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A critical role of hydrogen sulfide evolution during MOCVD of single phase thin film tin sulfide using ditertiarybutylsulfide as a less toxic precursor

Andrew J. Clayton¹, Cecile M. E. Charbonneau², Peter J. Siderfin¹ and Stuart J. C. Irvine¹

¹Centre for Solar Energy Research, College of Engineering, Swansea University, OpTIC, Ffordd William Morgan, St. Asaph Business Park, St. Asaph, Denbighshire, LL17 0JD, UK
²Sêr Solar, College of Engineering, Swansea University, Bay Campus, Crymlyn Burrows, Fabian Way, Swansea, West Glamorgan, SA1 8EN, UK

Thin film tin sulhide (SnS) was deposited on to molybdenum (Mo) substrates using metal organic chemical vapor deposition at 470°C using tetraethyltin and ditertiarybutylsulfide as precursors. In situ mass spectroscopy was used to study the exhaust gas species downstream of the reaction zone. The precursor vapor carrier gas was either nitrogen or hydrogen, thin film SnS only forming when the latter was used. Mass spectroscopy determined that hydrogen sulfide was being produced and playing a critical role in the vapor phase reaction process and adsorption of tin and sulfur on to the Mo surface. As-grown grain sizes were determined by scanning electron microscopy and were observed to be large averaging around 2 microns across. X-ray diffraction showed the films to be single phase SnS without any parasitic Sn₂S₃ or SnS₂ phases, with a small amount of MoS₂ also being detected.

1. INTRODUCTION

Thin film tin sulfide (SnS) is an attractive material for solar absorption in photovoltaics due to its high absorption coefficient at visible wavelengths [1]. Its earth abundant non-toxic constituents give potential for high throughput module production, which is an important consideration as energy demands increase and materials availability of existing technologies, such as cadmium telluride (CdTe) and copper indium gallium diselenide (CIGS) become uncertain [2]. To date, progress in conversion efficiencies for SnS solar cells has been slow, with a certified world record of 4.4 % [3]. This is very short of the theoretical conversion efficiency limit of 32 % [4]. The challenges with using SnS as a thin film solar cell absorber have mainly been associated to its small grains and poor band alignment with p-n junction counter-parts [3]. This leads to heavy recombination within the
bulk material due to grain boundaries acting as recombination centres and poor energy matches to n-type buffers creating losses at the junction. There are many reports focusing on the appropriate n-type buffer material to create small conduction band offsets with SnS, which has a low electron affinity [5]. Post-growth annealing steps are generally carried out to enlarge the SnS grains and reduce grain boundary defect concentration [3]. This is typically carried out in a sulfur atmosphere to reduce sulfur loss from the annealed film. Hydrogen sulphide (H₂S) has been shown [3] to be a successful sulfur precursor, also assisting in grain enlargement during post-growth annealing. Unfortunately, H₂S is a highly toxic gas so special measures are required for its use [6]. Ditertiarybutylsulfide (t-Bu₂S) is an alternative sulfur source, with less toxicity than H₂S and has been used by the authors employing the metal organic chemical vapor deposition (MOCVD) process [7]. Tetraethyltin (Et₄Sn) was used in this study as the tin precursor with successful growth of single phase SnS on to molybdenum (Mo) substrates. Post-growth annealing was not necessary with high growth temperatures of 470°C facilitating large grain growth. In situ mass spectroscopy was used to give insight into the reaction process.

2. EXPERIMENT

The MOCVD process used either nitrogen or hydrogen as carry gas to transport the Et₄Sn and t-Bu₂S vapor to the reaction chamber. The Mo substrates were 25 × 75 mm² in area and placed on to a heated graphite block with injector position 3 mm above over the upstream region of the substrate. The vapor flow followed a horizontal configuration towards the exhaust. The chamber was kept at atmospheric pressure and the concentration of the precursor vapor was determined by the partial pressure, which was 5.9 × 10⁻⁴ and 3.7 × 10⁻³ atmospheres for Et₄Sn and t-Bu₂S, respectively. It was necessary to use a 6-fold greater concentration of t-Bu₂S to Et₄Sn due to the higher vapor pressure of sulfur compensating for its re-evaporation from the growing SnS film. The authors have reported [7] these optimised parameters in another article.

A Cirrus portable mass spectrometer was used to sample exhaust gas species after the growth chamber to determine by-products produced from the chemical reaction process after SnS film formation. Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) were carried out with a Hitachi TM3000 bench top instrument and used to assess grain size/shape and approximate stoichiometry of the SnS deposits. High resolution (HR)-SEM was carried out with a Hitachi S-4800 instrument equipped with field emission gun (FEG) using beam settings at 2 - 10 keV and 10 μA. X-ray diffraction (XRD) was used with a Phillips X’PERT MPD instrument to determine the thin film crystal structure.

3. DISCUSSION

It was not possible to obtain thin film SnS when using nitrogen as the carrier gas. This was even the case at chamber temperatures up to 600°C. Thin film
SnS only deposited on to the substrates when using hydrogen as carrier gas and at temperatures greater than 410°C.

3.1 Thermal decomposition of Et₄Sn

The decomposition products of Et₄Sn, from Et₃Sn to EtSn, with loss of ethyl groups from the precursor, were all detected as soon as Et₄Sn was injected into the chamber using hydrogen as carrier (Figure 1). On heat up, detected concentrations of these by-products increased, correlating with outgassing of sulfur from parasitic wall deposits within the reactor chamber. At a critical temperature between 410 °C and 420°C, H₂S was detected. The temperature reached a maximum of 470°C with the hydrogen flow over the substrate. The carrier gas was then switched from hydrogen to nitrogen, resulting in an immediate drop in all detected exhaust gas by-products, even though the chamber temperature increased towards 600°C. This gave two observations, the first being that hydrogen was cooling the substrate surface to a certain degree and secondly that the Et₄Sn thermal decomposition was reliant on hydrogen being used as the carrier gas.

![Figure 1. In situ mass spectrum of exhaust gas species after Et₄Sn precursor injection as a function of time, temperature and type of carrier gas.](image)

3.2 Evolution of H₂S

The initial formation of H₂S during temperature increase with hydrogen flow is attributed by the sulfur release from parasitic wall deposits. Addition of t-Bu₂S results in approximately an order of magnitude increase in the partial pressure of H₂S detected (Figure 2). After t-Bu₂S injection, the sulfur follows a similar trend to H₂S, but at lower partial pressures. The t-Bu₂S decomposition products of t-Bu-S and butane were also detected upon t-Bu₂S injection. When Et₄Sn was then added to the reaction chamber, the detection of both t-Bu-S and butane increased and the butyl group released from t-Bu₂S became detectable, suggesting the Et₄Sn precursor enhanced t-Bu₂S decomposition. Also at the point of Et₄Sn injection,
some of the H$_2$S and sulfur was observed to be consumed. It was determined that this was due to SnS being formed at the substrate surface.

![Figure 2. In situ mass spectrum of exhaust gas species after t-Bu$_2$S injection followed by Et$_4$Sn precursor injection as a function of time and temperature.](image)

### 3.3 Thin film SnS structural properties

XRD showed (Figure 3) the film to have no other Sn-S phases present other than SnS. The dominant peak was that of Mo at $2\theta$ angle of 40.8°. The SnS peaks of the MOCVD-grown thin film correlated with the crystallography open database (COD) patterns for SnS (COD 9008785). There were two preferred orientations in the (101) and (040) planes. A small peak at $2\theta$ angle of 36.5° was present from MoS$_2$, which is known to form from the interaction of sulfur with Mo during deposition [8].

![Figure 3. XRD pattern of MOCVD-grown SnS deposited at 470°C on to Mo.](image)
The strong presence of Mo in the XRD pattern suggested the SnS film was thin, or that there was incomplete coverage of the SnS film on the Mo substrate. SEM was carried out on the film to get an indication of grain size (Figure 4). The grains were large, spanning 2 µm across and 4 µm in length in many cases. However, there were areas of significant contrast which were identified as Mo using EDX. This correlated with the strong peak associated with Mo observed in Figure 3. This signified a large vertical growth rate with incomplete coalescence of the grains. Further growth of the SnS should result in coalescence of the films.

Figure 4. SEM image of MOCVD-grown SnS deposited at 470°C on to Mo.

4. CONCLUSIONS

XRD determined that single phase thin film SnS was produced using t-Bu₂S as a less toxic sulfur precursor alternative to H₂S. However, high growth temperatures excessive of 410°C were required to produce SnS with use of hydrogen as carrier gas being essential. This resulted in the formation of H₂S within the growth chamber and was determined to be a necessity for Et₄Sn and its decomposition products to react and form SnS. Large grains were produced using the as-grown process, but vertical growth rate was high leading to incomplete coalescence of the SnS grains, exposing areas of the Mo substrate. Further growth of the SnS would be expected to lead to coalescence of the grains.

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