



Growth of $\text{Cu}_2\text{ZnSnS}_4$ absorber layer on flexible metallic substrates for thin film solar cell applications



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ABSTRACT

In this work, $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) absorber layers were fabricated using a two-stage process. Sequentially deposited Cu–Zn–Sn thin film layers on metallic foils were annealed in an $\text{Ar} + \text{S}_{2(g)}$ atmosphere. We aimed to investigate the role of flexible titanium and molybdenum foil substrates in the growth mechanism of CZTS thin films. The Raman spectra and X-ray photoelectron spectroscopy analyses of the sulfurized thin films revealed that, except for the presence of Sn-based secondary phases, nearly pure CZTS thin films were obtained. Additionally, the intense and sharp X-ray diffraction peak from the (112) plane provided evidence of good crystallinity. Electron dispersive spectroscopy analysis indicated sufficient sulfur content but poor Zn atomic weight percentage in the films. Absorption and band-gap energy analyses were carried out to confirm the suitability of CZTS thin films as the absorber layer in solar cell applications. Hall effect measurements showed the p-type semiconductor behavior of the CZTS samples. Moreover, the back contact behavior of these metallic flexible substrates was investigated and compared. We detected formation of cracks in the CZTS layer on the molybdenum foils, which indicates the incompatibility of molybdenum's thermal expansion coefficient with the CZTS structure. We demonstrated the application of the magnetron sputtering technique for the fabrication of CZTS thin films on titanium foils having lightweight, flexible properties and suitable for roll-to-roll manufacturing for high throughput fabrication. Titanium foils are also cost competitive compared to molybdenum foils.

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1. Introduction

To meet the worldwide energy demand in green technology in a cost competitive way, cheap and readily available clean energy systems are needed. Solar power is the most economic and powerful energy source among the renewable energy sources. Over the last few decades, the low cost and easy fabrication of thin film solar cell technology has allowed it to compete with conventional Si wafer technology and to take a major market share in the photovoltaic (PV) industry. Recently, the use of $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) as an absorber layer in thin film solar cell technology has been investigated. Moreover, this material is already being considered as a replacement for conventional chalcogenide-based absorber layers ($\text{CuIn}_x\text{Ga}_{1-x}\text{Se}_2$ and CdTe). In fact, this replacement is urgently needed in the PV industry due to the restrictions on the usage of the heavy metal Cd and the scarcity and high cost of In and Ga. CZTS is a p-type quaternary compound semiconductor that is stable in the kesterite structure. The CZTS kesterite crystal structure with a large absorption coefficient ($\geq 10^4 \text{ cm}^{-1}$) has a band gap energy of approximately 1.4–1.6 eV [1]. Beyond these beneficial physical properties,

CZTS consists of earth-abundant, cheap, and non-toxic elements. These features have led researchers to focus on the CZTS compound for use in solar cell technology. Currently, efficiencies up to 9.2% and 12.6% have been achieved for the kesterite structures $\text{Cu}_2\text{ZnSnS}_4$ [2] and $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ [3], respectively. Theoretical calculations based on the Shockley–Queisser limit for a single p–n junction with a band gap of 1.4 eV claim that an approximately 33.7% maximum solar conversion efficiency using an AM 1.5 solar spectrum can be generated [4]. For these reasons, the CZTS compound semiconductor will be the preferred material for thin-film PVs in the immediate future.

Several methods have been used in the fabrication of CZTS thin film absorber layers, such as atomic beam sputtering [5], e-beam evaporation [6], thermal evaporation [7], magnetron sputtering [8–11], electrodeposition [12,13], spray pyrolysis deposition [14,15], pulsed laser deposition [16], etc. Most of these techniques were carried out using rigid substrates such as bilayer molybdenum (Mo) coated soda lime glass (SLG). However, the deposition of the CZTS absorber layer on flexible substrates may open a wide range of application areas for large area thin film solar cell fabrication [17]. Metallic foils, such as Cr-steels, titanium (Ti), Mo, aluminum and some alloys are promising flexible substrates because they are cheap, lightweight, durable, and resistant to high-temperature fabrication processes. Additionally, metallic flexible substrate utilization eliminates

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the need for the deposition of a metallic conductive back contact layer. As a result, the cost of manufacturing and constructing solar cell modules would be substantially lowered by using flexible metallic substrates. The preferential flexible substrates should have well-matched coefficients of thermal expansion (CTE) (i.e., $5\text{--}12 \times 10^{-6} \text{ K}^{-1}$), sufficient thermal ($T \geq 400^\circ\text{C}$) and chemical resistivity (especially against S and Se), and should be suitable for a roll-to-roll deposition, in addition to being cost efficient [18].

Growth of CZTS layer on flexible Mo foil has only been investigated via the solvothermal approach [19]. Deposition of CZTS layers on flexible polyimide substrates was carried out using a screen printing process [20] and the electrochemical deposition technique [21]. Investigations of CZTS absorber layer growth on metallic flexible substrates via magnetron sputtering followed by sulfurization have not been reported in the literature yet.

In the present work, the magnetron sputtering technique was used in the first stage of the growth mechanism, since sputtering offers a wide range of advantages, such as easy adaptation to large-scale and reproducible manufacturing. Additionally, we chose to investigate both Ti and Mo foil substrates, due to the Ti's preferable CTE and chemical inertness behavior, as well as to compare the results of the two foils.

A chemically inert back contact layer with optimum electrical characteristics is necessary to achieve a high efficient solar cell. In the case of Mo back contact, high temperature sulfurization process leads to the decomposition of the CZTS absorber layer, resulting in MoS_2 phase formation [22,23], which restricts the hole transport from CZTS to Mo layer [24]. The interfacial MoS_2 layer may affect open circuit voltage (V_{oc}) and change the band alignment between the CZTS absorber layer and Mo substrate. Furthermore, impurities released from the substrate are another problem in the case of metal foil utilization. Pure metallic foil substrates like chromium and Ti can be used without a diffusion barrier since their diffusion rates into the absorber are comparably low [25] and have no detrimental effects on the conversion efficiency of the solar cells. Other intrinsic physical properties of the substrate, such as the CTE and surface roughness, affect the characteristics of the adjacent active layer. The CTE of the substrate and the adjacent active semiconductor layer should be in the same range. Adhesion problems may occur due to a high CTE of the substrate, while a low CTE may cause defects like crack formation. Formation of cracks decreases the performance of the device since it creates shunt paths between the back and front contacts of the device. Micro-cracks are also inactive cell domains and, thus, they reduce the active cell area. Therefore, back contact with a CTE nearly equal to that of the absorber layer is preferable to reduce the possibility of crack formation. Additionally, since surface roughness of the metal substrate causes leakage current and pinholes, surface smoothness of a metallic substrate is another important factor to achieve high efficient flexible solar cells [26]. Therefore, a smooth surface may ensure easier and more homogeneous active layer deposition.

Furthermore, the choice of substrate is crucially important to reduce the manufacturing costs for the high throughput fabrication of thin film solar cells. The cost of commercially available metal foils depends on the purity level and the Earth's reserve of the element. Ti is the fourth most abundant structural metal in the Earth's crust, and it is 600 times more abundant than Mo in [27]. Consequently, Mo foil is more expensive than Ti foil. Taking these factors into consideration, the careful selection of the substrate is crucially important to equip the growing thin film industry for mass production. The objective of this study is to establish a clear understanding of the substrate and back contact behavior of these promising Ti and Mo flexible substrates.

2. Material and methods

In the present work, we used $100 \mu\text{m}$ thick and $\geq 99.5\%$ pure Ti and Mo foils supplied by Sigma-Aldrich, and SLG substrate was used for optical and electrical characterization of CZTS material. Before the

sputtering process, to remove the oxidized layer and decrease the surface roughness, Ti and Mo foils were chemically etched with diluted HF and HCl, respectively. Additionally, the SLG substrate was cleaned by subsequent ultrasonication in acetone, ethanol and distilled water and then dried under a nitrogen stream. The CZTS layers were grown on these three substrates via sulfurization of the stacked metallic precursors, which were deposited sequentially by a multi-target DC magnetron sputtering system using 2-inch targets of Cu (99.999%), Zn (99.99%), and Sn (99.999%) at room temperature (Fig. 1). The deposition times were adjusted to 5 min for Cu, Sn and Zn targets by tuning the sputtering power. Deposition was conducted in attempt to achieve the desired layer thicknesses in the same time span for all three targets. With this approach, we would be able to use the co-sputtering method in our future work. After a base pressure below $1.3 \times 10^{-4} \text{ Pa}$ was reached, the sputtering process was started. Operating pressure was maintained at 2.0 Pa, and target-to-substrate distance was fixed at 8 cm. In this way, we sequentially grew layered metallic precursors, i.e. Cu/Sn/Zn layers, on the Ti and Mo foils as well as on the SLG substrate (Fig. 1(a)). The metallic precursors were produced using the same procedure for each process. Metallic precursors on Ti and Mo foils were obtained from a single sputtering run with a double-faced sample holder apparatus (Fig. 1(c)). The sulfurization procedure was performed in a Lindberg/Blue M tube furnace. The sulfur powder (99.98%) was placed in a custom-made quartz glass tube containing a small cylindrical outer partition. The cylindrical partition was heated to approximately 130°C via Joule heating to produce sulfur vapor. This system enabled the precursors to be quickly heated by transferring the precursor from the room temperature zone to the furnace central zone using a transfer rod (Fig. 2). The metallic precursors were loaded in the quartz tube installed in the tube furnace. Using a MKS 647C mass flow controller, 50 sccm of the carrier gas, Ar, was directed into the quartz tube during the sulfurization process. Ar was selected as the carrier gas rather than N_2 because the formation of TiN in the interface layer could deteriorate the CZTS on the foil substrate. The pressure was maintained at atmospheric pressure. The furnace temperature was set at 270°C , and we placed the metallic precursor into the furnace using the transfer rod. The furnace temperature was raised to 560°C in 10°C increments per minute. Fig. 3 represents the sulfurization process parameters of the CZTS films of this study.

Then, these samples were sulfurized in this setup for two hours at 560°C . After sulfur treatment, the current source was turned off, and just the Ar gas inlet was left on. Afterwards, the films were cooled

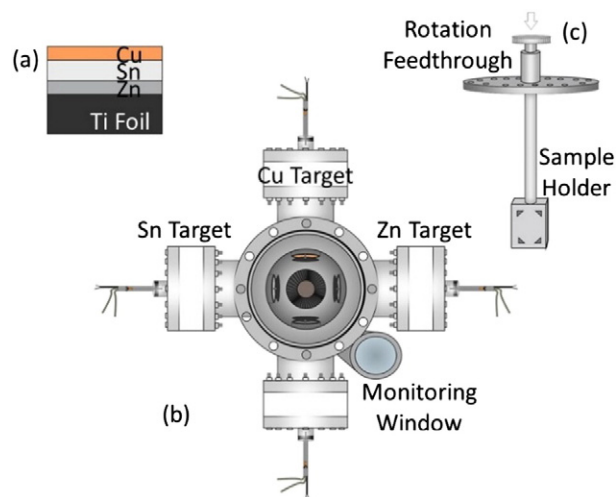


Fig. 1. (a) Illustration of sputtered metallic thin film layers on Ti foil, (b) schematic diagram of top view of multi-targeted sputtering system and (c) illustration of sample holder apparatus within the sputtering system.

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