

Growth of CuIn(Ga)Se_2 Thin Film Solar Cells

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Abstract and Introduction:

Copper indium diselenide (CuInSe_2) and copper indium gallium diselenide (CuInGaSe_2) thin film solar cells deposited by spray pyrolysis are a low cost way to provide solar energy. Although they are relatively cheap to fabricate, they suffer from low efficiencies because of their small grain sizes. In this work, we investigated the conditions of growth rate and temperature in order to obtain stoichiometric layers of these materials. We also investigated the conditions necessary to grow cadmium sulfide (CdS) by chemical bath deposition, which was used as the n-type window layer for our solar cell structure. Employing cadmium sulfide also increased the photovoltaic solar efficiency of our tandem structure.

CuInSe_2 and CuInGaSe_2 films were grown on soda lime glass substrates coated with 150 nm of evaporated molybdenum at 350-400°C for 30-60 minutes. Energy dispersive spectroscopy (EDS) data for CuInSe_2 indicated the presence of all three elements. Cadmium sulfide (CdS) films were grown in a bath of cadmium chloride (CdCl_2), thiourea and aqueous ammonia at 70°C with a pH of 11. EDS on cadmium sulfide indicated the presence of both elements in equal abundance.

Scanning electron microscopy (SEM) and optical microscopy indicated uniform deposition of CdS and CuInGaSe_2 films but non-uniform films for copper indium diselenide.

Experimental Procedure:

Before deposition on the surface of the soda lime glass substrate, the glass was cleaned thoroughly. The glass was first put in a bath with soap and water followed by a 10 minutes acetone rinse and then a 5 minute methanol rinse. The glass was then cleaned in a 30% hydrochloric acid bath for about 30 minutes, and finally, in aqua regia [1].

The back contact layer, molybdenum (Mo), was deposited on soda lime glass by a technique called electron-beam evaporation. The thickness of the layer was set to 150 nm. The CuInSe_2 layer was deposited on the Mo-coated soda lime glass by spray pyrolysis as seen in Figure 1. The thickness of this layer had to be between 1000-2000 nm in order to make the solar cell work efficiently. Initial stock solutions of copper chloride (CuCl_2) and indium chloride (InCl_3) were prepared. The concentrations of the solutions were 25 mM for CuCl_2 and 62.5 mM for InCl_3 . The dimethylselenide (DMS_{eu}) had

to be mixed two hours before each run and kept away from the light for about two hours until it was ready to be mixed. The concentration that was used was 165 mM [2]. To grow CuInGaSe_2 , gallium was incorporated in the form of gallium trichloride (GaCl_3). The concentration of indium and gallium was 62.5 mM in order to adjust the total concentration to 125 mM, which was double the original concentration that was used.

The growth temperature was kept between 350-400°C. The growth lasted between 30-60 minutes depending on spray rates, with 45 minutes being optimum. The spray rate was kept low to facilitate pyrolysis. In order to improve surface adhesion during pyrolysis, some glass surfaces were roughened with sand paper. The conditions for CuInSe_2 and CuInGaSe_2 growth can be seen in Table 1.

The CdS layer was deposited by chemical bath deposition and was the n-type contact for the cell. Initial stock solution of thiourea, CdCl_2 , and ammonium hydroxide (NH_4OH) were made with solution concentrations of 10 mM for CdCl_2 , 50 mM for thiourea and 1 M for NH_4OH . At first NH_4OH and CdCl_2 were mixed and heated in a water bath until the temperature reached 70°C. Thiourea was added to the bath and the pH was adjusted to 11 with 20% potassium hydroxide (KOH) and the substrate was then quickly immersed. The deposition time was 30 minutes [3].

Results and Conclusion:

The CuInSe_2 and CdS layers were deposited more uniformly when the concentrations of the solutions were doubled. EDS data for CdS indicated the presence of both elements as seen in Figure 2. The rate of deposition for the CdS layer was approximately 3 nm/min which produced an 80 nm thick layer. EDS on CuInGaSe_2 indicated the presence of all four elements as seen in Figure 3. When the concentration of Ga and In were split in half, we had a more uniform layer with the

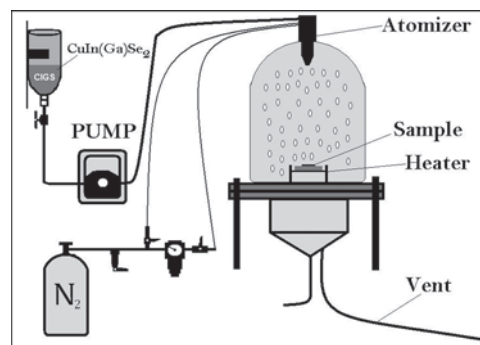


Figure 1: Spray pyrolysis system.

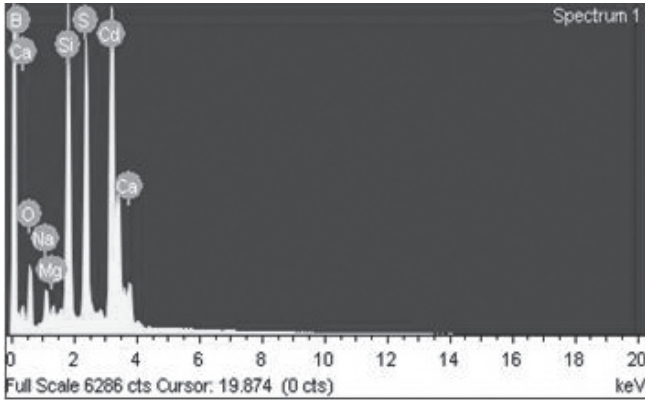


Figure 2: EDS data of CdS layer.

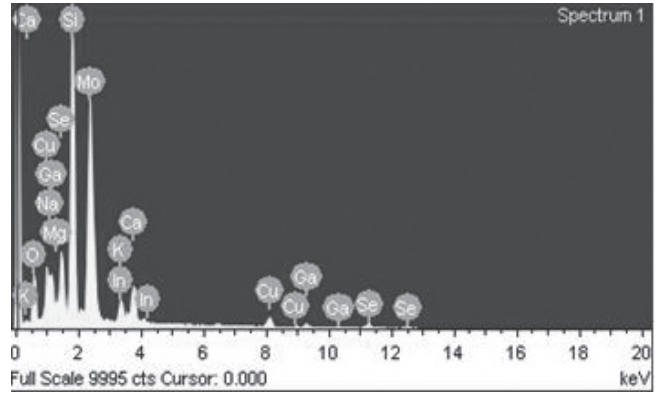


Figure 3 : EDS data of CIGS layer.

presence of all elements. We also had a better deposition rate when we roughened the surface of our sample. Uniform films of CdS were routinely obtained by chemical bath. Uniform films were more difficult to obtain by spray pyrolysis. Slower spray rates in general produced better films. CIGS films also appeared more uniform than CIS films.

Future Work:

Steps need to be taken to increase the growth rate for all layers. Efforts should also be undertaken to determine what parameters affect layer uniformity. Grain sizes need to be determined to see if they can be increase by rapid thermal annealing at high temperatures. Finally, solar cells should be fabricated so efficiency measurements can be performed.

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References:

- [1] Bachman, Mark. AMPEL Nanofabrication Facility. Fall 1999. 2 August 2009 <Mark Bachman>.
- [2] Varner, E; "Factors Influencing the Performance of Copper Indium Diselenide/ Cadmium Sulfide Solar Cells Made by Chemical Spray Pyrolysis";45-54(1996).
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Experiment	Substrate	Concentration	Temp	Atomizer	Chamber Pressure	Flow Rate	Time	Special Presidure	Results
1	soda lime glass	2.5x10 ⁻² M CuCl ₂ 6.25x10 ⁻² M InCl ₃ 0.165M dimethylselenide	275C-350°C	5psi	40-60psi	High	1 hour	Roughened surface Cleaned with H ₂ SO ₄ , HNO ₃ , DI Water	Some traces of selenium
2	70nm of Moly on soda lime glass	2.5x10 ⁻² M CuCl ₂ 6.25x10 ⁻² M InCl ₃ 0.165M dimethylselenide	300-350°C	5psi	40-60psi	constant	1 hour	Roughened glass Used a 4 step cleaning bath	Cu, In, Se present but in different areas so non-uniform
3	70nm of Moly on soda lime glass	2.5x10 ⁻² M CuCl ₂ 6.25x10 ⁻² M InCl ₃ 0.165M dimethylselenide	350-400°C	10psi	50psi	Low	1 hour	Smooth surface Used a 4 step cleaning bath	Cu,In,Se present (non-uniform)
4	70nm of Moly on soda lime glass	2.5x10 ⁻² M CuCl ₂ 6.25x10 ⁻² M InCl ₃ 0.165M dimethylselenide	350-400°C	10 psi	59 psi	constant	55 min	Used a 4 step cleaning bath	Cu,In,Se present (non-uniform)
5	70nm of Moly on soda lime glass	2.5x10 ⁻² M CuCl ₂ 6.25x10 ⁻² M InCl ₃ 0.165M dimethylselenide	300-350°C	10psi	60psi	High	20 min	High spray rate Used a 4 step cleaning bath	Some traces of copper and selenium, no indium
6	cadmium sulfide on soda lime glass	5x10 ⁻² M CuCl ₂ 12.5x10 ⁻² M InCl ₃ 0.330M dimethylselenide	350-400°C	5psi	59psi	constant	35 min	Doubled concentration and cadmium sulfide substrate Used a 4 step cleaning bath	Se, Cd and S present. Some traces of copper, no traces of Indium
7	85nm of Moly on soda lime glass + a top layer of cadmium sulfide	5x10 ⁻² M CuCl ₂ 12.5x10 ⁻² M InCl ₃ 0.330M dimethylselenide	300-400°C	5 psi	59psi	constant	45 min	85 nm of Molybdenum and doubled concentration Used a 4 step cleaning bath	Layer came off because of molybdenum some traces of selenium, cadmium and sulfur
8	150nm of Moly on soda lime glass	12.5x10 ⁻² M CuCl ₂ 6.25x10 ⁻² M InCl ₃ 6.25x10 ⁻² M GaCl ₃ 0.330M dimethylselenide	350-400°C	5psi	59psi	constant	1 hour	Added gallium chloride to make it a CuInGaSe ₂ cell Used a 4 step cleaning bath	Uniform layer of Cu,In,Ga,Se

Table 1: Spray pyrolysis growth conditions for CuInSe₂ and CuInGaSe₂.