M.L. 2014 Project Abstract

For the Period Ending June 30, 2017

PROJECT TITLE: Solar Cell Materials from Sulfur and Common Metals
PROJECT MANAGER: Lee Penn and Eray Aydil
AFFILIATION: University of MN – Twin Cities ; Department of Chemistry
Mailing Address: 207 Pleasant St. SE
City/State/Zip Code: Minneapolis, MN 55455
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FUNDING SOURCE: Environment and Natural Resources Trust Fund
LEGAL CITATION: M.L. 2014, Chp. 226, Sec. 2, Subd. 08a

APPROPRIATION AMOUNT: \$494,000 AMOUNT SPENT: \$476,496 AMOUNT REMAINING: \$17,504

Overall Project Outcomes and Results

We successfully synthesized the proposed transition metal sulfide materials with controlled composition. Preparing materials without impurities, which essential for success since impurities in the thin film of light absorbing material will cause solar cells to fail, was particularly challenging. We identified which synthetic variables are most important for preventing impurities. In addition, we can successfully control particle size, which is important for making high quality thin films of these materials. We developed a reproducible protocol for preparing thin films of the particles. We examined effects of annealing conditions (sulfur partial pressure, heating rate, heating time, pre-annealing compaction, the nature of the molybdenum layer beneath the CZTS particles, and more) on the CZTS films and were able to identify ideal conditions for the necessary annealing step.

A particularly exciting outcome was the development of a protocol for removing impurities from the thin films. During the annealing step, impurities often form even when the thin films are prepared using pure material. To solve this problem, we developed a selective etching method that effectively removes those impurities ("Selective Etching of Light Absorber Substrates", Application No. 62/328,851, which was filed April 28, 2016 but did not proceed to patent status).

Our biggest outcome expected was a fundamental advance in our ability to make high quality thin films of photovoltaic quality CZTS, and we did succeed in that regard. High quality thin films are required for the fabrication of high performing solar cells. In addition, we developed a green synthetic method for the controlled production of CZTS nanoparticles and can prepare high quality, microcrystalline thin films on conductive substrates using the microwave synthesis method. Unfortunately, we did not realize our final goal, which was to make a prototype solar cell fabricated using the aforementioned materials.

Project Results Use and Dissemination

We have published three papers in the peer-reviewed literature describing our results and two additional papers that are currently in review with scientific journals.

Unfortunately, Application No. 62/328,851, which was filed April 28, 2016, did not proceed to patent status. Our technology would have been used in the production of both copper indium gallium disulfide

(CIGS) and copper zinc tin sulfide (CZTS) thin film solar cells. The changing solar cell market landscape and continued significant dominance of silicon solar cells over CIGS and CZTS devalued our technology despite its green advantages. Silicon solar cells now dominate over 90% of the solar cell market. Moreover, the provisional patent application was returned with objections and to narrow the claims. Continuing the patent application for these reasons did not make economic sense.



Environment and Natural Resources Trust Fund (ENRTF) M.L. 2014 Work Plan

Date of Report:	30 January 2019			
Date of Next Status Update Report:	final report			
Date of Work Plan Approval:	4 June 2014			
Project Completion Date:	30 June 2017			
Does this submission include an amendment request?				

PROJECT TITLE: Solar Cell Materials from Sulfur and Common Metals

Project Manager:	Lee Penn and Eray Aydil
Organization:	Univerisity of MN – Twin Cities ; Department of Chemistry
Mailing Address:	207 Pleasant St. SE
City/State/Zip Code:	Minneapolis, MN 55455
Telephone Number:	612 626 4680
Email Address:	<u>rleepenn@umn.edu</u>
Web Address:	http://www.chem.umn.edu/groups/penn/

Location: Hennepin County (University of MN – Twin Cities ; Department of Chemistry and Department of Chemical Engineering and Materials Science); anticipated impact is expected to be at the statewide level.

Total ENRTF Project Budget:	ENRTF Appropriation:	\$494,000
	Amount Spent:	\$476,496
	Balance:	\$ 17,504

Legal Citation: M.L. 2014, Chp. 226, Sec. 2, Subd. 08a

Appropriation Language:

\$494,000 the second year is from the trust fund to the Board of Regents of the University of Minnesota to develop solar cell materials using nontoxic and common metals combined with sulfur. This appropriation is subject to Minnesota Statutes, section 116P.10. This appropriation is available until June 30, 2017, by which time the project must be completed and final products delivered.

I. PROJECT TITLE: Solar Cell Materials from Sulfur and Common Metals

II. PROJECT STATEMENT:

Safe and clean energy production is a grand challenge facing our society. The development of sustainable electrical energy sources is an urgent need in the state of Minnesota and in the United States. Solar energy is renewable and is a viable and attractive option. To become commonplace, solar cells must be inexpensive and robust, and they must be comprised of abundant, cheap, nontoxic materials. We propose to develop innovative methodology for producing thin films of metal sulfides for use in solar cells. Instead of using toxic elements like cadmium, we propose to use iron, copper, and other far less toxic metals combined with sulfide. By targeting sulfides for use in solar cells, sulfur waste from mining and other industrial operations could become a viable resource in the production of robust and inexpensive solar cells. Finally, we propose to exploit microwave energy so as to reduce the energy required to produce photovoltaic quality materials.

We aim to develop a method for producing CZTS, for example, with the high efficiencies required for realistic implementation of the affordable photovoltaic devices but without the hazards associated with using rare and/or toxic elements and other source materials.

The biggest outcome expected is a fundamental advance in our ability to make high quality thin films of photovoltaic quality CZTS.

Major Results Expected:

- 1. Generalized, green synthetic methods for the controlled production of kesterite nanoparticles.
- 2. Successful methods for preparation of high quality, microcrystalline thin films directly onto conductive substrates using the microwave synthesis method.
- 3. Prototype solar cell fabricated using promising candidate materials.

Deliverables: Open scientific presentations and papers addressing the above objectives; patents for methods to produce photovoltaic quality thin films of CZTS using our new method.

III. PROJECT STATUS UPDATES:

Project Status as of January 1, 2015: Two researchers are working on the project: Dr. Seung Wook Shin and Mr. Alex Pinto. The research-grade microwave has been purchased and installed, and the instrument is performing well. We have successfully synthesized transition metal sulfide materials, but a particular challenge is preparing materials without impurities. Impurities will cause solar cells to fail. We have determined which synthetic variables are most important for preventing the formation of impurities. We have also made progress in controlling particle size as well as controlling the stoichiometry of the resultant materials, with the ideal stoichiometry somewhat copper deficient. Both researchers have received the necessary training to effectively synthesize and characterize materials.

Amendment Request (December 29, 2014):

Due to accounting office schedules, the winter project report due dates are requested to occur on January 15, 2016 and January 15, 2017.

Approved by the LCCMR January 7, 2015.

Amendment Request (January 5, 2015):

Request transfer of \$466 from Equipment/Tools/Supplies to Capital Expenditures.

Project Status as of July 1, 2015: Two researchers continue on the project: Dr. Seung Wook Shin and Mr. Alex Pinto. We have successfully synthesized transition metal sulfide materials, and we can control the mixture of phases produced. However, a continuing challenge is preparing materials without impurities, which will cause solar cells to fail. We have further refined the synthetic conditions so as to prevent the formation of impurities and eliminate the need for surfactants. Even more importantly, we have developed a selective etching method that removes key impurities. We have achieved substantial control over the stoichiometry of the transition metal sulfides, with preparation of phase-pure materials containing differing amounts of copper, zinc, cobalt, tin, iron, sulfur, and selenium. Preparation of thin films of the transition metal sulfides has begun, with careful characterization before and after annealing.

Amendment Request (January 14, 2016):

We request a retroactive transfer of \$3,462 from Repairs and Maintenance (\$1,864 from activity 1 and \$1,568 from activity 2) and moving forward a transfer of \$22,000 from personnel into User Fees for instrumentation. Materials characterization is essential to the success of our proposed work. We have had excellent success producing materials with controlled stoichiometry and the work involving the preparation of thin films is also proceeding with great success. Our productivity has lead to a higher than expected number of samples requiring materials characterization for progress on this project. The user fees pay for the use of techniques such as transmission electron microscopy and Raman spectroscopy.

Amendment approved by LCCMR 1-25-2016

Project Status as of January 15, 2016: Two researchers continue on the project: Dr. Seung Wook Shin and Mr. Alex Pinto. We have successfully synthesized transition metal sulfide materials, and we can control the mixture of phases produced. We have addressed the challenge of preparing materials without impurities, which cause solar cells to fail. We have refined the synthetic conditions so as to prevent the formation of impurities and eliminate the need for surfactants. We have achieved substantial control over the stoichiometry of the transition metal sulfides, with successful preparation of phase-pure materials containing differing amounts of copper, zinc, cobalt, tin, iron, sulfur, and selenium. Preparation of thin films of the transition metal sulfides is in full swing, with careful characterization before and after annealing. During annealing, impurities sometimes form. Importantly, we have refined the selective etching method developed in the previous cycle. The method effectively removes those key impurities while leaving the mixed transition metal sulfide intact, and we are in the process of filing a patent on the process.

Project Status as of July 1, 2016: Two researchers continue on the project: Dr. Seung Wook Shin and Mr. Alex Pinto. Our synthetic conditions enable us to avoid the use of surfactants, which results in higher quality thin films of the transition metal sulfides. We have achieved substantial control over the stoichiometry of the transition metal sulfides, with successful preparation of phase-pure materials containing differing amounts of copper, zinc, cobalt, tin, iron, sulfur, and selenium. Our methods for preparing thin films of the transition metal sulfides are improving, and results from careful characterization before and after annealing demonstrate that the quality of the thin films is sensitive to sodium ion concentration as well as the temperature at which the films are annealed. During annealing, impurities sometimes form, and the selective etching method effectively removes those impurities ("Selective Etching of Light Absorber Substrates", Application No. 62/328,851. Filed April 28, 2016). In addition, a research article was submitted to *Green Chemistry*, and the paper is currently in revision. This paper reports on the experimental results demonstrating the efficacy of the selective etching process. Finally, a research article describing synthetic results is currently in review with *Inorganic Chemistry*.

Amendment Request (January 13, 2017):

We request a retroactive transfer of \$13,774 from Personnel and moving forward an additional transfer of \$20,000 from personnel into User Fees for instrumentation. Materials characterization is essential to the success of our proposed work. We have had excellent success producing materials and thin films but require additional materials characterization in order to obtain data to facilitate further refinement of the thin film methods. The user fees pay for the use of techniques such as transmission electron microscopy and Raman spectroscopy at the University of Minnesota Characterization Facility. Our higher-than-anticipated productivity means that we can decrease funds in the personnel category without compromising project aims.

Amendment Approved by LCCMR 1/30/2017

Project Status as of January 15, 2017: Two researchers continue on the project: Dr. Seung Wook Shin and Mr. Alex Pinto. We have spent substantial effort examining the effects of annealing conditions (sulfur partial pressure, heating rate, heating time, pre-annealing compaction, the nature of the molybdenum layer beneath the CZTS particles, and more) on the CZTS films. During annealing, impurities sometimes form, and the selective etching method effectively removes those impurities ("Selective Etching of Light Absorber Substrates", Application No. 62/328,851, which was filed April 28, 2016). An important result of ongoing research has been refining the etching process so that we can remove the impurity phases. In addition, a research article was submitted to *Green Chemistry*, and the paper is currently in revision. Finally, the research article submitted to *Inorganic Chemistry* that describes synthetic results is currently in revision.

Amendment Request (January 13, 2018):

We request a retroactive transfer of \$2,450 from User Fees for instrumentation into personnel. We spent \$2,450 more than anticipated with our amendment of January 2017 and substantially less than the \$20,000 that had been transferred into the area of User Fees for instrumentation.

Overall Project Outcomes and Results: We successfully synthesized transition metal sulfide materials with controlled composition. A particular challenge was preparing materials without impurities, which essential for success since impurities in the thin film of light absorbing material will cause solar cells to fail. We determined which synthetic variables are most important for preventing the formation of impurities. We can successfully control particle size and composition of the resultant materials. We have established a reproducible protocol for preparing thin films of the CZTS particles. We examined effects of annealing conditions (sulfur partial pressure, heating rate, heating time, pre-annealing compaction, the nature of the molybdenum layer beneath the CZTS particles, and more) on the CZTS films and were able to identify ideal conditions for the necessary annealing step. During annealing, impurities sometimes form, and the selective etching method effectively removes those impurities ("Selective Etching of Light Absorber Substrates", Application No. 62/328,851, which was filed April 28, 2016 but did not proceed to patent status). Our biggest outcome expected was a fundamental advance in our ability to make high quality thin films of photovoltaic quality CZTS, and we did succeed in that regard. High quality thin films are required for the fabrication of high performing solar cells. We developed a green synthetic method for the controlled production of CZTS nanoparticles and can prepare high quality, microcrystalline thin films on conductive substrates using the microwave synthesis method. Unfortunately, we did not realize our final goal, which was to make a prototype solar cell fabricated using the aforementioned materials.

We have published three papers in the peer-reviewed literature describing our results.

Pinto, A.H., S.W. Shin, E.S. Aydil, and R.L. Penn, "Selective removal of Cu2-x(S,Se) phases from Cu2ZnSn(S,Se)(4) thin films," Green Chemistry, 18, 5814-5821 (2016).

Pinto, A.H., S.W. Shin, E. Isaac, T. R. Knutson, E.S. Aydil, and R.L. Penn, "Controlling Cu2ZnSnS4 (CZTS) phase in microwave solvothermal synthesis" Journal of Materials Chemistry A, 5, 23179-23189 (2017).

Pinto, A.H., S.W. Shin, A. Sharma, R.L. Penn, and E.S. Aydil, "Synthesis of Cu2(Zn1-xCox)SnS4 Nanocrystals and Formation of Polycrystalline Thin Films from Their Aqueous Dispersions" Journal of Materials Chemistry A (Manuscript ID: TA-ART-07-2017-006295.R1) Status – In Press.

In addition, we have two additional papers that are currently in review with scientific journals.

Unfortunately, Application No. 62/328,851, which was filed April 28, 2016, did not proceed to patent status. Our technology would have been used in the production of both copper indium gallium disulfide (CIGS) and copper zinc tin sulfide (CZTS) thin film solar cells. The changing solar cell market landscape and continued significant dominance of silicon solar cells over CIGS and CZTS devalued our technology despite its green advantages. Silicon solar cells now dominate over 90% of the solar cell market. Moreover, the provisional patent application was returned with objections and to narrow the claims. Continuing the patent application for these reasons did not make economic sense.

IV. PROJECT ACTIVITIES AND OUTCOMES:

ACTIVITY 1: Develop synthetic process using sulfur, common metals, and a microwave-based method for producing mixed metal sulfides

Description: Using Nature as a guide and applying eight of the twelve principles of Green Chemistry, we will develop a rational approach to the green synthesis of CZTS thin films with properties ideal for incorporation into advanced technologies. Critical control parameters include the degree to which the material is nonstoiciometric (e.g., some degree of Cu deficiency is good from the perspective of electrical and optical properties), crystal size (i.e., hundreds of nanometers for the best photovoltaic properties), and defects (concentration, type, and distribution).

Using less toxic metals in combination with sulfur, we will develop methods for producing nanoparticles composed of common and less toxic elements. Systematic experiments will use metal salts in combination with sulfur sources in order to determine the best synthetic conditions for phase pure product. These experiments will enable development of a general synthetic procedure for producing pure materials that will have excellent performance in solar cells. Using microwaves will enable both faster production and dramatically reduced energy requirements.

The products of the above syntheses will be characterized using four primary methods: X-ray diffraction (XRD), Raman Spectroscopy, Scanning Transmission Electron Microscopy (STEM) with Electron Energy Loss Spectroscopy (EELS) and Energy Dispersive Spectroscopy (EDS), and UV-Vis Spectroscopy. XRD will enable quick determination if the material synthesized has a structure that is consistent with the kesterite structure and whether impurities of quite different structures (e.g., oxides or other sulfide structures) are present. In kesterites, it has been found that the S sublattice determines the unit cell dimensions. Consequently, it is difficult to identify and distinguish different kesterites based on XRD alone. Raman spectra are sensitive to the metal cations, making Raman spectroscopy a sensitive characterization method for kesterites. Thus, Raman spectroscopic characterization, UV-Vis spectroscopy will be used to determine the band gap of the material using methods well established in our laboratories. Finally, STEM with EELS and/or EDS will be employed to determine whether the elements are distributed homogeneously or heterogeneously.

Materials will be tested using established methods in order to predict performance in solar cell applications.

Summary Budget Information for Activity 1:

ENRTF Budget: \$241,568 Amount Spent: \$241,568 Balance: 0

Completion Date: Spring 2016								
Outcome	Completion Date	Budget						
1. Develop effective synthetic methods for pure transition metal	Summer 2015	\$140,000						
sulfides								
2. Preparation of photovoltaic quality materials and extensive testing	Spring 2016	\$ 101,568						

Activity Status as of January 1, 2015: We have made solid progress towards developing a green synthesis of metal sulfides with controlled particle size and stoichiometry. We have successfully synthesized phase-pure transition metal sulfide materials. A particular challenge is preparing materials without impurities. We have determined which synthetic variables are most important for preventing the formation of impurities since impurities will catastrophically impact the solar cells fabricated. We have also made progress in controlling particle size as well as controlling the stoichiometry of the resultant materials. Both researchers have received the necessary training to effectively synthesized. Results demonstrate that the oft added ethylenediamine, which is a hazardous chemical, is not a necessary additive to produce phase-pure materials. Rather, pH is the important control parameter. A combination of hydrothermal, which avoids the use of toxic solvents, and microwave processing has been employed. Microwave processing results in high quality materials in minutes rather than hours.

Products of syntheses have been characterized using X-ray diffraction (XRD), Raman Spectroscopy, Transmission and Scanning Electron Microscopy with Energy Dispersive Spectroscopy (EDS), and UV-Vis Spectroscopy. XRD results demonstrate phase pure material in the case of the cobalt iron sulfides. In the case of CZTS, a combination of results obtained using Raman spectroscopy and XRD demonstrate that we can prepare CZTS in both the wurtzite structure and in the kesterite structure. This is important because the preparation of thin films from wurtzite CZTS may enable the production of better thin films. EDS, which enables quantitatation of the composition of the produced materials demonstrates that we are improving our control over stoichiometry, with experiments aimed at producing copper deficient CZTS currently in progress.

The two researchers on the project have received training in standard operating procedures, safety protocols, and the synthesis and characterization methods to undertake the project. The tools required for annealing samples in the presence of sulfur vapor are now in place and have been tested using CZTS nanoparticles. The research-grade microwave has been purchased and installed, and the instrument is performing well.

Activity Status as of July 1, 2015: We are refining our green synthesis of metal sulfides with controlled particle size and stoichiometry. We have successfully synthesized phase-pure transition metal sulfide materials with controlled stoichiometry. We have achieved substantially improved control over the stoichiometry of the resultant materials. EDS enables quantitatation of the composition of the produced materials, and results demonstrate improved control over stoichiometry, with experiments aimed at producing copper deficient CZTS currently in progress. Microwave processing continues to produce superior materials in minutes rather than hours.

During the previous period, a combination of results obtained using Raman spectroscopy and XRD demonstrated that we can prepare CZTS in both the wurtzite structure and in the kesterite structure. This is important because the preparation of thin films from wurtzite CZTS may enable the production of better thin films. Now, we have learned how to control the phase composition of the CZTS produced from the reaction mixture. Key control parameters are the molar ratio of the sulfur source to the total metal cations added as well as the oxidation state of the tin ions.

A particular challenge is preparing materials without impurities. We have determined which synthetic variables are most important for preventing the formation of impurities since impurities will catastrophically impact the solar cells fabricated. However, we have developed a procedure for selective removal of key impurities – most notably – copper sulfide. A combination of mercapto ethanol and ethylenediamine results in the selective

dissolution of the copper sulfide, which is one of the most problematic impurities, but leaves the CZTS intact. This is a major step forward and will enable preparation of improved thin films.

Activity Status as of January 15, 2016: We have further improved our control over the stoichiometry of materials produced using the microwave method. Microwave processing continues to produce superior materials in minutes rather than hours. During the previous period, we demonstrated control over the phase of the product material, and we have successfully used those results to produce materials in larger quantities for use in preparing thin films.

The selective etching method has been put to the test, and we have demonstrated that the method effectively removes binary compounds (e.g., copper sulfide or tin sulfide) from the product material without significant loss of the desired mixed metal sulfide. Detailed characterization using EDS demonstrates that the method leaves the desired mixed metal sulfide intact.

A manuscript describing the etching process is currently in preparation. A manuscript describing our improved control over the stoichiometry of materials produced using the microwave method is currently in preparation. Both will be submitted to peer-reivewed scientific journals. Finally, a patent describing the selective etching of Cu sulfide and selenide impurities from CZTSSe thin films is currently in progress (Provisional Patent Application - OTC Case 20160046).

Activity Status as of July 1, 2016: Results from activity 1 are being applied to work in activity 2. The synthetic methods enable production of materials for the preparation of thin films, which is the focus of activity 2. The patent application describing the selective etching of Cu sulfide and selenide impurities from the thin films has been filed ("Selective Etching of Light Absorber Substrates", Application No. 62/328,851. Filed April 28, 2016). In addition, a research article was submitted to *Green Chemistry*, and the paper is currently in revision. This paper reports on the experimental results demonstrating the efficacy of the selective etching process. Finally, a research article describing synthetic results is currently in review with *Inorganic Chemistry*.

Activity Status as of January 15, 2017: Results from activity 1 are being applied to work in activity 2. The synthetic methods enable production of materials for the preparation of thin films, which is the focus of activity 2.

Final Report Summary: Results from activity 1 were successfully applied to work in activity 2. The synthetic methods enabled production of materials for the preparation of thin films, which was the focus of activity 2.

ACTIVITY 2: Preparation of Thin films

In order to prepare solar cells, the material must be made into a high quality thin film. The above methods will be adapted to enable production of thin films of metal sulfides on both rigid and flexible materials. Using the synthetic conditions determined from the above work, thin films will be synthesized directly onto conductive substrates. Important properties include an ideal thickness of on the order of 2 microns, a grain size in the range of hundreds of nanometers, and phase purity. Synthetic conditions may have to be modified in order to achieve these goals with a thin film. A major goal is to retain the low energy requirements and directly synthesize thin films that are pure, have excellent particle size, and optimal properties for use in solar cells.

Microwave heating of a conductive material submerged in a solution results in preferential heating of the conductive material while leaving the surrounding solution comparatively cool. We will exploit this effect in order to directly coat substrates with CZTS. Results from the work described above, in which CZTS is synthesized by precipitation from the solution phase, will inform the experimental design for the controlled synthesis of CZTS onto conductive substrates. In fact, we have successfully prepared CZTS thin films by submerging

substrates coated with conductive material into metal precursor solutions. When the microwave energy is absorbed strongly by the thin conductive coating, its temperature increases enough to deposit films exclusively onto the conductive layer, leaving the uncoated portions of the substrate CZTS-free and the surrounding solution free of precipitates. To date, resulting films are approximately 1-3 microns thick, which is a suitable thickness for use as a photovoltaic material. However, the crystal size is ca. ten nanometers in diameter, which is not large enough.

In addition, the ideal crystal size is hundreds of nanometers for the best photovoltaic properties. Post-deposition microwave annealing in neat solvent increased crystallite volume by eightfold, but this has only resulted in increasing the average crystal size to a few tens of nanometers. When nanocrystalline CZTS films are annealed in sulfur gas at high temperature (ca. 500 °C), substantial grain growth is achieved (results in the Aydil lab). At typical annealing temperatures, the S exists as vapor, and we have developed strategies to avoid S condensation on the films. Sintering and Ostwald ripening occur simultaneously, which results in substantial grain growth to sizes in the 0.5-2 µm size range. Here, we propose to tuning solution conditions during the microwave anneal step (see below) in order to achieve the larger size needed for the best photovoltaic properties. Experimental variables include the solvent properties and the solubility of S-bearing species in that solvent. Employing microwaves will enable drastic reduction in the energy required to anneal the films and may enable the use of flexible substrates.

The CZTS films will be annealed using the microwave approach, in which the sample is placed in a solution prepared using the target solvent and elemental sulfur or sulfur-containing molecules and exposed to microwaves so as to preferentially heat the underlying conductive layer and the CZTS film. In addition, CZTS films will be annealed using the more conventional high temperature approach, in which the sample is sealed into an ampule containing elemental sulfur or H2S gas and heated to high temperature, for comparison. Films will be characterized using the techniques described below. We hypothesize that employing a solvent in which CZTS is sparingly soluble but sulfur is moderately soluble will enable improved annealing so as to achieve the necessary crystal size (i.e., hundreds of nanometers).

The thin films produced will be characterized using four primary methods: X-ray diffraction (XRD), Raman Spectroscopy, Scanning Transmission Electron Microscopy (STEM) with Electron Energy Loss Spectroscopy (EELS) and Energy Dispersive Spectroscopy (EDS), and UV-Vis Spectroscopy.

Summary Budget Information for Activity 2:	ENRTF Budget:	\$ 252,432
	Amount Spent:	\$ 177,867
	Balance:	\$ 17,504
Completion Date: Summer 2017		

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Outcome	Completion Date	Budget
1. Photovolatic quality thin films combined with extensive testing	Summer 2017	\$ 154,000
2. Data synthesis, reporting, and recommendations	Summer 2017	\$ 98,432

Activity Status as of January 1, 2015: None to date.

Activity Status as of July 1, 2015: None to date.

Activity Status as of January 15, 2016: We have begun to prepare thin films using product materials. An important step in preparing high quality films is annealing in order to produce films suitable for use in a photovoltaic device. Thus far, the microwave annealing approach has not produced satisfactory results. However, annealing the thin films in sealed ampules containing elemental sulfur has proven very successful. Unfortunately, impurities such as copper sulfide sometimes form. We have applied the selective etching method to thin films with good success. The method is similar to what is described in Activity 1 except that the thin film is dipped directly into the etching solution. Characterization demonstrates that the thin film remains

intact as the copper sulfide impurity is removed. We are currently preparing a manuscript describing the results for publication, and a patent describing the selective etching of Cu sulfide and selenide impurities from CZTSSe thin films is currently in progress (Provisional Patent Application - OTC Case 20160046).

Activity Status as of July 15, 2016: Work refining our methods for preparing thin films continues. Work from activity 1 means that we have good materials to use in the preparation of the thin films. Critical variables include how films are compressed prior to annealing, the amount of sodium added, and annealing temperature. The best films will have crystallites with sizes in the micron range and no cracks. In addition, the molybdenum layer onto which the film is deposited must be preserved, and we have made progress in finding conditions that minimize the formation of a thick MoS₂ layer. The etching method is effective in removing copper sulfide impurities from thin films, and work continues to refine the method for further improvement. In addition, films subjected to the etching process will be tested for impact on properties related to solar cell performance.

Activity Status as of January 1, 2017: We have spent substantial effort examining the effects of annealing conditions (sulfur partial pressure, heating rate, heating time, pre-annealing compaction, the nature of the molybdenum layer beneath the CZTS particles, and more) on the CZTS films. During annealing, impurities sometimes form, and the selective etching method effectively removes those impurities ("Selective Etching of Light Absorber Substrates", Application No. 62/328,851, which was filed April 28, 2016). An important result of ongoing research has been refining the etching process so that we can remove the impurity phases. An additional challenge is that some conditions result in the CZTS thin film peeling away from the underlying substrate, which makes the thin film unsuitable for use in a solar cell. We continue experiments to attempt to solve this problem. Finally, we are completing the preparation of scientific reports for submission to the peer-reviewed scientific literature.

Final Report Summary: We established a reproducible protocol for preparing thin films of the CZTS particles. We examined effects of annealing conditions (sulfur partial pressure, heating rate, heating time, pre-annealing compaction, the nature of the molybdenum layer beneath the CZTS particles, and more) on the CZTS films and were able to identify ideal conditions for the necessary annealing step. During annealing, impurities sometimes form, and the selective etching method effectively removes those impurities ("Selective Etching of Light Absorber Substrates", Application No. 62/328,851, which was filed April 28, 2016 but has not proceeded to patent status). Our biggest outcome expected was a fundamental advance in our ability to make high quality thin films of photovoltaic quality CZTS, and we did succeed in that regard. We developed a green synthetic method for the controlled production of CZTS nanoparticles and can prepare high quality, microcrystalline thin films on conductive substrates using the microwave synthesis method. Unfortunately, we did not realize our final goal, which was to make a prototype solar cell fabricated using the aforementioned materials.

V. DISSEMINATION:

Description: Open scientific presentations and papers addressing the above objectives; patents for methods to produce photovoltaic quality thin films of CZTS using our new method; incorporation of solar cell in outreach activities.

Status as of January 1, 2015: None to date.

Status as of July 1, 2015: One manuscript is currently under preparation. It describes control over the phase composition of CZTS prepared using our microwave synthesis method. In addition, we are initiating the process for filing a patent for the selective dissolution of impurities from product materials.

Status as of January 1, 2016: Two manuscripts are currently under preparation, including the one started in the

previous period. The first describes control over the phase composition of CZTS prepared using the microwave synthesis method and will be submitted within the next six weeks. The second describes the selective etching method. Finally, the process for filing a patent describing the selective etching method is underway.

A patent describing the selective etching of Cu sulfide and selenide impurities from CZTSSe thin films is currently in progress (Provisional Patent Application - OTC Case 20160046).

Status as of July 1, 2016: Provisional Application (UMN 20160046) has been filed. "Purification of Thin Film Solar Cell Absorber Materials" was recognized as a 2016 TechConnect National Innovation Awardee at the May 2016 TechConnect-National Innovation Summit, Washington, D.C. In addition, a research article was submitted to *Green Chemistry*, and the paper is currently in revision. This paper reports on the experimental results demonstrating the efficacy of the selective etching process. Finally, a research article describing synthetic results is currently in review with *Inorganic Chemistry*. Two new manuscripts are also under preparation.

Status as of January 1, 2017: The research article submitted to *Green Chemistry* has been published. Finally, the research article submitted to *Inorganic Chemistry* that describes synthetic results is currently in revision. Two new manuscripts are nearing submission to journals, and one additional manuscript is in preparation.

Final Report Summary:

A Provisional Application (UMN 20160046) was filed. "Purification of Thin Film Solar Cell Absorber Materials" was recognized as a 2016 TechConnect National Innovation Awardee at the May 2016 TechConnect-National Innovation Summit, Washington, D.C.

We published three papers in the peer-reviewed literature describing our results.

Pinto, A.H., S.W. Shin, E.S. Aydil, and R.L. Penn, "Selective removal of Cu2-x(S,Se) phases from Cu2ZnSn(S,Se)(4) thin films," Green Chemistry, 18, 5814-5821 (2016).

Pinto, A.H., S.W. Shin, E. Isaac, T. R. Knutson, E.S. Aydil, and R.L. Penn, "Controlling Cu2ZnSnS4 (CZTS) phase in microwave solvothermal synthesis" Journal of Materials Chemistry A, 5, 23179-23189 (2017).

Pinto, A.H., S.W. Shin, A. Sharma, R.L. Penn, and E.S. Aydil, "Synthesis of Cu2(Zn1-xCox)SnS4 Nanocrystals and Formation of Polycrystalline Thin Films from Their Aqueous Dispersions" Journal of Materials Chemistry A (Manuscript ID: TA-ART-07-2017-006295.R1) Status – In Press.

In addition, we have two additional papers that are currently in review with peer-reviewed scientific journals.

VI. PROJECT BUDGET SUMMARY:

A. ENRTF Budget Overview:

Budget Category	\$ Amount	Explanation
Personnel:	\$104,250	Support for graduate student (3 years funding
		plus fringe); co-advised and working in close
		collaboration with the post-doctoral researcher;
		Design and execute synthetic methods for
		preparation of thin films using green methods.
		Characterize materials and films for suitability
		as photovoltaics. Prepare the prototype solar

		cell(s) in direct collaboration with the post-
		doctoral researcher.
Personnel:	\$166,635	Support for Post-doctoral researcher (; 3 years
		funding plus fringe); co-advised; Design and
		execute synthetic methods for preparation of
		thin films using green methods. Characterize
		materials and films for suitability as
		photovoltaics. Provide some supervision and
		mentoring towards the graduate student.
		Prepare the prototype solar cell(s) in direct
		collaboration with the graduate student.
Personnel:	\$60,841	Support for R. Lee Penn, project manager. 1.5
		months summer salary per year (plus fringe).
		Supervise post-doc and graduate student;
		perform electron micrscopy on samples;
		evaluate data and design experiments.
Personnel:	\$55,366	Support for Eray Aydil (co-project manager; 1
		months summer salary per year + fringe);
		supervise post-doc and graduate student;
		design characterization experiments; evaluate
		data and design experiments.
Equipment/Tools/Supplies:	\$36,000	User fees for instrumentation (electron
		microscopes, X-ray scattering equipment,
		spectroscopic methods) at the University of
		Minnestoa - College of Science and
		Engineering's Characterization Facility (\$12k/yr)
Equipment/Tools/Supplies:	\$35,908	Chemicals (metal precursors, elemental sulfur
		and other sulfur containing precursors,
		solvents), standards, conductive glasses as well
		as polymers for thin film support, lab supplies
		including reactors for microwave system, and
		supplies for materials testing
Equipment/Tools/Supplies:	\$10,000	Repairs and maintenance
Capital Expenditures over \$5,000:	\$25,000	Research-grade microwave system.
TOTAL ENRTF BUDGET:	\$494,000	

Details are provided in the accompanying excel file.

Explanation of Use of Classified Staff:

Explanation of Capital Expenditures Greater Than \$5,000: Research-grade microwave system optimized for thin film production (based on quote from one of the major equipment producers). This equipment is substantially more specialized than a conventional microwave oven. The system enables use of flow-through cells (fresh reagents can flow into the cell and concentrations of ingredients varied as a function of time) as well as enable monitoring of temperature and pressure during synthesis. Finally, the microwave enables very fine tuning of power output. This equipment will be used for its full useful life and made available to other researchers at no charge.

Number of Full-time Equivalents (FTE) Directly Funded with this ENRTF Appropriation: 6.62

Number of Full-time Equivalents (FTE) Estimated to Be Funded through Contracts with this ENRTF Appropriation:

B. Other Funds:

	\$ Amount	\$ Amount	
Source of Funds	Proposed	Spent	Use of Other Funds
Non-state			
	\$232,722	\$	In-kind Services During Project Period: During Project Period: Dr. Penn and Dr. Aydil will also devote 1% time per year in kind (\$2900). Because the project is overhead free, laboratory space, electricty, and other facilities/adminstrative costs (52% of direct costs excluding permanent equipment and graduate student academic year fringe benefits) are provided in-kind (\$229,822)
State	<u> </u>		
	\$	\$	
TOTAL OTHER FUNDS:	\$232,722	\$	

Add or remove rows as needed

VII. PROJECT STRATEGY:

A. Project Partners: Project Managers Lee Penn and Eray Aydil are the supervising partners on this project. The graduate student and post-doc will be recruited and hired once funding is in place. We do not have additional partners involved.

B. Project Impact and Long-term Strategy: Safe and clean energy production is a grand challenge facing our society. The development of sustainable electrical energy sources is an urgent need in the state of Minnesota and in the United States. Solar energy is renewable and is a viable and attractive option. To become commonplace, solar cells must be inexpensive and robust, and they must be comprised of abundant, cheap, nontoxic materials. Innovative methodology for producing thin films of metal sulfides for use in solar cells resulting from the proposed work will move us closer to commonplace installation of solar cells. Solar cells produced in the proposed work will be composed of less toxic elements like iron, copper, and other far less toxic metals, combined with sulfide. By targeting sulfides for use in solar cells, sulfur waste from mining and other industrial operations could become a viable resource in the production of robust and inexpensive solar cells. Finally, we propose to exploit microwave energy so as to reduce the energy required to produce photovoltaic quality materials.

c. spending mistory. Related to th	iis project				
Funding Source	M.L. 2008	M.L. 2009	M.L. 2010	M.L. 2011	M.L. 2013
	or	or	or	or	or
	FY09	FY10	FY11	FY12-13	FY14
NSF grant for previous data					\$42,000
analysis and testing					

C. Spending History: Related to this project

VIII. ACQUISITION/RESTORATION LIST:

IX. VISUAL ELEMENT or MAP(S):

X. ACQUISITION/RESTORATION REQUIREMENTS WORKSHEET:

XI. RESEARCH ADDENDUM: We have prepared a research addendum, which has been submitted to the LCCMR office separately. It is being kept confidential to protect against potential unintended release of information that could compromise patents that might result from the research.

XII. REPORTING REQUIREMENTS:

Periodic work plan status update reports will be submitted not later than January 1, 2015; July 1, 2015; January 15, 2016; July 1, 2016, and January 15, 2017. A final report and associated products will be submitted between June 30 and August 15, 2017.

Environment and Natural Resources Trust Fund								
M.L. 2014 Project Budget								*
Project Title: Solar Cell Materials from Sulfur and Common Metals							EN	VIRONMENT
Legal Citation: M.L. 2014, Chp. 226, Sec. 2, Subd. 08a								NATURAL RESOURCES
Project Manager: R Lee Penn								UST FUND
Organization: University of Minnesota								
M.L. 2014 ENRTF Appropriation: \$494,000								
Project Length and Completion Date: 3 Years, June 30, 2017								
Date of Report: 12 Janaury 2018								
ENVIRONMENT AND NATURAL RESOURCES TRUST FUND	Activity 1 Budget Revised	A	Activity 1	Activity 2 Budget Revised		Activity 2	TOTAL	
	1/15/2016	Amount Spent	Dalarice	1/13/2016	Amount Spent	Dalance	BUDGET	DALANCE
		* 4 7 4 040	\$ 0	.	\$400.4FF	**	\$000 700	\$ 0
Personnel (Wages and Benefits): overall	\$171,613	\$171,613	\$0	\$162,155	\$162,155	\$0	\$333,768	\$0
Support for graduate student (3 years funding plus fringe); co-advised and working in close collaboration with the post-doctoral researcher; Design and execute synthetic methods for preparation of thin films using green methods. Characterize materials and films for suitability as photovoltaics. Prepare the prototype solar cell(s) in direct collaboration with the post-doctoral researcher. [Estimated total \$104,250]								
Support for Post-doctoral researcher (; 3 years funding plus fringe); co-advised; Design and execute synthetic methods for preparation of thin films using green methods. Characterize materials and films for suitability as photovoltaics. Provide some supervision and mentoring towards the graduate student. Prepare the prototype solar cell(s) in direct collaboration with the graduate student. [Estimate \$166,635]								
Support for R. Lee Penn, project manager. 1.5 months summer salary per year								
(plus fringe). Supervise post-doc and graduate student; perform electron								
micrscopy on samples; evaluate data and design experiments. [Estimated								
S60841] Support for Eray Aydil (co-project manager; 1 months summer salary per year + fringe); supervise post-doc and graduate student; design characterization experiments; evaluate data and design experiments. [Estimated \$55,366]								
Equipment/Tools/Supplies								
User fees for instrumentation	\$21,462	\$21,462	\$0	\$71,324	\$58.576	\$12,748	\$92,786	\$12,748
These are the instruments, and their hourly rates, we intend to use. The budget is based on rough estimates of time required for materials characterization. We will report on the actual hours used for each piece of equipment. TEM \$44.00, SEM \$44.00, SAXS \$25.00, Raman \$25.00, XRD \$20.00, XPS \$40.00, Elliposmetry \$20.00, Maskmaking \$360.00, Metal Evap \$60.00, Sputtering \$40.25	, , , , , , , , , , , , , , , , , , ,	, , , , , , , , , , , , , , , , , , ,		<u> </u>		Ţ.=,. (V	¢21,100	¢.=,. 10
Equipment/Tools/Supplies	\$19,921	\$19,921	\$0	\$15,521	\$12,188	\$3,334	\$35,442	\$3,334

Chemicals (metal salts, sulfur sources, nitrogen gas, solvents)								
Vials and caps for microwave systems [Estimated \$4,500]								
Lab equipment (pH probe, balance, XRD sample holders, stir plate, UV- Vis flow cell, centrifuge) [Estimated \$3,900]								
Grids and stubs for electron microscopy [Estimated \$1,600]								
Lab supplies (safety supplies like gloves, pipets and pipet tips, vials, weigh boats, lab tape, centrifuge tubes, quartz cuvettes) [Estimated \$7,800]								
Glove box (for preparation of precursors in controlled atmosphere) [Estimated \$2,500]								
Substrates and materials for thin film preparation (e.g., conductive film (indium tin oxide) coated glass, flexible substrates, glass for use with molybdenum conductive films, silicon substrates) [Estimated \$6,305]								
Equipment/Tools/Supplies: Repairs and maintenance	\$3,106	\$3,106	\$0	\$3,432	\$2,010	\$1,422	\$6,538	\$1,423
Capital Expenditures Over \$5,000. Research-grade microwave system [\$25,466].	\$25,466	\$25,466	\$0	\$0	\$0	\$0	\$25,466	\$0
COLUMN TOTAL	\$241,568	\$241,568	\$0	\$252,432	\$234,928	\$17,504	\$494,000	\$17,504

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Chemically Deposited CdS Buffer/Kesterite Cu2ZnSnS4 Solar Cells: Relationship between CdS Thickness and Device...

Article in ACS Applied Materials & Interfaces · October 2017

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		Project
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Chemically Deposited CdS Buffer/Kesterite Cu₂ZnSnS₄ Solar Cells: Relationship between CdS Thickness and Device Performance

Chang Woo Hong,^{†,||} Seung Wook Shin,^{||,‡} Mahesh P. Suryawanshi,[†] Myeng Gil Gang,[†] Jaeyeong Heo,^{*,†} and Jin Hyeok Kim^{*,†}

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Supporting Information

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ABSTRACT: Earth-abundant, copper-zinc-tin-sulfide (CZTS), kesterite, is an attractive absorber material for thin-film solar cells (TFSCs). However, the open-circuit voltage deficit (V_{oc} -deficit) resulting from a high recombination rate at the buffer/ absorber interface is one of the major challenges that must be overcome to improve the performance of kesterite-based TFSCs. In this paper, we demonstrate the relationship between device parameters and performances for chemically deposited CdS buffer/CZTS-based heterojunction TFSCs as a function of buffer layer thickness, which could change the CdS/CZTS interface conditions such as conduction band or valence band offsets, to gain deeper insight and understanding about the V_{oc} -deficit behavior from a high recombination rate at the CdS buffer/kesterite interface. Experimental results show that device parameters and performances are strongly dependent on the CdS buffer thickness. We postulate two meaningful consequences: (i) Device parameters were improved up to a CdS buffer thickness of 70 nm, whereas they deteriorated at a thicker CdS buffer layer. The V_{oc} -deficit in the solar cells improved up to a CdS buffer thickness of 92 nm and then deteriorated at a thicker CdS buffer layer. (ii) The minimum values of the device parameters were obtained at 70 nm CdS thickness in the CZTS TFSCs. Finally, the highest conversion efficiency of 8.77% (V_{oc} : 494 mV, J_{sc} : 34.54 mA/cm², and FF: 51%) is obtained by applying a 70 nm thick CdS buffer to the Cu₂ZnSn(S,Se)₄ absorber layer.

KEYWORDS: earth-abundant elements, copper-zinc-tin-sulfide (CZTS), thin-film solar cells, CdS buffer, device performance

INTRODUCTION

Kesterite, copper-zinc-tin-sulfoselenide, and its related compounds, Cu₂ZnSnS₄ (CZTS), Cu₂ZnSnSe₄ (CZTSe), and $Cu_2ZnSn(S_x,Se_{1-x})_4$ (CZTSSe), have recently emerged as some of the most promising materials for thin-film solar cells (TFSCs) because of their natural abundance, outstanding lightabsorbing ability, and high theoretical efficiency.¹⁻⁹ A record power conversion efficiency (PCE) of $\eta = 12.6\%$ has been achieved by IBM using a CZTSSe absorber layer prepared by an approach requiring highly toxic and flammable hydrazine.¹ However, the achieved PCE for kesterite-based compounds is still far behind those of commercialized TFSCs such as $Cu(In,Ga)(S,Se)_2$ (CIGS) ($\eta = 22.6\%$)¹¹ and CdTe ($\eta =$ even though they possess higher theoretical 22.1%),¹² efficiencies (CZTS: 32.4% and CZTSe: 31.0% under singlejunction conditions).¹³ Among the factors causing the underperformance, the open-circuit voltage deficit (V_{oc} -deficit: $E_g/q - V_{oc}$ where E_g is the band gap energy of the kesterite and q is the electron charge) is a critical factor in kesterite-based TFSCs.^{5,14–21} The value of V_{oc} -deficit in kesterite-based TFSCs with outstanding performance is more than 600 mV, which is slightly higher than that of the CIGSSe TFSCs (about 440 mV).^{19,22} Several possible reasons have been proposed to explain the V_{oc} -deficit in kesterite-based TFSCs. Secondary phases usually formed during annealing in chalcogenide atmospheres, located at the absorber material surface, near the back contact, or within the kesterite layer, can hinder the charge carrier transport and lead to an increase in the

Received: June 27, 2017 Accepted: October 5, 2017 Published: October 5, 2017 recombination rate, leading to underperformance in the device. 1,5,23 Other persuasive reasons for losses in $V_{\rm oc}$ include band gap fluctuations because of the locally varying ionization of defects ($V_{\rm Cu}$) and atomic-level antisite defects such as $\rm Cu_{Zn'}$ $\rm Zn_{Cu'}$, $\rm Cu_{Sn'}$, $\rm Sn_{Cu'}$, $\rm Zn_{Sn}$, and $\rm Sn_{Zn'}$, resulting from the nonuniformities in the crystal structure or the compositional ratio of the kesterite. $^{4,14,15,18-21,24-28}$ Specifically, multioxygen state elements such as Cu and Sn in CZTS commonly generate deep defects that increase the nonradiative carrier recombination and thus significantly affect the $V_{\rm oc}.^{23}$

Another possible reason for V_{oc} -deficit is the high recombination rate at the buffer/kesterite interface, resulting from the mismatched band alignment between CdS and kesterite layers.¹⁹ Several values of conduction band offset (CBO) have been reported for CdS/kesterite heterojunction devices by various measurement techniques under different interface conditions.^{29,30} On the basis of first-principles calculations, the value of CBO is negative, a so-called "clifflike" CdS/kesterite heterojunction.²⁹ It has been suggested that the cliff-like CBO leads to the high interface recombination rate and thereby V_{0c} -deficit behavior. The cliff-like band alignment between the CdS/kesterite layers acts as a barrier to injected electrons (majority carriers) from the CdS buffer to the kesterite absorber under forward bias.^{30–33} The electrons lead to the interface recombination current between the holes in kesterite and electrons at the CdS/kesterite interface. This electrical behavior impacts the reduction of $V_{\rm oc}$ under wide band gap conditions in the sulfide-rich kesterite absorber.¹⁴ On the other hand, many reports have proposed that the optimal band alignment of the CdS/kesterite interface, a so-called "spike-like" type (positive offset), is more favorable than that of the cliff-like type because it can reduce the CdS/kesterite interface recombination of majority carriers, which prevents the reduction of V_{oc} .^{19,30,32,33} Some researchers have proposed the following to solve this problem: (i) alkali elements such as Na and K or Ge in the kesterite compounds during synthesis to enhance the growth of grains to large size as well as to reduce antisite defects in the kesterite layer^{9,24,25,27,34–38} and (ii) buffer layers such as Zn_{1-x}Cd_xS, (Zn,Mg)O, Zn(O,S), and In₂S₃ compounds to achieve the spike-like type band alignment.^{33,39-42}

Although the introduction of additive elements in the kesterite and alternatives to CdS in the buffer layers has been suggested as a promising possibility for the improvement of performance, improvements over kesterite-based TFSCs with CdS buffer have not been realized. On the basis of literature surveys and to our best knowledge, there are a few research papers on the effect of chemical-bath-deposited CdS buffer thickness on the performances of kesterite-based solar cells with efficiencies below 3%.43,44 On the other hand, a few research papers reported the effect of sputtered CdS buffer thickness on the performances of CZTS-based TFSCs from 4.0 to 7.1% efficiencies.^{45,46} Furthermore, Winkler et al. reported the improved performance of CZTSSe TFSCs, prepared by a hydrazine-based process, more than 11% through the precise optical designs such as transparent conducting oxide (TCO) and buffer layers.⁴⁷ Even though the solar cell device parameter analysis regarding the relationship with the device performance as a function of buffer thickness is desirable to deeply understand the loss of V_{oc} resulting from a high recombination rate at the CdS/kesterite interface, above research studies only reported the performances of the kesterite. The relationship between the buffer thickness and device performances is not

clear yet. In particular, the various thicknesses of CdS buffer layers may change the CdS/CZTS interface conditions such as CBO values because of the quantum size effect in CdS without introducing an additive element in the absorber layer and alternative buffer materials.⁴⁸

In this paper, we report the preparation of the CZTS thin film prepared by annealing the sputtering-deposited metallic precursor in the chalcogenide atmospheres and chemically deposited CdS buffer and fabrication of CdS/CZTS TFSCs as a function of CdS buffer thickness. We systematically demonstrate the deeper insight and understanding on $V_{\rm oc}$ -deficit behavior resulting from the recombination rate at the buffer/ absorber interface through the study on the relationship between device performances and parameters of CZTS-based TFSCs. Finally, an efficiency of 8.77% in the CZTSSe TFSC was achieved by applying a 70 nm thick CdS buffer to the CZTSSe absorber.

EXPERIMENTAL PROCEDURES

Preparation of the Metallic Precursor Thin Films. A 1 μ m thick Mo thin film was prepared by the direct current (dc) magnetron sputtering technique at room temperature on a soda-lime glass (SLG) substrate. The substrates were cleaned ultrasonically using acetone, methanol, isopropyl alcohol, and deionized (DI) water for 10 min consecutively. The metallic precursor stacked with Cu/Sn/Zn was prepared on Mo-coated SLG substrates (0.5 Ω/sq , sheet resistance) using the dc magnetron sputtering technique. The Mo-coated SLG substrates were placed in the sputtering chamber under 1.0×10^{-6} Torr. Each metallic target used had a 99.999% purity (TASCO, Korea). The sputtering conditions of each metallic layer were as follows: Cu (0.68 W/cm², 8 mTorr, 2600 s), Sn (0.68 W/cm², 8 mTorr, 1852 s), and Zn (0.68 W/cm², 8 mTorr, 1525 s). The substrates were rotated at 5 rpm during the sputtering process. The Mo-coated SLG substrates were cooled using a custom cooling chuck. To improve the morphologies and microstructures of the as-deposited Zn and Sn layers, the growth rate was controlled by maintaining the substrate temperature at 0 °C. The metallic precursor thin films were then soft-annealed at 300 $^\circ C$ for 10 min under an N_2 atmosphere to improve their morphology. Detailed information on Experimental Procedures can be found elsewhere.¹³ The composition of the metallic precursor was Cu-poor and Zn-rich (Cu/(Zn + Sn) = 0.61, Zn/Sn =2.17), as measured by X-ray fluorescence (XRF).

Formation of CZTS and CZTSSe Thin Films by a Rapid Thermal Annealing Process. Metallic precursor thin films were individually annealed to synthesize CZTS and CZTSSe absorber thin films in an Ar + chalcogenide vapor atmosphere. Chalcogenide powders including S or S + Se were purchased from Sigma-Aldrich (with 99.999% purity), and the soft annealed metallic precursor thin films were placed into a rapid thermal annealing system. Details can be found in ref 13. The heating rate was 10 °C/s. The CZTS thin films were prepared by sulfurization at 580 °C for 10 min under 20 Torr (amount of S: 3 mg), whereas the CZTSSe thin films were prepared by sulfo-selenization at 520 °C for 10 min under 50 Torr (amounts of S and Se: 3 and 3 mg). After the annealing process, the annealed thin films were cooled at ambient temperature for 1 h. The compositional ratios of annealed thin films are Cu/(Zn + Sn) = 0.65 and Zn/Sn =1.23 (CZTS) and Cu/(Zn + Sn) = 0.57, Zn/Sn = 1.6, and Se/(S + Se) = 0.81 (CZTSSe), as measured by XRF.

Deposition of CdS Buffer on Kesterite Films and Glass Substrates. Before CdS buffer deposition, each of the CZTS and CZTSSe thin films was soaked in DI water for 300 s and etched with 0.2 M potassium cyanide at room temperature for 300 s, which removes the oxide-based compounds and the $Cu_{2-x}(S,Se)_x$ phase located at the kesterite surface. The thin films were then rinsed using DI water for 60 s. Details of the removal process can be found in ref 13. Prior to the CdS buffer deposition process, the SLG substrates were cleaned ultrasonically using acetone, methanol, isopropyl alcohol, and DI water for 10 min consecutively. Further, CdS buffer deposition



Figure 1. Surface and cross-sectional FE-SEM images of (a,c) metallic precursor prepared at 0 °C with the soft annealing process at 300 °C for 10 min and (b,d) CZTS thin film by sulfurization at 580 °C for 10 min. The metallic precursor thin film shows a dense, crack-, and void-free microstructure with a thickness of ~600 nm. The sulfurized thin films have a dense microstructure with a thickness of ~1.2 μ m and a grain size ranging from 500 nm to 1.6 μ m.

was carried out on the SLG substrates and CZTS and CZTSSe absorber layers prepared by the chemical bath deposition using a precursor solution of 0.2 M CdSO₄, 0.84 M ammonia, and 1.02 M thiourea at 80 °C under different deposition times ranging from 11 to 20 min. The cleaned SLG substrate and CZTS and CZTSSe thin films were immersed vertically in the reaction bath after the etching process. The color of the precursor solution was initially transparent; it changed from transparent to yellow after 6 min, and then it appeared orange after 15 min (see Figure S2a). The color of the CdS layer on SLG and CZTS absorber substrates changed from transparent to deep yellow and from gray to violet, respectively, with increasing reaction time (see Figure S2b). After deposition, the SLG substrates and kesterite thin films were taken out of the reaction bath, rinsed with DI water, and dried in air at room temperature.

Fabrication of Kesterite-Based Solar Cells. The CZTS and CZTSSe TFSCs were fabricated with a multilayer structure of SLG/ Mo/kesterite/CdS/i-ZnO/AZO/Al. The highly resistive, 50 nm thick i-ZnO was deposited using the radio frequency (RF) magnetron sputtering technique at room temperature, with an RF power of 75 W and a working pressure of 1 mTorr under Ar and O₂ mixed plasma. The 400 nm thick AZO layers were deposited using the RF sputtering technique at room temperature, with an RF power of 150 W and a working pressure of 1 mTorr under Ar plasma. The Al top grid layer was deposited using the thermal evaporation technique. The active area of the fabricated TFSCs was 0.30 cm².

Characterization. The structural properties of thin films were measured using a high-resolution X-ray diffraction (XRD, X'pert PRO, Philips, Eindhoven, the Netherlands) instrument operated at 40 kV and 100 mA and analyzed using Raman scattering spectroscopy (Jobin Yvon T6400 Raman scattering system with an Olympus microscope equipped with a 100× magnification lens and in the backscattering configuration). The excitation source was an Ar laser operating at different wavelengths of 332, 532, and 632 nm. The surface morphology of the thin films was characterized by field emission scanning electron microscopy (ZSX Primus II Rigaku Corp.). The conversion efficiency and external quantum efficiency (EQE) for CZTS and CZTSSe TFSCs were characterized by a class AAA solar simulator (WXS-15SS-L2, Wacom, Japan) satisfying the conditions of AM 1.5G, 100 mW/cm², and 25 °C and with an incident PCE

measurement unit (PV measurement, Inc.). To characterize the device parameters including shunt conductance ($G_{\rm sh}$), ideality factor (A), reverse saturation current density ($J_{\rm o}$), and series resistance ($R_{\rm s}$) for CZTS and CZTSSe TFSCs, the J-V behavior was determined using the one-diode model described by eq 1⁴⁹⁻⁵¹

$$J - J_{\rm L} = J_0 \exp\left[\frac{q}{AkT}(V - R_s J)\right] + \frac{V}{G_{\rm sh}}$$
(1)

where $J_{\rm L}$ is the photocurrent, q is the electronic charge, and k is Boltzmann's constant. Hegedus et al. have extracted the diode parameters using the model shown in eq 1.⁵⁰ The derivative, dV/dJ, is plotted as a function of $(J + J_{\rm L})^{-1}$. A linear fit to the data gives an intercept of $R_{\rm s}$ and a slope of AkT/q as defined by eq 2

$$\frac{\mathrm{d}V}{\mathrm{d}J} = R_{\mathrm{s}} + \frac{AkT}{q} (J + J_{\mathrm{L}})^{-1} \tag{2}$$

The values of $G_{\rm sh}$ can be determined using the plots of dJ/dV versus V. The value of J_0 is estimated from the *y*-intercept in the plots of $(J + J_{\rm sc} - GV)$ versus (V - RJ).

RESULTS AND DISCUSSION

Characterization of Metallic Precursor and Cu₂ZnSnS₄ Thin Films. It is well-known that the morphologies and microstructures of Zn or Sn prepared by sputtering techniques are usually quite poor because of the low melting points of Zn and Sn. The Cu/Sn/Zn-stacked metallic precursor thin films were prepared at 0 °C during the sputtering process to improve the morphologies and microstructures of Zn and Sn. The Cu/ Sn/Zn-stacked metallic precursor thin films were annealed at 300 °C for 10 min under an N₂ atmosphere to form the Cu-Sn and Cu-Zn alloys. These alloys can act as a temporary chalcogenide diffusion barrier during the annealing process, which can further reduce the formation of MoS₂ at the interface between Mo and absorber layers and form large-sized grains in the kesterite. Additional details on the effect of substrate temperature, the soft annealing process on the morphology and microstructure of Cu-Zn-Sn metallic precursor thin films, and

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the relationship between the soft annealing temperature and the thickness of Mo-chalcogenide can be found in ref 13.

Figure 1a,c shows the surface and cross-sectional FE-SEM images of Cu/Sn/Zn/Mo-stacked metallic precursor prepared at 0 °C with soft annealing at 300 °C for 10 min. Figure 1b,d shows sulfurized thin films prepared at 580 °C for 10 min. The surface FE-SEM image of the metallic precursor thin film shows a rough morphology consisting of large-sized grains (600-1000 nm) and small-sized grains (100-200 nm). The microstructure of the metallic precursor thin film shows a dense microstructure with voids and a thickness of ~ 600 nm (Figure 1c). The sulfurized thin film shows very smooth surface morphology consisting of grain sizes ranging from 500 nm to 1.6 μ m. The microstructure of the sulfurized thin film is dense and compact without any voids and with grains extending from the top to the bottom of the substrate. Additionally, the formation of a thin MoS₂ interfacial layer between the absorber and the Mo back contact layer is also observed. The thickness of the sulfurized thin film is approximately 1.2 μ m. The sulfurized thin film consists of large-sized grains more than 1 μ m located in the upper region and small-sized grains ranging from 400 to 600 nm located in the lower region. The large grain size positively affects the device performance because smaller grains can lead to both unfavorable hopping electron transport and a higher recombination rate for charge carriers at grain boundaries in the absorber.^{6,7,52–54}

Figure 2 shows the (a) XRD pattern and (b) Raman spectrum of the sulfurized thin film at 580 °C for 10 min. The XRD pattern of a sulfurized thin film shows strong peaks located at 28.5°, 47.3°, and 56.1° corresponding to the (112), (204), and (312) planes, respectively, for the kesterite CZTS structure (JCPDS card no. 26-0575). Several weaker peaks located at 23.1°, 29.6°, 31.8°, 33.0°, 37.0°, 37.9°, 45°, 58.9°, and 69.2° corresponding to the (110), (103), (200), (202), (211), (105), (224), and (008) planes, respectively, of the kesterite CZTS structure (JCPDS card no. 26-0575).52 The diffraction peak located near 40° is originated from the Mo substrate. Figures 2b and S2 show Raman spectra of the sulfurized thin films using different excited lasers such as 325, 532, and 632 nm to clearly distinguish the secondary phases such as ZnS₂, $Cu_{2-x}S_{xy}$, Sn_xS_{yy} and Cu_2SnS_3 . Each of the excitation wavelengths is particularly powerful in detecting the ZnS (325 nm), $Cu_{2-x}S_x$ and Sn_xS_y (532 and 632 nm), and Cu₂SnS₃ (632 nm) secondary phases. The Raman spectrum using 325 nm wavelength shows no detection of the ZnSrelated peak located at 347 cm⁻¹ shown in Figure S2.⁵² The formation of prominent kesterite CZTS was further confirmed from the presence of the major peak located at 338 cm^{-1} as well as several weak peaks located at 249, 287, 350, and 375 cm⁻¹ in the Raman spectrum using 532 nm wavelength.⁵² No observable Raman peaks from $Cu_{2-x}S_x$ and Sn_xS_y were detected. At 632 nm wavelength, only CZTS-related Raman peaks were detected at 287, 338, and 367 cm⁻¹; however, the Cu₂SnS₃-related Raman peaks located at 265 and 305 cm⁻¹ were not observed⁵² (Figure S2). The XRD pattern and Raman spectrum characterizations suggest that the secondary phases such as $Cu_{2-x}S_{x}$, Sn_xS_{y} , ZnS, and Cu_2SnS_3 are not present in the kesterite thin film. Additionally, the compositional ratios of the CZTS thin film are Cu/(Zn + Sn) = 0.65 and Zn/Sn = 1.23, as measured by XRF characterization.

Characterization of Chemically Deposited CdS Buffer on the Cu₂ZnSnS₄ Absorber and SLG Substrates. A chemically deposited CdS buffer layer is favorable in the CIGS Research Article



Figure 2. (a) XRD pattern and (b) Raman spectrum for the CZTS thin film using different wavelengths by sulfurization of the metallic precursor at 580 °C for 10 min. The compositional ratios of the CZTS thin film are Cu/(Zn + Sn) = 0.65 and Zn/Sn = 1.23. Indexed diffraction pattern in (a) and spectrum in (b) are the stimulated information corresponding to the tetragonal CZTS structure. All of the peaks of the CZTS thin film are matched with stick patterns and spectrum. Additional Raman spectra for CZTS thin films are found in Figure S3 in the Supporting Information using 325 and 632 nm wavelength.

and CZTSSe multilayered structured TFSCs because of the protection provided from the following: (i) modification from chemical species in the sensitive surface of the absorber and junction regions, (ii) damage caused by the subsequent physical deposition of the TCO layer, and (iii) alteration of the interface charge during the deposition process.55-59 The chemically deposited CdS thin films are generally prepared using aqueous solutions consisting of Cd salts, thiourea, and ammonia in a hot, basic medium. A typical reaction proceeds as shown in eq $3.^{57}$ According to previous studies on the growth of the chemically deposited CdS thin film in the reaction solution, there are three different mechanisms at work: (i) the primary adherent layer is formed by the ion-by-ion deposition of Cd²⁺ and S^{2-} on the substrate surface (heteronucleation and growth), (ii) the less adherent and more powdery films are formed by the cluster-by-cluster mechanism through the adsorption and aggregation of CdS cluster precipitated in a bulk solution (homonucleation and growth), and (iii) a mixed mechanism where the predominance of one mechanism over another is governed by the extent of ion-by-ion and cluster-bycluster deposition.

$$Cd(NH_3)_4^{2+} + CS(NH_2)_2 + 2OH^-$$

 $\rightarrow CdS + CH_2N_2 + NH_3 + 2H_2O$ (3)

The key factors include the degree of supersaturation of the solution and the catalytic activity of the substrate surface.^{55–59}



Figure 3. Representative surface and cross-sectional FE-SEM images of CdS thin films prepared on the SLG substrate (a,b) and on the Cu₂ZnSnS₄ thin film (c,d) at 80 °C for 13 min. The morphologies and microstructures of CdS thin films are quite different on the SLG substrate and on the CZTS thin films.

Figure 3 shows the representative surface and cross-sectional FE-SEM images of CdS thin films prepared on the SLG substrate (a,c) and on the CZTS absorber (b,d) at 80 °C. The CdS thin film prepared on the SLG substrate (Figure 3a,b) exhibits a nonuniform distribution of spherical grains with different sizes ranging from 100 to 400 nm and with many empty regions. The cross-sectional FE-SEM image shows a microstructure with many voids with a thickness of approximately 150 nm. It was also observed that some large (400 nm) grains on the SLG substrate were formed via the cluster-by-cluster mechanism at long reaction times. By contrast, the chemically deposited CdS thin film deposited on the CZTS absorber layer (Figure 3c) shows very smooth, nanoscale crystalline morphology with the presence of few large grains ranging from 100 to 300 nm in size. The microstructure of CdS on the CZTS absorber layer (Figure 3d) is uniform, compact, and densely packed with small CdS grains, is pinholefree, and has a thickness of 83 nm. Figure 4 shows the variation in the CdS buffer thickness on the CZTS absorber layer as a function of reaction times at 80 °C, which were obtained from the cross-sectional FE-SEM images (see Figure S4). The thickness of the CdS buffer increases rapidly from 48 to 123 nm up to a reaction time of 17 min and then saturates. This growth behavior is attributed to the decrease in the Cd-ammonia ligand concentration during the reaction process. Similar behavior has been observed in the chemically deposited CdS and ZnS by several researchers.^{55–59} The significantly different morphologies of CdS on the SLG substrate and CZTS absorber layer may be attributed to the different CdS growth mechanisms during the reaction process. Previous reports of chemically deposited metal sulfide thin layers on amorphous and crystallized substrates have suggested that the growth of CdS on amorphous substrates is dominated by the cluster-bycluster mechanism, whereas the growth on crystalline substrates is dominated by the ion-by-ion mechanism or by the mixed



Figure 4. Variation of CdS buffer thicknesses on CZTS absorber layers as a function of reaction times at 80 °C. The thicknesses of CdS buffer were obtained from the cross-sectional FE-SEM images shown in Figure S3.

mechanism because of the catalytic activity of the substrate surfaces. $^{57-59}$

Solar Cell Performances as a Function of CdS Thickness. V_{oc} -deficit characteristics in kesterite-based TFSCs are affected by the mismatched band alignment at interfaces between CdS buffer and kesterite or CIGS absorber layers which leads to the high interface recombination rate.^{18,19,21,26,60} It has been reported that the band alignment of CdS buffer/kesterite or CdS buffer/CIGS TFSCs could be altered by adjusting the thickness of the CdS buffer or by the postannealing treatment.^{4,48,60,61}

Therefore, we selected several thicknesses of the CdS buffer, namely, 48, 62, 70, 92, and 123 nm, to study the relationship between interface conditions and device performances in the CdS buffer/CZTS heterojunction. Figure 5 shows the device performance of the CZTS TFSCs with different thicknesses of



Figure 5. Device performances of the CZTS TFSCs as a function of CdS buffer thickness; (a) V_{oct} (b) J_{scr} (c) FF, and (d) η under AM 1.5G illuminations. Each dataset was obtained from five to six solar cells.

the CdS buffer: (a) open-circuit voltage (V_{oc}) , (b) short-circuit current density (J_{sc}) , (c) fill factor (FF), and (d) efficiency (η) under AM 1.5G illumination. Each dataset was obtained from five or six solar cells. The average performance of the CZTS TFSCs improved when the CdS buffer thickness is increased up to 70 nm, whereas the average performance deteriorates with further increase in the CdS layer thickness. Surprisingly, the average values of J_{sc} and η of CZTS TFSCs are dramatically improved with increased thickness up to 70 nm compared to the other device parameters.

Figure 6 shows the (a) current-voltage (J-V) curve and (b) EQE of devices with the best performance as a function of CdS



Figure 6. (a) J-V, (b) EQE, and (c) integrated current densities from the EQE of the best performance among each solar cell as a function of CdS buffer thickness.

buffer thickness. All of the performance parameters (except $V_{\rm oc}$) of the CZTS TFSCs improve with increased CdS buffer thickness up to 70 nm and then deteriorate with CdS thickness thicker than 70 nm. The CZTS solar cell with a 92 nm thick CdS buffer showed the best value of $V_{\rm oc}$. The CZTS TFSCs with the 70 nm thick CdS buffer showed the best performance parameters: $\eta = 5.77\%$, $V_{\rm oc} = 623$ mV, FF = 61%, and $J_{\rm sc} = 15.23$ mA/cm² (see Table 2). The EQE of the CZTS TFSCs exceeds 70% in the visible region from 520 to 700 nm, except for the device with 42 nm thick CdS buffer. This poor EQE is related to the insufficient p–n formation at the interface between the CdS and CZTS layers.³ The insufficient or thin CdS buffer may lead to shunt or leakage currents. The EQE in higher wavelength regions decreased regardless of the CdS buffer thickness. This behavior results from the low minority

Table 1. Obtained J_{sc} Values from $J-V$ Curves, Integrated Current Densities from EQE Values, and Values of J_{sc} -Integrated E	QE
for CZTS-Based TFSCs as a Function of Buffer Thickness ^a	

thickness (nm)	48	62	70	92	123	70 (CZTSSe)
$J_{\rm sc}~({\rm mA/cm^2})$	7.46	9.14	15.23	13.53	12.76	34.54
integrated EQE (mA/cm ²)	6.57	12.58	14.47	13.49	12.09	34.60
$J_{\rm sc}$ -integrated EQE (mA/cm ²)	+0.89	-3.44	+0.76	+0.04	+0.67	-0.06
^a The integrated EQE values were obt	tained from integ	rated calculation	in the Origin sof	ftware.		

charge carrier lifetime and short carrier diffusion caused by the high defect density in the kesterite absorber layer, and it is a common problem for kesterite-based solar cells.^{10,62}

The EQE at wavelengths ranging from 360 to 500 nm, which is attributed to the absorption in the CdS buffer, decreases with increasing thickness of CdS buffers except for the 42 nm thick CdS layer. The band gap energy of the CZTS absorber layer as estimated from the EQE graph is 1.51 ± 0.02 eV (Figure S5). Figure 6c and Table 1 show integrated current densities and gap values between measured and integrated current densities from EQE graphs (Figure 6b) of the best performance among each solar cell as a function of CdS buffer thickness. It is similar values between integrated current densities from EQE graph and measured J_{sc} except for that at 62 nm. This difference between the integrated current density from EQE and J_{sc} at 62 nm may be attributed to the higher R_s and G_{sh} than those of other devices. The device parameters for CZTS TFSCs as a function of different CdS buffer thicknesses will be discussed in next section.

Relationship between Device Performances and Parameters as a Function of CdS Buffer Thickness. The aforementioned experimental results yielded information about the strong dependence of device performances of CZTS TFSCs on CdS buffer thickness. The observed tendency may be caused by the following:^{49,51} (i) recombination rate at the CdS/CZTS interface, (ii) decreased R_s , and (iii) change in the values of the CBO or valence band offset (VBO) at the CdS/CZTS interface.

For change in the values of the CBO at the CdS/CZTS interface as a function of CdS thickness, we calculated the CBO and VBO at the CdS buffer/CZTS interface as a function of CdS thickness through the measured band gap energies of CdS buffers, literature surveys on the band alignment of CdS buffer/ CIGS with different CdS thicknesses, and the band structure of CZTS. Figure S1 shows (a) the band gap energies of CdS and (b) the calculated CBO and VBO between the CdS/CZTS interfaces as a function of different CdS thicknesses. Table S1 summarizes the detailed values of band gap energies, E_{CBM} – $E_{\rm F'}$ CBO, $E_{\rm F} - E_{\rm VBM}$, and VBO at CdS/CZTS interfaces as a function of CdS thickness. The band gap energies of CdS prepared on glass substrates decreased from 3.3 to 2.3 eV with increasing CdS thickness. The slightly wide band gap energies of CdS below 25 nm were related to the quantum size effect from nanosized grains of the CdS thin film. At the initial growth stage of CdS by chemical bath deposition at relatively low temperature, the nucleation process is more dominant than the growth process, indicating that the size of grains is below 5 nm.^{52,53} On the basis of this reason, the band gap energies showed the values more than 3.0 eV at a film thickness below 25 nm. Figure S1b shows the calculated VBO values, which are not significantly changed because the VBM positions are not changed regardless of CdS thickness. However, the calculated CBO values decreased from +0.6 to -0.40 eV with increasing CdS thickness. On the basis of the above discussion, the values

of CBO may be adjusted by controlling the CdS thickness. The detailed calculation process can be found in the Supporting Information.

The recombination rate at the CdS/CZTS interface and R_s can be demonstrated by calculating device parameters using single-diode equations (eqs 1 and 2). To clearly demonstrate the relationships between device performances, parameters, and interface conditions in the CdS buffer/CZTS heterojunction, we calculated the device parameters obtained from the best performance cell among each solar cell under different thicknesses of the CdS buffer. Figure 7 shows the device



Figure 7. Device parameters obtained from the light J-V curve and device performances of CZTS TFSCs with different thicknesses of CdS buffer: (a) $J_{0'}$, A, FF, and $E_g/q - V_{oc}$ and (b) $R_{s'}$, $G_{sh'}$, η , and $J_{sc'}$. All of the data were collected in the best efficiencies of solar cells as a function of CdS thickness.

Table 2. Device Characteristics of CZTS and CZTSSe TFSCs and Their Comparison with the Best Reported CZTSSe TFSCs Using the Hydrazine-Based Process

samples	$J_{\rm sc}$ (mA/cm ²)	$egin{array}{c} V_{ m oc} \ ({ m mV}) \end{array}$	FF (%)	η (%)	$(eV)^{E_g}$	$E_{\rm g}~({\rm eV})/q - V_{\rm oc}~({\rm mV})$	$\frac{G_{\rm sh}}{({\rm mS/cm}^2)}$	$\binom{R_s^b}{(\Omega \text{ cm}^2)}$	A^{b}	$\int_{o} (mA/cm^2)^b$
48 nm CdS/CZTS	7.46	485	48	1.74	1.49	1005	6.68	5.78	1.98	8.12×10^{-5}
62 nm CdS/CZTS	9.14	537	59	2.89	1.51	973	3.47	4.31	1.78	9.24×10^{-6}
70 nm CdS/CZTS	15.23	623	61	5.77	1.53	907	2.28	2.14	1.71	7.81×10^{-6}
92 nm CdS/CZTS	13.53	624	52	4.22	1.53	906	4.48	2.98	1.89	2.24×10^{-5}
123 nm CdS/CZTS	12.76	561	54	3.89	1.52	959	4.71	3.47	1.81	2.13×10^{-5}
70 nm CdS/CZTSSe ^c	34.54	494	51	8.77	1.16	666	2.14	2.12	1.52	4.73×10^{-6}
solution (hydrazine, Se	35.2	513.4	69.8	12.6	1.13	617	1.61	0.72	1.45	7.0×10^{-8}

^{*a*}Band gap energies were obtained from the plot of $(\ln(1 - EQE))^2$ vs energy in the Supporting Information (Figure S4). ^{*b*}Light shunt conductance (G_{sh}) , series resistance (R_s) , ideal factor (A), and reverse saturation current density (J_0) were calculated from the J-V curve under light conditions. ^{*c*}All of the performance and parameters are taken from the CZTSSe TFSC with a 70 nm thick CdS buffer. ^{*d*}All of the performance and parameters are taken from the hydrazine-based CZTSSe TFSC reported by IBM researchers. ¹⁰

parameters from the light J-V curve and device performance of CZTS TFSCs as a function of CdS thickness: (a) J_{0} , A, FF, and $E_g/q - V_{oc}$ and (b) R_{s} , G_{sh} , J_{sc} , and η . Additionally, the values of E_{σ}° in the CZTS absorber layers were obtained from the plots of $(ln(1 - EQE))^2$ versus energy shown in Figure S4. Device performance and parameters of the CZTS solar cells with different CdS buffer thicknesses are summarized in Table 2. All of the solar cell devices show V_{oc} -deficit characteristics, which are closely related to the recombination rate at the CdS buffer/ kesterite interface.^{14,15} Interestingly, we observe a similar relationship between the device performance and parameters. The device parameters including J_{0} , A, R_{s} , and G_{sh} (and notably not including $E_g/q - V_{oc}$) are improved up to a CdS buffer thickness of 70 nm, whereas they deteriorate at larger CdS thickness. The V_{0c} -deficit in the solar cells is improved up to a CdS buffer thickness of 92 nm and then deteriorated at a thicker CdS buffer layer. The tendencies of FF, $J_{\rm sc}$ and η are opposite to those of J_0 , A, R_s , $E_g/q - V_{oc}$, and G_{sh} . The values of $E_{\rm g}/q - V_{\rm oc}$ and device parameters such as J_0 and A with a CdS buffer thickness are reduced up to 70 nm.

Another possible reason for the enhanced performance and parameters is the reduced value of both CBO and VBO at the CdS/CZTS interface with increasing thickness of the CdS layer. The previous literature surveys for band alignment at buffer compounds such as CdS, Zn(O,S), ZnO, (Zn,Sn)O, and In_2S_3 buffer-/thin-film-based absorber materials such as kesterite, CdTe, and CIGS heterojunction interfaces suggested that the CBO and VBO values for the buffer/absorber interface can be controlled by adjusting the thickness owing to the quantum size effect and the band gap engineering in the buffer.⁴⁸ The values of CBO and VBO decreased with increasing thickness of buffer and the device performances were dramatically worse at negative or highly positive values of CBO conditions.⁴⁸ On the basis of the above discussion point, we assume that a causal relationship between the conditions at the CdS/CZTS interface (values of CBO and VBO) can be adjusted by controlling the thickness of the CdS buffer. In the case of a relative thin buffer layer, the values of the CBO and VBO at the CdS/CZTS interface are highly positive (spike type), indicating that the interface acts as a barrier to the generated charge carrier flow, leading to the poor performance.³³ With increasing thickness of the CdS buffer, the values of the CBO and VBO decrease, leading to the enhanced performance. The deteriorated performance of the devices with the CdS buffer thickness greater than 92 nm is attributed to the higher Rs and the negative values of CBO and VBO. The resistivity of the

chemically deposited CdS buffer is more than $10^4 \Omega$ cm because it consists of nanoscale grains and contains many O and OH species. This higher resistivity of the CdS buffer leads to the higher $R_{\rm s}$ and lower $J_{\rm sc}$ and η . The increased $G_{\rm sh}$ in the thicker CdS buffer is attributed to the nonuniform microstructure consisting of a few nanoscale grains and large grains more than 200 nm in size, which is formed by the mixed mechanism over long reaction times. Previous papers on the growth of chemically deposited metal-sulfides-based buffer on the absorber layers report the nonuniform microstructure consisting of different sized grains for long reaction times and high reaction temperatures.^{48,55,56,63,64} Additionally, the negative values of CBO and VBO at thicker CdS buffer produce a cliff-type band alignment between CdS and CZTS, which leads to the loss of $V_{\rm oct}^{-48}$

Performance through Applying 70 nm Thick CdS to the CZTSSe Absorber. To improve the efficiency of kesteritebased TFSCs, we further apply the compositional ratio of (S/(S+ Se)) in the kesterite layer because the band gap energy near 1.1-1.2 eV shows the best performance, even though the best theoretical performance is expected at a band gap energy of 1.5 eV.^{14,15} The compositional ratios of the CZTSSe absorber layer are Cu/(Zn + Sn) = 0.57, Zn/Sn = 1.6, and Se/(S + Se) = 0.89, as measured by XRF. The Se-rich CZTSSe absorber thin film shows a dense microstructure consisting of submicron grains and many voids located near the Mo back contact. No secondary phases were observed in the XRD pattern or Raman spectrum, and the cross-sectional FE-SEM images are shown in Figure S5. Figure 8 shows the (a) J-V curve, (b) EQE spectrum and integrated current from the EQE graph, and a (c) plot of $(\ln(1 - EQE))^2$ versus energy of the most efficient CZTSSe TFSC. The solar cell has a PCE of 8.77% with an active area of 0.30 cm² under an AM 1.5G illumination. The performance parameters of the CZTSSe TFSC with the best efficiency are as follows: $V_{\rm oc}$ = 494 mV, FF = 51%, and $J_{\rm sc}$ = 34.54 mA/cm². The value of the FF in the CZTSSe TFSC is quite low as compared to that of the kesterite-based TFSCs with a PCE greater than 10%. The EQE spectrum of the CZTSSe solar cell shows an EQE more than 75% in the visible region and decreased EQE in the high wavelength region. The estimated band gap energy from the EQE spectrum in the CZTSSe solar cell is approximately 1.06 eV. Although the CZTSSe TFSC with a 70 nm CdS buffer layer showed an efficiency more than 8%, the tendency of performance was quite different from those of CZTS TFSCs.



Figure 8. (a) J-V curve, (b) EQE spectrum and integrated current from the EQE graph, and (c) plot of $(\ln(1 - EQE))^2$ vs energy of the best efficient CZTSSe TFSCs after process optimization. The compositional ratios of the CZTSSe thin film are Cu/(Zn + Sn) = 0.57, Zn/Sn = 1.6, and Se/(S + Se) = 0.89 under annealing condition at 520 °C for 10 min.

The performance of CZTSSe TFSCs was improved from 8.8 to 10% with decreasing thickness of CdS from 70 to 25 nm because of the enhanced amount of light to the absorber layers. (Data are not shown here.) They were saturated over a 70 nm thick CdS buffer layer. The difference behavior about device performances as a function of different thicknesses for the CdS buffer layer between CZTS and CZTSSe may be attributed to the difference in their roughness, band alignment between CdS and the absorber, and thickness of the absorber. The performance and parameters of the most efficient CZTSSe solar cell and the previously reported CZTSSe solar cell using a hydrazine-based process are summarized in Table 2 to clearly illustrate the poor performance. The difference in FF and $V_{\rm oc}$ deficit is clearly observed between the present results (51% and 666 mV) and the previously reported CZTSSe solar cell (69.8% and 617 mV). Furthermore, the device parameters such as $G_{\rm sh}$ $R_{\rm s}$, A, and J_0 for the present results ($G_{\rm sh}$: 2.14 mS/cm², $R_{\rm s}$: 2.12 Ω cm², A: 1.52, and J_0 : 4.73 × 10⁻⁶ mA/cm²) are higher than those of the previously reported CZTSSe solar cell ($G_{\rm sh}$: 1.61 mS/cm², R_s : 0.72 Ω cm², \bar{A} : 1.45, and J_0 : 7.0 × 10⁻⁸ mA/cm²). Particularly, the values of R_s and G_{sh} in the present results are 3 and 1.5 times higher, respectively, than those of the previously

reported CZTSSe solar cell. Our previous paper on CZTSSe solar cells showed the presence of secondary phases and voids at the interface between the CZTSSe absorber layer and the Mo back contact, which led to the lower values of the device parameters. The V_{α} -deficit characteristic of the present solar cell is higher than that of the previously reported CZTSSe solar cell in spite of having similar J_{sc} values and optical band gap energies. This $V_{\rm oc}$ -deficit characteristic, caused by the higher recombination rate at the buffer/absorber interface and the low minority charge lifetime, is evidence of higher defect densities on the CZTSSe surface in the present cell than in the previously reported CZTSSe TFSC. On the basis of these comparisons, the poor performance in the present case compared to that previously reported is attributed to the presence of unexpected secondary phases, voids, and higher defect densities on the CZTSSe surface. This implies that the performance of our CZTSSe TFSC can be improved by controlling the defect densities on the kesterite surface through surface modification using alkali elements and by removing the secondary phases and voids near the Mo back contact using optimized annealing parameters.

CONCLUSIONS

CdS buffer/CZTS heterojunction solar cells have been successfully fabricated by systematically studying the relationship between the device performance and device parameters as a function of different CdS buffer thicknesses. An 8.8% efficiency is achieved by applying 70 nm thick CdS buffer to the CZTSSe absorber layer. All aspects of device performance except for that related to V_{oc} are enhanced with increased CdS buffer thickness up to 70 nm and are diminished with thicker CdS buffer thickness. The V_{oc}-deficit improves with increased CdS buffer thickness up to 92 nm and then deteriorates with greater CdS buffer thickness. The tendencies of FF, $J_{\rm sc\prime}$ and η are opposite to those of J_{0} , A, R_{s} , $E_{g}/q - V_{oc}$, and G_{sh} . These tendencies synergistically affect the recombination rate at the CdS/CZTS interface and the microstructure of the CdS to a degree dependent on the CdS buffer thickness. We believe that this detailed systematic study is useful for deeper insight into the relationship between the device performance and device parameters as a function of CdS buffer thickness.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.7b09266.

Band gap energies of CdS with different thicknesses, the CBO and VBO values at CdS buffer/CZTS interfaces as a function of CdS thickness through literature surveys, images of a reaction solution during the CdS deposition, images of CdS thin films on the CZTS and SLG substrates, Raman spectra of CZTS thin films using different wavelengths such as 325 and 623 nm, FE-SEM images of full-structured CZTS TFSCs devices, band gap energy plots of CdS/CZTS heterojunction solar cells as a function of CdS thickness, XRD, Raman spectrum of the CZTSSe thin film, and FE-SEM images of CZTSSe devices (PDF)

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Notes

The authors declare no competing financial interest.

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Introduction

Thin film solar cells based on direct band gap semiconductors such as Cu(In,Ga)Se₂ (CIGS) and CdTe require a hundred times less absorber material than silicon solar cells and are therefore expected to be less expensive.^{1,2} Solar cells based on CIGS have already reached efficiencies as high as 21.7%, comparable to silicon solar cells.³ However, CIGS-based solar cells are difficult to implement in large scale because indium is scarce and high in demand as an element in transparent conductive oxides used widely in the display industry.⁴ A potential substitute for CIGS in



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The semiconductor Cu_2ZnSnS_4 (CZTS) is a promising sustainable photovoltaic material and colloidal dispersions of wurtzite or kesterite CZTS nanocrystals are often used to make thin polycrystalline films for solar cells. This requires control of the nanocrystal phases *via* the synthesis. We studied the microwave-assisted solvothermal synthesis of CZTS nanocrystals from metal salts and thiourea in ethylene glycol in the presence of various excess sulfur sources. Relative fractions of the kesterite and wurtzite phases depend on the excess sulfur source, the oxidation state of Sn, and the sulfur-to-total-metal -cation (S : M) ratio used in the synthesis. When the excess sulfur source contains an amino group, a Zn–Sn intermediate forms and allows the CZTS phase to be varied between kesterite and wurtzite *via* the Sn initial oxidation state and S : M ratio. When the excess sulfur source contains an amino group, synthesis using Sn(II) salts and low S : M (1.9) favors the formation of the wurtzite phase, whereas solution state of Sn ratio (>4) favors the formation of the kesterite phase. Only the kesterite phase is obtained when Sn(IV) reagent is used, regardless of S : M ratio. When the excess sulfur source does not have an amino group, only the wurtzite phase is obtained under the conditions studied, regardless of the oxidation state of the Sn precursor or the S : M ratio; in these cases, the Zn–Sn intermediate does not form and the precursor to wurtzite appears to be copper sulfide.

thin film solar cells is Cu_2ZnSnS_4 (CZTS). CZTS is a p-type semiconductor with a band gap of 1.5 eV and high absorption coefficient (>10⁴ cm⁻¹) so that a few micrometer thick film absorbs nearly all photons with energies greater than the band gap. Moreover, CZTS is comprised of abundant and non-toxic elements,⁵⁻⁷ and CZTS-based solar cell efficiencies have already reached 12.7%.⁸

CZTS can crystallize in kesterite, stannite, primitive mixed Cu-Au (PMCA), and wurtzite crystal structures.9 Besides these, other structures derived from wurtzite do also form, such as, wurtzite-derived monoclinic, and wurtzite-derived orthorhombic, which are also known as wurtzite-kesterite and wurtzite-stannite phases, respectively.^{10,11} The thermodynamically stable crystalline phase of CZTS is tetragonal kesterite (space group $I\overline{4}$), whereas wurtzite ($P6_3mc$) is considered to be metastable.¹⁰ Because the kesterite and stannite phases differ only in the ordering of the Cu⁺ and Zn²⁺ cations, routinely used characterization methods such as X-ray diffraction and Raman spectroscopy cannot distinguish between these two phases regardless of the underlying lattice (tetragonal or hexagonal, i.e., wurtzite). Perhaps the only characterization technique that can possibly distinguish between kesterite and stannite phases is neutron diffraction. Indeed, using neutron diffraction Schorr et al.12 have shown that tetragonal kesterite forms when the synthesis is carried out in a way to favor the equilibrium phase. However, Schorr *et al.* also showed that there could still be Cu⁺



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[†] Electronic supplementary information (ESI) available: Rietveld refinement procedure, crystal size estimates, elemental mapping using STEM-HAADF, X-ray diffraction patterns, additional synthesis experiments and characterization. See DOI: 10.1039/c7ta06086f

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and Zn^{2+} cation disorder in the product. The analogous study to distinguish between wurtzite–kesterite and wurtzite–stannite was recommended by Regulacio *et al.*¹³ but to our knowledge has not been carried out yet. In this manuscript, we refer to the tetragonal phase as kesterite. We refer to the wurtzite phase without any qualification on whether it is kesterite–wurtzite or stannite–wurtzite because we cannot tell the difference without conducting neutron diffraction on nearly phase pure samples. Of course, cation disorder can also be present but is also difficult to quantify.

In 2011, Lu et al.14 synthesized the metastable wurtzite phase of CZTS by injecting metal chloride solutions in dodecanethiol into a hot mixture of dodecanethiol, oleylamine, and oleic acid. They hypothesized that dodecanethiol played an important role in obtaining the metastable wurtzite phase. Indeed, most methods for synthesizing wurtzite CZTS employ a surfactant such as hexadecanethiol, dodecanethiol, oleylamine, and trioctylamine during synthesis.15,16 Regulacio et al.13 showed that, in one mechanism, the role of the surfactant is to stabilize intermediate products that help the formation of wurtzite CZTS while restricting the formation of the tetragonal phase. Regulacio et al.13 also found that wurtzite CZTS formation was favored when long chain alkanethiols helped nucleation and growth of hexagonal Cu1.94S nanocrystals, which in turn allowed wurtzite CZTS to template on these Cu1.94S nanocrystals. The heterostructured wurtzite-CZTS-Cu_{1.94}S nanocrystals eventually converted to wurtzite CZTS via cation diffusion.13 Thus, the surfactants appear to stabilize a copper sulfide intermediate that locks in the crystal structure.

Another approach to synthesize wurtzite CZTS phase is via cation substitution into a wurtzite intermediate. For instance, Wang and co-workers prepared wurtzite CZTS by diffusing Zn into wurtzite Cu₂SnS₃ and replacing half the copper cations with Zn.17 This idea is related to that used by Regulacio because it allows the system to choose the final crystal structure through an intermediate nanocrystal with hexagonal symmetry. Li et al.18 varied the phase composition of their product from wurtzite to kesterite CZTS by varying the sulfur sources mixed into oleylamine. Using elemental sulfur dissolved in oleylamine produced kesterite CZTS via a rapid reaction, whereas moderating the reaction rate by using dodecanethiol allowed the formation of a copper sulfide intermediate (Cu₇S₄) and produced wurtzite CZTS. Lin et al.19 used a microwave solvothermal method and varied the volume fraction of ethylenediamine and water as solvents. When only ethylenediamine was used, they obtained wurtzite CZTS whereas a 50-50% mixture of ethylenediamine and water lead to kesterite CZTS. Again, wurtzite formation was preceded by the formation of a sulfide, this time Cu₂S, as the intermediate.

Thus, the work to date shows that wurtzite is obtained when the reaction is slowed and copper sulfide intermediates are allowed to form though not all the copper sulfide intermediates identified by various groups were the same. The reaction rate and the formation of the intermediate could be controlled by varying the capping ligands, sulfur source, or the solvent. Although, there have been numerous studies that showed the synthesis of wurtzite nanocrystals, mechanisms of their production and the factors that control the phase composition remain unclear in many cases.²⁰⁻²⁴

One approach to making thin polycrystalline kesterite CZTS films for solar cells is to anneal coatings cast from nanocrystal dispersions in sulfur or selenium vapour.^{25–28} During annealing the microstructure of the coatings cast from wurtzite or kesterite nanocrystals evolve differently.²⁹ For example, grain growth is faster, begins at lower temperature, and is more facile when metastable wurtzite nanocrystals are transformed into kesterite grains. This motivates the search for controlled synthetic routes that are able to selectively give one crystalline phase (*e.g.*, wurtzite) over the other (*e.g.*, kesterite).^{29,30}

Herein, we studied several factors that play a key role in the control of the CZTS phase from wurtzite to kesterite. These factors include the sulfur source, molar ratio of sulfur to total metal ions, and the initial oxidation state of the Sn reagent. Surfactant or capping agents were not used in any of the syntheses. There are multiple paths to the metastable wurtzite phase. Instead of the copper sulfides that appeared to be the key intermediate in previous work, we show that the intermediate that leads to the wurtzite phase in our work is a Zn-Sn intermediate complex, whose formation is controlled by the oxidation state of Sn and the presence of an amino group in the sulfur source. The absence of surfactants is a also a significant advantage of our method, since long chain organic ligands are difficult to remove from particle surfaces after synthesis, and can hinder charge transport in films prepared from these particles.31 Additionally, the microwave based solvothermal approach described here is reproducible, fast, and scalable. In a typical synthesis significant amounts (0.4 g) of CZTS particles can be synthesized in just 20 minutes.

Experimental

Materials

Copper(II) acetate monohydrate (CuAc₂·H₂O ACS reagent, >98% Sigma-Aldrich), copper(I) acetate (CuAc 97% Sigma Aldrich), zinc acetate dihydrate (ZnAc₂·2H₂O ACS reagent Acros Organic), tin(II) chloride (SnCl₂ 98% Sigma Aldrich), tin(IV) chloride pentahydrate (SnCl₄·5H₂O Sigma Aldrich), thiourea (CH₄N₂S \geq 99.0% Sigma Aldrich), L-cysteine (C₃H₇NO₂S 97% Sigma Aldrich), thioglycolic acid (C₂H₄O₂S 98% Sigma Aldrich), 3mercaptopropionic acid (C₃H₆O₂S \geq 99.0% Sigma Aldrich) ethylene glycol (Fisher Scientific), methanol (Sigma Aldrich), and ethanol (Decon – 200 Proof) were used as received and without additional purification.

CZTS nanoparticles synthesis

In a typical synthesis, 1.7×10^{-3} mol of CuAc₂·H₂O, 1.0×10^{-3} mol of ZnAc₂·2H₂O, and 1.0×10^{-3} mol of SnCl₂ were added to 30 mL ethylene glycol with stirring. Variable amounts of thiourea were added to achieve a sulfur to total (Cu, Zn and Sn) metal ion molar ratio (S : M) between 1 and 6.2, *i.e.*, S : M = $n_{\rm S}/(n_{\rm Cu} + n_{\rm Zn} + n_{\rm Sn})$, where n_i is the number of moles of species *i*. After sonicating for 30 minutes, this reaction mixture was sealed in a Teflon vial, which was placed inside a SiC sleeve and

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loaded into an Anton Parr Multiwave Pro microwave. The reaction mixture was heated from room temperature to 160 $^{\circ}$ C in 15 minutes, using 300 W of power. Following this temperature ramp, the reaction mixture was maintained at 160 $^{\circ}$ C for 5 minutes. After 5 minutes, the power was turned off, and the reaction mixture was cooled to 55 $^{\circ}$ C in 20 minutes *via* convective flow induced by the fans in the microwave. The microwave is equipped with a turntable, which spins the vial at 2 rpm during the entire procedure. Magnetic stirring was not used during the synthesis. The reaction mixture temperature was measured using an infrared sensor.

After cooling, the contents of the Teflon vial were transferred to a centrifuge tube and centrifuged at 8500 rpm (8450 rcf) for 15 minutes. The supernatant was discarded, ethanol was added, and the resulting dispersion in ethanol was centrifuged at 8450 rcf for 5 minutes. This centrifugation–redispersion cycle was repeated four times. Finally, the precipitate was dispersed in methanol. The effect of the excess sulfur sources other than thiourea was studied by adding appropriate moles (to achieve a particular S : M ratio) of L-cysteine, thioglycolic acid or 3mercaptopropionic acid to the mixture of CuAc₂·H₂O (1.7×10^{-3} mol), ZnAc₂·2H₂O (1.0×10^{-3} mol), SnCl₂ (1.0×10^{-3} mol), and thiourea (4.0×10^{-3} mol) in 30 mL ethylene glycol.

Experiments varying the synthesis temperature

To study the effect of temperature, the microwave heating was stopped during the ramp at different temperatures. For instance, a reported synthesis temperature of 75 $^{\circ}$ C means that the microwave heating was turned off when the temperature reached 75 $^{\circ}$ C; after the microwave heating was turned off, the reaction mixture immediately started to cool.

Experiments varying the copper and tin oxidation states

In addition to the synthesis with $\text{CuAc}_2 \cdot \text{H}_2\text{O}$ and SnCl_2 , the following combinations of copper and tin reagents were also used: CuAc and SnCl_2 , CuAc and $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$; and $\text{CuAc}_2 \cdot \text{H}_2\text{O}$ and $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$. In all these experiments, 1.7×10^{-3} mol of the copper reagent, 1.0×10^{-3} mol of ZnAc}_2 \cdot 2\text{H}_2\text{O}, and 1.0×10^{-3} mol of the tin reagent were used. Thiourea was added in the appropriate amounts to vary the S : M ratios between 1.9 and 6.2. The ultrasonication and microwave heating procedures were the same as used in the synthesis with CuAc_2 \cdot \text{H}_2\text{O} and SnCl_2.

Product labelling convention

Because of the large number of synthesis variables, we use a convenient product-labelling scheme. The synthesis products are labeled as $Cu(N)_Sn(L)_XCS_S: M_T$, where N and L represent copper and tin oxidation states, respectively; XCS represents the source of sulfur excess, where Tu, Cyst, TGacid and MCPacid stand for thiourea, L-cysteine, thioglycolic acid, and 3-mercaptopropionic acid, respectively. S : M is the sulfurto-total-metal-cation ratio; and *T* is the maximum temperature reached during the microwave heating.

Characterization

Products were characterized using X-Ray Diffraction (XRD), Raman scattering, optical and infrared spectroscopy, and various electron microscopies. Specifically, XRD patterns from the products were collected using a Pananalytical X'Pert Pro Xray diffractometer (Co K α radiation with a wavelength of 1.7890 E) equipped with a X'Celerator detector. The XRD patterns were collected from 16 to 85° (2 θ), with an effective step size of 0.0167° and 50 s dwell time per step. The crystalline phase percentage was estimated using Rietveld refinement, with the details provided in the ESI.†

Raman spectra were collected from dried powders using a Witec Confocal micro-Raman spectrometer with a green 532 nm laser as the excitation source. The laser power was fixed at 1 mW, and each spectrum was integrated over 150 seconds. Optical absorption spectra were collected from diluted methanol dispersions of the nanocrystals, using an Agilent 8453 spectrophotometer. For infrared spectroscopy analyses, nanocrystals were drop cast from methanol dispersions onto NaCl windows, which were then dried in air. Infrared spectra were collected using a Nicolet Series II Magna-IR System 750 FTIR in the transmittance mode. For elemental analysis using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES), 20 μ L of supernatant were dissolved in 50 mL of H₂O and injected in a iCap 7600 Duo ICP-OES Analyzer.

For SEM analyses, the nanocrystals dispersed in methanol were sonicated for 15 minutes, drop cast onto silicon substrates, and dried in air. The dried nanocrystals were then examined in a JEOL 6500 SEM, at an acceleration voltage of 5 kV. Elemental composition of the nanocrystals was determined using Energy Dispersive X-ray Spectroscopy (EDS) using a Thermo-Noran Vantage system equipped with an EDS detector coupled to the JEOL 6500 SEM. The acceleration voltage was adjusted to 15 kV for all EDS measurements, the EDS spectra were collected in the standardless mode, with the ratio of the elements calculated based on the reference spectra provided by the software System SIX. For each sample, the elemental compositions were averaged.

Samples for TEM characterization were prepared by drop casting nanocrystals onto Cu TEM grids (SPI 200 mesh holey carbon coated) from methanol dispersions after sonicating for at least 30 minutes. The nanocrystals were imaged using a FEI T12 microscope, with acceleration voltage of 120 kV. Highresolution images were collected using a FEI Tecnai G2 F-30, with acceleration voltage of 300 kV. Selected area electron diffraction patterns were collected using this same microscope. Scanning transmission electron microscopy (STEM) was performed using an FEI Tecnai G2 field-emission S/TEM operating at an accelerating voltage of 80 kV. High-angle annular dark field (HAADF) images were collected using an E. A. Fischione annular detector. Energy-dispersive X-ray spectroscopy (EDS) spectra were collected using the ChemiSTEM EDX spectrometer. EDS maps were collected while rastering the beam over the sample, which facilitated

minimization of beam damage. A probe current of ~ 0.1 nA was used, and maps were collected over a minimum of five minutes. Data were analyzed using ESPRIT software (version 1.9.4).

Results and discussion

Effect of S : M ratio on the phase of the nanocrystals synthesized using Cu(n) and Sn(n) reagents

When $Cu(\pi)$ and $Sn(\pi)$ precursors were used and the sole sulfur source was thiourea, the kesterite-to-wurtzite ratio in the synthesis product could be changed by varying the S : M ratio. Fig. 1a shows the XRD patterns from nanocrystals synthesized using $Cu(\pi)$ and $Sn(\pi)$ reagents and thiourea as the sole sulfur source while varying the S : M ratio. The stoichiometric reaction mixture (S : M = 1) results in the formation of impurity phases such as Cu_3SnS_4 , Cu_4SnS_4 , and elemental sulfur. The kesterite-to-wurtzite ratio



Fig. 1 (a) XRD patterns from nanocrystals synthesized using Cu²⁺, and Sn²⁺ at 160 °C using different S : M ratios. The sulfur source was thiourea (*i.e.*, Cu(II)_Sn(II)_Tu_S : M_160 °C where S : M was varied between 1.0 and 6.2). XRD patterns for wurtzite (simulated) and kesterite (PDF# 00-0026-0575) CZTS are shown at the bottom. Peaks labeled as Ω are consistent with Cu₃SnS₄ (PDF 00-036-0218), α with Cu₄SnS₄ (PDF 00-029-0584), and × with elemental sulfur (PDF 00-008-0247) (b) phase composition estimated from Rietveld refinement analysis of the XRD patterns shown in (a). Error bars were determined from triplicate analyses, as described in the ESI.†

increases with increasing S : M ratio (Fig. 1b). The nanocrystal product is comprised of approximately 50% wurtzite and 50% kesterite for S : M between 2 and 4. When S : M is greater than 4, the kesterite fraction rises to 80% (see ESI Table S2[†] for details).

The nanocrystal size estimated using Scherrer equation, for the peak located at 2θ around 32° , corresponding to the (112) planes of the wurtzite phase, and (002) planes of the kesterite phase, varied between 6.4 and 3.7 nm and decreased with increasing S : M. The product containing mostly kesterite had the smallest average crystallite size (ESI Table S3†).

Raman spectra (Fig. 2) are consistent with the XRD results and exhibit a high intensity peak at 328 cm⁻¹ for all products prepared with a S : M of 1.9 or greater. The most intense Raman peak from CZTS is expected around 336–339 cm⁻¹.^{32,33} However, it is common to observe this peak shifted to lower wavenumbers (*e.g.*, 328–331 cm⁻¹). This peak shift is thought to be due to inhomogeneity within the disordered cation sublattice.^{34,35} Peaks related to secondary phases such as Cu₂S, SnS, SnS₂, ZnS, Cu₂SnS₃, and Cu₃SnS₄ were not detected, though some of these compounds (ZnS, Cu₂SnS₃, and Cu₃SnS₄) have partially overlapping peaks with CZTS and presence of amounts undetectable *via* XRD and Raman can not be ruled out.³³

Bright field TEM images of the Cu(II)_Sn(II)_Tu_1.9_160 °C nanocrystals (Fig. 3a) revealed the presence of two types of nanocrystal shapes. Some nanocrystals were anisotropic and oblate while others were more spheroidal (see also Fig. S1 in ESI†). Anisotropic oblate nanocrystal shapes have been observed previously when wurtzite CZTS was present.³⁶ The observation of two types of morphology is consistent with the XRD results, which demonstrate that the product is a mixture of kesterite and wurtzite CZTS: we associate the oblate morphology with wurtzite CZTS and the spheroid morphology with kesterite CZTS. The SAED patterns (Fig. 3b and e) exhibit rings with *d*-spacings that are consistent with both the wurtzite and the kesterite phases. The SAED pattern (Fig. 3b) is consistent with the XRD results, showing more intense reflections



Fig. 2 Raman spectra of the nanocrystals synthesized from Cu^{2+} , and Sn^{2+} at 160 °C, while varying the S : M ratio. The sulfur source was thiourea: (*i.e.*, $Cu(II)_Sn(II)_Tu_S$: M_160 °C where S : M was varied between 1.0 and 6.2).



Fig. 3 (a) TEM, (b) SAED (c) HR-TEM images of the Cu(II)_Sn(II) _Tu_1.9_160 °C and (d) TEM, (e) SAED (f) HR-TEM of the Cu(II)_Sn(II) _Tu_6.2_160 °C nanocrystals.

related to the wurtzite phase than for kesterite phase. Highresolution images from an oblate nanocrystal show lattice fringes with spacing consistent with the (002) of wurtzite CZTS (Fig. 3c). This would be consistent with our association of the oblate anisotropic nanocrystals with the wurtzite phase. In contrast, in the TEM image of $Cu(\pi)_Sn(\pi)_Tu_6.2_{-}160$ °C (Fig. 3f), the nanocrystals appear spheroidal in shape, and the reflections consistent with the kesterite phase are substantially more intense, which is consistent with the XRD results. The spheroid nanocrystals showed lattice fringes with spacings that match the (112) *d*-spacing of kesterite (Fig. 3f). The $Cu(\pi)_Sn(\pi)_Tu_{-}1.9_{-}160$ °C and $Cu(\pi)_Sn(\pi)_Tu_{-}6.2_{-}160$ °C samples were analyzed using HAADF-STEM. The STEM-EDS maps revealed that Cu, Zn, Sn and S are homogeneously distributed in both samples (Fig. S2 in ESI†).

Effect of Cu and Sn initial oxidation states

Varying the oxidation states of the Sn and Cu precursors led to the conclusion that the initial tin oxidation state is an important parameter and is one of the factors in the synthesis that determines the crystalline phase of the product. To support this conclusion Fig. 4 shows the XRD patterns from nanocrystals synthesized using different pairings of Cu(i) and Cu(ii) reagents with Sn(ii) and Sn(iv) reagents while holding S : M constant at 1.9 or 6.2: the excess sulfur was provided using thiourea. The



Fig. 4 XRD patterns for (a) Cu(i)_Sn(II)_Tu_S : M_160 °C (bottom), and Cu(i)_Sn(IV)_Tu_S : M_160 °C (top) (b) Cu(II)_Sn(II)_Tu_S : M_160 °C (bottom), and Cu(II)_Sn(IV)_Tu_S : M_160 °C (top).

nanocrystal compositions are in ESI Table S4.† When the S : M is 6.2, the majority phase is always kesterite, regardless of the oxidation states of Sn and Cu. However, when the S : M is 1.9, the dominant product is wurtzite when Sn(n) is used and kesterite when Sn(n) is used, regardless of the copper oxidation state.

Effect of excess sulfur source

We also studied the effect of changing the excess sulfur source by substituting L-cysteine, thioglycolic acid or 3-mercaptopropionic acid for excess thiourea. We conducted experiments where we varied the excess sulfur source, Sn oxidation state (Sn(π) or Sn(π)), and S : M ratio, S : M = 1.9 or 3.6. Fig. 5 shows the XRD patterns from the products of these experiments. There are two noticeable trends with the source of sulfur excess. First, the molecules containing an amino group (NH₂), *e.g.*, thiourea and L-cysteine, produce mostly kesterite CZTS when Sn(π) is used as tin source but tend to produce wurtzite when Sn(π) is used. On the other hand, molecules without NH₂ groups, like thioglycolic acid and 3-mercaptopropionic acid, when used as source of excess sulfur always produce wurtzite CZTS, regardless of the initial tin oxidation state.

On the mechanism and precursors to CZTS formation

Table 1 summarizes the dominant phases obtained with different excess sulfur sources, tin sources and S:M ratios. Thiourea was always necessary in at least stoichiometric amounts to form CZTS. Use of other sulfur sources without thiourea did not produce CZTS (see ESI Fig. S3†). While there are combinations of synthesis variables that lead to predominantly wurtzite or kesterite phases, there does not appear to be neat and obvious trends, perhaps with the exception of the trend with amino groups: it appears that presence of the amino group in the excess sulfur source differentiates the Sn(π) and Sn(τ v) sources. Infrared spectra of the surfaces of these nanocrystals were consistent with the presence of ethylene glycol (ESI Fig. S4†). The explanation of Table 1 requires experiments aimed at revealing the formation mechanisms. Towards this end we conducted experiments at lower temperatures in



Fig. 5 XRD patterns of the CZTS nanocrystals synthesized using different excess sulfur sources, Sn oxidation states, and S : M = 1.9 or 3.6. Sulfur excess sources were (a) thiourea, (b) L-cysteine, (c) thio-glycolic acid, (d) 3-mercaptopropionic acid (see also Table S5† for wurtzite and kesterite fractions calculated *via* Rietveld refinement).

attempts to slow the formation of the CZTS nanocrystals and observe any reaction intermediates.

Considering the possibility that the preferential synthesis of one phase over another may be related to the differences in their formation mechanisms we explored the synthesis at temperatures lower than 160 °C. Fig. 6a shows the XRD patterns from products synthesized at various temperatures between 25 °C and 160 °C for S: M = 1.9 with Sn(n) source and thiourea,

Table 1Summary of the dominant phases formed using differentcombinations of tin and excess sulfur sources and with low and highS : M ratios. TGAcid is thioglycolic acid and MPAcid is 3-mercapto-propionic acid

Excess S	Low S : M		High S : M	1	
Source	Sn(II)	Sn(rv)	Sn(II)	Sn(rv)	
Thiourea	W	К	К	К	
L-Cysteine	W	K	W	K	
TGacid	W	W	W	W	
MPacid	W	W	W	W	



Fig. 6 XRD pattern from the nanocrystals synthesized at different temperatures, *T* from Sn(II) source: (a) Cu(II)_Sn(II)_Tu_1.9_*T*, (b) Cu(II) _Sn(II)_Tu_6.2_*T*; \blacklozenge denotes the diffraction from the Zn–Sn intermediate.

conditions that favor the formation of the wurtzite phase. At and below 100 °C, we find multiple diffraction peaks The reaction of the Zn and Sn(II) in ethylene glycol yields a product with 1:1 Zn: Sn ratio, with XRD peaks identified with black diamonds in Fig. 6 (see also Fig. S5 and S6 in ESI[†]), corresponding to Zn-Sn intermediates, as discussed by Wang,37 Ng,38 and Das.39 The XRD peaks for the wurtzite CZTS begin to appear at 130 °C. Zn-Sn intermediate intermediates are the only products below 100 °C. It is well known that Zinc(II) acetate can react with thiourea to form the bisthiourea zinc acetate complex (Zn((NH₂CSNH₂)₂(CH₃COO)₂)).^{40,41} It is also known that SnCl₂ can form complexes with thiourea. For instance, when Sn²⁺ and thiourea are mixed in 1:1 mole ratio, they form thioureatin(II) chloride (Sn(NH₂CSNH₂)Cl₂), and when the Sn : thiourea ratio is between 1:2 and 1:6, the pentathioureadi-[tin(π)chloride] dihydrate (Sn₂(NH₂CSNH₂)₅Cl₄·2H₂O) complex.⁴² Thus, the formation of a Zn-Sn complex is not surprising. Unfortunately, we have been unable to grow large single crystals of this Zn-Sn intermediate to conduct X-ray diffraction, which leaves us unable to assign a definite formula and structure. However, after a thorough search on Cambridge Structural Database (CSD), we found that the XRD pattern of this Zn-Sn intermediate resembles a pattern formed by a mixture of thioureatin(II) chloride (CSD code: CAPWEV)43 and a zinc succinate thiourea

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complex called catena-((m2-Succinato-O,O')-bis(thiourea-S)zinc) (CSD code: FELXEA).44 Based on the similarity between the XRD pattern of this zinc succinate thiourea complex and the Zn-Sn intermediate, one possibility is that the intermediate is a mixture of the thioureatin(π) chloride complex and another complex that contains intermediate and thiourea ligands.44 Further information about the XRD patterns of the thioureatin(II) chloride and catena-((m2-Succinato-O,O')-bis(thiourea-S)-zinc) can be found in the ESI (Fig. S5, the additional data in Fig. S6-S9 and the accompanying discussion).† Another possibility is that the Zn-Sn intermediate may be a bi-nuclear complex containing Zn and Sn. A Zn-Sn intermediate is also formed when L-cysteine is used as the excess sulfur source but not with other sulfur sources such as TGAcid and MPAcid, implicating the amino group in the formation of this complex intermediate. Another possibility is that the Zn-Sn intermediate could be a compound with the formula similar to {[Zn(amine containing ligand)_x]₂[Sn₂S₆])_n. Similar compounds containing Ni instead of Zn with this structure have already been synthesized at room temperature and reported in the literature.45 Importantly, the Zn-Sn intermediate obtained at 25 °C did not contain any copper. Copper begins to incorporate as the temperature is raised (Fig. S6[†]). Analysis of the supernatant from the reaction that produces solid Zn-Sn intermediate at 25 °C using ICP-OES contained \approx 900 times more Cu than Zn, indicating clearly that copper remains in solution, perhaps as an amino complex. The same analysis on the supernatant from the reaction at 90 °C contained \approx 20 times more Cu than Zn, consistent with increased Cu incorporation into the solid as temperature is raised.

In contrast, when the synthesis is conducted using higher sulfur excess (S : M = 6.2), Zn–Sn intermediates are observed only up to 75 °C, with CZTS peaks just beginning to appear at lower temperature. However, these CZTS peaks are those expected from the kesterite phase and not the wurtzite phase. For S : M = 6.2 at and above 100 °C only the XRD peaks from kesterite CZTS are observed, with no evidence of wurtzite formation. The XRD data from the products synthesized with a high S: M ratio (S: M = 6.2) show that the kesterite phase is formed directly, without the formation of the wurtzite phase. Similarly, the XRD data from the products synthesized with a low S: M ratio (S: M = 1.9) show that the wurtzite phase is formed directly without the formation of the kesterite phase. In other words, there is no phase transition from wurtzite to kesterite or vice versa during synthesis. This indicates that the S : M ratio directly influences the nucleation and growth of CZTS, an issue that we will revisit shortly.

The same low temperature experiments conducted with the Sn(tv) precursor did not yield the Zn–Sn intermediate complex. Instead, the XRD and SEM-EDS data show that the room temperature synthesis starting with Cu(tr) and Sn(tv) precursors resulted in the formation only of elemental sulfur, with no evidence for the presence of any Zn–Sn intermediates, regardless of the S : M ratio (ESI Fig. S9 and Table S6†). The fact that thiourea does not bind Sn(tv) can be explained based on Pearson's Hard and Soft Acid Base Theory (HSAB),⁴⁶ since thiourea is a soft base and thus more likely to bind to Sn(tr) and Zn(tr),

which are both borderline acids, than to Sn(IV), which is a hard acid. Consequently, thiourea remains in the solution and decomposes, producing elemental sulfur. At higher temperatures Cu(II) and Sn(IV) precursors always lead to the formation of the kesterite phase. This observation implicates Zn–Sn intermediate as the precursors in the formation of the wurtzite phase when thiourea is used as sulfur excess source. That the Zn–Sn intermediates also form with other amine containing sulfur sources such as L-cysteine and leads to wurtzite formation supports this conclusion.

Fig. 7 compares SEM images of the Zn-Sn intermediate products, specifically, Cu(II)_Sn(II)_Tu_1.9_25 °C (Fig. 7a) and Cu(II)_Sn(II)_Tu_6.2_25 °C (Fig. 7c) with SEM images of the CZTS nanocrystals produced with the same tin and sulfur sources at 160 °C, specifically, Cu(II) Sn(II) Tu 1.9 160 °C (Fig. 7b) and $Cu(\pi)$ _Sn(π)_Tu_6.2_160 °C (Fig. 7d). The morphologies of the Zn-Sn intermediate intermediates are sensitive to S : M ratio. When the S : M ratio employed is 1.9, the Zn-Sn intermediate particles are micron-sized hexagonal prisms (Fig. 7a), and the product formed after heating to 160 °C is wurtzite particles agglomerated into submicron spherules. In contrast an S: M ratio of 6.2 leads to the formation of hexagonal plates that have holes and this donut morphology is retained in the kesterite product that forms upon heating to 160 °C (Fig. 7c). The similarity between this morphology and those of CZTS nanocrystals (e.g., Fig. 7d) is striking and immediately reinforces the conclusion that these Zn-Sn intermediate intermediates are precursors to CZTS formation. It thus seems that the hexagonal donuts transform to kesterite CZTS directly.

Even though the morphologies of the particles synthesized with S : M = 1.9 and S : M = 6.2 (*e.g.*, at 25 °C) are very different,



Fig. 7 SEM images of the nanocrystals (a) $Cu(II)_Sn(II)_Tu_1.9_25 \, ^{\circ}C$, (b) $Cu(II)_Sn(II)_Tu_1.9_160 \, ^{\circ}C$, (c) $Cu(II)_Sn(II)_Tu_6.2_25 \, ^{\circ}C$, and (d) $Cu(II)_Sn(II)_Tu_6.2_160 \, ^{\circ}C$. (a) and (c) are the Zn–Sn intermediate precursor nanocrystals whereas (b) and (d) are the CZTS nanocrystals formed from these precursors (see ESI Fig. S10† for additional SEM images).

their XRD patterns are nearly indistinguishable. These different precursor morphologies lead to the formation of wurtzite CZTS when S: M = 1.9 and kesterite CZTS when S: M = 6.2. We believe that the morphologies of the Zn–Sn intermediate precursor mediate the rate of transformation to CZTS. We hypothesize that the formation of wurtzite CZTS is favored by slow conversion of the Zn–Sn intermediate precursor to CZTS *via* Cu diffusion. The hollow morphology presents a larger surface area facilitating faster diffusion of Cu into the intermediate and faster transformation, which favors the formation of the kesterite phase. In contrast, the transformation is slower with larger hexagonal prisms with less surface area, which slows the transport rate of Cu into the precursor particles favoring the slow formation of the wurtzite phase.

Table 1 also shows that wurtzite is always the major CZTS phase when thioglycolic acid or 3-mercaptopropionic acid are used as the excess sulfur source in the synthesis, regardless of the S : M ratio or the Sn oxidation state. This is in direct contrast to synthesis where amine containing excess sulfur sources are used where both the S : M ratio and the Sn oxidation state affects whether one obtains kesterite or wurtzite phases. We now show that the mechanism of the wurtzite CZTS formation when thioglycolic acid or 3-mercaptopropionic acid are used as the excess sulfur source is different than the mechanism discussed above where the precursor is a Zn–Sn intermediate. We further show that when thioglycolic acid or 3-mercaptopropionic acid are used that previously revealed by Regulacio and others, and is *via* a copper sulfide intermediate as discussed in the Introduction.

Again, to reveal the intermediates we conducted the CZTS synthesis at temperatures lower than 160 °C, varying the Sn oxidation state. We changed the excess sulfur source to a molecule that does not have an amino group and cannot form the Zn-Sn intermediate precursor. Fig. 8 shows the XRD patterns from nanocrystals synthesized using thioglycolic acid as the excess sulfur source. Indeed, the Zn-Sn intermediate is not observed at any temperature. Instead, an amorphous powder is formed at temperatures lower than 75 °C. This amorphous powder begins to convert to crystalline $Cu_{2-x}S$, above 100 °C. We see clear diffraction peaks from $Cu_{2-x}S(e.g.,$ sample Cu(II)_Sn(IV)_TGacid_1.9_100 °C in Fig. 8b) when the tin source is Sn(w) and weaker and broader diffraction peaks when the tin source is $Sn(\pi)$ (e.g., sample $Cu(\pi)_Sn(\pi)$ _TGacid_1.9_100 °C in Fig. 8a). We thus conclude that when the excess sulfur source does not have an amino group, the synthesis of the wurtzite CZTS phase proceeds through an $Cu_{2-x}S$ intermediate. The presence of $Cu_{2-x}S$ as intermediate leading to the formation of wurtzite CZTS and CuInS₂ was previously observed and reported in the literature.^{20,47}

While the amino group is necessary for the formation of the Zn–Sn intermediate, its precise role is not clear. One possibility is that the amino group is a part of the Zn–Sn intermediate. Alternatively, and perhaps more likely, the amino group complexes with copper present in solution, forming soluble copper–amino complexes leading to the formation of a copper-free Zn–Sn intermediate. Sequestration of copper in the soluble complex is also consistent with no $Cu_{2-x}S$ intermediate



Fig. 8 XRD pattern of the samples Cu(II)_Sn(II)_TGacid_1.9_T and Cu(II)_Sn(IV)_TGacid_1.9_T, with T between 25 and 160 °C. The sample Cu(II)_Sn(IV)_TGacid_1.9_25 °C did not produce any solid. Peaks labelled as \triangle are consistent with Cu_{2-x}S matching the following patterns CuS – PDF# 00-006-0464, Cu₉S₈ PDF# 00-036-0379, and Cu₃₉S₂₈ PDF# 00-036-0380 (see also Table S7 in the ESI† for the elemental analysis results).

forming. It is also consistent with copper not becoming incorporated into the Zn–Sn intermediate by complexing with thiourea like $Zn(\pi)$ and $Sn(\pi)$ do as would be expected from Pearson's HSAB theory. As the temperature is increased these amino complexes dissociate, allowing copper to react with the Zn–Sn intermediate to form CZTS.

Summary and conclusions

Scheme 1 is a schematic summary of our findings. Our main conclusion is the existence of two distinct pathways to wurtzite CZTS nanocrystals. One of these (Scheme 1a) is *via* copper sulfide intermediates as previously reported and discussed in the literature.^{13,20} In this pathway, the oxidation state of the tin and S : M ratio does not play a role in determining the phase of the CZTS: it seems that wurtzite CZTS is formed as long as copper sulfides are formed as intermediates. The second pathway (Scheme 1b) is new and involves an intermediate Zn-



Scheme 1 (a) Reaction scheme for S excess source containing NH₂ group, according to the S : M variation, leading to kesterite or wurtzite CZTS; (b) reaction scheme for S excess source without NH₂ group, leading mostly to wurtzite CZTS.

Sn intermediate that appears to form only when the sulfur precursor contains $-NH_2$ groups. In this second pathway, the oxidation state of the tin and S : M ratio does play a significant role. The former determines whether the intermediate can form and the latter determines the morphology of the precursor and thus the transformation rate of the precursor to CZTS. The Zn-Sn intermediate forms only when the Sn source is in the +2 oxidation state and does not form when the tin is in +4 oxidation state.

In the new mechanism (Scheme 1b) the first step is the formation of Zn-Sn intermediate precursor particles upon mixing of the reagent solutions. This reaction proceeds even at room temperature. The morphology of these Zn-Sn intermediate particles depends on the S: M ratio. At low thiourea concentration (*i.e.*, S : M = 1.9) large hexagonal prisms form. On the other hand, at higher thiourea concentrations (*i.e.*, S: M = 6.2), dissolution-reconstitution rates will increase and faster localized Ostwald ripening will produce hollow hexagonal plate-like structures.48-51 The second step is the transformation of the Zn-Sn intermediate precursor to CZTS, in either the wurtzite or the kesterite phase. This transformation requires the diffusion into and reaction of copper with the intermediate. After Cu(II) adsorbs on to the Zn-Sn intermediates, the high temperature in the microwave promotes the mixing, interdiffusion, and reaction of the species present in the Zn-Sn intermediate particles and Cu(II) ions. The rate of this transformation depends on the morphology of the intermediate. Small, hollow structures promote faster conversion while large hexagonal prisms slow down the transformation. A major consequence of the morphological difference between the products synthesized with S: M = 1.9 and S: M = 6.2 is

that the interdiffusion rate of the elements within the hexagonal prism shaped Zn-Sn intermediate particles (obtained with S: M = 1.9) is slower than the interdiffusion rate in the hollow hexagonal plate-like particles (obtained with S: M = 6.2) (it is easier to diffuse into a small hollow structure with high surface to volume ratio that it is to diffuse into a larger one with low surface to volume ratio). Consequently, the Zn-Sn intermediates prepared with S: M = 1.9 require a higher temperature in order to convert to CZTS. To test this hypothesis, we examined the SEMs of the products whose XRD patterns are shown in Fig. 6 (see Fig. S11 in ESI[†]). These SEM images show that, indeed, the large hexagonal prisms (S : M = 1.9) still persist at 100 °C with small spherical CZTS particles growing around them while the hollow hexagonal plates (S: M = 6.2) have been completely converted. The slower diffusion rate of Cu into the hexagonal prism shaped large Zn–Sn-intermediate particles (obtained with S: M = 1.9) slows the transformation of the intermediate to CZTS. This slow transformation leads to the formation of the metastable wurtzite phase.

Conflicts of interest

There are no conflicts to declare.

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Synthesis of $Cu_2(Zn_{1-x}Co_x)SnS_4$ nanocrystals and formation of polycrystalline thin films from their aqueous dispersions[†]

Alexandre H. Pinto, (); * Seung Wook Shin, (); * Aastha Sharma, * R. Lee Penn * and Eray S. Aydil * *

Quintenary $Cu_2(Zn_{1-x}Co_x)SnS_4$ is an analog of the promising solar absorber material Cu_2ZnSnS_4 (CZTS). The initial rapid progress in CZTS has stalled because the similar sizes of Cu and Zn cations lead to facile formation of antisite defects, which are thought to limit the solar cell performance. Cobalt substitution for Zn may reduce cation disorder. Herein, we report the synthesis of wurtzite Cu₂(Zn_{1-x}Co_x)SnS₄ across the entire composition range and a systematic study of the substitution of Co into the wurtzite CZTS lattice. The synthesis is based on microwave heating to only 160 °C and uses metal salts and thiourea as precursors and ethylene glycol as the solvent. The $Cu_2(Zn_{1-x}Co_x)SnS_4$ nanocrystals were phase pure wurtzite within the detection limits of X-ray diffraction and Raman scattering. The wurtzite lattice parameters, nanocrystal sizes, and A1 Raman mode peak positions depend on the Co concentration, x. The lattice parameters follow Vegard's law within the accuracy of our measurements, and the A1 Raman mode shifts nearly linearly with x. The nanocrystal size decreases from 8 nm to 4 nm as x increases from 0 to 1. The absorption band edge blue shifted from 1.1 eV for x = 0 to 1.35 eV for x = 1. These values are lower than those predicted by density functional theory calculations and previous attempts at determining the optical band gap for wurtzite Cu_2ZnSnS_4 (x = 0) and Cu_2CoSnS_4 (x = 1). Either the band gaps of wurtzite Cu_2ZnSnS_4 (x = 0) and Cu_2CoSnS_4 (x = 1) are lower or these materials have significant band tails due to defects. We also prepared polycrystalline $Cu_2(Zn_{1-x}Co_x)SnS_4$ thin films by thermal annealing, in sulfur, of coatings comprised of $Cu_2(Zn_{1-x}Co_x)SnS_4$ nanocrystals. Upon annealing in sulfur, the wurtzite $Cu_2(Zn_{1-x}Co_x)SnS_4$ nanocrystals transformed into larger grains (100 s of nm to microns) that have a kesterite structure. The films with $x \le 0.4$ were phase pure kesterite within the detection limits of XRD and Raman scattering, but, for $x \ge 0.6$, secondary phases such as Cu_{1.96}S and Co_{0.24}Zn_{0.76}S were also detected.

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Introduction

Kesterite Cu_2ZnSnS_4 (CZTS) and the related compound Cu_2 - $ZnSn(S_xSe_{1-x})_4$ (CZTSSe) are being considered as absorber layers in thin-film solar cells^{1,2} because they have high absorption coefficients in the visible range of the electromagnetic spectrum³ (>10⁻⁴ cm⁻¹), direct and easily tunable band gaps between 1.0 eV and 1.5 eV by adjusting the S-to-Se ratio,⁴ and a high theoretical efficiency (\sim 32%).⁵ Moreover, CZTSSe is comprised of abundant metals with low toxicity relative to other solar cell materials such as CdTe. Although CZTSSe-based thinfilm solar cells have already achieved a record efficiency of 12.7%,⁶ this performance still falls significantly short of the 21.7% efficiency of Cu(In,Ga)Se₂ (CIGS)-based solar cells⁷ and of theoretical efficiencies (32.4% for CZTS and 31% for CZTSe).⁸

Alarmingly, the initial rapid rise achieved in record efficiencies between 2010 and 2014 has stalled. Among the reasons responsible for this underperformance is the relatively large open circuit voltage, $V_{\rm oc}$, deficit (600 mV) with respect to the theoretical maximum (*i.e.*, the band gap, $E_{\rm g}$, divided by the electron charge).^{9,10} This deficit is much larger for CZTSSe than for CIGS-based solar cells (440 mV).⁶ One possible reason proposed for this relatively high $V_{\rm oc}$ -deficit is band gap and

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band edge fluctuations due to cation disorder and antisite defects such as CuZn, ZnCu, ZnSn, and SnZn.11,12 Moreover, Cu and Sn have multiple oxidation states and favor the formation of deep-level defects in CZTSSe.13 These defects may increase the non-radiative carrier recombination rate and lower the $V_{\rm oc}$.¹¹ Higher $V_{\rm oc}$ values are achieved by substituting some of the cations in CZTSSe. For example, replacing Sn with Ge improves $V_{\rm oc}$ by reducing defect concentrations.¹⁴ The main problem, however, is the similar sizes of Cu⁺ (0.91 Å), Cu²⁺ (0.87 Å), and Zn^{2+} (0.88 Å) cations, which allow them to easily substitute for each other resulting in substantial cation disorder in wurtzite and kesterite phases of CZTS.^{10,11} One solution to this problem is to substitute a smaller cation such as Co^{2+} (0.68 Å) for Zn^{2+} (0.88 Å) to form $Cu_2(Zn_{1-x}Co_x)SnS_4$ alloys with band gaps similar to that of CZTS.^{15,16} The smaller size of Co²⁺ is expected to result in reduced cation disorder and antisite defects in Cu₂CoSnS₄ as compared to Cu₂ZnSnS₄. Thus, $Cu_2(Zn_{1-x}Co_x)SnS_4$ alloys may lead to solar cells with a higher V_{oc}.

In one approach to making polycrystalline thin films for solar cells, CZTS coatings are cast on substrates from nanocrystal dispersions, and the resulting coatings are annealed in sulfur or selenium vapor.17-20 CZTS nanocrystals have been synthesized using a variety of routes, and methods for controlling their size and composition have been explored.²¹⁻²⁴ Making $Cu_2(Zn_{1-r}Co_r)SnS_4$ films using this method will require the synthesis of nanocrystals with the desired cation composition, x. A few studies have reported the synthesis of Cu₂CoSnS₄ nanocrystals.²⁵⁻³⁰ To our knowledge, there is only one recent report of stannite $Cu_2(Zn_{1-x}Co_x)SnS_4$ ($0 \le x \le 1$) nanocrystals across the entire composition range: Huang et al. synthesized stannite Cu₂(Zn_{1-x}Co_x)SnS₄ nanocrystals by reacting metal salts with thiourea in oleylamine for more than 24 hours at temperatures greater than 260 °C.31 More recently, Thompson et al. synthesized wurtzite $Cu_2(Zn_{1-x}Co_x)SnS_4$ nanocrystals from metal salts in octadecene using trioctylphosphine oxide but only for x between 0 and 0.11. To our knowledge, wurtzite $Cu_2(Zn_{1-x}Co_x)SnS_4$ nanocrystals and polycrystalline thin films have not been synthesized previously across the entire composition range (*i.e.*, $0 \le x \le 1$). Moreover, previous synthesis of Cu2CoSnS4 nanocrystals used chemicals such as trioctylphosphine oxide and oleylamine,25,30,31 which are known to be cytotoxic.32,33

Herein, we report the synthesis of $\text{Cu}_2(\text{Zn}_{1-x}\text{Co}_x)\text{SnS}_4$ nanocrystals ($0 \le x \le 1$) and thin polycrystalline films formed by annealing coatings cast from dispersions of these nanocrystals. Specifically, we made $\text{Cu}_2(\text{Zn}_{1-x}\text{Co}_x)\text{SnS}_4$ nanocrystals using a microwave-assisted solvothermal synthesis in ethylene glycol and investigated the formation of polycrystalline $\text{Cu}_2(\text{Zn}_{1-x}\text{Co}_x)\text{SnS}_4$ films on Mo-coated soda lime glass substrates when coatings cast from aqueous dispersions of these nanocrystals are annealed in sulfur vapor. Advantages of microwave synthesis have been reviewed by Baghbanzadeh *et al.*: they include significant reduction in synthesis times and efficient use of energy by coupling it selectively with the solvent.³⁴

Experimental procedure

Materials

Copper(II) acetate monohydrate (Cu(II)Ac₂·H₂O ACS reagent, >98%, Sigma-Aldrich), zinc acetate dihydrate (ZnAc₂·2H₂O ACS reagent Acros Organic), cobalt(II) acetate tetrahydrate (Co(II)Ac₂·4H₂O, >97%, Acros Organic), tin(II) chloride (Sn(II)Cl₂ 98% Sigma Aldrich), thiourea (CH₄N₂S, \geq 99.0%, Sigma Aldrich), sodium thioglycolate (HSCH₂COONa \geq 96.5%, Sigma Aldrich), ethylene glycol (Fisher Scientific), methanol (Sigma Aldrich), and ethanol (Decon-200 Proof) were used as received.

Synthesis of Cu₂(Zn_{1-x}Co_x)SnS₄ nanocrystals

In a typical ${
m Cu_2ZnSnS_4}$ synthesis, 1.7 imes 10⁻³ mol of Cu(II)Ac₂·H₂O, 1.0 \times 10⁻³ mol of ZnAc₂·2H₂O, and 1.0 \times 10^{-3} mol of Sn(II)Cl₂ were added to 30 mL ethylene glycol while stirring. To synthesize Cu_2CoSnS_4 , 1.0 \times 10⁻³ mol of $ZnAc_2 \cdot 2H_2O$ was replaced by 1.0×10^{-3} mol of $CoAc_2 \cdot 4H_2O$. To synthesize $Cu_2(Zn_{1-x}Co_x)SnS_4$ solid solutions, the amounts of $ZnAc_2 \cdot 2H_2O$ and $CoAc_2 \cdot 4H_2O$ were adjusted according to the desired solid solution composition, x, where x is the nominal Co fraction in the precursor solutions as calculated from the ratio of the moles of CoAc2 to the sum of the moles of CoAc2 and $ZnAc_2$ (*i.e.*, $[CoAc_2]/[Co(II)Ac_2 + ZnAc_2]$). Following this, 4.0 × 10^{-3} mol of thiourea and 3.4×10^{-3} mol of HSCH₂COONa were added to the metal acetate solution. After sonication for 30 minutes, this mixture was sealed in a Teflon vial, placed inside a SiC sleeve, and loaded into an Anton Parr Multiwave Pro microwave. The solution temperature was measured using an infrared sensor. The solution was heated from room temperature to 160 °C in 15 minutes and maintained at 160 °C for 5 minutes. Following this, the power was turned off, and the solution was cooled to 55 °C in approximately 20 minutes with the aid of the fans inside the microwave. The microwave is equipped with a turntable, which spins at 2 revolutions per minute (RPM) during the entire synthesis, but the solution is not stirred. Using conventional heating, instead of microwave heating, produces a brown amorphous powder as evidenced by the lack of any XRD peaks.

Formation of polycrystalline films

After synthesis, the wurtzite $\text{Cu}_2(\text{Zn}_{1-x}\text{Co}_x)\text{SnS}_4$ nanocrystals were centrifuged at 8450 RCF for 15 minutes, the ethylene glycol supernatant was discarded, and the remaining nanocrystals were dispersed in water to make $36 \pm 10 \text{ mg mL}^{-1}$ dispersions. These dispersions agglomerate in approximately one day and must be redispersed by sonication before use. The nanocrystal coatings were cast from dispersions that were sonicated for at least 1 hour prior to casting. Soda lime glass substrates covered with 700 nm of Mo were coated with the wurtzite $\text{Cu}_2(\text{Zn}_{1-x}\text{Co}_x)\text{SnS}_4$ nanocrystals by drop casting 400 µL of the aqueous dispersions onto 6.25 cm^2 area defined by a metal frame. After drop casting, the coatings were dried at room temperature for 2 days as described previously.^{35,36} The substrates coated with nanocrystals were annealed in air at 200 °C for 10 minutes to remove any residual water trapped in between the nanocrystals. These nanocrystal coatings were porous and rough because the nanocrystals agglomerate as the dispersion cast on the substrate dries. The coatings were compacted using a hydraulic press at 6000 kPa for 15 seconds (Caver Autopellet 3887) as described previously.^{37,38} A thin sheet of Kapton film was placed on top of the nanocrystal coating to prevent the nanocrystals from adhering to the press.

The compacted wurtzite $\text{Cu}_2(\text{Zn}_{1-x}\text{Co}_x)\text{SnS}_4$ nanocrystal coatings were placed in pre-cleaned quartz ampoules (1 cm inner diameter and 10 cm length) with 14 mg of solid sulfur and 3×10^{-5} moles of NaOH, which were introduced as described by Johnson *et al.*³⁹ Following this, the quartz ampoule was evacuated to 10^{-6} Torr and flame-sealed. The sealed quartz ampoule at room temperature was loaded into a preheated furnace at 600 °C. At this temperature, 14 mg of sulfur corresponds to approximately 500 Torr of sulfur vapor. Details of the annealing process can be found in our previous papers.^{19,37,39} After maintaining the quartz ampoule at 600 °C for 1 hour, the furnace was turned off and the ampoule was allowed to cool naturally to 150 °C before removing it from the furnace. The furnace took approximately 4 hours to cool to 150 °C.

Characterization

The nanocrystal coatings were characterized, before and after annealing in sulfur, using X-ray diffraction (XRD), Raman scattering, optical absorption, and field emission scanning electron microscopy (FE-SEM). The as-synthesized nanocrystals were also characterized using transmission electron microscopy (TEM). Specifically, XRD patterns from the products were collected using a PANalytical X'Pert Pro X-ray diffractometer (Co Kα radiation with a wavelength of 1.7890 Å) equipped with an X'Celerator detector. The XRD patterns were collected from 20 to 70° (2 θ) with an effective step size of 0.0167° and 50 s dwell time per step. Lattice parameters were calculated by Rietveld refinement using the X'pert High Score Plus software. Raman spectra were collected from dried powders and annealed thin films using a Witec Confocal micro-Raman spectrometer, with a green (532 nm) laser as the excitation source. The laser power was fixed at 1 mW, and each spectrum was integrated over 150 seconds. The absorption spectra were collected in the transmission mode using an Agilent Cary 5000 UV-Vis-NIR spectrometer. A constant small background below the bandgap due to reflection and scattering was subtracted from each spectrum. For FE-SEM examination, the nanocrystals dispersed in methanol were sonicated for 1 hour, dropcast onto soda lime glass substrates, and dried in air. The dried nanocrystal coatings and annealed thin films were then examined on a JEOL 6500 FE-SEM, at an acceleration voltage of 5 kV. The elemental composition of the nanocrystals was determined using energy dispersive X-ray spectroscopy (EDS) using a Thermo-Noran Vantage system equipped with an EDS detector coupled to the JEOL 6500 FE-SEM. The acceleration voltage was adjusted to 15 kV for all EDS measurements. The ratios of the elemental concentrations were calculated based on the reference spectra provided by the software system SIX and converted to atomic%. For each sample, the elemental compositions were determined

at ten different locations and the values were averaged. Grain sizes were estimated from SEM images of the thin films by randomly drawing lines on several plan view SEM images and the average grain sizes were determined from the number of grain boundaries intersected by the line per unit length. Samples for TEM characterization were prepared by drop casting nanocrystals onto Ni TEM grids (SPI 200 mesh holey carbon coated) from methanol dispersions after sonication for at least 30 minutes. The nanocrystals were imaged using an FEI T12 TEM, operating at an accelerating voltage of 120 kV. Highresolution images were collected using an FEI Tecnai G2 F30, with an accelerating voltage of 300 kV. The elemental composition of the nanocrystals was also measured using inductively coupled plasma mass spectroscopy (ICP-MS) using a Thermo Scientific XSERIES 2 ICP-MS with an ESI PC3 Peltier cooled spray chamber, SC-FAST injection loop, and SC-4 auto sampler. Samples were diluted as appropriate and 40 ppb of indium internal standard was added. The powders were digested in a mixture of 4 mL of concentrated trace metal grade HNO₃, 1 mL of deionized water, 1.5 mL of concentrated trace metal grade HCl, and 1.5 mL of concentrated trace metal grade HF. The powders were digested by heating this dispersion in a CEM Corp Discover SP-D microwave to 150 °C for 4 minutes. We use a capital X to denote the measured (by ICP-MS and SEM-EDS) Co fraction, which is defined as $C_{\rm Co}/(C_{\rm Zn} + C_{\rm Co})$ in the nanocrystals, where C_i is the concentration of species i (Co or Zn). We use small x in $Cu_2(Zn_{1-x}Co_x)SnS_4$ nanocrystals to denote the nominal Co fraction calculated from the ratio of the moles of Co(II) acetate monohydrate to the sum of Co(II) acetate monohydrate and Zn(II) acetate monohydrate in the precursor solutions. These values (X and x) are within measurement error and are virtually the same as shown in ESI Fig. S1.† Even though Na is present in the synthesis, it was not detected in the product. If present, its concentration is below the detection limit of EDS $(\sim 0.3\%).$

Results and discussion

Cu₂(Zn_{1-x}Co_x)SnS₄ nanocrystals

Fig. 1 shows (a) XRD patterns, (b) lattice parameters, and (c) sizes of $Cu_2(Zn_{1-x}Co_x)SnS_4$ nanocrystals as a function of x. All XRD patterns show three strong peaks located near 30.5° , 32° , and 35° , which correspond to diffraction from the (100), (002), and (101) planes in wurtzite Cu₂(Zn_{1-x}Co_x)SnS₄ (P6₃mc). Additionally, the XRD patterns exhibit several weak diffraction peaks near 46° , 55° , 60° , and 66° , corresponding to the (102), (110), (103), and (112) planes, also in wurtzite Cu₂(Zn_{1-x}Co_x)SnS₄.⁴⁰ No secondary phases such as Zn-, Sn-, Cu- and Co-based sulfide compounds are detected regardless of x. Generally, the relative intensities of the XRD peaks are consistent with those expected for a powder diffraction pattern of the wurtzite phase, indicating that the kesterite and/or stannite phases are present at very low concentrations or completely absent; were a significant fraction of these phases present, the (002) peak intensity would have increased substantially as compared to the (100) and (101) peaks (see ESI Fig. S2[†]). In fact, careful examination of the XRD patterns for samples with x = 0 and x = 0.05 shows that the



Fig. 1 (a) XRD patterns, (b) lattice parameters, and (c) sizes of $Cu_2(Zn_{1-x}Co_x)SnS_4$ nanocrystals as a function of the Co fraction, *x*. Simulated XRD patterns of wurtzite Cu_2ZnSnS_4 and Cu_2CoSnS_4 are shown as stick patterns. Lines in (b) are linear extrapolation (Vegard's law) between the lattice parameters of Cu_2ZnSnS_4 and Cu_2CoSnS_4 . Nanocrystal sizes were obtained from the Scherrer equation using the measured XRD patterns. Co K α emission was used for XRD. Also see ESI Fig. S2† for XRD patterns on an expanded scale between $2\theta = 30^{\circ}$ and $2\theta = 37^{\circ}$, and for simulation details.

(002) peak is slightly higher than expected for wurtzite, indicating the possible presence of small amounts of the kesterite phase. The *a* and *c* lattice parameters in the wurtzite $Cu_2(Zn_{1-x}Co_x)SnS_4$ nanocrystals decrease with increasing Co fraction, *x*, because the ionic radius of Co^{2+} (0.68 Å) is smaller than the ionic radius of Zn^{2+} (0.88 Å). For x = 0 and x = 1wurtzite Cu_2ZnSnS_4 and wurtzite Cu_2CoSnS_4 , the calculated lattice parameters are in excellent agreement with those reported previously (Table 1). 4,41,42

The sizes of the $Cu_2(Zn_{1-x}Co_x)SnS_4$ nanocrystals, calculated from the full width at half maximum of the (002) diffraction peak using the Scherrer equation, remain approximately constant up to x = 0.5 and decrease thereafter. The decrease in the nanocrystal size with increasing doping or alloying (*i.e.* increasing x) has been observed previously in other systems⁴³ and may be expected when two different types of ions compete for the same lattice position because this competition can reduce both the nucleation and the growth of the nanocrystals.^{44,45} For example, lattice strain induced upon incorporation of ions with different radii can increase the critical nucleation size.

Fig. 2 shows the Raman spectra of the $Cu_2(Zn_{1-x}Co_x)SnS_4$ nanocrystals as a function of nominal Co fraction, x. The A1 mode peak position shifts from 328 cm⁻¹ for x = 0 (Cu₂ZnSnS₄) to 319 cm⁻¹ for x = 1 (Cu₂CoSnS₄). The A₁ mode peak in wurtzite CZTS has been reported to range from 325 cm⁻¹ to 335 cm^{-1} . ⁵⁰⁻⁵⁴ There is evidence that the A₁ mode peak position may depend on the shape and size of the nanocrystals.¹⁹⁻²³ For example, Li et al. reported the A1 mode peak position for wurtzite CZTS nanoplates at 335 cm^{-1} as compared to 325 cm^{-1} for oblate rice shaped nanocrystals.⁵¹ Our nanocrystals were a mixture of oblate and spherical nanocrystals (vide infra) and gave rise to a broad Raman scattering peak that peaked at 328 cm⁻¹ for wurtzite CZTS (x = 0). To our knowledge, there is no Raman scattering reported for wurtzite Cu2CoSnS4. Gillorin et al. synthesized kesterite Cu2CoxSnS4 and reported a broad Raman scattering peak peaking at 315 cm⁻¹ for 3 nm diameter nanocrystals.25 For larger Cu2CoSnS4 kesterite crystals (e.g., 100 s of nm), Krishnaiah observed the A1 peak at 325 cm⁻¹.²⁹ Huang *et al.* reported a shift from 335 cm⁻¹ to 325 cm⁻¹ for stannite or kesterite $Cu_2(Zn_{1-x}Co_x)SnS_4$ as x increased from 0 to 1.31 Thus, substituting Co for Zn in kesterite CZTS appears to shift the A_1 mode from 337 cm⁻¹ to 325 cm⁻¹. Such a Raman shift to lower wavenumbers has also been observed when Zn was substituted with Fe to form Cu₂(Zn_{1-x}Fe_x)SnS₄ and Co to form Cu₂(Zn_{1-x}Co_x)SnS₄.⁵⁵ Both alloying and the small nanocrystal size broaden the Raman peaks and reduce the scattering intensity, making it difficult to ascertain the phase purity by Raman measurements alone. However, there is no obvious presence of large amounts of secondary phases such as Cu-, Zn-, Co-, and Sn-sulfides via XRD. The impurity phases that are most difficult to distinguish from Cu₂(Zn_{1-x}Co_x)SnS₄ are Cu₃SnS₄ and ZnS. ZnS Raman scattering at \sim 350 cm⁻¹ is weak and can be easily masked by the main broad A1 mode.⁵⁶⁻⁵⁸ Similarly, the most intense Raman scattering from Cu_3SnS_4 is at 318 cm⁻¹.⁵⁶ To complicate matters, these phases have overlapping XRD peaks with $Cu_2(Zn_{1-x}Co_x)SnS_4$. However, the presence of both of these phases in significant amounts would alter the intensity ratios of the (100), (002), and (101) XRD peaks as shown in Fig. 1. This is not the case and the diffraction intensity ratios closely match those expected from a powder of $Cu_2(Zn_{1-x}Co_x)SnS_4$.

Fig. 3 shows the representative high resolution (HR)-TEM images of $Cu_2(Zn_{1-x}Co_x)SnS_4$ nanocrystals. The

Table 1 Lattice parameters of the $Cu_2(Zn_{1-x}Co_x)SnS_4$ phases

	Crystal structure	Space group	<i>a</i> (Å)	<i>c</i> (Å)
Cu_2ZnSnS_4 (<i>x</i> = 0) ref. 46	Wurtzite	P6 ₃ mc	3.8387	6.3388
Cu_2CoSnS_4 (x = 1) ref. 47	Wurtzite	$P6_3mc$	3.806	6.295
Cu_2ZnSnS_4 (x = 0) ref. 48	Kesterite	$I4_{2m}$	5.427	10.848
Cu_2CoSnS_4 (x = 1) ref. 49	Kesterite	I4 _{2m}	5.396	10.789
Cu_2ZnSnS_4 (x = 0) this work	Wurtzite	$P6_3mc$	3.837	6.339
Cu_2CoSnS_4 ($x = 1$) this work	Wurtzite	$P6_3mc$	3.809	6.281

Cu₂(Zn_{1-x}Co_x)SnS₄ nanocrystals are either spherical or oblate. Oblate nanocrystals have been observed previously when wurtzite Cu₂ZnSnS₄ and Cu₂CoSnS₄ nanocrystals were synthesized in other solvents.^{26,41} On average the nanocrystals observed in the TEM are smaller for larger *x*, which is consistent with sizes obtained from the XRD patterns (Fig. 1(c)). The HRTEM images show lattice fringes with spacings consistent with the (101), (102), (100) planes of wurtzite CZTS and wurtzite Cu₂CoSnS₄. The fast Fourier transform (FFT) patterns well match with the wurtzite structure of Cu₂(Zn_{1-x}Co_x)SnS₄ and are shown in the ESI (Fig. S3[†]).

The Cu₂(Zn_{1-x}Co_x)SnS₄ nanocrystals show strong absorption in the visible region of the electromagnetic spectrum, with the absorption edge (Fig. 4) blue shifting from ~1120 nm (1.1 eV) to ~920 nm (1.35 eV) as x is increased. The band gap of wurtzite



Fig. 2 (a) Raman spectra and (b) A_1 mode peak positions of $Cu_2(Zn_{1-x}Co_x)SnS_4$ nanocrystals as a function of *x*.

Cu₂ZnSnS₄ has been reported to be between 1.4 and 1.5 eV, but these analyses rely on plotting $(\alpha h\nu)^2 \nu s$. $(h\nu)$, arbitrarily deciding the region where this plot appears linear, and extrapolating this line to $(\alpha h\nu) = 0$ to find where it intercepts the $(h\nu)$ axis; this intercept is an estimate of the band gap energy, E_{g} .⁵⁹ However, this analysis is fraught with difficulties and potential pitfalls, particularly when there is significant reflection and scattering or when there is absorption near the band edge due to plasmons or tail states. Indeed, all the reported measurements for wurtzite CZTS show absorption below the reported band gap values^{41,46,59} (see also the discussion in the ESI[†]). Using density functional theory within hybrid functional PBE0, Zhao et al. calculated the wurtzite CZTS band gap to be 1.372 eV.60 Like the previous experimental absorption spectra, absorption from our wurtzite CZTS films also begins to rise at \sim 1200 nm, indicating either a lower band gap value than the reported 1.43 eV or a significant absorption tail below the conduction band edge, possibly due to defects. There is only one report of optical absorption in $Cu_2(Zn_{1-x}Co_x)SnS_4$, but these are in kesterite or stannite nanocrystals.³¹ Based on the changes in the Raman peak widths, the authors claimed that the crystal structure changed from kesterite to stannite, around x = 0.3-0.6, as x was increased. The XRD, however, shows that these crystals were either kesterite or stannite and not wurtzite. These authors reported that the band gap of $Cu_2(Zn_{1-x}Co_x)SnS_4$ (kesterite or stannite) red shifted from 1.45 eV at x = 0 to 1.21 eV at x = 1. These values are again determined from extrapolation of the $(\alpha h\nu)^2$ vs. $(h\nu)$ plot, which showed a significant tail and absorption below the extrapolated values. In fact, one cannot discern a band edge from the unprocessed absorption spectra in this article. Our absorption edge gradually blue shifts to \sim 1.35 eV as more Co is substituted for Zn (*i.e.*, x increases), the opposite trend to that reported by Huang et al.31 (see also the discussion in the ESI[†]). One possibility is that the nanocrystals become increasingly more quantum confined as their sizes decrease with increasing Co concentration (see Fig. 1), but Khare et al. showed that the CZTS nanocrystal sizes must be approximately 3 nm or less to observe this effect.61 Thus, quantum confinement is an unlikely explanation for the shift observed in the spectra of Fig. 4.

Polycrystalline $Cu_2(Zn_{1-x}Co_x)SnS_4$ thin films

Encouraged by the formation of wurtzite $Cu_2(Zn_{1-x}Co_x)SnS_4$ solid solutions without any detectable secondary phases, we proceeded to study the formation of polycrystalline $Cu_2(Zn_{1-x}Co_x)SnS_4$ thin films from coatings comprising the nanocrystals. We made



Fig. 3 Representative TEM images of $Cu_2(Zn_{1-x}Co_x)SnS_4$ nanocrystals with (a) x = 0, (b) x = 0.25, (c) x = 0.4, (d) x = 0.6, (e) x = 0.75, and (f) x = 1, respectively. TEM samples were made by drop casting the nanocrystal dispersion in methanol onto Ni carbon mesh grids.

polycrystalline $\text{Cu}_2(\text{Zn}_{1-x}\text{Co}_x)\text{SnS}_4$ thin films by annealing, in sulfur vapor, coatings dropcast onto Mo-coated soda lime glass substrates from aqueous dispersions of the nanocrystals. Fig. 5 shows the XRD patterns and lattice parameters of the polycrystalline films formed on Mo-coated soda lime glass substrates by annealing coatings of $\text{Cu}_2(\text{Zn}_{1-x}\text{Co}_x)\text{SnS}_4$ nanocrystals. The XRD patterns collected from the annealed films with x = 0 are



Fig. 4 Optical absorption spectra of $Cu_2(Zn_{1-x}Co_x)SnS_4$ nanocrystals as a function of Co fraction, *x*. The absorption spectra were obtained from films dropcast from nanocrystal dispersions in methanol on soda lime glass substrates after compaction. The baseline was offset for *x* > 0 for clarity. The baseline for the offset spectra (*A* = 0) is indicated with a dashed line.

consistent with the kesterite CZTS phase, Mo, and MoS₂. When annealed, the wurtzite nanocrystals transform into larger kesterite grains. When x is less than 0.4, no secondary phases were detected by XRD, and the films appear to consist primarily of polycrystalline $Cu_2(Zn_{1-x}Co_x)SnS_4$. On the other hand, when $x \ge x$ 0.6, secondary phases such as Cu_{1.96}S and Co_{0.24}Zn_{0.76}S were also detected. We assign the peak appearing at 33.4° to cubic $Co_{0.24}Zn_{0.76}S$. This peak appears at around x = 0.75 and increases in intensity as the Co concentration is increased and *x* reaches 1. It may seem odd that this particular composition of this alloy forms, but Becker and Lutz et al. showed that there is a limit to the solubility of Co in zinc blende ZnS. It so happens that 24% is indeed the solubility limit at 600 °C, our annealing temperature.⁶² The diffraction peaks at 22° and 45.6° are from tetragonal Cu_{1.96}S. The Mo peak at 38° overlaps with diffraction from some of the secondary phases, most notably the strong (103) diffraction from $Cu_{1.96}S$ also at 38°. One can still see the Cu_{1.96}S diffraction emerging from the top of the broad Mo diffraction for films with x = 0.6 and x = 0.75. Although wurtzite $Cu_2(Zn_{1-x}Co_x)SnS_4$ forms across the entire composition range, kesterite $Cu_2(Zn_{1-x}Co_x)SnS_4$ via this route could only be formed up to x = 0.4. It is interesting to note that $Cu_2(Zn_{1-x}Fe_x)SnS_4$ transforms from kesterite to stannite with changes in the cation ordering when $x \approx 0.4-0.5$.^{49,63,64} Because Co^{2+} and Fe^{2+} have similar sizes, like $Cu_2(Zn_{1-x}Fe_x)SnS_4$, kesterite $Cu_2(Zn_{1-x}Co_x)SnS_4$ also becomes destabilized near this value of x.³¹ For this reason, we surmise that the formation of kesterite from the wurtzite structure may become inaccessible around $x \approx 0.4$ –0.5, leading instead to phase separation into $Cu_{1.96}S$ and $Co_{0.24}Zn_{0.76}S$.



Fig. 5 XRD patterns of Cu₂(Zn_{1-x}Co_x)SnS₄ polycrystalline thin films formed on Mo-coated soda lime glass substrates *via* thermal annealing, in sulfur, of Cu₂(Zn_{1-x}Co_x)SnS₄ nanocrystal coatings. Annealing was conducted in 500 Torr of sulfur at 600 °C for 1 hour. 3.0×10^{-5} mol of Na was added to the annealing ampule as described in the experimental procedure. The XRD patterns of kesterite Cu₂ZnSnS₄ (00-026-0575), kesterite Cu₂CoSnS₄ (00-026-0513), tetragonal Cu_{1.96}S (00-012-0224), cubic Co_{0.24}Zn_{0.76}S (00-047-1656), and cubic CoS₂ (98-001-3473) are also shown for comparison. Co K α emission was used for XRD.

The lattice parameters of polycrystalline $\text{Cu}_2(\text{Zn}_{1-x}\text{Co}_x)\text{SnS}_4$ thin films extracted from the XRD decrease from a = 0.5429 nm and c = 1.0832 nm at x = 0 to a = 0.5425 nm and c = 1.0828 nm at x = 0.4, and this trend is consistent with the results obtained with the $\text{Cu}_2(\text{Zn}_{1-x}\text{Co}_x)\text{SnS}_4$ nanocrystals (Fig. 1(b)). For $x \ge 0.4$, we cannot determine the true x in the kesterite phase since there are significant secondary phases in the films. Annealing at 500 °C showed similar results to annealing at 600 °C in that the films with $x \le 0.4$ were phase pure kesterite, but, for $x \ge 0.6$, secondary phases such as $\text{Cu}_{1.96}$ S and $\text{Co}_{0.24}\text{Zn}_{0.76}$ S were also detected. On the other hand, the grain sizes of films annealed at 500 °C were smaller (0.1–0.6 µm) than those at 600 °C (0.5–2 µm).

Fig. 6 shows the Raman spectra and A1 mode peak positions for polycrystalline $Cu_2(Zn_{1-x}Co_x)SnS_4$ thin films formed on Mocoated soda lime glass substrates. The film made from nanocrystals without Co (x = 0) exhibits a strong peak located at 337 ± 2 cm⁻¹, which corresponds to the A₁ mode Raman peak of the kesterite CZTS structure. As x increases to x = 0.4 (Fig. 6(a)), this peak shifts towards lower wavenumbers (324 cm⁻¹), broadens, and decreases in intensity. This behavior would be expected if Co was substituting for Zn and forming a solid solution. If the Co and Zn were to phase segregate into Cu₂ZnSnS₄ and Cu₂CoSnS₄ domains, we would expect two sharper peaks, with one at 337 cm⁻¹ for Cu₂ZnSnS₄ and the other around 324 cm⁻¹ for Cu_2CoSnS_4 .^{29,31} For $x \le 0.4$, we do not observe any other Raman scattering that can be assigned to secondary phases. However, we begin seeing Raman scattering from secondary phases in films synthesized with $x \ge 0.6$, in addition to that



Fig. 6 (a–d) Raman spectra and (e) A_1 mode peak positions of $Cu_2(Zn_{1-x}Co_x)SnS_4$ thin films formed on Mo coated soda lime glass substrates by thermal annealing of $Cu_2(Zn_{1-x}Co_x)SnS_4$ nanocrystal coatings. A_1 mode Raman peaks were collected from large grains in the $Cu_2(Zn_{1-x}Co_x)SnS_4$ films as shown in (e). Annealing conditions were the same as for Fig. 5. The Raman spectra of $Cu_2(Zn_{1-x}Co_x)SnS_4$ thin films at $x \ge 0.6$ (b–d) were collected from different grains, which were selected to show the different phases present.

from kesterite $Cu_2(Zn_{1-x}Co_x)SnS_4$, which appears between 337 cm⁻¹ (x = 0) and 324 cm⁻¹ (x = 1). For example, Fig. 6(b) shows Raman spectra collected from three different locations on the same film (x = 0.6). Region (i) shows intense Raman scattering from copper-sulfur vibrations characteristic of copper sulfides (475 cm^{-1}). An additional peak at 400 cm^{-1} can be identified both in this region (i) and elsewhere on the film, e.g., region (ii), and is assigned to characteristic Co-S vibrations in $Co_{0.24}Zn_{0.76}S$, which are expected around 390–400 cm⁻¹.^{65,66} Region (ii) in Fig. 6(b) shows Raman scattering from $Cu_2(Zn_{1-x}Co_x)SnS_4$ and $Co_{0.24}Zn_{0.76}S$ but not from $Cu_{1.96}S$. The vast majority of the film, however, is $Cu_2(Zn_{1-x}Co_x)SnS_4$ and exhibits Raman scattering like that shown for region (iii) in Fig. 6(b). In some regions like region (i) in Fig. 6(d) a particularly strong Raman peak at 476 cm⁻¹ from copper sulfide is observed when x = 1.

Fig. 7 shows the plan view and cross-sectional FE-SEM images of the polycrystalline thin films formed on Mo-coated soda lime glass substrates *via* thermal annealing of $Cu_2(Zn_{1-x}Co_x)SnS_4$ nanocrystal coatings in sulfur. FE-SEM images for the polycrystalline $Cu_2(Zn_{1-x}Co_x)SnS_4$ thin film for



Fig. 7 Plan view and cross-sectional FE-SEM images of the $Cu_2(Zn_{1-x}Co_x)SnS_4$ thin films formed on Mo coated soda lime glass substrates by thermal annealing of the $Cu_2(Zn_{1-x}Co_x)SnS_4$ nanocrystal coating: ((a) and (b)) x = 0, ((c) and (d)) x = 0.25, ((e) and (f)) x = 0.4, ((g) and (h)) x = 0.6, ((i) and (j)) x = 0.75, and ((k) and (l)) x = 1. Annealing conditions were the same as for Fig. 5.

x = 0 show a 2.0 µm thick film consisting of submicron sized grains ranging from 0.2 to 2.4 µm. The grains appear densely packed though some voids are visible. As the Co fraction, *x*, increases, the microstructure and grain size undergo dramatic changes. When x = 0.25 and 0.4, we observe large abnormal grains that have grown to over 2 µm on top of a layer comprised of smaller 200 to 800 nm grains. The average grain size, increases from 0.6 ± 0.3 to 1.1 ± 0.5 µm as *x* increases from 0.6 to 1. Although the annealed Cu₂(Zn_{1-x}Co_x)SnS₄ thin films show

micron sized grains, there are also many voids. Further optimization of the annealing parameters, such as S partial pressure, temperature, and annealing time as well as Na concentration, will be needed.

Conclusions

We report the synthesis of wurtzite $Cu_2(Zn_{1-r}Co_r)SnS_4$ nanocrystals across the entire composition range using a microwave assisted solvothermal method. The Cu₂(Zn_{1-x}Co_x)SnS₄ nanocrystals have an average size that decreases from 8 to 4 nm as x increases from 0 to 1. The absorption band edge blue shifted from 1.1 eV for Cu_2ZnSnS_4 (x = 0) to 1.35 eV for $Cu_2Co_xSnS_4$ (x =1). These values are lower than those predicted by density functional theory calculations and previous attempts at determining the optical band gap for Cu_2ZnSnS_4 (x = 0) and $Cu_2Co_xSnS_4$ (x = 1). Either the band gaps of wurtzite Cu_2ZnSnS_4 (x = 0) and Cu₂Co_xSnS₄ (x = 1) are lower, or these materials have significant band tails due to defects. The lattice parameters of $Cu_2(Zn_{1-x}Co_x)SnS_4$ nanocrystals also decrease with increasing x. Finally, we made polycrystalline $Cu_2(Zn_{1-x}Co_x)SnS_4$ thin films by annealing, in sulfur vapor, coatings comprised of $Cu_2(Zn_{1-x}Co_x)SnS_4$ nanocrystals. Upon annealing, the coatings transformed into larger grained (100 s of nm to several microns) kesterite films if $x \le 0.4$. At higher $x (x \ge 0.6)$ annealing wurtzite nanocrystals produced secondary phases such as Co_{0.24}Zn_{0.76}S, $Cu_{1.96}S$ and Co_2S , in addition to kesterite $Cu_2(Zn_{1-x}Co_x)SnS_4$. Although this work shows that $Cu_2(Zn_{1-r}Co_r)SnS_4$ films can be synthesized for $x \le 0.4$ from nanocrystal dispersions, it may be difficult to form phase pure films for higher values of x. Future work should focus on improving the film morphology and phase purity as well as on the electrical characterization of thin films towards making solar cells.

Conflicts of interest

There are no conflicts to declare.

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