

Nucleation and growth study of SnS nanostructures prepared by electrodeposition method

A. Nouri*, D. Dekhil, H. Guessas

Laboratory of Photonics Systems and Nonlinear Optics, Institute of Optics and Precision Mechanics, University Setif 1, Algeria

SnS nanostructures were prepared using the electrodeposition technique in aqueous solutions containing 0.1M of SnSO₄ and Na₂SO₄. Three concentrations (0.05M, 0.10M, and 0.15M) of Na₂SO₄ were tested. The electrodeposition of SnS nanostructures on ITO substrates was investigated by cyclic voltammetry, chronoamperometry, SEM microscopy, and X-ray diffraction techniques. The concentration-dependent nucleation and growth mechanisms of electrodeposited SnS were analyzed using current transients. For the concentrations (0.05M and 0.10 M), the SnS films follow 3D growth in instantaneous nucleation mode. For a concentration of 0.15M, the SnS films start with progressive nucleation before switching to the instantaneous nucleation mode. The SnS nanostructures produced were found to be polycrystalline with an orthorhombic structure. XRD measurement shows that the preferred orientation of SnS nanostructures is in the (111) and (101) directions for the lower concentrations. SEM images reveal the 3D growth model of the samples, which is consistent with the electrochemical analysis.

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1. Introduction

Recent interest in the preparation and study of the physical properties of ternary and binary chalcogenide compounds has increased for their potential applications in optoelectronic devices and photovoltaic conversion. These physical properties are well affected by several parameters, such as the deposition method [1], concentration [2], temperature [3], and mode of nucleation and growth [4]. However, a typical optoelectronic device can only measure a few microns and expand in size over the course of minutes or even hours. Therefore, understanding the nucleation and growth of thin films is a significant challenge for physicists and material scientists.

Binary chalcogenide compounds can be prepared using a variety of methods, including spray pyrolysis, CVD, chemical bath deposition, and electrodeposition [1]. Among these methods, electrodeposition is a low-cost, convenient, and economic method for large-scale production with a relatively high growth rate. The electrodeposition method has been demonstrated to be a suitable method for studying nucleation and growth modes while utilizing transition current [5,6].

The aim of this work is to study the influence of the concentration of the precursor on the nucleation process and structural properties of the binary chalcogenide compound tin sulfide (SnS) electrodeposited on an ITO-coated glass substrate.

2. Experimental technique

Tin sulfide (SnS) thin films were formed using the electrodeposition method from an aqueous solution of thiosulfate of sodium (Na₂SO₄) and 0.1M of tin sulfate (SnSO₄). Three concentration of Na₂SO₄ were tested 0.05M, 0.1M and 0.15M. The PH of the solution was fixed at 4 by adding H₂SO₄. The electrochemical process of SnS thin films was carried out in a standard cell doted of three electrodes comprising ITO-coated glass, platinum plate and saturated calomel

* Corresponding author: ahak2009@univ-setif.dz
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electrode (SCE) as working, counter and reference electrodes respectively. Cell temperature and chemical reactions were maintained at room temperature. Prior the deposition process, the ITO-coated glass substrate was cleaned ultrasonically in acetone, ethanol and distilled water. The SnS thin films were deposited at fixed potential of -1V during 1h by using potentiostat/galvanostat (Autolab) as potential source. Structural and morphological analyses were performed using an X-ray diffractometer (XRD) and scanning electron microscope (SEM) respectively.

3. Results and discussion

3.1. Electrochemical study

In order to investigate the electrochemical behavior, the voltammetry cyclic was used. Fig. 1 shows the voltammogram onto ITO-coated glass from the aqueous solution of 0.1 SnSO₄ on a potential range of [0.6, -1.5] V/ECS with a scan rate of 20 mV/s. As shown in Fig. 1, the increase in cathodic current from -0.8 V to -1.4 V is quite clear. So, this means that all potential from this range can reduce the SnS nanostructure on the substrate. This result is in good agreement with that reported by Ichimura et al [7].

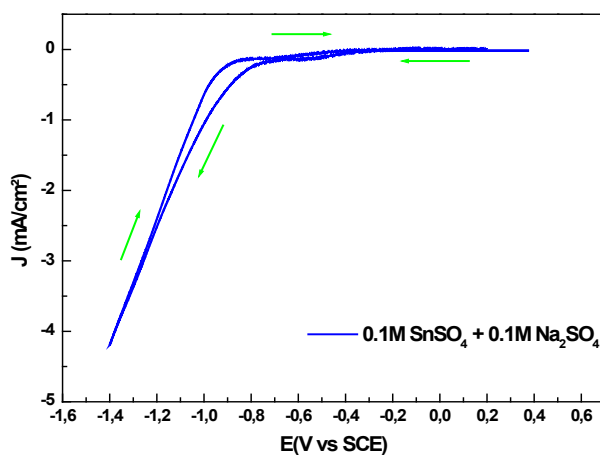


Fig. 1. Cyclic voltammogram (0.1M SnSO₄, 0.1M Na₂SO₄).

The following reactions show the formation of SnS nanostructures on the cathode (ITO):



The Sn⁺² and S are reduced at the cathodic to form SnS



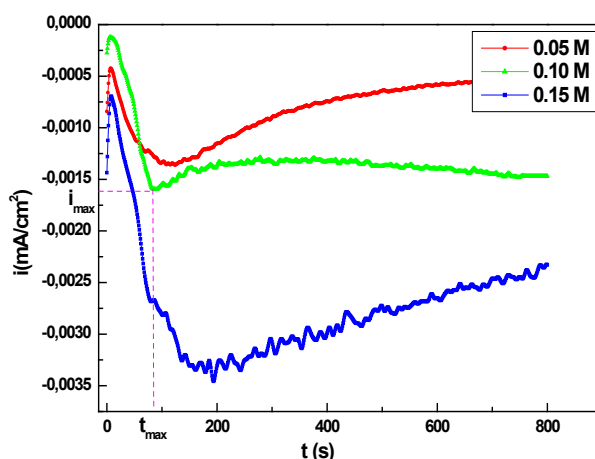


Fig. 2. Current transients of SnS nanostructures electrodeposited at -1 V vs. SCE.

Fig. 2 depicts the variation of current transients (i - t) obtained from the electrodeposition of SnS nanostructures at -1 V vs SCE. As shown in Fig. 2, the i - t curves of different concentrations tested are similar to each other. Thus, the current increases cathodically and rapidly, followed by a rapid decay. This is due to the discharging of the double layer formed at the interface of the ITO substrate and aqueous solution. Thereafter, the current rose again, revealing the birth of the new nuclei on the surface and the growth of the SnS films. This process is compatible with the formation of hemispherical diffusion zones encircling the growing nuclei, which eventually collide and combine in a manner that corresponds to linear diffusion. These characteristics are in alignment with the concept of 3D Island proposed by Scharifker et al [8]. According to Scharifker et al., the 3D island growth model has two modes of nucleation, depending on the rate of the nucleation and that of the growth. When succeeding nuclei develop quickly at all potential growth sites in a short period of time, nucleation is regarded as instantaneous. This occurs when the rate of nucleation is high relative to the rate of growth that results. Whereas, nucleation is referred to as progressive if it occurs at a slow rate and continues to occur at the surface while the prior nucleation sites continue to expand.

To investigate the mode of nucleation and growth of SnS nanostructures, the following equations are used [8]:

- Instantaneous nucleation:

$$\frac{i^2}{i_{max}^2} = 1.9542 \left(\frac{t_{max}}{t} \right) \left[1 - \exp \left(-1.2564 \frac{t}{t_{max}} \right) \right]^2 \quad (4)$$

- Progressive nucleation:

$$\frac{i^2}{i_{max}^2} = 1.2254 \left(\frac{t_{max}}{t} \right) \left[1 - \exp \left(-2.3367 \frac{t^2}{t_{max}^2} \right) \right]^2 \quad (5)$$

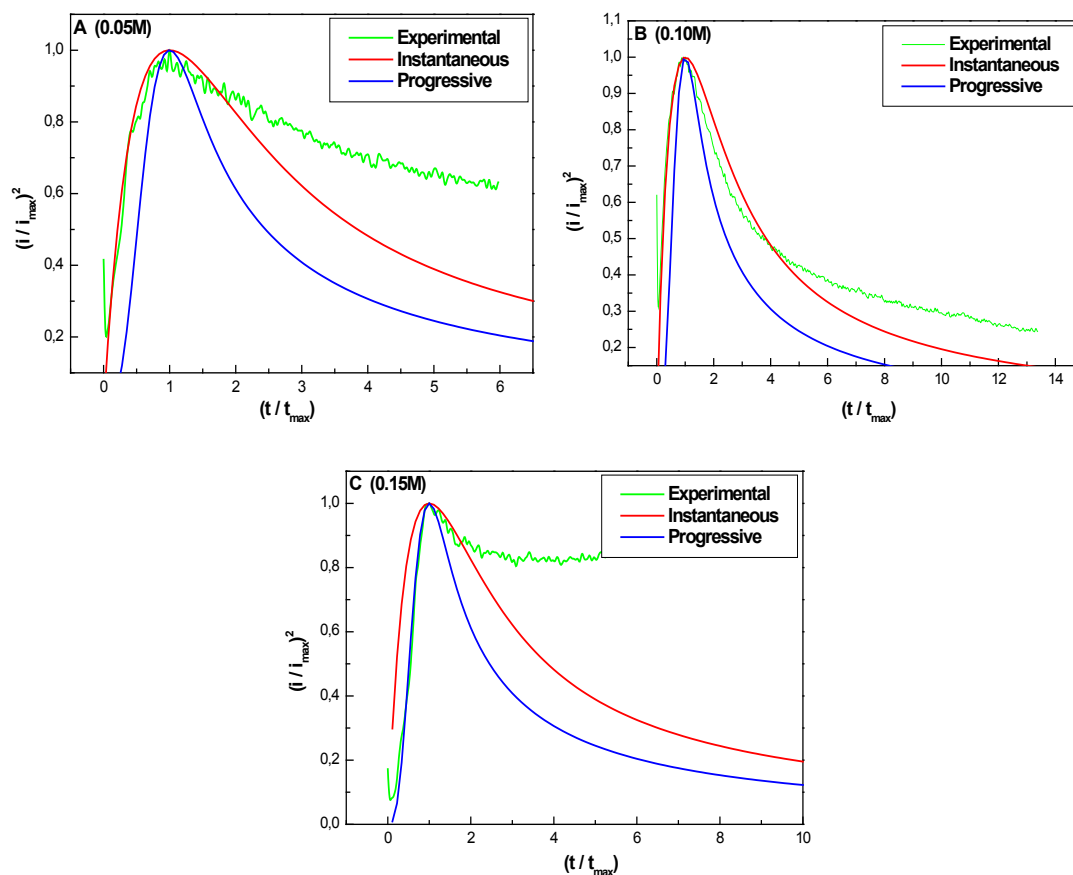


Fig. 3. Plot of theoretical model (red line) instantaneous nucleation, (blue line) progressive nucleation and (green line) experimental normalized current results, a)0.05M, b)0.10M, c)0.15M of Na_2SO_4 .

The mode of nucleation can be determined by comparing the theoretical model of equations (4) and (5) to the normalized current results. Fig. 3(a-b-c) displays the plot of the theoretical curves of instantaneous, progressive nucleation, and normalized experimental data. As can be seen in the figure, there is a high match between the experimental curves and the theoretical instantaneous and progressive curves. For the 0.05M and 0.1M concentrations of (Na_2SO_4), there is a perfect coincidence between the experimental curve and the theoretical curve of the instantaneous mode Fig.3 (a-b). This means that the mode of nucleation is instantaneous. In this mode of nucleation, at the very first instant of the deposition process, the incoming Sn and S atoms are typically reduced and simultaneously occupy all the active nucleation sites available on the ITO substrate. On the other hand, Fig. 3c demonstrates that at the early moment of deposition, the nucleation starts out in progressive mode before switching to instantaneous mode. For the first mode (Progressive), the wall-like structure formed by a high concentration (0.15M of Na_2SO_4) of S atoms in front of the ITO substrate's surface restricts the emergence of new nucleation sites at the same time as a slow rate of SnS nanostructure deposition. Then, with an increase in the rate of nucleation and growth by increasing the cathodic transient current (Fig. 2), the electrochemical process switched to an instantaneous mode (Fig. 3c)[9].

3.2. Structural study

XRD measurements were carried out in order to follow the microstructural evolution of the SnS nanostructures. Fig. 4 illustrates the XRD patterns of SnS nanostructures at different concentrations of Na_2SO_4 that were deposited at -1V vs SCE. The peaks (0 2 1), (1 0 1), (1 1 1), and (1 3 1) located at 26.19° , 30.58° , 31.61° , and 39.15° are in good agreement with the typical orthorhombic structure of the SnS diffraction pattern (JCPDS card No. 75-2115) and that reported by Dekhil et al[3]. Other phases' or impurities' characteristic diffraction peaks were not found. The SnS nanostructures have a high degree of crystallinity and purity, which is shown by the sharp

shape and narrow diffraction peaks. As shown in Fig. 4, it is evident that the intensity of the (0 2 1), (1 0 1), (1 1 1), and (1 3 1) peaks of the SnS nanostructures varied with the concentration of the aqueous solution, indicating a change in the film's degree of crystallinity. Furthermore, as the concentration of Na_2SO_4 was increased from 0.05M to 0.15M, the preferred orientation of the nanostructures shifted from the (101) and (111) peaks to the (021) peaks. In fact, the (111) and (101) planes are more growth-active than other planes. The high concentration (0.15M of Na_2SO_4) of S atoms in solution inhibits growth in the (111) and (101) directions, which makes the (021) plane more favorable as a growth direction [10].

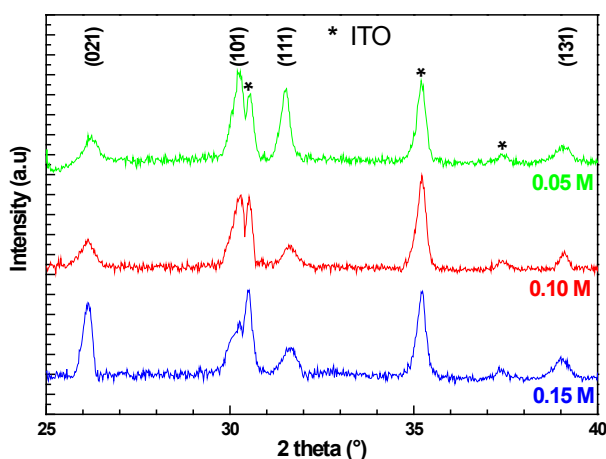


Fig. 4. XRD patterns of the films electrodeposited at $-1V$ at different concentrations of Na_2SO_4 (0.05 M, 0.1 M, and 0.15M) and SnSO_4 (0.1 M).

3.3. Surface morphology

Fig. 5, depict the images of the samples deposited with different concentration during 1 hour at $-1V$ vs SCE.

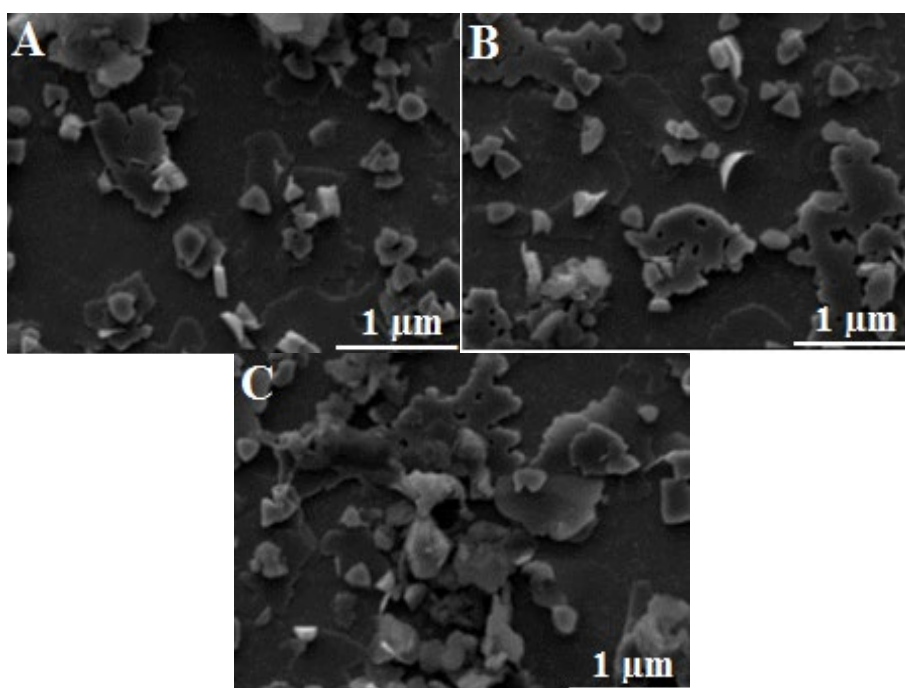


Fig. 5. SEM images of SnS nanostructures electrodeposited at $-1V$ vs SCE at different concentrations a) 0.05M, b) 0.10M, and c) 0.15M.

As shown in Fig. 5, the deposition of SnS nanostructures is plate-shaped and parallel to the substrate surface. Additionally, 3D island formation is quite evident for the lower concentrations, as illustrated in Fig. 5(a, b). The result is well consistent with the electrochemical investigation. On the other hand, at higher concentrations (0.15M), SnS nanostructure growth starts to lose its plate-shaped growth characteristic and turns into an aggregation. This result is in good agreement with that discussing the change in the mode of nucleation [11].

4. Conclusion

In this work, SnS nanostructures were synthesized using the electrochemical method with different concentrations of aqueous solution and a potential of -1 V vs. SCE. The electrochemical study shows the effect of the concentrations on the growth and nucleation modes. The SnS nanostructures follow a 3D growth model with instantaneous nucleation mode at the lower concentrations investigated (0.05M, 0.10M) of Na₂SO₄. Whereas, at higher concentrations (0.15M) of Na₂SO₄, SnS nanostructures begin with a progressive nucleation mode before switching to an instantaneous nucleation mode. The SEM images demonstrate the 3D growth of SnS nanostructures and support the results of the electrochemical analysis. The SnS nanostructures are of the highest quality of crystallinity, with a typical orthorhombic structure, according to XRD measurements.

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