

# Nanoparticle Oxides Precursor Inks for Thin film Copper Indium Gallium Selenide (CIGS) Solar Cells

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## ABSTRACT

The paper describes ISET's patented non-vacuum process for low cost mass production of CIGS solar cells. In this process, the water based precursor inks of mixed oxides are deposited on various conducting substrates by a variety of non-vacuum coating techniques. The oxides are converted to CIGS by annealing and the device is completed by deposition of CdS by CBD followed by ZnO deposition by MOCVD. Small area solar cells with efficiency >13% have been fabricated by this process. The advantages of this non-vacuum process are: high compositional control of the absorber layer, high materials utilization and low cost.

## INTRODUCTION

A number of labs working on thin film CIGS solar cells have clearly demonstrated their potential in achieving respectable conversion efficiency and their outdoor stability. Also, CIGS solar cells have been found to be robust against radiation damage in space and, therefore, are being favored as the candidate for fabricating light weight and flexible solar cells and modules for space power application. Most of the labs developing CIGS solar cells have used physical vapor deposition (PVD) techniques such as evaporation or sputtering for depositing the absorber layer of CIGS. The champion solar cell with conversion efficiency 18.8% (1) was first fabricated more than two years ago by the research team at the National Renewable Energy Laboratory (NREL), USA. Since then a number of other laboratories have demonstrated CIGS solar cells with conversion efficiencies in the 15–17% range. However, utilizing this knowledge and experience gained in labs around the world in defining a commercial process for manufacturing *low cost* CIGS modules remains a big challenge.

It is well known that the electronic properties of chalcopyrite materials such as CIGS are affected by slight changes in their composition. Deposition of CIGS absorber layers with specific electronic properties and with uniform composition on large areas using PVD methods is very challenging. In PVD systems the composition of the deposited materials is affected by the relative geometry of the source and the substrate on which the material is being deposited. The geometry in a system changes as the deposition process progresses affecting the composition of the deposited material continuously. Variations in the composition of the CIGS absorber layers result in poor process yields. These limitations can be overcome by using a variety of feed back loops and controls in deposition systems, however at a substantially increased costs of the deposition equipment. Cost analysis of large-scale manufacturing reveals that the major cost-contributing factor in manufacturing thin film PV modules is the cost of materials. Even though, in principle thin film solar cells use very little amount of materials, the cost of materials can be a serious issue if the manufacturing process used is inefficient in materials utilization. In PVD manufacturing processes the materials utilization of active materials is generally low.

The major challenge in commercializing a new thin film PV technology lies in lowering the cost of manufacturing PV modules. Three main factors that affect the manufacturing costs of PV

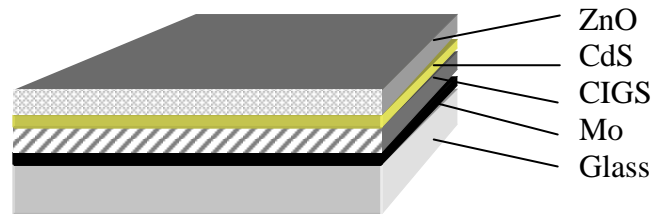
modules are; (i) process yield, (ii) materials utilization, and (iii) cost of the capital equipment. These parameters are not the best attributes of PVD techniques. In this paper we discuss a novel approach to fabricating CIGS solar cells in which a non-vacuum process is used for depositing the CIGS absorber layer. Results on solar cells fabricated on the CIGS layers deposited by this new method are also discussed.

## EXPERIMENTAL

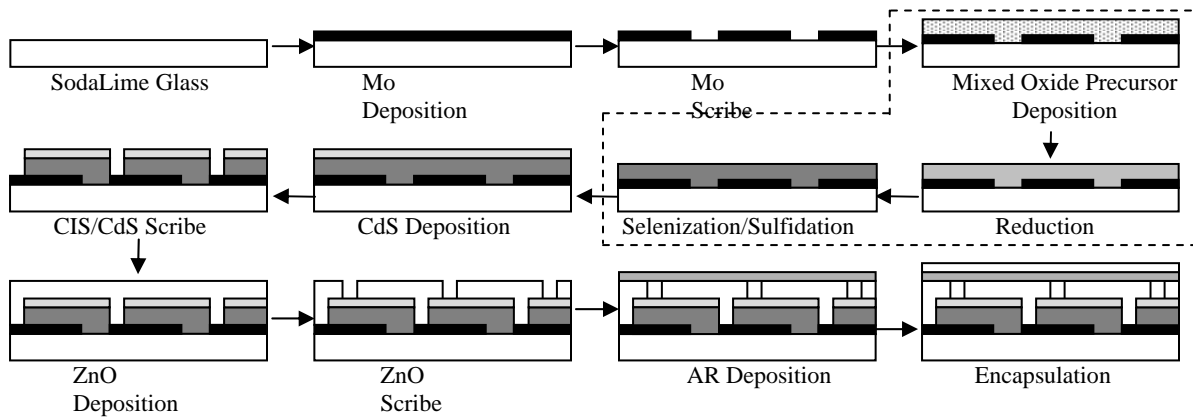
### Fabrication of CIGS solar cell and module

Figure 1 shows a schematic CIGS solar cell in a substrate structure and figure 2 shows a schematic of CIGS module fabrication process. Almost all of the R&D labs use ‘Soda Lime’ glass substrate, which is metallized by sputter deposition of Mo. The thickness of Mo layer is typically between 0.5–1.0  $\mu\text{m}$ . Likewise most of labs deposit the CdS window layer with thickness ranging between 0.05–0.15  $\mu\text{m}$  via a chemical bath deposition (CBD) technique. The top transparent conducting ZnO layer is deposited either by sputtering from a ZnO target or by low pressure chemical vapor deposition (LPCVD) using di-ethyl zinc and water vapor. At ISET we deposit ZnO using the LPCVD method.

For depositing CIGS absorber layer, majority of the labs use vacuum evaporation method. Every lab has a different approach within the evaporation scheme to distinguish itself from others. A few labs use PVD deposition of metallic precursors followed by their selenization using  $\text{H}_2\text{Se}$  gas. ISET uses a unique non-vacuum process for CIGS deposition, which is quite different from commonly used PVD techniques. *ISET uses coatings of water based precursor*



**Figure 1.** Schematic of CIGS solar cell on glass substrate



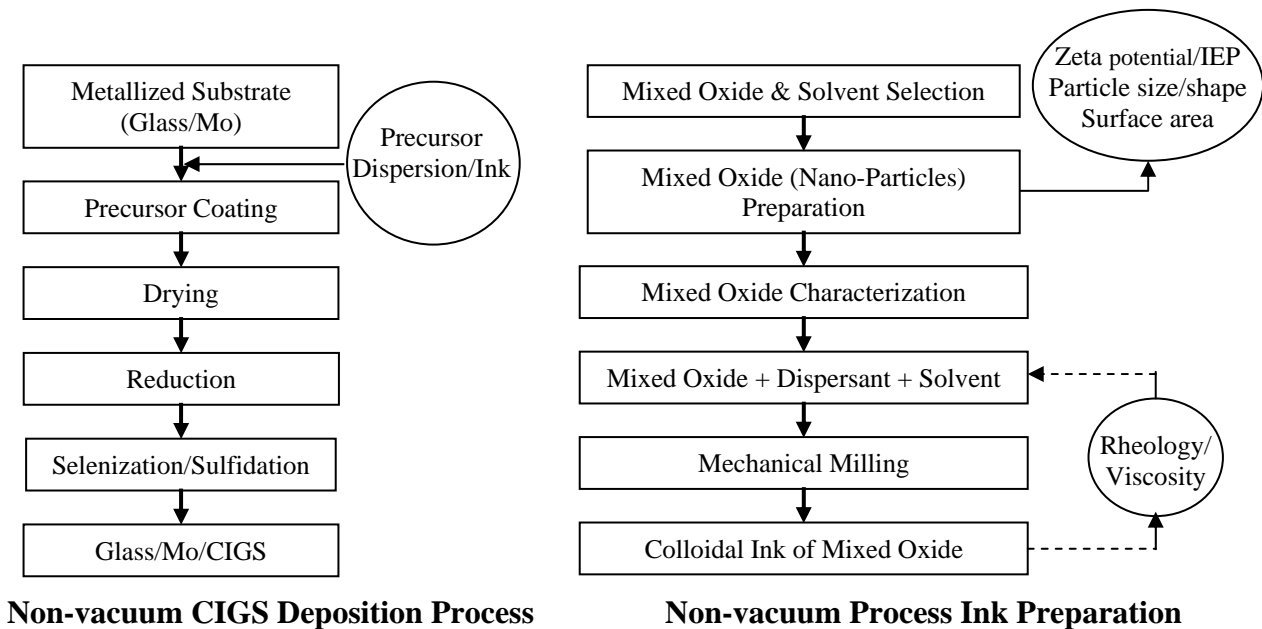
**Figure 2.** Schematic of CIGS module fabrication process

*inks made of nano-particles of mixed oxides of Cu, In and Ga that are converted to yield CIGS absorber layers of desired electronic properties.*

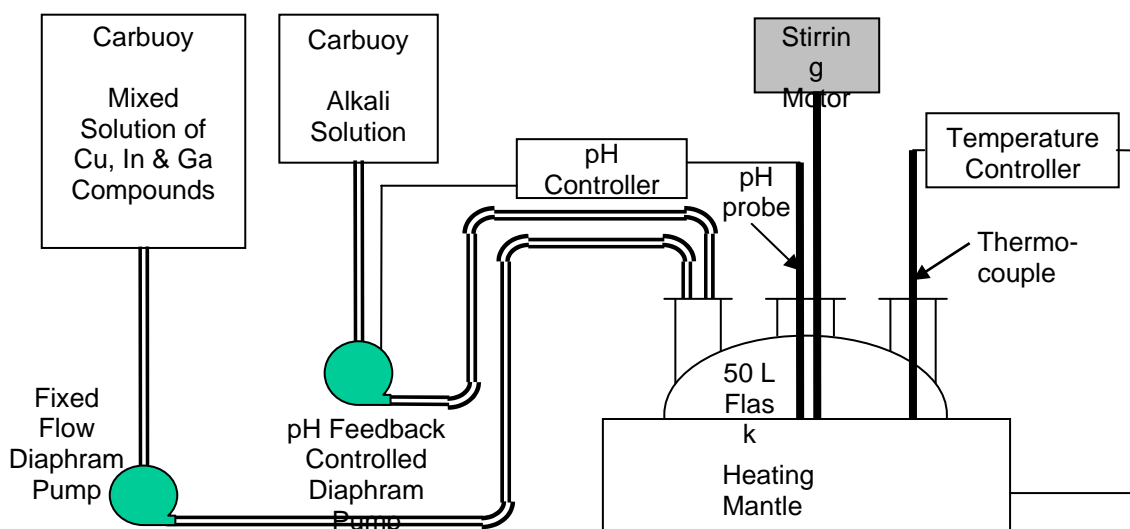
Figure 3. Shows ISET’s approach to the deposition of CIGS absorber layer (2). A precursor coating of water based inks is applied to a metallized glass substrate using ‘knife blade’ coating technique. After drying, a layer of mixed oxides of thickness about 2.5–3.0  $\mu\text{m}$  is left on the glass/Mo substrate. This oxide layer is then reduced under a forming gas mixture of  $\text{H}_2$  and  $\text{N}_2$  gases at temperatures in the range of 475–525  $^\circ\text{C}$  to obtain a compact coating of metal alloys consisting of Cu, In and Ga. This alloy coating is then selenized using  $\text{H}_2\text{Se}$  gas at temperatures in the range of 440–475  $^\circ\text{C}$  to form CIGS layer. Solar cell fabrication is completed by depositing CdS and ZnO layers on the CIGS layer using techniques described above.

**Preparation of mixed oxide powders and inks**

Figure 4 shows the schematic diagram of a co-precipitation set for preparing mixed oxides of Cu, In and Ga. In our lab we prepare mixed oxides of Cu, In and Ga by first co-precipitating hydroxides of these metals followed by their firing to get oxides. In a glass flask of volume 50.0 liters a solution of mixed compounds of Cu, In and Ga in which the Cu/(In+Ga) is fixed to a desired value and a solution of an NaOH are delivered simultaneously using metering pumps. The solution mixture is continuously stirred with a mechanical stirrer. The pH and the temperature of the precipitation reaction are controlled throughout the precipitation process. The pH of the reaction mixture is controlled by connecting a pH controller in a feed back loop that controls the delivery rate of the NaOH solution to the reaction. The quality of the hydroxide precipitate depends upon the temperature, pH, and the delivery rate of the reactants. Generally a gelatinous precipitate of mixed hydroxides is obtained which is filtered and washed to remove soluble sodium compounds. The filter cake obtained at the completion of washing and filtration,



**Figure 3.** Ink preparation and CIGS process by ISET’s non-vacuum process.



**Figure 4.** Co-precipitation setup for preparing inks.

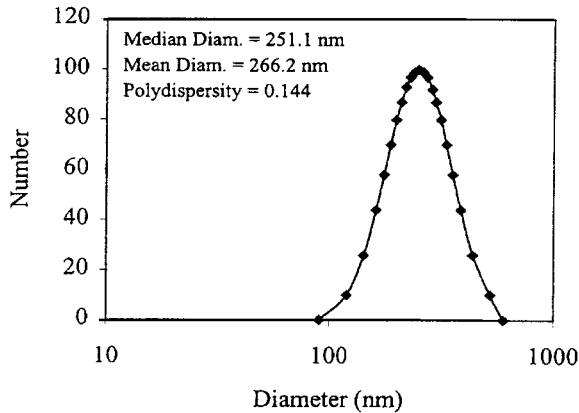
is dried to remove water and then fired at 450 °C to obtain the mixed oxides powder. The mixed oxide powder is characterized by measuring its surface area and the particle size. Figure 5 shows the distribution of the particle size of the powder with an average particle size of about 260 nanometers. However, by adjusting the preparation conditions, we have prepared particles with an average size of about 100 nanometers. The surface area of the powder can vary from 10–70 m<sup>2</sup>/gm and the average surface area of powder that we use is about 15 m<sup>2</sup>/gm.

### **Ink preparation**

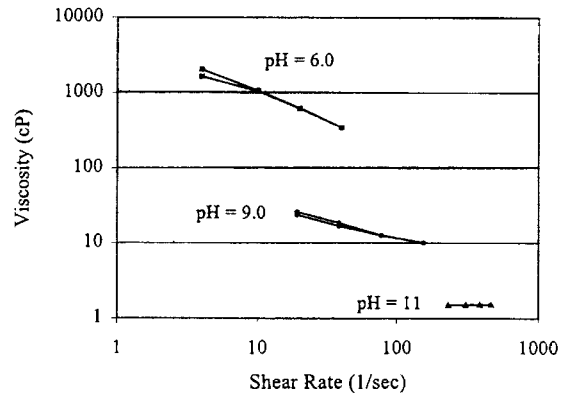
After characterization, the oxide powder is mixed with a proper dispersing agent and water and the mixture is milled using zirconia balls to prepare an ink. The water-based ink is a stabilized colloidal dispersion of mixed oxide powder. The rheology of this ink can be adjusted by changing the particle size of the powder, by changing the dispersant and also by adjusting the pH of the ink. We have made inks with their rheology varying from ‘ketchup’ like which is thixotropic to Newtonian which is water like. Figure 5 shows the change of viscosity of inks with sheer stress. Clearly we could change the viscosity of inks by orders of magnitude. This flexibility is very useful because it allows us to match the ink rheology to meet the requirements of precursor coating technique. We are evaluating a number of techniques such as ‘doctor blade’, ink jet printing, roller coating and spraying for applying the precursor ink on the metallized substrate. Each of these techniques requires a different rheology of the ink and our ink making process can meet those requirements.

### **Process rationale**

The basic philosophy of this ink-based technique is to avoid compositional non-uniformity by designing precursors powders in which the compositional ratio of Cu/(In +Ga) is fixed almost at the molecular level. Making colloidal dispersions of oxides is appealing because the published literature is full of information about dispersing oxide particles into stable dispersions. As a first response using oxides as precursors is counter intuitive because the oxides used are quite stable



**Figure 5.** Particle size distribution of ISET's pigments



**Figure 6.** Viscosity of the inks used in ISET's process

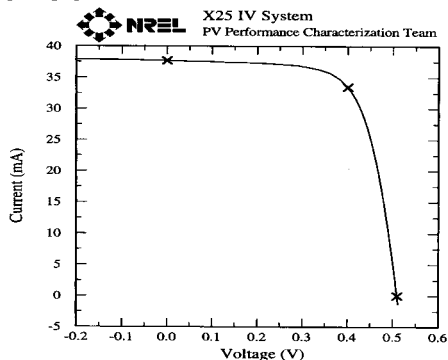
CuO ( $\Delta G_f^\circ = -31$  kCal/Mole),  $\text{In}_2\text{O}_3$  ( $\Delta G_f^\circ = -221.3$  kCal/Mole) and  $\text{Ga}_2\text{O}_3$  ( $\Delta G_f^\circ = -238.6$  kCal/Mole). In particular, the indium and gallium oxides are substantially more stable than the copper oxide. Since we carry out the oxide reduction at temperature around  $500^\circ\text{C}$ , we examined the free energy values of the reduction reaction at  $800^\circ\text{K}$  in which the oxides are reduced by  $\text{H}_2$  gas to metals. Whereas the reduction of CuO is thermodynamically favored ( $\Delta G = -25.0$  kCal/Mole), the reduction of  $\text{In}_2\text{O}_3$  ( $\Delta G = +15.7$  kCal/Mole) and  $\text{Ga}_2\text{O}_3$  ( $\Delta G = +50.0$  kCal/Mole) are not favored. These observations are based on the equilibrium thermochemical numbers. Even though the reduction of indium and gallium oxides is not favored, we could reduce them under non-equilibrium conditions. Additionally, because of the nanoparticles, the surface areas of these fine oxide powders are very large and therefore the kinetics of reduction reactions is fast and they assist in carrying out the '**oxide-to-metal alloys**' conversion relatively easily. The next step of conversion of '**metal alloys-to-selenides**' is carried out by reacting the alloy with  $\text{H}_2\text{Se}$  and  $\text{N}_2$  gas mixture at  $475^\circ\text{C}$ . The selenized films are finally exposed to  $\text{H}_2\text{S}$  and  $\text{N}_2$  mixture to open the bandgap of CIGS by replacing Se with S.

## RESULTS

CIGS solar cells and sub-modules fabricated using the ink process described above were tested for their performance at the National Renewable Energy Laboratories (NREL) under standard conditions of global AM1.5 at  $25^\circ\text{C}$ . Figure 6 shows the test result for a CIGS solar cell of area  $1.094\text{ cm}^2$  with conversion efficiency of 12.3% and figure 7 shows the test result for a sub-module of area about  $65\text{ cm}^2$  with conversion efficiency of about 8%. There are seventeen (17) solar cells monolithically integrated in this module. These results validate ISET's process for fabricating CIGS solar cells and modules. However, there is a plenty of room to improve these devices. The open circuit voltage in the single cell ( $V_{oc} = 509$  mV) is quite low, with process optimization  $V_{oc}$  value approaching 600 mV can be obtained. In the sub-module the major challenge is in improving the monolithic integration scheme. The current activities at ISET are focused on improving the device performance with a goal of fabricating 15% efficient CIGS solar cells using ISET's promising low cost and patented (3) process.

**International Solar Electric Technology  
CIGSS Cell**

Device ID: CO 1580B (Best)      Device Temperature: 25.0 ± 1 °C  
 Mar 7, 2000 1:37 PM      Device Area: 1.094 cm<sup>2</sup>  
 Reporting Spectrum: Global AM1.5      Irradiance: 1000.0 W/m<sup>2</sup>



$V_{oc} = 0.5097$  V       $I_{max} = 33.49$  mA  
 $I_{sc} = 0.03767$  A       $V_{max} = 0.4002$  V  
 $J_{sc} = 34.44$  mA/cm<sup>2</sup>       $P_{max} = 13.40$  mW  
 Fill Factor = 69.79 %      Efficiency = 12.3 %

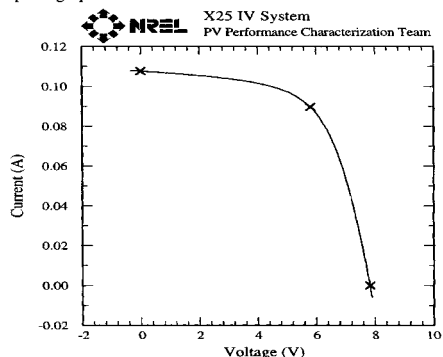
After 10 minute soak at  $P_{max}$ , 2 minute cool.

Contact to both Indium strips.

**Figure 7.** Current-Voltage characteristics of CIGSS solar cell

**International Solar Electric Technology  
CIGSS Module**

Device ID: CO-1577C      Device Temperature: 25.0 ± 1 °C  
 Mar 8, 2000 10:34 AM      Device Area: 64.91 cm<sup>2</sup>  
 Reporting Spectrum: Global AM1.5      Irradiance: 1000.0 W/m<sup>2</sup>



$V_{oc} = 7.837$  V       $I_{max} = 89.72$  mA  
 $I_{sc} = 0.1076$  A       $V_{max} = 5.817$  V  
 $J_{sc} = 1.658$  mA/cm<sup>2</sup>       $P_{max} = 521.9$  mW  
 Fill Factor = 61.89 %      Efficiency = 8.04 %

After 10 minute soak at  $P_{max}$ , 2 minute cool.

Aperture area.

**Figure 8.** Current-Voltage characteristics of CIGSS Module

**Other attributes of the ink process**

In the formulation of the ink since we fix the composition of the mixed oxide powders, therefore the absorber CIGS films deposited are quite uniform. The amount of the ink used to coat the metallized glass substrate can be easily monitored and controlled without wasting any material. We estimate that our material utilization can be >85%. Finally, with the exception of the sputtering equipment used for metallizing glass with Mo coating, most of the equipment used is not expensive. Combination of all of these factors makes this process very promising for large scale production of CIGS solar cells and modules. Cost estimates show that by using this process the cost of manufacturing CIGS modules can be lowered to <\$1.0/watt even in pilot plants of nominal capacity 10.0 MW/Yr.

**CONCLUSIONS**

We have demonstrated that using water based inks made of nanoparticles of mixed oxides of Cu In and Ga can be used to fabricate CIGS solar cells and sub-modules. The simplicity and the fact that various techniques used in this process are commonly used in other mature industries such as ceramics and paints will help in rapid scale and commercialization of this process.

**ACKNOWLEDGEMENTS**

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