

Influence of pH Values on Chemical Bath Deposited FeS₂ Thin Films.

K. Anuar, Ph.D.^{1*}, W.T. Tan, Ph.D.¹, N. Saravanan, Ph.D.², S.M. Ho, M.Sc.¹,
and S.Y. Gwee, B.Sc.¹

¹Department of Chemistry, Faculty of Science, Universiti Putra Malaysia,
43400 Serdang, Selangor, Malaysia.

²Department of Bioscience and Chemistry, Faculty of Engineering and Science,
Universiti Tunku Abdul Rahman, 53300 Kuala Lumpur, Malaysia.

*E-mail: anuar@fsas.upm.edu.my

ABSTRACT

FeS₂ thin films have been deposited from an aqueous solution onto microscope glass substrates by chemical bath deposition method. The structural, morphological, and optical properties of the deposited films have been studied using X-ray diffraction, atomic force microscopy and UV-Vis spectrophotometer, respectively. The XRD patterns of FeS₂ films showed polycrystalline nature and orthorhombic structure. It is also clearly shown that increasing pH from 0.5 to 2.5 improved the crystalline phase of FeS₂ film. The film deposited at higher pH value showed complete surface coverage with bigger grain size when compared with lower pH value according to AFM images. All films showed direct band gap transition. The band gap of the film varied from 1.85 to 2.25 eV. Deposition at pH 2.5 proved to offer a reasonably good quality of FeS₂ thin film.

(Keywords: chemical bath deposition, semiconductor, thin films, X-ray diffraction)

INTRODUCTION

Metal chalcogenide thin films have been a subject of interest for many years mainly due to their possible application to the manufacture of large area photodiode arrays, solar selective coatings, solar cells and sensors. The main advantage of binary (Rashwan et al., 2007; Inamdar et al., 2008) and ternary (Lin et al., 2008; Anuar et al., 2007) chalcogenide semiconductors is their promise of lower costs, since less energy for processing and relatively lower costs for the materials are required and large scale production is feasible.

FeS₂ thin film has attracted considerable attention in recent years, because of is composed of very abundant, cheap, nontoxic elements and posses semiconducting properties. Various processes such as flash evaporation (Ferrer et al., 1990), metal organic chemical vapor deposition (Thomas et al., 1997), sputtering (Birkholz et al., 1992), chemical vapor transport (Willeke et al., 1992), electodeposition (Nakamura and Yamamoto, 2001) and molecular beam deposition (Bronold et al., 1997) method have been employed to produce FeS₂ thin films. However, there is no literature review for the preparation of FeS₂ thin film using chemical bath deposition method so far. In present investigation, we report the growth and characterization of FeS₂ thin films deposited by chemical bath deposition method.

Chemical bath deposition technique is a relatively inexpensive, simple and convenient method for large area deposition and a variety of substrates can be used to grow thin films (Ugwu and Onah, 2007; Okoli et al., 2006; Khefacha et al., 2004; Bari et al., 2007; Hankare et al., 2006; Larramendi et al., 2001). This method does not require complicated instrumentation.

FeS₂ thin films were deposited by using aqueous solutions of iron nitrate, triethanolamine, hydrochloric acid and sodium thiosulfate, where triethanolamine was used as the complexing agent and hydrochloric acid as the pH adjuster. The effect of pH values on structural, morphological and optical properties of these films is investigated in order to optimize the conditions of deposition process.

EXPERIMENTAL DETAILS

All the chemicals used for the deposition were analytical grade and all the solutions were prepared in deionized water (Alpha-Q Millipore). The FeS₂ thin films were prepared from an acidic bath using aqueous solutions of iron nitrate (Fe(NO₃)₃·9H₂O) and sodium thiosulfate (Na₂S₂O₃·5H₂O) act as a source of iron and sulfide ion, respectively. The triethanolamine ((HOC₂H₄)₃N) is used as a complexing agent during deposition process. In order to investigate the influence of the pH values on the chemical bath deposited films, the deposition was carried out under different pH values ranging from 0.5 to 3.5. Firstly, 10 mL of triethanolamine (TEA) and 20 ml of 0.15 M iron nitrate were mixed and stirred for several minutes to get a homogeneous solution. Thereafter, 20 ml of 0.15 M Na₂S₂O₃ was added under stirring condition. Finally, hydrochloric acid was added into this solution to adjust the pH at the desired pH value.

The microscope glass slides were used as the substrate for the chemical bath deposition of FeS₂ thin film. Before deposition, the glass slides were degreased with ethanol for 10 min. Then, ultrasonically cleaned by deionized water for 10 min and dried in air. The cleaned glass substrate was immersed vertically into acidic bath. The deposition process was carried out for 90 min at 90 °C. The film deposition was carried out with the same bath composition for different pH values, ranging from 0.5 to 3.5. After completion of film deposition, the glass slide was removed from the beaker and was cleaned with deionized water.

The crystal structure of the film was monitored by X-ray diffraction (XRD) with a Philips PM 11730 diffractometer equipped with a CuK_α (λ=1.5418 Å) radiation source. Data were collected by step scanning from 25° to 60° (2θ) with a step size of 0.05° (2θ) and 1s counting time per step. Surface morphologies of the films were observed by using a Q-Scope 250 (Quesant Instrument Corporation) atomic force microscope in a contact mode. The optical properties of the films were measured with a Perkin Elmer UV/Vis Lambda 20 Spectrophotometer ranging from 400 to 700 nm. The film-coated glass slide was placed across the sample radiation pathway while the uncoated glass slide was put across the reference path. The data obtained from the film was used to determine the band gap energy and transition type of the semiconductor film.

RESULTS AND DISCUSSION

The structure changes and identification of phases were studied with the help of X-ray diffraction (XRD) technique. Figure 1 shows the X-ray diffraction patterns of the films deposited at different pH values. All the samples show a polycrystalline nature. The diffraction angle 2θ was varied between 25 and 60°. It can be observed that FeS₂ thin film prepared at pH 0.5 showed a single peak (Figure 1a) at 2θ = 52.3° which can be assigned to the (211) plane. In addition, the diffraction peak of silicon oxide (JCPDS reference No.: 01-074-0201) also appeared at lower pH value. However, when the film deposited at pH 2.5, it disappeared. At pH 2.5 (Figure 1b), five peaks can be found corresponding to (110), (011), (111), (210) and (121) planes, which are definitely attributed to the orthorhombic structure of FeS₂. The crystallinity of films also increased as evidenced by the sharpness of the XRD peaks. The peaks were identified by comparing the *d*-spacing values obtained from the XRD patterns with JCPDS data for FeS₂ (reference No.: 00-024-0074). The lattice parameters of the orthorhombic structure are equal to a = 4.436 Å, b = 5.414 Å and c = 3.381 Å.

As the pH value was increased to 3.5, the total peaks attributable to FeS₂ reduced to four peaks. This indicates that deposition of film at higher pH value proved unfavorable condition towards films under current condition. This is accompanied by the appearance of two other peaks attributable to silicon oxide (SiO₂) at 2θ = 33.5° and 41.3° with interplanar distances of 2.20 and 2.69 Å, respectively. Figure 2 shows the three dimensional AFM images (20 μm x 20 μm) of the surface of the FeS₂ thin films deposited under different pH values ranging from 0.5 to 3.5. It was found that the surface morphologies and roughness of the thin films were obviously different. Fig. 2a shows that the FeS₂ thin film deposited at pH 0.5 had smaller grain sizes with lower surface roughness and its root mean square (RMS) roughness is 6.5 nm. The films deposited at pH 2.5 and 3.5 showed well-covered entire substrate surface as shown in Fig. 2b and 2c. There were many larger aggregate grains dispersed on the surface of substrate. Their roughness was 72.8 and 147.1 nm, respectively. Therefore, it could be concluded that deposition of thin film in higher pH value probably caused aggregation of FeS₂ thin films.

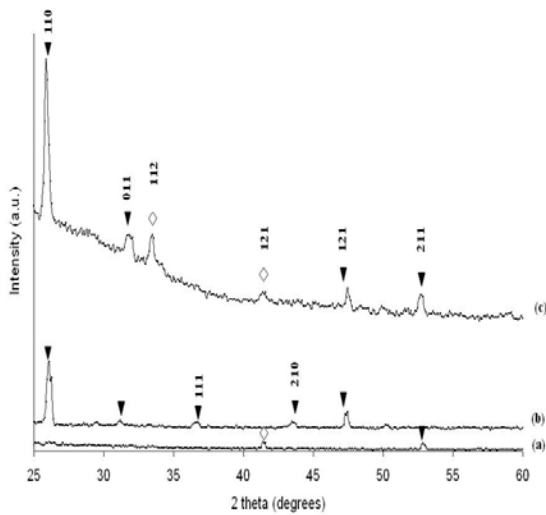


Figure 1: X-ray diffraction patterns of the FeS₂ thin films deposited at different pH values (a) pH 0.5 (b) pH 2.5 (c) pH 3.5. [▼ FeS₂; ◇ SiO₂]

The band gap energy and transition type can be derived from mathematical treatment of data obtained from optical absorbance versus wavelength with the following relationship for near-edge absorption:

$$A = \frac{[k(h\nu - E_g)^{n/2}]}{h\nu} \quad (1)$$

where ν is the frequency, h is the Planck's constant, k equals to constant while n carries the value of either 1 or 4. The value of n is 1 and 4 for the direct transition and indirect transition, respectively. Plot of $(Ah\nu)^{2/n}$ versus $h\nu$ and extrapolate the straight line to $(Ah\nu)=0$ and thus, the band gap is obtained. Figure 3 shows the linear dependence of $(Ah\nu)^{2/n}$ against $h\nu$ when $n=1$, which indicates a direct band gap transition. The band gap determined from optical measurement is in range between 0 and 3.5 eV and given in Table 1. The band gaps deduced for all thin films in this manner decreased from 2.25 to 1.85 eV as the pH value was increased from 0.5 to 2.5. This band gap closes to solar spectrum makes it possible to use as solar cells materials. However, the band gap was found increased to 2.15 eV as the pH was further increased to 3.5. Therefore, the pH value has some influence on the band gap of FeS₂ thin film.

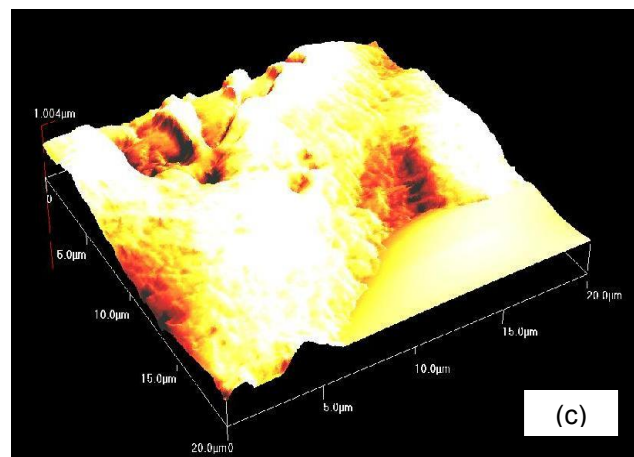
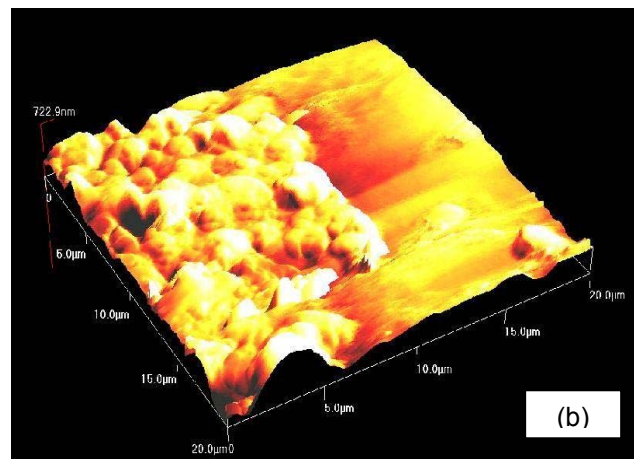
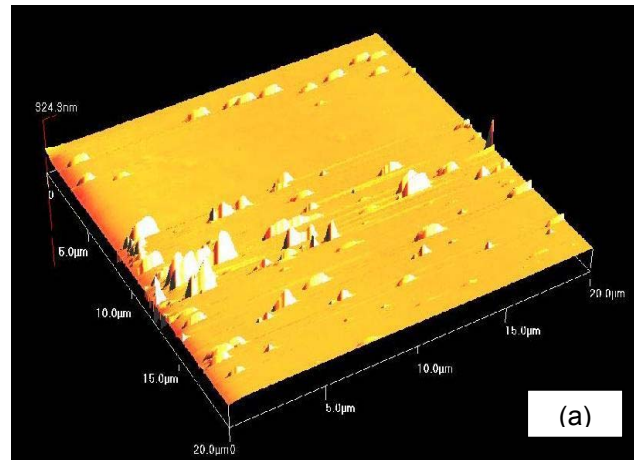


Figure 2: The Atomic Force Microscopy Images of the FeS₂ Thin Films Deposited at Different pH Values (a) pH 0.5 (b) pH 2.5 (c) pH 3.5.

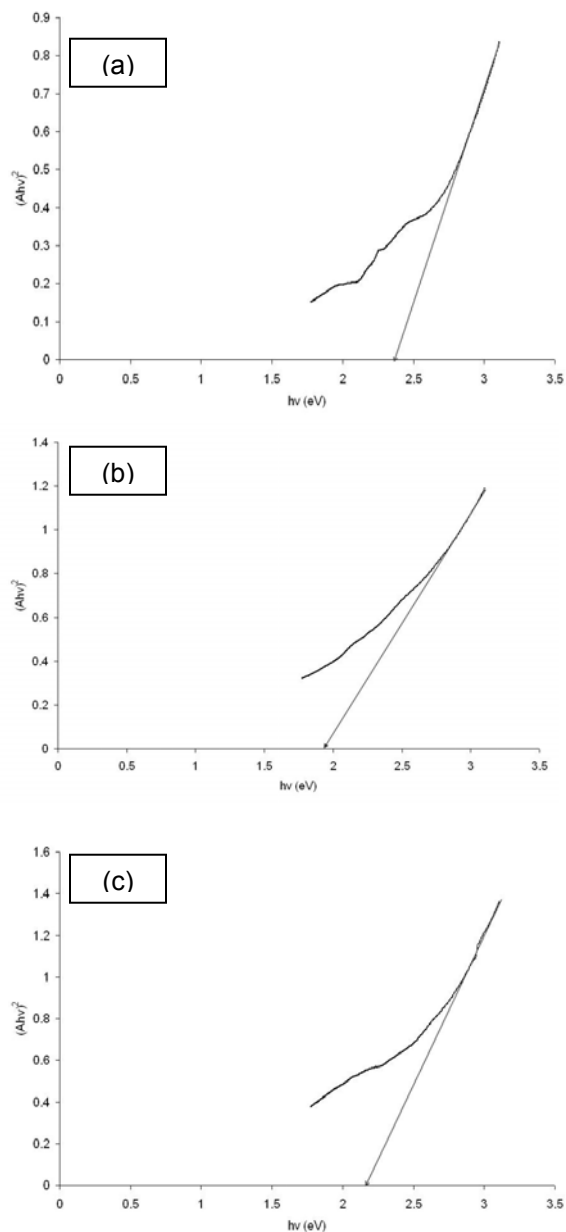


Figure 3: Plot of $(Ah\nu)^{2/n}$ versus $h\nu$ when $n=1$ of the FeS_2 Thin Films Deposited at Different pH Values (a) pH 0.5 (b) pH 2.5 (c) pH 3.5.

Table 1: The Band Gap Energy for FeS_2 Thin Films Deposited at Different pH Values.

Band Gap (eV)	pH
2.25	0.5
1.85	2.5
2.15	3.5

CONCLUSION

The FeS_2 thin films were chemical bath deposited on microscopy glass slides at various pH values from an aqueous solutions. The XRD patterns revealed that the formation of orthorhombic structure of FeS_2 for all the samples. The grain sizes of FeS_2 films which prepared at higher pH value are larger than those deposited at lower pH value. The band gap of the films varied from 1.85 to 2.25 eV. The films deposited at pH 2.5 showed good crystallinity, surface coverage and band gap energy.

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ABOUT THE AUTHORS

Anuar Kassim, Ph.D. is a Professor of Chemistry in the Faculty of Science, Universiti Putra Malaysia. His research interests include conducting polymers, thin films, and surfactants.

Tan Wee Tee, Ph.D. is a Associate Professor of Chemistry in the Faculty of Science, Universiti Putra Malaysia. His research interests include electrochemistry.

Saravanan Nagalingan, Ph.D. is a Lecturer in the Department of Bioscience and Chemistry, Faculty of Engineering and Science, Universiti Tunku Abdul Rahman. His research interests include material science and thin films.

Ho Soon Min, M.Sc. is a Researcher in the Department of Chemistry, Universiti Putra Malaysia. He research interests include thin films.

Gwee Siew Yong, B.Sc. (Chemistry) obtained her degree from Department of Chemistry, Universiti Putra Malaysia. She studied chalcogenide thin films for solar cell applications.

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