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Development of smooth CuInGa precursor films for $\text{CuIn}_{1\,-\,x}\text{Ga}_x\text{Se}_2$ thin film solar cell applications

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1. Introduction

Polycrystalline thin film material based on $CuIn_{1-x}Ga_xSe_2$ (CIGS) is a promising candidate as an absorber material for low-cost and high-efficiency photovoltaic devices. High efficiencies were achieved with CIGS thin films, with a world-record efficiency cell of 19.9% [1]. These CIGS thin films were deposited by co-evaporation through a three-step process. However, co-evaporation has difficulties in scaling-up for a large manufacturing system because of its complexity. In addition, large area development of high quality and uniform CIGS films is a challenging task. On the other hand, a two-step process, in which the selenization step follows the sputtering step of the metallic precursors, is easier to scale up and seems to be the most feasible approach for industrial production use.

Co-sputtering of CulnGa precursor thin films, from a dual target approach was proposed to form homogeneous precursor material [2,3]. However, for deposition at room temperature and higher temperatures, In segregates, and forms In-rich islands on the film surface, while the CulnGa precursor film becomes rough and inhomogeneous in structure. In order to obtain compositional uniformity of precursor films, stacked-metal or alloy layers, such as In/CuGa, CuGa/In, CuGa/In/CuGa or In/CuGa/In films, have been investigated [4,5]. Nevertheless, these precursors give rise to In-rich phases on the surface and turn out to have a rough surface morphology. In addition, the surface morphology has an impact on the CdS/CIGS interface properties

ABSTRACT

CulnGa precursor thin films were deposited using a CuGa (75–25 at.%) and an In 3" diameter target material simultaneously by RF magnetron sputtering. The precursor films were deposited on Si and glass substrates at -80 °C and room temperature, and characterized by Rutherford backscattering spectroscopy, Auger electron spectroscopy, scanning electron microscopy, atomic force microscopy and X-ray diffraction. The effects of gun power density and substrate temperatures on resulting precursor film properties were investigated. Precursor films deposited at -80 °C have a smooth morphology with a 75% reduction in all roughness values and are more dense and homogeneous in structure compared to precursors deposited at room temperature. Therefore these precursors will result in better selenization process reproducibility.

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[6]. Since smooth morphology of the precursor results in smooth morphology of the CIGS films, the preparation of CuInGa precursors with a smooth surface is important [3,6–9]. Also, the selenization kinetics and chalcopyrite syntheses depend strongly on the state of the metallic precursor film after deposition. Therefore the precursor film morphology and homogeneity also have a great influence on the reaction process. Because inhomogeneous precursors with In-rich phases on the surface result inhomogeneous precursor/Se interfaces, it is possible that, in this system, substantial fluctuations in the absorber synthesis kinetics yield problems of inhomogeneous absorber synthesis. Co-sputtered precursors deposited at room temperature vield smoother and more homogeneous thin films then sequentially sputtered precursors at room temperature and the smooth precursor films presented in this work are even more homogeneous and have a better surface morphology then the co-sputtered precursors deposited at room temperature and, therefore, could result in more homogeneous absorber layers, and may result in better device efficiencies [10,11]. Because of the strong influence of the precursor sputter process on the surface morphology, homogeneity and the related absorber formation, it is of great importance to have smooth and homogeneous precursor thin films.

It has been reported that evaporation of single elemental layers on a substrate cooled to -160 °C resulted in smooth Cu and Ga thin films [12]. However, the cooled-substrate approach was not further investigated in the form of multi-compound thin films obtained by co-sputtering.

In this work, we report the deposition of CuInGa precursor films at substrate temperature below and at room temperature. The dependence of the chemical composition, sticking coefficient, morphology

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and crystal structure of the precursor thin films on the temperature of the substrate was also investigated.

2. Experimental details

CulnGa precursor thin films were deposited by RF-magnetron cosputtering on $1'' \times 1''$ Si and glass substrates. The sputter deposition of the precursor films was performed in an ATC 1800F PVD high vacuum sputtering chamber (AJA International, Inc), equipped with a load-lock and two co-focal sputtering guns for both a CuGa (75–25 at.%) (99.9% purity) and an In (99.995% purity) 3" diameter target material. Prior to film deposition, the chamber base pressure was $1.01*10^{-6}$ Pa Before deposition, the substrates were cleaned with ethanol and DI-water and plasma-cleaned for 2 min in an Ar plasma.

The precursor films were deposited at a pressure of 0.56 Pa, with an Ar flow of 80 sccm and a deposition time of 2700 s with a target-to-substrate distance of ~10 cm, and the substrate temperatures were -80 °C and room temperature, this resulted in ~600 nm films. The process parameters varied in this work were the ln gun power, and substrate temperature. The gun power study was performed to obtain the desired chemical composition in the precursor films of 0.25<Ga/(ln+Ga)<0.30 and 0.88<Cu/(ln+Ga)<0.95 [13,14]. The substrate temperature was measured with a thermocouple attached to the substrate surface before and after each deposition, while the samples were in the load-lock.

The In gun power was varied from 99 to 123 W with 6 W increments resulting in 5 samples for each substrate temperature. The CuGa gun power was fixed at 138 W and the substrate temperature was approximately -80 °C or room temperature. During precursor film deposition at -80 °C, the substrate temperature increased from -80 °C to -35 °C as a result of particle bombardment and heat conduction of the sample holder.

For depositions at -80 °C, the substrates were mounted on the Al sample holder using carbon tape to increase heat conductance, this was placed in a sealed bag filled with N₂ gas and cooled to -80 °C in liquid N₂ before being loaded into the vacuum chamber. Because the substrate temperature increased significantly during the depositions at -80 °C, a 1″ thick, 8″ diameter Al slab was used as a sample holder in this case. This increased the heat capacity of the substrate holder and kept the substrate temperature, a regular Inconel sample holder was used.

The precursor films where characterized by Rutherford backscattering spectroscopy (RBS), Auger electron spectroscopy (AES), scanning electron microscopy (SEM), atomic force microscopy (AFM) and X-ray diffraction (XRD) for chemical composition, surface morphology and crystallographic structure.

Bulk chemical composition was measured using RBS on a Dynamitron linear accelerator at a 1×1 mm primary He⁺ ion beam energy of 2.0 MeV with a 2 μ C collected current. The RBS data was simulated by XRump to obtain the chemical composition versus film depth. By integrating the chemical compositions as a function of depth and dividing this by the film thickness, the bulk chemical composition was obtained.

Compositional depth profiles were measured using AES. Auger analyses were performed using a Perkin-Elmer Physical Electronics Model 660 Scanning Auger Microprobe. The samples were mounted on stainless steel stages and inserted into the analytical chamber via a vacuum load lock. All of the analyses were performed using a primary electron beam energy of 5 keV producing $1.0 \,\mu$ A of specimen current with a beam diameter of approximately 5 μ m. Compositional sputter depth profiling was accomplished by milling the surface with a 3 keV argon ion beam, while monitoring the elemental peaks for the film species as a function of sputter time. These data were later converted to relative atomic composition versus depth by applying the most appropriate relative sensitivity factors, measured by Rutherford Backscattering Spectroscopy, and the sputter rate for SiO₂, of ~14 nm/min under these conditions. The vacuum in the analytical chamber was typically $< 6.67 * 10^{-7}$ Pa before introducing the sputter gas.

Surface morphology by top view imaging and thickness by cross section imaging of the precursor films were performed using a Carl Zeiss 1550 Schottky source electron microscope operating at 10 keV. The Z-range, average roughness and root mean square (RMS) roughness values of the precursor film surfaces were measured by a Veeco AFM, using tapping mode on a $10 \times 10 \,\mu\text{m}$ scan size having 256×256 data points.

The crystallographic structure of the film was analyzed by XRD and carried out using a Scintag X-ray diffractometer equipped with a Cu $\kappa\alpha$ X-ray source ($\lambda=1.54$ Å) and a horizontal wide-angle four-axis goniometer with stepping motors which allowed independent or coupled theta/2-theta axes motion. XRD patterns were collected using a Theta/2-theta scan. The collected XRD patterns were compared to reference patterns from the standard Joint Committee or Powder Diffraction Standards (JCPDS) powder diffraction file (PDF).

3. Results and discussion

A chemical property investigation and a thorough micro-structural film property investigation were performed for the set of precursors. For the precursor samples, the desired chemical composition was obtained using an In gun power ranging from 117 to 123 W and 111 to 117 W with a fixed CuGa gun power of 138 W at approximately -80 °C and room temperature substrates, respectively. The RBS results for this series of sample are shown in Fig. 1. It can be seen that the sticking coefficient of Ga relative to Cu stayed constant while the sticking coefficient of In relative to Ga and Cu increased from the temperature range of -80 °C to room temperature. It has already been reported that the sticking coefficient of In versus Ga and Cu increases in the temperature range of room temperature to 140 °C [15]. Based on the results published by R. Diaz et al., we estimate that the sticking coefficient of In versus Ga and Cu further decreases as the substrate temperature decreases from room temperature to -80 °C while the sticking coefficient of Cu versus Ga remains constant.

Fig. 2a displays an AES profile of Cu, In and Ga composition versus depth for precursor films with the desired chemical composition deposited on a Si substrate at -80 °C with a 117 W In gun power. The Cu, In and Ga concentrations versus thin film depth stayed constant in the



Fig. 1. RBS chemical composition results of CulnGa precursors versus In gun power for -80 °C and room temperature substrates with fixed CuGa gun power of 138 W.

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Fig. 2. AES results of CulnGa precursors with desired chemical composition deposited at (a) -80 °C and (b) room temperature respectively.

bulk with an In content of roughly at 37 at.% and a Cu:Ga ratio was roughly 3:1. It was observed that In segregates toward the surface of the film but its diffusion is retarded due to the low deposition temperature, as can be seen in comparison with Fig. 2b, which displays a similar depth profile and chemical composition of a precursor film deposited on a room

temperature Si substrate with a 111 W In gun power. In this AES profile the In content in the bulk is not constant versus depth and increases from 22 to 32 at.% while the Cu:Ga ratio is roughly 3:1. The chemical potential of the Cu-In-Ga system can be reduced by In segregation, according to the Ga-In phase diagram which shows that only a small fraction of In can be dissolved in Ga at room temperature [16]. If the temperature could be kept constant at -80 °C or lower by using a cooling stage in the vacuum chamber, the In content could be completely quenched in the CuGa system resulting in a lateral and transversal homogeneous deposition of precursor thin films. For surface diffusion of In on a Cu surface, the diffusion constant D (cm²/s) increases linearly by one order of magnitude with an increase of 30 °C in the range of room temperature to 70 °C [17]. It can be assumed that the diffusion constant will decrease further in the range of room temperature to -80 °C, and will result in less In diffusion toward the film surface and prevent In agglomeration in the form of islands on the surface for precursor films deposited at -80 °C. The morphology of the precursor thin films stays virtually unchanged even though the crystallographic phases become similar at a post anneal at 200 °C [10,11]. The oxide on the Si interface shown in Fig. 2a was due to water crystallizing on the cold substrates when moving the substrate from the cooling set up into the vacuum chamber, and reacting with the bombarding Cu-In-Ga flux.

The surface morphology and thickness of the precursor films with the desired chemical composition can be seen in the SEM top view and cross section images shown in Fig. 3 for films deposited with a 117 and 111 In gun power at -80 °C and room temperature Si substrates respectively. Both films had an approximate thickness of 600 nm and showed a significant difference in surface morphology. The precursor film deposited at -80 °C, Fig. 3a and c had a smooth, homogeneous and dense appearance and was therefore laterally more homogeneous in structure. The precursor films deposited at room temperature, Fig. 3b and d, had an open structure with In islands on the surface.

To obtain roughness values, the precursors deposited at -80 °C and room temperature glass substrates were analyzed by AFM. The surface roughness comparison of the precursors with desired chemical composition deposited with a 117 and 111 ln gun power at -80 °C and room temperature glass substrates, respectively, is displayed in Fig. 4a and b. Precursor films deposited at -80 °C had a smooth morphology with a 75% reduction in all roughness values and are laterally more



Fig. 3. SEM cross section and top view images of a CulnGa precursors with the desired chemical composition on Si substrates deposited at (a and c) - 80 °C and (b and d) at room temperature, respectively.

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Fig. 4. AFM top view images of CulnGa precursors with the desired chemical composition deposited at (a) -80 °C and (b) room temperature respectively.

homogeneous in structure compared to precursors deposited at room temperature. All precursor films deposited at -80 °C had RMS roughness values <35 nm, while precursor films deposited at room temperature exhibited RMS roughness values >150 nm.

The crystallographic structure of the precursor films was revealed by XRD. There were ternary CulnGa peaks present for the precursors deposited at -80 °C but these were absent in the precursor material deposited at room temperature. For precursors deposited at -80 °C, the Cu₁₁In₉ phase will incorporate Ga to form Cu₁₁(In,Ga)₉. As a result the Cu₁₁In₉ (002) and (313) diffract, the reflection will shift from 29.85° 20 to 30° 20 and from 42.31° 20 to 42.75° 20.

A change in In content of 31 to 41 at.% did not result in a difference in peak position in precursor films deposited at the same temperature. Different metallic peak positions were observed for precursor films deposited at -80 °C compared to those at room temperature. Fig. 5a shows an XRD pattern of a precursor film with the desired chemical composition deposited on a -80 °C glass substrate with a 117 W In gun power. It had dominant Cu₁₁(In,Ga)₉, CuIn and In peaks along with less dominant Cu₃Ga and Cu₉Ga₄ peaks, indicating a thorough mix of the Cu–In–Ga content in the precursor film, which is in agreement with its AES and RBS spectra. The PDF card files used for analysis were PDF#: 41-0883, 35-1150, 05-0642, 44-1118, 44-1119 and 71-0458.

Fig. 5b shows an XRD pattern of a precursor film with the desired chemical composition deposited on a room temperature glass substrate with a 111 W In gun power. Here we can see multiple In peaks, which reveal a large presence of elementary In, which is also in agreement with its AES and RBS spectra. Furthermore, there were dominant $Cu_{11}In_9$ and CuIn peaks and less dominant Cu_9Ga_4 and $CuGa_2$ peaks present, indicating a significantly less homogeneous precursor material compared to the precursor films deposited at -80 °C. The PDF card files used for analysis were PDF#: 41-0883, 35-1150, 05-0642, 02-1253, 71-0458 and 25-0275.

The characterization results revealed information on the microchemical and micro-structural properties of the precursor films. The findings supported the hypothesis that depositions at -80 °C result in dense, homogeneous and smooth precursor films due to the retardation of diffusion of In out of the Cu–Ga system. There is a strong correlation between substrate temperature and crystallographic structure, density, homogeneity and surface morphology. The precursor material was quenched on cold substrates, locking the particles in place and resulting into homogeneous, smooth and dense thin films. The precursor films were deposited for 2700 s to obtain 600 nm films. Other groups have reported CuInGa precursor thin films with RMS roughness values <200 nm [18] for the same precursor film thickness. In this work we were able to produce dense, smooth and



Fig. 5. XRD patterns of CulnGa precursors with the desired chemical composition deposited at (a) -80 °C and (b) room temperature, respectively.

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homogeneous CuInGa precursor thin films with RMS roughness values below 35 nm.

4. Conclusions

In summary, a low substrate temperature CuInGa precursor sputter process has been developed which yields dense, smooth, and homogeneous precursor films with RMS roughness values <35 nm compared to rough and inhomogeneous precursors deposited at room temperature with RMS roughness values >150 nm. This dense, smooth and homogeneous morphology leads to a better precursor/Se interface which ultimately results in better process control and uniform chalcopyrite syntheses. By depositing at -80 °C, it is possible to alloy Cu, In and Ga to form the ternary phase Cu₁₁(In,Ga)₉, which gives rise to a homogeneous mixture of species. This ternary phase leads to device-quality CIGS [19]. With depositions below room temperature it is possible to lock the particles in place and retard diffusion of the constituents, leading to a smooth surface morphology. It is also possible to give rise to a concentration gradient of the constituents for instance to have a CuGa rich surface that leads to higher device performance [20]. By quenching the particles in place, this technique gives rise to a broad scale of possibilities for precursor formation leading to uniform chalcopyrite synthesis kinetics because of the homogeneous nature of the precursor/Se interface.

Results were presented from the RF magnetron co-sputtering of CuGa and In targets for the deposition of CuInGa precursor thin films with the desired chemical composition of 0.25 < Ga/(In + Ga) < 0.30 and 0.88 < Cu/(In + Ga) < 0.95. Tight control of films' morphology, density and process reproducibility were achieved through the deposition parameters. The desired chemical composition was obtained for an In gun power of 117 to 123 W and 111 to 117 W for -80 °C and room temperature substrates, respectively, with a fixed CuGa gun power of 138 W.

When comparing samples deposited at -80 °C with those deposited at room temperature, a difference in sticking coefficient was observed. In the literature, an increase of the In sticking coefficient versus Ga and Cu and a constant sticking coefficient of Ga versus Cu was reported in the temperature range of room temperature to 140 °C.

With the results reported in this work we can conclude that the sticking coefficient of In versus Ga and Cu further decreases in a substrate temperature range of room temperature to -80 °C, while the sticking coefficient of Ga versus Cu remains constant, and is an extrapolation of the results published by R. Diaz et al. [13].

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