DEVELOPMENT OF CIGS2 THIN FILMS ON ULTRALIGHTWEIGHT FLEXIBLE LARGE AREA FOIL SUBSTRATES

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Introduction

The development of thin film solar cells is aimed at reducing the costs for photovoltaic systems [1]. Use of thin film technology and thin foil substrate such as 5-mil thick stainless steel foil or 1-mil thick Ti would result in considerable costs savings. Another important aspect is manufacturing cost. Current single crystal technology for space power can cost more than $ 300 per watt at the array level and weigh more than 1 kg/m^2 equivalent to specific power of ~ 65 W/kg. Thin film material such as $CuIn_{1-x}Ga_xS_2$ (CIGS2), $CuIn_{1-x}Ga_xSe_{2-y}S_y$ (CIGSS) or amorphous hydrogenated silicon (a-Si:H) may be able to reduce both the cost and mass per unit area by an order of magnitude. Manufacturing costs for solar arrays are an important consideration for total spacecraft budget. For a medium sized 5kW satellite for example, the array manufacturing cost alone may exceed $ 2 million. Moving to thin film technology could reduce this expense to less than $ 500K [2]. Earlier publications have demonstrated the potential of achieving higher efficiencies from CIGSS thin film solar cells on 5-mil thick stainless steel foil as well as initial stages of facility augmentation for depositing thin film solar cells on larger (6"x 4") substrates [3]. This paper presents the developmental study of achieving stress free Mo coating; uniform coatings of Mo back contact and metallic precursors. The paper also presents the development of sol gel process, refurbishment of selenization/sulfurization furnace, chemical bath deposition (CBD) for n-type CdS and scrubber for detoxification of H_2S and H_2Se gases.

Sol Gel Process

A new sturdy and robust set up for carrying out sol-gel SiO_2 coating by dip coating method was prepared at FSEC (Figure 1). A structure of adequate height was fabricated for large samples to be raised easily from the container (beaker of capacity 4 liters) holding the sol-gel solution. A DC gear motor of shaft diameter = 0.312"(0.79 cm) with 4 rpm and a pulley assembly for raising and lowering the sample were mounted atop the structure. A 12V DC, 1500 mA power supply was used to control the motion of the DC motor. Special bushings of various dimensions were designed and fabricated for attaching to the motor for variable speeds for carrying out experiments with speeds ranging from 8-16 cm/min. The speed of withdrawal was one of the important factors and attempts were made to optimize the speed for improving the quality of the coating. Weights attached to the bottom of the foil kept it vertical so that the foil enters the sol-gel solution and is withdrawn normal to the sol surface. This prevents the thickness variation during coating. After withdrawal of the foil, it was left hanging to dry for a period of 5 minutes. Later the foil was placed in an Isotemp Muffle Furnace for sintering along with other foils. A batch of four foils could be heat-treated at a time in the furnace in one run. Adequate care was taken to place the foils in a specially prepared fixture without bending or stressing. Samples were sintered in air at a temperature of 450ºC for a period of 1 hour. After cooling for approximately 2 hrs the samples were removed from the furnace, rinsed with deionized water and dried with compressed N_2 gas prior to storing them in a desiccators. Atomic Force Microscopy (AFM) was carried out at National Renewable Energy Laboratory to study the morphology and roughness of the SiO_2 layer on Ti foil substrate at a high resolution. The images were obtained for an area of (100 X 100) µm^2.
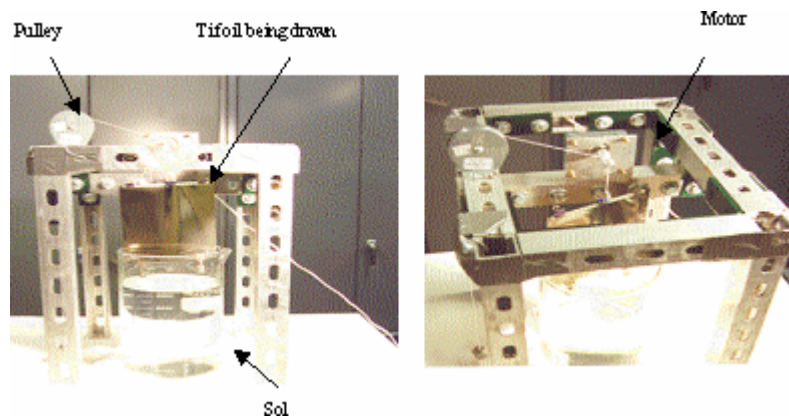
Figure 1. Sol gel setup

AFM images show both the 3-dimensional and normal 2-dimensional images. Figure 2 shows both these images for a plain Ti foil surface without any SiO_2 deposition. The average roughness value obtained was Ra = 543 Å. Figure 3 shows Ti foil coated with SiO_2 where the average roughness value was measured to be 146 Å [4].
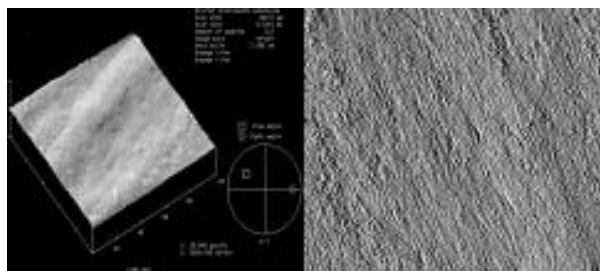

Figure 2: AFM images (100 X 100 μm^2) of plain Ti foil, Ra = 543 Å.
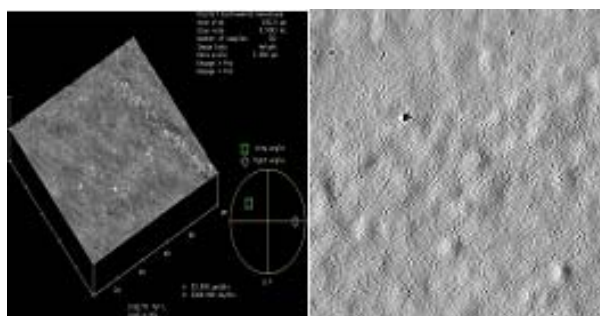
Figure 3: AFM images (100 X 100 μm^2) of Ti foil + 1 thick (0.55 μm) + 2 thin (0.35 μm) SiO_2 layer, Ra = 146 Å.

CIGS2 thin film was deposited on the foil after cleaning in distilled deionized water and drying with compressed N_2 gas. Figure 4 shows a stacked layering sequence for the thin film deposition of CIGS2 on SiO_2 coated titanium foil substrate. Ti was chosen because of its good compromise between cost and physico-chemical properties.
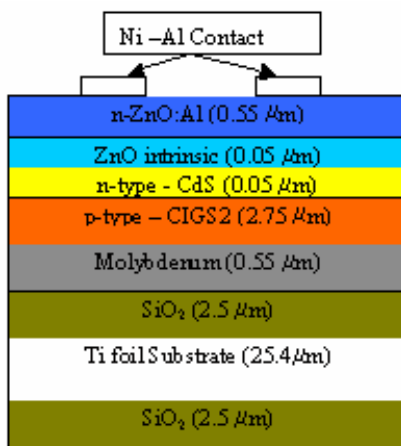

Figure 4: Structure of completed Polycrystalline CIGS2 Thin film Solar Cell.

Mo Back Contact

Depending on the working gas pressure, residual stresses are developed in refractory metal films prepared by magnetron sputtering. Films deposited below transition pressure develop compressive stresses, whereas those deposited above the transition pressure develop tensile stresses. Gross stress may be determined by visual inspection in that highly compressed films tend to buckle up, frequently in zigzag patterns, whereas films under extreme tensile stress develop a system of stress lines that appear like scratches.

Thin flat strips of clean titanium foil of 1cm x 15cm were attached at their ends to a glass substrate prior to deposition (Figure 5) using vacuum compatible tape. It was observed that films deposited at high power of 300W and low argon pressure of 3 x 10^{-4} Torr resulted in compressive stresses. The thin foil deposited under these parameters showed convex bending (Figure 6). On the other hand films deposited at power of 200W and argon pressure of 5 x 10^{-3} Torr resulted in tensile stresses showing concave bending and stress lines (Figures 7-8) [5].

Figure 5: Thin strips of flat foil attached to glass substrate prior to deposition.
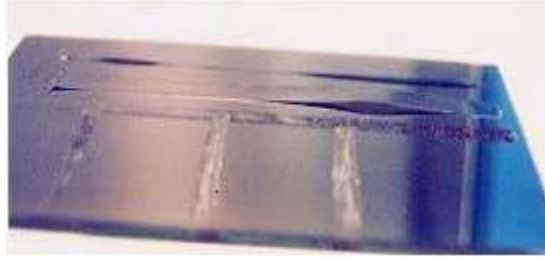
Figure 6: Films deposited at high power of 300W and low argon pressure of 3 x 10^{-4} Torr resulting in compressive stresses leading to lifting of the flat foil.

Figure 7: Films deposited at low power of 200W and high argon pressure of 5 x 10^{-3} Torr resulting in tensile stresses leading to lifting of the inverted deposited foil.
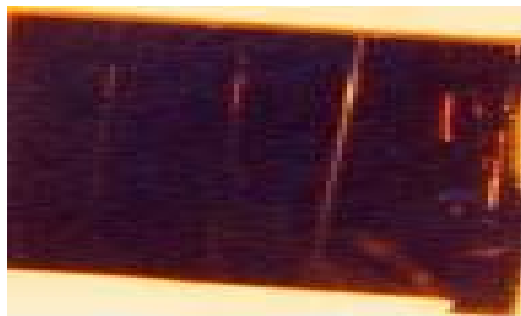

Figure 8: Scratches observed due to tensile stresses on films deposited 200W/ 5 x 10^{-3} Torr.

A simple bending foil technique was used to estimate the magnitude of stress present in the foils. Loads were applied to the concave and convex region of the foil and weight required to make the foil flat similar to its position prior to deposition was measured. The load required and the curvatures in the cycles mentioned above are provided in Table I.

Table I: Loads applied to make foil flat.

Power / Argon Pressure	Height of curvature	Loads applied
300W / 3 x 10^{-4}	0.88 mm	450 mg
200W / 5 x 10^{-3}	0.48 mm	130 mg

The applied loads as well as the curvature of the foil were used for estimating the stress. These samples were sulfurized in 4% H_2S in argon mixture at 475°C for 20 minutes. The reactivity of the molybdenum in sulfur/ selenium atmosphere has been reported to occur at temperatures over 600°C. However, it was observed that the sample under compressive stress peeled off from several regions and turned reddish pink indicating a chemical reaction occurring even at 475°C. On the other hand, the sample under tensile stress remained, mostly as it was with slight change in color from brownish to brownish red.

Foils were deposited with a number of combinations of the cycles of high power/low pressure and low power/high pressure to obtain a very flat foil after deposition. It is reported that such stress reversal is dependent on energetic bombardment by reflected neutral and/or sputtered atoms. At relatively low pressure, the mean free path is high, as a result of which the arriving atoms have higher kinetic energy and the resulting film has dense microstructure thereby experiencing compressive stresses. At higher working pressure the mean free path is reduced resulting in moderate flux of atoms reaching the substrate leaving the film in tensile stress. However, for producing highly efficient 4"x 4" size solar cell, the back contact molybdenum has to be fairly free of residual stresses. Therefore, the deposition started with low power and high pressure to reduce chemical reactivity. Two compressive stress cycles sandwiched between three tensile cycles were deposited in order to lower the stress and to achieve required thickness uniformity.

Thickness Uniformity

Molybdenum back contact and zinc oxide thin films were deposited on large-area glass substrates using optimized parameters of DC or RF sputtering power, working gas pressure, target-to-substrate distance, sputtering time and linear substrate movement parallel to the 4" width of the target.
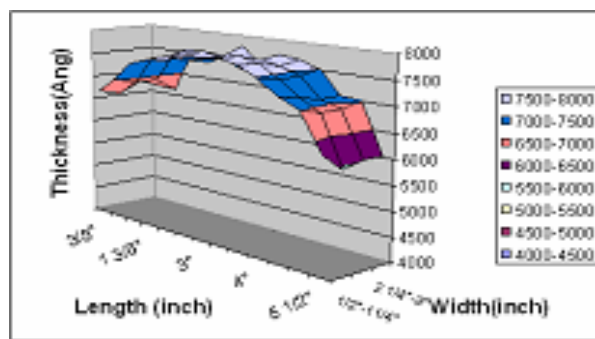

Figure 9. Thickness distribution profile.

After depositions, the grid design initially drawn on the substrates together with the overlaying thin film was removed by ultrasonic cleaning in isopropanol, thus providing a distinct step for measurements with a Dektak[3] thickness profilometer. Thickness variation of ±11% over the central 4"x4" region was observed. Series of experiments were carried out for improving thickness uniformity by empirically modifying the magnetic field distribution. Experiments were carried out using various permutations and combinations of

nickel coated soft iron strips arrangements. The strips were replaced by similar-size rubber strips to maintain the shape integrity. The optimum configuration resulted in a thickness uniformity of ±3% over central 4" x 4" region for molybdenum thin films (Figure 9) while it continued to drop beyond this region [6].

Based on the continued thickness drop beyond 4", it was realized that the magnetic field must be boosted at the extremities to achieve better thickness uniformity. The sputtering sources were also found to produce non-uniform plasma distribution within the racetrack leading to varying plasma intensity glow, again confirming the need to modify magnetic array. In the mean time, the manufacturer had modified the magnetic array with a better magnetic field distribution and stronger magnetic field at the extremities. Two such new magnetron-sputtering sources were procured. The old and new modified magnetic arrays are shown in Figures 10 and 11 respectively.
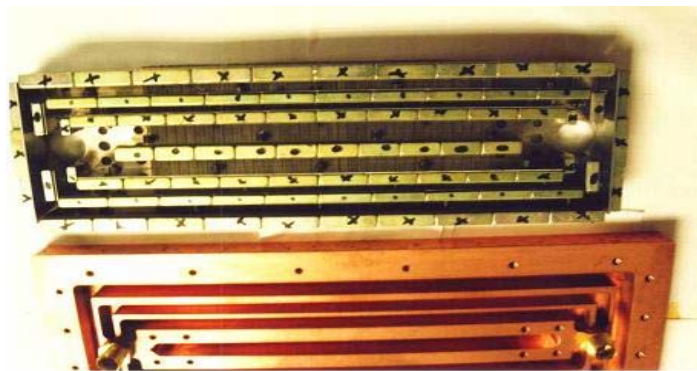

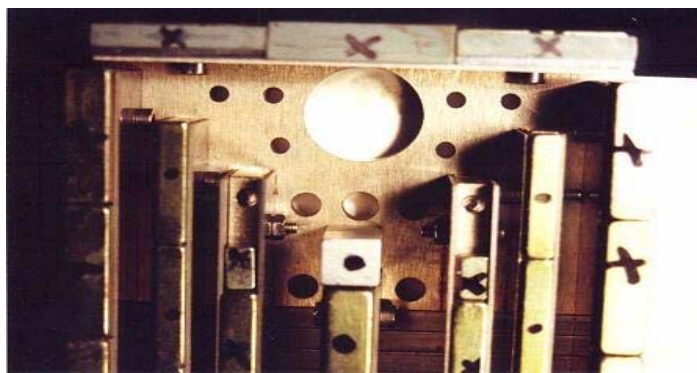
Figure 10: Older Magnetic Array design

Figure 11: Modified magnetic array.

However, in the absence of specific information of their being substantially different, they were assumed to be similar to the older sources and no thickness profiling experimentation was carried out with them. The new magnetic array design and the necessary additional magnets were obtained from the manufacturer for upgrading the remaining three magnetron-sputtering sources. The design introduced extra magnets at and near the periphery. The copper body holding the magnetic assembly was machined to accommodate the modified assembly. The problem of non-uniform plasma was resolved after modifying magnetic assembly. The initial non-uniform plasma was modified into the dumbbell shape of the racetrack region with the modified magnetic arrays having boosted magnetic field at extremities (Figure 12 a, b).
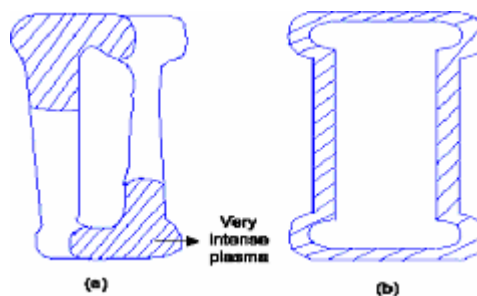
Figure 12. a) Non-uniform plasma b) Uniform plasma.

Figure 13 shows variation of thickness of molybdenum deposited by DC sputtering and zinc oxide by RF magnetron sputtering averaged over 2.75" distances along the linear movement direction with the length parallel to the 12" dimension of sputtering sources. The thickness uniformities over central lengths were: Molybdenum: ±2.24 % over 4", ±2.40% over 5", ±2.95% over 6" and zinc oxide: ±2.46 % over 4", ±3.84% over 5", ±5.60% over 6". Fortunately the thickness uniformity for ZnO/ZnO:Al is slightly less critical. These results pave the way for deposition of large area (6"x4") thin film solar cells.
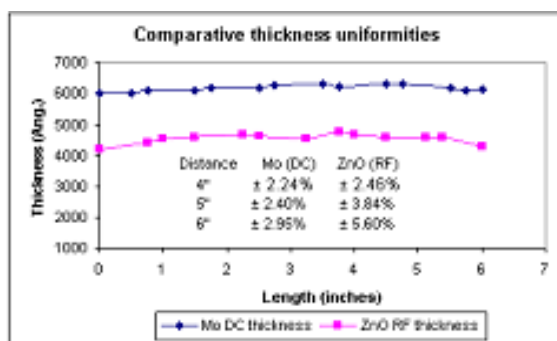

Figure 13. Thickness variation plots Mo (DC sputtering) and ZnO (RF sputtering).

Selenization/Sulfurization Furnace

Deposition of metallic precursors on the substrate is followed by sulfurization to get p-type CIGS2 absorber layer. A furnace was donated by Shell (formerly Siemens) Solar capable of Selenization/Sulfurization of metallic precursors on large 6"x 4" size substrates. The furnace is capable of sulfurizing one hundred 4"x4" or sixty-six of 6"x 4" substrates in a single run. The furnace in as received condition needed upgrade. The major part of upgrade included; the computer, mass flow controllers, valves, thermocouples and cables. The furnace is now fully operational and produces CIGS2 absorber layer on routine basis.

Figure 14. Selenization/Sulfurization furnace

CdS by Chemical bath deposition

Having augmented the substrate size to 4"x 4", next step was to design and construct chemical bath deposition (CBD) setup for four such substrates. The setup was built using teflon sheets of ½" and 1/8" thickness, and a teflon rods of 1/8" diameter. The setup can hold two1/8" thick glass samples and two 1-5 mil thick stainless steel or titanium foil substrates. Holes were drilled in the bottom and top teflon plate to insert 1/8" diameter rods for holding the two top and bottom sheets assembly. 4 5/8" length of the rods allowed 4" clearance between top and bottom plates for placing 4" x 4" substrates. The bottom plate has a central circular hole for the stirrer movement. The top plate had openings for insertion of the thermometers and pH control sensors. The final assembly is shown in the figure 15. Experiments were carried out with the new designed set up, thus scaling up from 1.25" x 1" to 1" x 4" to 4" x 4" as shown in Figure 16. Table 2 provides the bath composition for carrying out deposition on 4"x 4" substrates.

Table II. Chemical bath composition for 4" x 4" substrates

Sr.No.	Type of solution	Concentration	Quantity (milliliters)
1	Distilled and Deionized water	-	1320
2	Ammonium Hydroxide $(NH)_4OH$	28 to 30%	309
3	Cadmium Sulfate $CdSO_4$	0.015 M	181.5
4	Thiourea	1.5 M	90.75

Composition of the bath was chosen so that the substrates would be completely immersed inside the chemical bath. The bath is prepared in a beaker of 3500 ml capacity for the new set up of 4" x 4" substrates to fit snugly [7].
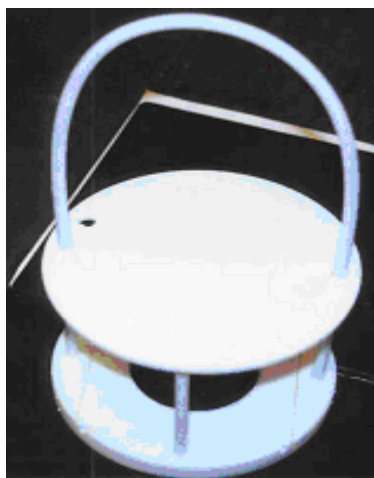
Figure 15. CDS setup for 4"x 4" substrates

Figure 16. Increase in substrate sizes from 1.25" x 1" to 1" x 4" to 4" x 4"

Scrubber

A scrubber was designed and fabricated to detoxify H_2S and H_2Se gases coming out of the furnace reaction tube. Reaction tube having a volume of 15.3 liters is filled with process gas [N_2+H_2S (<4%) or N_2+ H_2Se (<4%)] and heated to 500 ^{o}C in a furnace. A mechanical pump pumped the process gas from the reaction tube through a mass flow controller. The effluent gas was further diluted with nitrogen by factor of 60. The process gas was fed through a venturi that is propelled by nitrogen gas used for dilution. The total flow of diluted hydrogen selenide (666 ppm) or diluted hydrogen sulfide (666 ppm) gas was calculated to be 132 liters/min equivalent to 4.7 scfm. The diluted process gas flows through the first wet scrubber and then through the first packed-bed column. The total height of the packed bed was calculated to be 6.9 feet for H_2S in order to achieve less than 10 ppm at exhaust. The height of the total packed bed was calculated to be 17.14 feet for H_2Se to achieve 50 ppb prior to exhaust according to Occupational Safety and Health Administration (OSHA). The packed-bed column was split in two. The height of the first column was 10.25 feet and the second was 9.25 feet. The extra height was provided to accommodate the packed bed column internals. Prior to entering the second packed-bed column, the gas passes through the second wet scrubber. The effluent gas from the packed-bed column(s) passes

through drums containing activated carbon impregnated with KOH and from there will be exhausted to the atmosphere [8].

The four point CM4 analyzer for H_2Se has been installed, to detect the H_2Se gas concentration at various levels. This CM4 analyzer has been connected to the present building alarm system in FSEC.

Figure 17. Inside (left) and outside (right) scrubber assembly including CM4 connections

Figure 18. Drums containing activated carbon impregnated with KOH and exhaust fans assembly

Conclusion

The paper demonstrates the potential of PV Materials Lab at the Florida Solar Energy Center (FSEC) for carrying out research and development of $CuIn_{1-x}Ga_xSe_{2-y}S_y$ (CIGSS) thin-film solar cells on large area ultralightweight flexible metallic foil for space applications. This facility equipped with large area deposition systems, sulfurization/selenization furnace along with CBD setup for CdS deposition and the scrubber unit is one of its kinds amongst University Labs and could serve as a nucleus of a small pilot plant for CIGSS thin film solar cell fabrication.

Acknowledgements

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