glass substrate by the screen printing method. The postdeposition treatment step consisted of annealing the precursor film in nitrogen gas at 700°C. As a result, a compound film was formed on the substrate. For evaluating the electronic properties of the resulting compound, the authors fabricated CdS/CIS solar cells, but the reported conversion efficiencies of such devices were lower than 1%. X-ray diffraction (XRD) data from Arita et al. indicated that indium powder partially oxidized during the milling process when water was used as the solvent, and that Cu, In, and Se reacted with each other to some extent forming CIS particles in the ink.

Thin layers of CIS deposited by screen printing were also studied by Vervaet et al. who (i) milled a CIS powder for particle size reduction, (ii) added excess Se powder and other agents such as 1,2-propanediol into the formulation to prepare a screen printable paste, (iii) screen printed precursor layers onto borosilicate and alumina substrates, and (iv) sintered the precursor layers at high temperature (>500°C) to form the compound films.<sup>4</sup> The major problem in this approach was finding a suitable sintering aid or fluxing agent for CIS film formation. Among many agents studied, Cu-selenide was the best for grain growth. But films containing this phase could not be used for solar cell fabrication since they had Cu/In ratios larger than 1.0. More recently, the same research group experimented with CuTiSe<sub>2</sub>, a compound with a melting point of about 400°C, as a fluxing agent and demonstrated grain growth for films with Cu/(In+Ti) ratios in the acceptable range of 0.9-1.0. However, the solar cells fabricated on the resulting layers were still poor with conversion efficiencies of only about 1%. The sintering temperature >600°C used in this process was also high for low-cost glass substrates.

As can be seen from the review of previous work, the nature of the ingredients in the formulation of a paste or an ink is very important for the formation of a precursor layer which can later be converted into a high quality CIS-type compound film with properties that are desirable for solar cell applications. In this article we report a low-cost ink coating technique that was successfully employed for the deposition of CIS absorbers that could be used for the fabrication of over 9% efficient thin film solar cells.

### Experimental

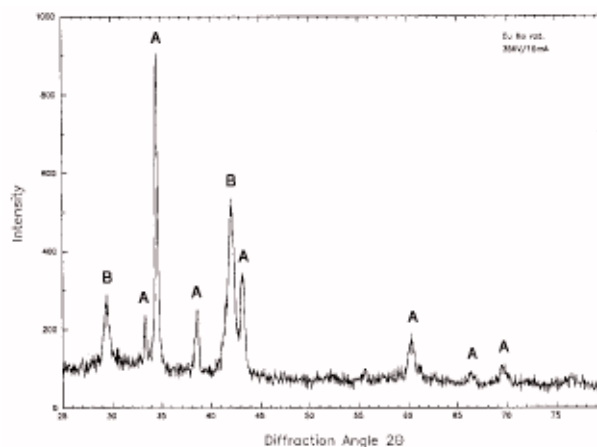
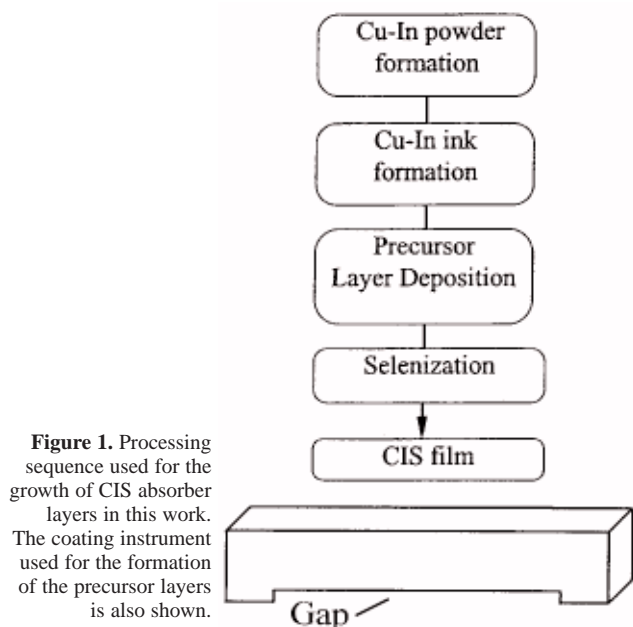
The general steps of the low-cost process used in this work for the growth of thin film CIS absorbers are schematically shown in Fig. 1. As can be seen from this figure, the method involves preparation of a metallic powder, formation of a metallic ink using the powder, deposition of this ink in the form of a thin metallic precursor layer over a substrate, and finally, reaction of the metallic precursor layer with gaseous selenium at high temperatures to form the CIS compound.

The source of Cu and In in this work was a Cu-In alloy powder with a preselected and fixed Cu/In stoichiometric ratio. The Cu-In alloy powder was obtained by the melt atomization technique. To prepare the powder, 99.99% pure Cu and 99.99% pure In were melted under a hydrogen curtain at above 900°C. The Cu/In ratio of the melt corresponded to the targeted value range of 0.87-0.9. The melted alloy was transformed into powder in a gas atomizer employing Ar as the quenching gas. Quenched powder was collected at the bottom of the reactor and sieved to separate the particles that were smaller than 20 μm in size which were used in this work as the pigment.

About 10 g of the Cu-In pigment was mixed with 23 g of water. A small amount (about 1.5 wt %) of a wetting agent and dispersant were added to this aqueous formulation. The mixture was milled in a ball mill for 42 h. The resulting metallic ink was water-thin. Particle size analysis was done on a sample of this ink using a

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**Figure 2.** XRD data taken from a precursor film deposited on a glass substrate. Peaks associated with the  $\text{CuIn}_2$  and  $\text{Cu}_{11}\text{In}_9$  phases are labeled as A and B, respectively.

### Results and Discussion

As indicated above, the largest particle size in the Cu-In alloy powder used here was  $20\ \mu\text{m}$ . After this powder was milled into an ink the largest particle size was  $2.0\ \mu\text{m}$ , the mean particle size was about  $0.5\ \mu\text{m}$ .

Figure 2 shows the XRD data obtained from a metallic precursor layer deposited on a soda-lime glass substrate using the  $150\ \mu\text{m}$  edge of the coating cup. The dried thickness of this layer as measured by a surface profilometer was about  $20\ \mu\text{m}$ . By depositing a relatively thick film on a plain glass substrate the phase content of the ink could easily be determined. All of the peaks in the data of Fig. 2 are identified and indexed to the known In-rich and Cu-rich alloy phases of  $\text{CuIn}_2$  (peaks labeled A, Ref. 7) and  $\text{Cu}_{11}\text{In}_9$  (peaks labeled B, JCPDS card 41-883). Based on the fixed Cu/In ratio in the starting alloy powder, the molar ratio of the  $\text{CuIn}_2$  phase to the  $\text{Cu}_{11}\text{In}_9$  phase in the precursor layer is expected to be about 3.6.

There are no peaks associated with  $\text{In}_2\text{O}_3$  in the diffraction pattern of Fig. 2. It is interesting to note that previous work on milling Cu, In, and Se powders in water-based solvents resulted in the formation of an  $\text{In}_2\text{O}_3$  phase as reported by the XRD data of Arita et al., indicating excessive oxidation of indium in the water-based formulation.<sup>3</sup> In our approach, indium is in the form of Cu-In alloys. Oxidation of indium which is tied in an alloy phase is expected to be less energetically favorable compared to the oxidation of pure indium, and this is confirmed by the data of Fig. 2. As evidenced by the particle size analysis results, the milling step has been effective in reducing the size of the relatively brittle Cu-In alloy particles. Pure indium powder is soft and when milled in a ball mill, it forms platelets that coat the milling media instead of forming a dispersion. Ease of milling and reduced oxidation during processing in water solutions are some of the attractive and unique features of the pigment chemistry that was developed and employed here.

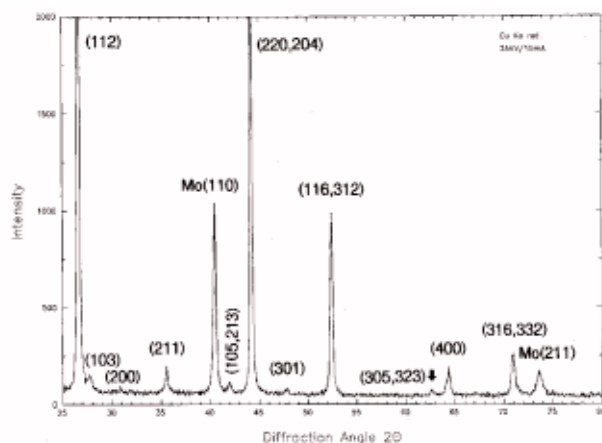
Figure 3 shows the XRD patterns taken from a precursor film selenized in the  $\text{H}_2\text{Se}$  reactor under the conditions previously specified. This film was deposited on a glass/Mo substrate and the thickness of the dried precursor was only about  $3\ \mu\text{m}$ . Two of the reflection peaks in Fig. 3 correspond to the underlying Mo layer as noted on the figure. All the other peaks index well with the chalcopyrite CIS phase (JCPDS card 40-1487) indicating the capability of the present technique to yield single-phase material. The preferred orientation of the compound layer is  $\langle 112 \rangle$  as is commonly observed in films grown by the coevaporation or vacuum-based two-stage processes.

Figure 4 shows the illuminated I-V characteristics and the relative quantum efficiency of a solar cell fabricated on a CIS absorber grown by the ink coating method. The efficiency of this  $0.426\ \text{cm}^2$  area device is 8.6% with the open-circuit voltage ( $V_{oc}$ ), short-circuit current density ( $J_{sc}$ ), and fill factor ( $FF$ ) values of 0.424 V, 31.52

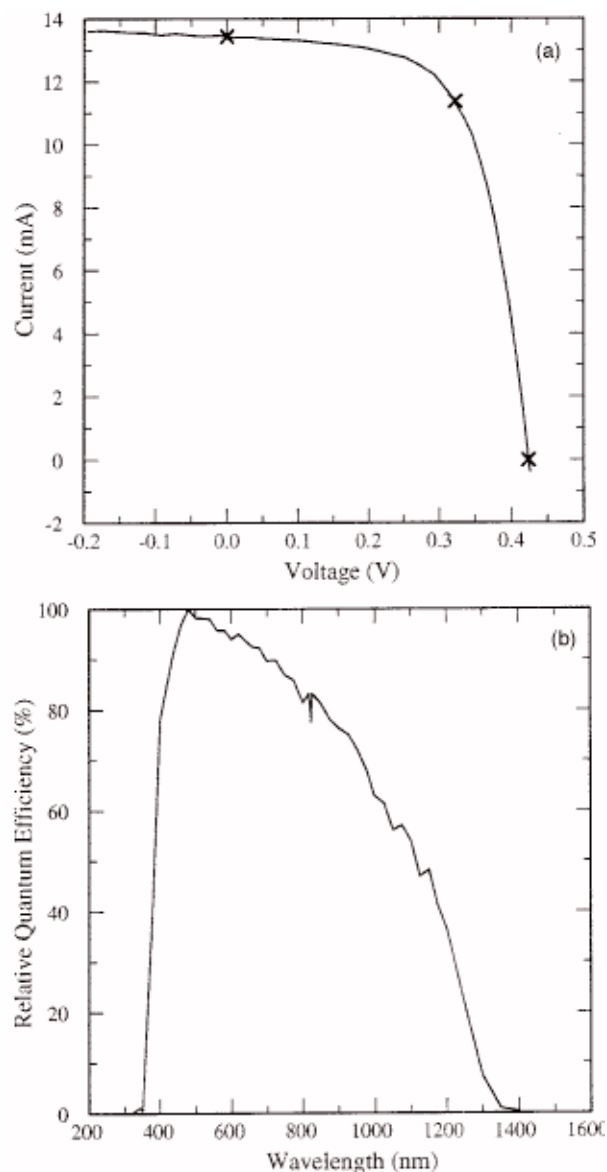
Horiba particle size analyzer. Glass/Mo substrates were prepared by depositing  $0.5\ \mu\text{m}$  thick Mo layers on 3 mm thick soda-lime glass sheets in an in-line dc magnetron sputtering system. Precursor films containing the milled Cu-In metallic pigment were coated over the glass or glass/Mo substrates by the cup-coating (or doctor blading) technique using a few drops of the prepared ink. In this technique the coating instrument was a stainless steel bar of approximately  $1 \times 1 \times 6$  in. The coating edge of this bar was machined so that when the bar was placed on the flat surface of the glass substrate, there was a gap between the bar and the substrate surface as is schematically shown in Fig. 1. A few drops of the Cu-In ink was placed in front of the gap of the bar and the bar was dragged on the substrate. In this way a wet film was formed behind the moving bar. The film thickness in this method is a function of the gap dimension. The cup used in this work had coating edges with openings (gaps) ranging from 12 to  $150\ \mu\text{m}$ , to spread the ink over the surface of the substrate in a uniform manner. In this way, films with various thicknesses could be obtained. After coating, the wet films were dried in an oven at  $60^\circ\text{C}$ .

Selenization of the precursor layers was carried out in a reactor that employed 5%  $\text{H}_2\text{Se} + 95\% \text{N}_2$  gas mixture. Selenization temperature was  $440^\circ\text{C}$  and the selenization time was 30 min. XRD analysis was carried out to determine the phases in the precursor layers as well as the selenized films.

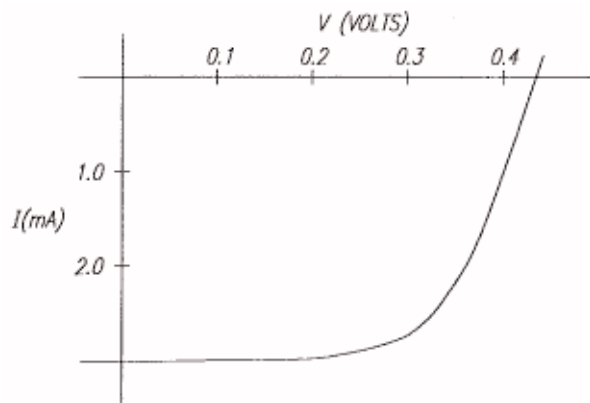
Solar cells with the glass/Mo/CIS/CdZnS/ZnO structure were fabricated on the CIS absorbers by depositing CdZnS buffer layers and ZnO window films. Thin layers ( $500\text{-}1000\ \text{\AA}$ ) of CdZnS with about 10% Zn were coated by the commonly used chemical bath deposition technique. The deposition bath consisted of 5 mL of 0.5 M zinc acetate, 10 mL of 1.0 M cadmium acetate, 7 mL of triethanolamine, 4.5 mL of ammonium hydroxide, and 55 mL of distilled water. The solution was heated to  $55^\circ\text{C}$  and then the glass/Mo/CIS sample was placed in the beaker containing the solution. 12 mL of 1.0 M thiourea was then added to the beaker initiating the CdZnS deposition which lasted 10 min. CdZnS deposition was followed by the deposition of a transparent ZnO layer at  $175^\circ\text{C}$  by the metallorganic chemical vapor deposition technique employing diethyl zinc as the zinc source, water vapor as the oxygen source, and diborane as the n-type dopant.<sup>6</sup> The thickness and the sheet resistance of the ZnO layers were about  $2.5\ \mu\text{m}$  and  $10\ \Omega$  per square, respectively. Solar cells of  $0.09\text{-}0.5\ \text{cm}^2$  area were isolated by photolithography followed by an etching step in HCl which removed the excess CdZnS/ZnO layers around the defined area of the device. Solar cells were characterized by illuminated I-V measurements under AM1.5 conditions.



**Figure 3.** XRD data taken from a precursor layer which was first deposited on a glass/Mo substrate and then selenized in  $H_2Se$ . All reflections are either associated with Mo or with the tetragonal CIS phase.



**Figure 4.** (a) Illuminated I-V characteristics of an 8.6% efficient solar cell fabricated on a CIS absorber. Area =  $0.426 \text{ cm}^2$ ,  $V_{oc} = 0.424 \text{ V}$ ,  $J_{sc} = 31.52 \text{ mA/cm}^2$ , and  $FF = 64.35\%$ ; (b) relative quantum efficiency of the device in a.



**Figure 5.** Illuminated I-V characteristics of a  $0.09 \text{ cm}^2$  CIS solar cell.  $V_{oc} = 0.43 \text{ V}$ ,  $J_{sc} = 33.33 \text{ mA/cm}^2$ ,  $FF = 65.7\%$ , and efficiency =  $9.42\%$ .

$\text{mA/cm}^2$ , and  $64.35\%$ , respectively. The rather steep decline of the quantum efficiency curve at longer wavelengths in Fig. 4b indicates that the current collection from the rear of this device was poor. This is at least partially responsible for the low  $J_{sc}$  value. The shunt and series resistance values of the cell were also obtained from the dark I-V measurements and they were  $4 \text{ k}\Omega$  and  $4.74 \Omega$ , respectively. The illuminated I-V characteristics of a smaller area ( $0.09 \text{ cm}^2$ ) solar cell fabricated on another CIS absorber layer is shown in Fig. 5. This device has a conversion efficiency of  $9.42\%$  ( $V_{oc} = 0.43 \text{ V}$ ,  $J_{sc} = 33.33 \text{ mA/cm}^2$ ,  $FF = 65.7\%$ ).

The above results demonstrate the potential of a truly low-cost ink coating technique for the manufacture of CIS-type thin film solar cells. In addition to its low cost, the technique has other desirable features such as nearly 100% materials utilization, absolute control over the Cu/In stoichiometric ratio which is critical in CIS-type absorbers, and the capability of coating large area substrates using methods such as spraying or screen printing. The technique can also utilize nanoparticle pigments to eliminate the milling step for the preparation of inks or pastes. Work is now in progress to develop inks containing Ga to be able to grow CIGS absorbers for even higher efficiency solar cell fabrication.

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