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Reactively sputtered films in the Cu_xS – ZnS – SnS_y system: From metastability to equilibrium

Yi Ren^{*}, Jonathan J. Scragg, Tove Ericson, Tomas Kubart, Charlotte Platzer-Björkman

Ångström Solar Center, Div. Solid State Electronics, Department of Engineering Science, Uppsala University, Box 534, SE-75121 Uppsala, Sweden

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ABSTRACT

$\text{Cu}_2\text{ZnSnS}_4$ is a promising photovoltaic absorber containing earth abundant elements. Using a two stage process, low temperature reactive co-sputtering followed by heat treatment, we have previously achieved a 7.9% efficient solar cell. Because the sputtered precursors contain non-equilibrium phases with unusual crystal structures, it is crucial to understand their nature and their conversion into $\text{Cu}_2\text{ZnSnS}_4$ (and secondary phases) during heat treatment. In this study, we report phase analysis of reactively sputtered binary and ternary sulfides in the Cu_xS – ZnS – SnS_y system before and after annealing. In the as deposited films, Raman spectroscopy with 532 and 325 nm excitation wavelengths reveals expected phases for the binaries (CuS , ZnS and SnS_2) and the ternary (Cu_2SnS_3), and unique metastable phases for the Cu – Zn – S and Zn – Sn – S precursors. Upon annealing, the non-equilibrium phases disappear, accompanied by additional chemical changes. Excess S content in the films is removed, and in the Sn – S and Zn – Sn – S films, further S loss from decomposition of SnS_x ($x > 1$) and CuS respectively generates SnS and Cu_xS ($x > 1$). Due to the presence of SnS vapor, $\text{Cu}_2\text{ZnSnS}_4$ is generated from the Cu – Zn – S precursor. Additionally, the range of sulfur partial pressure in the annealing process is estimated according to the temperature–pressure phase diagram. This gives us useful insight allowing better control of annealing conditions.

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1. Introduction

The photovoltaic absorber material – $\text{Cu}_2\text{ZnSn}(\text{S,Se})_4$ (CZTSSe) – is attracting considerable attention with its suitable semiconducting properties [1] and earth-abundant elements. A record conversion efficiency of 12.6% has been demonstrated by IBM recently [2]. The two stage process, precursor deposition followed by (reactive) heat treatment at high temperature, is the widely used route employed so far. We have achieved 7.9% efficient $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) with 0.5 cm^2 total area by this method [3]. However, the high temperature heat treatment can give rise to surface decomposition of the CZTS phase due to the loss of volatile sulfur and SnS from the film, generating unfavorable secondary phases [4]. Since our reactively sputtered precursors contain metastable phases arising from the highly energetic sputtering process, it is essential to understand their nature and conversion into respective equilibrium states during heating. This is also true for the secondary phases that are difficult to characterize alongside the CZTS phase. To clarify the possible transitions of secondary phases from the metastable to equilibrium condition, Cu – S , Zn – S , Sn – S , Zn – Sn – S , Cu – Sn – S and Cu – Zn – S films are prepared and compared. From the observed phase transitions, we can infer an estimation of the sulfur partial pressure in the heat treatment by comparing with the sulfur partial pressure–temperature phase diagram of the Cu_xS – ZnS – SnS_y system.

2. Experimental details

Precursors were reactively (co-)sputtered in a Von Ardenne CS600 sputtering system described in detail elsewhere [5]. The system was equipped with three magnetrons in co-sputtering configuration facing the substrate with an angle of 45° at a distance of 16 cm. Planar circular targets with a diameter of 100 mm of Cu_2S (purity 99.95%), Zn (purity 99.994–99.995%) and Sn (99.994–99.995%) were used. All the targets were operated in pulsed DC mode. For Zn and Sn targets, pulsed DC with a frequency of 20 kHz was supplied by two Huttinger PFG 3000 DC power supplies, which were equipped with Advanced Energy Sparc-le 20 pulsing units. For the Cu_2S target, an Advanced Energy pinnacle® plus + 5 kW pulsed DC power supply was used and the pulsing frequency was set to 150 kHz. All targets were operated in constant power mode yielding a power density of 2.20 W/cm^2 for the Cu_2S target, 2.45 W/cm^2 for the Zn target and 2.45 W/cm^2 for the Sn target. Base pressure of the system was below 10^{-4} Pa, and the sputtering atmosphere was pure H_2S (99.5%), flowing at 30 sccm to provide a constant pressure of about 0.7 Pa. The sputtering time was typically 30–90 min without intentional substrate heating. Next, the as sputtered films (Cu – S , Sn – S , Zn – S , Zn – Sn – S , Cu – Sn – S and Cu – Zn – S) were all placed into a closed graphite box together with about 80 mg of elemental sulfur. Similar to the process for our best device fabrication, a baseline annealing process in a tube furnace under a static Ar atmosphere (35 kPa) at 560 °C for 10 min was used for the heat treatment of the sputtered precursors [3,6].

^{*} Corresponding author. Tel.: +46 18 4717255.
E-mail address: yi.ren@angstrom.uu.se (Y. Ren).

Three different substrates were used in depositions: glass for thickness measurement via a Veeco Dektak 150 profilometer, silicon wafer for sulfur measurement and Mo-coated soda lime glass for other material characterizations. The morphology of the samples was studied in the Scanning Electron Microscopy (SEM) cross section and top view images. Energy Dispersive X-ray Spectroscopy (EDS) was performed at 20 kV, in a LEO 1550 with a Zeiss EDS system, to characterize the sample composition. This measurement was done on the Si wafer to avoid the overlap of S $K\alpha$ and Mo $L\alpha$ peaks. The phase identifications were analyzed from the results made by the green and ultra-violet (UV) laser (532 nm and 325 nm excitation wavelengths) Raman spectroscopy (Renishaw inVia system), and the Siemens D5000 grazing incidence X-ray diffraction (GIXRD) at 0.5° incidence angle in parallel beam geometry.

3. As deposited binary thin films

Fig. 1 shows the morphologies of each binary thin film before and after annealing. Unique morphologies are formed in the Cu–S, Zn–S

and Sn–S thin films after reactive sputtering, as shown in Fig. 1A), C) and E). The layer thickness of the as-deposited films varies for constant sputtering time of 30 min, as shown in Table 1. Upon annealing, recrystallization occurs and the poor wettability of the materials (i.e. CuS and SnS) on Mo layer gives limited coverage of the substrate. The Cu–S thin film exhibits isolated grains, whereas small uniformly distributed crystals are formed in the Zn–S thin film and large flat crystals ($\sim 15 \mu\text{m}$) span and connect over the entire Sn–S sample. Besides, thick MoS_2 layers of about 140 nm, measured from SEM cross section, appear between the synthesized film and substrate in all the samples. This phase can be confirmed by measuring with the green laser Raman (408 cm^{-1} , 383 cm^{-1} and 287 cm^{-1} [7] in Fig. 2B) and F) on the exposed area (Fig. 1F). This sulfur required for formation of this interfacial layer can come either from the sulfur excess in the graphite box or from the as-deposited sample.

In the Cu–S thin film before annealing, a hexagonal CuS phase can be assigned by the green laser Raman as shown in Fig. 2B) and by GIXRD in Fig. 2A). The GIXRD pattern of the film is altered after annealing. Beside the peak intensity variation, unclear peaks appear at 46.7° , 55.3° and

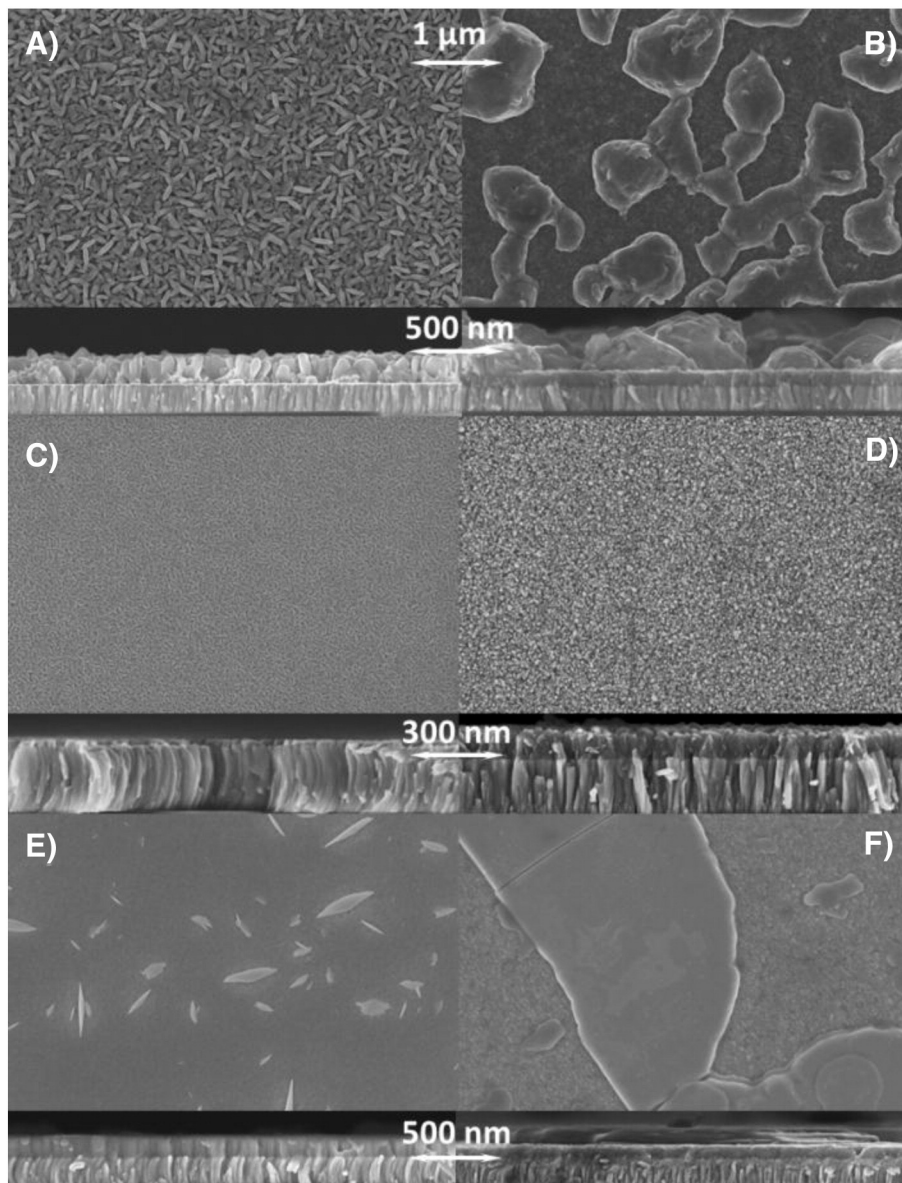


Fig. 1. SEM images of the binary thin films, the inset is the SEM cross section of each film: A), B) Cu–S film; C), D) Zn–S film; E), F) Sn–S film; A), C), E) are the precursors and B), D), F) are the annealed samples.

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