Influence of substrate temperature on Cu$_x$SnS$_{x+1}$ thin films prepared by Co-sputtering and H$_2$S annealing

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Abstract

Cu$_x$SnS$_{x+1}$ (CTS) thin films were deposited by co-sputtering of Cu and Sn targets and annealing the films in an Ar:H$_2$S atmosphere. The substrate temperatures were fixed at room temperature, 100, 175, and 250 °C during film deposition. The deposited films were then annealed in an Ar:H$_2$S atmosphere at 550 °C for 1 h. The Cu/Sn ratio decreased sharply with substrate temperature. In the annealed samples, the Cu/Sn ratio increased for films deposited at room temperature, 100, and 175 °C, and decreased for films deposited at 250 °C, showing the temperature dependence of Cu$_x$Sn alloy formation. Additionally, Cu$_3$SnS$_4$ phase formation was observed in the films grown at room temperature, whereas the films showed a Cu$_2$SnS$_3$ phase at higher substrate temperatures.

1. Introduction

Advances over the last decade have resulted in material alternatives to CdTe and Cu(In,Ga)(S,Se)$_2$, which are conventionally used as absorber layers in solar cells; these materials include toxic elements such as Cd, and tend to be expensive [1]. Quaternary and ternary chalcogenide semiconductors are promising candidates for cost-effective thin-film solar cells [2–7]. In particular, copper (zinc) tin sulphurs, including Cu$_2$ZnSnS$_4$ (CZTS), Cu$_2$SnS$_3$, and Cu$_3$SnS$_4$, are expected to play a crucial role in the power conversion of thin-film solar cells as an absorber layer [8, 9].

The maximum power conversion efficiency of Cu$_x$SnS$_{x+1}$ (CTS) and CZTS-based solar cells is still much lower than that of copper indium gallium selenide solar cells [10, 11]. The main reason for this is the inability to form high-quality CZTS and Cu$_2$SnS$_3$ thin films due to secondary phase formation, such as ZnS and CuS [12, 13]. To enhance the performance of solar cells, it is crucial to examine the factors affecting film formation.

Many different methods have been used to deposit CTS thin films, some of which require a vacuum (e.g. thermal evaporation and scattering); others are solution-based, such as spin coating and spray coating, and do not require a vacuum [14–17]. Sputtering is one of the most common methods used to deposit metallic and ceramic thin films on many substrate types. The sputtering process allows control over the homogeneity and thickness of the films for high-quality film production, by varying deposition parameters including the substrate bias, substrate temperature, chamber pressure, and power applied to the targets. The intensive use of the sputtering method for the fabrication of commercialised thin film-based solar cells shows the importance of investigating the effects of sputtering conditions during CTS thin film deposition.

In this study, Cu and Sn were sputtered simultaneously to deposit Cu$_x$Sn thin films under various substrate temperatures. After deposition, the films were annealed in an Ar:H$_2$S atmosphere to obtain CTS thin films. The influence of substrate temperature on CTS phase formation was investigated.

2. Experimental procedures

CTS thin films were prepared on soda-lime glass (SLG) substrates using a two-step process, involving the co-sputtering of Cu and Sn and annealing in an H$_2$S:Ar (1:9) mixed gas atmosphere. The SLG substrates were
washed with detergent, rinsed, and then ultrasonically vibrated in acetone and 2-propanol. A Nanovak NVTS-400 vacuum system (Nanovak, Ankara, Turkey) was used for thin film deposition. Before deposition of the thin films, Cu and Sn were sputtered separately to control the Cu:Sn ratio on room-temperature substrates. The film thickness was monitored using a scanning electron microscope (SEM). The base pressure was $2 \times 10^{-7}$ Torr. Then, Cu and Sn were simultaneously sputtered onto SLG substrates at room temperature, 100 °C, 175 °C, and 250 °C under 20 mTorr of ionizing gas pressure. After formation of the CuxSn thin films, the films were annealed at 550 °C in a quartz tube furnace under a 40-sccm H2S:Ar (1:9) flow for 1 h. Before the heating process, the tube was loaded with 99.99% pure nitrogen gas for about 30 min to remove oxygen and water vapor. The morphological properties of the films were analysed using a field emission gun (Quanta 250; FEI, Hillsboro, OR, USA) equipped with an energy dispersive spectroscopy (EDS) apparatus. The SEM was operated at 15 keV, and the images were acquired under 10,000 × magnification. The structural properties of the films were analysed using x-ray diffraction (XRD; Bruker D8 Advance; Bruker Corp., Billerica, MA, USA) with Cu-Kα radiation ($\lambda = 1.540056$ Å) and Raman spectroscopy (Alpha300 RS; WITec GmbH, Ulm, Germany) with 532-nm excitation. The XRD data were collected in 2θ mode. Finally, the optical properties of the films were determined with a Shimadzu UV-3600 spectrophotometer (Shimadzu Corp., Kyoto, Japan). Ultraviolet-visible-near-infrared (UV–vis-NIR) spectroscopy measurements were performed over the range of 700–1500 nm.

### 3. Results and discussion

Figure 1 shows SEM images of the films after the annealing procedure. The films deposited at room temperature, 100 °C, and 175 °C exhibited homogeneous surfaces with micro-sized particles thereon. The number of particles decreased with the substrate temperature and eventually the particles disappeared. The film surface was relatively smooth for films deposited at 250 °C, and the few remaining particles were less than 1 μm in size. The results show the influence of substrate temperature on film morphology; a higher substrate temperature produced more homogeneous films. The EDS results for the films before and after annealing are listed in table 1. Although the same power was applied to the targets during film deposition, the Cu/Sn ratio decreased as the substrate temperature increased. Before the annealing procedure, the Cu/Sn ratio was 2.42 for the film obtained at room temperature, decreasing to 2.13 for the film deposited at 250 °C.

Thus, Sn metal cannot adhere to the film surface at higher temperatures due to its lower evaporation point. After annealing the CuxSn thin films in an H2S:Ar atmosphere at 550 °C, the Cu/Sn ratio increased for films
deposited at room temperature, 100 °C, and 175 °C, and decreased to 2.08 for films grown under 250 °C. The increase in the Cu/Sn ratio from 2.42 to 2.96 implies the evaporation of Sn metal from the film surface during the annealing procedure. Notably, the Cu/Sn ratio changed from 2.14 to 2.08 for films deposited at 250 °C. The significant change at lower substrate temperatures and small change at higher substrate temperatures imply the formation of a Cu₅Sn₅ alloy, effectively preventing Sn atoms from escaping easily from the film surfaces. Finally, the S/metal ratio, which varied between 1.05 and 1.11, was observed to be nearly ideal for all samples. Taken together, these results indicate the importance of substrate temperature in controlling the ratio of the components during Cu–Sn–S film formation, including the temperatures reached during both the sputtering and annealing procedures.

The XRD patterns of the co-sputtered CuxSn thin-films deposited at room temperature, 100 °C, 175 °C, and 250 °C are shown in figure 2. As presented in the figure, the film obtained at room temperature had no peaks, which indicates the formation of an amorphous Cu-Sn thin film on the SLG substrate. The film deposited at 100 °C exhibited peaks at 27.95°, 30.42°, and 43.24°, related to the Cu₆Sn₅ phase, and peaks at 32.62°, 37.7°, 41.98°, and 57.61° corresponding to the Cu₃Sn phase [18, 19]. When the substrate temperature increased to 175 °C, the peak at 32.62° disappeared, and the peak at 57.77° associated with the Cu₅Sn₅ alloy became evident [18]. The intensities of the peaks at 30.42° and 43.24° correspond to Cu₆Sn₅, and that at 37.7° is related to the Cu₃Sn peak, which increased sharply with the deposition temperature. Thus, these results indicate the formation of Cu₅Sn₅ alloy crystals at higher substrate temperatures.

Figure 3 shows the XRD pattern of the CTS thin films between 20 and 70 °C. The films deposited at various substrate temperatures showed similar XRD patterns, including peaks at 28.53° and 33.02°. A peak at 47.41° was evident for the film samples deposited at room temperature and 100 °C; this peak shifted to 47.32° for films deposited at 175 °C, and to 47.36° for the film grown at 250 °C. Similar XRD patterns were obtained for films deposited at room temperature and 100 °C, showing a peak at 56.27°; however, this peak shifted to 56.14° for the films grown at 175 and 250 °C. The XRD peaks of tetragonal Cu₂Sn₃ have been reported at 28.54°, 33.07°, 47.47°, and 56.32° (JCPDS NO. 089-4714). The peaks for cubic Cu₂Sn₃ are reportedly positioned at 28.44°, 32.96°, 47.31°, and 56.13° [20]. The peaks at 28.49°, 47.46°, and 56.03° are associated with the tetragonal Cu₂Sn₃ phase (JCPDS NO. 33–0501). It is understood that the XRD patterns are not sufficient to fully characterise the structural properties of the films. Therefore, Raman spectroscopy analysis is required to resolve the structural features. Figure 4 shows

| Substrate temperature (°C) | Before annealing | After annealing |
|---------------------------|------------------|-----------------|
|                           | Cu   | Sn   | Cu/Sn | Cu   | Sn   | S    | Cu/Sn | S/(Cu+Sn) |
| Room                      | 70.80| 29.20| 2.42  | 36.14| 12.18| 51.51| 2.97  | 1.07      |
| 100                       | 70.61| 29.39| 2.40  | 36.12| 12.67| 51.22| 2.85  | 1.05      |
| 175                       | 68.78| 31.23| 2.20  | 33.16| 14.51| 52.34| 2.29  | 1.10      |
| 250                       | 68.14| 31.86| 2.14  | 31.98| 15.45| 52.58| 2.07  | 1.11      |

Figure 2. X-ray diffraction (XRD) patterns of co-sputtered CuxSn thin-films deposited at various substrate temperatures.
the Raman spectra of CTS films deposited at various substrate temperatures; the film deposited at room temperature showed four peaks, at 290, 314, 346, and 472 cm\(^{-1}\). The main peaks at 290 and 314 cm\(^{-1}\) are associated with the monoclinic phase of Cu\(_2\)SnS\(_3\) \([21]\). The peak at 346 cm\(^{-1}\) is related to the orthorhombic symmetry of Cu\(_3\)SnS\(_4\). The other peak, at 472 cm\(^{-1}\), indicates the formation of the Cu\(_x\)S phase \([22]\). The peaks at 472 and 346 cm\(^{-1}\), related to Cu\(_x\)S and Cu\(_3\)SnS\(_4\) phases, respectively, disappeared for films deposited at higher temperatures. For the films obtained at 100, 175, and 250 °C, the main Raman peaks occurred at 290 and 352 cm\(^{-1}\). The plot shows the formation of A' modes of monoclinic Cu\(_2\)SnS\(_3\) thin films \([23]\); the additional weaker peak at 374 cm\(^{-1}\) implies the A'' mode of monoclinic Cu\(_2\)SnS\(_3\). Therefore, it can be said that the films deposited at room temperature formed Cu\(_x\)S, Cu\(_2\)SnS\(_3\), and Cu\(_3\)SnS\(_4\) crystal structures; in contrast, at higher substrate temperatures, Cu\(_x\)S crystals were absent from the deposited films and the Cu\(_3\)SnS\(_4\) structure had disappeared completely.

Figure 5 shows the UV–vis-NIR spectra of films deposited at various substrate temperatures. As shown in the figure, all of the thin films absorbed light up to the NIR region. It is well known that Cu\(_2\)SnS\(_3\) and Cu\(_3\)SnS\(_4\) thin films have a direct band gap. The inset of figure 5 shows the square of the absorption as a function of the photon energy of the thin film samples. The band gaps of the film, determined by plot extrapolation, were 1.10, 1.03, 1.01, and 1.00 eV for films deposited at room temperature, 100 °C, 175 °C, and 250 °C, respectively. The results showed a decrease in the band gap from 1.10 to 1.00 eV as the substrate temperature increased.
According to the EDS and Raman spectra results, the reduction in band gap corresponded to the disappearance of the Cu$_3$SnS$_4$ and CuS phases. Chino et al. [24] deposited a Cu/ Sn stacked-layer by electron beam evaporation and obtained Cu$_2$SnS$_3$ thin films by sulphuring the precursors under temperatures of 450–580 °C for 2 h in an atmosphere of N$_2$ and sulphur vapor. They also reported a direct optical band gap between 0.96 and 1.00 eV for the films [24]. Therefore, our results are in good agreement with those from the literature.

4. Conclusion

To understand the influence of substrate temperature on the formation dynamics of CTS structures, Cu$_x$Sn thin films were deposited by sputtering of Cu and Sn metal targets, followed by an annealing treatment in an H$_2$S:Ar atmosphere. Firstly, the measurements showed that the substrate temperature has a strong effect on the Cu:Sn ratio during sputtering; hence, the Cu/ Sn ratio decreased sharply with an increasing substrate temperature. The Cu/ Sn ratio of the films increased for films deposited at lower substrate temperatures, whereas it decreased for films deposited at 250 °C after annealing in an H$_2$S:Ar atmosphere. These results are attributable to Cu$_x$Sn alloy formation at higher temperatures. Finally, clear Cu$_3$SnS$_4$ and CuxS phases were present in the films deposited at room temperature; these phases disappeared in films deposited at higher temperatures. By controlling the phase, it is possible to obtain phase-pure, high-quality crystalline, low-cost CTS for use in high-performance solar cell applications.

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Figure 5. Absorption–wavelength plots of CTS thin films obtained at various substrate temperatures [inset, (ahv)$^2$–energy plots derived from ultraviolet-visible (UV–vis) data].

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