UNIVERSITY OF CENTRAL FLORIDA

Development of High Throughput CIGS Manufacturing Process

PI: Neelkanth Dhere
Students: Sachin Kulkarni, Ph.D.; Ph.D.; Ashwani Kaul, Ph.D.

Description: A reduction in the cost of CIGS and other thin PV film modules is required for broad PV applications. The objective is to develop a high-rate deposition process for synthesis of CIGS absorbers and other layers by employing in-line and batch deposition techniques. The goal is finally to attract a PV manufacturing company to Florida by developing a high-rate manufacturing process for CuIn$_x$Ga$_{1-x}$Se$_2$ (CIGS) solar cells.

Budget: $151,611
Universities: UCF/FSEC

Progress Summary

It is essential to develop a process that has high yield and low production cost in order to initiate a high volume manufacture of thin film PV technology. A versatile methodology was adopted in order to improve and optimize the deposition parameters for each of the layers for preparation of CuInxGa1-xSe2 (CIGS) thin film solar cell. The initial effort were directed towards increasing the deposition rates of metallic precursors deposited by DC magnetron sputtering and the rate was increased to ~7.5 Å/sec which is significant for laboratory level. Further increment in the deposition rate was achieved by changing the working distance between the metallic targets and the substrate. Reducing the working distance from 90 mm to 70 mm further increased the deposition rate to 11.4 Å/sec, which is an increase by 1.5 times. In an industrial set up, there is possibility for further improvements in the deposition rates with efficient cooling mechanism for the metal targets. The cost of production can also be reduced by reducing the total material utilization without adversely affecting the device performance. Experimentation focused on the reduction of the absorber layer thickness in the range of ~1 µm to ~1.5 µm has been discussed in the prior reports.

Optimization of silicon nitride barrier layer was also carried out to minimize the sodium out-diffusion from the sodalime glass substrate. The optimum thickness of silicon nitride barrier layer determined empirically was 800 Å. Efforts were focused on optimizing the parameters for molybdenum back contact. Molybdenum back contact in CuIn1-xGaxSe2 (CIGS) solar cells is usually deposited with DC magnetron sputtering. Properties of thin films are dependent on process conditions. Films deposited at high power and low pressure, tend to be more conductive. However, such films exhibit poor adhesional strength since the films are under compressive stress. Films deposited at low power and high pressure tend to be under tensile stress and exhibit higher roughness and resistivity, while the films adhere very well to the sodalime glass substrate. Therefore, it has been a practice to deposit multi-layered Mo back contact to achieve properties of good adhesion and higher conductivity. Deposition of multi-layered back contact results in either increase in deposition time if a single target is used or increase in foot print if multiple targets are used resulting in increase in the total cost of production. Hence experiments were carried out to understand effects of working pressure, sputtering power and working distance on molybdenum film properties with the final aim to develop a process recipe for deposition of a single molybdenum film with acceptable properties of both good adhesion and higher conductivity. Adhesive tape test was performed on each film to determine the adhesional strength of the films. Moreover, the sheet resistance and the average roughness for each film were measured using a four probe measurement setup and the Dektak Profilometer, respectively. Resistivity was found to be dependent on working gas pressure. All experiments were also carried out on narrow and long glass strips in order to estimate the residual stress in the film by using the bend test method. It was found that the residual stress is strongly influenced by the kinetic energy of the incident sputtered atoms and the backscattered argon atoms which in turn is determined by the sputtering power and working gas pressure. Electron back scattered diffraction (EBSD) has also been introduced in this work for characterization of CIGS solar cells.

Part of the work carried out during this period has not been mentioned herein because a patent is being filed, which, therefore, restricts and further discussion on this matter in open literature.

2010 Annual Report

For the development of a high-rate manufacturing process for $CuIn_xGa_{1-x}Se_2$ (CIGS) solar cells it is essential that all the processes involved in preparation of the device be optimized in terms of the deposition rate as well as yield of each process. Moreover, it is important to consider the uniformity of each process in terms of performance when deposited over large areas. Therefore, systematic and simultaneous experiments are being carried out on various layers of the CIGS solar cell device. Efforts were taken to increase the deposition rate of the metallic precursors, to develop single layered molybdenum back contact, to reduce the absorber thickness, to develop and optimize a silicon nitride barrier layer and to develop mechanical and laser scribing techniques.

Deposition Rates for Metallic Precursors:

DC magnetron sputtering is used for deposition of metallic precursors from Cu-Ga alloy and In target. In case of sputtering the deposition rate changes with the changes in sputtering power and pressure and the working distance between the metallic target and the substrate. However, the deposition rate versus sputtering power and pressure follows a U shaped curve and therefore, it is essential to optimize the sputtering power and pressure in order to get the highest possible deposition rates for a given system. In the previous experiments, the sputtering power employed for the Cu-Ga target was varied while keeping the sputtering pressure constant at 1.5 mT. The sputtering power was varied from 200 W to 350 W and the thickness calibration was carried out using a Dektak Profilometer. Realizing the possibility of being able to reduce the working distance, experiments were carried out to determine the effect of reducing the working distance on the deposition rates. It was observed that the deposition rate increased linearly with increase in the sputtering power for each set of working distance. Figure 1 shows the variation of deposition rate at a given working distance with respect to the sputtering power and Table I shows the total thickness deposited for each sputtering power and the total time taken for deposition.

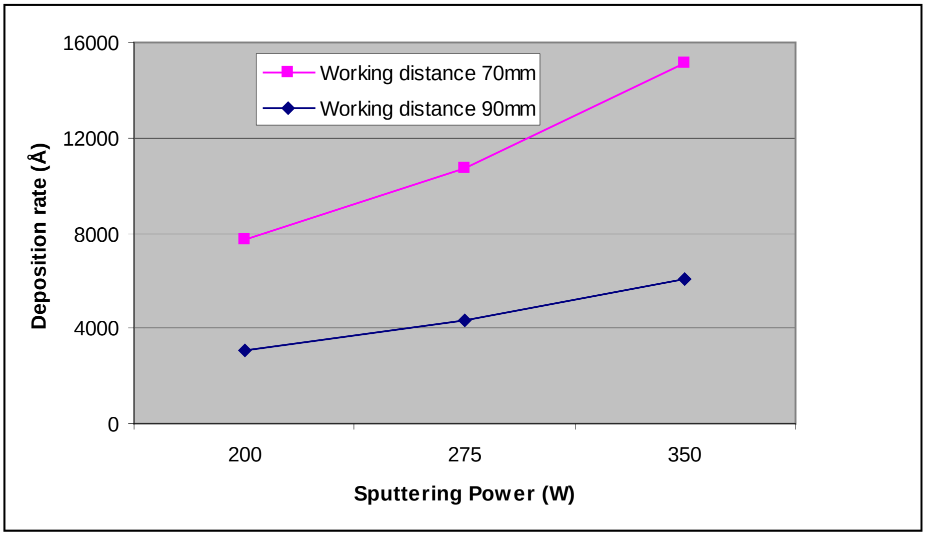

Figure 1. Effect of Sputtering power on deposition rate.

Table I: Sputtering Power with corresponding thicknesses

Sputtering Power (W)	Deposition Time (Seconds)	Average Thickness (Å) (90mm working distance)	Average Thickness (Å) (70mm working distance)
200	800	3100	4650
275	800	4300	6400
350	800	6050	9115

Development of Mo Back Contact:

Molybdenum back contact in CIGS solar cells is usually deposited using DC magnetron sputtering. Properties of thin films are dependent on process parameters. The working distance between the sputtering target and the substrate was maintained at ~90 mm for all depositions. To achieve thickness uniformity over a 6” X 4” area, the substrate was slowly moved over the sputtering target using an in-house developed moving mechanism. The rate at which the substrate moves determines the total thickness of the film. Experiments were carried out by systematically changing the working gas pressure while keeping the sputtering power constant and then changing the sputtering power while keeping the working gas pressure constant. The working gas pressure was varied in the range of 0.1 to 5 milli torr and the sputtering power was varied in the range from 200-300 W. On the main glass substrate, very thin glass strip, 0.15 mm thick, and of 10mm × 150mm dimension was attached during each deposition. Since the glass strips were extremely thin and narrow, any stress developed by the deposited film resulted in change in the curvature of the glass strips. The residual stress was then measured by the bending beam method using the formula;

$$S = \left[\frac{4E_s h_s^2}{3(1-\upsilon)L_0^2}\right] \times \left[\frac{\delta}{h_c}\right]$$

Where, E_s is the Young’s modulus of the glass strip, h_s is the thickness of the strip, h_c is the film thickness, υ is the Poisson’s ratio of the strip, S is the average stress of the film, L_0 is the length of the glass strip, δ is the deflection.

The working gas pressure and the sputtering power were systematically varied one at a time keeping the other parameter constant. The resulting films were then analyzed to determine the effect of each parameter on the residual stress and the resistivity of the film.

1.1 Adhesion

All the films deposited in this investigation passed the Scotch-tape test. It has been reported that Mo films in compressive stress adhere poorly to the glass substrate, and those in tensile stress have a good adhesion. Since the films obtained in this investigation were all in tensile stress state, they are considered to exhibit a good adherence to the glass substrate

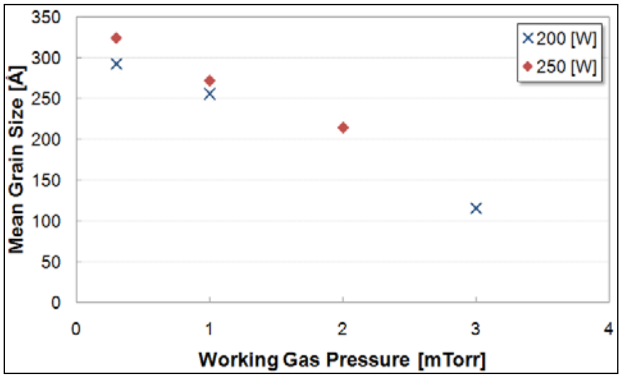

Figure 2: Mean grain size of Mo thin films as a function of working gas pressure

1.2 Surface Morphology

The average roughness of the films was determined using AFM (figure 3) and it was found that the films deposited at lower gas pressures were rougher than those deposited at intermediate pressures and the roughness increased as the gas pressured increased. The increase in the average roughness at lower pressures was attributed to the coarse grains and at higher pressure it was attributed to the self–shadowing effect resulting in porous films.

Figure 4 shows the relation pseudo-kinetic energy of incident atoms and average roughness. The kinetic energy of the incident atoms was calculated as follows;

$$E_{in} = E_{out} \exp\left(-\frac{\sigma p l}{kT}\right)$$

Where, E_{in} is the kinetic energy of the incident atom, E_{out} is the initial kinetic energy of the atom, l is the distance between the substrate and the target, σ is the cross section for momentum transfer collision with background gas atom, k is the Boltzmann constant, and T is the temperature. It should be noted that an assumption made here is that E_{out} is equal to the sputtering voltage. In lower energy region, porous microstructure is grown due to low kinetic energy of incident atoms resulting in rougher surface. The roughness decreases with increase in kinetic energy of incident atoms; however, it increases again in higher energy region. Rougher surfaces in higher energy region are attributed to the large coarse grains.

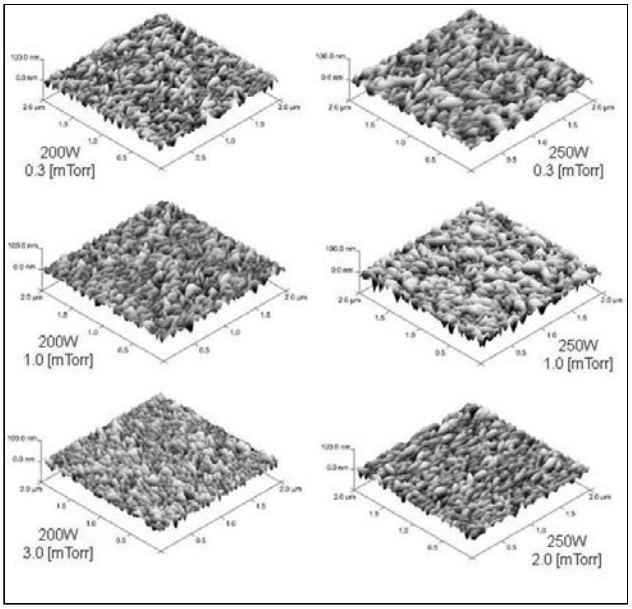

Figure 3: AFM images of Mo thin film deposited at various sputtering conditions

Figure 4: Average roughness variation of Mo thin film as a function of pseudo-kinetic energy of incident atoms

1.3 Resistivity

As noted in figure 5 the working gas pressure strongly influences the resistivity of the molybdenum films. The resistivity does change with sputtering power but change in the working gas pressure is more dominant mechanism in determining the resistivity of the film. The lowest resistivity of 11.9 μΩcm was obtained in films prepared at a working gas pressure of 0.1 mTorr and a power of 250 W, which is roughly twice the room temperature bulk value of 5.4 μΩcm. The observed increase in resistivity shown at higher gas pressure is deduced to be the direct result of the porous microstructure and small grains.

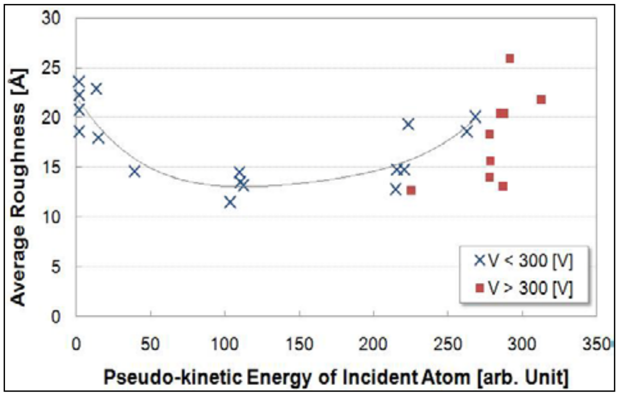

Figure 4: Average roughness variation of Mo thin film as a function of pseudo-kinetic energy of incident atoms

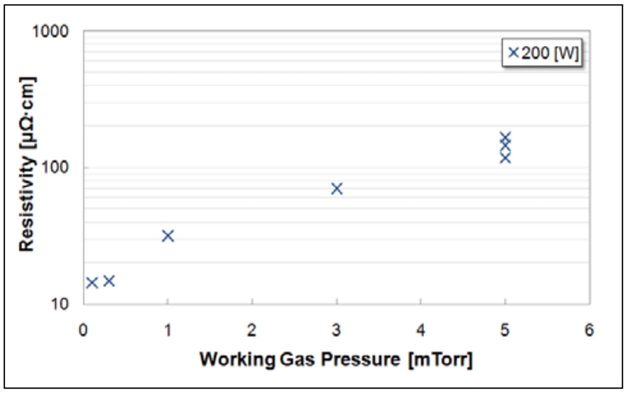

Figure 5: Resistivity variation of Mo thin films as a function of working gas pressure (deposited at 200W)

1.4 Stress Analysis

Figure 6 shows the images of glass strips which were bent by the residual stress of deposited Mo thin film. As can be seen from the tables II and III, the residual stress is inversely proportional to the sputtering voltage. As the sputtering voltage decreases the energy of the incident sputtered atoms and the neutralized argon atoms reduces thus resulting in an open structure. Such an open structure results in an increase in the intergranular spacing which in turn results in the decrease in the attractive force. Hence, the tensile stress increases with decreasing sputtering voltage. Similarly, at higher sputtering voltages the films are more compactly packed thus resulting in the reduction in the tensile stress developed in the films. At higher working gas pressures, the number of collisions that the sputtered atom and the neutralized argon atom encounter before getting deposited on the substrate increases. The increase in number of collisions results in the reduction of the kinetic energy of the sputtered atoms as well as that of the neutralized argon atoms. This leads to an open structure resulting in an increase in the tensile stress in film. The magnitude of attractive force, which is responsible for tensile stress among grains is inversely proportional to the intergranular spacing. Therefore, with decreasing the target voltage, the films developed a tensile stress with increasing the intergranular spacing, and reversely, increasing the discharge voltage results in lowering of the number of open sites within the film, and thereby reduces the tensile stress. If film is deposited at higher pressures, it can be expected that collisions with background Ar gas atoms reduce the kinetic energy of sputtered Mo atoms and reflected neutral Ar gas atoms, resulting in more porous and less densely packed Mo film with significant tensile stress state. Below the gas pressure of 0.3 mTorr, this holds true, however, further increase in gas pressure results in attenuation of the tensile stress.

Figure 6. Bending of glass strips at various sputtering conditions.

Table II: Residual stresses of Mo thin film deposited at different pressures

Power (W)	Pressure (mTorr)	Residual Stress (MPa)
200	0.1	322
	0.3	358
	1	101
	3	0

Table III: Residual stresses of Mo thin film deposited at different powers

Power (W)	Pressure (mTorr)	Residual Stress (MPa)
200	0.1	322
225		249
250		213
275		204
300		152

Electron back scattered diffraction (EBSD)

EBSD study of CIGS thin film solar cells has also been initiated in this study. This is a powerful technique which allows crystallographic information such as the grain orientation, grain boundaries and also the grain size to be obtained. A more detailed account of this work will be provided in the following reports. Figure 7 shows the EBSD map and the Kikuchi pattern obtained for a CIGS2 thin film.

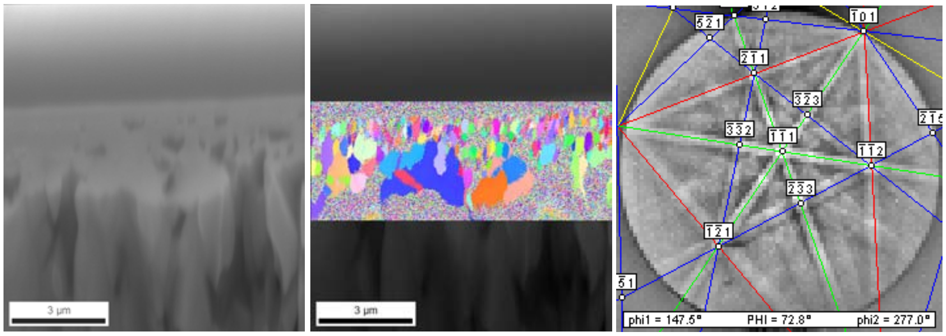

Figure 7: EBSD maps and indexing for CIGS2 samples

Human Resources:

Eigo Takahashi (M.S. in Material Science) graduated in spring 2010. Shirish Pethe (PhD in Electrical Engineering) is graduating in fall 2010 and Ashwani Kaul (PhD in Material Science) will graduate in spring 2011.

Publications:

1. S. A. Pethe, E. Takahashi, A. Kaul and N. G. Dhere, “Effect of sputtering process parameters on film properties of molybdenum back contact”, submitted in the Journal of Solar Energy Materials and Solar cells.
2. S. A. Pethe, E. Takahashi, and N. G. Dhere , “Correlation between preparation parameters and properties of molybdenum back contact layer for CIGS thin film solar cells”, Proc. PVSC35, June 20-25, Hawaii.