A national laboratory of the U.S. Department of Energy
Office of Energy Efficiency & Renewable Energy

National Renewable Energy Laboratory

Innovation for Our Energy Future

Spray Deposition of High Quality $CuInSe_2$ and CdTe Films

Preprint

C.J. Curtis, M. van Hest, A. Miedaner, P. Hersh, J. Leisch, and D.S. Ginley
National Renewable Energy Laboratory

J. Nekuda
Colorado School of Mines

Presented at the 33rd IEEE Photovoltaic Specialists Conference
San Diego, California
May 11–16, 2008

Conference Paper
NREL/CP-590-42538
May 2008

NREL is operated by Midwest Research Institute • Battelle Contract No. DE-AC36-99-GO10337

Spray Deposition of High Quality $CuInSe_2$ and CdTe Films

Calvin J. Curtis[1], Maikel van Hest[1], Alex Miedaner[1], Jennifer Nekuda[2], Peter Hersh[1], Jennifer Leisch[1], and David S. Ginley[1]
[1]National Renewable Energy Laboratory, Golden, CO 80401
[2]Colorado School of Mines, Golden, CO 80401

ABSTRACT

A number of different ink and deposition approaches have been used for the deposition of $CuInSe_2$ (CIS), $Cu(In,Ga)Se_2$ (CIGS), and CdTe films. For CIS and CIGS, soluble precursors containing Cu, In, and Ga have been developed and used in two ways to produce CIS films. In the first, In-containing precursor films were sprayed on Mo-coated glass substrates and converted by rapid thermal processing (RTP) to In_2Se_3. Then a Cu-containing film was sprayed down on top of the In_2Se_3 and the stacked films were again thermally processed to give CIS. In the second approach, the Cu-, In-, and Ga-containing inks were combined in the proper ratio to produce a mixed Cu-In-Ga ink that was sprayed on substrates and thermally processed to give CIGS films directly. For CdTe deposition, ink consisting of CdTe nanoparticles dispersed in methanol was prepared and used to spray precursor films. Annealing these precursor films in the presence of $CdCl_2$ produced large-grained CdTe films. The films were characterized by x-ray diffraction (XRD) and scanning electron microscopy (SEM). Optimized spray and processing conditions are crucial to obtain dense, crystalline films.

INTRODUCTION

The use of ink based precursors deposited and processed under atmospheric conditions to produce high quality semiconductor absorber layers, metals and TCOs offers an attractive alternative to conventional vacuum based deposition approaches in terms of process simplicity and cost. The key element to atmospheric processing is to develop and formulate precursors and inks that can be sprayed or printed and which decompose to give the desired materials with the proper composition, morphology, optical and electrical properties.

Solar cells based on thin film absorber layers are attractive because of the reduced material cost compared to Si wafers. Two of the most attractive thin film absorber materials are CdTe and CIGS. Currently, the favored technology for deposition of CdTe is closed-space sublimation under vacuum[1], while the best large-grained CIGS films are produced by deposition of the metals by evaporation followed by selenization with Se or H_2Se[2, 3]. This CIGS process has produced very efficient laboratory scale devices, but translation into a manufacturing environment has proven difficult, and high temperature selenization is hazardous. The use of ink based precursors that can be deposited and processed under atmospheric conditions could be a simple and inexpensive alternative method for deposition of these absorber materials. The key element in this approach is to develop precursors and formulate inks that decompose to give the desired materials with the proper composition, morphology and properties for the application. The inks must also be formulated to wet the substrate properly in order to obtain smooth, continuous films. In addition, thermal processing conditions that allow volatile materials to escape and lead to formation of dense films must be found. The objective of this work is to demonstrate the feasibility of depositing high quality absorber layers of CIGS and CdTe by spray deposition of precursor inks coupled with rapid thermal processing under atmospheric conditions.

TECHNICAL APPROACH

For CIS deposition, a variety of soluble Cu, In and Ga-containing precursors to binary selenide materials have been developed. These were dissolved in organic solvents, along with dispersants and other additives, to produce the proprietary inks used in this study. For CdTe deposition, an ink consisting of CdTe nanoparticles dispersed in methanol was prepared by the reaction of CdI_2 with Na_2Te in methanol at low temperature, as shown[4].

$$CdI_2 + Na_2Te \xrightarrow[-78^oC]{\text{methanol}} \text{nano-CdTe} + 2\text{NaI}$$

The CdTe nanoparticles were collected by centrifugation, washed with methanol to remove the NaI co-product and re-dispersed in methanol for spray deposition.

The inks were deposited using an ultrasonic spray head (SonoTek Corp.) fed by a variable speed liquid pump (Fluid Metering, Inc.). A substrate heater mounted on a computer-controlled X-Y motion system allowed for movement of heated substrates under the sprayed stream. The thickness of the sprayed film was controlled by varying the ink concentration, the flow rate through the sprayer and the number of coats sprayed. Conditions were found such that smooth, uniform precursor films were obtained for all of the sprayed inks.

The precursor films were converted to the desired materials using rapid thermal processing (RTP) in a controlled atmosphere. The RTP conditions were varied systematically to ascertain the effect of conditions on the film compositions and morphologies obtained. The film compositions were characterized by x-ray fluorescence (XRF), crystalline phases were identified using x-ray diffraction (XRD) and film morphology was examined using scanning electron microscopy (SEM).

RESULTS

Spray Deposition of CIS Films

The inks developed for deposition of binary selenide materials have been used in two ways to produce CIS and CIGS films. In the first approach, an In-containing precursor film was first sprayed on a heated, Mo-coated glass substrate and processed by RTP to give In_2Se_3. Figure 1 shows XRD scans of thickened In_2Se_3 films processed under these conditions. After processing the

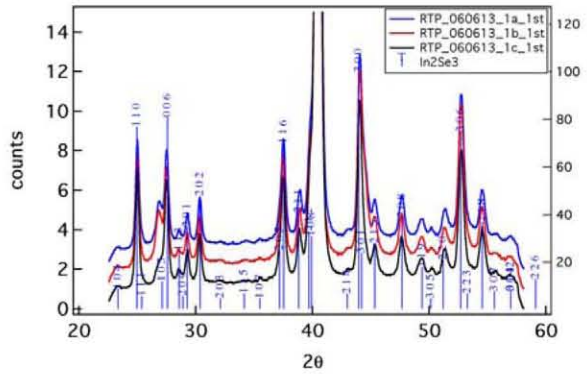

Figure 1. XRD scans of In_2Se_3 films of different thickness deposited using the In-containing ink. The large peak at ~40° is due to Mo.

first film to In_2Se_3, the Cu-containing ink was used to spray a precursor film on top of the In_2Se_3 film, and the stacked films were then processed again by RTP, which caused the films to react to form a CIS film. Figure 2 shows XRD scans of the initial In_2Se_3 film and the CIS film that was produced by reaction with the Cu-containing precursor.

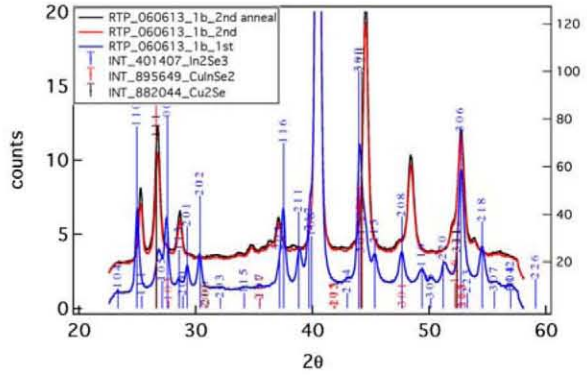

Figure 2. XRD scans of In_2Se_3 film and CIS film that resulted from treatment with Cu-containing ink and processing. The large peak at ~40° is due to Mo.

In the second approach, the Cu, In, and Ga-containing inks were mixed in the proper ratio to produce a Cu-In-Ga ink. This ink was sprayed on to Mo-coated glass substrates to produce precursor films that were then annealed at various temperatures to produce CIGS films. Figure 3 shows the XRD scans for films sprayed at low temperature and annealed at increasing temperatures. With the exception of the as-sprayed film, which was amorphous, all of the temperatures examined produced CIGS films from this mixed ink. However, films processed

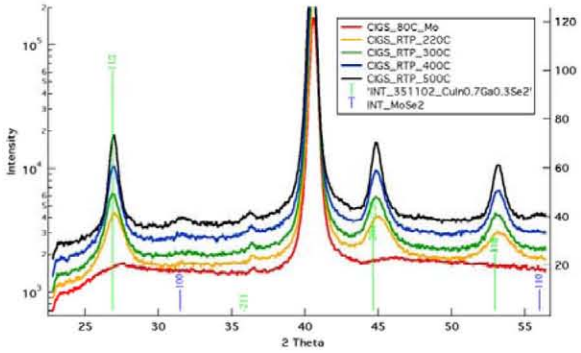

Figure 3. XRD scans of CIGS films produced from the mixed Cu-In-Ga ink annealed at increasing temperatures. The large peak at ~40° is due to Mo.

under these conditions were found to be cracked and somewhat porous. It was found that spraying the precursor film at low temperature, followed by processing with a slower temperature ramp to high temperature gave a dense film, as shown in Figure 4. This result represents a breakthrough for solution-based precursors.

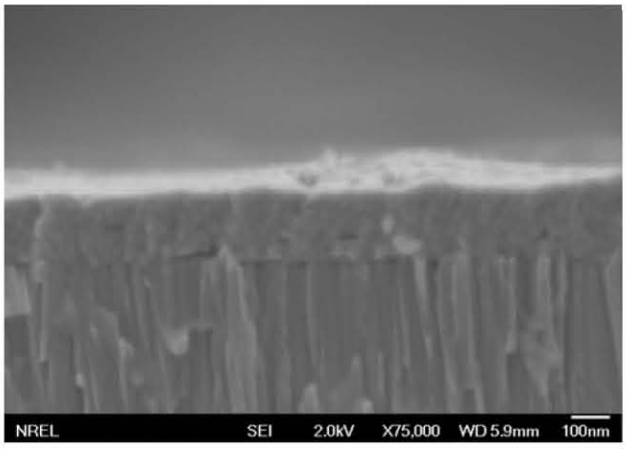

Figure 4. SEM image of a CIS film produced from the mixed ink sprayed at low temperature and processed with a slower temperature ramp.

Spray Deposition of CdTe Films

The CdTe ink consists of nanoparticles 2.5-7.5 nm in diameter suspended in methanol, as determined by TEM and XRD analysis. Ink with a concentration of about 25

mg of CdTe per ml was spray deposited on glass substrates coated with layers of F:SnO_2 and CdS at a temperature of 150ºC to produce precursor films 1 to 5 μm thick, depending on the number of coats sprayed. The precursor films were annealed at temperatures ranging from 250 to 500ºC in argon and forming gas (10%H_2 in N_2) atmospheres. Sharp XRD patterns corresponding to cubic CdTe were observed for films annealed at all temperatures, with the sharpest XRD peaks exhibited by films annealed at 400ºC and above, as shown in Figure 5. Little difference was observed between films annealed in argon or forming gas.

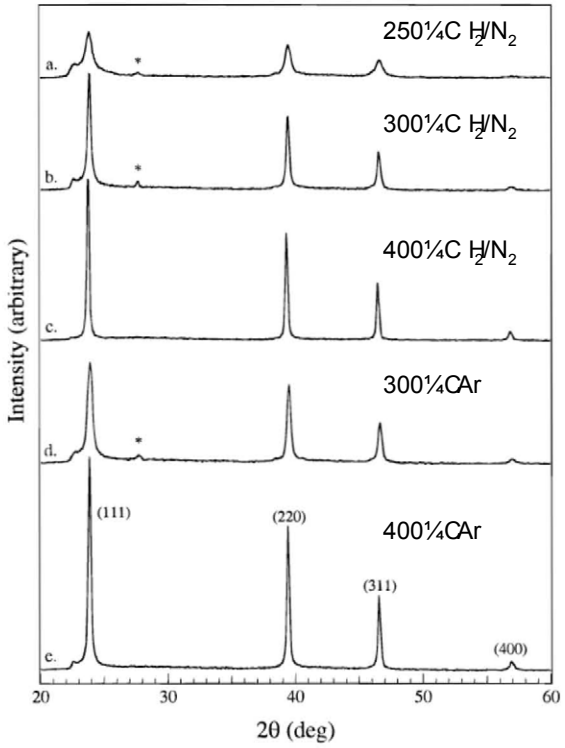

Figure 5. XRD data for CdTe films sprayed at 150ºC and annealed in forming gas or argon at the temperatures shown (* denotes Te).

The use of $CdCl_2$ to promote grain growth during annealing was also examined. Sprayed precursor films were dipped into $CdCl_2$ solutions in methanol at 10% and 20% of saturation at 50ºC for 5 min, followed by annealing at 400ºC for 30 min in argon. Figure 6 shows atomic force microscopy (AFM) images of sprayed films annealed with and without $CdCl_2$ treatment. The $CdCl_2$ treatment definitely promotes grain growth compared to untreated films, with grains larger than 1 μm observed after treatment with $CdCl_2$ at the higher concentration. These films were finished into solar cells by addition of a standard doped carbon top contact. Cells based on nanoparticle-derived absorber layers have shown efficiencies of 6% to date.

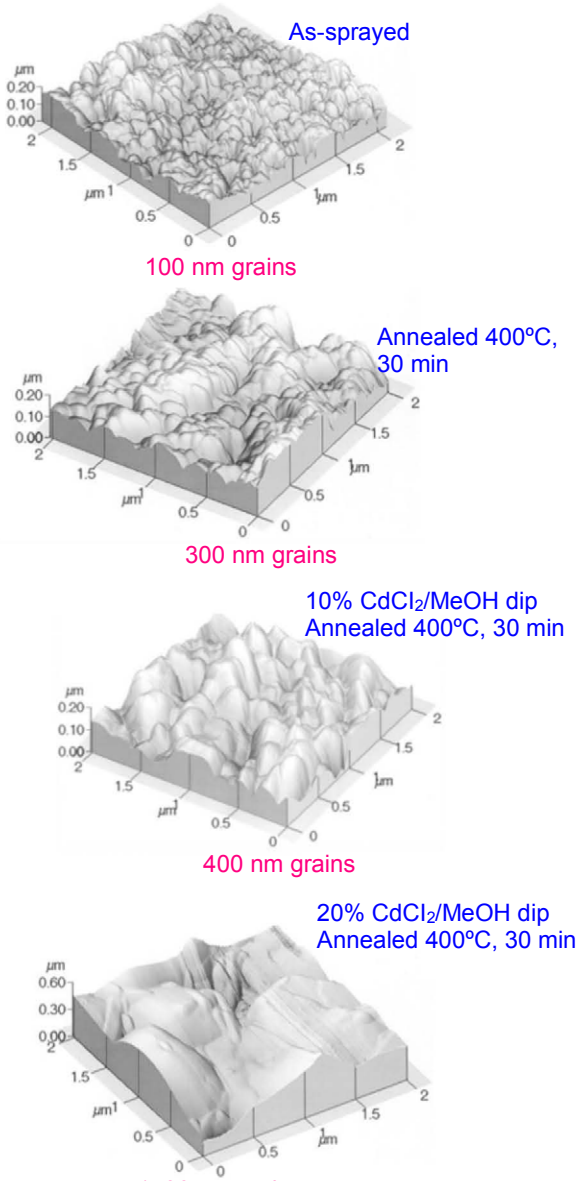

Figure 6. AFM images of as-sprayed and annealed films with and without $CdCl_2$ treatment.

CONCLUSION

Inks containing Cu, In and Ga have been formulated from new soluble precursors and have been used to deposit CIS and CIGS films by two approaches. The first approach involved deposition of stacked layers of In- and Cu-containing precursor materials followed by thermal processing to give CIS. The second approach consisted

of mixing Cu, In, and Ga inks in the proper stoichiometry for CIGS. This mixed ink was then spray deposited on Mo-coated glass substrates and thermally processed to give CIGS films. A nanoparticle CdTe ink was used to spray deposit CdTe films. Treatment of the sprayed films with a $CdCl_2$ solution followed by annealing produced grain growth in the CdTe film. Solar cells with conversion efficiencies of 6% have been produced using these films. For both CIGS and CdTe films, optimized spray and thermal processing conditions are key to obtaining films with the desired composition and morphology.

ACKNOWLEDGEMENT

This work was supported by the U.S. Department of Energy under Contract No. DE-AC36-99GO10337 with the National Renewable Energy Laboratory.

REFERENCES

1. Chopra, K.L., P.D. Paulson, and V. Dutta, "Thin-film solar cells: An overview." *Progress in Photovoltaics*, 2004. **12**, 69-92.

2. Lundberg, O., M. Edoff, and L. Stolt, "Optimized growth conditions for Cu(In,Ga)Se/sub 2/ layers grown by co-evaporation at high deposition rates." Compound Semiconductor Photovoltaics. Symposium. *Mater. Res. Soc. Symposium Proceedings,* **763**, 2003, 365-70.

3. Ramanathan, K., G. Teeter, J.C. Keane, and R. Noufi, "Properties of high-efficiency CuInGaSe2 thin film solar cells." *Thin Solid Films*, 2005. **480**, 499-502.

4. Schulz, D.L., M. Pehnt, D.H. Rose, E. Urgiles, A.F. Cahill, D.W. Niles, K.M. Jones, R.J. Ellingson, C.J. Curtis, and D.S. Ginley, "CdTe Thin Films from Nanoparticle Precursors by Spray Deposition." *Chem. Mater.*, 1997. **9**, 889-900.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ORGANIZATION.

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
May 2008	Conference Paper	11-16 May 2008

4. TITLE AND SUBTITLE
Spray Deposition of High Quality CuInSe2 and CdTe Films: Preprint

5a. CONTRACT NUMBER
DE-AC36-99-GO10337

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
C.J. Curtis, M. van Hest, A. Miedaner, J. Nekuda, P. Hersh, J. Leisch, and D.S. Ginley

5d. PROJECT NUMBER
NREL/CP-590-42538

5e. TASK NUMBER
PVA74201

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
National Renewable Energy Laboratory
1617 Cole Blvd.
Golden, CO 80401-3393

8. PERFORMING ORGANIZATION REPORT NUMBER
NREL/CP-590-42538

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR'S ACRONYM(S)
NREL

11. SPONSORING/MONITORING AGENCY REPORT NUMBER

12. DISTRIBUTION AVAILABILITY STATEMENT
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

13. SUPPLEMENTARY NOTES

14. ABSTRACT *(Maximum 200 Words)*
A number of different ink and deposition approaches have been used for the deposition of CuInSe2 (CIS), Cu(In,Ga)Se2 (CIGS), and CdTe films. For CIS and CIGS, soluble precursors containing Cu, In, and Ga have been developed and used in two ways to produce CIS films. In the first, In-containing precursor films were sprayed on Mo-coated glass substrates and converted by rapid thermal processing (RTP) to In2Se3. Then a Cu-containing film was sprayed down on top of the In2Se3 and the stacked films were again thermally processed to give CIS. In the second approach, the Cu-, In-, and Ga-containing inks were combined in the proper ratio to produce a mixed Cu-In-Ga ink that was sprayed on substrates and thermally processed to give CIGS films directly. For CdTe deposition, ink consisting of CdTe nanoparticles dispersed in methanol was prepared and used to spray precursor films. Annealing these precursor films in the presence of CdCl2 produced large-grained CdTe films. The films were characterized by x-ray diffraction (XRD) and scanning electron microscopy (SEM). Optimized spray and processing conditions are crucial to obtain dense, crystalline films.

15. SUBJECT TERMS
CIGS; spray deposition; ink-based precursors; x-ray diffraction, scanning electron microscopy; crystalline film; large grain;

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER (*Include area code*)
Unclassified	Unclassified	Unclassified	UL		

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18