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Chemical Bath Deposition of tin sulphide thin films in acid solution

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Abstract

Sn_xS_y thin films have been grown on glass or on SnO_2/glass substrates by Chemical Bath Deposition in acid solution. The crystallography, the morphology, and the chemical properties of the layers have been characterized using X-ray Diffraction, Atomic Force Microscopy, Energy Dispersive X-ray Spectroscopy, and Auger Electron Spectroscopy. The value of the [Sn]/[Thioacetamide] concentration ratio is optimized in order to obtain good quality layers satisfying stoichiometry. ***To cite this article: M. Mnari et al., C. R. Chimie 12 (2009).***

Keywords: Tin sulphide; Thin films; Chemical Bath Deposition in acid solution; Chemical composition; Roughness

1. Introduction

Tin sulphide compounds Sn_xS_y present physico-chemical properties, optical quality, and electronic characteristics (bandgap varying between 1 and 2.3 eV depending on x and y values, high charge carrier mobility, high radiation strength…) adapted to the fabrication of optoelectronic devices such as solar cells [1−13]. Sn_xS_y thin films can be prepared by different methods [1−4,13] among which the Chemical Bath Deposition (CBD) technique in a basic solution. However, basic solutions carry an unwanted precipitate [14]. Therefore we have chosen an acid solution to prepare Sn_xS_y films by CBD and we have characterized the crystallography, the morphology, and the chemical properties of the obtained layers by using X-ray Diffraction (XRD), Atomic Force Microscopy (AFM), Energy Dispersive X-ray Spectroscopy (EDS), and Auger Electron Spectroscopy (AES). Results exhibit the role of the substrate nature, the deposition time, and the ratio between tin and thioacetamide (TA) concentrations [Sn]/[TA], on the layer properties.

2. Experimental procedure

Thin films are grown on glass and on SnO_2/glass substrates for 60 min. Glass substrates are more particularly devoted to the optical characterization of thin films, while SnO_2/glass substrates present good electrical conductivity and are used in techniques where charge flows are needed. SnO_2/glass substrates are also used in the final solar cell fabrication process.

Glass substrates are initially soaked for 10 min in aqueous hydrofluoric acid (HF) solution at 7%, then rinsed in distilled water. SnO_2/glass substrates are prepared by spray pyrolysis of a 0.6 μm tin oxide thin film on glass [14,15].

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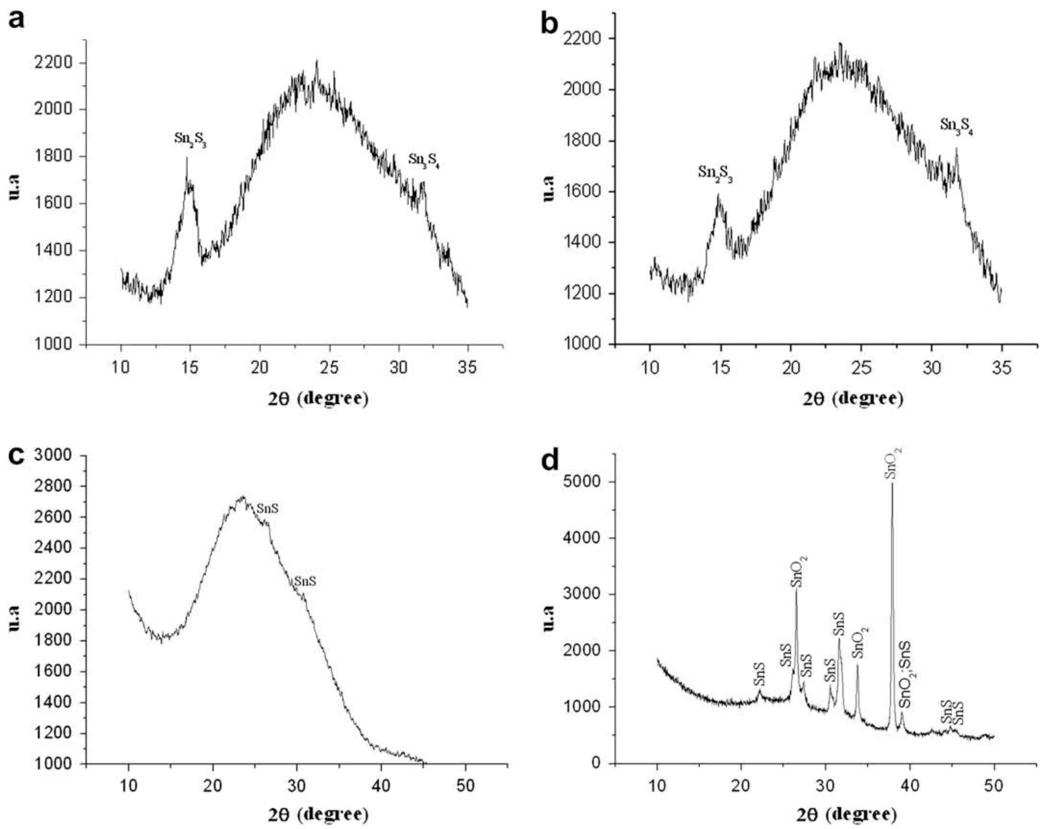

Fig. 1. XRD spectra of tin sulphide layers grown by CBD: (a) on glass with [Sn]/[TA] = 1, (b) on glass with [Sn]/[TA] = 0.5, (c) on glass with [Sn]/[TA] = 0.25 and (d) on SnO_2/glass with [Sn]/[TA] = 0.25.

Sn_xS_y thin films are grown by CBD using two precursors, tin chloride $SnCl_2$ with concentration equal to 2×10^{-2} M and Thioacetamide with concentration varying from 10^{-2} M to 8×10^{-2} M. Growth is carried out in an acid solution using acetic acid at pH = 0.41 [14], in order to prevent $Sn(OH)_2$ precipitation. Infact, it precipitates from pH = 1.87 and tin concentration of 10^{-2} M according the solubility product $K_{S1} = 5.45.10^{27}$ of following reaction: $Sn^{2+} + 2OH^- \rightarrow Sn(OH)_2$ solid; whereas thioacetamide hydrolyses, when heated in strong acid solution according to the reaction:

$$CH_3CSNH_2 + H_2O + H_3O^+ \rightarrow CH_3COOH + NH_4^+ + H_2S$$

which, in turn, allows tin sulphide precipitation following:

$$Sn^{2+} + H_2S \rightarrow SnS + 2H^+$$

with $K_{S2} = 3.25 \times 10^{-28}$ [16].

Such experimental conditions are fulfilled as we chose to maintain the bath temperature at 80 °C.

3. Results and discussion

Complementary characterization techniques are applied to the obtained films in order to study different aspects related to their fabrication: crystallography, surface morphology, volume and surface composition. Glass or SnO_2/glass substrates are used, and post-growth annealing is applied in some cases as mentioned below.

Tin sulphide thin film crystallography is studied using Philips XPer diffractometer and the (Cu)Kα energy ($\lambda = 1.5418$ Å). Thin films grown at 80 °C on glass and on SnO_2/glass substrates present an amorphous structure as reported in the literature [2]. A crystal structure appears when the layers are annealed during 40 min at 320 °C under nitrogen gas. Fig. 1a and b represents XRD spectra of annealed layers on glass, for [Sn]/[TA] equal to 0.5 and 1 respectively.