

A CHEMICAL BATH PROCESS FOR DEPOSITING $\text{Cu}_2\text{ZnSnS}_4$ PHOTOVOLTAIC ABSORBERS

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ABSTRACT

Thin films of $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) were fabricated through a combination of chemical bath deposition, ion exchange and sulfurization heat treatment. Scanning electron microscopy was used to study the morphology of the thin films, Auger electron spectroscopy for compositional analysis, X-ray diffraction and Raman scattering for structural characterization, and diffuse reflectance UV-Vis measurements for optical properties. With the method described, compositionally uniform microcrystalline CZTS with kesterite structure and a bandgap of 1.45 eV have been produced, and a preliminary solar cell device was fabricated to demonstrate that this material is applicable in earth-abundant, non-toxic thin film photovoltaics.

INTRODUCTION

Crystalline silicon solar cells—comprising over 90% of photovoltaics produced today—are relatively efficient, but remain expensive due to requirements of high crystallinity and thickness. Inorganic thin films, which circumvent these requirements, are therefore an attractive technology for achieving large-scale deployment of inexpensive, stable, and efficient photovoltaics. However, current leading thin-film materials, such as CdTe and CIGS, face production limitations at a global scale as they contain both non-abundant and toxic elements [1]. A material that has gained significant attention is $\text{Cu}_2\text{ZnSnS}_4$ (CZTS), which is not constrained by the drawbacks of CdTe and CIGS and has an ideal bandgap of 1.4-1.5 eV [2].

Several groups have studied the fabrication of CZTS solar cells using a variety of methods ranging from sol-gel processing to sputter deposition [3-7]. Most recently, Todorov *et al.* reported a record 9.6% efficiency for a $\text{Cu}_2\text{ZnSn}(\text{Se},\text{S})_4$ device fabricated by a hydrazine-slurry method in an inert atmosphere, demonstrating the potential of CZTS and similar kesterite materials as efficient photovoltaic absorbers [8].

In the present work, we report an alternative method for large area deposition of CZTS thin films that is potentially high throughput and inexpensive when used to produce monolithically integrated solar panel modules. Specifically, we have developed an aqueous chemical approach based on chemical bath deposition (CBD) [9] of chalcogenide thin films and ion

exchange [10], with a subsequent sulfurization heat treatment. CBD has been previously demonstrated to have high materials utilization [11].

Samples produced by our method were analyzed by scanning electron microscopy (SEM), Auger electron spectroscopy (AES), X-ray diffraction (XRD), Raman spectroscopy, and diffuse reflectance UV-vis spectroscopy. The results show that this inexpensive and relatively benign process produces thin films of CZTS exhibiting uniform composition, kesterite crystal structure, and good optical properties. A preliminary solar cell device was fabricated to demonstrate rectifying and photovoltaic behavior.

EXPERIMENTAL

The chemical bath processes were carried out in a fume hood. SnS_x was grown at room temperature on glass, Si and Mo-coated substrates after the method of Nair *et al.* [12]. The substrates were first cleaned using acetone, ethanol, and deionized water and then mounted in the CBD bath (see Fig. 1).

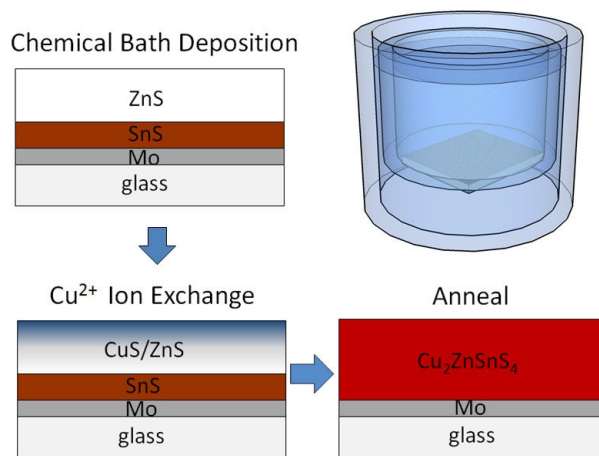


Figure 1. Chemical bath process steps and substrate mounting scheme for depositing CZTS.

ZnS was next grown in the manner of Cheng *et al.* [13]. After immersing the substrates, the bath was maintained for 1 hour at 70°C using a silicone oil bath. This process was repeated twice to obtain a sufficiently thick ZnS

layer of approximately 400 nm. Cu was next incorporated into the bath-deposited films via ion exchange [14-16]. The SnS/ZnS-coated substrates were immersed in an aqueous Cu^{2+} (0.1 M) bath for 1 min.

The precursor stacks were next sulfurized at 500 °C for 2 hours to form the desired $\text{Cu}_2\text{ZnSnS}_4$ phase. Using a custom-built reactor, a gas delivery system generated H_2S *in situ* through the decomposition of thioacetamide [17] and delivered it to the sample in the tube furnace. In this way we generate on demand the minimum amount of H_2S necessary. A complete device was fabricated with the addition of KCN treatment, CBD-deposited CdS, sputtered ZnO and Al:ZnO, and a screen printed Ag grid.

RESULTS AND DISCUSSIONS

An AES depth profile of the film after sulfurization indicate that the Cu, Sn, and Zn interdiffuse and the composition becomes uniform throughout (see Fig. 2). There is no significant presence of MoS₂ or O, an element which is present before sulfurization and difficult to avoid in aqueous processes.

The film is Zn rich, which may be beneficial to photovoltaic CZTS thin films. For instance, Katagiri *et al.* have empirically found that Zn-rich films achieve superior photovoltaic performance [18], and a recent theoretical study by Chen *et al.* concluded that Zn-rich films are beneficial for the defect properties of photovoltaic CZTS [19].

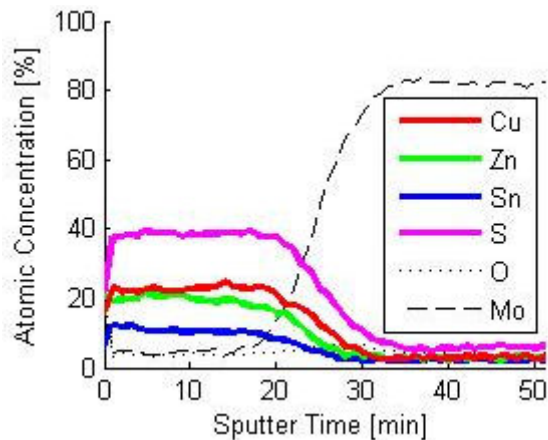


Figure 2. AES depth profile of the sulfurized precursor film exhibiting uniform composition and the absence of O.

XRD analysis of a sulfurized Cu-Sn-Zn precursor film on Si (see Fig. 3) indicates major $\text{Cu}_2\text{ZnSnS}_4$ peaks at (112), (200), (220) and (312) [20]. No evidence of crystalline SnS, SnS_2 , or Cu_2S was observed in the diffraction pattern. However, because the XRD spectra of CZTS and β -ZnS are similar for visible peaks and the angle differences too small to distinguish within

instrument accuracy, the existence of CZTS was further investigated by Raman spectroscopy (data not shown), as performed previously by Fernandes *et al.* for sputtered samples [21].

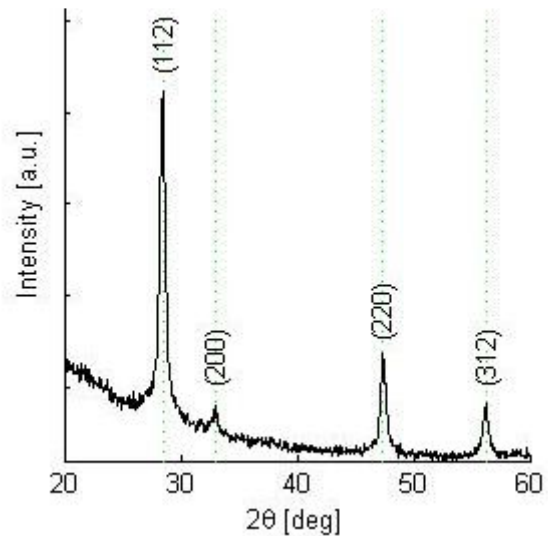


Figure 3. XRD spectrum of the sulfurized precursor film containing the major CZTS peaks.

The major Raman peaks are well defined, suggesting that the sulfurized Cu-Sn-Zn precursor film has good CZTS kesterite structure. A secondary phase of β -ZnS may be present, though the Raman data indicate minimal contribution of that phase if any. A very weak Cu_{2-x}S peak is also present in the spectrum, which may be eliminated through a KCN treatment [22].

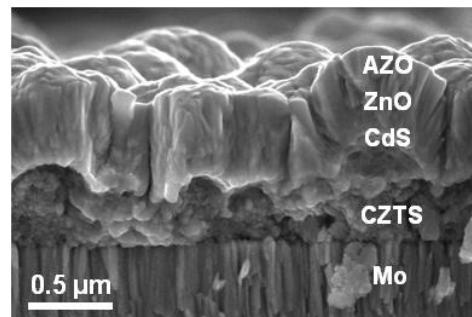


Figure 4. SEM cross section of CZTS device

In order to obtain the bandgap of CZTS produced by our method, we performed diffuse reflectance UV-vis measurements and obtained a bandgap of 1.45 eV, agreeing well with other CZTS studies [7,23,24].

A complete solar cell device was fabricated (see Fig. 4) and tested under one sun illumination to demonstrate photovoltaic and rectifying behavior (see Fig. 5). The

device achieved 210 mV open circuit voltage, 2.4 mA/cm² short circuit current, and 0.16 % efficiency.

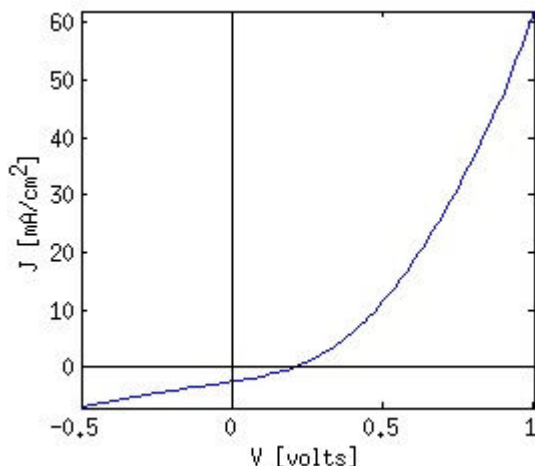


Figure 5. Device current-voltage curve under AM 1.5G illumination demonstrating rectifying and photovoltaic behavior.

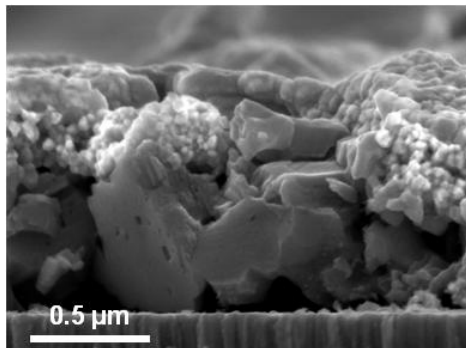


Figure 6. A chalcogenide thin film deposited by the chemical bath process and sulfurized.

Factors contributing to the low device performance most likely include extremely small grains, an insufficiently thick absorber layer, and the absence of an anti-reflective coating. We believe that most of these issues can be addressed given further research, as our most recent studies show that chalcogenide polycrystalline thin films with larger grains can be produced by this method (see Fig. 6).

CONCLUSION

This work demonstrates that CZTS thin-film photovoltaic absorber layers can be produced through a water-based method. The four elements of interest were incorporated through chemical bath deposition, ion exchange and sulfurization. The method is not only conducive to large area production but also avoids the use of complicated equipment. Also notable are the relatively benign

processes and materials required. In particular, we generate on demand the minimum amount of H₂S necessary and do not use toxic solvents. Given that Cd-free, thin-film buffer layers can be deposited by CBD [24] and that new transparent conductors deposited by solution have been reported [25,26], the method presented here can be integrated into a largely solution process for an inorganic photovoltaic device of earth-abundant and non-toxic materials. The chemical bath technique can also be tailored to produce materials of various optical and electronic properties. For instance, a process could be designed for Cu₂ZnSn(Se,S)₄, since CBD of ZnSe and CuSe have been established [27].

ACKNOWLEDGEMENT

We thank Justin Opatkiewicz for help with Raman spectroscopy and Dan Chawla for assistance with XRD. The Global Climate and Energy Project is gratefully acknowledged for initial funding of this research. Studies were carried out as part of the Center on Nanostructuring for Efficient Energy Conversion, an EFRC funded by the U.S. Department of Energy, Office of Basic Energy Sciences under Award Number DE-SC0001060. AW received supported under National Science Foundation Grant CBET 0930098.

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