PROGRAM DESCRIPTION

1. Introduction

The conversion of sunlight directly into electricity using the photovoltaic (PV) properties of suitable materials is a distinctively green but underutilized energy conversion process. Solar cell technology has been historically used in providing electrical power for spacecraft, and more recently for terrestrial systems. The driving force for the recent and ongoing technological development is the realization that the traditional fossil energy resources, coal, oil and gas, are not only limited, but are harmful to the environment, depleting the ozone layer through the emission of carbon dioxide. The use of alternate green resources, such as sunlight offers a favorable and promising alternative to the worldwide energy problems.

Solar cells are made of semiconductor materials. The first semiconductor materials that showed a significant light-dependent voltage between two contacts were selenium and later cuprous oxide [1]. Almost simultaneous with the beginning of silicon solar cell technology was the first development of cuprous sulfide/cadmium sulfide heterojunctions, which served as the basis for intense research on thin-film solar cell devices [2]. The solar cell using a diffused silicon p-n junction was first developed by Chapin, Fuller, and Pearson [3]. Subsequently, the cadmium-sulfide solar cell was developed by Reynolds et al [2]. The demand for a reliable, long-lasting power source was the major reason for the application of solar cells, and by 1958 the first silicon solar cells were used in spacecraft.

Interest arose in solar cells as an alternative energy source for terrestrial applications in the mid-1970s after the political crisis in the Middle East, the oil embargo, the realization that fossil fuel sources were limited. We peaked in domestic oil production in the 1970's. The gap between the United States oil consumption and production will continue to widen. The cost target for electricity from a photovoltaic plant operating for 30 years was established in 1986 to be equal to about 0.06 US$/kWh. The performance of the solar cell is measured in terms of its efficiency at turning sunlight into electricity. Today's commercial solar cells operate at an efficiency of 15%, using only about one-sixth of the sunlight striking the cell. It was estimated that this requires module efficiencies in the range of 15% to 20% for a flat panel system and 25% to 30% for a system operating under concentrated sunlight [1].

Photovoltaics have experienced extraordinary growth during the last few years with overall growth rates between 30% and 40% making further increase of production facilities and attractive investment [4]. In 2008, the world-wide photovoltaic industry delivered some 6,941 MW of photovoltaic generators [5].

The PV market is dominated by crystalline silicon solar modules which require thicknesses of approximately 200-300 μm and high energy intensive processes. Expensive materials and processes limit the potential for future long term cost reductions. Thin film polycrystalline low cost alternatives to silicon have emerged. Thin film solar cells require only a few microns of film thickness and less energy intensive processes. The market share for thin-film PV in the US continues to grow rapidly and was reported at more than 44% in 2006 [6].

The typical range of the thin-film technology is a layer of about 3-5 μm thickness or less. A variety of thin-film deposition techniques are available, offering great flexibility for the thin-film preparation. Other advantages of thin-film solar cells are that less material is required and that the thin layers can be deposited using different deposition techniques.

The choice of materials for photovoltaic conversion is based on a number of requirements including:

1. A direct band gap with nearly optimum values for either homojunction or heterojunction devices.
2. A high optical absorption coefficient, which minimizes the requirement for high minority carrier lengths.
3. The possibility of producing *n*- and *p*-type material, so that the formation of homojunction as well as heterojunction devices is feasible. Generally *p*-type material is preferred because electrons in many cases have a higher mobility, and the materials therefore exhibit a higher minority carrier length. Another reason is that most suitable window materials have an n- type character, and a *p*- type absorber is needed in a heterojunction device.
4. A good lattice and electron affinity match with large band gap (window) materials such as CdS or ZnO so that heterojunctions with low interface state densities can be formed and device limiting conduction band spikes can be avoided.

These requirements can be fulfilled by a number of semiconductor materials including cadmium telluride (CdTe) and copper indium gallium di-selenide ($CuIn_{(1-x)}Ga_xSe_2$), CIGS solar cells. However, some elements of these solar cells are expensive due to their scarcity in the earth's crust (In and Ga) [7] and toxic due to their carcinogenic effects (Cd and Se). In contrast, copper zinc tin sulfur (Cu_2ZnSnS_4), CZTS is a semiconductor material consisting of abundant, low-cost, non-toxic elements. CZTS is one of the most promising absorber layer materials for low-cost thin-film solar cells providing both an economical and green solution to the current thin-film technologies. CZTS has a suitable optical band gap of ~1.5 eV and a large optical absorption coefficient of over 10^4 cm^{-1}.

This research will focus on the fundamental development of CZTS thin films and solar cells by non-vacuum, liquid-based techniques. CZTS is a new semiconductor material with a very high potential for use in solar cells. Little is known and reported about the properties of CZTS, about the optimum fabrication process, and the performance relationship. This research will develop well controlled deposition methods for CZTS that will result in a high quality absorber material for CZTS solar cells. It will establish the relation between film deposition conditions, and electrical, optical and structural properties of CZTS films that result in high efficiency solar cells.

2. Research Plan

Research into PV alternatives is imperative to make the technology competitive. This includes the development of low-cost techniques, higher efficiency cells using new, low cost/abundant, non-toxic materials and thin film solar cell concepts. Several research groups have attempted the use of CZTS thin film for PV solar energy conversions. Ennaoui et al. [8] reported on CZTS thin-film solar cells with CZTS absorbers fabricated by solid-state reaction in a H_2S atmosphere of electrodeposited Cu-Zn-Sn precursors. Their highest solar cell efficiency was 3.4%. Ito et al. [9] reported on solar cells with CZTS absorbers prepared by atom beam sputtering on a stainless steel substrate, showing an open circuit voltage of 165 mV. Friedlmeier et al. [10] prepared CZTS thin films from thermally evaporated elements and binary chalcogenides in high vacuum, resulting in a solar cell with a conversion efficiency of 2.3%. Katagiri et al. [11] prepared absorbers by the reaction of electron-beam evaporated precursors followed by solid-state reaction in a H_2S atmosphere. Their highest solar cell conversion efficiency was 5.7% [12]. Recently, T. Todorov et al. [13] reported on high-efficiency CZTS solar cell of 9.6% efficiency.

Several of the CZTS crystal growth and thin film techniques are carried out at high temperatures. It is important for the determination of the stoichiometry of the compounds to control the vapor pressure of the components at these temperatures. The microstructure of the films is mainly determined by the substrate temperature, the lattice match of the compound, the substrate properties, the process direction (substrate versus superstrate configurations), and the growth rate and pressure during deposition of the films. The electronic behavior of the films may also vary considerably with deposition conditions. CZTS have been studied as potential alternatives for the two leading technologies [9, 14-16], reaching promising but not yet marketable efficiencies of 6.7% and 3.2%, respectively by multiplayer vacuum deposition [14, 15].

This research will focus on the fundamental development of CZTS thin films and solar cells by a non-vacuum, liquid-based coating method that combines advantages of both solution processing [17-20] and particle based deposition [21-24] enabling fabrication of high-efficiency CZTS solar cell devices. The PI's doctoral research focused on the development of thin film solar cells with the University of South Florida thin film solar cell group. This group is recognized around the world for its accomplishments, including the most notable being the first thin film solar cell ever to exceed the 15% efficiency mark [25]. The knowledge, experience and relationships gained working with this group, soundly and strategically positions the PI for pursuing the proposed research project.

The major tasks to implement this research plan of the fundamental development of CZTS thin films and solar cells by a non-vacuum, liquid-based coating method include:

1. Development and characterization of CZTS thin films (Years 1 and 2)

   Task 1 – CZTS Composition Ratios, Stoichiometry and Film Preparation

   Task 2 – CZTS Thin Film Grain Size and Thickness Profile

   Task 3 – CZTS Thin Film Stress and Adhesion Analysis

2. Development of CZTS solar cells (Year 2)

   Task 4 – CZTS Solar Cells and Device Fabrication

2.1 CZTS Composition Ratios, Stoichiometry and Film Preparation

To address the issue of cost, a non-vacuum liquid-based approach, from both solutions and suspensions will be developed for the CZTS absorber layer deposition to replace potentially more expensive vacuum-based techniques. True solutions allow intermixing of the constituents at a molecular level and the formation of smooth homogeneous films. Suspension approaches use solid particles designed to be deposited on a substrate and reacted of fused with each other, to form a desired crystalline phase and grain structure [21, 22]. This research will develop a solution-particle (slurry) approach using the CZTS constituents. In the work of others, it was found that the Cu-poor and Zn-rich compositions were preferable to improve the solar cell conversion efficiency [13, 26-30]. In order to clarify the region of composition ratio to achieve high conversion efficiency, CZTS thin film absorber layers will be developed having a wide range of composition ratios (Cu/(Zn+Sn); 0.75-1.25, Zn/Sn; 0.80-1.35). Initial research has found that the stable crystal structure of CZTS is kesterite and that the stable chemical potential region for the formation of the stoichiometric compound is small [13, 14, 31]. In this task, the research will focus on the development and growth optimization of Cu-poor/Zn-rich CZTS thin films.

Using this hybrid slurry method successfully combines the advantages of solution and suspension deposition routes by use of solutions containing solid particles, wherein both components (i.e., solution and particle) contain metal and chalcogen elements that integrate into the final film. Using the hybrid slurry method (i) solubility limitations are resolved, as virtually any materials system can be constituted by a combination of solid and dissolved components; (ii) the dissolved components can be engineered as an efficient binding media for the particles, eliminating the need of separate organic binders; (iii) solid particles act as stress-relief and crack-deflection centers allowing the deposition of thicker layers than pure solution processes; and (iv) the intimate contact between the two phases allows rapid reaction and homogenous phase formation.[13]

Film preparation will begin by mixing together in a single batch of hydrazine (N_2H_4) solution all the components: Cu_2S, SnS, S and Zn powder, resulting in the in situ formation of $ZnS(N_2H_4)$. The chemically reducing character of hydrazine stabilizes solutions of anions with direct metal-chalcogen bonding for select elements without the necessity to introduce typical impurities [17, 18, 32]. Prepare solutions six separate solutions that span the range of composition ratios (Cu/(Zn+Sn); 0.75-1.25, Zn/Sn; 0.80-1.35). Initially, for each film, spin coat at 800 rpm five successive layers and anneal at a range of different temperatures, from 300°C to 600°C, for different lengths of time, from 5 minutes to 60 minutes, developing the optimum deposition conditions.

Figure 1 shows the surface SEM image of CZTS films deposited by the sol-gel sulfurization method [30, 33, 34]. The CZTS is composed of smaller than 1 μm size of CZTS grains and the thickness of the CZTS film is ~1.7 μm. The objective of this research is the grow CZTS films with larger grains and thicker films, using a different deposition technique and a range of composition ratios.

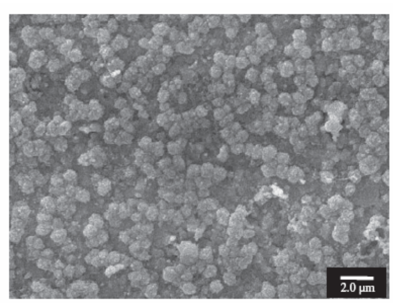


Figure 1. Surface morphology of a CZTS thin film.

Th. M. Friedlmeier et. Al. analyzed the structural properties of CZTS in detail with a pseudo-ternary ZnS-SnS2-Cu2S phase diagram [35]. Figure 2 shows the entire pseudo-ternary phase diagram [27]. Theoretically, this material should phase separate into CZTS (p-type) and ZnS (n-type) [36]. The goal of this research is to control that phase separation and develop stoichiometric CZTS thin films. The filled circle in the near middle of the phase diagram on the left represents pure CZTS, which consists of CuS of 50%, ZnS of 25% and SnS of 25%. The stoichiometric ratio of Cu/Sn is 2.0 on the green line, so the green line indicates the traces of (CZTS+ZnS) [27]. This research will study the influence of the composition ratio on photovoltaic properties, focused upon the area within small orange triangle, representing a small range of composition ratios.

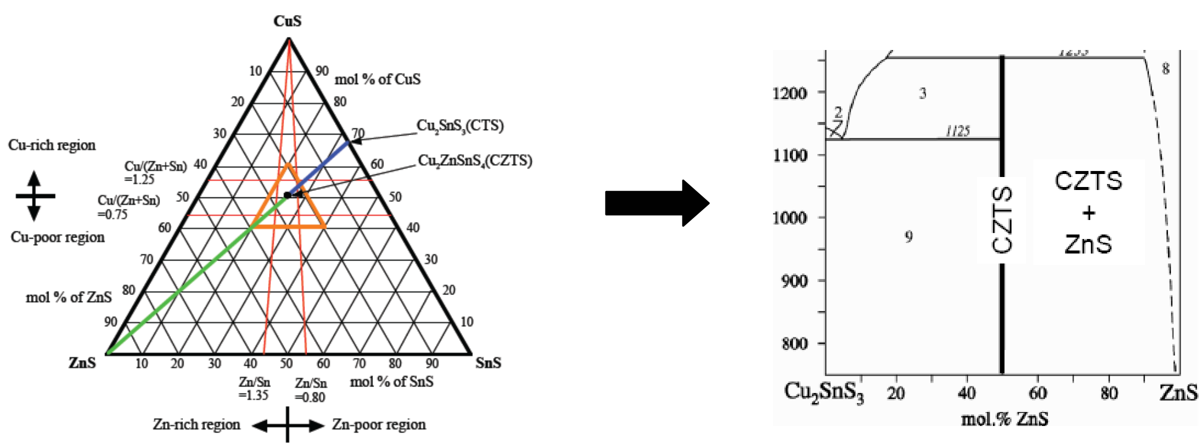


Figure 2. Pseudo-ternary phase diagram on the left with CuS, ZnS and SnS. Binary phase diagram on the right with temperature dependencies. This material should separate into CZTS (p-type) and ZnS (n-type) within a small range of composition ratios.

The X-ray diffraction pattern of the CZTS films deposited by the sol-gel sulfurization method is shown in Figure 3 [30]. The XRD peaks attributed to CZTS and their orientation are denoted by solid circles. This CZTS XRD pattern is similar to one previously reported [33], but slightly off-stoichiometric. This CZTS film was oriented to (1 1 2), same as with other reports [9, 37-39]. This research will perform XRD analysis of orientation and stoichiometry of the CZTS films prepared in this project and compare to that of the XRD data of films prepared by other deposition and preparation techniques, working towards the development of a single-phase kesterite film.

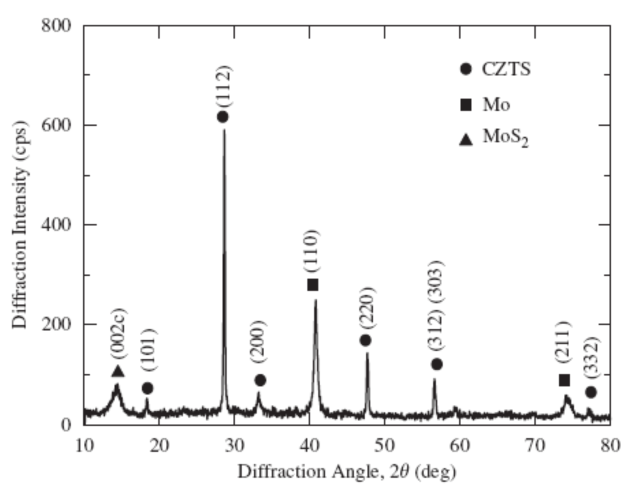


Figure 3. XRD pattern of CZTS film deposited by sol-gel sulfurization.

2.2 CZTS Thin Film Grain Size and Thickness Profile

One approach to advance solar cell device efficiencies and reduce cost is by using ultra-thin layers of the CZTS absorber and scaled down deposition process conditions. This research will focus on developing the optimal CZTS film thickness for maximum absorption in the long range wavelength. A thin film CdTe solar cell is similar to that of CZTS, in that a small thickness of CdTe ranging from 2-4 μm will absorb 100% of the incident photons, due to its high absorption coefficient of 10^5 cm^{-1} [40]. The CdTe layers grown by high temperature (~550°C) close spaced sublimation (CSS) processes have grain sizes equivalent to the CdS grain size at the interface, but develop into much larger grains of several microns in diameter near the CdTe top surface. Figure 4 show the effects of deposition processes on grain size, and that small CdTe grains re-crystallize into large grains, after a heat treatment process. However, large CdTe grains do not re-crystallize. A lattice mismatch at the absorber/buffer interface that results in dislocations can also impact the grain size.

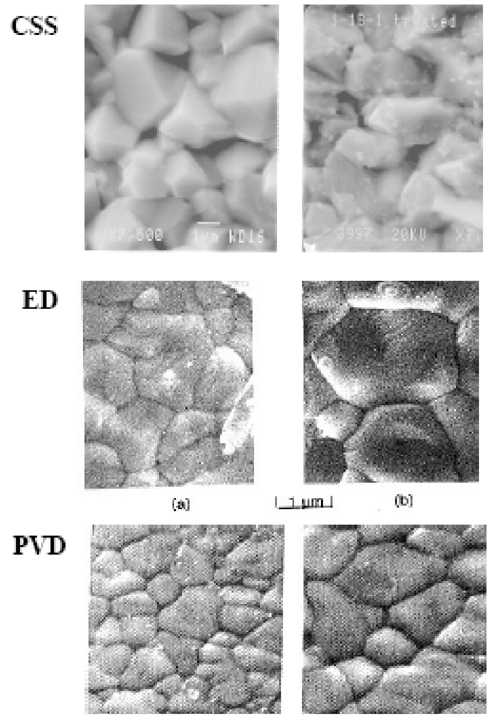


Figure 4. CdTe grain size, as grown (left), and re-crystallized after heat treatment process (right).

Figure 5 show SEM cross-section images comparing three different thin film solar cells. The first SEM image on the left is a CZTS thin film solar cell with the absorber deposited by reactive sputtering [36]. CZTS grains vary at the Mo/CZTS interface, and are large and columnar away from the interface. The middle SEM image is a CZTSe thin film solar cell with the absorber deposited by spin-coating [13]. CZTSe grains are not as large and densely packed, and have defects and voids, compared to the SEM image of a CdTe solar cell on the right, with large, densely packed CdTe grains, deposited by CSS.

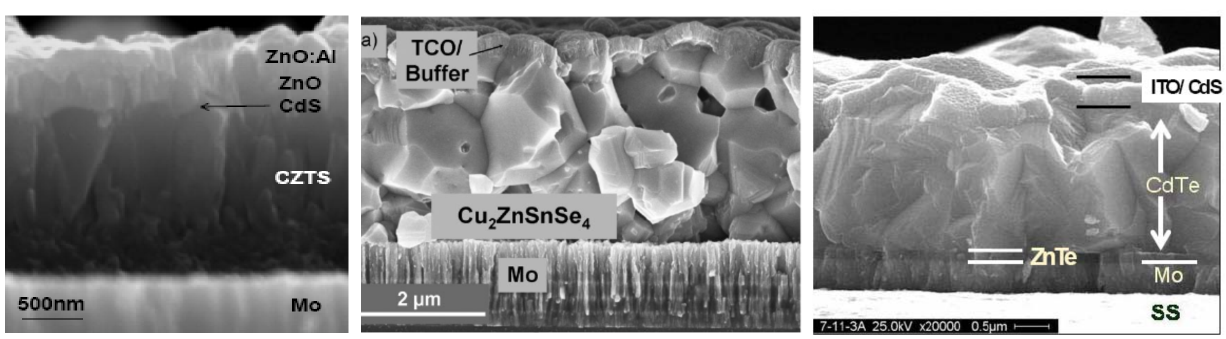


Figure 5. SEM images for CZTS by reactive sputtering (left), CZTSe by spin-coating (middle) and CdTe by CSS (right). Both CZTS and CZTSe thin film grains are not large and densely packed as the CdTe grains, and the middle CZTSe film has defects and voids which degrades solar cell performance.

Using the results from Task 1, "CZTS Composition Ratios, Stoichiometry and Film Preparation", a heat treatment process will be developed for complete conversion of all constituents of the spin-coated hybrid slurry films into a single-phase, highly crystalline, large-grained CZTS film. In order to optimize the CZTS thickness for maximum absorption, several CZTS thin films will be fabricated with thickness ranging from 1 to 6 microns. Films will be characterized by XRD and used in solar cell devices. Devices will be characterized by transmission data, light and dark J-V (current density-voltage) measurements, and spectral responses. Device parameters including open circuit voltage, short circuit current density, fill factor and efficiency will be reported.

2.3 CZTS Thin Film Adhesion and Stress Analysis

The adhesion of deposited films used in CZTS thin film solar cell devices must be excellent both as deposited, and after subsequent processing. Typically, for low values of adhesion, the electron shells of the adsorbed atoms remain intact, and these atoms are held to the surface by Van der Waals forces. These atoms are said to be physisorbed on the substrate. For high values of adhesion, sharing of electrons between the film and the substrate occurs, and the atoms are chemisorbed. Generally adhesion is greater the higher the absorption energy of the deposit and/or the higher the number of nucleation centers in the early growth stage of the film. Chemisorption due an intermediate-layer or "adhesion layer" formation that allows a continuous transition from one lattice to the other results in excellent adhesion. Adhesion is also improved if intermetallic metal alloys are formed. In addition, adhesion is strongly affected by the cleanliness of the substrate, and the surface roughness of the substrate. Substrate roughness strongly influences growth, crystal orientation and other properties of subsequent layers. Grain boundaries, defects, size, orientation and packing density directly impacts the overall solar cell device performance.

Stress in a thin film is generally not sufficient to result in delamination, unless the film is extremely thick. More often, high stress results in the cracking of films. Typically, a thin film or multi-layer material bonded to a substrate supports some state of residual stress, which has a direct dependence on the film thickness. This residual stress can trigger significant undesirable consequences, including excessive deformation, fracture, delamination, microstructural changes in the materials, and device failure. This stress may be compressive or tensile. Compressively stressed films tend to expand parallel to the substrate surface, and buckle up on the substrate. Tensile stressed films tend to contract parallel to the substrate surface, and crack if their elastic limits are exceeded. Highly stressed films tend to exhibit poor adhesion, and the resistivity of stressed metallic films is higher than that of their annealed counterparts. Growth or intrinsic stresses are dependent on the materials, substrate temperature, and growth flux and deposition process conditions.

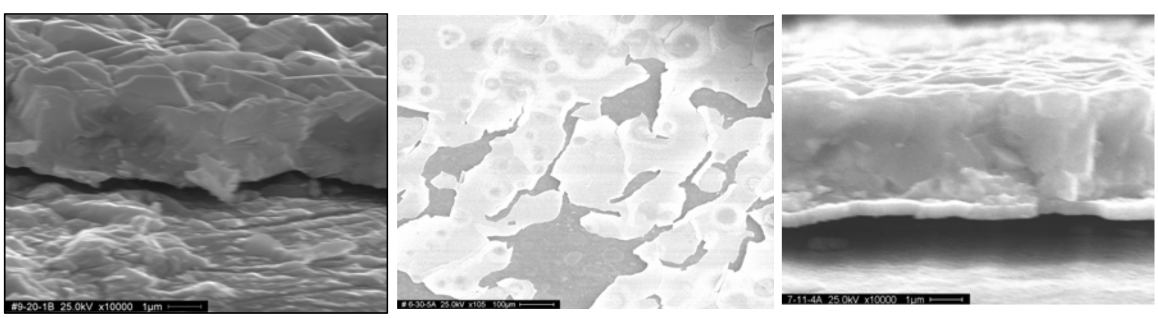
The development of intrinsic stress dependencies include the bonding of the deposit to the substrate, the mobility of adatoms on the film material itself, and the mobility of grain boundaries formed during growth. The final growth structure is typically metastable. Proposed mechanisms for stress generation during film material deposition include:

1. Surface and/or interface stress
2. Cluster coalescence to reduce surface area
3. Grain growth, or grain boundary area reduction
4. Vacancy annihilation
5. Grain boundary relaxation
6. Shrinkage of grain boundary voids
7. Incorporation of impurities
8. Phase transformations and precipitation
9. Moisture adsorption or desorption
10. Structural damage as result of sputtering or other energetic deposition process.

The coefficient of thermal expansion (CTE) of the substrate must lie in the range of the CTE of the CZTS solar cell thin film layers, otherwise adhesion problems can occur as a result of thermal expansion mismatch, as listed in Table 1 [41, 42]. The largest CTE mismatch exists between the substrate/back contact and between the back contact/absorber interfaces. Figure 6 illustrates the effects of stress in thin film CdTe solar cells fabricated on flexible stainless steel foil substrates. These effects include film delamination, flaking and debonding all as a result of stress, poor adhesion and CTE mismatch. Use of an intermediate adhesion layer with a similar CTE can promote adhesion.

Table 1. Thermal Expansion Properties

Sequence	**Function**	**Material**	**CTE ($x10^{-6}$/°K)**
5	Front Contact	Zinc Oxide (ZnO)	4.8
4	Window	Cadmium Sulfide (CdS)	7.0
3	Absorber	Cu_2ZnSnS_4 (CZTS)	8.2
2	Back Contact	Molybdenum (Mo)	5.1
1	Substrate	Soda Lime Glass (SLG)	9.0



(a) Delamination (b) Flaking (c) Debonding

Figure 6. Film (a) delamination, (b) flaking, and (c) debonding all as a result of stress, poor adhesion and CTE mismatch.

This research will perform CZTS thin film adhesion and stress analysis and employ techniques and mechanisms that alleviate stress, promote adhesion and improve the overall quality of the films.

2.4 CZTS Solar Cells and Device Fabrication

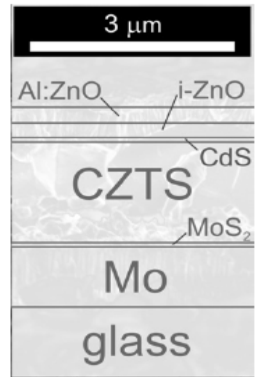


Figure 7. CZTS thin film solar cell basic device structure

The band gap of CZTS, ~1.5 eV is suitable for a single junction solar cell [43, 44]. CZTS films have shown p-type behavior, suggesting that there is an internal mechanism for generating acceptor states in the band gap. Charge carrier concentrations have been reported between $5x10^{15}$ and $6x10^{16}$ cm^{-3}, suitable for thin film devices [45-47]. As yet there is no consensus on the best way of preparing CZTS thin films [48]. The CZTS thin film solar cells in this project are of the substrate configuration. The basic device structure of the substrate cells proposed is: SLG/Mo/CZTS/CdS/ZnO/ZnO:Al shown if Figure 7 [48].

Different substrates have different influences on the film microstructure, growth of the layers, and the device characteristics. The substrate should withstand high temperatures experienced during the cell fabrication process. In addition, elemental impurities from the substrate must not diffuse into the layers of the solar cell device structure during high temperature processing. The substrate is a passive component in the device and is required to be mechanically stable, matching thermal expansion coefficient with deposited layers during the device fabrication.

The substrate selected for this project is Mo-coated SLG. Prior to solar cell fabrication, substrates will be cleaned by an ultrasonic solvent clean of three successive 30 minute rinses in acetone, methanol and deionised (DI) water. Substrates will be given a final rinse in DI water and dried with a nitrogen gas. The CZTS films prepared in Tasks 1 and 2 will be deposited by spin-coating onto the Mo-coated SLG substrates. Successive layers will be spin-coated at 800-1000 rpm until the desired thickness of 2-4 microns is achieved, and annealed at respective high temperature established in the prior tasks.

The primary function of a window layer in a heterojunction is to form a junction with the absorber layer while admitting a maximum amount of light to the junction region and absorber layer. For high optical throughput with minimal resistive loss the bandgap of the window layer should be as high as possible and as thin as possible to maintain low series resistance. The optical transmission, thickness and film resistivity can be optimized to improve the solar cell device output. CdS will be used as the window layer. Layers of *n*-conducting CdS are easily grown by various deposition methods including chemical bath deposition (CBD) as well as physical vapor deposition (PVD). CdS grows under most deposition conditions in a stable stoichiometric phase, α-CdS, which has the hexagonal wurtzite structure. Under high pressure growth conditions or in thin films, CdS may be found in the cubic, metastable zincblende structure. Thin layers of CdS films ranging from 0.1-0.3 microns will be deposited by CBD in this research project. In order to produce Cd-free CZTS thin film solar cells, other materials will be investigated for use as the window layer in this device structure.

A highly transparent and conducting oxide (TCO) front contact layer with an electron affinity below 4.5 eV is required to form an ohmic contact and a good band alignment with CdS. If the electron affinity of the TCO is higher than that of CdS, a blocking Schottky contact is formed.

Transparent conducting oxides in general are *n-type* semiconductors with good electrical conductivity and high transparency in the visible spectrum. A low resistance contact to the device and transmission of most of the incident light to the absorber layer is ensured. The conductivity of the TCO depends on the carrier concentration and mobility.

The most commonly used TCOs and window layers for thin film solar cells and their transmission spectra are shown in Figure 8. Intrinsic (high resistivity) TCO facilitates the use of a thinner CdS layer for reducing photon absorption losses for wavelengths smaller than 500 nm [49]. The use of a bi-layer transparent contact, one that consists of a low/high resistivity (ρ) stack of transparent films has been found to effectively minimize efficiency losses resulting from the use of thin CdS films [50, 51]. Table 2 lists typical values of resistivity and transmission in the visible region for various TCOs of interest for photovoltaic application [52, 53].

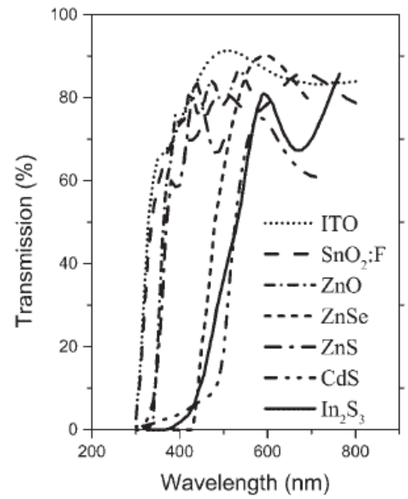


Figure 8. Optical transmission of different front contacts and window layers.

Table 2. Typical resistivity and transmission for various TCO and window materials investigated for thin film solar cells [52, 53].

Material	Resistivity (Ω cm)	Transparency (%)
SnO_2	8×10^{-4}	80
In_2O_3:Sn (ITO)	2×10^{-4}	>80
In_2O_3:Ga (IGO)	2×10^{-4}	85
In_2O_3:F	$2{\cdot}5 \times 10^{-4}$	85
Cd_2SnO_4 (CTO)	2×10^{-4}	85
Zn_2SnO_4 (ZTO)	10^{-2}	90
ZnO:In	8×10^{-4}	85

The baseline transparent front contact ZnO will be used in this research in the CZTS thin film solar cell. A ZnO/ZnO:Al bi-layer will also be used and evaluated in this research project. The thickness of the ZnO films will range from 0.2-0.3 microns. Films will be deposited the conventional sol-gel method.

The crystallinity of CZTS thin films will be analyzed with an X-ray diffractometer. Surface morphology and thickness will be investigated using a scanning electron microscope. The transmittance and reflectance of the thin films will be studied with an optical spectrometer. A solar simulator and four-point probe will be used for the determination of the conversion efficiency and current density-voltage (*J-V*) characteristics of illuminated CZTS solar cells to characterize the devices fabricated in this research.

The defined tasks timetable is provided below in Table 3. There will be several tasks performed in parallel due to the anticipated interdependence of the various cell components and processes. The ultimate objective is to optimize the performance of the CZTS thin film solar cell.

Table 3. Task Timetable

Task #	Task Description	Months
1	CZTS Composition Ratios, Stoichiometry and Film Preparation	9/11-2/13
2	CZTS Thin Film Grain Size and Thickness Profile	3/12-8/13
3	CZTS Thin Film Stress and Adhesion Analysis	3/12-2/13
4	CZTS Solar Cells and Device Fabrication	9/12-8/13

3. Impact on underrepresented groups

The proposed research and tasks will broaden the participation of underrepresented groups in engineering, including electrical, mechanical and chemical engineering disciplines. This unique interdisciplinary approach will provide outreach, opportunity, networking and interdisciplinary research to larger group of students by cutting across traditional boundaries between chemistry, physics and engineering. The students involved with this research will be educated in a culture that values interdisciplinary collaboration. Students from underrepresented groups, K-12 STEM fields and girls from “Introduce a Girl to Engineering” will have a unique opportunity will have the opportunity to be involved in the developing a solution to the issue related to providing energy to approximately ten billion people using a sustainable, alternative renewable energy technology. The technology addressed in this proposal will provide invaluable skills, experience, knowledge and insight into thin-film fabrication, materials characterization, stress and adhesion studies, and photovoltaics. In summary, the research described in this proposal brings together concepts from electrical engineering, chemistry, electronic materials, physics and mechanical engineering.

Past undergraduate research students trained in photovoltaics and thin-film CdTe solar cell fabrication and materials characterization by the PI:

3.1 Outreach and integration with education

Educational Synergies: Southern Polytechnic State University (SPSU) is a university within the University System of Georgia. SPSU offers bachelors and masters degrees in engineering technology, engineering, the sciences, the computing sciences, business, architecture, technical communication, social sciences, and several other related fields. SPSU offers seven degree programs in engineering (Civil Engineering, Construction Engineering, Electrical Engineering, Mechanical Engineering, Mechatronics Engineering, Software Engineering, and Systems Engineering), all at the B.S. level, with Software and Systems Engineering also at the masters level. It also offers six engineering technology programs (Civil Engineering Technology, Computer Engineering Technology, Electrical Engineering Technology, Industrial Engineering Technology, Mechanical Engineering Technology, and Telecommunications Engineering Technology), all at the B.S. level, with Electrical Engineering Technology also at the masters level.

New Course Development: The outcomes of this research will also be integrated into a new 3 credit-hour senior level course, "*Optoelectronics and Solar Cells". This course will be developed during the course of the proposed project. By disseminating the research results of this project into the classroom, students from a broad cross-section of disciplinary interests will benefit. Pre-requisites will include Circuit Analysis I, Semiconductor Devices, Engineering Materials, Physics I and Chemistry I. "*Optoelectronics and Solar Cells"* will include solar cell simulation software and assignments, intended to familiarize students with design principles and industry standardized software. The course will also be project-based. A final term-project and presentation will be required and tied to real-world photovoltaics, and provide the opportunity to provide design solutions and simulated results.

Minority Outreach: The 2009 edition of *Profiles of Engineering and Engineering Technology Colleges*, published by the American Society for Engineering Education, ranked SPSU as #1 in the number of African-American male students receiving engineering technology degrees, #4 in the number of engineering technology bachelor's degrees awarded, #2 in the number of students enrolled in engineering technology programs, and #7 in the number of engineering technology degrees awarded to women. SPSU has been one of the largest partners in **PSLSAMP,** the Peach State Alliance of the NSF Louis Stokes Award for Minority Participation, from 2005-present. With over 91 scholarships to minority STEM participants during the first year of this project. SPSU hosted the first Annual Fall Forum, opened a PSLAMP office on campus, and has expanded outreach tutoring/mentoring programs within the Marietta City and Cobb County School Districts for middle school students. Scholarship students are required to maintain a 2.75^{+} GPA to continue to qualify for this program. PSLSAMP participants have an 80% retention rate, well above the institutional average.

The synergy with the research outcomes of training grants also facilitates participation by underrepresented groups, such as PSLSAMP. Successful mentoring of these students is evident from the fact of their 80% retention rate. These activities will be further enhanced through this proposal. Undergraduate students appointed to this research project will work in collaboration with some PSLSAMP students, and research activities will be used to enhance recruitment initiatives. In previous work, the PI has worked with the Florida-Georgia Louis Stokes Alliance for Minority Participation (**FGLSAMP**) and is committed in continuing that work with the proposed research project.

K-12 STEM and Solar Cell Education: This research will be integrated into the outreach and educational activities beyond the training of undergraduate students. The PI has been engaged in developing early awareness outreach programs to stimulate interest in Science and Engineering, Alternative Renewable Energy and Solar Cells. The PI's past and planned outreach activities involvements include the following components:

- Introduce A Girl to Engineering
- Girl Scout Engineering Expositions
- K-12 STEM Middle and High School Outreach Activities
- High School Robotics Competitions
- Recruitment Activities at Regional Events

Past K-12 STEM and Introduce-A-Girl to Engineering community outreach activities with PI initiation and involvement:

3.2 The university and researchers

As part of a $100 million dollar expansion, SPSU's new Engineering Technology Center, a $38 million dollar facility, opened in January 2011. The Center will house the Electrical and Computer Engineering Technology and Mechanical Engineering Technology departments, as well as the Division of Engineering. SPSU is proud to be Georgia's technology university. Our academic, professional, outreach and service programs embrace all aspects of technology, including the practical applied skills needed to solve today's real-world problems and the theoretical knowledge necessary to meet tomorrow's challenges. SPSU graduates are well prepared to lead the scientific and economic development of an increasingly complex state, nation and world. The 2009 edition of *Profiles of Engineering and Engineering Technology*

Colleges, published by the American Society for Engineering Education, ranked SPSU as #1 in the number of African-American male students receiving engineering technology degrees, #4 in the number of engineering technology bachelor's degrees awarded, #2 in the number of students enrolled in engineering technology programs, and #7 in the number of engineering technology degrees awarded to women.

SPSU mission is to serve both traditional and non-traditional students at the undergraduate, graduate and continuing education levels; in engineering and engineering technology, the sciences, applied liberal arts, business and professional programs. We work to develop the broader community's intellectual, cultural, economic and human resources. Facilitated by our innovative faculty, dedicated staff, and supportive campus environment, or learning community empowers SPSU students with the ability and vision to transform the future. SPSU is a non-Ph.D.-granting institution that serves a large number of students from underrepresented groups in engineering. More than one third of the students are non-Caucasian. The university also has a large number of first-generation and non-traditional students, with an average undergraduate age of 25.3 years. Many students work full-time while attending school.

The PI has significant contact with the students as an assistant professor, an advisor, and an instructor of a requisite engineering courses required by all engineering majors. As the only female and African-American faculty member in the EE department, she serves as a mentor to many of the female and underrepresented groups of students in the program. The PI is committed to working with underrepresented groups and females at the university. This includes continued work with them as researchers in this research project.

4. Dissemination of research results

The main aim of this proposal is to develop a liquid-based process for the deposition of low-cost non-toxic materials necessary to fabricate a CZTS thin-film solar cell. Once this is accomplished, the intent is to design a pilot pre-production type of deposition system (not under this project) that can be presented to companies interested in pursuing this technology. As university researchers, our main objectives are to advance the state of understanding and performance, to build collaborations with researchers in the field, and to disseminate the results through publications, communications, media, peer networking and conferences. The PI has already begun developing a network with photovoltaic researchers from the University of South Florida, the Department of Energy's National Renewable Energy Laboratory, the University of Toledo and Georgia Tech. The PI has already orally presented at the Materials Research Society conference in San Francisco, CA and given a poster presentation at the 34th IEEE Photovoltaic Specialists conference in Philadelphia, PA. This grant will fund the attendance at the annual IEEE PV Specialists conferences. This will give the research team the opportunity to share their early results and be evaluated by researchers in the field. In addition to publishing the research in solar energy and materials science journals, the PI plan to pursue patents under this project as novel methods and processes are identified and developed. The university will pursue licensees for its intellectual property.

5. Conclusions

The driving force for the recent and ongoing technological development is the realization that the traditional fossil energy resources, coal, oil and gas, are not only limited, but are harmful to the environment through the emission of carbon dioxide. The use of alternate green resources, such as sunlight offers a favorable and promising alternative to the worldwide energy problems. Photovoltaics have experienced extraordinary growth during the last few years with overall growth rates between 30% and 40%. The PV market is dominated by crystalline silicon solar modules which require thicknesses of approximately 200-300 μm and high energy intensive processes. Expensive materials and processes, limit the potential for future long term cost reductions. Thin film polycrystalline low cost alternatives to silicon have emerged. In contrast, Cu_2ZnSnS_4 (CZTS) is a semiconductor material consisting of abundant, low-cost, non-toxic elements. CZTS is one of the most promising absorber layer materials for low-cost thin-film solar cells providing both an economical and green solution to the current thin-film technologies. This research will focus on the fundamental development of CZTS thin films and solar cells by non-vacuum, liquid-based techniques.

This research will be a critical step toward the PI's long-term research goals of contributing to our nation's photovoltaics growth rate, reducing the need for fossil fuels and developing a model for a cost effective "solar farm" that can used by local communities, universities and individual homeowners. The proposed "solar farm" is a small footprint power plant of solar panels that would allow users to become less-dependent on the grid and to generate power, and sale power back to the local power companies, thereby, becoming self-sustaining and revenue generating simultaneously.

This work will contribute to the recruitment and retention of engineers from underrepresented groups. The host university is a non-Ph.D. granting institution that serves a large number of students from underrepresented groups. The PI is committed to incorporating these students into the research and the results of the research into a proposed new course that will be developed. The proposed research and tasks will broaden the participation of underrepresented groups in engineering. The PI has experience in training and developing undergraduate research students and in K-12 STEM and 'Introduce-A-Girl to Engineering" community outreach activities.

The PI is well qualified to perform this proposed research, having been mentored and trained by a researcher who has set a world record in thin-film photovoltaics. Through previous research in this area, the PI has developed significant depth of knowledge of thin-film photovoltaics materials fabrication and characterization. Additionally, the PI has existing relationships and intends to develop new relationships and collaborations with researchers. The results of this research will be broadly disseminated to other researchers and the photovoltaics industry.

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