

## COMPLEXING AGENT EFFECT ON THE PROPERTIES OF IRON SULPHIDE THIN FILMS

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### ABSTRACT

Thin films of iron sulphide were prepared by chemical bath deposition technique in aqueous solutions. The influence of complexing agent for the formation of thin films was determined. The structure, morphology and optical properties of thin films of iron sulphide grown on microscope glass slide were investigated by X-ray diffraction, scanning electron microscopy and UV-Vis spectrophotometer. The films deposited using 0.1 M of sodium tartrate indicated the highest number of FeS peaks and covered substrate surface completely based on X-ray diffraction data and scanning electron microscopy results, respectively. However, when the concentration of sodium tartrate was increased to 0.2 M and above, the number of FeS peaks decreased and the films showed incomplete coverage of material over the surface of the substrate with inhomogeneous grain size.

**Keywords:** Chemical bath deposition, complexing agent, thin films, iron sulphide.

### INTRODUCTION

The iron sulphide thin films have attracted considerable attention in recent years, because of abundant and possess semiconducting properties. Numerous deposition techniques including 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.*, 2009) have been employed for the growth of iron sulphide thin films. Among these deposition techniques, the chemical bath deposition is a very common deposition method (Sonawane *et al.*, 2004; Goudarzi *et al.*, 2008; Hankare *et al.*, 2008; Moualkia *et al.*, 2009; Asenjo *et al.*, 2010; Ekuma *et al.*, 2010; Gopakumar *et al.*, 2010; Anuar *et al.*, 2011) with respect to economic considerations.

In this investigation, deposition of iron sulphide thin films on microscope glass slides using chemical bath deposition method is presented. To our knowledge, a study on the properties of the chemical bath deposited iron sulphide thin films in the presence of sodium tartrate as a complexing agent has not been reported so far. Here, we report the influence of sodium tartrate on the structure, morphology and optical properties of thin films using X-ray diffraction, scanning electron microscopy and UV-Visible spectrophotometer, respectively.

### 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 using 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 15min. 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. 20ml of iron nitrate (0.1M) was complexed with 20ml of various concentrations of sodium tartrate (0.1M, 0.2M and 0.3M) in order to study the influence of complexing agent on the properties of thin films. Then 20ml of sodium thiosulfate (0.1M) was added slowly to the mixture. The cleaned glass slide was immersed vertically into beaker. The pH was adjusted to 1.5 by adding hydrochloric acid using pH meter. During deposition process, the beaker was kept undisturbed at 75°C. After the completion of deposition (1.5h), the glass slide was removed, washed several times with distilled water and dried naturally in desiccators for further characterization.

In order to investigate the crystallographic properties of the iron sulphide thin films, we carried out the X-ray diffraction analysis using Philips PM 11730 diffractometer with  $\text{CuK}_\alpha$  ( $\lambda=1.5418 \text{ \AA}$ ) radiation. The surface morphology was observed by a scanning electron

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microscopy (JEOL, JSM-6400). All the samples taken at 20 kV with a 1000 X magnification. The elemental composition of the films was studied by scanning electron microscope attached with energy dispersive analysis of X-ray (EDAX) analyzer. The optical properties of the film were measured with a Perkin Elmer UV/Vis Lambda 20 Spectrophotometer in the wavelength range of 300 to 800nm. The film-coated microscope glass slide was placed across the sample radiation pathway while the uncoated microscope glass slide was put across the reference path. Thus, the absorbance measurement included only the contribution from FeS thin films.

## RESULTS AND DISCUSSION

Table 1 indicates the X-ray diffraction (XRD) data for the films deposited at various concentrations of sodium tartrate. Five peaks at  $2\theta = 25.2^\circ, 38.6^\circ, 43.7^\circ, 47.3^\circ$  and  $62.5^\circ$  corresponding to  $d$ -spacing values of 3.5, 2.4, 2.1, 1.9 and 1.5 Å are attributed to the (110), (210), (202), (301) and (213) planes, which belong to FeS, are detected from the films deposited using 0.1M of sodium tartrate. All of the peaks are coincident well with the corresponding diffraction peaks of FeS (Keller-Besrest and Collin, 1990) compound (JCPDS reference code: 01-080-1028). The lattice parameter values for the dominant structure are:  $a=b=6.958$  Å and  $c=5.824$  Å. However, the number of hexagonal phase of FeS peaks decreased to four and three peaks as the concentration of sodium tartrate is increased to 0.2M and 0.3M, respectively. It is believed that the complexing reaction is complete with high concentration of complexing agent (0.2M and 0.3M) and therefore hinders the deposition of films. In this study, the position of several peaks is used to determine the iron sulphide as shown in table 1. The use of complexing agent is very common in the preparation of thin films through chemical bath deposition method. Iron sulphide thin films are deposited on microscope glass

slides by the decomposition of iron nitrate and sodium thiosulphate in acidic medium containing sodium tartrate as complexing agent. Iron nitrate is the source to produce  $Fe^{2+}$  while sodium thiosulphate is the source to produce  $S^{2-}$ . Sodium tartrate played the important role on this study that is to react with  $Fe^{2+}$  ions to form Fe-tartrate complex. It is to release the  $Fe^{2+}$  ions on slowly and improved the lifetime of the deposition bath as well as adhesion of the deposition thin films on substrate.

The investigation of scanning electron microscopy (SEM) micrographs from figure 1 brings to a comparison of the surface morphologies from the deposited films under different concentrations of sodium tartrate. For the films deposited using 0.1M of complexing agent, the films indicate complete coverage of material over the surface of the substrate. In contrast, SEM micrographs show incomplete coverage of material over substrate surface for the films deposited using 0.2M and 0.3M of complexing agent. The number of grains decreased as the concentration of complex agent is increased to 0.2M and 0.3M, respectively. Furthermore, various grain sizes can be seen from SEM micrographs which indicating irregular growth rate of the grains. The distributions of grains are randomly throughout the substrate with certain sites only occupied by the grains. Therefore, we can conclude that the morphology of iron sulphide thin films is strongly dependent on the complexing agent.

Optical absorbance spectra of FeS thin films deposited under different concentrations of sodium tartrate are given in figure 2. As it can be observed that the absorbance spectrum of the films deposited using 0.1M sodium tartrate is very high in comparison with other samples in the visible region. The higher absorbance can be due to more FeS materials deposited (five prominent FeS peaks) and these materials are found to cover the surface of the substrate completely (Fig. 1a).

Table 1. Comparison of the JCPDS  $d$ -spacing data for iron sulphide thin films to experimentally observed values for the sample deposited at various concentrations of sodium tartrate.

Sodium tartrate (M)	$2\theta / (^\circ)$	$hkl$	$d$ -spacing (Å) Observed value	JCPDS value
0.1	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
0.2	25.2	110	3.5	3.5
	39.1	210	2.3	2.3
	43.5	202	2.1	2.1
	47.3	301	1.9	1.9
0.3	25.1	110	3.5	3.5
	43.6	202	2.1	2.1
	51.9	220	1.8	1.8

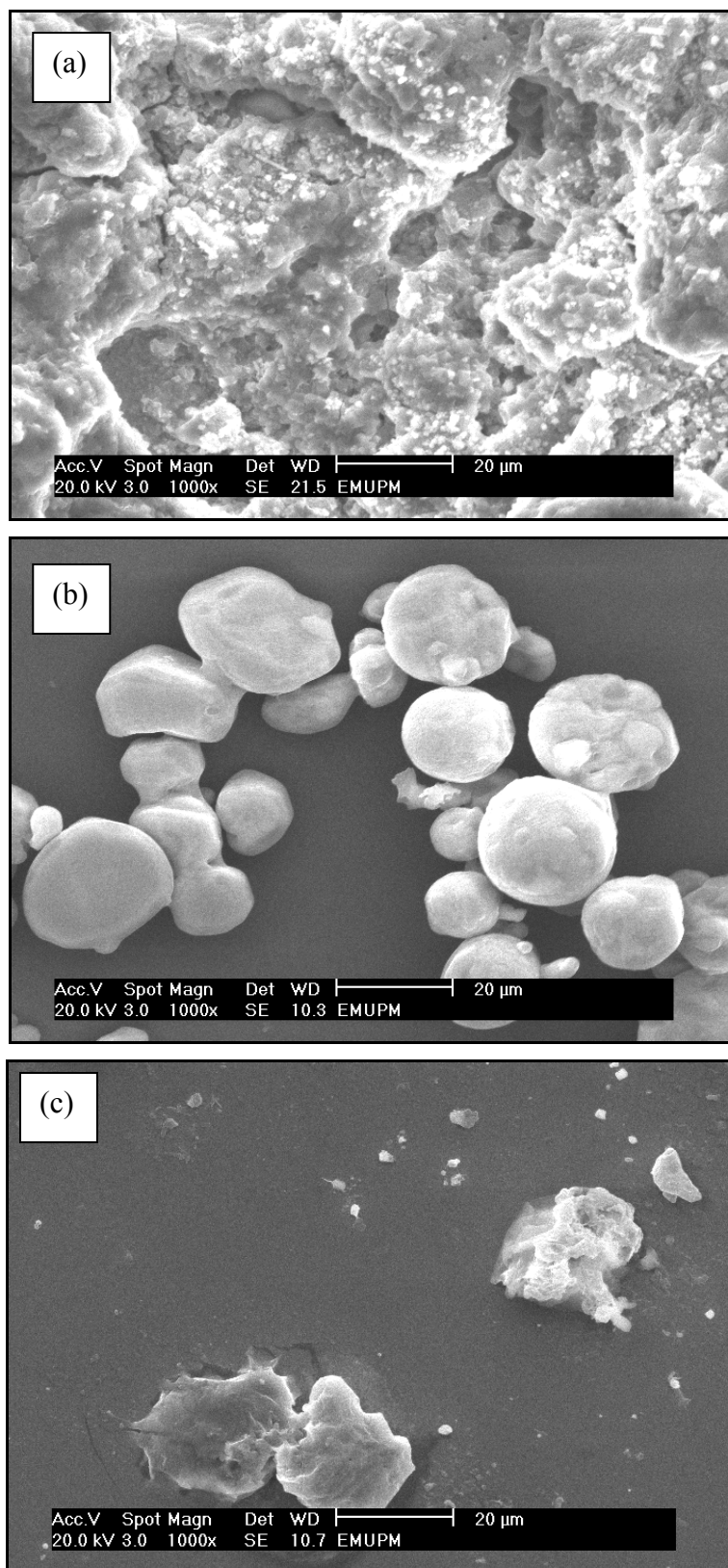


Fig. 1. The scanning electron microscopy (SEM) micrographs of FeS thin films deposited at various concentrations of sodium tartrate (a) 0.1M (b) 0.2M (c) 0.3M.

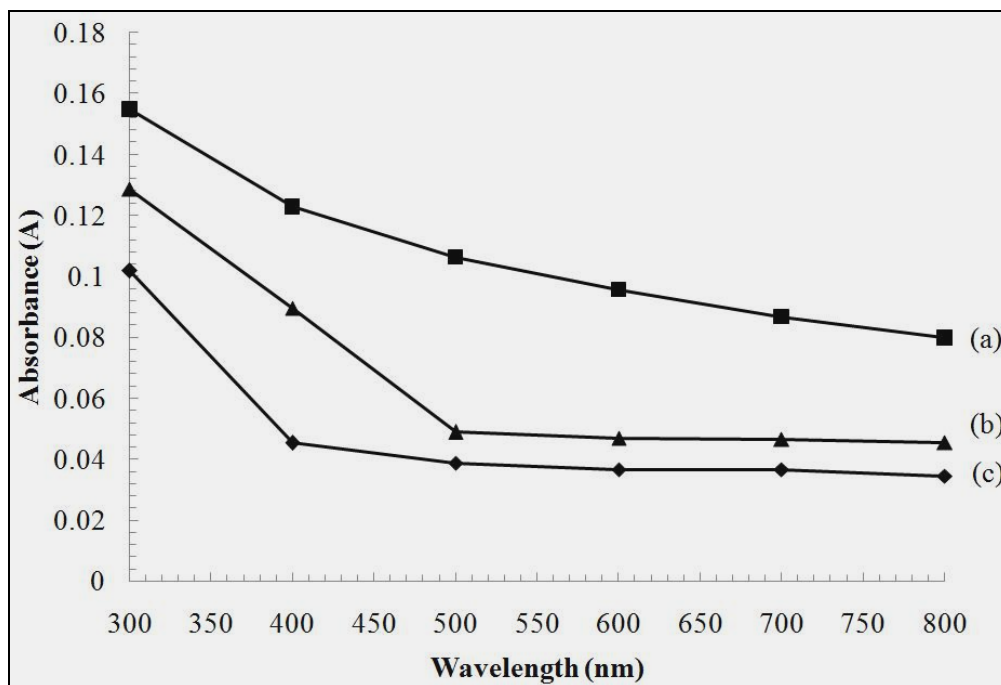


Fig. 2. Optical absorbance versus wavelength of FeS thin films deposited at various concentrations of sodium tartrate (a) 0.1M (b) 0.2M (c) 0.3M.

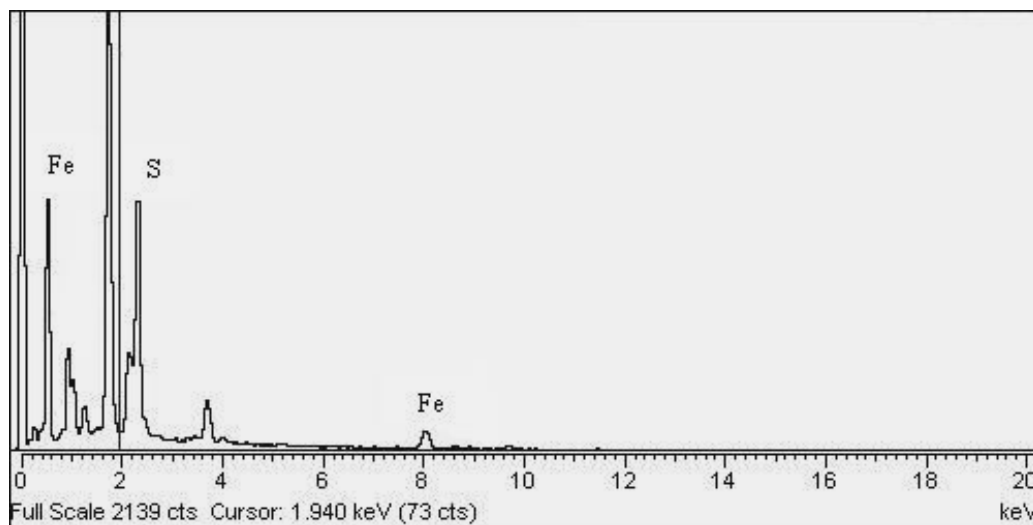


Fig. 3. EDAX spectrum of FeS thin films prepared using 0.1M of sodium tartrate as complexing agent.

The compositional analysis of the thin films was investigated by energy dispersive analysis of X-ray (EDAX) technique. The EDAX spectrum of FeS thin films prepared using 0.1M of sodium tartrate is shown in figure 3. The quantitative elemental analysis is carried out only for Fe and S. The atomic percentage (%) for these elements is 49.1% and 50.9%, respectively. The ratio of 1:1 of iron and sulphur has been confirmed by EDAX analysis.

## CONCLUSION

In this paper, we presented the influence of complexing agent on the properties of FeS thin films. Overall, we concluded that 0.1M of sodium tartrate is the most favourable condition for growth of thin films. These films showed presence of higher number of FeS peaks and completely covered substrate surface based on X-ray diffraction and scanning electron microscopy results, respectively.

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