

Spray Deposition of High Quality CuInSe_2 and CdTe Films

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Spray Deposition of High Quality CuInSe₂ and CdTe Films

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ABSTRACT

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.

INTRODUCTION

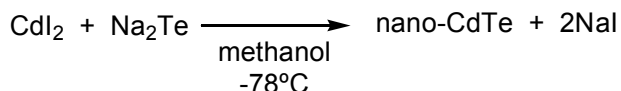
The use of ink based precursors deposited and processed under atmospheric conditions to produce high quality semiconductor absorber layers, metals and TCOs offers an attractive alternative to conventional vacuum based deposition approaches in terms of process simplicity and cost. The key element to atmospheric 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 H₂Se[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 CdI₂ with Na₂Te in methanol at low temperature, as shown[4].



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

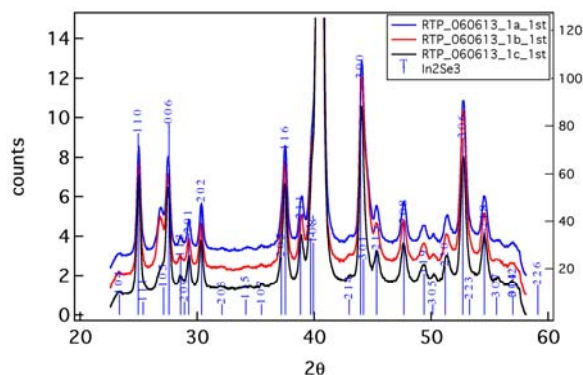
The inks were deposited using an ultrasonic spray head (SonoTek Corp.) fed by a variable speed liquid pump (Fluid Metering, Inc.). A substrate heater mounted on a computer-controlled X-Y motion system allowed for movement of heated substrates under the sprayed stream. The thickness of the sprayed film 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



mg of CdTe per ml was spray deposited on glass substrates coated with layers of F:SnO₂ and CdS at a temperature of 150°C 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 500°C in argon and forming gas (10%H₂ in N₂) 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 400°C and above, as shown in Figure 5. Little difference was observed between films annealed in argon or forming gas.

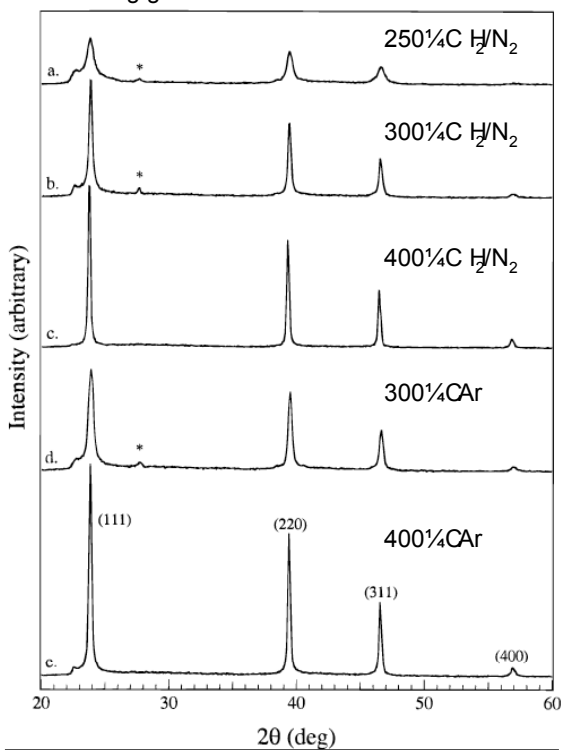


Figure 5. XRD data for CdTe films sprayed at 150°C and annealed in forming gas or argon at the temperatures shown (* denotes Te).

The use of CdCl₂ to promote grain growth during annealing was also examined. Sprayed precursor films were dipped into CdCl₂ solutions in methanol at 10% and 20% of saturation at 50°C for 5 min, followed by annealing at 400°C for 30 min in argon. Figure 6 shows atomic force microscopy (AFM) images of sprayed films annealed with and without CdCl₂ treatment. The CdCl₂ treatment definitely promotes grain growth compared to untreated films, with grains larger than 1 μm observed after treatment with CdCl₂ 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.

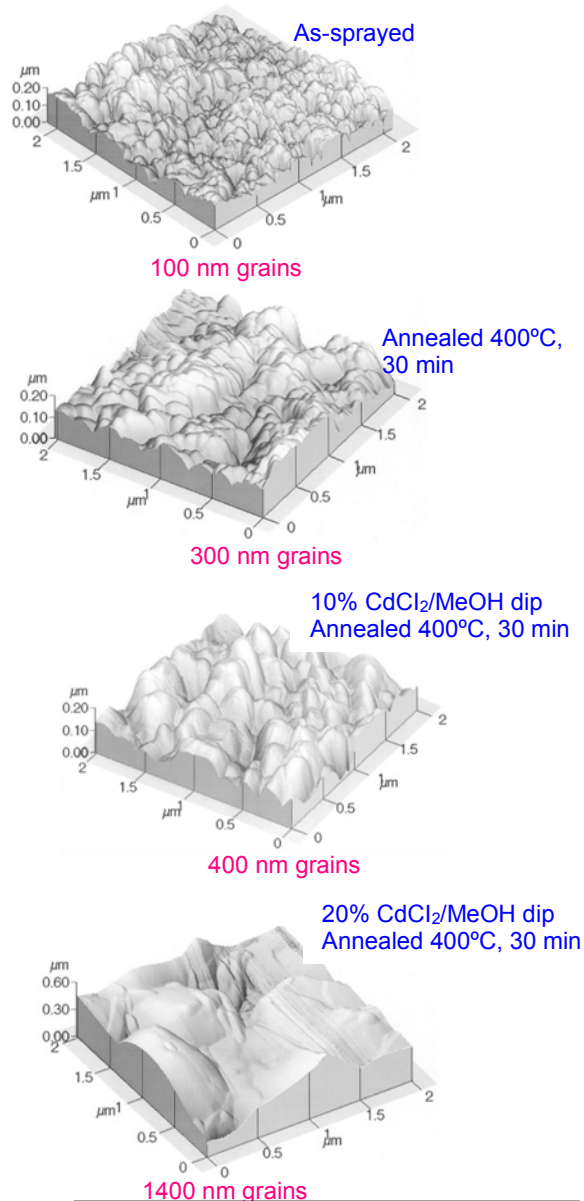


Figure 6. AFM images of as-sprayed and annealed films with and without CdCl₂ treatment.

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 CdCl₂ 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

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