Spray Pyrolysis of $CuInSe_2$ for Thin Film Photovoltaic Solar Cells

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Abstract/ Introduction:

With the increasing costs of traditional sources of energy, and depleting resources, photovoltaic energy is becoming a feasible energy alternative. Copper indium diselenide ($CuInSe_2$) cells may provide a cost effective way to produce electricity as their efficiencies are increased. The focus of this project was to grow $CuInSe_2$ cells by spray pyrolysis using a solution of copper chloride, indium chloride, and dimethylselenide, onto soda-lime glass coated with molybdenum (Mo). After deposition of $CuInSe_2$, cadmium sulfide (CdS) was deposited by chemical bath deposition. This arrangement of cells is called "tandem," or stacked, which also decreases costs and space. Molybdenum acts a back contact and it was deposited by evaporation or sputtering. The deposition rate was determined to be 50 Å/ min for sputtering, and the rate for evaporation depended on filament current. The $CuInSe_2$ serves as the light absorbing layer, and was grown at 250-350ºC in a chamber where the pressure was kept at atmosphere or slightly above atmospheric pressure. Electron dispersive spectroscopy (EDS) confirmed the presence of copper, indium, and selenium. The CdS acted as a window layer, and was deposited in a chemical bath of thiourea, cadmium chloride, and ammonium hydroxide at 70ºC. Spectrophotometer measurements of the CdS layer determined the band gap to be 2.1eV, which is slightly lower than the 2.30-2.60eV range reported in the literature. Discrepancies could be attributed to the non-uniform surface.

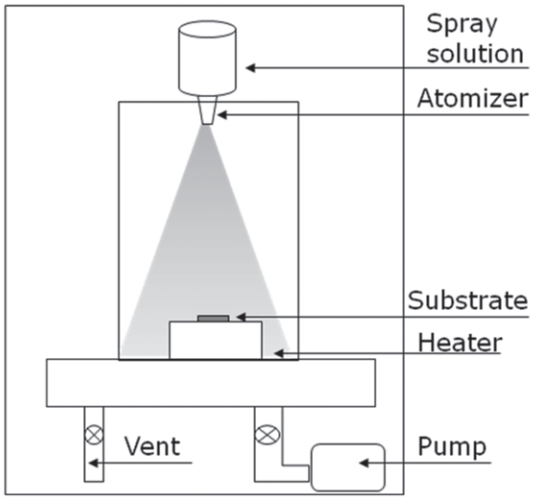

Figure 1: Schematic drawing of spray pyrolysis system.

Experimental Procedure:

The molybdenum (Mo) layer was deposited on a clean soda-lime glass slide by electron beam evaporation or by sputtering using a Mo target. Mo sputter rates were determined by surface profilometry measurements [1]. The $CuInSe_2$ layer was deposited onto a Mo-coated substrate by spray pyrolysis (see Figure 1). Initial stock solutions of copper chloride ($CuCl_2$) and indium chloride ($InCl_3$) had to be made. A vial of 5 grams of $CuCl_2$ was dissolved in 1.48 L of de-ionized water for a 2.5×10^{-2} M solution. A vial of 5 grams of $InCl_3$ was dissolved in 362 mL of 0.1 M HCl to form a 6.25×10^{-2} M solution. The dimethylselenide (DMS) was mixed fresh before each run and was mixed in 0.1 M to 0.165 M solutions, then left to dissolve for 2 hours, shielded from light. Two drops of hydrochloric acid were added to the selenium solution after dissolving. In the final solution, 4.5 mL of $CuCl_2$, 2.0 mL of $InCl_3$, 2.5 mL of DMS, 48.2 mL of ethanol, and 198.2 mL of deionized water were used.

Growth temperatures were kept between 250-350°C, and growth lasted between 1-2 hours. Modifications to this procedure included doubling concentrations of $CuCl_2$, $InCl_3$, and selenium, pH adjustments using acid/base to a value of pH = 3, and slower spray rates. The conditions for $CuInSe_2$ growth are tabulated in Table 1 [2].

The cadmium sulfide layer was deposited by chemical bath deposition. Initial stock solutions of thiourea, cadmium chloride, and ammonium hydroxide were made. Given a 10 gram vial of thiourea, 96 mL of de-ionized water was used to make a 50 mM solution. Given a 5-gram vial of cadmium chloride, 92 mL of de-ionized water was used to make a 10 mM solution. Ammonium hydroxide was added in a 14.8 M solution, and 278.2 mL of de-ionized water was added to dilute it to 1 M. The deposition process started with 92 mL of cadmium chloride added to 33.78 mL of ammonium hydroxide. The solution was heated to 70°C in a water bath. Next, 96 mL of thiourea was added. The acid/base levels were adjusted to maintain a pH of 11. A clean glass substrate was

	Substrate	Concentrations (20% ethanol in DI water)	Temp./Atomizer and Chamber Pressure	Results
1	Molybdenum on glass slide	$CuCl_2$ $4.5x10^{-4}$M $InCl_3$ $5.0x10^{-4}$M DMSeU $1.65x10^{-3}$M	340ºC 60 psi/ 0.5 psi	No traces of copper, indium, or selenium
2	Molybdenum on half of a soda-lime glass		290ºC 60 psi/ 0.4 psi	Traces of indium
3	Molybdenum on soda-lime glass		340ºC 35 psi/ 0.5 psi	No traces of copper, indium, or selenium
4	Molybdenum on soda-lime glass	$CuCl_2$ $9x10^{-4}$M $InCl_3$ $10x10^{-4}$M DMSeU $3.33x10^{-3}$M PH adjustment with NaOH and HCl.	330ºC 35 psi/ 0.3 psi	Traces of copper, indium, and selenium
5	Molybdenum on soda-lime glass		210ºC 35 psi/ 0 psi	Traces of copper, indium, and selenium
6	Molybdenum on half of a soda-lime glass		240ºC 35 psi/ 0 psi	No growth
7	Molybdenum on soda-lime glass.		392ºC 35 psi/ 0 psi	Traces of copper, indium, and selenium
8	Molybdenum on soda-lime glass. (evaporated)		Temp. not measured 35 psi/ 0 psi	More uniform traces of copper, indium, and selenium

Table 1: Spray pyrolysis growth conditions for $CuInSe_2$.

lowered into the solution and left for 45 minutes. Modifications to this procedure included reducing the solution concentration by 40%, and using a magnetic stirrer [3].

Results and Conclusions:

The sputter rate for Mo was found to be approximately 50 Å/ min after measurements with a profilometer. Electron dispersion spectroscopy performed on the initial samples showed no traces of copper, indium, or selenium, but after the modifications were made, all the elements were present as seen in Figure 2 in a good ratio. To confirm that cadmium sulfide was deposited, spectrophotometer measurements were taken to obtain an absorbance vs. wavelength graph, as seen in Figure 3. The wavelength axis was converted into energy to reveal a bandgap of 2.1eV, which is very similar to literature values of 2.3-2.6eV. Ellipsometry readings of the surface revealed a CdS layer thickness of approximately 100 nm.

Future Work:

In the future, layer uniformity would have to be improved so that all the layers can be stacked. With the stacked cell, tests for efficiency could be made. Gallium could also be added to form copper indium gallium diselenide, which should also improve efficiencies.

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[1] Albin, D.; Ballard, B.; Duda, A; Predecki, P; Scofield,J; "Sputtered Molybdenum Bilayer Back Contact for Copper Indium Diselenide-Based Polycrystalline Thin-Film Solar Cells"; 1-5 (1994).

[2] Varner, E; "Factors Influencing the Performance of Copper Indium Diselenide/ Cadmium Sulfide Solar Cells Made by Chemical Spray Pyrolysis"; 45-54 (1996).

[3] Hodes, G; "Chemical Solution Deposition of Semiconductor Films"; 50-55 (2003).

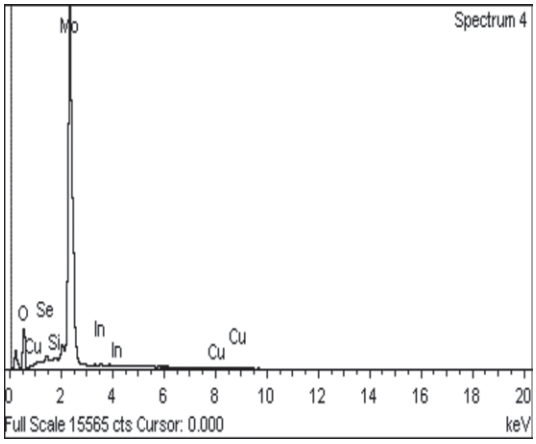

Figure 2: EDS results from the $CuInSe_2$ layer.

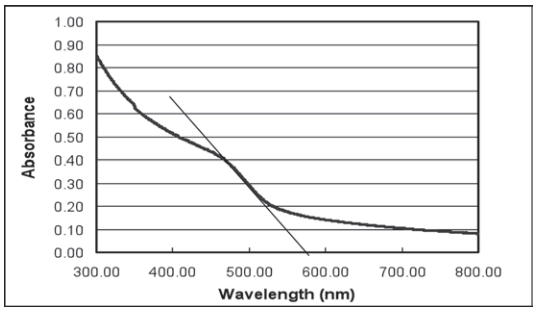

Figure 3: Spectrophotometer results of cadmium sulfide layer.