Materials for CZTS Photovoltaic Devices

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Abstract and Introduction:

Thin film solar cells made of copper indium gallium selenide ($CuIn_{1-x}Ga_xSe_2$ or CIGS) combined with cadmium sulfide (CdS) to form a *pn* heterojunction are nearing the commercial production stage. However, indium and selenium are rare, and cadmium is toxic, so CIGS solar cells are not a good option for large scale energy production. Copper zinc tin sulfide (Cu_2ZnSnS_4 or CZTS) is modeled after CIGS, but uses abundant, environmentally friendly materials. CdS, which forms the heterojunction with CZTS, must be replaced with zinc sulfide (ZnS). Zinc is also useful in the compound CdZnS in CIGS solar cells to tune the band gap. In the first half of this project, deposition of ZnS and CdZnS was explored. ZnS deposition on glass slides looks promising and merits further investigation. CdZnS deposition on molybdenum coated glass slides was unsuccessful as x-ray diffraction (XRD) and energy-dispersive x-ray spectroscopy (EDX) revealed no Zn was present in the film. In the second part of this project, a method for depositing CZTS was developed. Zinc, copper and tin were deposited using thermal evaporation on molybdenum coated quartz slides. The CZT stack was annealed with sulfur powder in a Petri® dish. The CZTS films were analyzed using XRD and scanning electron microscopy (SEM).

Methods and Results:

Cadmium and zinc sulfide films were deposited using chemical bath deposition. CdS films are easily deposited in a chemical bath consisting of deionized water (DI water), $CdSO_4$, thiourea, and NH_4OH at temperatures between 50°C and 90°C in under an hour. Replacing some or all of the $CdSO_4$ in the CdS bath with $ZnSO_4$ did not lead to ZnS or CdZnS deposition. O'Brien and McAleese [1] suggest adding hydrazine, triethanolamine, or ethanolamine to promote ZnS deposition. ZnS films were deposited on scratched glass slides using the bath described above, with the addition of triethanolamine at 70°C for 1.5 to 4.5 hours. The transmission measurements are shown in Figure 1. It was found that a deposition time of at least 2.5 hours was needed for an appreciable film thickness.

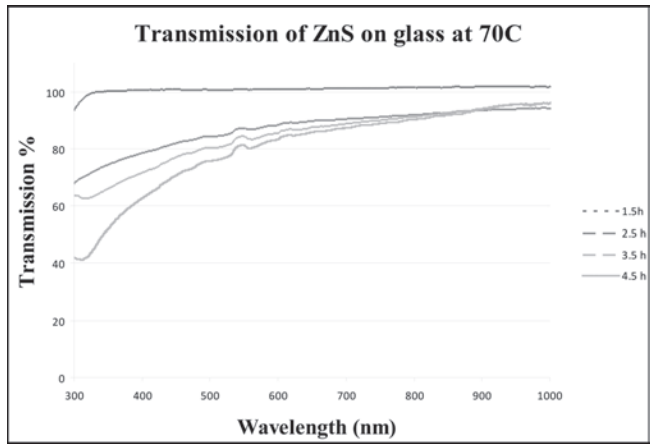

Figure 1: Transmission through ZnS deposition on glass slides.

Next, the deposition of CdZnS was attempted using the bath composition described above for ZnS. The ratio of 3:7 for Cd:Zn was chosen because Dona and Herrero [2] determined that ratio yields the highest stability CdZnS compound. Deposition was first done on scratched glass slides, then on molybdenum coated glass slides. The transmission measurements on the glass slides suggested some Zn may have deposited, but XRD and EDX on the molybdenum coated slides showed the film contained only CdS.

CZTS films were deposited on quartz slides coated with molybdenum, using e-beam evaporation or sputtering. Sputtered films were found to be better quality than e-beam evaporated films. Layers of zinc, copper, and tin were deposited using thermal evaporation. The order Zn/Cu/Sn was used because Araki et al. [3] showed it produced the most efficient solar cell. Ratios of Cu/(Zn+Sn) between 0.85 and 0.96 and Zn/Sn between 1.05 and 1.3 were used.

The CZT stack was placed in a fused silica Petri® dish with sulfur powder and annealed at 560°C, so the film was exposed to a sulfur vapor environment. Previously, the annealing step had been done in an atmosphere of hydrogen

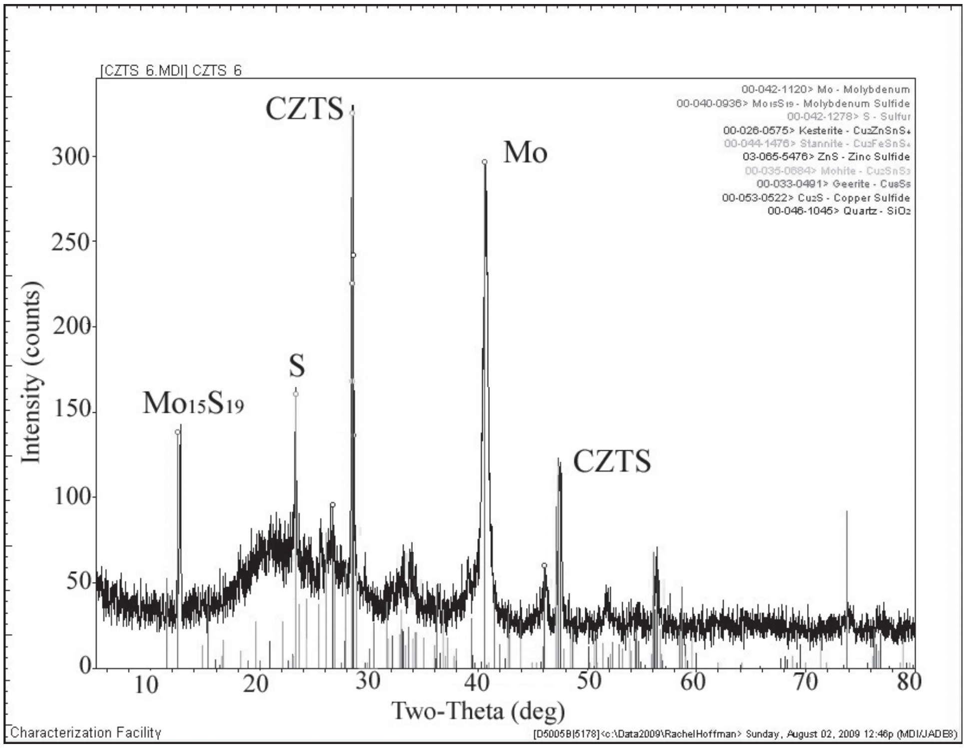

Figure 2: XRD: 30 mg sulfur anneal CZTS peaks show stannite structure so S was incorporated. The existence of S and MoS peaks suggest too much sulfur was added.

sulfide and nitrogen gases, but this project elected to use the sulfur powder method because of the toxicity of H_2S. Sulfur amounts between 4 mg and 20 mg were tested. XRD of the resulting films showed remaining copper and zinc suggesting that sulfur was not being incorporated into the film. SEM images showed that the crystalline CZTS structure was not obtained.

A weight, of approximately 470g, was obtained to hold down the lid of the Petri dish so that the increasing pressure from the evaporating sulfur would not lift the lid, allowing the sulfur vapor to escape. The amount of sulfur added was increased to 30 mg, resulting in higher CZTS peaks. XRD of this film is shown in Figure 2. Part of the CZTS film was scratched off after deposition to obtain a molybdenum contact.

Complete solar cells are formed by depositing CdS in a chemical bath followed by sputtering zinc oxide and aluminum doped zinc oxide.

Conclusions and Future Work:

Zinc sulfide deposition on glass slides looks promising and merits further investigation. Deposition on molybdenum coated slides will allow verification that it is ZnS, and then deposition on CZTS films can be attempted. The addition of a weight during the sulfur anneal step led to CZTS formation. This process will be used to characterize CZTS films and relate deposition parameters to solar cell efficiencies.

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References:

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