Large cubic tin sulfide–tin selenide thin film stacks for energy conversion

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A R T I C L E I N F O

A B S T R A C T

Large cubic (CUB) polymorphs of SnS and SnSe were identified in nanocrystals and in thin films during 2015–16. We present how thin films of SnS-CUB and SnSe-CUB can be stacked in different sequences to thickness of 450 nm by chemical deposition. Grazing incidence X-ray diffraction pattern of the films establishes how these stacks of materials with a lattice constant $a = 11.59$ Å for SnS-CUB and 11.96 Å for SnSe form, upon heating at 300 °C, composite layers of SnS-CUB + $SnS_{0.75}Se_{0.25}$-CUB + SnSe-CUB. The layers so formed have optical band gap of nearly 1.52 eV, intermediate to that of SnSe-CUB and SnS-CUB, of 1.38 and 1.73 eV, respectively. With optical absorption coefficient exceeding 10^5 cm^{-1} in the visible region, the stacks would produce light generated current density of 28–31 mA/cm^2 in solar cells for air mass 1.5 global solar radiation. Electrical conductivity of 0.01 Ω^{-1} cm^{-1}, and Seebeck coefficient of up to 0.48 mV/K of the layers suggest their possible application in thermoelectric converters as well.

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1. Introduction

Large cubic tin sulfide (SnS-CUB) and tin selenide (SnSe-CUB) are polymorphs of tin chalcogenides identified during 2015–2016 in nanocrystals [1–3] and in thin films [4–6]. Their unit cells are simple cubes of lattice constant $a = 11.5873$ and 11.9632 Å, respectively, reported in thin films, with a basis of 32 formula units of SnS or SnSe per cell. The lattice constants of the more commonly reported ortho-rhombic SnS (SnS-ORT) of the mineral herzenbergite are: $a = 11.1923$, $b = 3.9838$ and $c = 4.3291$ Å [powder diffraction file, PDF 39-0354] and that for SnSe-ORT are: $a = 11.42$, $b = 4.19$ and $c = 4.46$ Å [PDF 32-1382]. Thus the CUB unit cells are nearly eight times "larger" (cell volumes, 1556 and 1712 Å^3) than those of the ORT unit cells holding four formula units. The optical band gap (E_g) of SnS-CUB and SnSe-CUB are distinctively larger, 1.7 and 1.4 eV, respectively [5,6] compared with 1.07 and 0.90 eV (indirect) and 1.30 and 1.05 eV (direct) for SnS-ORT and SnSe-ORT, respectively [7]. Theoretical models suggest that thermal stability of these newly identified CUB-polymorphs are comparable with that of their more common ORT-polymorphs [2,3]. Such a finding agrees with experimental results on nanocrystals [8] and in thin films [9] reported prior to identification of the large cubic structure for the materials. In view of these results, one could seek to produce solid solutions of SnS$_x$Se$_{1-x}$-CUB using precursor stacks of SnS-CUB/SnSe-CUB so that E_g may be varied in the 1.4–1.7 eV interval. We report here that thin films of SnS-CUB and SnSe-CUB produced by chemical deposition may be stacked with much versatility in sequential deposition. Heating of these stacks at 300 °C produces materials with E_g of 1.5 eV and electrical conductivity (σ) higher by three orders of magnitude compared with that of SnS-CUB or SnSe-CUB thin films. Applications of these materials as a photo-carrier generation layer in thin film solar cell and as a thermoelectric material are considered.

2. Experimental details

2.1. Thin film deposition

Substrates – chemical deposition of the thin films were made on Corning glass substrates of 1 mm in thickness and area 2.5 cm × 7.5 cm. These substrates were immersed for 15 h at room temperature in a dilute solution of sodium sulfide prepared by dissolving 3 g of Na$_2$S · 9H$_2$O in 200 ml of deionized water. They were rinsed in deionized water and dried. This pre-treatment of glass substrates has been found to produce compact thin films of SnSe in chemical deposition [10] and generally useful in other cases, too.

SnS-CUB [4–6] – a solution of SnCl$_2$ was prepared in a standard volumetric flask by dissolving 2.26 g of SnCl$_2$·2H$_2$O (Aldrich) in 30 ml of glacial acetic acid and 2 ml of concentrated HCl and making the volume up to 100 ml by adding deionized water, as described in [9].

To 10 ml of this solution were added 30 ml of 3.7 M triethanolamine (TEA), 16 ml of 30% NH_3 (aq.), and 10 ml of 0.1 M thioacetamide. De-ionized water was added to take the final volume of the solution to 100 ml. 'Baker-Analyzed' reagents were used. The pre-treated glass substrates were immersed in this deposition bath (initial pH 11) that was subsequently placed in a temperature controlled circulation bath maintained at 17 °C to proceed with the deposition for 15 h (overnight). Specularly reflective films of SnS-CUB of thickness 110 nm were obtained. Three such successive depositions, each from a freshly prepared bath, increased the film thickness to approximately 290 nm.

SnSe-CUB – as reported previously [6,10], we required a pre-coating of a SnS-CUB thin film on the glass substrates to grow SnSe-CUB thin films. For this, a thin film of 140 nm SnS-CUB from a single deposition was used as the substrate-film. A solution of Na_2SeSO_3 (SSS - sodium selenosulfate) of 0.2 mol dm^{-3} in concentration was prepared by refluxing 2 g of Se-powder (ASARCO) and 12.3 g Na_2SO_3 (Aldrich) in 100 ml deionized water. For preparing the deposition solution, 0.7 g of $SnCl_2$ (anhydrous, Aldrich) was dissolved in 5 ml of acetone in a 100 ml beaker. To this was added with stirring 30 ml of 3.5 M triethanolamine, $(CH_2CH_2OH)_3N$, followed by 18 ml of 1.0 M solution of sodium hydroxide (NaOH), 0.25 ml of 0.5% polyvinyl pyrrolidone (PVP) w/w solution in water, 4.0 ml of 0.2 M SSS-solution, and 16 ml of water. Small variations in these solution concentrations would still yield good film quality. The reagents not specified were 'Baker Analyzed'. It was suggested previously that the use of PVP in the solution contributes toward better quality for tin selenide thin films [11]. Initial pH of this deposition bath was 14, which causes some dissolution of SnS-CUB, of about 50 nm, before the deposition of SnSe-CUB film starts. As the deposition of SnSe proceeds, part of SnS-CUB (which is retained after dissolution) is converted to SnSe-CUB. Following the growth mechanism suggested in ref. [6], formation of a solid solution SnS_xSe_{1-x} was not observed. In the present case, a residual SnS-CUB film would be left on the glass substrate on which SnSe-CUB film has grown. Deposition for 2 h at 17 °C in the SnSe bath resulted in a total film thickness of 180 nm. A successive chemical deposition in a fresh SnSe deposition bath takes the total film thickness to 280 nm.

Glass/SnS-CUB-SnSe-CUB stack – thin film stack was prepared with two successive depositions of SnS-CUB (2 × 15 h) followed by two depositions of SnSe-CUB (2 × 2 h) at 17 °C. The total film thickness of this stack is nearly 450 nm.

Glass/SnS-CUB-SnSe-CUB-SnS-CUB stack – this stack consisted of SnS-CUB thin film prepared in two successive depositions, followed by one deposition of SnSe-CUB, and another deposition of SnS-CUB film. The final thickness of this stack is nearly 460 nm.

The sample scheme is illustrated in Fig. 1.

Heating of the thin films: Samples of the films were heated at 300 °C under nitrogen pressure of 20 Torr for 30 min. Such heating is reported

here to significantly affect the optical and electrical properties of the thin film stacks, not seen in either SnS-CUB [5] or SnSe-CUB [6] thin films.

2.2. Thin film characterization

Thickness of the thin films was measured in Alpha-Step 100 (Tencore, CA). The chemical composition of the films was analyzed using energy dispersive X-ray emission spectral (EDS) data from the films. For this, an Oxford X-act energy dispersive X-ray spectrum analyzer attachment to a Hitachi-SEM SU1510 was used. The electron beam energy was fixed at 7 keV to minimize excitation of emission lines from the glass substrate. The intensity of emission lines in the EDS data was normalized with respect to the $Sn-L_{\alpha 1}$ emission line for each sample-type. These data helped to assess any notable relative loss of an element from the film if it had occurred during its heating at 300 °C.

Grazing Incidence X-Ray Diffraction (GIXRD) data on the samples were recorded on a Rigaku ULTIMA IV diffractometer using Cu-K_α radiation making incident angles (δ) at 0.5°, 2° and 2.5° with the sample plane. The mass absorption coefficient (μ_{mass}), linear absorption coefficient (α), penetration depth (PD) and sampling depth (SD) with respect to these angles were estimated following standard procedure [12] using standard data [13] and lattice parameters reported for SnS-CUB and SnSe-CUB [5,6]. The procedure is described in Table 1. At $\delta = 0.5°$, XRD pattern from a sample will be dominated by the material of thickness 75–77 nm of the SnSe-CUB or SnS-CUB at the surface of a layer. At $\delta = 2°$, SD (300 nm) the analysis would cover most of the film thickness. At $\delta = 2.5°$, the SD of 380 nm would surpass the film thickness in SnS-CUB and SnSe-CUB, but still would fall short of the entire film thickness of 450-460 nm in the stacks. The broad intensity distribution from the amorphous glass substrate would be superimposed on the XRD pattern of the sample when the SD is more than the thin film thickness.

The optical transmittance (T) was measured with air in the reference beam. Specular reflectance (R) was measured with a front-aluminized standard mirror in the reference beam. Measurements were made for film-side incidence for the heated samples. A JASCO 670 spectrophotometer was used. The optical absorption coefficient (α) was evaluated for any wavelength (λ) from T, R data and film thickness (d) by considering multiple reflections [14]: $T = (1 - R)^2 e^{-\alpha d} / (1 - R^2 e^{-2\alpha d})$. Since diffuse transmittance/reflectance was present in most samples, $T + R$ did not add up to unity prior to the onset of band-to-band excitation of electrons, responsible for strong optical absorption. Acceptable estimate for α was obtained by substituting the value of 1 in the equation (valid for specular reflection) with the $T + R$ fractional value (for example 0.8) observed for a sample prior to the onset of the absorption.

For electrical measurements, pairs of silver-paint electrodes of 5 mm length at 5 mm separation printed on the film surface served as contacts. The measurement and data acquisition system consisted of a Keithley 619 electrometer/multimeter and Keithley 230 voltage source interfaced with a computer. The samples were allowed to stabilize in the dark under a bias of 10 V. The samples were always subjected to some background illumination during loading into the measurement chamber. A computer software tracked the dark current under the bias every second and started the photocurrent response measurement once the variation in current was less than 0.2% per second. On-plane current (I) was recorded for 20 s in the dark, 20 s under tungsten-halogen radiation (temp., 3200 K) of intensity 850 W/m^2 at the sample plane and again for 20 s in the dark. The current recorded against time was converted to electrical conductivity σ ($\sigma = (I)/(V \times d)$). Here, the composition of the film across the film thickness is assumed to be homogeneous; the validity of which is limited as would be seen in the GIXRD result.
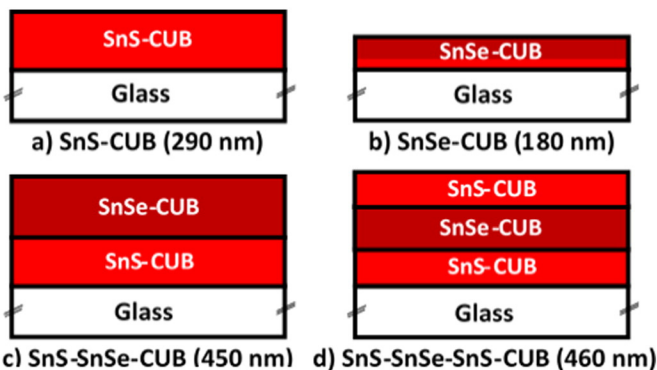

Fig. 1. Sample scheme for a) Glass/SnS-CUB, b) Glass/SnSe-CUB thin films, and c) Glass/SnS-CUB-SnSe-CUB and d) Glass/SnS-CUB-SnSe-CUB-SnS-CUB thin film stacks.