Electrodeposition of Tandem Solar Cells

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Abstract

According to the International Energy Agency (IEA), solar energy is set to lead the charge of clean energy over the next 30 years.[1] This growth will increase demand for cost-effective photovoltaic technology, making the research in this field essential. Tandem solar Cells are a relatively new approach to enhancing the efficiencies of low-cost solar cells. $CuInS_2$ thin films are ideal for tandem solar cells with silicon due to their band gap (1.5 eV), high absorption coefficient, relatively low cost, and ease of fabrication when electrodeposited. Electrodeposition can be performed at standard temperatures and pressures. This method of fabrication also enables the recycling of waste chemicals, improving the environmental and economic viability of this process. As a first step in developing a $CuInS_2$/Si tandem cell, thin films of $CuInSe_2$ and $CuInS_2$ were successfully formed directly onto etched Si(111) wafers by electrochemical and annealing methods. The resulting $CuInS_2$ /Si samples were characterized by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and X-ray Diffraction (XRD). These early results may provide a path forward for the future development of low-cost Si-based tandem solar cells.

Introduction

The first paper that self-consistently analyzed the electronic structure of $CuInSe_2$ and $CuInS_2$ was published in 1983 by Jaffe & Zunger [2]. They found that the band gaps were ~1.0 eV and ~1.5 eV, respectively. Later, efforts shifted to applying electrodeposition to these semiconductors using a multistep deposition process with an aqueous bath [3-4]. Previously, these films had to be grown on conducting seed layers on top of the substrate, but it was found that the films can be deposited directly onto a semiconductor. The most cost-efficient semiconductor was found to be silicon [5]. Epitaxial growth of copper-gallium disulfide in vacuum was achieved on Si (111) wafers in 2002 [6]. This is pertinent to this work due to the similar compound and the same type of silicon wafers (111). An essential part of the electrochemical approach used here is the one-step co-deposition of the $CuInSe_2$ film. This means that the entire film is deposited in a single process from the same bath, which saves time and is more cost-effective than other methods. The viability of this method was first demonstrated in 2000 by the University of Helsinki, achieving conversion efficiencies above 18% [7], and has been reproduced multiple times [8-11]. To convert the thin film to the larger band gap $CuInS_2$, the $CuInSe_2$ must be annealed with sulfur.

Methods and Materials

Etching: The silicon wafers were ultrasonically cleaned in a bath composed of 1ml Micro-90 cleaner and 500ml DI water, then rinsed with DI water. The wafers were placed into a60-rpm stirred etching bath at 80 °C for 1 hour. The etching solution consisted of 400 mL of DI water, 100 mL of isopropyl alcohol, and 100 g of KOH pellets dissolved within. At the end of the hour, the heat was turned off, and the wafer was left etching at room temperature overnight. The next day, the etched wafer was cleaned in a 37% HCl + DI water ultrasonic bath followed by a final DI water rinse. The back of the wafer was coated with a liquid gallium layer serving as electrical contact for the deposition process.
Depositing: An acidic electrochemical bath consisting of 1.0 mM $CuCl_2$, 1.0 mM $InCl_3$,2.0 mM SeO_2, 25.0 mM Na-citrate (a complexing agent), was used for all experiments. The pH of the bath was adjusted to 3.0 with diluted HCl. A $CuInSe_2$ thin film was deposited using a 3-electrode system comprising the etched Si working electrode (WE), a Pd disc/ Pt wire counter electrode (CE) and a Ag/AgCl reference electrode (RE). All films were deposited potentiostatically vs Ag/AgCl (RE). For all samples, a Pine Instruments Rotating Disc Electrode (RDE) was rotated at 300 rpm for 5 minutes at room temperature during the electrodeposition process.

Methods and Materials, cont.

Annealing: After being deposited, annealing with S flakes converts most of the $CuInSe_2$ film into a $CuInS_2$ film. Four wafers at a time were placed in a quartz boat for the sulfurization process. The sulfurization was achieved by sliding the boat into a tube furnace with 0.1g of sulfur flakes, flooding the tube with argon gas, and heating to 350°C for 30 minutes. The samples were then left to cool overnight.
Analysis: During the fabrication process, the samples were analyzed by SEM, EDS and XRD before and after sulfurization. SEM was used to study the morphology, EDS was used to study the bulk composition, and XRD was used to study the crystal structure of the thin films.

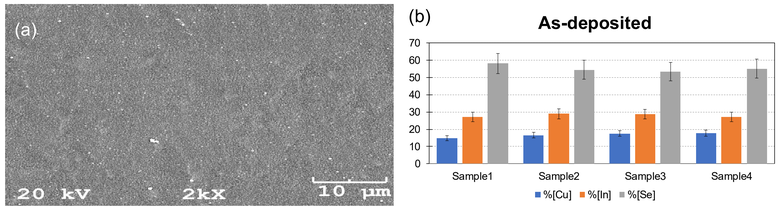

Figure 2: (a) SEM image and (b) EDS composition of as-deposited $CuInSe_2$ thin film deposited at -1.0V (The SEM micrograph in Fig. 2 (a) belongs to Sample 4)

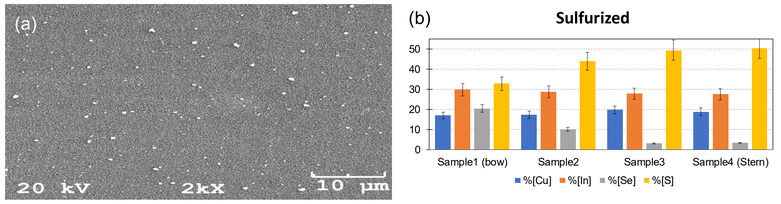

Figure 3: (a) SEM image of sulfurized thin film and (b) EDS composition of sulfurized thin film. (The SEM micrograph in Fig. 3 (a) belongs to Sample 4)

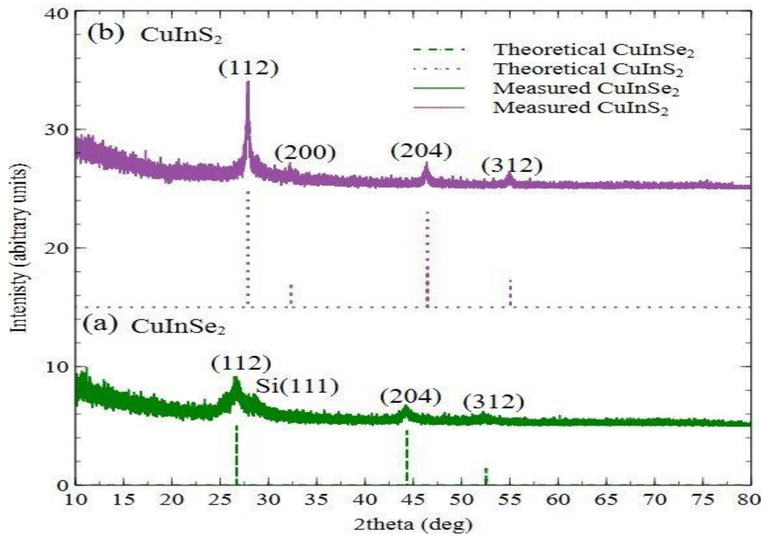

Figure 1: XRD Patterns of (a) As-deposited $CuInSe_2$ deposited at -1.0V and (b) Annealed/Sulfurized thin film forming $CuInS_2$

Results

Samples were characterized before (as-deposited) and after sulfurization. The films that exhibited the best morphology by SEM analysis were selected for sulfurization. XRD was performed on four sulfurized samples. A representative pattern is shown in Fig. 1. It can be noted that the main chalcopyrite peaks (112), (204), and (312) are slightly shifted to the right and are of higher intensity after sulfurization. These shifts in angle and intensity of the XRD peaks give an indication of the successful conversion from $CuInSe_2$ to $CuInS_2$.The morphology of an as-deposited and sulfurized film are shown in Fig. 2 (a) and Fig. 3 (a), respectively. The films appear as dense, two-dimensional polycrystalline films. Dense, two-dimensional films (as opposed to three dimensional-dendritic films) are better suited for device fabrication. Figures 2 (b) and 3 (b) show the elemental compositions for the as-deposited ($CuInSe_2$) and sulfurized ($CuInS_2$) samples, respectively. It can be seen that while the compositions of the as deposited films shown in Fig. 2 (b), closely match the correct stoichiometries for $CuInSe_2$, the ones in Fig. 3 (b) reveal a trend of increasing [S] and decreasing [Se] with the sulfurization process. This is to be expected for a conversion from $CuInSe_2$ to $CuInS_2$. However, after the sulfurization and characterization, it was discovered that the samples near the bow of the boat, (far from the center of the tube furnace) experienced less sulfurization than the samples near the stern of the boat (center of tube furnace). This indicates that the tube furnace has a nonuniform temperature profile. Finally, EDS analysis of the as-deposited films ($CuInSe_2$) showed varying compositions based on the deposition potential. This means that the film composition and therefore the semiconducting properties, can be controlled to a degree by the deposition potential.

Conclusions

1) As evidenced by SEM, dense, two dimensional $CuInS_2$ thin films can be formed directly on Si(111) by electrochemical and annealing methods without the need for high vacuum or conductive seed layer.
2) As evidenced by EDS and XRD analysis, near 100% conversion of deposited $CuInSe_2$ to $CuInS_2$ can be achieved with a simple sulfurization process in a tube furnace with an argon atmosphere.
3) The electrodeposition process is very sensitive to bath composition. The acidic (pH=3) bath of 1mM $CuCl_2$, 1mM $InCl_3$, 2 mM SeO_3 with 25mM Na-citrate (a complexing agent) yielded dense 2D polycrystalline films with a uniform composition.

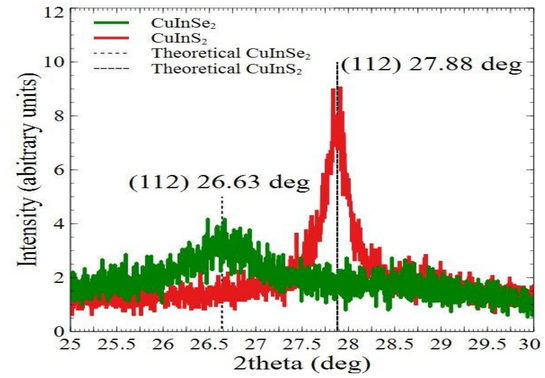

Figure 4: XRD 112 Peak shift after annealing/sulfurization.

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