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Morphological and thermal properties of β-SnS_2 crystals grown by spray pyrolysis technique

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ABSTRACT

In this work, β-SnS_2 crystals were grown on glass substrates by the spray pyrolysis technique using tin chloride and thiourea precursors. Ex-situ characterizations of the crystals by means of scanning electron microscope, atomic force microscope and X-ray diffraction measurements have revealed a homogeneous and relatively smooth surface. The X-ray diffraction analysis of 910 nm thick β-SnS_2 layers grown at substrate temperature T_s=280 °C revealed an obvious crystallographic orientation in the hexagonal phase with a strong (0 0 1) diffraction line. Microprobe analyses as well as X-ray photoelectron spectroscopy show the presence of undesirable phase of SnO_2. On the other hand, the photothermal properties have been studied, the thermal diffusivity was D_c=16.2 × 10^{-6} m^2 s^{-1}.

1. Introduction

The tin disulfide compounds have attracted attention in recent years due to its numerous applications. Its band-gap energy varying inside the solar spectrum range [1–4] makes it suitable as an absorber or window layers in photovoltaic solar cells due to the possibility of the change of its character, n- or p-type. Moreover, this material does not contain toxic constituents. Several of its structural and optical characteristics have been reported.

Hai et al. [5] studied single crystals of SnS_2 synthesized via a solvothermal process and yielded interesting spectral response of photoconductivity measurements. Later, their results were confirmed by the works of Amalraj et al. [6] who investigated quaternary doped tin sulphide crystals fabricated for solar energy conversion purposes. In 2004, Di Chen et al. [7] prepared nanoscale $SnS_x|_{x=1,2}$ crystals for heterojunction diodes. More recently, Premchander et al. [8] reported structural and optical analyses of SeS and $SeSnS_2$ microcrystals.

In this work, tin disulfide crystals were fabricated by the mini-spray pyrolysis technique, we tried to model the thermal behavior of this material in order to evaluate its thermal conductivity taking into consideration the effect of the structure defaults.

2. Crystals preparation and characterisation

The tin disulphide crystals were obtained using a spray flow on a heated substrate. The precursor solutions were a mixture of methanol and tin tetrachloride and a thiourea concentrated solution. The value of the concentration ratio x=[S]/[Sn] and the substrate temperature T_s were, respectively, 2.5 and 280 °C [9].

The composition of the crystals was obtained by photoelectrons spectroscopy and via microprobe analysis. The identification of the type of characteristics of this compound has been made via infrared spectroscopy. X-ray diffraction spectra were obtained by means of a Philips X'Pert diffractometer using two monochromatic radiations CuK_α (λ_1=1.54056 Å; λ_2=1.54438 Å). The surface analyses were carried out by scanning electron microscopy (SEM) and atomic force microscopy (AFM). The surface quality and the growth rate were monitored periodically during the growth by reflectometry.

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The thermal behavior was studied using an enhanced photothermal technique [10].

3. Morphology and absorbance investigations

The MEB observations reveal a homogenous surface and a dense columnar structure (Fig. 1). This result has been confirmed by X-ray diffraction analysis. These analyses confirmed that the crystal is well crystallized with a strong (0 0 1) X-ray diffraction line showing a highly *c*-axis-oriented crystallites perpendicular to the substrate.

The reflections (Fig. 2) obtained by infrared spectroscopy (FTIR) show the presence of a first peak corresponding to tin sulphide situated at 210 cm^{-1} and a second one related to tin oxide located at 500 cm^{-1}. These results are consistent with those obtained by precedent studies [11,12].

Fig. 3 shows conjointly the optical transmittance and reflectance spectra of the as-grown β-SnS_2 crystal. The major feature in this figure appears to be a rise of the optical transmittance within the wavelength range 400–1400 nm.

Using the measured spectral transmittance and reflectance (Fig. 3), and the crystal film thickness $h = 910$ nm, the absorption coefficient α was calculated as a mean value of the expressions given by Moss [13] and Martinez et al. [14]:

$$\alpha = \frac{1}{h} \ln \frac{1-R}{T} \quad (1)$$

$$\alpha = \frac{1}{h} \ln \left(\frac{(1-R)^2}{T} \right) \quad (2)$$

$$\alpha = \frac{1}{h} \ln T^{-1} \quad (3)$$

Fig. 3 (bold line) shows the variations of the absorption coefficient α as a function of the incident wavelength.

4. Thermal properties

4.1. Photothermal measurements

An enhanced 'mirage effect' [15,16] disposal (Fig. 4) has been carried out for determining the glass-layer set effective

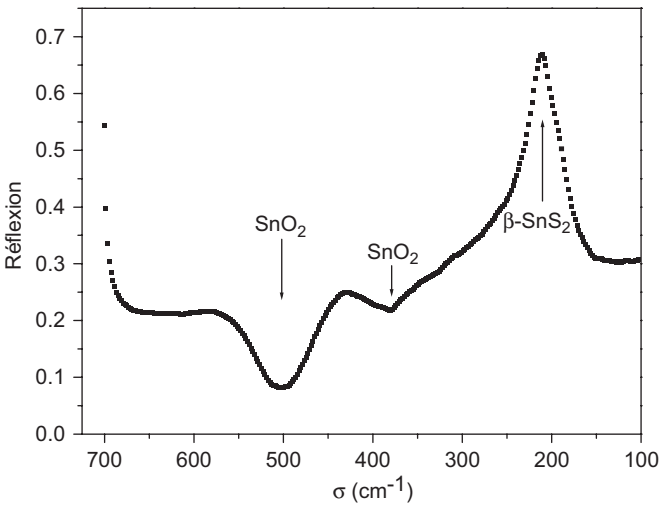

Fig. 2. IR reflection spectrum of β-SnS_2 crystal deposited on glass substrate.

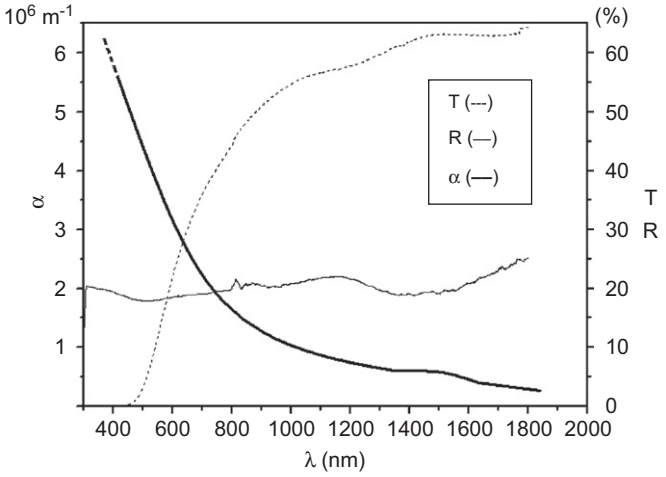

Fig. 3. β-SnS_2 crystal optical transmittance and reflectance spectra. (The bold line corresponds to the variations of the absorption coefficient α.)

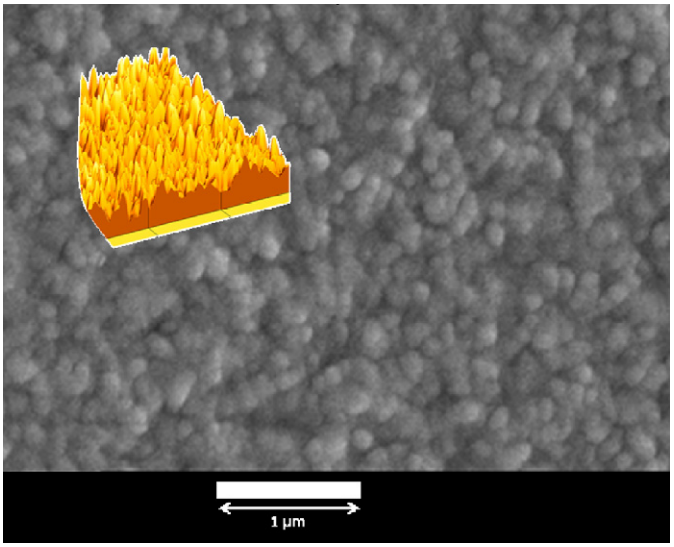

Fig. 1. SEM and 3D AFM micrographs of β-SnS_2 crystals.

Fig. 4. Experimental setup.