

# A Novel Approach to Amine-Thiol Molecular Precursors for Fabrication of High Efficiency Thin Film CISSe/CIGSSe Devices

David Rokke, Swapnil D. Deshmukh, and Rakesh Agrawal

Davidson School of Chemical Engineering, Purdue University, West Lafayette, IN 47907, USA

**Abstract** — A new approach is presented for solution-processing of thin film chalcogenide materials which utilizes amine-thiol chemistry in a novel and judicious manner. Using this new approach, CISSe and CIGSSe films were fabricated with complete prevention of the carbonaceous fine grain layer, which has been a persistent impurity in molecular precursor systems. Using the standard device architecture, total area (active area) efficiencies of up to 11.5% (12.6%) and 11.8% (12.9%) were achieved for the CISSe and CIGSSe systems, respectively.

**Index Terms** – chemical analysis, photovoltaic cells, semiconductor devices, thin films

## I. INTRODUCTION AND BACKGROUND

Thin film photovoltaic devices have shown great promise with lab scale power conversion efficiencies reaching as high as 22.9% for CIGSe [1] and 22.1% for CdTe.[2] Despite such high lab scale device efficiencies, module efficiencies for these materials are significantly lower, making it difficult to compete with the progress of the silicon photovoltaic industry which has been successful in significantly reducing the cost/ $W_{DC}$ . [3] Large throughput production capabilities along with high efficiency module fabrication are required for the commercialization of these thin film technologies. Solution processing will enable the use of roll-to-roll production techniques which will effectively improve the rate of production and lower production costs. Recently, a new branch of research has started to investigate tandem architecture devices with high bandgap perovskite materials which has reached lab scale efficiencies up to 23.7%. [4] A printable, low bandgap material like CISE (bandgap of 1eV) would be appropriate for such an application to achieve higher efficiencies.

Hydrazine has already been used to demonstrate solution processed CIGSe device fabrication with a champion certified efficiency of 17.3%. [5] Although this confirms the potential of solution processing, the use of hydrazine on a large scale is not feasible due to its explosive and toxic nature. Among alternative solution processing routes, the amine-thiol route has shown impressive results in dissolving various metal salts, metal chalcogenides and even pure metals. [6], [7] A CIGSe device efficiency of 13.1% has been achieved by using metals and metal chalcogenides with the amine-thiol dissolution route. [8]

Similar to many other solution processing routes, this route suffers from residual carbon and carbonaceous impurities in

the final film, which affects photovoltaic performance. [9]–[12] Due to its versatile dissolution ability, this solvent system can also corrode materials that it encounters, complicating the handling procedures.

To address these issues, we developed a novel solution processing route which takes advantage of amine-thiol chemistry for pure metal dissolution to formulate an ink that diminishes the likelihood of impurity formation while using safer solvents, increasing the likelihood of successful scale up.

## II. EXPERIMENTAL DETAILS

The CIS ink (0.4M metals basis) was prepared by co-dissolution of copper and indium in an argon atmosphere with stoichiometric quantities of hexylamine and ethanedithiol in an acetonitrile solvent. Similarly, 0.2M (metals basis) CIGS ink was prepared using stoichiometric propylamine and ethanedithiol in acetonitrile solvent. After complete dissolution, (which takes anywhere between 24 hr to 10 days depending on concentration as well as type of solution) a doctor blading technique was used to cast absorber layer films from the corresponding inks on molybdenum coated soda lime glass substrates. The films were annealed at 300 °C for various durations ranging from 30 sec to 2 min to evaporate the solvent and form the CIS/CIGS material. These films were then subjected to a selenization process by heating with selenium pellets in a non-pyrolytic graphite box in a tube furnace assembly at 500-550 °C. Different selenization time intervals ranging from 15-40 min were used depending on initial film thicknesses. The devices were finished by depositing a 50 nm CdS layer via chemical bath deposition followed by the deposition of ~80 nm i-ZnO and ~220 nm ITO using RF sputtering. Ni/Al grids were deposited as metal contacts by e-beam evaporation to make devices with a total area of 0.47 cm<sup>2</sup>. The J-V characteristics were then measured under simulated AM1.5G illumination.

## III. RESULTS AND DISCUSSION

Metal dissolutions in amine-thiol mixtures can be treated as reactions rather than simple dissolutions. In this reaction, metals are oxidized to form organometallic complexes with amines and thiols. Our analysis with EXAFS/XANES, ESI-MS, and NMR suggests that the metals form dithiolate complexes in the solution in an amine-catalyzed reaction. [13] Taking advantage of this insight, an ink was prepared with the

minimum quantities of amines and thiols required to form the desired metal complexes. The metals consume nearly all of the added thiols, leaving no excess amine-thiol reactant available for further reaction, ultimately resulting in a more benign final solution.

FTIR analysis was performed on annealed inks for detection of any carbon residue. For comparison, a standard ink which has been used previously by researchers, was prepared with copper and indium salts along with selenium in a pure amine-thiol solution. The typical annealing temperature used in previous studies for CIGS amine-thiol film fabrications is around 300 °C,[9]–[12] so both the inks were drop cast on NaCl crystals and annealed at 200 °C and 300 °C for 5 min in a N<sub>2</sub> atmosphere.

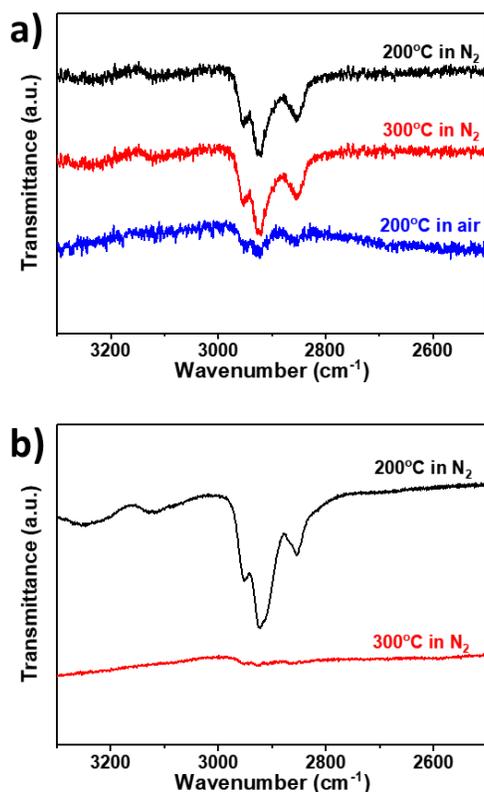


Fig. 1. FTIR spectrum of inks annealed on NaCl crystals at various temperatures: a) Standard CIS ink with copper acetylacetonate, indium acetate and elemental selenium dissolved in hexylamine and ethanedithiol solution; b) New CIS ink with elemental copper and indium dissolved in stoichiometric hexylamine and ethanedithiol with acetonitrile as a solvent.

Results from this analysis are shown in Fig. 1, which focuses on the alkane C-H stretching absorption peak obtained from FTIR. Both inks show C-H stretches when baked at 200 °C, confirming the presence of organometallic complexes. When annealed at 300 °C, the standard ink still shows the presence of C-H stretches (Fig. 1a) while the new stoichiometric ink shows almost complete removal of the C-H stretch from the film (Fig.

1b). Annealing the standard ink in air at 200 °C does remove some carbon from the film (Fig. 1a) but introduces the possibility of oxidizing the metal complexes which will ultimately affect the selenization process.

The residual carbon in the film fabricated from the standard ink interacts with selenium at high temperature during the process of selenization and gets trapped in the final film forming a carbon-rich fine grain layer in an uncontrolled manner that limits the effective implementation of amine-thiol inks. In contrast, the inks with stoichiometric amine-thiol have been shown to reliably decompose in to thiirane, hydrogen sulfide, and free amine allowing for the reproducible realization of carbon-free films.

Similar to the CIS ink, a CIGS ink formulation was developed by incorporating gallium in the ink. Previously, researchers have dissolved Cu, In, Ga and Se together in a diamine-dithiol solution for the fabrication of CIGSSe films. Previous studies have proposed that the presence of selenium is necessary for gallium dissolution in amine-thiol solutions, [8,11] but we successfully demonstrated gallium dissolution in the presence of copper and indium without the addition of selenium with the new stoichiometric amine-thiol solutions.

After confirming carbon removal from drop cast inks for both CIS and CIGS solution, films were coated using a doctor blading technique. Multiple layers were coated to control the film thickness and each layer was annealed at 300 °C. Once the desired thickness was achieved, the films were selenized as described in the experimental section and analyzed in SEM for the presence of a fine grain layer (Fig. 2). Fig. 2a shows the SEM cross section of the thin device fabricated from the standard amine-thiol ink which clearly indicates a ~100nm thick fine grain layer underneath the sub-micron (~500 nm) CIGSSe grains, while CIGSSe and CISSe films fabricated from new inks (Fig. 2b and 2d respectively) show complete absence of such a fine grain layer.

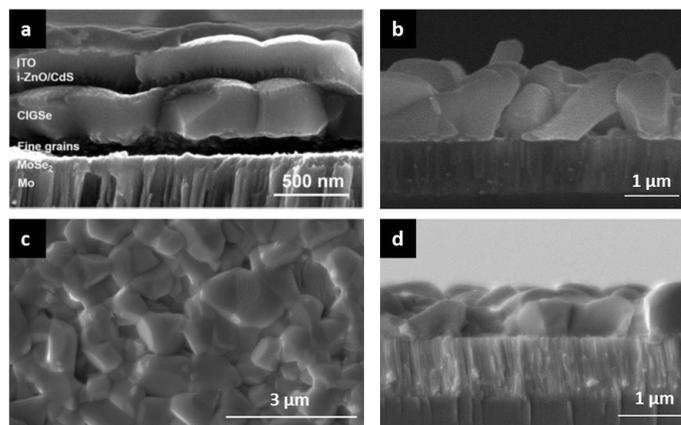


Fig. 2. SEM micrographs: a) Cross section of entire CIGSSe device fabricated with standard CIGS ink[9]; b) Cross section of selenized CIGSSe film fabricated from new CIGS ink; c) & d) Top view and cross section of selenized CISSe films fabricated from new CIS ink, respectively.

The devices were finished with CdS, ZnO, and ITO layers followed by Ni/Al grids. 100 nm of MgF<sub>2</sub> was deposited on top of these devices through e-beam evaporation to act as an anti-reflective coating. Both devices were light soaked for 20 min under AM1.5G illumination. J-V curves obtained for the devices are shown in Fig. 3.

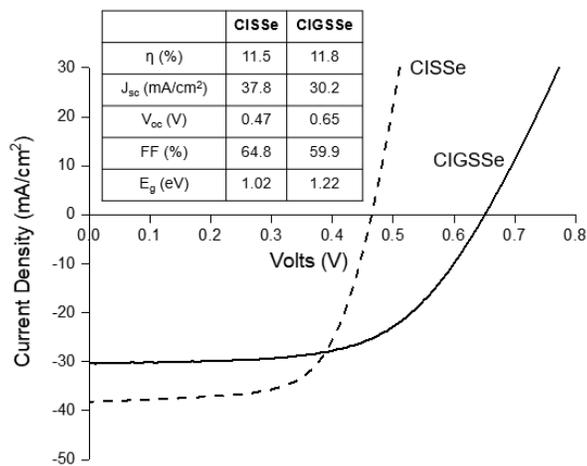


Fig. 3. J-V curve of CISSe and CIGSSe solar cells fabricated using stoichiometric inks. The insert table gives the device parameters for both devices.

For the champion CISSe device, a total area power conversion efficiency of 11.5% (active area efficiency of 12.6%) was achieved with cell area of 0.47 cm<sup>2</sup>. This efficiency, obtained through a solution processing route, is promising for applications in tandem architectures with perovskite materials which are generally processed through solution processing techniques. Preliminary results with CIGSSe devices show total area efficiency up to 11.8% for the champion device (active area efficiency of 12.9%). The device demonstrated a high  $V_{oc}$  of 650 mV, which is comparable to the  $V_{oc}$  obtained by the 17.3% efficient hydrazine device (660 mV)[5] and 65 mV higher than the highest efficiency amine-thiol CIGSSe device (585 mV).[8] Further optimization of processing conditions and window layer depositions along with gallium grading is required for improvement of these devices in terms of  $J_{sc}$  and FF to achieve high efficiencies.

#### IV. CONCLUSIONS

We have studied the versatile amine-thiol dissolution chemistry and have proposed a new approach to utilize it. The new approach is equally effective in terms of precursor dissolution abilities when compared with prevalent amine-thiol routes. In addition, it provides various advantages such as a tunable bulk solvent which is of great interest for scale up processes, and the elimination of any impurities or carbon residue in the final films, which will improve the performance of the device. We have demonstrated the highest power

conversion efficiency for amine-thiol processed CISSe devices and also have achieved one of the highest  $V_{oc}$  values for solution processed CIGSSe device. Further development of this route will enable the fabrication of high efficiency CIGSSe devices along with possible tandem architectures for CISSe devices.

#### V. ACKNOWLEDGEMENTS

The authors would like to thank Xianyi Hu, Essam Alruqobah, and Joseph Andler for their assistance in providing the Mo-coated soda lime glass. The authors would also like to acknowledge NSF funding under grants #1735282-NRT (SFEWS) and #1534691-DMR (DMREF)

#### REFERENCES

- [1] "Solar Frontier Achieves World Record Thin-Film Solar Cell Efficiency of 22.9%," 20-Dec-2017.
- [2] "First Solar Achieves Yet Another Cell Conversion Efficiency World Record," 23-Feb-2016.
- [3] K. A. W. Horowitz *et al.*, "An Analysis of the Cost and Performance of Photovoltaic Systems as a Function of Module Area An Analysis of the Cost and Performance of Photovoltaic Systems as a Function of Module Area," 2017.
- [4] <https://www.nrel.gov/pv/assets/pdfs/pv-efficiency-chart.20190103.pdf> Accessed Jan. 14 2019.
- [5] T. Zhang *et al.*, "High efficiency solution-processed thin-film Cu(In,Ga)(Se,S) 2 solar cells," *Energy Environ. Sci.*, vol. 9, no. 12, pp. 3674–3681, 2016.
- [6] D. H. Webber and R. L. Brutchey, "Alkahest for V2VI3 chalcogenides: Dissolution of nine bulk semiconductors in a diamine-dithiol solvent mixture," *J. Am. Chem. Soc.*, vol. 135, no. 42, pp. 15722–15725, 2013.
- [7] R. Zhang *et al.*, "Metal-metal chalcogenide molecular precursors to binary, ternary, and quaternary metal chalcogenide thin films for electronic devices," *Chem. Commun.*, p. DOI: 10.1039/C5CC09915C, 2016.
- [8] Q. Fan *et al.*, "Regulating the starting location of front-gradient enabled highly efficient Cu(In,Ga)Se 2 solar cells via a facile thiol-amine solution approach," *J. Mater. Chem. A*, vol. 6, no. 9, pp. 4095–4101, 2018.
- [9] X. Zhao, M. Lu, M. J. Koeper, and R. Agrawal, "Solution-processed sulfur depleted Cu(In,Ga)Se<sub>2</sub> solar cells synthesized from a monoamine-dithiol solvent mixture," *J. Mater. Chem. A*, vol. 4, no. 19, pp. 7390–7397, 2016.
- [10] Z. Zhao *et al.*, "Solution-based synthesis of dense, large grained CuIn(S, Se)<sub>2</sub> thin films using elemental precursor," *Ceram. Int.*, vol. 43, no. 8, pp. 6257–6262, 2017.
- [11] D. Zhao *et al.*, "Solution-deposited pure selenide CIGSe solar cells from elemental Cu, In, Ga, and Se," *J. Mater. Chem. A*, vol. 3, no. 38, pp. 19263–19267, 2015.
- [12] P. Arnou, C. S. Cooper, A. V. Malkov, J. W. Bowers, and J. M. Walls, "Solution-processed CuIn(S,Se)<sub>2</sub> absorber layers for application in thin film solar cells," *Thin Solid Films*, vol. 582, pp. 31–34, 2015.
- [13] P. Murria *et al.*, "Speciation of CuCl and CuCl<sub>2</sub> Thiol-Amine Solutions and Characterization of Resulting Films: Implications for Semiconductor Device Fabrication," *Inorg. Chem.*, vol. 56, no. 23, pp. 14396–14407, Dec. 2017.