Structural and Electronic Characteristics of Cu(In,Ga)Se₂ Thin Films Sputtered From Quaternary Targets

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Abstract — Although the advantages of sputter deposition for large area, uniform deposition are well known, it has long been believed that sputtering Cu(In,Ga)Se₂ (CIGS) from a quaternary sputtering target yields films with morphological and electronic properties that make them unsuitable for use in high-efficiency photovoltaic devices. Recent work, however, has demonstrated that this deposition method can produce dense, polycrystalline, highly oriented films with the desired stoichiometry. Devices built with these films exhibit efficiencies >10%. While effective parameters for target composition and deposition conditions have been achieved, variation from these conditions can result in a wide array of morphologies, even while composition remains near that of stoichiometric CIGS. In this paper, we review the broad range of structural and electronic properties that result from various sets of target compositions and deposition conditions. Films deposited under some conditions are similar in important respects — their composition, a dense structure composed of ~1 μm sized grains, and the presence of a MoSe₂ layer — to those of evaporated CIGS. We discuss how these results point towards the possibility of higher-efficiency sputtered CIGS.

Index Terms — copper compounds, grain size, photovoltaic cells, solar energy, sputtering, thin film devices, thin films.

I. INTRODUCTION

Thin film Copper Indium Gallium Diselenide (CIGS) has rapidly become an important photovoltaic material, competing for market share with silicon and other more established technologies. Device efficiencies have increased significantly, with recent reports of approximately 20% efficiency for an individual cell [1], [2] and 15.7% for a module [3].

One common deposition method, for both laboratory and commercial devices, is co-evaporation from multiple sources. This method has yielded the best efficiencies in laboratory devices [1], [2] and is one of the standard methods used in the manufacture of commercial devices. While much progress has been made in scaling co-evaporation for production, there are several disadvantages associated with this technique. As a result of the point source nature of typical evaporation sources, uniform deposition over large areas is difficult. In addition, simultaneous control of all four sources can be challenging, with variations in relative deposition rate potentially leading to incorrect stoichiometry and diminished device performance.

Another method of fabricating CIGS films is by sputtering the metals, Cu, In, and Ga, either in a selenium environment or followed by a post-deposition selenization step [3]. Alternately, multiple metal depositions can be interspersed with Se treatments. These techniques have the advantages typically associated with sputtering – good uniformity over large areas and high deposition rates. For these metal sputtering methods, Se is typically supplied either by use of H₂Se gas or by Se vapor thermally generated from a solid source. While both of these methods of supplying Se have been shown to produce good quality CIGS films, each method has drawbacks. H₂Se gas, though widely used, is highly toxic. Supplying Se vapor from a solid source complicates the deposition process, requiring the Se concentration to fall within a prescribed range.

Sputtering from a single quaternary target could maintain the advantages of sputtering while greatly simplifying the fabrication process. This approach has received only limited treatment in the literature. Several groups have used sputtering to deposit CIGS [4]-[7] films directly from compound chalcopryte targets (i.e., targets that contain the metals as well as Se), and only recently, working devices that incorporate such films have been demonstrated [5]-[7]. We have deposited films using a large variety of target compositions and processing conditions. Many sets of parameters have led to films with undesirable morphologies or poor electronic properties. A set of processing conditions has been found, however, that results in films with stoichiometric composition, a dense structure composed of ~1 μm sized grains highly oriented in the (112) direction, and an observable MoSe₂ layer at the Mo-CIGS interface. Devices using films produced under these conditions exhibit efficiencies as high as 10.6%.

II. EXPERIMENT

Bulk CIGS was formed by heating high purity (>99.999%) precursors in a vacuum-sealed quartz ampoule. The bulk material was ground into a powder inside a nitrogen-purged glovebox, and sputtering targets were formed by hot pressing the powder into 3” diameter disks. The disks were then
machined to the proper dimensions and indium bonded to a copper backing plate.

Soda lime glass (SLG) samples with a 500 nm to 1 µm thick layer of sputtered Mo were used as substrates. CIGS films, approximately 2 µm in thickness, were prepared by RF magnetron sputtering in a sputter-up geometry. This process was carried out in an Ar atmosphere, typically at a pressure of 3 mT. The substrate temperature, RF power, post-annealing conditions, and the excess selenium content in the deposition chamber were varied. After removal from the deposition chamber, some samples were used for CIGS film characterization, and others remained in the process line for device fabrication. For device samples, approximately 50 nm of CdS was deposited via chemical bath deposition, and 50 nm of ZnO was deposited by sputtering. A 200 nm thick layer of Al2O3:ZnO was deposited by sputtering to serve as the top contact. Ni/Al grids, composed of 50 nm of Ni followed by 400 nm of aluminum, were deposited via evaporation. Samples were scribed by hand to obtain individual cells, each with an area of approximately 0.45 cm².

Samples for cross sectional scanning electron microscope (SEM) analysis were obtained by mechanically breaking samples. Energy dispersive spectroscopy (EDS) with standardless calibration was employed to determine the film’s composition. Samples for transmission electron microscope (TEM) analysis were capped with Pt and prepared for imaging by the focused ion beam (FIB) lift-out technique. Composition as a function of depth was obtained by use of secondary ion mass spectroscopy (SIMS) with ion beam milling. Light J-V curves were obtained in a solar simulator under one sun, AM 1.5G illumination. External quantum efficiency (EQE) was also measured.

III. RESULTS AND DISCUSSION

Sputtering targets with a variety of compositions were fabricated. These include a stoichiometric target with a composition of CuIn0.53Ga0.47Se2, a Cu-poor target with a composition of Cu0.7In0.3Ga0.7Se2, and a near-stoichiometric target with a composition of CuIn0.3Ga0.7Se2.06. The composition of the latter target was chosen so that even with a small amount of Se lost to the vapor phase during target fabrication or sputter deposition, there is still sufficient Se present. The excess Ga is added in stoichiometric proportions for Ga2Se3, in order to incorporate the Se into a secondary phase that is more stable during heating. Interestingly, EDS measurements showed that all target compositions resulted in films with the same stoichiometry, within the sampling error of the detection method, providing that the substrate temperature was maintained above 400 °C during deposition. Morphology, however, varied significantly. Targets with far-from-stoichiometric compositions, as well as co-sputtering from a Se target to incorporate excess Se, resulted in undesirable µm-scale pillars, platelets, and boulders. The morphology most closely resembling that of evaporated films was obtained with the near-stoichiometric target, a substrate temperature near 550 °C, sputtering power of 200 W, and no excess Se introduced during deposition. The latter set of parameters will be referred to as “standard conditions.” Fig. 1 shows some representative images of desirable and undesirable morphology. The images show films sputtered from a Cu-poor target, films co-sputtered with Se, and films deposited from the near-stoichiometric target with standard conditions.

![Fig. 1. SEM images showing the (a) top view, and (b) cross section of a film sputtered from a Cu-poor target; the (c) top view, and (d) 45° inclination image of films co-sputtered with Se; and the (e) top view, and (f) cross section of films deposited with standard conditions.](image)

Using the near-stoichiometric target, deposition conditions were varied to examine their effects on film properties. Fig. 2 shows grain size, estimated from SEM images, as a function of substrate temperature during deposition. The maximum temperature used was about 600 °C, higher than the 550 °C maximum working temperature of the glass. While these substrates were warped after deposition, it was still possible to obtain images of the films. Fig. 2(a) shows that grain size exhibits an exponential dependence on substrate temperature, similar to the behavior observed in evaporated CIGS [8]. The same data is plotted on an Arrhenius plot in Fig. 2(b). The activation energy for grain growth can be found using the equation

\[
E_A = -R \frac{\partial (\ln(d))}{\partial (1/T)}
\]

(1)

Where \(E_A\) is the activation energy, \(d\) is grain size, \(T\) is temperature in Kelvin, and \(R\) is the gas constant. In this case,
$E_a=18.7 \text{ kJ/mol}=193 \text{ meV}$. It has previously been shown that deposition power also affects film properties [6], [7].

TEM images reveal further details about the films’ structure. Fig. 3 shows a cross section of a device sample. Large grains, continuous from the base to the top of the CIGS layer, are evident. During FIB thinning, some of the smaller grains near the Mo interface pulled out, exaggerating the appearance of pores near the base. This image shows that small grains are present near the base of the CIGS film while there are larger grains with fewer boundaries near the top. The inset shows a high resolution TEM image of the Mo-CIGS interface. The presence of MoSe$_2$ layer is evident at atomic resolution.

SIMS measurements with depth profiling, shown in Fig. 4, indicate that composition throughout most of the thickness is nearly constant. The Na content is higher near the Mo/CIGS interface, and Cu content is lower near the top surface. The presence of Mo within the base of the film is consistent with the presence of a MoSe$_2$ layer.

![Fig. 3. TEM image showing the cross section of a CIGS device. The inset shows HRTEM profile of the MoSe$_2$ layer at the Mo-CIGS interface.](image)

The fact that the film is Cu-poor near the surface is consistent with the absence of a significant amount of CuSe$_2$, a phase that is present with many deposition processes and necessitates etching in KCN.

![Fig. 4. SIMS profile of a CIGS film. Na and K concentration are shown on the left axis, and the concentrations of other constituents are shown on the right axis.](image)

Device samples were fabricated using the near-stoichiometric target and the standard processing conditions described above. After CIGS deposition, no further processing steps (i.e., no KCN etch, selenization, or annealing) were carried out before deposition of the rest of the stack. Fig. 5(a) shows light $J$-$V$ curves for such a device with a conversion efficiency of 10.6%. For this device, $J_{sc}=33.8 \text{ mA/cm}^2$, $V_{oc}=489 \text{ mV}$, and the fill factor is 64.3%. The dark $J$-$V$ curve for this device is shown in Fig. 5(b). The EQE, shown in Fig. 5(c), is greater than 80% for short wavelengths but is degraded at the base. This behavior may be due to the presence of the
small grains near the Mo-CIGS interface evident in the SEM and TEM images.

The presence of grain boundaries would affect the diffusion length and transport of carriers through this layer reducing the short circuit current at longer wavelengths as shown in Fig. 5(c). Taken together, these results suggest that the greatest gains in performance for these devices may be achieved by understanding the nucleation and grain growth during deposition and finding ways to mitigate the formation of small grains near the base.

I. CONCLUSIONS

We describe the structure and composition of CIGS films deposited from a single sputtering target by RF magnetron sputtering. When used to make photovoltaic devices they yield efficiencies >10% without any additional processing. The films are similar in structure and composition to evaporated CIGS. While grain sizes are on the order of ~1 μm through most of the film, small grains form near the base. Mitigating this effect has the potential to greatly improve device performance.

REFERENCES