

CVD-grown Tin Sulphide for Thin Film Solar Cell Devices

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Abstract

Chalcogenide materials are emerging as leading thin film photovoltaic (PV) technology. Tin mono-sulphide, a p-type semiconductor with a band gap of ~1.3 eV, has attracted great interest for the use as an absorber layer in chalcogenide thin film solar cells due to its desirable properties as an absorber layer in scalable, inexpensive, and non-toxic solar cells. In this work thin films of tin sulphide have been deposited by chemical vapour deposition (CVD) at room temperature onto soda-lime substrates then annealed at five different temperatures 200, 250, 350, 400 and 450°C with the aim of optimizing the properties of the thin films to achieve the required phase for use in solar cell device structures. These annealed CVD-grown tin sulphide thin films were further characterized with SEM, EDX, XRD, Raman and UV-VIS-NIR spectroscopy. The preliminary results of these tin sulphide thin films show great promise for PV applications.

Introduction

The search for low cost, low toxicity and earth abundant high efficiency absorbing materials has been carried on. In the past few decades, tin(II) sulphide (SnS) has gained much attention as a possible alternative absorber material for the next generation of thin-film solar cells to replace the current best developed technology based on Cu(In,Ga)Se₂ and CdTe [1].

Tin can form many sulphides, SnS₂, Sn₂S₃, Sn₃S₄, Sn₄S₅, SnS and several sulphide anions. The two most important tin sulphides are SnS, which has a distorted GeS structure [2], and SnS₂ which adopts a PbI₂ layer structure, both materials are semiconductors and can act as either an n-type or p-type conductor [3]. Tin sulphide thin films have been deposited by a range

of methods such as thermal evaporation processes [4], chemical bath deposition, sputtering [5], chemical vapour deposition (CVD) [6], atomic layer deposition (ALD) [7] and others.

In this work CVD was performed at room temperature and the effect of annealing on the phase purification was also investigated.

Experimental Details

Atmospheric pressure chemical vapour deposition (APCVD) of SnS₂, Sn₂S₃, and SnS has been achieved onto soda-lime glass substrates (30x20 mm) from the reaction between SnCl₄ and H₂S at room temperature and atmospheric pressure. The CVD system for Sn-S deposition is shown in Figure 1. In the experiment, Tin (IV) chloride (99.99% from Alfa Aesar) placed in a glass bubbler was used as the precursor vapourized and delivered by argon gas through the mass flow controller (MFC). The SnCl₄ vapours were then react with the H₂S/argon gas mixture through another two MFCs to form Sn-S thin film on soda-lime glass substrates at room temperature.

The as-deposited Sn-S thin film samples were then annealed at five different temperatures 200, 250, 350, 400, 450°C in a three zone furnace with a gas mixture of argon and H₂S.

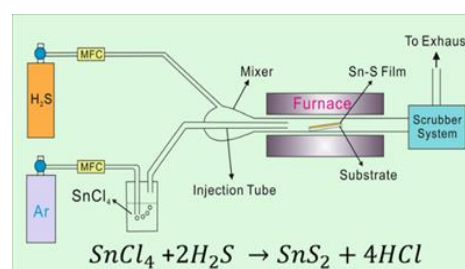


Fig.1 Schematic diagram of the CVD apparatus.

Results and Discussion

Energy-dispersive X-ray (EDX): EdX was used to determine the tin to sulphur ratio for the as-deposited and annealed Sn-S thin film samples. The tin to sulphur ratio for the films determined by EDX showed the variation of tin to sulphur ratio changing with different annealing temperature. From the EDX results shown in Figure 2 and the summary in Table 1. It appeared that the as-deposited Sn-S thin films contain some un-reacted Chlorine at room temperature.

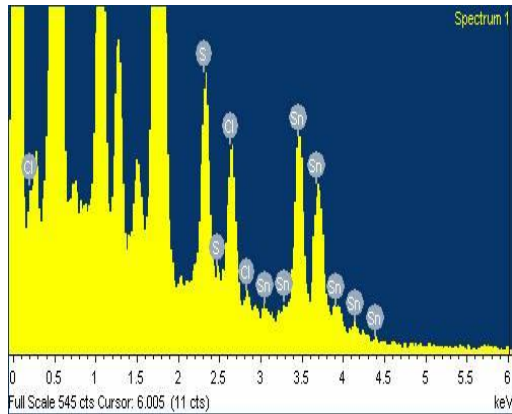


Fig. 2 EDX of the as-deposited Sn-S thin films.

	Weight%	Atomic%
S K	35.82	67.38
Sn L	64.18	32.62
Cl K	16.00	29.33
Totals	100.00	

Table 1 The element ratio of as-deposited Sn-S thin films.

The annealed Sn-S thin films at 350°C revealed that the slightly deficiency of sulphur in the mono phase of SnS composition shown in Figure 3 and the summary in Table 2. However, the Sn-S phase can be further characterized by XRD and Raman techniques.

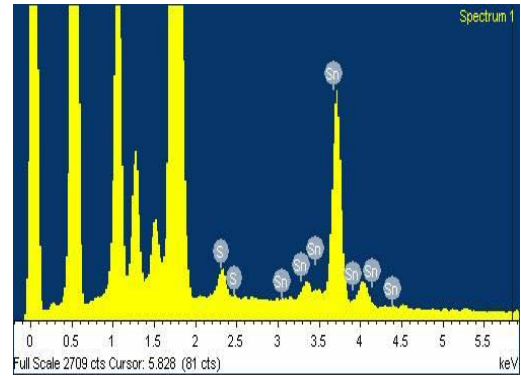


Fig. 3 EDX of the annealed Sn-S thin films at 350°C.

Element	Weight%	Atomic%
S K	18.09	44.98
Sn L	81.91	55.02
Totals	100.00	

Table 2 The element ratio of annealed SnS thin films at 350°C

X-ray diffraction (XRD): The absence of the peaks in the as deposited thin films suggests that the samples are amorphous in nature: this is common since the films were deposited in room temperature. By annealing the pattern of single-phase orthorhombic SnS appears at 350°C. The patterns show some preferred orientation in the (100) direction at the annealing temperature of 350°C as shown in Figure 4.

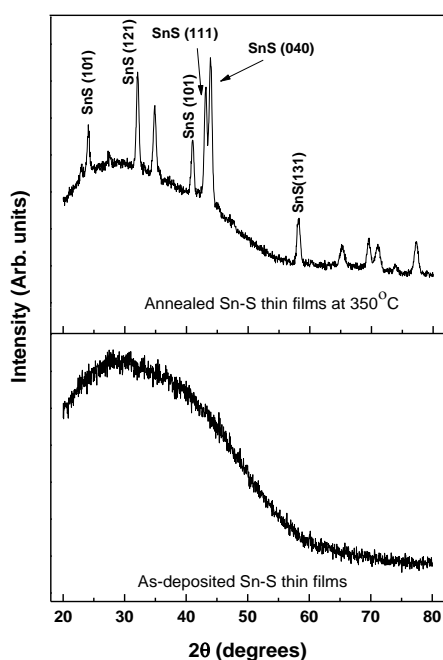


Fig. 4 XRD patterns for as-deposited and annealed tin sulphide thin films at mentioned temperatures.

Raman studies: To confirm the phase purity, Raman spectra were taken of Sn-S films annealed at different temperatures. The films annealed at 350°C show the Raman peaks of Sn-S at 160, 187, 220 and 302 cm^{-1} , which confirms that at this annealing temperature pure SnS without any appearance of the SnS_2 phase, Figure 5.

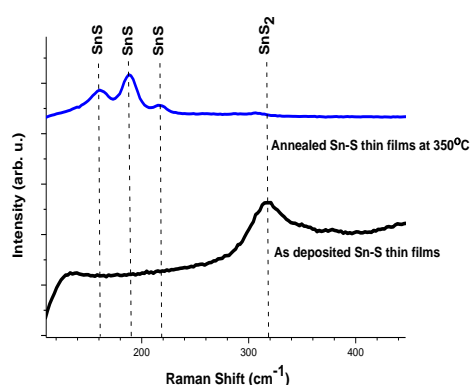


Fig. 5. Raman spectra of Sn-S films before and after annealing at temperatures indicated, major peak assignment is performed using the following references [8], [9].

Conclusion

It is possible to produce tin sulphide thin films by APCVD reaction of tin (IV) chloride and H_2S at room temperature. The as-deposited thin films show an amorphous structure and two phases of tin sulphide appear SnS and SnS_2 . A single phase of SnS is possible to achieve at an annealing temperature of 350°C. We consider that this method is appropriate for the production of Sn-S films in thin film solar cell devices.

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