Phase Engineering of Tin Sulphide Grown by Atmospheric Pressure Chemical Vapour Deposition at Ambient Temperature

Ghadah Al Zaidy, Chris Craig, Daniel W. Hewak, Kevin Chung-Che Huang, Ioannis Zeimpekis-Karakonstantinos, Katrina Morgan and Ed Weatherby

Optoelectronics Research Centre, University of Southampton, Southampton, SO17 1BJ, U.K.

Considerable efforts have been made in the search for new photovoltaic (PV) materials that satisfy requirements such as low toxicity, optimum energy gap, high stability as well as the ability to synthesize by a wide range of methods. Tin (II) monosulfide (SnS), a binary metal (IV-VI) compound semiconductor offers many attributes. SnS is a p-type with high optical absorption coefficient $>10^4$ cm^{-1} and a band gap of E_g =1.1–1.32 eV making it a favourable material for PV applications and optical devices.

Depending on the deposition temperature and the percentage of precursors the SnS phase is accompanied with other Sn complexes such as Sn_2S_3 and SnS_2 and thus achieving a single phase material can be a challenge.

Tin sulfide thin films have been synthesised by several methods such as thermal evaporation, chemical bath deposition, spray pyrolysis, sulfurization and electrodeposition [1]. Among these, atmospheric pressure chemical vapour deposition (APCVD) which is a low cost and high-throughput deposition method, is attractive for large scale production. In this work, we demonstrate a novel phase engineering process of tin sulphide thin films grown by APCVD at room temperature using $SnCl_4$ precursor and H_2S/Ar gas mixture. Additionally, we explore the effect of post annealing treatment on the phase of the thin films.

The deposition was achieved by using a metal halide precursor, which allows the deposition to take place at room temperature, despite most studied cases, where the deposited films were formed at relatively high temperatures. A further post-deposition annealing process was performed in a tubular furnace in a 6% H_2/Ar atmosphere varying the temperature from 250 to 450 °C. The impact of annealing temperature on the phase and quality of material were investigated by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and scanning electron microscope (SEM). The spectral behaviour of the optical energy gap as a function of annealing temperature was obtained by UV–vis transmission and absorption spectra.

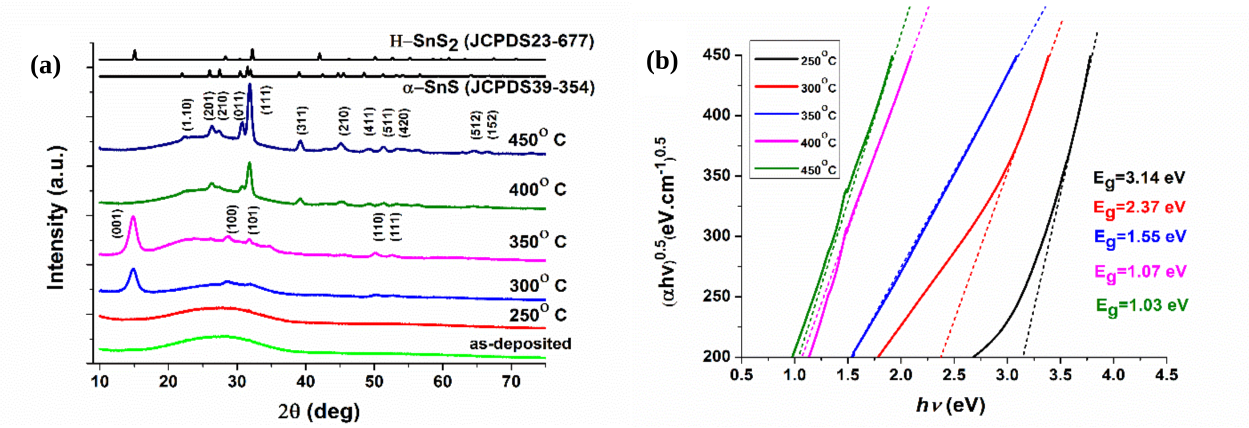

Fig. 1 (a) XRD spectra for the APCVD-grown tin sulphide on annealed at various temperatures. (b) The Tauc plots for APCVD-grown tin sulphide thin films annealed at various temperatures as a function of the photon energy.

Figure 1(a) shows the XRD spectra of all the samples under study with SnS_x phases appearing as a function of the annealing temperature. Amorphous-to-polycrystalline phase transition occurred after post-annealing treatment at 300° C and a signal intensity is observed at 14.9° corresponding to the crystallographic plane (001) which indicates a hexagonal SnS_2 phase. With increasing annealing temperature loss of sulphur occurs leading to a change in the Sn/S ratio which results in a single orthorhombic SnS phase that starts to form at 400° C. XPS and Raman spectra support the existence of pure phase SnS at temperatures between 400-450°C. UV−vis spectroscopy shown in figure 1(b) reveals that the band gap of the annealed tin sulphide thin films varies with the S concentration and can be tuned in the range of 1.03−3.14 eV. The comparison between structural and optical measurements show that an increased annealing temperature of up to 450 °C can produce high quality single tin SnS phase which can be promising for photodetectors and solar cell applications.

References

[1] M. Steichen, R. Djemour, L. Gütay, J. Guillot, S. Siebentritt, and P. J. Dale, "Direct Synthesis of Single-Phase p-Type SnS by Electrodeposition from a Dicyanamide Ionic Liquid at High Temperature for Thin Film Solar Cells," *The Journal of Physical Chemistry C,* vol. 117, pp. 4383-4393, 2013/03/07 2013.