Polycrystalline CuInSe_2 and CdTe Solar Cells

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MASTER

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SUMMARY

Objectives

The principal objective of the research project is to develop processes for the fabrication of cadmium-telluride, CdTe, and copper-indium-gallium-diselenide, $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$, polycrystalline-thin-film solar cells using techniques that can be scaled-up for economic manufacture on a large scale. The aims are to fabricate CdTe solar cells using Cd and Te layers sputtered from elemental targets; to promote the interdiffusion between Cd/Te layers, CdTe phase formation, and grain growth; to utilize non-toxic selenization so as to avoid the use of extremely toxic H_2Se in the fabrication of $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ thin-film solar cells; to optimize selenization parameters; to improve adhesion; to minimize residual stresses; to improve the uniformity, stoichiometry, and morphology of CdTe and $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ thin films, and the efficiency of CdTe and $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ solar cells.

Discussion

This is an annual technical report on the Phase I of a three year phased research program. CdTe and $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ polycrystalline-thin-film solar cells are emerging as the leading candidates for meeting the DOE long-range cost goals. A new laboratory has been established at FSEC, for research and development on thin-film solar cells. The structure of CdTe thin-film solar cells consisted of glass/ SnO_2 :F/CdS/CdTe/back contact. Optimum conditions for slow ion-by-ion growth of conformal CdS 500-2600 Å thick layers with direct bandgap of ~2.40 eV for use as heterojunction partner in CuInSe_2 and CdTe thin-film solar cells, were cadmium salt concentration Q in the range 0.001-0.003 M, thiourea concentration 5xQ, ammonium salt concentration 20xQ, pH ~9.11, deposition temperature of ~85° C, and deposition time of 6-30 min. FSEC has developed a new technique for the deposition of elemental layers of cadmium and tellurium by magnetron-sputtering followed by interdiffusion, CdTe phase formation, and grain growth. Parameters for heat treatments were optimized to minimize the loss of tellurium and cadmium during the heat-treatment of Cd/Te multilayers. Use of vacuum melted sputtering targets, efficient water cooling, and good thermal and electrical contacts improved the controllability, repeatability, and efficiency of the sputter-deposition from tellurium targets. Even though lower deposition rates of ~0.25 $\mu\text{m min}^{-1}$ have been utilized during the first phase both for Cd and Te so as to be able to accurately control the thickness of individual layer by controlling the deposition time manually, it is estimated that the deposition rates could be enhanced so as to deposit Cd and Te layers required for obtaining a 4 μm thick CdTe thin films in 5-7 minutes. Adhesion, and formation of pinholes in heat-treated CdTe thin films were found to be influenced by the type and cleanliness of substrate, and the adhesion and compactness of individual Cd and Te layers. After a careful study, various factors which can cause pinholes in the Cd/Te layered films on glass/ SnO_2 :F/CdS substrates prior to the heat treatment were identified and eliminated. Heat treatments were carried out on Cd/Te multilayer structures on glass, glass/CdS, and glass/ SnO_2 :F/CdS substrates in partially-closed or open graphite crucibles, in an

evacuated quartz tube in a tube furnace. The rate of temperature rise during heat treatment was limited to $20^{\circ}\text{C min}^{-1}$ to avoid peeling off of CdTe layers especially on plain glass substrates. The maximum temperature during the heat treatment was limited to 400°C to avoid the formation of blisters on the film. Uniform 2-6 μm thick CdTe films were obtained by heat treatment of Cd/Te multiple layers on glass/SnO₂:F/CdS substrates. However, samples showed a few pin-holes. X-ray diffraction studies on the heat-treated samples indicated good CdTe compound formation with highly crystalline, single phase, thin films with a weak (111) texture of face centered cubic structure with $a_0 = 6.48\text{ \AA}$, without any trace of the precursor elements cadmium and tellurium. After the chloride treatment, a significant increase in the grain size was observed in CdTe sample especially those heat-treated at somewhat lower maximum temperature. CdTe thin-film solar-cell fabrication was completed by applying graphite paste contacts after etching the surface of CdTe thin films. Most of the contacting was carried out at NREL. Also an arrangement has been made for deposition of Cu/Au back contacts in a renovated vacuum system at FSEC. Completed CdTe solar cells showed open-circuit voltages, V_{∞} in the range 320-380 mV, low short-circuit-current densities, J_{sc} of $\sim 5\text{ mA cm}^{-2}$, and poor values of the fill factor, FF because of the shorting across the few existing pin-holes and possibly some problems with the ohmic contacts. Experiments are continuing for the elimination pin-holes in CdTe thin films after which it would be possible to obtain solar cells with high PV conversion efficiencies.

The structure of CuInSe₂ thin-film solar cells consisted of glass/Mo/CuInSe₂/CdS/ZnO:Al/Al contact fingers. Attempts were made to overcome problems of residual stress in molybdenum layers by varying sputtering gas pressure, power, and angle of vapor incidence. Some of the samples were tested at ORNL. Initially the depositions consisted of a Cu/In bilayer. Selenized films were found to be more homogeneous if there was a proper intermixing of Cu/In bilayer prior to placement in the selenization chamber. RBS spectra of Cu-In precursor bilayers pre-heat-treated *in situ* at $90\text{--}95^{\circ}\text{C}$ for 10 minutes showed completely intermixed layer having a composition Cu_{0.79}In_{1.0}. Thorough cleaning, minimization of residual stress in the Mo, and the use of moderate ($25\text{--}50\text{ \AA sec}^{-1}$) selenium evaporation rates improved adhesion of selenized layers. An innovative two-stage-selenization process has been developed at FSEC. It uses a first copper-indium bilayer consisting of the entire thickness of copper required to form the compound and only a fraction ($\sim 25\%$) of the indium with an objective of improving the grain size. It also improved adhesion. Experiments were carried out to increase the bandgap by adding gallium to form selenized Cu(In_{1-x}Ga_x)Se₂ thin films with $x = 0.2\text{--}0.25$. Addition of gallium mostly near the Mo back contact improved the film properties still further. A new process has been developed for the successful incorporation of gallium while avoiding the deleterious interaction between indium and gallium. Initial proportions of Cu:In were adjusted to 0.85:1.0 so as to obtain Cu:In proportion of 0.95:1.0 after an estimated loss of $\sim 10\%$ In during selenization. However, the loss of indium during the selenizations was found to be negligible. Copper content in Cu(In_{1-x}Ga_x)Se₂ thin films was varied systematically over a wide range. Rough estimates of the composition of Cu(In_{1-x}Ga_x)Se₂ thin films were obtained by measuring the electrical resistance through the film by contacting molybdenum back layer and the front of Cu(In_{1-x}Ga_x)Se₂ films. Structure and morphology were studied by XRD and SEM. The composition of the films was analyzed by EPMA at NREL, XPS at KSC, and RBS and PIXE at UNC. The resistance of Cu(In_{1-x}Ga_x)Se₂ thin films with Cu:In:Ga:Se atomic proportions of 18.9:28.1:2.5:50.5 was in the range of several

hundred kilo ohms even approaching 1 M Ω . XRD patterns of these films showed the formation of Cu(In_{1-x}Ga_x)Se₂ and CuIn₂Se_{3.5} phases. Heterojunction-partner- and window layers and front contact grids were deposited at NREL and IEC. Solar cells prepared using these films gave a open circuit voltage of ~300 mV and a very low short circuit current of ~1 mA. The resistance through the Cu(In_{1-x}Ga_x)Se₂ thin film having Cu:In:Ga:Se atomic proportions of 19.3:27.6:1.3:51.8 was 100-200 K Ω . Solar cell fabricated using this film showed an open circuit voltage of 331 mV, a short circuit current of 18 mA, with a very low fill factor of 28% due to the excessively large series resistance resulting from the copper deficiency. The copper content in Cu(In_{1-x}Ga_x)Se₂ thin films was adjusted to obtain near the optimum atomic proportion of Cu:In:Ga:Se of 23.5:25.5:1.5:49.5. These films have shown resistance in the range of 50-100 k Ω . XRD pattern showed the formation of Cu(In_{1-x}Ga_x)Se₂ phase. Several cells were completed at IEC by deposition of 1- μ m thick CdZnS:In\ITO\Al fingers on glass\Mo\Cu(In_{1-x}Ga_x)Se₂ samples prepared at FSEC with this near optimum composition. Morphological properties of Cu(In_{1-x}Ga_x)Se₂ thin films and photovoltaic characteristics of completed cells reaffirmed the importance of proper intermixing of Cu:In:Ga precursors prior to selenization. Cu(In_{1-x}Ga_x)Se₂ thin films in which the precursors were homogenized showed large, well-faceted grains, whilst the grain morphology was inferior in Cu(In_{1-x}Ga_x)Se₂ thin films prepared from unhomogenized precursor layers. Solar cells prepared from Cu(In_{1-x}Ga_x)Se₂ thin films in which the precursors were not homogenized showed V_{oc} of 378 mV, J_{sc} of 33.4 mA, a fill factor of 60.2% and a conversion efficiency of 7.6%. The best cell obtained with films prepared using precursors homogenized *in situ* prior to selenization gave an open circuit voltage V_{oc} of 377 mV, J_{sc} of 34.8 mA, a fill factor 62.5% and photovoltaic conversion efficiency of 8.2%. It may be noted that a 1- μ m thick CdZnS heterojunction layer was used in these cells. This resulted in the loss of spectral response from high energy photons above the CdZnS bandgap. Also the values of fill factors were low. Based on expected improvements in the fill factor, high photon energy response, and further optimization of elemental proportions and film properties, it is expected to obtain significant improvements in the performance of these solar cells.

1. INTRODUCTION

This is an annual technical report on the Phase I of a three year phased research program subcontract no. XG-2-11036-5, entitled "Polycrystalline CuInSe₂ & CdTe PV Solar Cells". The principal objective of the research project is to develop the process for the fabrication of cadmium-telluride, CdTe, and copper-indium-gallium-diselenide, Cu(In_{1-x}Ga_x)Se₂, polycrystalline-thin-film solar cells using techniques that can be scaled-up for economic manufacture on a large scale. The aims are to develop a process for the fabrication of CdTe solar cells using Cd and Te layers sputtered from elemental targets; to promote the interdiffusion between Cd/Te layers, CdTe phase formation, and grain growth; to develop a process for the non-toxic selenization so as to avoid the use of extremely toxic H₂Se in the fabrication of Cu(In_{1-x}Ga_x)Se₂ thin-film solar cells; to optimize selenization parameters; to improve adhesion; to minimize residual stresses; to improve the metallic back-contact; to improve the uniformity, stoichiometry, and morphology of CdTe and Cu(In_{1-x}Ga_x)Se₂ thin films; and to improve the efficiency of CdTe and Cu(In_{1-x}Ga_x)Se₂ solar cells.

1.1 Background

Cadmium telluride (CdTe) and copper-indium diselenide (CuInSe₂) polycrystalline-thin-film solar cells are emerging as the leading candidates for meeting the DOE long range cost goals for 30-year, levelized PV electricity cost in constant 1986 dollars of 6¢ (kWh)⁻¹, equivalent to the module cost for 15%-20%-efficient, fixed, flat-plate cells of \$ 45-80 m⁻² [1-3]. Moreover these cells are free from intrinsic degradation mechanisms. CuInSe₂ and CdTe solar cell modules have been shown to maintain their efficiency for several years without appreciable degradation in outdoor tests carried out at NREL.

The thickness of the active layer of the present day CdTe-based solar cells manufactured by chemical spray or screen printing is >10 µm. Because of the direct bandgap of ~1.5 eV of CdTe it would be possible to absorb the sunlight efficiently within a thickness of 1-2 µm. Recently, 15.8% (AM1) efficient CdTe/CdS polycrystalline-thin-film solar cells have been prepared by close space sublimation. Several other methods such as electrodeposition, metalorganic, chemical vapor deposition, laser ablation, and sputtering from a compound CdTe target have resulted in conversion efficiencies in excess of 10% (AM1). Sputtering from elemental targets can be scaled up for economic coating on large areas. The present project aims at developing the process of sputtering from Cd and Te elemental targets for the fabrication of CdTe solar cells. It is estimated that achieving such high rates of deposition would be very difficult with a compound CdTe target.

Solution growth of CdS layers was investigated for use as heterojunction partner in CuInSe₂ and CdTe polycrystalline-thin-film solar cells. Growth from aqueous solutions is an inexpensive, highly reproducible, and easily controllable technique which can yield conformal CdS layers with

excellent optoelectronic properties [4-7].

Plasma-assisted deposition of semiconducting thin films is playing a major role in microelectronics and solid state device technologies. Bombardment of energetic ions and neutrals can lead to reduced temperatures for compound formation and increased probability of the incorporation of dopants. The technique would be useful for the selenization of Cu-In and Cu-Ga-In layers to form CuInSe_2 and $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ without employing the highly toxic H_2Se gas.

High-efficiency CuInSe_2 solar cells can be prepared by sputter-depositing a 1- μm Mo thin film on glass or alumina, followed by the formation of 2- μm thick CuInSe_2 thin films by post-deposition selenization of distinct 200 nm Cu and 450 nm In layers deposited by sputtering. The selenization is usually accomplished by heat treatment of the glass/Mo/Cu/In structure in 10%-15% H_2Se and Ar, ramping the substrate temperature to 400° C, soaking at 400° C for 90 min, and cooling down. In a typical post-deposition selenization process, thin films are deposited by magnetron sputtering on unheated glass substrates at deposition rates around 0.1 $\mu\text{m min}^{-1}$ (controlled to <0.1%). Cu and In target temperatures are held below 200° and 150° C, respectively. Special care is needed for targets situated over the substrates to insure that the In does not melt (melting point ~157° C) and splatter onto the substrate. It has been indicated that the best efficiencies are obtained when the CuInSe_2 films are heated to a maximum temperature of 550° C.

Further research and development is needed to optimize selenization parameters to improve adhesion, to minimize the residual stress, to avoid the use of extremely toxic H_2Se , to reduce CuInSe_2 layer thicknesses to minimize the requirements of rare In metal, and to improve the quality (uniformity, stoichiometry and morphology) of CuInSe_2 thin films. The poor adhesion to the Mo-coated substrates has been attributed to a three-fold volume expansion during selenization. The problem is especially acute in the case of electrodeposited films in which the Cu/In layers consist mostly of two separate elemental phases. In evaporated and also in sputtered films, the significant alloying between Cu-In layers during the deposition even on uncooled substrates, seems to result in an approximately two-fold volume expansion. The additional expansion during selenization of these films may not produce excessive stress and hence the problem of peeling off could be minimized. Recently, indium layer has been deposited prior to the deposition of copper layer in an attempt to improve the intermixing. The problem of globule formation of indium was avoided by depositing an extremely thin layer of tellurium which provided well-dispersed nucleation sites.

It is necessary to minimize residual stress in the molybdenum coatings which are used as back contact in these cells, so as to minimize problems of adhesion to commonly used soda-lime glass substrate. Internal stresses in refractory-metal films prepared by magnetron-sputter deposition have been found to depend strongly on the sputtering-gas pressure. The compressive stress developed below a transition pressure has been attributed to atomic peening caused by the impact of energetic reflected neutrals and sputtered atoms. Higher working-gas pressure moderates the flux and energy of the gas neutrals and sputtered atoms and thus lowers the amount of kinetic energy incident on depositing species leading to a more open porous microstructure. Interatomic

forces producing tensile stress can act most effectively in such a structure. Other factors affecting the stress in the Mo coatings are the dc sputtering power and the angle of incidence. The microstructure of the compressively stressed films seems to consist of tightly packed columns while a void network surrounding the microcolumns is observed in films with tensile stress. Improved understanding of the mechanisms of residual stress formation in Mo coatings would lead to methods of stress reduction and thus would directly contribute to improved efficiency, reliability, and manufacturability of CuInSe₂ solar cells. The columnar grains have been observed to be oriented partially towards the obliquely placed deposition source. The residual stress in molybdenum films may be arising from the tightly packed microstructure of oriented columnar grains. Mitchell *et al* have deposited molybdenum films with low internal stress by adding O₂ and H₂O to sputtering argon gas [8].

Large-grain CuInSe₂ thin films prepared by co-evaporation maintaining initially a higher proportion of copper followed by a high proportion of indium in the second phase have resulted in high efficiency [9]. The desired final composition of copper-indium diselenide is known to be Cu_{0.95}In_{1.0}Se₂ and the recommended thickness for present device quality CuInSe₂ is in the range 2.0-2.5 μm. Moreover, it has been estimated that during the selenization there is a loss of indium of approximately ~10% in the form of indium selenide. Hence the initial proportions of Cu:In need to be adjusted to 0.85:1.0.

1.2 New Laboratory Facilities

A new laboratory has been established at the Florida Solar Energy Center (FSEC), University of Florida (UCF) for research and development on thin-film solar cells. The equipments and other facilities created at FSEC are briefly described in the following for the information of the PV community. A multichamber vacuum deposition system being used at present for growth of thin films by magnetron sputtering was constructed at FSEC under a project from the Florida High Technology and Industry Council using FSEC/UCF equipment funds [10]. The system consists of a large deposition chamber (~18" diameter x 24" height) pumped with a 1500 l/s cryopump and two-stage rotary pumps lubricated with fluorocarbon pump fluid for corrosion resistance, and a throttled gate valve. The second chamber consists of a 6" six-way cross pumped with a corrosion resistant (200 l/s N₂) hybrid turbomolecular pump equipped with a helical groove stage which provides molecular-drag action for high pressure operation, a two-stage rotary pumps lubricated with fluorocarbon pump fluid, and 4" throttled gate valve. It has mostly ultra high vacuum (UHV) type oxygen-free high-conductivity copper seals. Both the high-vacuum pumps provide clean hydrocarbon-free ambient and also operate in a range of pressures of interest for magnetron processes. The chosen cryopump provides very high pumping speeds for water and other vapors, a high pumping speed for nitrogen and oxygen, and a high capacity for argon, the working gas, for sputtering applications.

The system has three 3" diameter planar magnetron sputtering sources in the large chamber and two UHV type 3" magnetron sputtering sources in the 6"-six way cross chamber. The system is equipped with a dc power supply (~1 KW) and a rf power supply (~750 W) with an air cooled

matching network. Both the supplies can be connected to any of the sputtering sources. Process control and data acquisition is being carried with a microcomputer, data acquisition cards, and RS 232 interfaces. Capacitance and convection gauges with a vacuum gauge control unit fitted with several modules and RS 232 interface are utilized to monitor the pressures in each of the chambers and backing lines. The gas lines and the mass flow indicators and controllers have been mounted for rf and dc sputtering.

At present, the larger 18" diameter chamber is being used for sequential depositions of Mo, Cu, and In thin films for CuInSe₂ thin-film solar cells while the smaller 6" diameter six-way cross is being used for the deposition of Cd, Te, and CdTe thin films for solar cells.

Another vacuum unit having a small chamber consisting of a 6" diameter six-way cross pumped to a base chamber pressure of ~0.02 Torr with a Fomblin-lubricated mechanical vacuum pump was constructed for selenization of Cu/In layers. Since the smaller size, higher base pressure, and limited accessibility were limiting the experimental flexibility, an old vacuum system donated by Martin Marietta Missile Systems was renovated and made available for selenizations. High vacuum of $< 4 \times 10^{-6}$ Torr is obtained routinely in the large (18" diameter and 24" height) bell jar of this vacuum system pumped with a diffusion pump and liquid-nitrogen cooled trap for the purpose of selenization. The system was fitted with electrodes and holders for vacuum evaporation using a power supply (5-10 V, 600 A). With the availability of this system, the selenization process can be controlled fairly well because of the high vacuum, large size, and good accessibility of vacuum evaporation and substrate heating set ups. Also an arrangement has been made for vacuum deposition of Cu/Au back contacts to CdTe solar cells in this system.

A new Lindberg furnace (3" diameter tube, 3 zone, 24" heated length) model 55347 with the control console model 58434-P has been installed in a fume hood with gas-exhaust lines. It has been fitted with a quartz tube and graphite crucibles for the heat treatment, mechanical vacuum pump and gas flow set-up. A new wet chemistry laboratory was installed with a distilled water and 18 M Ω deionizing water units, fume hood, exhaust lines, pH meters, hot plates, ultrasonic cleaners, etc specifically for the thin-film solar cell research.

2. TECHNICAL DISCUSSION

2.1 CdTe THIN-FILM SOLAR CELLS

The structure of CdTe thin-film solar cells consisted of glass/SnO₂:F/CdS/CdTe/back contact (Fig. 1). Soda-lime float-glass substrates coated with SnO₂:F transparent and conducting coatings provided by Libbey Owens Ford (LOF) were utilized in this project. Development of processes for the preparation of CdS and CdTe layers and fabrication of CdTe solar cells is described in the following sections. An arrangement has been made for vacuum deposition of Cu/Au back

contacts.

2.1.1 Solution Growth of CdS Thin Films

Heterojunction partner layers of CdS were prepared by solution growth. $\text{SnO}_2\text{:F/CdS}$ coated glass substrates provided by Solar Cells Inc. were also utilized for the fabrication of some of the solar cells. Solution growth of CdS layers was investigated for use as heterojunction partner in CuInSe_2 and CdTe polycrystalline-thin-film solar cells. Growth from aqueous solutions is an inexpensive, highly reproducible, and easily controllable technique which can yield conformal CdS layers with excellent optoelectronic properties [4-7].

Ammonium acetate or ammonium chloride was added to the buffer solution depending on whether cadmium acetate or cadmium chloride was employed as the Cd source. Thiourea was employed as the source of sulphur ions. The complexing agent was ammonium hydroxide. The experimental set up is shown in Fig. 2. 300 ml experimental solution was prepared by adding preheated stock solutions of cadmium salt and ammonium salt into continuously stirred deionized water at the desired temperature. Stirring has been found to be helpful in promoting ion-by-ion heterogeneous growth on the substrates. The pH was adjusted with ammonium hydroxide. Then clean plain- and $\text{SnO}_2\text{:F}$ -coated soda-lime glass and Si/SiO_2 substrates mounted on a teflon substrate holder were lowered in the solution. A plastic wrap helped in avoiding excessive loss of ammonia. Finally preheated thiourea stock solution was added to the solution. Preheating of the reactants and buffer solutions in the same water bath helped in minimizing temperature fluctuations. CdS layers were grown for 5-30 min. Initially the films were grown without the addition of the ammonium salt into the buffer solution. Optimum conditions for the growth of good quality CdS layers were determined by investigating the CdS films prepared by varying the primary parameters that control the reaction rates over wide ranges viz. cadmium salt concentration (0.001-0.1 M), S/Cd ratio (0.5-5), ammonium salt/Cd salt ratio (0-30), temperature (70-95° C), pH (8-11.5), and reaction time (5-30 min).

A direct relationship was found between the deposition rate of CdS thin films and the growth temperature. Higher kinetic energy at higher temperatures increases the decomposition of the reactants providing a greater amount of cadmium and sulphide ions which become available for deposition. In the CdS thin films grown without the ammonium salt in the buffer solution, the rate of deposition was found to increase with an increase in the pH of the solution up to a pH of 11. The CdS films became much thinner above pH of 11. For CdS growth without the ammonium salt in the buffer solution, uniform and well-adherent CdS films with thickness up to 1000 Å were obtained in the range of pH of 10 to 11. When ammonium salt was added to the buffer solution, the deposition rate of CdS films was found to decrease with an increasing value of pH.

Growth on plain-glass substrates was found to be difficult, slow, and patchy whereas the growth was steady and uniform on a $\text{SnO}_2\text{:F}$ coated glass or Si/SiO_2 substrates, no doubt due to the availability of nucleation sites for the heterogeneous growth.

There was considerable precipitation of homogeneously reacted particulates in CdS layers deposited using cadmium chloride. With cadmium acetate, the homogeneous growth was significantly less and a smoother heterogeneously grown CdS film was visible beneath the homogeneous growth. The films became smooth and specularly reflecting and the amount of precipitated homogeneously grown particles became significantly less when CdS films were grown after adding the ammonium salt to the buffer solution. After considerable experimentation, the following range of optimum conditions was established for the depositions of CdS thin films using the ammonium salt in the buffer solution: growth temperature of $\sim 85^{\circ}\text{C}$, pH of ~ 9.11 , deposition time 6-30 minutes, cadmium-salt concentration in the range 0.001-0.003 M, ammonium salt concentration of 20 times the cadmium salt concentration, and thiourea concentration of 5 times the cadmium salt concentration. Increasing the growth temperature increased the amount of precipitate particles while lowering the growth temperature lowered the amount of precipitate particles. Figure 3 shows a scanning electron micrograph (SEM) of a CdS thin film deposited at 80°C and pH of 9.5 in 30 minutes using the concentrations of cadmium acetate, ammonium acetate, and thiourea of 0.002 M, 0.04 M, and 0.01 M, respectively. It was found that lowering the concentration of cadmium acetate to 0.001 M or increasing the pH of the solution also reduced the amounts of homogeneously precipitated particles in the film still further in conjunction with the ammonium salt in the buffer solution. However, the deposition rates were also reduced in each of these cases. Surface morphologies of CdS thin films deposited using cadmium acetate and cadmium chloride were similar when the ammonium salt was added to the buffer solution.

CdS thin film thicknesses up to $1000\text{ \AA}$ were obtained in the solution growth without the use of the ammonium salt in the buffer solution. Higher thicknesses up to $2600\text{ \AA}$ were achieved when the buffer solution contained the ammonium salt which enhanced the heterogeneous ion-by-ion growth. It was found to be essential to minimize the homogeneous precipitation of CdS particulates in the solution because some of the precipitates reached the substrate and were incorporated in the growing film. However, experimental parameters aimed at minimizing the homogeneous growth also led to a reduced deposition rate and consequently a lower thickness. Attempts to build up the thickness by two or three successive coatings by solution growth were not too successful. The parameters were, therefore, chosen to minimize the density of precipitated particulates.

X-ray diffraction (XRD) patterns from CdS thin films grown on glass substrates using cadmium acetate without the ammonium salt in the buffer solution revealed well defined 111, 220, 311, and 222 reflections from the sphalerite type of face-centered-cubic phase of CdS equivalent to 00.2, 11.0, 11.2, and 00.4 reflections from the wurtzite type of hexagonal CdS phase with an indication of a weak preferential (111) or (00.1) orientation of these phases. Similar but very weak reflections from these phases were observed in the XRD patterns from CdS films grown on glass substrates using cadmium chloride without the ammonium salt in the buffer solution. Very strong (111) or (00.2) reflection indicating a preferential texture of the cubic or hexagonal CdS was observed in the XRD patterns from CdS films grown with the ammonium salts in the buffer solution and either with cadmium acetate or cadmium chloride salt.

Rutherford backscattering spectra (RBS) were obtained at an angle of 185° using a 2 MeV He^+ ion beam incident at an angle of 30° to the normal to the CdS thin film surface. RBS spectrum from CdS thin films deposited on Si/SiO₂ substrates with cadmium acetate or cadmium chloride salt and ammonium salt in the buffer solution under optimum conditions showed the proportion of Cd:S of 1:1. Figure 4 shows the RBS spectrum from CdS thin films deposited on Si/SiO₂ substrates with CdCl₂ and ammonium salt in the buffer solution. The density change during the formation of CdS and void content are indicated by the formula $\text{CdSH}_{2.8}$ where H represents the molar volume of vacancies. X-ray photoelectron spectroscopy indicated deviation from stoichiometry in the surface layers. Here the RBS results are representative of the entire film thickness.

CdS thin films deposited with the ammonium salt in the buffer solution were highly transparent and specularly reflecting, while the films deposited without the ammonium salt in the buffer solution were significantly less transparent because of considerable internal scattering. The superiority of coatings deposited using the ammonium salt in the buffer solution could be seen clearly. The optical transmission of CdS thin films grown using the ammonium salt in the buffer solution and either the cadmium acetate or cadmium chloride salt as the source of cadmium was found to be nearly the same. At lower wavelengths, films grown with cadmium acetate showed better optical transmission while the optical transparency of CdS thin films prepared using cadmium chloride was better at higher wavelengths. Higher transmission at lower wavelengths in the case of the thinner CdS layer represents an additional amount of photons above the bandgap of CdS available for improving the photocurrent of a solar cell. Only those cells such as thin-film CuInSe_2 solar cells in which any diffusion and phase formation occurring during the subsequent process steps would not destroy such a very thin film could benefit from the higher transmission. In these cells, the thin CdS layer is not affected adversely during the subsequent low temperature deposition of ZnO:Al transparent-conducting coating and aluminum front contact grid. Thin film CdTe solar cells, on the other hand, may require CdS thickness of 2500 Å or higher because of the high temperature processing utilized subsequently in the fabrication of CdTe absorbing layer.

The best overall optical properties were obtained for cadmium salt concentration Q in the range of 0.001-0.003 M, thiourea concentration of 3 times the cadmium ion salt concentration i.e. $3 \times Q$, and concentration of ammonium salt in the buffer solution of 20 times the cadmium ion salt concentration i.e. $20 \times Q$ with pH in the range of 9.0 to 9.5 deposition temperature of $\sim 85^\circ \text{C}$, and deposition time of 6-30 min. Much thinner CdS films were obtained when the proportion of ammonium salt in buffer solution was decreased to $10 \times Q$ or when thiourea concentration was reduced to that of the cadmium salt concentration, Q. Higher concentrations of $30 \times Q$ of the ammonium salt in the buffer solution resulted in overall lower optical transmission. Optical transmission at longer wavelengths suffered considerably at lower thiourea concentrations of Q.

Bandgap and direct energy levels calculated from the linear regions of plots of square of optical absorption coefficient versus photon energy were found to be close to the bulk CdS bandgap of $\sim 2.4 \text{ eV}$ in CdS films grown using the ammonium salts in the buffer solution. The value of the direct bandgap was closer to the bulk CdS value in the films grown with cadmium acetate than

in those grown using cadmium chloride.

2.1.2 Preparation of CdTe Thin Films

FSEC has developed a new technique for the deposition of elemental layers of cadmium and tellurium by magnetron-sputtering followed by interdiffusion, CdTe phase formation, and grain growth.

2.1.2.1 Deposition of Cd/Te Layers

Optimization of the deposition process of CdTe solar cells started with the process optimization of individual layers of cadmium and tellurium. The thickness and mass of deposited thin films was measured using profilometry and microbalance respectively. Initially the quantities and elemental proportions of Cd/Te multilayer structures deposited were adjusted to result in a total thickness of 6 μm with an additional amount of tellurium of up to 10 at.%. Excess tellurium was added with an intention of compensating the loss, if any, of Te during the heat-treatment. As discussed below, parameters for heat treatments were optimized to minimize the loss of tellurium and cadmium during the heat-treatment of Cd/Te multilayers. Hence a stoichiometric proportion between quantities of cadmium and tellurium could be chosen. The quantities were adjusted to obtain a thickness of CdTe thin films in the range of 2-6 μm .

Process optimization for deposition of cadmium thin films did not present any problems. The depositions were fairly repeatable. Process optimization basically consisted of adjusting the desired rates of deposition. The deposition was optimized to obtain a rate of $\sim 0.2 \mu\text{m min}^{-1}$ under a sputter-power of 50 W. It has been experimentally verified that the rate could be easily increased several fold. However, a low rate of $\sim 0.2 \mu\text{m min}^{-1}$ has been utilized in the first stage so as to be able to accurately control the thickness of individual layer by manually controlling the deposition time.

The process optimization of tellurium depositions was very challenging. The initial depositions gave a variable rate of 0.02 to 0.04 $\mu\text{m min}^{-1}$. With process conditions optimized for individual layers, the total time taken for the deposition of 4-6 μm CdTe was very high, making the process commercially non-viable. This long duration was mainly due to the time taken by deposition of tellurium layers. Deposition of tellurium needed further optimization so as to reduce the total time of deposition. Optimization of tellurium was very complex; the Ar plasma during magnetron sputtering of tellurium was highly unstable, giving rise to sudden discharges and frequent sputtering-power interrupts. The sputtering-power supply was programmed to reignite the plasma by reaching the maximum set power which is different from the sputtering power set for regular depositions. Hence the maximum set power was carefully adjusted to avoid breakage of the target during reignition of plasma. The sudden discharges were attributed to the nature of the target. Moreover, an appearance of a reacted layer on exposure to atmosphere indicated problems with the target fabrication. After a number of attempts to adjust the parameters, the

target finally broke because of the frequent sudden discharges, sputtering-power interruption and automatic reignition cycles. Even though a vacuum-melted Te target had been ordered, it turned out that because of the processing difficulties, the manufacturer had delivered a powder-pressed target. The manufacturer had not informed FSEC about the change in the process. On being informed about the considerable difficulties being encountered in obtaining repeatable results and final breakage of the target, the manufacturer readily volunteered the information about the change in the process and agreed to refund the total cost of the target. A new manufacturer of a vacuum melted target was identified and a vacuum-melted Te target was procured.

The process of optimizing the individual layers was carried out again. With the new target the deposition rate could be increased considerably. Even though the deposition rates were considerably higher, the sputtering process was not completely smooth. Sudden discharges and occasional sputtering power interrupts still persisted. The occurrence of sudden discharges was found to be related to inadequate cooling of the target, which was believed to cause excessive localized heating. New cooling water lines for target cooling were installed to ensure fast and even cooling. With this modification tellurium sputtering process was optimized to give a controllable deposition at a rate of $\sim 0.25 \mu\text{m min}^{-1}$. Careful analysis of the sputtering source and target installation arrangement have shown that a repeatable and controlled operation of the sputtering process can be achieved only when a good thermal contact between the target and the water-cooled sputtering source is guaranteed. Targets have been found to corrode also from the back side if the thermal contact is not good. Secondly a good electrical contact was found to improve further the controllability, repeatability, and efficiency of the sputtering process. Careful optimization of the sputtering process has allowed to attain a considerable increase in the rates of sputter-deposition. However, as in the case of sputter-deposition of cadmium, a lower rate of $\sim 0.25 \mu\text{m min}^{-1}$ has again been utilized in this first phase so as to be able to accurately control the thickness of individual layer by controlling the deposition time manually. It is estimated that it would be possible to enhance the deposition rates of both cadmium and tellurium so as to achieve the deposition of Cd and Te layers required for obtaining a $4 \mu\text{m}$ thick CdTe thin films in total time of 5-7 min. Achieving such high rates of deposition by sputtering from a compound CdTe target would be very difficult because of the low thermal conductivity and the difficulty of obtaining a satisfactory electrical contact to CdTe.

Improved conditions of target cooling and good electrical contacts were provided to a second powder-pressed tellurium target. The sputtering conditions became controllable. However, heat-treated Cd/Te films sputtered using the powder-pressed tellurium targets were found to be more prone to peeling off than those sputtered using a vacuum-melted tellurium targets. Hence only vacuum melted targets were used for subsequent depositions.

Adhesion and compactness of individual Cd and Te layers were found to influence the adhesion, and formation of pinholes in heat-treated CdTe thin films. The adhesion of Cd and Te layers was found to depend on the nature and cleanliness of the substrate and also on the deposition conditions. Careful cleaning was found to be essential for assuring good adhesion of the individual Cd and Te as well as heat-treated CdTe thin film. Some SnO_2/CdS coated substrates were cut using a diamond wheel. In the process, there was a contamination of the samples by

the oil used as lubricant during the cutting process. Considerable problems of peeling off of heat-treated CdTe layer were encountered when using these substrates. It may be because the lubricant could not be removed thoroughly with common organic solvents such as acetone, petroleum ether, ethyl alcohol, etc. or because the solvents themselves left a contaminant layer which could not be removed during dilute etch of the substrate CdS thin film. Even traces of the contaminants remaining on the laboratory utensils proved quite problematic. The peeling off problem was completely eliminated only after a thorough cleaning of all the substrate-cleaning utensils in ethanol/KOH bath. Adhesion of individual and multiple layers was tested with a peel-off test using an adhesive tape. Cleanliness of the substrates was found to improve adhesion. Cadmium and tellurium layers did not adhere very well to plain-glass substrates probably because of the inert nature of glass. Adhesion improved but was not too good for Cd and Te layers deposited on glass\CdS substrates. This may be due to a weaker bond between CdS and glass.

Very good adhesion was obtained between tellurium films deposited on glass\SnO₂:F\CdS samples especially when CdS layer had received a mild etch in dilute HCl for removal of surface layer prior to mounting in the deposition chamber.

Some of the sputtering conditions were also found to influence the adhesion. These are duration of the time of exposure of the targets to the atmosphere, presputtering of the targets after exposure to atmosphere, sputtering gas pressure, and rate of deposition. Minimization of the duration of exposure to the atmosphere as well as presputtering of the target prior to deposition on the substrate improved adhesion and reduced pinhole density. Further problems can be caused by handling of Cd/Te layered samples. After a careful study, various factors which can cause pinholes in the Cd/Te layered films on glass\SnO₂:F\CdS substrates prior to the heat treatment were identified and eliminated.

2.1.2.2 Heat Treatment of Cd/Te Multilayers

Heat treatments were carried out on Cd/Te multilayer structures on the following substrates: glass, glass\CdS, glass\SnO₂:F\CdS. Optimization of the heat treatment of Cd/Te films was done by controlling the following parameters: pressure, temperature, and rate of temperature rise. The samples were placed in a partially-closed or open graphite crucibles and heated at nitrogen pressures up to 300 Torr in an evacuated quartz tube in a tube furnace. Partial closing obtained by placing thin wires between the crucible and the lid was meant to maintain the vapors of re-evaporating species in the vicinity at the same time allowing equalization of pressure between the quartz tube and the crucible. The heating was done under different pressure conditions. The heating in the tube furnace was programmed to ramp steadily and stop at intermediate levels to obtain equilibrium. At the final stage of heating, the sample was soaked at a maximum temperature for a certain duration. The maximum temperature was determined based on the estimated rates of Cd and Te interdiffusion, vapor pressures of tellurium and cadmium, and their melting points. The heat-treatment aimed at accomplishing the following results without an excessive re-evaporation of reacting species and excessive interdiffusion between CdS and the Cd/Te overlayers: i) complete interdiffusion between Cd/Te layers; ii) CdTe phase formation; and

iii) re-evaporation of excess individual components. Thus attempts were made to avoid re-evaporation of cadmium and tellurium during the initial phases of their interdiffusion and compound formation by maintaining a reasonably high partial pressure of an inert gas viz. nitrogen. On the other hand, a lower background pressure was maintained in the final phase of heat treatment of most experiments, to facilitate the re-evaporation of unreacted cadmium and tellurium.

Heat treatment was initially done for Cd/Te multilayer samples deposited on glass. Excessively high rates of temperature rise were found to result in peeling off of CdTe layers especially on plain glass substrates. Hence the rate of temperature rise was limited to $20^{\circ}\text{C min}^{-1}$. Employing the maximum temperatures considerably in excess of 400°C resulted in the formation of blisters on the film. This can be verified in figure 5 which shows a SEM image of CdTe thin films heated to a maximum temperature of 440°C . Hence the maximum temperature during the heat treatment was limited to 400°C .

For the first set of samples a base pressure of a mechanical vacuum pump was obtained initially. The tube furnace was purged with nitrogen. This process was repeated twice. The tube was continuously supplied with nitrogen while the pumping was throttled so as to maintain a pressure of 300 Torr. The heating process followed is as follows: A ramp rate was adjusted at $20^{\circ}\text{C min}^{-1}$ to successively reach temperatures 200°C , 300°C and 400°C , with a dwell at each of these levels to attain equilibrium. Even though the heat treatment was done in nitrogen atmosphere, the films lost their adhesion and presented a powder-like appearance. SEM study of the films showed that powder-like appearance was due to the globule formation in thin film on glass (Fig. 6).

In the last stage of the earlier heating process, even though the maximum temperature was set to be 400°C , initially there was a small overshooting of the temperature over this limit. In order to avoid this, the heating in the last step was changed as follows: rate of $20^{\circ}\text{C min}^{-1}$ to reach 380°C and a brief dwell, rate of $4^{\circ}\text{C min}^{-1}$ to reach the final value of 400°C and a dwell of 30 minutes. Hence the pressure conditions in the heating process were changed as follows: A base pressure of the mechanical vacuum pump was obtained. The quartz tube was purged with nitrogen gas. The pumping was throttled and the tube was continuously supplied with nitrogen to maintain a pressure of 300 Torr. When the temperature reached 380°C the pressure was brought down to a pressure of 0.2 Torr of flowing nitrogen. Under these conditions, heat treatment was done on Cd/Te multilayer structures on glass\CdS placed in partially-closed graphite crucibles again using the maximum temperature of 400°C . With the new process, the top layer of the samples peeled off from the underlying layer the appearance of which was metallic grayish. The film was partly reflective with numerous pinholes. The peeling off was attributed to poor adhesion of CdS without a $\text{SnO}_2\text{:F}$ underlayer and also because the films had not been etched to remove the surface layer.

Heat treated Cd/Te multilayers on glass\SnO₂:F\CdS substrates in partially-closed graphite crucibles usually presented an uniformly dark appearance. In the heat-treatment process of these structures, the quartz tube in the tube furnace was maintained at a dynamic pressure of ~300 Torr

of nitrogen. In the final stage, the sample was soaked at a maximum temperature in a low vacuum of <0.02 Torr obtained with a mechanical pump filled with inert fluorocarbon fluid Fomblin and fitted with a oil-filtration device. These samples did not show any peeling off. Fairly uniform CdTe thin films have been obtained by this process in most cases. Reaction zones were observed in some cases. The presence of reaction zones was attributed to uneven heating and uneven material loss. Uneven heating was avoided by proper positioning of samples. Very uniform CdTe thin films with thicknesses in the range 2-6 μm have been obtained in these experiments. However, the films were found to possess pin-holes.

Considerable efforts were made to identify the factors which lead to the formation of pin-holes in unheated Cd/Te layers. Based on these efforts, all such factors have been identified and eliminated. Cd/Te multilayers without any pin-holes or blemishes are being routinely fabricated. X-ray diffraction patterns as deposited Cd/Te layers on glass/SnO₂:F/CdS substrate showed the presence of mainly reflections from Cd, Te, and a few weak reflections from face centered cubic form of CdTe $a_0 = 6.48 \text{ \AA}$. (Fig. 7). Use of these samples has resulted in heat-treated samples with a significantly small number of pin-holes. Further experiments were carried out with systematic reduction in the maximum temperature of heat treatment. Samples continued to show only a few pin-holes.

X-ray diffraction studies on the heat-treated samples indicate good CdTe compound formation. XRD pattern in figure 8 shows complete transformation to a highly crystalline, single phase, face centered cubic CdTe thin films with a weak (111) texture of CdTe $a_0 = 6.48 \text{ \AA}$, without any trace of the precursor elements cadmium and tellurium. The peaks are fairly narrow showing a reasonably large grain size even prior to the chloride treatment.

2.1.2.3 Chloride Treatment

Chloride treatment of heat-treated CdTe samples was carried out for improving the grain size. Several of the chloride treatments were carried out at NREL. Samples were dipped in CdCl₂ solution in methanol of various concentrations for varying periods of time and were heated in air or inert gas:oxygen mixtures at $\sim 400^\circ \text{C}$. Samples were cleaned ultrasonically in deionized water and methanol and dried. Uniform, large grain CdTe films have been obtained after experimentation with the various parameters. A significant increase in the grain size was observed in CdTe sample especially those heat-treated at somewhat lower maximum temperature.

2.1.3 Fabrication of CdTe Solar Cells

CdTe thin-film solar-cell fabrication was completed by applying graphite paste contacts after etching the surface of CdTe thin films. Most of the contacting was carried out at NREL. Also an arrangement has been made at FSEC for vacuum deposition of Cu/Au back contacts in the renovated system having a large (18" diameter x 24" height) chamber pumped with a diffusion pump having a liquid-nitrogen cooled trap. Initially, there were problems in applying contacts

to some of the CdTe films because of uneven heat treatment which lead to appearance of different reaction zones. These problems have been solved after ensuring uniformity of heat treatment. Initially most of the cells were badly shorted because of a large number of pin-holes. With the considerable reduction of the density of pinholes, it was possible to measure photovoltaic activity in the completed solar cells. CdTe solar cells showed open-circuit voltages, V_{oc} in the range 320-380 mV. The short-circuit current-densities, J_{sc} were very low. Best values of J_{sc} were only $\sim 5 \text{ mA cm}^{-2}$. Values of the fill factor, FF was very poor. Because of the shorting across the few existing pin-holes and possibly some problems with the ohmic contacts, the current x voltage, $I \times V$ curves showed resistive behavior. Figure 9 shows photograph of a completed CdTe thin-film solar cell. Experiments are continuing for the elimination pin-holes in CdTe thin films after which it would be possible to obtain solar cells with high photovoltaic conversion efficiencies.

2.2 Cu(In_{1-x}Ga_x)Se₂ THIN-FILM SOLAR CELLS

The structure of Cu(In_{1-x}Ga_x)Se₂ thin-film solar cells consisted of glass\Mo\Cu(In_{1-x}Ga_x)Se₂\CdS/ZnO:Al contact fingers (Fig. 10). Soda-lime float-glass was used as substrate material. Development of processes for the preparation of molybdenum, Cu(In_{1-x}Ga_x)Se₂, and CdS thin films and Cu(In_{1-x}Ga_x)Se₂ thin-film solar cells is described in the following sections. The thickness and mass of molybdenum, copper, indium, and CuInSe₂ thin films were measured by profilometry and microbalance techniques.

2.2.1 Deposition of Molybdenum Thin Films

Molybdenum thin films were utilized as back contact layers. Molybdenum coated glass substrates provided by Solarex and Siemens Solar were also utilized in this project. Molybdenum layers presented problems of adhesion mainly because of residual stress. Molybdenum films deposited by magnetron sputtering under normal argon pressure of 5×10^{-3} Torr and high sputtering power $> 150 \text{ W}$ were found to possess considerable residual stress. Some molybdenum films showed cracking and partially peeled off as the thickness was increased to the desired range of 0.9-1.5 μm . This is clearly evident in SEM images in figure 11 a and b.

As discussed earlier the residual stress in refractory-metal films of molybdenum prepared by magnetron sputter deposition probably arise from atomic peening of energetic neutrals incident on the depositing films and the microstructure of tightly packed and oriented grains. Increasing the sputtering gas pressure, reducing the sputtering power, and varying the angle of incidence of sputtered species and reflected neutrals would reduce the kinetic energies of incident species and thus would reduce atomic peening as well as result in a more open, multiply textured structure. Residual stress in such a structure would be less compressive or even tensile.

Experiments were carried out initially to systematically increase the sputtering-argon gas pressure and reducing the power to minimize the residual stress in these films. It was possible to deposit

molybdenum films having thickness of $\sim 1.5 \mu\text{m}$ which did not peel off. However, the deposition rate was found to reduce considerably and it took ~ 90 minutes to deposit a film of $\sim 1.5 \mu\text{m}$ at very high sputtering gas pressures of ~ 0.015 Torr and low sputtering power of < 50 W. Moreover, the resistivity of the films was found to increase partially, counterbalancing advantage of using a thicker molybdenum back contact.

In a second set of experiments moderate argon pressures were maintained and sputtering power was varied alternatively between lower sputtering power for a shorter duration and a higher sputtering power for a longer duration. Films of $\sim 1.3 \mu\text{m}$ were obtained by alternatively sputtering at 50 W for 2 minutes followed by sputtering at 100 W for 5 min. However, films began to peel off at higher thicknesses when alternative depositions were carried out at 50 W for 1 minute and at 100 W for 2.5 minutes.

In a third set of experiments, molybdenum atoms were made incident on the substrates at -45° , 0° , and $+45^\circ$ for equal intervals using moderate sputtering gas pressure and low sputtering power of 50 W. It was possible to obtain routinely thicknesses of $1.5\text{--}1.6 \mu\text{m}$.

Empirical observations have shown that a combination of varying angles of incidence and sputtering power, with an intermittent leak of $\text{O}_2 + \text{H}_2\text{O}$ would lead to a more open microstructure of multiply oriented grains resulting in molybdenum thin films reasonably free of residual stress.

Because of the importance of reducing residual stress in Mo back-contact layers, it was decided to carry out a quantitative evaluation of the residual stresses in these films at the High Temperature Materials Laboratory (HTML) of the Oak Ridge National Laboratory (ORNL). The state-of-art Scintag PTS goniometer with high flux rotating anode x-ray source available at HTML can provide stress and texture analysis with unrestricted 2θ range without serious defocusing problems encountered in 2θ - θ goniometer. Another Scintag PTS goniometer has been added recently enhancing their capabilities still further. After verifying that the samples were suitable for residual stress measurements, a proposal entitled, "Residual Stress Minimization in Mo Thin Films Used as Back Contact in CuInSe_2 Solar Cells" was submitted to ORNL. It was approved. It is proposed to study the residual stress in Mo thin films prepared by magnetron sputtering at FSEC under varying conditions of sputtering-gas pressure, power, and incidence angle. After carrying out the stress analysis at ORNL, the effect of the residual stress on the adhesion and efficiency of CuInSe_2 solar cells will be studied at FSEC. It is also planned to analyze through this project a few Mo samples from each of the participating U.S. manufacturers of CuInSe_2 solar cells.

2.2.2 Preparation of $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ Thin Films

Use of the highly toxic H_2Se gas in the selenization of Cu-In-Ga layers to form CuInSe_2 and $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ thin films was avoided by carrying out the selenization in selenium vapor in a vacuum system.

2.2.2.1 Depositions of Copper-Indium-Gallium Thin Films

Initially copper and indium thin films were deposited on plain soda-lime, float-glass substrates. After optimization of parameters for magnetron sputtering of copper and indium thin films, depositions were carried out on molybdenum coated glass substrates. Most of the depositions consisted of bilayers of copper followed by indium. The residual stress in molybdenum coatings was found to affect the adhesion of Cu/In bilayers in a few cases.

Deposition of copper and indium by magnetron sputtering did not present any undue problems. Earlier it was anticipated that there would be some surface melting and splattering of the indium target at high sputtering power. There was no evidence of surface melting and splattering even at high power especially because of very efficient cooling of the sputtering source. Optimization of the sputtering process, therefore, consisted of calibrating the deposition rate with sputtering power and choosing sputtering power so as to obtain the requisite deposition rates consistently. This made it possible to obtain the desired thicknesses of each layer by adjusting the sputtering conditions and deposition time. As discussed above, the desired final composition of copper-indium diselenide is known to be $\text{Cu}_{0.95}\text{In}_{1.0}\text{Se}_2$ and the recommended thickness for present device quality CuInSe_2 is in the range 2.0-2.5 μm . Moreover, it has been estimated that during the selenization there is a loss of indium of approximately ~10% in the form of indium selenide. The initial proportions of Cu:In were adjusted to 0.85:1.0 to compensate for the possible loss of indium during selenization. Thicknesses of copper and indium were chosen so as to result in the final thickness of CuInSe_2 thin films of 2-2.5 μm .

As discussed below, selenized films were found to be more homogeneous if there was a proper intermixing of Cu/In bilayer prior to placement in the selenization chamber. Hence Cu-In precursor bilayers received a pre-heat-treatment *in situ* immediately after the deposition without breaking the vacuum. Experiments were carried out to study the phase changes in Cu-In layers by *in situ* heat-treatments. Time-temperature profiles were varied with the maximum temperatures in the range 80-155° C. Temperatures above 155° C were avoided because they were found to be detrimental to the formation of a uniform precursor phase. The morphology of the films was studied by SEM. A reaction zone was observed to pass through the film heated to temperatures approximately 10-30° C below the melting point of indium. Globule formation on the surface was observed in extreme cases. SEM photographs of Cu/In precursor bilayer pre-heat treated at >130° C shows surface protrusions (Figure 12 a) and pitting (Figure 12 b). Such a transfer of mass below the melting point has been attributed to large surface velocities of a small (~10%) fraction of atoms at temperatures above 0.8 T_m (where T_m is the melting point of indium).

Intermixing of Cu/In bilayers was analyzed by Rutherford backscattering spectroscopy (RBS) at the University of North Carolina, by X-ray photoelectron spectroscopy (XPS) at the Kennedy Space Center, and Auger Electron Spectroscopy at the University of Central Florida. Samples for RBS analysis were deposited on single-crystal silicon wafers having a ~1 μm thick thermally grown SiO_2 surface layer on the surface. The total thickness of Cu/In layers was limited to ~1000 Å so as to avoid overlap of copper and indium peaks in the RBS spectra. Considerable

intermixing was found to occur either during the deposition itself or during the storage at room temperature. Comparison with simulated spectra showed that neglecting the interdiffusion with the SiO₂ layer, prior to heat treatment intermixing of the bilayer had resulted in a 330 Å thick bottom layer having a composition Cu_{1.0}In_{1.0}, a 250 Å thick middle layer of composition Cu_{0.72}In_{1.0}, and a 600 Å thick top layer with a composition Cu_{0.54}In_{1.0}. After the heat treatment at ~90° C for 10 minutes, the intermixing was found to be complete. The composition of the resultant layer was Cu_{0.79}In_{1.0}. Figures 13 a and b shows RBS spectra of a Cu/In bilayer before and after heat treatment. The simulated spectra in the figures show Cu-In layers interdiffusing with the SiO₂ layer on the substrate. This interdiffusion with the SiO₂ layer has been neglected in the above discussion for the sake of simplicity. As can be seen from the XPS scan of the surface of the Cu/In bilayer prior to heat treatment in figure 14, copper was present on the surface. Depth profiling by XPS and Auger electron spectroscopy, in conjunction with argon-ion etching showed results similar to those from RBS analysis described above. XRD patterns also showed the formation of a completely intermixed Cu₁₁In₉ + In phases. Because of these results showing a complete intermixing and phase formation at the maximum temperatures of pre-heat-treatment of 90-95° C for 10 minutes, the pre-heat-treatments in subsequent experiments were limited to the maximum temperature of 90-95° C for 10 minutes.

Further experiments were carried out to increase the bandgap by adding gallium to form selenized Cu(In_{1-x}Ga_x)Se₂ thin films with $x \approx 0.2-0.25$. Interaction between indium and gallium can lead to a liquid phase because of the formation of a low-melting-point (16° C) In-Ga eutectic. A new process has been developed for the successful incorporation of gallium. Gallium has been incorporated successfully using this process which helps in avoiding the deleterious interaction between indium and gallium. The depth-profiles of the gallium content were varied as follows. Most of the gallium was added near the Mo back contact and a small fraction near the surface.

2.2.2.2 Selenization of Cu/In Layers

Selenization of Cu/In bilayers was carried out mostly using selenium vapor in a vacuum evaporation chamber. Selenium was evaporated from a Knudsen cell type molybdenum boat on to a sample mounted under a ceramic plate heater. Initial selenizations were carried out in a chamber consisting of a 6" diameter six way cross pumped with a Fomblin-lubricated mechanical vacuum pump. The base chamber pressure of ~0.02 Torr obtained with the mechanical vacuum pump excessively limited the mean free path of selenium vapors and hence considerable amount of selenium diffused to other parts of the chamber and was not available for selenization. The smaller size, and limited accessibility also placed considerable constraints on the experimental set-up. Hence an old vacuum system donated by Martin Marietta Missile Systems was renovated and made available for selenization. High vacuum of $< 4 \times 10^{-6}$ Torr is obtained in the large (18" diameter and 24" height) bell jar of this vacuum system pumped by liquid-nitrogen cooled diffusion pump. The selenization process can be controlled fairly well because of the high vacuum, large size, and good accessibility of the vacuum evaporation and substrate heating set-ups in this vacuum system. Initially a backing copper plate was utilized between the heater and the sample for better temperature uniformity. However, at the high substrate temperatures

employed for selenization, the stress caused by the weight of the backing plate caused breakage of the glass in some cases. There was also partial softening of the glass at the corners. Hence the backing plate was removed.

Heating cycle during the selenization consisted of initiating a slow ramp for heating of the selenium boat and warming the sample to $\sim 100^\circ\text{C}$. After achieving the desired selenium evaporation rate, ramping the temperature to 450°C at a rate of $50^\circ\text{C min}^{-1}$, soaking the sample in selenium vapor at that temperature for 40-45 minutes, slow cooling at a rate of $10^\circ\text{C min}^{-1}$ to 350°C with continued selenium evaporation, and finally cooling to room temperature without selenium evaporation. As discussed in the following, the rate of selenium incidence was adjusted equivalent to $25\text{-}50\text{ \AA sec}^{-1}$. As discussed earlier, other groups have achieved the best efficiencies by heating CuInSe_2 films to a maximum temperature of 550°C . Hence in the later experiments, the maximum temperature for selenization of the samples was adjusted at 550°C .

Severe problems of peeling off of the selenized CuInSe_2 thin films have been encountered because of several causes. Firstly, the peeling off of the selenized Cu/In layers was found to be intricately related to the residual stress in Mo films. Hence only the Mo back-contact films having a reasonably low residual stress were utilized for cell fabrication.

Another important factor for avoiding peeling off is the cleanliness of Mo coated samples. The peeling off of selenized layers was seen to be more frequent in the case of Cu-In layers deposited on molybdenum back contact thin films which had received a considerable exposure to the ambient. This was true even for films which had been stored in atmospheric pressure desiccators for a few days. Hence the procedure was modified so as to install one sample immediately after molybdenum films deposition for subsequent Cu-In thin film deposition, minimizing the time of exposure of the film and the vacuum chamber walls to the ambient. The other molybdenum coated samples were kept in the same high vacuum chamber, shielded from Cu and In sputtering fluxes. It has also been found that the peeling off from Mo samples which have been stored for a prolonged period, could be avoided by cleaning by mechanical scrubbing and ultrasonic cleaning in neutral soap solution and deionized water prior to being mounted for Cu/In deposition. This procedure has been found to reduce the peeling off problem after selenization.

A minimum rate of incidence of selenium vapor equivalent to $25\text{ \AA sec}^{-1}$ was found to be essential for complete selenization. Selenization process was quite reproducible when the selenium vapor incidence rate were maintained between $25\text{-}300\text{ \AA sec}^{-1}$. However, the problems of peeling off of selenized films became more frequent when excessive ($>350\text{ \AA sec}^{-1}$) rates of selenium vapor incidence were utilized. Rates of selenium evaporation were found to increase excessively when the selenium source was inadvertently overheated by the sample heater because of their proximity. The source to substrate distances were increased suitably to obtain a uniform deposition rate in the desired range at the same time avoiding the excessive heating of the selenium source. As mentioned above, routine selenizations are being carried out using equivalent selenium evaporation rates of $25\text{-}50\text{ \AA sec}^{-1}$.

The other major improvement was obtained through the use of an innovative two-stage-

selenization process developed at FSEC. As discussed above, large-grain coevaporated CuInSe_2 thin films used in the high efficiency solar cells were prepared by initially maintaining a higher proportion of copper followed by a higher proportion of indium [9]. Experiments were carried out to improve the grain size of CuInSe_2 by first selenizing a Cu(rich)-In layer having Cu proportions of 60-80%, followed by the deposition and selenization of a complementary Cu-In(rich) layer. The process was found to improve the adhesion of selenized films. Hence the new two-stage-selenization process was standardized. The first copper-indium bilayer consisted of the entire thickness of copper required to form the film and only a fraction (~25%) of the indium thickness. As before, this bilayer was homogenized by heating to $\sim 95^\circ \text{C}$ for 10 min *in situ* prior to being removed from the sputtering chamber for selenization in a high vacuum chamber in the presence of selenium vapor. A complementary In layer was then deposited to complete the necessary stoichiometric amount. In this case, no attempt was made to homogenize by heating *in situ* in the sputter-deposition chamber so as to avoid selenium contamination of the chamber. The second selenization was carried out after deposition of the second In layer. The two-stage selenization has been found to eliminate the peeling off and to minimize the pinholes in the selenized CuInSe_2 thin film. This process has been used successfully for the preparation of several well-adherent and homogeneous CuInSe_2 thin films. Figure 15 shows a SEM image of CuInSe_2 thin film.

As discussed above, experiments were carried out to increase the bandgap by adding gallium to form selenized $\text{Cu(In}_{1-x}\text{Ga}_x\text{)Se}_2$ thin films with $x \approx 0.2-0.25$. Addition of gallium mostly near the Mo back contact improved the film properties still further. Well-adherent $\text{Cu(In}_{1-x}\text{Ga}_x\text{)Se}_2$ thin films free from pin-holes are being prepared routinely.

As mentioned earlier, the initial proportions of Cu:(In+Ga) were adjusted to 0.85:1.0 so as to obtain Cu:In proportion of 0.95:1.0 after an estimated loss of $\sim 10\%$ In during selenization. Rough estimates of the composition of CuInSe_2 and $\text{Cu(In}_{1-x}\text{Ga}_x\text{)Se}_2$ ($x = 0.2-0.25$) thin films were obtained by measuring the electrical resistance through the film by contacting molybdenum back layer and the front of CuInSe_2 and $\text{Cu(In}_{1-x}\text{Ga}_x\text{)Se}_2$ films. Very large values of resistance measured through the selenized films indicated a copper deficiency. This was confirmed by composition analysis by electron-probe microanalysis (EPMA) at NREL; proton-induced X-ray emission spectroscopy (PIXE) at UNC, Chapel Hill, NC; and X-ray photoelectron spectroscopy (XPS) at the Kennedy Space Center (KSC), Cape Canaveral, FL. Thus the loss of indium during the selenizations was probably negligible. Copper content in $\text{Cu(In}_{1-x}\text{Ga}_x\text{)Se}_2$ thin films was varied systematically over a wide range. Structure and morphology were studied by XRD and SEM. The resistance of $\text{Cu(In}_{1-x}\text{Ga}_x\text{)Se}_2$ thin films with Cu:In:Ga:Se atomic proportions of 18.9:28.1:2.5:50.5 was in the range of several hundred kilo ohms even approaching 1 M Ω . XRD patterns of these films showed the formation of $\text{Cu(In}_{1-x}\text{Ga}_x\text{)Se}_2$ and $\text{CuIn}_2\text{Se}_{3.5}$ phases (Figure 16). As can be seen in the top and bottom patterns in figure 16, the positions of peaks correspond to reflections from both CuInSe_2 and $\text{CuIn}_2\text{Se}_{3.5}$. However, the intensities correspond to a mixture of the two phases. The resistance through the $\text{Cu(In}_{1-x}\text{Ga}_x\text{)Se}_2$ thin film having Cu:In:Ga:Se atomic proportions of 19.3:27.6:1.3:51.8 was 100-200 K Ω . The copper content in $\text{Cu(In}_{1-x}\text{Ga}_x\text{)Se}_2$ thin films was adjusted to obtain near optimum atomic proportion of Cu:In:Ga:Se of 23.5:25.5:1.5:49.5. These films showed resistance in the range of 50-100 k Ω . XRD pattern

showed the formation of $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ phase (Fig. 17). Study of the morphology by SEM of $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ thin films with the near optimum atomic proportion showed the importance of proper intermixing of Cu:In:Ga precursors prior to selenization. SEM photographs of $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ thin films in which the precursors were homogenized showed large, well-faceted grains (Fig. 18a). On the other hand the grain morphology was inferior in $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ thin films prepared from unhomogenized precursor layers (Fig. 18b).

2.2.3 Solution Growth of CdS Thin Films

The solution growth of CdS on CuInSe_2 followed a process similar to that described above for CdTe solar cells, except that the thickness was limited to ~ 500 Å and that the deposition rate is lower.

2.2.4 Fabrication of CuInSe_2 Solar Cells

Heterojunction-partner and window layers and front contact grids were deposited at NREL and IEC. Undoped- and In-doped bilayer of CdS and aluminum front-contact grid were deposited by vacuum evaporation at NREL. The first set of very-copper-poor and very-high-resistivity CuInSe_2 and $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ thin films with atomic proportions Cu:In:Ga:Se of 18.9:28.1:2.5:50.5 gave open circuit voltages of ~ 300 mV and a very low short circuit current of ~ 1 mA. Six solar cells were fabricated using another sample $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ with some more copper, having a resistance measured through the thickness of the film of 100-200 K Ω , and Cu:In:Ga:Se atomic proportions of 19.3:27.6:1.3:51.8. Even though still quite copper-poor, all the six 0.45 cm² area cells completed with this sample showed photovoltaic conversion with $V_{oc} > 296$ mV, $J_{sc} > 16$ mA, and FF $> 27\%$. Three cells gave an $V_{oc} > 330$ mV, $J_{sc} > 16.9$ mA, FF > 27.7 . One cell showed an open circuit voltage of 331 mV, a short circuit current of 18 mA, however again with a very low fill factor of 28%. The low fill factor was attributed to the excessively large series resistance resulting from the copper deficiency.

At IEC, the heterojunction partner layer consisting of 1- μm thick In-doped CdZnS thin film were deposited on several $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ thin films with the near optimum atomic proportion of Cu:In:Ga:Se 23.5:25.5:1.5:49.5 by vacuum coevaporation. It was followed by deposition of an indium-tin oxide (ITO) window layer and Al contact fingers. Photovoltaic properties of solar cells prepared using the $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ thin films with the near optimum atomic proportion reaffirmed the importance of proper intermixing of Cu:In:Ga precursors prior to selenization. Cells prepared from $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ thin films in which the precursors were not homogenized showed V_{oc} of 378 mV, J_{sc} of 33.4 mA, a fill factor of 60.2% and a conversion efficiency of 7.6%. The best cell obtained with films prepared using precursors homogenized *in situ* prior to selenization gave an open circuit voltage V_{oc} of 377 mV, J_{sc} of 34.8 mA, a fill factor 62.5% and photovoltaic conversion efficiency of 8.2%. A photograph of a completed $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ thin-film solar cell is shown in figure 19. It may be noted in these cells a 1- μm thick CdZnS:In heterojunction layer was used which resulted in the loss of spectral response from high energy

photons. The values of fill factors are low. Based on expected improvements in the fill factor, high photon energy response, and further optimization of elemental proportions and film properties, it is expected to obtain significant improvements in the performance of these solar cells.

3. CONCLUSIONS

A new laboratory has been established at FSEC, for research and development on thin-film solar cells. The process chosen for the preparation of the cadmium telluride layer in CdTe thin-film solar cells consisted of deposition of elemental layers of cadmium and tellurium by magnetron-sputtering followed by interdiffusion, phase formation, and grain growth. Solution growth of CdS layers was investigated for use as heterojunction partner in CuInSe₂ and CdTe polycrystalline-thin-film solar cells. Use of vacuum melted sputtering targets, efficient water cooling, and a good thermal, and electrical contact improved the controllability, repeatability, and efficiency of the sputtering process. Adhesion and compactness of individual Cd and Te layers were found to influence the adhesion, and formation of pinholes in heat-treated CdTe thin films. After a careful study, various factors that can cause pinholes in the Cd/Te layered films on glass/SnO₂:F/CdS substrates prior to the heat treatment were identified and eliminated. Heat treatments of Cd/Te multilayers were carried out in graphite crucibles, in an evacuated quartz tube avoiding excessively high rates of temperature rise and temperatures >400° C. Very uniform, highly crystalline CdTe thin films with thicknesses in the range 2-6 μm and partial (111) texture of face centered cubic CdTe with $a_0 = 6.48 \text{ \AA}$ were obtained. Photovoltaic activity has been measured in CdTe thin-film solar-cell which were completed at NREL. CdTe solar cells showed open-circuit voltages, V_{oc} in the range 320-380 mV, low short-circuit-current densities, J_{sc} of ~5 mA cm⁻², and poor values of the fill factor, FF because of the shorting across the few existing pin-holes and possibly some problems with the ohmic contacts. It is expected to obtain solar cells with high PV conversion efficiencies by elimination pin-holes in CdTe thin films and improvement of ohmic contacts.

Attempts were made to overcome problems of residual stress in molybdenum layers by varying sputtering gas pressure, power, and angle of vapor incidence. The initial proportions of Cu:In were adjusted at 0.85:1.0. Homogeneous Cu-In precursor bilayers were formed by *in situ* pre-heat-treatment to improve selenization using selenium vapor in a vacuum evaporation chamber. The problem of peeling off encountered in some cases was most probably due to the residual stress in molybdenum back-contact layer. An innovative two-stage selenization process has been developed. It has resulted in larger grains and also has helped in elimination of the problems of peeling off. A new process has been developed for the successful incorporation of gallium while avoiding the deleterious interaction between indium and gallium. Cu(In_{1-x}Ga_x)Se₂ thin films in which the precursors were homogenized showed large, well-faceted grains. On the other hand the grain morphology was inferior in Cu(In_{1-x}Ga_x)Se₂ thin films prepared from unhomogenized precursor layers.

Solar cells completed at NREL from the first set of very-copper-poor and very-high-resistivity CuInSe_2 and $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ thin films prepared at FSEC having atomic proportions Cu:In:Ga:Se of 18.9:28.1:2.5:50.5 gave open circuit voltages of ~ 300 mV and a very low short circuit current of ~ 1 mA. Solar cells were fabricated using a $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ sample having Cu:In:Ga:Se atomic proportions of 19.3:27.6:1.3:51.8 showed photovoltaic conversion with $V_{oc} > 296$ mV, $J_{sc} > 16$ mA, and FF $> 27\%$, one cell showing V_{oc} of 331 mV, J_{sc} of 18 mA, and a very low fill factor of 28%, because of an excessively large series resistance.

Several cells were completed at IEC by deposition of 1- μm thick CdZnS:In\NTO\Al fingers on glass\Mo\Cu(In_{1-x}Ga_x)Se₂ samples prepared at FSEC with the near optimum atomic proportion of Cu:In:Ga:Se 23.5:25.5:1.5:49.5. Photovoltaic characteristics of completed cells using $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ thin films having the near optimum composition reaffirmed the importance of proper intermixing of Cu:In:Ga precursors prior to selenization. Solar cells prepared from $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ thin films in which the precursors were not homogenized showed V_{oc} of 378 mV, J_{sc} of 33.4 mA, a fill factor of 60.2% and a conversion efficiency of 7.6%. The best cell obtained with films prepared using precursors homogenized *in situ* prior to selenization gave an open circuit voltage V_{oc} of 377 mV, J_{sc} of 34.8 mA, a fill factor 62.5% and photovoltaic conversion efficiency of 8.2%. Low values of fill factor were attributed to the 1- μm thick CdZnS:In heterojunction layer which also resulted in the loss of spectral response from high energy photons. It is expected to obtain significant improvements in the performance of these solar cells through the use of thinner, conformal CdS layers and cell optimization.

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Fig. 1. Structure of CdTe thin-film solar cells.

Fig. 2. Experimental set up for solution growth of CdS layers.

Figure 3. SEM of a CdS thin film deposited using 0.002 M concentration of cadmium acetate at 80°C.

Figure 4. RBS spectrum from CdS thin films deposited on Si/SiO₂ substrates with CdCl₂ and buffer solution.

Figure 5. SEM image of CdTe thin films heated to a maximum temperature of 440°C showing blister formation due to heat treatment at an excessive temperature.

Figure 6. SEM photograph of CdTe thin film formed by heat treatment of CdTe layers on plain glass.

Fig. 7. X-ray diffraction pattern from as deposited Cd/Te layers on glass/SnO₂:F/CdS substrate.

Fig. 8. X-ray diffraction pattern from a CdTe thin film formed by heat treatment of Cd/Te layers on glass/SnO₂:F/CdS substrate.

Fig. 9. Photograph of a completed CdTe thin-film solar cell.

Fig. 10. Structure of CuInSe₂ thin-film solar cells.

(a)

(b)

Figure 11. SEM images of molybdenum films showing (a) cracking and (b) partially peeling off.

(a)

(b)

Figure 12. SEM photographs of Cu/In precursor bilayer pre-heat-treated at $> 130^{\circ}\text{C}$ showing (a) surface protrusions and (b) pitting.

(a)

(b)

Fig. 13. RBS spectra of a Cu/In bilayer together with simulated spectra: a) before and b) after heat treatment.

Title: CU-IN FILM ON SI(111)/SI02
 Run:042102 Reg: 1 (WIDE) Scan: 1 Base Cts: 3726 Max Cps:1.47787M

Fig. 14. XPS scan of the surface of Cu/In bilayer prior to heat treatment.

Fig. 15. SEM image of CuInSe₂ thin film.

Fig. 16. XRD pattern of $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ thin film having the proportions of Cu:In:Ga:Se of 18.9:28.1:2.5:50.5.

Fig. 17. XRD pattern of $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ having the near-optimum copper content of Cu:In:Ga:Se of 23.5:25.5:1.5:49.5.

Fig. 18. SEM images of $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ thin film prepared using a) unhomogenized precursors and b) precursors homogenized *in situ* prior to selenization.

(b)

(a)

Fig. 19. Photograph of a completed $\text{Cu}(\text{In}_{1-x}\text{Ga}_x)\text{Se}_2$ thin-film solar cell.

REPORT DOCUMENTATION PAGE

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13. ABSTRACT (Maximum 200 words) This report describes work to develop processes for the fabrication of cadmium telluride (CdTe) and copper indium gallium diselenide (Cu(In _{1-x} Ga _x)Se ₂), polycrystalline thin-film solar cells using technologies that can be scaled up for economic manufacture on a large scale. The aims are to fabricate CdTe solar cells using Cd and Te layers sputtered from elemental targets; to promote the interdiffusion between Cd/Te layers, CdTe phase formation, and grain growth; to utilize non-toxic selenization so as to avoid the use of extremely toxic H ₂ Se in the fabrication of Cu(In _{1-x} Ga _x)Se ₂ thin-film solar cells; to optimize selenization parameters; to improve adhesion; to minimize residual stresses; and to improve the uniformity, stoichiometry, and morphology of CdTe and Cu(In _{1-x} Ga _x)Se ₂ thin films and the efficiency of CdTe and Cu(In _{1-x} Ga _x)Se ₂ solar cells.					
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