Investigating the effect of Sodium and Potassium on the formation of Copper Zinc Tin Sulfide Films

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INTRODUCTION

As of 2008, global energy consumption reached 15 TW and is expected to double by the year 2050 [1]. Over 80% of this energy is produced from carbon based fossil fuels, including coal, petroleum, and natural gas, which are non-renewable and are largely responsible for the release of anthropogenic carbon dioxide, which is recognized as a leading factor in global climate change [2]. One prospective renewable source of electricity lies in solar cells, which directly convert sunlight into electricity. Despite its enormous potential, solar power currently provides less than 0.1% of the world's energy demand [3]. The major impedance to large scale deployment of solar cells lies in the capital cost. The most commonly used commercial solar cells are made using thick, highly pure layers of silicon which require expensive high temperature processing. One possible alternative to silicon solar cells are thin film solar cells. These solar devices utilize materials that absorb more sunlight than Si, and therefore require thinner absorber layers. Currently there are two commercially available types of thin film solar cells, one utilizes cadmium telluride (CdTe) as an absorber and the other copper indium gallium diselenide (CIGS). Power conversion efficiencies of up to 20 % have been attained using CIGS in the lab and CdTe is relatively easy to make on a large scale [4]. Unfortunately, these layers have constituent elements that are toxic (Cd), rare within the earth's crust (Te), or expensive (In) [5,6]. In order for large scale

solar deployment to be feasible it is necessary to find a solar cell design that incorporates the use of thin layers of benign and abundant elements.

One semiconductor Cu_2ZnSnS_4 (CZTS) meets all of these criteria. CZTS, which is highly absorbing, is made entirely of nontoxic earth abundant elements. Over a relatively short period of time, CZTS solar cells have already reached conversion efficiencies of over 12 % [7]. This is particularly impressive as the solar cell geometry was adopted from CIGS and has not been optimized for CZTS. Limiting the advancement of CZTS performance, however, is the significant knowledge gap between processing conditions and CZTS material properties.

One area of CZTS processing that warrants closer examination is the effect of the substrate that CZTS is grown on. The best performing CZTS devices were all grown on Mo coated soda lime glass (SLG). Like most glass, SLG is primarily silicon dioxide, but it also contains several impurities such as Na, K, and Ca to aid in processing. In fact, SLG is 9% Na on an atomic basis according to an elemental analysis conducted using inductively coupled plasma mass spectrometry (ICP-MS). Results of this analysis can be found in Table 1. The choice of SLG as a substrate is a holdover from CIGS devices where it has been shown that Na diffusion from the SLG into the CIGS drastically improves solar cell performance as well as increases grain size. In previous experiments, larger grains of pure CZTS have been formed on SLG substrates as opposed to quartz, which contains no impurities, and Pyrex, which contains significantly lower levels of impurities [8]. However, it was shown that similar grain sizes to those on SLG could be attained by including a piece of uncoated SLG alongside a precursor film deposited on quartz or Pyrex. It was experimentally shown

that the Na, K, and Ca present in the SLG volatilize and are incorporated into the adjacent film, thus promoting grain growth [8]. This is thought to be beneficial as increasing the grain size of CZTS decreases the grain boundary concentration and may potentially boost the carrier mobility. Based on these results, it was of interest to test exactly which impurities in SLG are responsible for the enhanced grain growth and to determine in what amounts they should be added during film synthesis to achieve a large grain size without the formation of secondary phases or voids. Specifically, optimal impurity concentrations and addition methods are desired for films on a variety of substrates including SiO_2 based substrates like quartz as well as Mo coated substrates and Mo foils which may be used as back contacts in solar cell devices.

Table 1 – Elemental analysis of SLG results.

Element	Al	Ca	Mg	Na	Si	O
Atomic % in SLG	0.25	4.36	3.41	9.00	23.40	59.50

EXPERIMENTAL

CZTS films were synthesized by the *ex situ* sulfidation method, which involves reacting a metallic precursor film in a S atmosphere at elevated temperatures. The precursor films were co-sputtered from Cu/Zn (35 at% Cu) and Cu/Sn (60 at% Cu) targets at 10 mTorr using Ar as the working gas with a chamber base pressure of $2x10^{-7}$ Torr. The precursor films were deposited on a variety of substrates, including SLG, quartz, and Mo foil. Following deposition, the precursor films were placed into quartz tubes alongside 1 mg of solid S. The tube walls were coated with various amounts KOH, NaOH, or $Ca(OH)_2$. Coating was done by making aqueous solutions of known molarity of KOH, NaOH, and $Ca(OH)_2$ made from solid KOH and $Ca(OH)_2$ or a 50 wt% NaOH in water solution, which were micropipetted into the bottom the tubes in

0.1 ml quantities. The water was removed by drying the tubes vertically in a convection oven overnight at 100 ^{0}C which left a radially uniform hydroxide coating on the bottom portion of the tube. After adding the precursor film and S into the tube, the tubes were pumped to a base pressure of 10^{-6} Torr and flame sealed. The sealed ampoules were loaded into a box furnace and heated at a rate of 6.5 ^{0}C/min to 600 ^{0}C. The precursor films were sulfidized isothermally at 600 ^{0}C for 8 hours. At this elevated temperature, S, Ca, K, and Na can be volatilized and incorporated into the CZTS film. Following sulfidation, the films were allowed to cool to room temperature naturally. The ampoules were broken open to remove the precursor films which were characterized using X-ray diffraction (XRD), confocal Raman scattering microscopy, scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS). XRD patterns were collected using a Bruker D8 Discover system equipped with a Cu $K\alpha$ X-ray source, 0.5 mm beam collimator, and a Bruker Hi-Star two-dimensional X-ray detector. Raman spectra were collected at room temperature using a WiTec alpha 300R confocal Raman microscope equipped with a UHTS300 spectrometer and a DV401 CCD detector. An Omnichrome Ar ion laser (514.5 nm, ~300 nm beam spot size) was used to illuminate films for collecting Raman spectra. Raman scattering was collected in a backscattering geometry and dispersed with an 1800 lines/mm grating resulting in a spectral resolution of 0.02 cm^{-1}. A JOEL 6500 SEM equipped with a Thermo-Noran Vantage EDS detector was used to examine the morphologies and elemental compositions of sulfidized films. The electron energy was set at 15 keV both for imaging and EDS measurements. At this energy, the EDS probe depth is estimated to be near 2 μm. This ensures that the entire depth of the sulfidized films was examined. The average

gran size of the CZTS films was determined from SEM images by averaging the sizes of at least 100 grains along randomly chosen lines for each film.

RESULTS AND DISCUSSION

Initial experiments tested the effects of K, Na, and Ca individually on the size of CZTS grains, the main results of which are shown in Figure 1. The amounts of impurities used were varied over several orders of magnitude. Specifically, amounts between 95 μmol and 0.006 μmol of NaOH, 50 μmol and 0.003 μmol of KOH, and 50 μmol and 0.04 μmol of $Ca(OH)_2$ were tested. After sulfidizing the precursor films deposited on impurity free quartz, larger grains were observed in ampoules loaded with KOH or NaOH (Figure 1(c) and (d)). In fact grain sizes as large (1.4 μm) as the CZTS synthesized on SLG (Figure 1(b)) were achieved. The addition of Ca proved to have no effect on the grain size of the film (Figure 1(e)) and the film appeared similar to the film synthesized on quartz without added impurities (Figure 1(a)). This conclusively showed that the Na and K found in SLG are responsible for the enhancement in grain size. Based on these results, only the NaOH and KOH delivery processes were optimized.
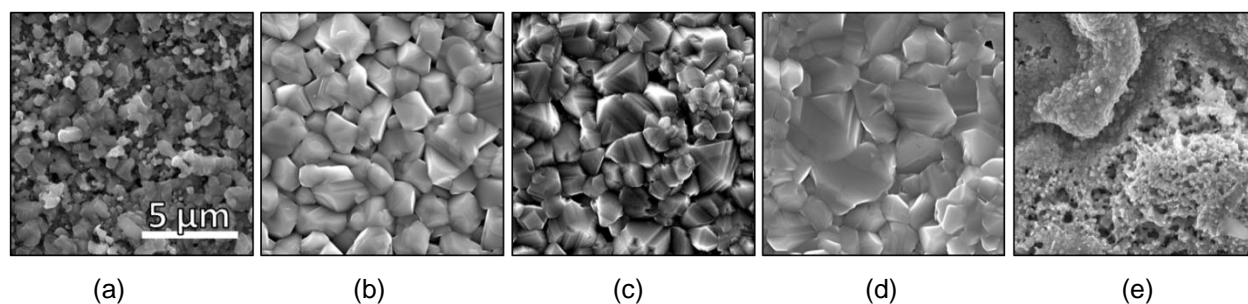

(a) (b) (c) (d) (e)

Figure 1 – SEM images of CZTS films synthesized on (a) quartz, (b) SLG, (c) quartz with added NaOH, (d) quartz with added KOH, and (e) quartz with added $Ca(OH)_2$. Same scale bar applies for all images.

While testing the wide ranges of NaOH and KOH additions, it was determined that grain size varied with the amount of impurity that was coated onto the tube walls.

When too little was included in the ampule, minimal grain growth occurred while adding too much KOH or NaOH caused grain sizes to become so large that the CZTS layer became discontinuous and secondary phases containing either Na or K to appear. Figure 2 shows a film with grains that are on the order of 2 μm across and areas of exposed substrate (dark areas in between grains). To form a continuous film, the lateral grain size should not exceed the film thickness, which is between 1 and 2 μm. In completed solar cells a discontinuous or impure CZTS layer would result in poor performance as it could lead to shorting or recombination centers. To ensure a the formation of continuous films while varying grain size, the amount of NaOH and KOH added to the ampoule were swept carefully. The results of such a sweep for NaOH are shown in Figure 3 which shows the incremental increase in the average grain size as the amount of NaOH added to the ampoule is increased in increments of 0.5×10^{-7} mol. Such a technique allows for an increase in grain size while stopping grain growth before the formation of voids between the grains begins.
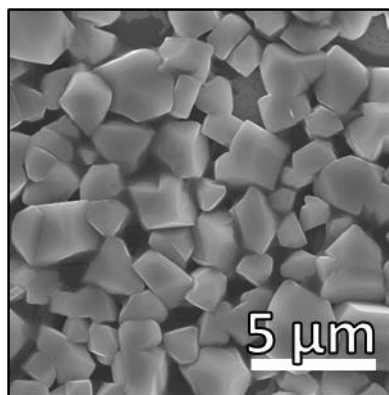

Figure 2 – SEM image of a discontinuous CZTS film. Dark areas between light grains are areas of uncovered substrate.
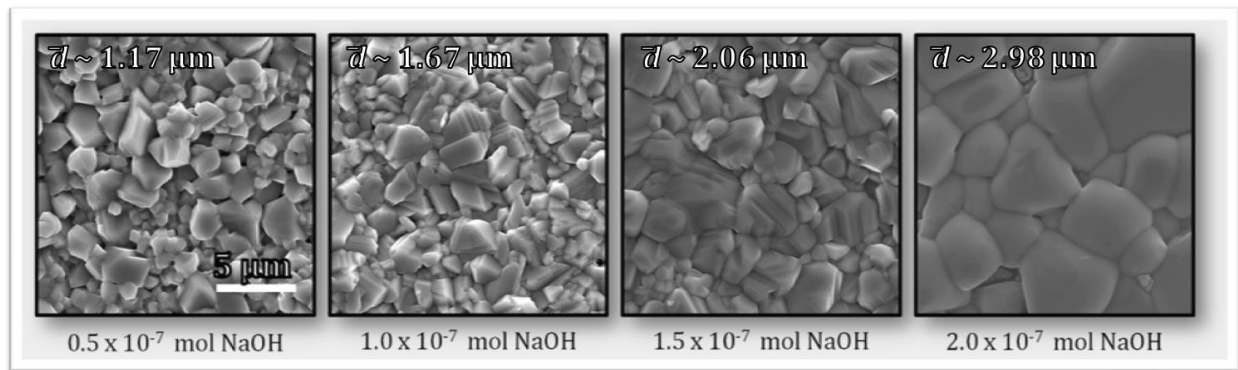
Figure 3 – SEM images of films made with between 0.5 and 2 x10^{-7} mol NaOH coated on the annealing tube. The average grain size of the film is indicated within each image. The scale bar applies to all images.

Interestingly, it was found that different substrates required different amounts of NaOH or KOH to achieve similar grain sizes. This is shown in Figure 4 which compares samples prepared on sapphire (a) and Mo foil (b) with an identical amount of NaOH added to the ampoule. While the film on Mo foil is continuous, the film on sapphire is not, indicating an excess of NaOH. It is hypothesized that this occurs due to Na diffusion into the Mo layer, inhibiting the Na from promoting CZTS grain growth.
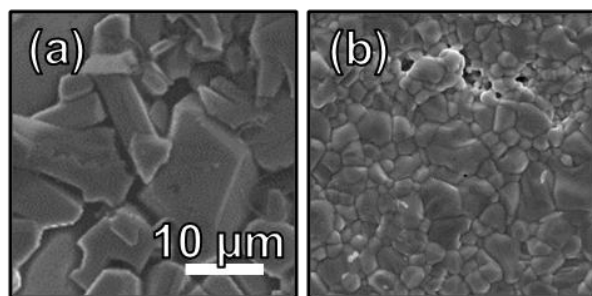

Figure 4 – SEM images of CZTS films grown on sapphire (a) and Mo foil (b) with 2.0 x 10^{-7} mol of NaOH.

The lateral size of the CZTS films examined was approximately 0.5 cm x 0.5 cm. In order to make solar cell devices, the area of these films must be increased. This means that the method for delivering NaOH and KOH must be modified. Since impurity

solution volumes added to sulfidation tubes were limited to 2 ml to allow ampoules to dry within a day, only the bottom 1-2 cm of the tube wall was coated with NaOH or KOH. When larger precursor films with lengths that exceeded the coated area on the tube wall were sulfidized, a gradient in grain size was observed. A diagram of the relationship between the large precursor and the area of dried KOH or NaOH can be found in Figure 5. Grain growth was more extensive on the portion of the film that was within the coated portion of the ampoule, while the grain size gradually decreased towards the end that was not within the coated portion of the ampoule. This gradient is shown in Figure 6 which contrasts SEM images on several points along a sulfidized film. The contrast in grain size can be seen most easily between images (a) and (c) which were on opposite ends of the film and show average grain sizes of 3 µm and 0.5 µm respectively. To address this problem and make a more uniform film, a known amount of NaOH or KOH solution was micropipeted onto a quartz strip longer than the precursor film. Care was taken to ensure the solution covered the entire surface of the strip. The solution was dried onto the strip using a hot plate creating an even coating of NaOH or KOH. Instead of coating the tube walls with hydroxide, this strip was included inside the tube. The strip was situated such that it was below the precursor with the precursor film being wide enough to be supported by the tube walls and not the strip. A diagram showing the relationship between the precursor and the glass strip is shown in Figure 7. This technique was effective in eliminating grain size gradients as can be seen in Figure 8, which shows SEM images of several points along the length of a long CZTS film sulfidized with a glass strip at similar points to Figure 6. No significant grain size gradient can be seen in this film.
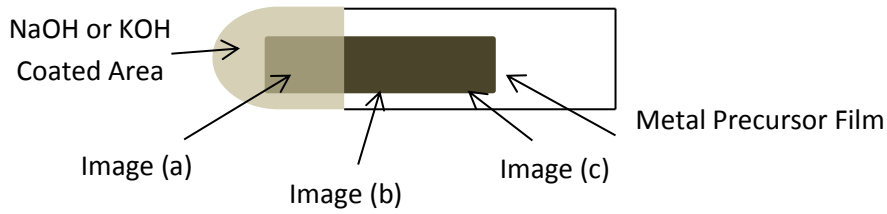
NaOH or KOH
Coated Area

Image (a)

Image (b)

Image (c)

Metal Precursor Film

Figure 5 – Diagram of a long precursor film in relation to the area of the ampoule coated with NaOH or KOH. Locations of each area imaged in Figure 6 on the precursor film are indicated. The hydroxide coating is radially uniform.
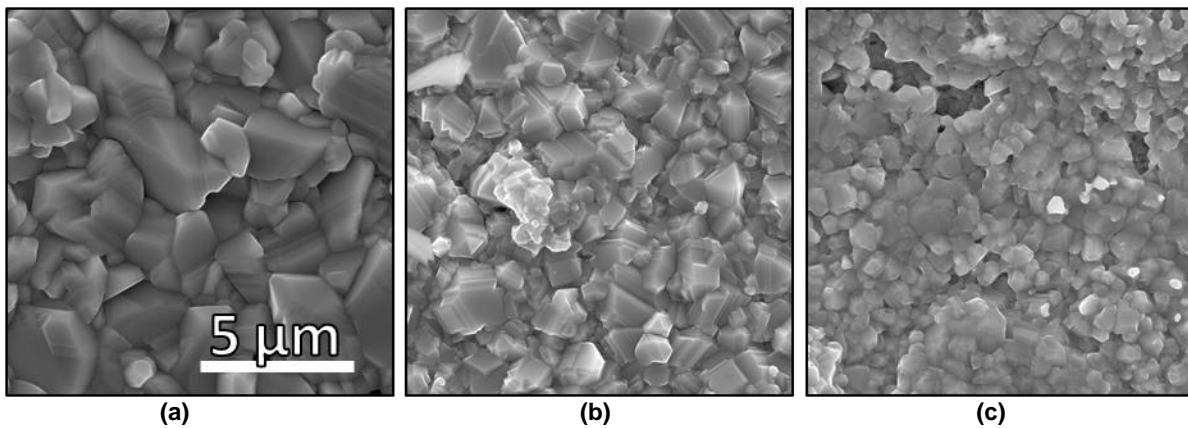

5 μm

(a)   **(b)**   **(c)**

Figure 6 – SEM images of one precursor film sulfidized (a) near the added NaOH, (b) in the middle of the ampoule, and (c) the opposite end of the ampoule from the added NaOH. Locations are depicted in Figure 5. Scale bar applies to all images.
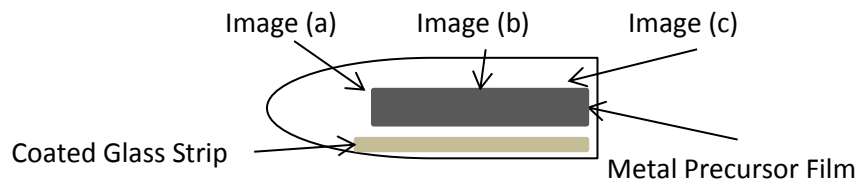

Image (a)   Image (b)   Image (c)

Coated Glass Strip

Metal Precursor Film

Figure 7 – Diagram of a long precursor film in relation to a hydroxide coated glass strip. Locations of each area imaged in Figure 8 on the precursor film are indicated.
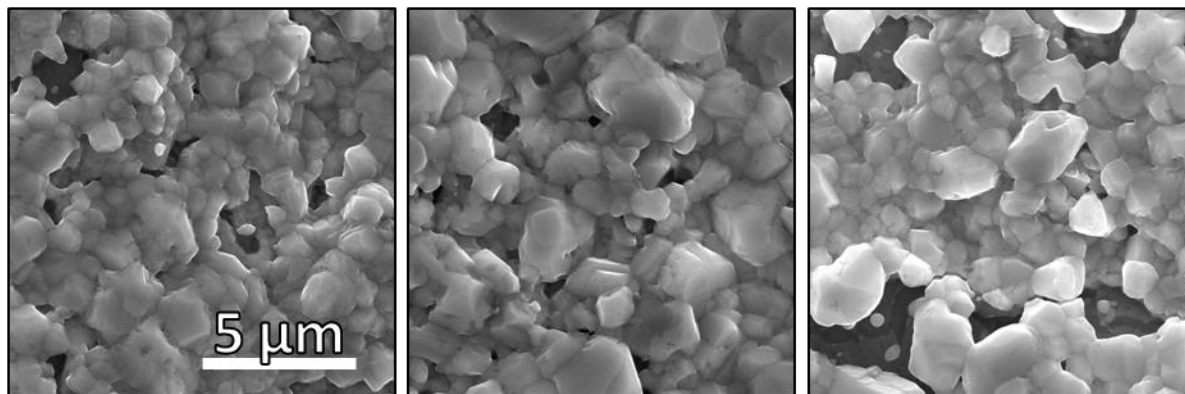
(a)   **(b)**   **(c)**

Figure 6 – SEM images of a CZTS film sulfidized at the points indicated in Figure 7 along with a glass strip loaded with NaOH. Scale bar applies to all images.

CONCLUSIONS

The effects of Ca, K, and Na on the grain size of CZTS films produced by sulfidizing Cu-Zn-Sn precursor films were investigated. A method of coating the sulfidation ampoule with solutions of NaOH, KOH, and $Ca(OH)_2$ was first developed to provide controlled amounts of each element. It was found that both K and Na caused increases in the average CZTS grain size while Ca had no beneficial effects. At high loads of Na and K, the CZTS grains reached sizes on the order of 10 µm and Na and K impurity phases formed. This resulted in discontinuous films unsuitable for solar cell production. Experiments determined the optimal amounts of NaOH and KOH respectively needed to make films with large grains that were free of voids on quartz substrates. Additional NaOH and KOH were required for substrates containing Mo which we believe may be due diffusion of Na and K into the Mo layer. If the precursor was too long, such that the precursor length exceeded the length of the hydroxide coating, grain size gradients were observed. A method was also developed to provide Na and K to longer precursors in a way that did not produce grain size gradients. This was done by coating long glass strips with hydroxide solution instead of the ampoule

walls. These methods for manipulating the physical characteristics of CZTS films will be valuable in the future processing of CZTS based solar cells. Future experiments must be conducted to optimize sulfidation conditions for Mo containing substrates which will be used for constructing solar cell. Of particular interest are the effect of sulfidation time on Na diffusion and the formation of MoS_2. Solar cell devices must also be constructed to determine ranges of Na and K that give optimal electronic performance.

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