Research Article

Structural and Morphological Characterization of Chemical Bath Deposition of FeS Thin Films in the Presence of Sodium Tartrate as a Complexing Agent

Anuar Kassim[1*], Ho Soon Min[1], Loh Yean Yee[1] and Saravanan Nagalingam[2]

[1]*Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia*
[2]*Faculty of Science, Universiti Tunku Abdul Rahman, 31900 Kampar, Perak, Malaysia*
[*]*Corresponding author. E-mail address: soonminho@gmail.com*

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Abstract

In this paper, we presented the results of X-ray diffraction and scanning electron microscopy of the iron sulphide thin films prepared using a simple and cost effective chemical bath deposition method. The effects of solution concentration and pH on the structural and morphological properties of thin films were studied in the presence of sodium tartrate as a complexing agent. The thin films deposited using higher solution concentration showed higher number of FeS peaks and larger grain size according to X-ray diffraction and scanning electron microscopy results, respectively as compared with other solution concentrations. On the other hand, when the thin films were deposited at higher pH, the number of FeS peaks reduced to two peaks and the films showed incomplete coverage of material over the surface of the substrate with the smaller grain size.

***Key Words*:** Chemical bath deposition; Iron sulphide; Scanning electron microscopy; Thin films

Introduction

Iron sulphide thin films are very attractive materials for a wide variety of technological applications such as photoelectrochemical and photovoltaic applications. Various methods are used for the preparation of iron sulphide thin films such as chemical vapor transport (Willeke et al., 1992), metal-organic chemical vapour deposition (Thomas et al., 1997), sputtering (Birkholz et al., 1992), molecular beam deposition (Bronold et al., 1997), flash evaporation (Ferrer et al., 1990), electrodeposition (Nakamura and Yamamoto, 2001) and chemical bath deposition (Anuar et al., 2010). Among various other methods, the chemical bath deposition method is found to be a cheap and simple way to deposit large area polycrystalline metal chalcogenide thin films. The preparations of various thin films using chemical bath deposition technique such as CdS (Moualkia et al., 2009), As_2S_3 (Mane et al., 2004), MnS (Gumus et al., 2007), PbS (Larramendi et al., 2001), ZnS (Ubale et al., 2007), $Cd_{0.5}Zn_{0.5}Se$ (Kale et al., 2007) and Cu_4SnS_4 (Anuar et al., 2009) have reported by several authors.

However, there is no attempt made on the chemical bath deposition of the iron sulphide thin films, using sodium tartrate as a complexing agent.

In view of this, the synthesis of iron sulphide thin films was performed at different pH values and solution concentrations. The crystal structure and surface morphology of iron sulphide thin films were then investigated.

Materials and methods

All the chemicals used for the deposition were analytical grade reagents and all the solutions were prepared in deionised water (Alpha-Q Millipore). The iron sulphide thin films were prepared from an acidic bath containing aqueous solutions of iron nitrate, sodium thiosulfate and sodium tartrate. The microscope glass slide was used as the substrate for the chemical bath deposition of iron sulphide thin films. Before deposition, the microscope glass slide was degreased with ethanol for 15 min, then, ultrasonically cleaned with distilled water for another 15 min and dried in desiccators. Deposition of iron sulphide thin films was carried out using following procedure. 20 mL of iron nitrate was complexed with 20 mL of 0.2 M sodium tartrate. Then, 20 mL of sodium thiosulfate was added slowly to the mixture. The cleaned glass slide was immersed vertically into the solution. The deposition process was carried out by varying solution concentrations (0.1, 0.15 and 0.2 M) and pH values (2 and 2.5). During deposition process, the beaker was kept undisturbed. After the completion of deposition (2 h), the glass slide was removed, washed several times with distilled water and dried in desiccators for further characterization.

In order to investigate the crystallographic properties of the iron sulphide thin films, the X-ray diffraction analyses were carried out using Philips PM 11730 diffractometer with CuK_{α} (λ=1.5418 Å) radiation for the 2θ ranging from 20 to 65°. The surface morphology was observed by a scanning electron microscopy (JEOL, JSM-6400). All the samples were taken at 20 kV with a 1000 X magnification.

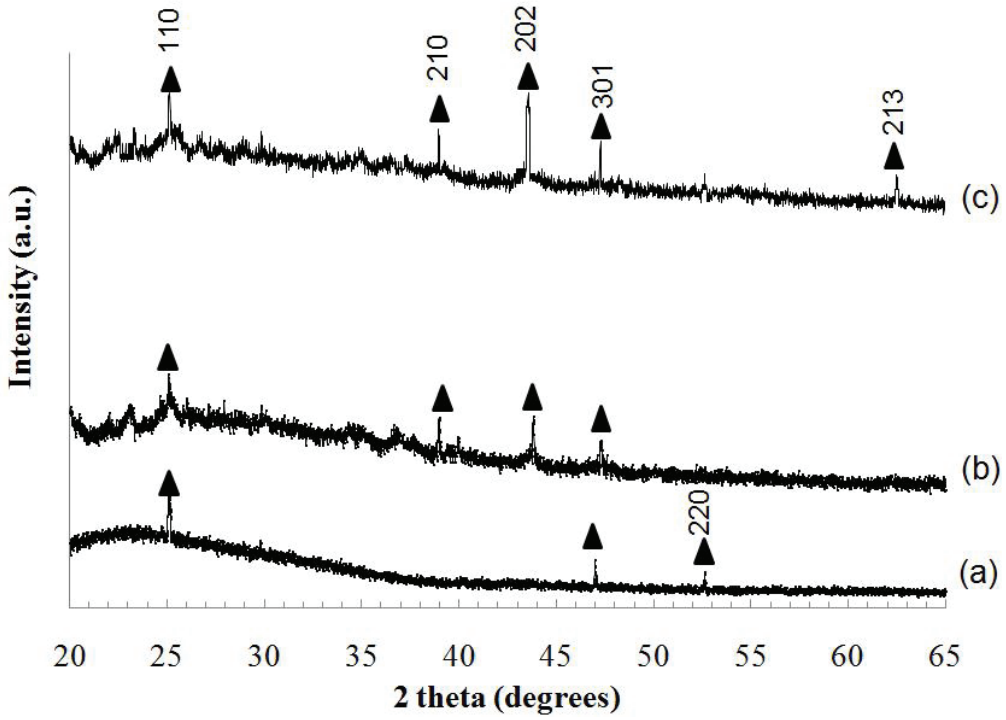

Figure 1 X-ray diffraction patterns for iron sulphide thin films deposited at various solution concentrations at pH 2. (a) 0.1 M (b) 0.15 M (c) 0.2 M

Table 1 Comparison of the JCPDS *d*-spacing data for iron sulphide thin films to experimentally observed values for the sample deposited at various solution concentrations at pH 2

Solution concentration (M)	2θ (°)	*hkl*	*d*-spacing (Å)	
			Observed value	JCPDS value
0.1	25.1	110	3.5	3.5
	46.9	301	2.0	1.9
	52.6	220	1.8	1.7
0.15	25.2	110	3.5	3.5
	38.9	210	2.3	2.3
	43.7	202	2.1	2.1
	47.0	301	1.9	1.9
0.2	25.2	110	3.5	3.5
	38.6	210	2.4	2.3
	43.7	202	2.1	2.1
	47.3	301	1.9	1.9
	62.5	213	1.5	1.5

Results and discussion

Figure 1 and Table 1 show the X-ray diffraction (XRD) patterns and data for the thin films deposited at various solution concentrations at pH 2, respectively. For the thin films prepared using 0.1 M iron nitrate and sodium thiosulfate, three peaks at 2θ= 25.1°, 46.9° and 52.6° are observed, which referred to the (110), (301) and (220) planes of FeS, respectively. However, the number of peaks increased to four (Figure 1b) and finally five peaks (Figure 1c) when the concentration is increased to 0.15 and 0.2 M, respectively. The position of several peaks is used to determine the iron sulphide as shown in Table 1. These peaks are well matched with the Joint Committee on Powder Diffraction Standard (JCPDS) data for FeS (JCPDS reference code: 01-080-1028) (Keller-Besrest and Collin, 1990). The lattice parameter values are a=b=6.958 Å, c=5.824 Å, α=β=90°, γ=120°.

Figure 2 shows the scanning electron microscopy (SEM) micrographs of the FeS thin films prepared using different solution concentrations at pH 2. Based on the Figure 2a, the films prepared using 0.1 M $Fe(NO_3)_3$ and $Na_2S_2O_3$ show incomplete coverage of material over the surface of the substrate. This may be caused by insufficient amount of iron and sulfide ions in the mixture. The thin films deposition process on a substrate depends mainly on the formation of nucleation sites and subsequent growth of the thin films from this centre. However, further increment in the solution concentration to 0.15 M $Fe(NO_3)_3$ and $Na_2S_2O_3$ indicates almost complete coverage of the FeS material over the substrate compared to the films prepared at lower concentration. At higher concentration (0.2 M), the material is found to cover the surface of the substrate completely. Formation of granules, which is uniformly distributed over the deposit layer, can

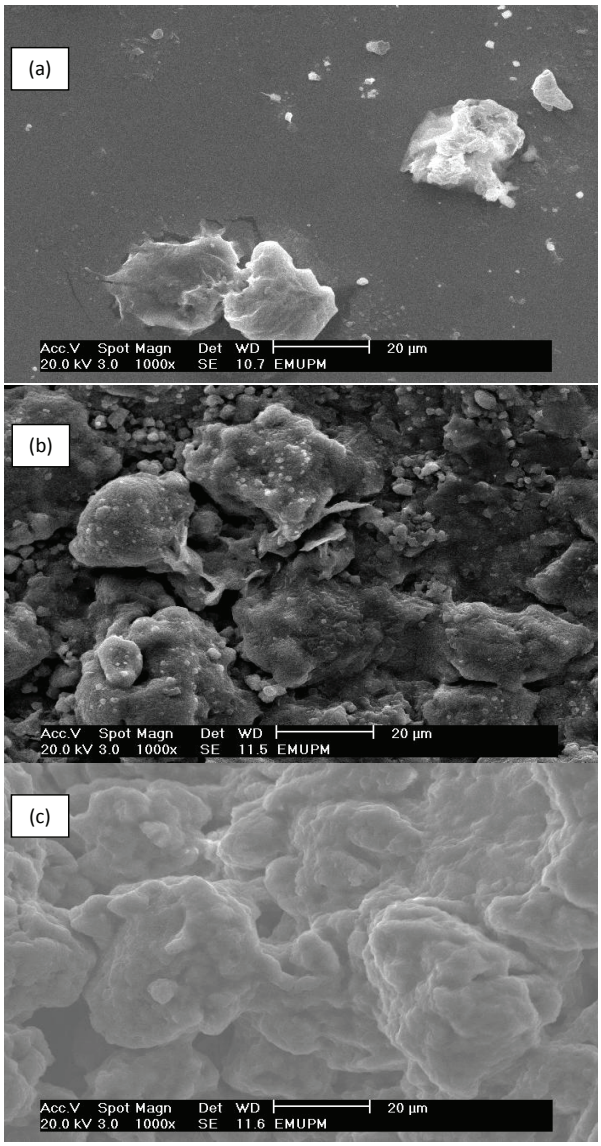

Figure 2 Scanning electron microscopy micrographs of the FeS thin films prepared using different solution concentrations at pH 2. (a) 0.1 M (b) 0.15 M (c) 0.2 M

be seen in Figure 2c. The grain sizes (4-6 µm) were almost similar to each other. Based on the SEM micrograph, the grains structures are formed in an agglomerated morphology (average size is about 20 µm).

Figure 3 and Table 2 show the X-ray diffraction (XRD) patterns and XRD data for the iron sulphide thin films prepared at various pH values using 0.2 M iron nitrate and sodium thiosulfate, respectively. Comparison between the thin films deposited at pH 2 and 2.5 reveals that the number of FeS peaks increased, indicating better crystalline phase for the films prepared at lower pH. The films deposited at pH 2 show five peaks and the d-spacing values obtained match with the standard JCPDS data (Table 2). The positions of the peaks obtained indicate that hexagonal FeS structure with (110), (210), (202), (301) and (213) planes have been deposited. On the other hand, we observed that the intensity of the peaks were much better for the films deposited at pH 2. At lower pH value, the peak intensities were increasing which showed the improvement in the crystallinity of the films. As the pH was decreased from pH 2.5 to 2, the intensity of the peaks corresponding to (110) and (202) planes increased. These planes seem dominant at this stage of experiment.

The scanning electron microscopy (SEM) micrographs of the iron sulphide thin films prepared at different pH solutions using 0.2 M $Fe(NO_3)_3$ and $Na_2S_2O_3$ are shown in Figure 4.

The SEM micrograph of the thin films deposited at pH 2 shows distribution of grains, which covers the surface of the substrate completely (Figure 4a). However, as the pH is increased to 2.5, the distribution of grains has been reduced and resulted in a lower surface coverage. These films have smaller grains compared to the other films (Figure 4b). The pinholes can be observed on the surface of these films. The pinholes are areas which were not covered by thin films.

Conclusions

FeS thin films have been successfully deposited by chemical bath deposition method. XRD study revealed polycrystalline nature of the films with hexagonal phase. Based on the XRD data, the films prepared at lower pH and higher solution concentration indicated higher number of FeS peaks. The surface morphology of these films was observed quite uniform and well covered on the substrate than

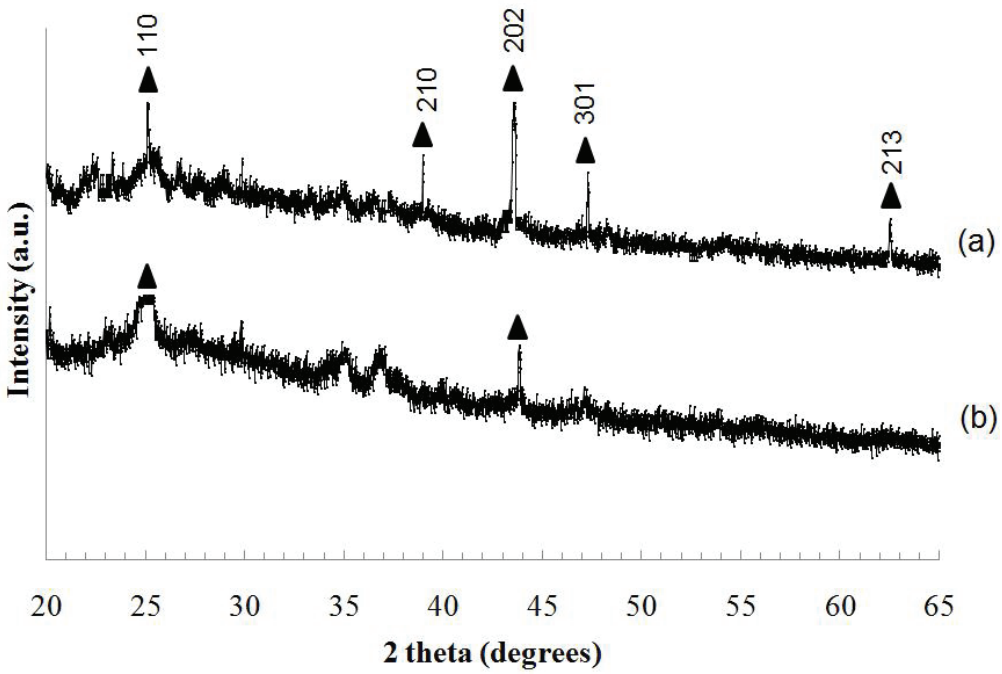

Figure 3 X-ray diffraction patterns for iron sulphide thin films deposited at various pH values using 0.2 M iron nitrate and sodium thiosulfate (a) pH 2 (b) pH 2.5

Table 2 Comparison of the JCPDS *d*-spacing data for iron sulphide thin films to experimentally observed values for the sample deposited at various pH values using 0.2 M iron nitrate and sodium thiosulfate

pH	2θ (°)	*hkl*	*d*-spacing (Å)	
			Observed value	JCPDS value
2	25.2	110	3.5	3.5
	38.6	210	2.4	2.3
	43.7	202	2.1	2.1
	47.3	301	1.9	1.9
	62.5	213	1.5	1.5
2.5	25.2	110	3.5	3.5
	43.7	202	2.1	2.1

other samples. Experimental results indicated that the deposition at pH 2 using 0.2 M iron nitrate and sodium thiosulphate was the optimum condition for the preparation of FeS films.

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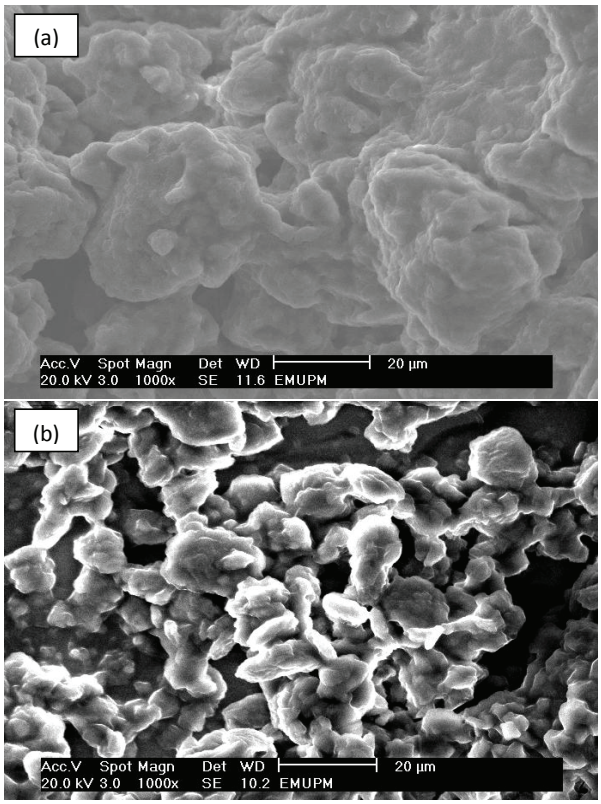

Figure 4 Scanning electron microscopy micrographs of the iron sulphide thin films prepared at different pH solutions using 0.2 M $Fe(NO_3)_3$ and $Na_2S_2O_3$. (a) pH 2 (b) pH 2.5

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