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Detailed characterization of good-quality SnS thin films obtained by chemical solution deposition at different reaction temperatures

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ABSTRACT

A process for the chemical deposition of good-quality SnS thin films is presented. This process consists of a careful substrate sensitization; the placement of the substrate in a particular angle in the reaction solution; and the use of an aqueous reaction solution composed of stannous chloride, ethanol, triethanolamine, thioacetamide, and ammonium hydroxide. This process enables the deposition of good-quality SnS thin films that are homogenous and strongly adhered to the substrate, even at a temperature of 70 °C. The effect of reaction temperature (40, 45, 50, 55, 60, 65, and 70 °C) on the properties of the SnS thin films was studied by means of X-ray diffraction (including a Rietveld analysis), scanning electron microscopy, X-ray photoelectron spectroscopy, optical spectroscopy, and current photo-response. Rietveld analysis shows the presence of two tin sulfide orthorhombic phases (α-SnS and β-SnS) and a platelet-like microstructure with less than 20% of the total volume oriented in the (111) plane. Surface morphology confirms that grains have platey-like habits. It is found that with increasing reaction temperature the thin films increase in thickness, become more crystalline, and the conductivity photo-response improves, making the prepared SnS thin films suitable for optoelectronic applications.

1. Introduction

Tin sulfur binary compounds expressed as Sn_xS_y, represent an emergent class of electronic materials that have been studied for several decades [1–8]. Three Sn_xS_y compounds are known to exist at ambient conditions, all of which are semiconducting materials: SnS, SnS_2, and Sn_2S_3 [9–11]. From these, SnS, which is a non-toxic material, is of great interest due to its good chemical stability [12], its absorption coefficient greater than 10^4 cm^{-1} [13], and its *p*-type conductivity [14]. Additionally, SnS has a polymorphic nature and is able to adopt orthorhombic and cubic structures at ambient conditions by changing certain chemical parameters [15–19]. Furthermore, each phase has its own energy band gap; around 1.13 eV for orthorhombic and 1.73 eV for the cubic phase [15–20]. This means that it is possible to modulate the energy band gap by tuning the SnS structure.

The previous reasons make SnS a useful semiconductor material for a variety of applications, such as photovoltaics, optoelectronics, chemical sensors, water-splitting, and others [21,22]. Also, SnS is especially important because it can be employed as a precursor in the synthesis of quaternary semiconductors like Cu_2ZnSnS_4 (CZTS) [23,24]. However, the performance of SnS devices critically depends on the employed method of synthesis. SnS thin films can be prepared by several physical and chemical methods. Physical methods usually employ high vacuum and complex experimental systems that make the synthesis process expensive; among which sputtering [25], pulsed laser deposition, and evaporation by e-beam [26] are worth mentioning. On the other hand, chemical methods based on chemical solutions provide an affordable and technically simple process; these may include sol-gel [27], successive ionic layer adsorption reaction (SILAR) [28], and chemical bath deposition (CBD) [19,20,29–33].

Chemical bath deposition (or better, chemical solution deposition) has been one of the simplest, inexpensive, and effective techniques employed for the synthesis of metallic chalcogenides and, of course, for the synthesis of SnS. There are plenty of reports of SnS thin films obtained by chemical solution deposition with different formulations and reaction conditions [8,19,20,29–33]. Among them, perhaps the *recipe*

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formulated by Nair & Nair [8] is the simplest and most versatile one to deposit SnS thin films; for this reason, it was effectively used with no modifications during years [15,16,19,20,34–41]. In fact, this formulation allows to deposit SnS thin films in a cubic or orthorhombic structure depending on the temperature used in the deposition reaction [19]; cubic is predominant at 30 °C and below, and at 35 °C and above the predominant structure is orthorhombic. This polymorphic characteristic detonated a pursuit for the real structural composition of SnS in the years 2014–2016, especially for SnS thin films obtained at low temperatures [9,11,19,20,42–44]. However, the structural composition of SnS films obtained by chemical solution deposition at higher temperatures was not addressed in the same way, even when it is evident that experimental X-ray diffraction peaks commonly reported in literature do not exactly match the peak positions of the reference pattern. This observation suggests that another phase, alongside the typical proposed one, is probably present in the SnS films obtained at temperatures at 35 °C and above (in a similar way to that suggested by Banai et al. [45] for SnS films obtained by radio-frequency magnetron sputtering).

Furthermore, it is worth noting that above 50 °C the formulation by Nair & Nair leads to SnS thin films that tend to be fragile to touch [19], thus limiting the temperature range for film deposition, and, in turn, limiting the study of temperature effect on structural composition and other relevant characteristics and properties. Other authors who claimed to study the effect of reaction temperature on SnS thin films by chemical solution deposition were focused on simple and rapid characterizations of films obtained from a few temperature values and without delving on detailed structural or chemical compositions [33,46–48]. Thus, in this paper, we present a complete research about the effect of reaction temperature by using a process based on the Nair & Nair formulation [8] but allowing depositions of good-quality thin films in a wide range of temperatures. Specifically, in this paper we shall present:

a) A chemical formulation, based on that presented by Nair & Nair [8], in which ethanol is used instead of acetone (which improves solubility of the tin salt and lengthens the durability of the prepared solution, as we observed experimentally) and where the thioacetamide concentration is reduced in 38%. We found that these changes permit the deposition of SnS thin films at temperatures above 50 °C, which additionally permits the reduction of deposition time.
b) The incorporation of reported methodologies that improve the quality of the deposited films, such as the use of a substrate presensitized with tin oxide species [49–53] and the placement of the substrate at a particular angle with respect to the horizontal line [17,18,30].
c) A complete and detailed morphological, structural, chemical, optical, and photoelectrical characterization of good-quality SnS thin films obtained in the temperature range where the orthorhombic structure is predominant: 40, 45, 50, 55, 60, 65, and 70 °C. Also, the digital photographs of the films are presented to convince the reader of the homogeneous appearance of the films, since this is not explicitly shown in the literature.
d) A Rietveld analysis to assess the structural composition of the SnS thin films deposited at temperatures where the orthorhombic structure is predominant, similarly to that performed by Banai et al. [45] in SnS obtained by radio-frequency magnetron sputtering, a high-energy deposition technique. We made an emphasis in this section to correlate structural composition with the other film characteristics.

2. Experimental details

2.1. Materials

Tin(II) chloride dihydrate, $SnCl_2{\cdot}2H_2O$, with 99.6% purity; triethanolamine (TEA), $N(CH_2CH_2OH)_3$, with 99.8% purity; and ammonium hydroxide, NH_4OH, with 29.3% purity, were supplied by Fermont. The 96%-ethanol, CH_3CH_2OH, was purchased from *Alcoholera de Zapopan*. The thioacetamide (TA) reagent, CH_3CSNH_2, with 99.6% purity, was acquired from Fischer Scientific. Lauka® microscope glass slides (2.5 cm × 7.5 cm × 0.1 cm) were used as substrates.

2.2. Film deposition

The substrates were manually cleaned by a thorough rinse with Alconox® detergent and distilled water and were later treated with a sensitization procedure. The latter involves the immersion of the substrates in a magnetically stirred solution of 0.01 M $SnCl_2{\cdot}2H_2O$ for 1 h at a temperature of 70 °C. We observed in our preliminary experiments that the sensitization procedure enables the deposition of a strongly adhered film that does not separate from the substrate even after a soft rub with a moistened cotton swab.

The chemical solution deposition formulation employed here is a modified version of the one reported by Nair & Nair [8]. This modified formulation enables the deposition of good-quality thin films in a deposition time of 3 h at least in the temperature range from 40 to 70 °C. For a good comparison, Table 1 explicitly shows the formulation followed in this paper to prepare 100 mL of the reaction solution, as well as the formulation originally presented by Nair & Nair [8]. According to this, we firstly dissolve by ultrasonication 1 g of $SnCl_2{\cdot}2H_2O$ in 5 mL of ethanol for 10 min. Later, the rest of the reagents were added to this tin solution by following the sequence presented in Table 1. The resulting 100 mL reaction solution is composed by $SnCl_2$ in 0.044 M, ethanol in 0.822 M, TEA in 0.674 M, TA in 0.050 M, and NH_4OH in 0.400 M. The initial pH value of this solution is ~10.

One pre-sensitized substrate is then immersed in the fresh reaction solution and is supported on the wall of the beaker forming a ~ 30° angle between the substrate and beaker wall (details on the purpose of this tilt will be given later). The bath temperature was controlled using a Lauda Ecoline E100 thermostat. Finally, after the deposition terminated, the substrate with the film is withdrawn, rinsed with distilled water, and dried naturally in the air.

2.3. Thin film characterization

The thickness of the thin films was determined using an Alpha-Step 100 (Tencor, CA) stylus profilometer. Surface morphology was recorded with a JEOL JSM-5410LV scanning electron microscope (SEM) equipped with a Bruker Quantax 200 analytical system for energy dispersive X-ray spectroscopy (EDXS).

X-ray diffraction (XRD) patterns were recorded in grazing incidence mode employing a Rigaku DMAX-2200 diffractometer using a Cu K_α (λ = 1.54 Å) X-ray source. The incidence angle was set to 0.5° and the 2θ collection range was from 10° to 70°. The instrumental broadening was determined with a LaB_6 standard and intensity correction to a Bragg-Brentano geometry was done employing the James

Table 1
Formulation details to prepare 100 mL of reaction solution for chemical solution deposition of SnS thin films, according to the work by Nair & Nair [8] and the present research.

Stock reagent solution or diluent	Quantity according to Nair & Nair formulation	Quantity according to the present work
$SnCl_2{\cdot}2H_2O$	1 g	1 g
Acetone	5 mL	0 mL
Ethanol	0 mL	5 mL
3.75 M (50%) N $(CH_2CH_2OH)_3$ (TEA)	12 mL	18 mL
Distilled water	65 mL	62 mL
1.0 M CH_3CSNH_2 (TA)	8 mL	5 mL
4.0 M NH_4OH	10 mL	10 mL