

# ATMOSPHERIC PRESSURE SPRAY CHEMICAL VAPOR DEPOSITED $\text{CuInS}_2$ THIN FILMS FOR PHOTOVOLTAIC APPLICATIONS

J. D. Harris  
Cleveland State University, Cleveland, OH 44115

R. P. Raffaele  
Rochester Institute of Technology, Rochester, NY 14623

K. K. Banger, M. A. Smith and D.A. Scheiman  
Ohio Aerospace Institute, Brookpark, OH 44142

A. F. Hepp  
NASA Glenn Research Center, Cleveland, OH 44135

## ABSTRACT

Solar cells have been prepared using atmospheric pressure spray chemical vapor deposited  $\text{CuInS}_2$  absorbers. The  $\text{CuInS}_2$  films were deposited at  $390^\circ\text{C}$  using the single source precursor  $(\text{PPh}_3)_2\text{CuIn}(\text{SEt})_4$  in an argon atmosphere. The absorber ranges in thickness from  $0.75 - 1.0 \mu\text{m}$ , and exhibits a crystallographic gradient, with the leading edge having a (220) preferred orientation and the trailing edge having a (112) orientation. Schottky diodes prepared by thermal evaporation of aluminum contacts on to the  $\text{CuInS}_2$  yielded diodes for films that were annealed at  $600^\circ\text{C}$ . Solar cells were prepared using annealed films and had the (top down) composition of  $\text{Al/ZnO/CdS/CuInS}_2/\text{Mo/Glass}$ . The  $J_{\text{sc}}$ ,  $V_{\text{oc}}$ , FF and  $\eta$  were  $6.46 \text{ mA/cm}^2$ ,  $307 \text{ mV}$ ,  $24\%$  and  $0.35\%$ , respectively for the best small area cells under simulated AM0 illumination.

## INTRODUCTION

The National Aeronautics and Space Administration is interested in developing low temperature deposition techniques for producing thin-film photovoltaics (1-5). Low temperature routes ( $<400^\circ\text{C}$ ) allow devices to be deposited onto lightweight polymer substrates such as Kapton<sup>TM</sup> or polybenzobisoxazole (PBO). These lightweight devices would not only offer cost savings over present technologies, but in many cases would be mission enabling (6). One of the most promising family of materials for photovoltaic applications are the chalcopyrite  $\text{Cu}(\text{Ga,In})(\text{S,Se})_2$  alloys. These materials exhibit high absorption coefficients in the visible to near IR spectrum range, are generally prepared as p-type but can also be prepared n-type by adjusting the stoichiometry of the material, have good electrical characteristics and terrestrial stability, and in the case of  $\text{CuInSe}_2$  (2), has been demonstrated to be more radiation tolerant than crystalline silicon and gallium arsenide (7). Tests on laboratory scale  $\text{CuInSe}_2$  based devices have achieved efficiencies approaching  $18\%$  (8). Likewise,  $\text{CuInS}_2$  based devices have achieved conversion efficiencies over  $11\%$  and its direct band gap of  $1.5 \text{ eV}$  is near optimal for solar radiation utilization (9, 10). In addition, from an environmental standpoint,  $\text{CuInS}_2$  is free from the toxicity concerns associated with the selenium containing analog, and thus may be a more suitable material for terrestrial applications.

To facilitate low temperature deposition, organometallic molecules are used because of their low decomposition temperatures. To avoid premature decomposition of the precursor, atmospheric pressure spray chemical vapor deposition (CVD) was used. Spray CVD combines the benefits of traditional MOCVD with those of spray pyrolysis, while avoiding the disadvantages of each. The technique not only offers film growth in inert

atmospheres, large area deposition and laminar flow over the substrate, which are features usually associated with MOCVD, but it also offers a low temperature solution reservoir, an advantage which comes with spray pyrolysis. The latter feature is an important benefit which can prevent premature precursor decomposition when using thermally sensitive precursor compounds. In addition, this technique allows low volatile precursors to be easily put into the vapor phase, without using high vacuum and/or elevated precursor temperatures, since the precursor solutions are sprayed as aerosols and then swept into the reactor.

In the early 1990's, Kanatzidis and coworkers reported the synthesis of a new family of single source molecular precursors for  $\text{CuInQ}_2$ , (where  $Q = \text{S}$  or  $\text{Se}$ ) (11). Several compounds of the type  $(\text{PPh}_3)_2\text{CuIn}(\text{QR})_4$  (where  $R =$  ethyl or propyl) were structurally characterized, and it was observed that all the compounds decomposed at temperature below  $300^\circ\text{C}$  to yield  $\text{CuInQ}_2$ . In follow on work, Hollingsworth and coworkers demonstrated that spray CVD and  $(\text{PPh}_3)_2\text{CuIn}(\text{SEt})_4$  could be used to deposit high quality  $\text{CuInS}_2$ , as characterized by SEM-EDS, Rutherford Backscattering Spectroscopy and X-ray diffraction (12, 13). However, the only electrical property that was measured for the films was sheet resistivity, which was less than  $100 \Omega \text{ cm}$  for a  $1 \mu\text{m}$  thick film. The work reported here demonstrates that photovoltaic device quality  $\text{CuInS}_2$  can be deposited using single source precursors and atmospheric pressure spray CVD.

## EXPERIMENTAL

All operations of moisture- and air-sensitive materials were performed under an argon atmosphere employing standard Schlenk techniques and a double-manifold vacuum line. Solids were manipulated in an argon filled glovebox. Solvents were freshly distilled from appropriate drying agents under Ar prior to use. The single source precursors,  $(\text{PPh}_3)_2\text{CuIn}(\text{SEt})_4$  was prepared using a procedure reported elsewhere (11, 12, 14, 15). Precursor purity was monitored by nuclear magnetic resonance spectroscopy (NMR).

Using a spray CVD reactor similar to Hollingworth's (12, 13),  $1 \mu\text{m}$  thick films of  $\text{CuInS}_2$  were deposited in 70-90 minutes from 150 ml of 0.01 M solution of  $(\text{PPh}_3)_2\text{CuIn}(\text{SEt})_4$  in toluene. The solution was atomized by a 2.5 MHz nebulizer and swept into a two-zone hot-wall reactor by argon carrier gas (4 l/min) that was presaturated with the solvent. Zone one (evaporation zone) of the reactor was held at  $128 \pm 1^\circ\text{C}$ , and zone two (deposition zone) was held at  $390 \pm 1^\circ\text{C}$  during depositions. For films given a post-deposition anneal at higher temperatures, the carrier gas was reduced to a minimal flow and both zones of the furnace were heated to  $600 \pm 1^\circ\text{C}$  in 4 minutes, held isothermal for 8 minutes and then allowed to cool to room temperature.

Films were characterized by transmission spectroscopy (Perkin Elmer, Lambda-19), scanning electron microscopy (SEM) (Hitachi S-3000N), Energy Dispersive Spectroscopy (SEM-EDS) (EDAX), profilometry (KLA-Tencor HRP 75) and X-ray diffraction (Philips). Schottky barriers were prepared by thermally evaporating aluminum contacts onto the  $\text{CuInS}_2$  films and the diode curves measured. Complete cells with the (top down) composition of  $\text{Al/ZnO/CdS/CuInS}_2/\text{Mo/glass}$  were also prepared using the spray CVD deposited films. Films were etched in a 1.5 M KCN solution for one minute, prior to chemical bath deposition of CdS to form the heterojunction. A  $1 \mu\text{m}$  thick layer of fluorine-doped  $\text{ZnO}_2$  was sputtered on top of the CdS, followed by thermally evaporated aluminum contacts. Complete cells were characterized under a simulated AM0 solar spectrum and diode curves were measured (Tektronix 370A).

## RESULTS AND DISCUSSION

As deposited, the well adhering  $\text{CuInS}_2$  films were dark blue to black, depending on film thickness. The thickness for a typical film ranged from 0.75 to  $1.0 \mu\text{m}$ , with grain size for the films less than  $0.5 \mu\text{m}$  (Figure 1). As evident from the SEM images, grain growth appears dense and columnar, despite the small grain size (Figure 2). The film thickness varies along the sample, with the thinner portion of the film growing in the "up stream" end of the substrate, and the thick portion of the film growing on the "down stream" end. It is believed this gradient is a

product of temperature inhomogeneity, carrier gas flow rate and incline angle of the substrate holder. Experiments are in progress to minimize the thickness gradient.

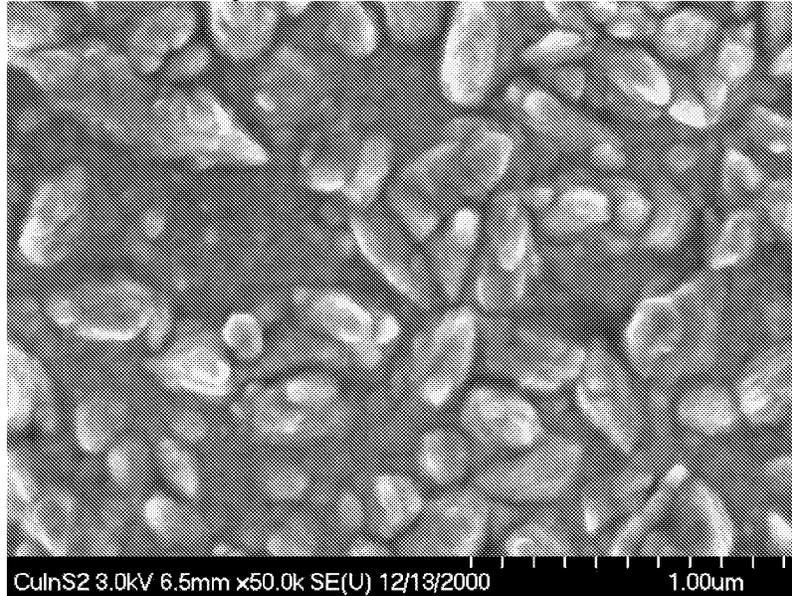


Figure 1. SEM image of CuInS<sub>2</sub> deposited on Mo foil at 390°C at a flow rate of 4 L/min.

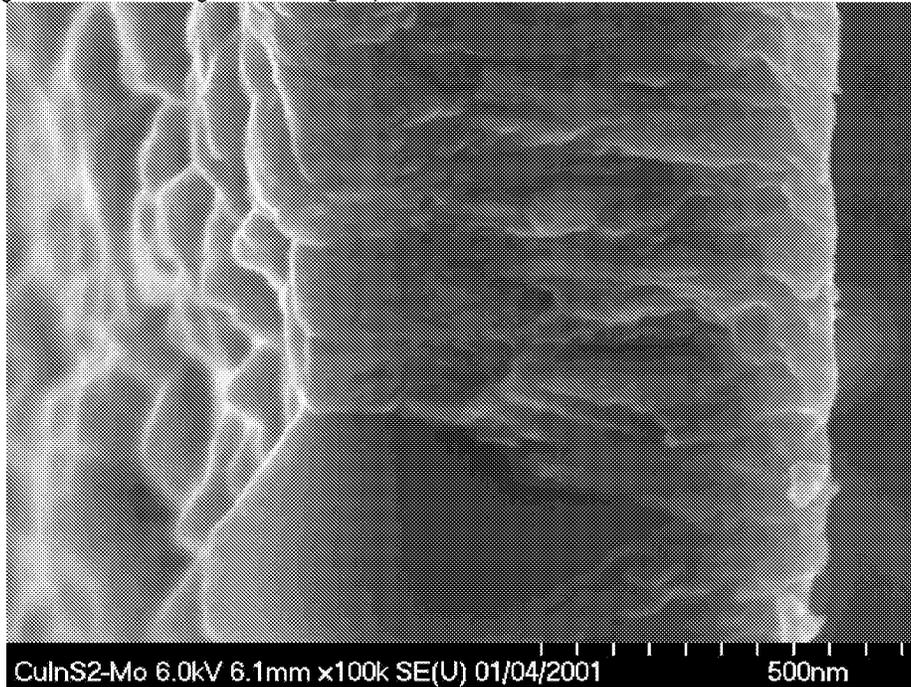


Figure 2. SEM edge-on view of a CuInS<sub>2</sub> film showing film thickness and columnar grain growth.

Along with the thickness gradient, there is also a gradient in the crystallographic orientation of the films. As deposited, the majority of the film is highly (112) oriented. Over the length of the 76 mm long substrate, the

leading 1/3 of the film is (220) oriented, whereas the downstream 2/3 of the film are strictly (112) oriented (Figure 3). Siemer and co-workers have demonstrated that devices prepared from preferred (112) oriented  $\text{CuInS}_2$  films have better performance than photovoltaic devices fabricated from other oriented films due mainly to a lower series resistance (16). The reflection at  $2\theta = 27^\circ$  in the front film, labeled with an \* has been identified as arising from  $\text{In}_2\text{S}_3$  and  $\text{In}_2\text{Se}_3$  in films of  $\text{CuInS}_2$  and  $\text{CuInSe}_2$ , respectively, prepared by spray pyrolysis. However, spray pyrolyzed films only yield the spurious reflection when indium rich solutions were sprayed. For films grown by spray CVD, the reflection is only observed on the leading 1/3 of the film, yet as will be discussed later, composition of the films remain constant from front to back. Films deposited by spray CVD also lack the (101) reflection at  $2\theta = 17.914^\circ$ . It is unknown whether this is a product of preferred orientation or lack of long range order since chalcopyrite has the zinc-blend structure with a doubled c-axis and alternating Cu and In atoms replacing the Zn atoms. Using a similar spray CVD reactor, Hollingsworth demonstrated that crystal orientation is a function of both carrier gas flow rate and solution concentration (13). It is anticipated that experiments to reduce the thickness gradient will improve the orientation gradient as well.

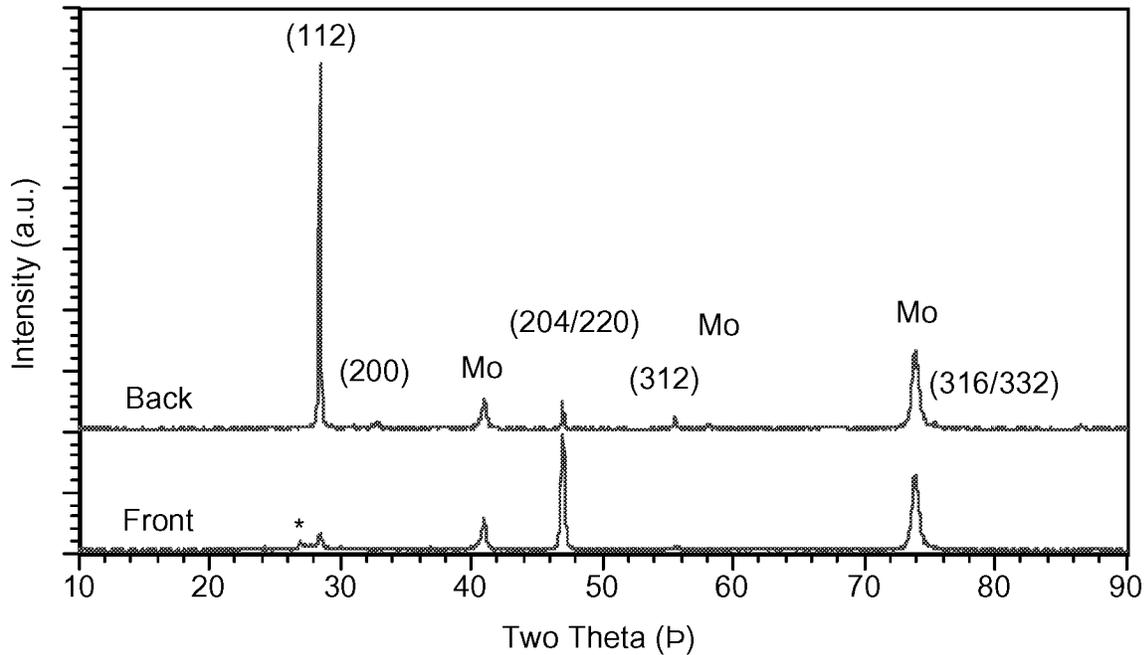


Figure 3. X-ray powder diffraction spectra of a  $\text{CuInS}_2$  film on Mo coated glass.

Films were deposited onto a variety of substrates, including Ti, Mo and Ni foils, Kapton™, PBO,  $\text{SiO}_2$ , and Mo coated glass. In all cases, SEM-EDS measurements revealed the films were nearly stoichiometric  $\text{CuInS}_2$ , or only slightly indium and sulfur rich, (with atomic percents for Cu, In and S as 23%, 24% and 53%, respectively). Films deposited on all substrates, except nickel, show no evidence of phosphorous or carbon by SEM-EDS, indicating that the precursor molecules decompose cleanly. Within experimental error of SEM-EDS, the stoichiometry of the films remain constant along their length. SEM-EDS data for films deposited on nickel substrates revealed large quantities of phosphorous (16%) in the material. SEM-EDS measurements of as deposited films on nickel gave atomic percents for Cu, In, S and P as 24%, 17%, 43% and 16%, respectively. This implies that nickel substrates promote the cracking of the phosphine during deposition, and would thus be unacceptable for device preparation without a passivating layer.

To evaluate the electrical properties of the deposited films, current versus voltage (IV) measurements were recorded for the films using thermally evaporated aluminum point contacts ( $10 \mu\text{m}^2$ ) to make Schottky barrier diodes. Many of the Schottky barriers were excellent diodes on films annealed at  $600^\circ\text{C}$ , with "turn on" voltages of 0.6 - 0.8 volts and little leakage when reverse biased. However, many of the contacts on the as-deposited films gave large reverse bias currents and nearly ohmic response. This behavior is indicative of degeneracy of the semiconductor due to a high carrier density resulting from native defects. The improvement in the diode behavior of the annealed films is attributed to enhanced crystallinity and reduction of defects, as considerable narrowing of the diffraction lines was observed in the annealed films.

Solar cells were prepared from annealed films deposited on Mo coated glass substrates. The  $10 \text{ mm} \times 76 \text{ mm}$  cell was mechanically scribed into many smaller cells, with an IV curve for each being measured under a simulated AM0 light source. The maximum efficiency achieved by one of the small area cells was 0.35% (Figure 4), which was located on the back third of the substrate and had a total area of  $0.15 \text{ cm}^2$ . The most obvious feature of the JV curve is the lack of a "knee," given that the curve is nearly linear. From the data near the open circuit voltage ( $V_{oc}$ ), the device appears to have high series resistance. At this time it is unknown whether the series resistance is from the absorber layer, from the interfaces between the different layers or both. From the slope of the line near the short circuit current ( $J_{sc}$ ), the film also has high shunt resistance. The mechanical scribing of the small area cells could have caused the shunting; future small area cells will be prepared lithographically.

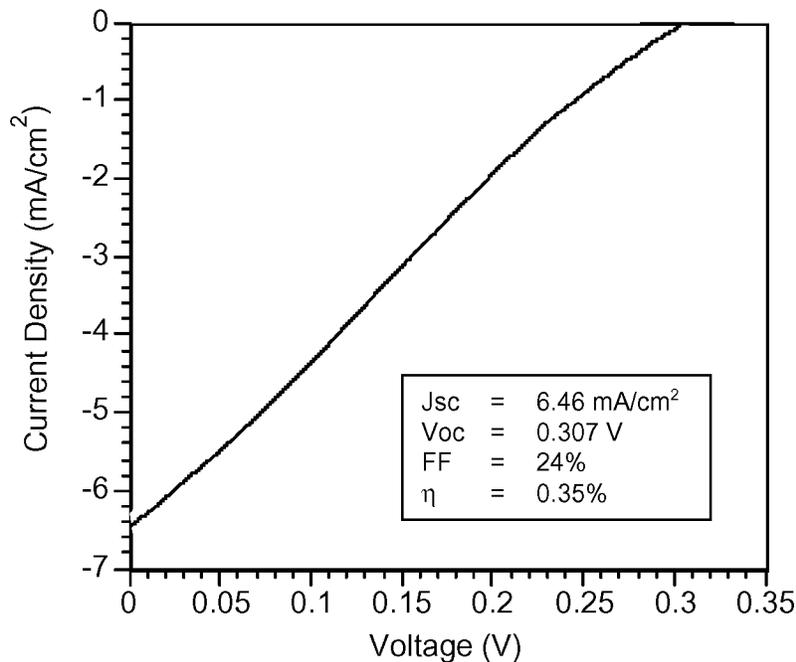


Figure 4. JV curve for small area  $\text{CuInS}_2$  cell on Mo coated glass.

### CONCLUSION

Working photovoltaic devices have been prepared from atmospheric pressure spray CVD deposited  $\text{CuInS}_2$  thin films using the single source precursor  $(\text{PPh}_3)_2\text{CuIn}(\text{SET})_4$ . Although the  $V_{oc}$ ,  $J_{sc}$  and fill factor are low, it is anticipated that these will increase as deposition parameters are optimized. X-ray diffraction of the films reveals there is a preferred orientation gradient along the substrate, with only the back two thirds of the film having the

desired (112) crystal orientation. The films also range in thickness, with the leading edge being thinner than the trailing edge. Spray CVD is a promising technique for depositing  $\text{CuInS}_2$  on to low temperature substrates such as Kapton™ and PBO and temperatures below 400°C. However, the films with the best electrical properties were annealed at 600°C following deposition.

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