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Effects of Deposition Period on the Properties of FeS_2 Thin Films by Chemical Bath Deposition Method

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Abstract

Iron sulfide thin films were deposited onto microscope glass substrates by chemical bath deposition technique from aqueous solutions containing iron nitrate and sodium thiosulfate. The effects of deposition time toward the properties of the thin films were investigated. The deposited thin films were characterized with X-ray diffraction, scanning electron microscopy and UV-Vis Spectrophotometer. The X-ray diffraction patterns indicate that the films have orthorhombic structure with better crystalline phase for the films deposited for 90 min. According to SEM micrographs, the sizes of the grains were noticed to increase as the deposition time was increased to 90 min. The values of band gap energy, calculated from the absorption spectra, decreased from 2.65 to 1.85 eV as the deposition time was increased from 30 to 90 min. Therefore, deposition for 90 min was suitable to produce good quality FeS_2 thin films.

Keywords: Iron sulfide, X-ray diffraction, Chemical bath deposition, Thin films

1. Introduction

Recently, much attention has been focused to study properties of various metal chalcogenide thin films. This is due to their possible application to the manufacture of large area photodiode arrays, solar selective coatings, solar cells [1-4] and sensors. The main advantage of 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.

FeS_2 thin film has attracted considerable attention in recent years, as it is composed of very abundant, cheap, nontoxic elements and possesses semiconducting properties. Various techniques have been used to prepare FeS_2 thin films. These include flash evaporation [5], metal organic chemical vapour deposition [6], sputtering [7], chemical vapour transport [8], electrodeposition [9] and molecular beam deposition [10].

However, to our knowledge, a study on the properties of the chemical bath deposited iron sulfide thin film has not been reported so far. In the present investigation, we report the growth and characterization of FeS_2 thin films deposited using this method. Chemical bath deposition as a method for thin film preparation is a good approach with respect to economic considerations. An important advantage of this method is that thin films with a large area can be prepared without vacuum, using simple and low-cost equipment. The chemical bath deposition method has been proved as a suitable method of preparing chalcogenide thin films such as CdS [11], ZnS [12], CdSe [13], PbS [14], $Cd_{1-x}Zn_xSe$ [15], $Cd_{0.5}Zn_{0.5}Se$ [16] and $CuInSe_2$ [17].

In this work, we prepare iron sulfide thin films using the chemical bath deposition technique from aqueous medium. We investigate the influence of the deposition time (30, 60 and 90 min) on structural, morphological and optical properties of thin films. The thin film has been characterized by X-ray diffraction (XRD) for structure determination, scanning electron microscopy (SEM) analysis for surface morphology study and optical properties for band gap calculation.

2. Materials and Methods

2.1 Sample preparation

All the chemicals used for the deposition were analytical grade. They include iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$), sodium thiosulfate ($Na_2S_2O_3.5H_2O$), triethanolamine [$(HOC_2H_4)_3N$] and hydrochloric acid [HCl]. All the solutions were prepared in deionised water (Alpha-Q Millipore). During the deposition, the triethanolamine (TEA) is used as a complexing agent while iron nitrate and sodium thiosulfate act as a source of iron and sulfide ion, respectively.

The microscope glass substrates of the dimension 25.4 mm x 76.2 mm x 1 mm were degreased in ethanol for 10 min and then ultrasonically cleaned with distilled water for another 15 min before deposition of films. Deposition of FeS_2 thin film was carried out by using the following procedure: 20 ml of 0.15 M iron nitrate solution was put in a 100 mL beaker. Then, 10 mL of triethanolamine solution was added. Following that, 20 mL of 0.15 M sodium thiosulfate solution was added into the above mentioned mixture. By adding drop-wise hydrochloric acid solution, the pH of resultant solution was adjusted to 2.5. The beaker containing resultant solution was kept in the water bath. The temperature of the bath was then allowed to increase slowly up to 80 °C. The clean microscope glass slides were placed in the bath, supported vertically on the wall of the beaker. In order to determine the best conditions for the deposition process, the films were deposited at different deposition periods, ranging from 30 to 90 min. During the deposition period the beaker was kept undisturbed. After completion of film deposition, the glass slide was removed, washed several times with distilled water and dried naturally in desiccators for further characterization.

2.2 Characterization method

In order to investigate the crystallographic properties of the FeS_2 thin films, we carried out the X-ray diffraction analysis using a Philips PM 11730 diffractometer with CuK_α (λ=1.5418 Å) radiation. The surface morphology was observed by scanning electron microscopy (JEOL, JSM-6400). The optical absorption measurement was carried out in the wavelength range from 350 to 800 nm by using a Perkin Elmer UV/Vis Lambda 20 Spectrophotometer. The film-coated glass substrate was placed across the sample radiation pathway while the uncoated glass substrate was put across the reference path. The absorption data were studied for the determination of the band gap energy.

3. Results and discussion

Figure 1 is the X-ray diffractogram of the iron sulfide thin films deposited at different deposition periods. The film deposited for 30 min shows only a single peak at 2θ = 33.8° corresponds to interplanar distances of 2.65 Å (Fig. 1a). As the deposition time was increased to 60 min, three prominent diffraction peaks were observed at 2θ values = 31.9°, 33.5° and 47.5° corresponding to (011), (101) and (121) planes. Comparison between the films deposited for 60 and 90 min revealed that the number of peaks increased to six peaks, indicating a better crystalline phase for the film deposited in longer time (Fig. 1c). In addition, the preferred orientation is changed from (011) to (101) plane at this period. The peaks were identified by comparing the *d*-spacing values obtained from the XRD patterns with Joint Committee on Powder Diffraction Standards (JCPDS) data for FeS_2 (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. The peaks observed at 2θ values of 37.5° (*d*-spacing = 2.38 Å) and 41.3° (*d*-spacing = 2.17 Å) are caused by the glass substrate. The data indicated the formation of orthorhombic phase of SiO_2 (JCPDS reference No.: 01-074-0201).

Scanning electron microscopy (SEM) is a useful technique analysis of the surface morphology of a film. It can give the grain size and structure of samples. The examination of SEM micrographs from Figure 2 brings a comparison of the surface grains from the deposited films under different deposition periods. All the samples were examined at 20 kV with 250 X magnification.

The morphology study shows that the FeS_2 thin films deposited for 30 min are not compact and do not have good coverage of glass substrate (Fig. 2a). These films have smaller grains compared to the other films. This observation is supported by data obtained from XRD pattern. This can be explained by the broadening of the peaks, which can be due to the small size of the crystals. The sizes of the grains were noticed to increase as the deposition time was increased to 90 min (Fig. 2c). The films are composed of largely irregular-shaped grains of diameter 100-150 μm.

The optical properties of FeS_2 thin films are determined from absorbance measurement in the range of 350 to 800 nm. Figure 3 shows absorbance spectra for FeS_2 thin films deposited at different deposition periods. All the films show a gradually increasing absorbance throughout the visible region, which makes it possible for this material to be used in a photo-electrochemical cell. As it can be seen, the thin films deposited for 90 min (Fig. 3c) display high absorption characteristics in the visible region when compared with the other films. This confirmed that the thicker film has higher absorption properties. This response also is associated with the fact that more FeS_2 materials are formed at this period.

Band gap energy and transition type can be derived from mathematical treatment of data obtained from optical absorbance versus wavelength with the Stern relationship of near-edge absorption (Equation 1):

$$A = \frac{[k(hv - E_g)^{n/2}]}{hv} \tag{1}$$

where *v* is the frequency, *h* is the Planck's constant, *k* equals a 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. The plots of $(Ahv)^2$ versus *hv* are shown in Figure 4. The linear nature of the plots indicated the existence of direct transitions. The band gap energy is obtained by extrapolating the linear portion of $(Ahv)^{2/n}$ versus *hv* to the energy axis at $(Ahv)^{2/n} = 0$. The results reveal that the band gap energy decreases linearly from 2.65 to

2.60 and 1.85 eV when the deposition time was increased from 30 to 60 and 90 min, respectively. Clearly, the grain size increases gradually with deposition time. This statement is also supported by the data obtained from XRD and SEM analysis.

4. Conclusions

FeS_2 thin films can be chemically deposited by using iron nitrate and sodium thiosulfate solutions. The triethanolamine solution was used as a complexing agent during the deposition process. The film deposited for 90 min showed larger grain size and more peaks attributed to FeS_2, as could be observed from SEM and XRD results, respectively. The band gap energy was decreased from 2.65 to 1.85 eV as the deposition time was increased from 30 to 90 min. Therefore, deposition for 90 min was suitable to produce good quality of FeS_2 thin films.

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6. References

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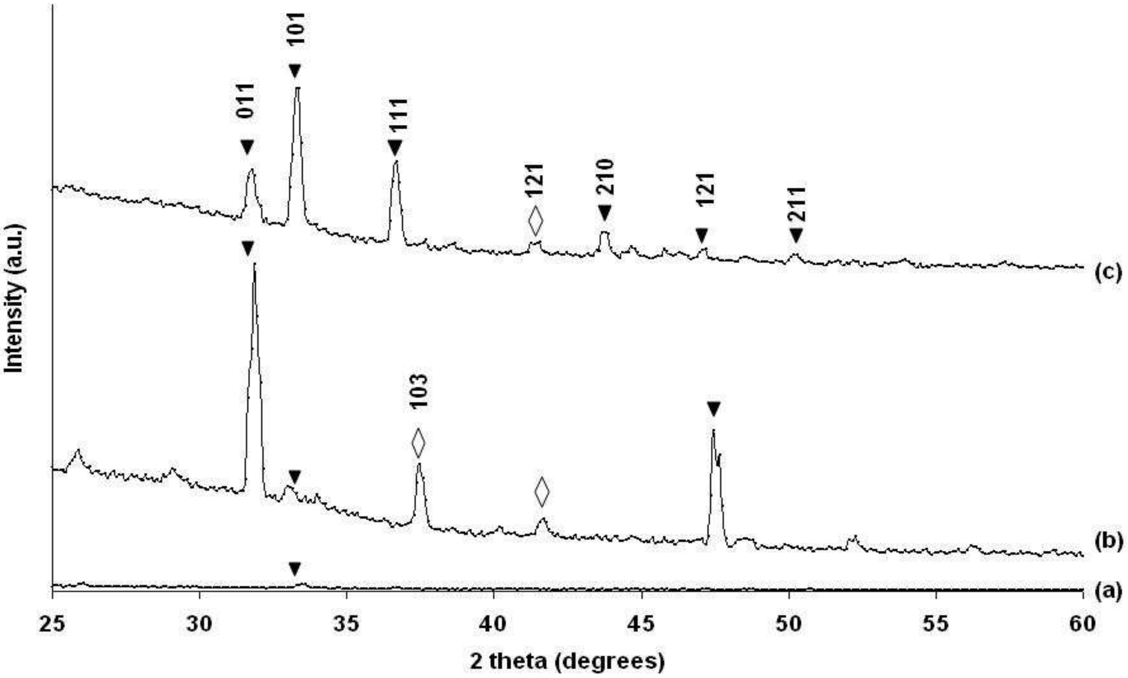


Fig. 1 X-ray diffraction pattern of FeS_2 thin films deposited at different deposition periods. (a) 30 min (b) 60 min (c) 90 min (▼ FeS_2; ◊ SiO_2)

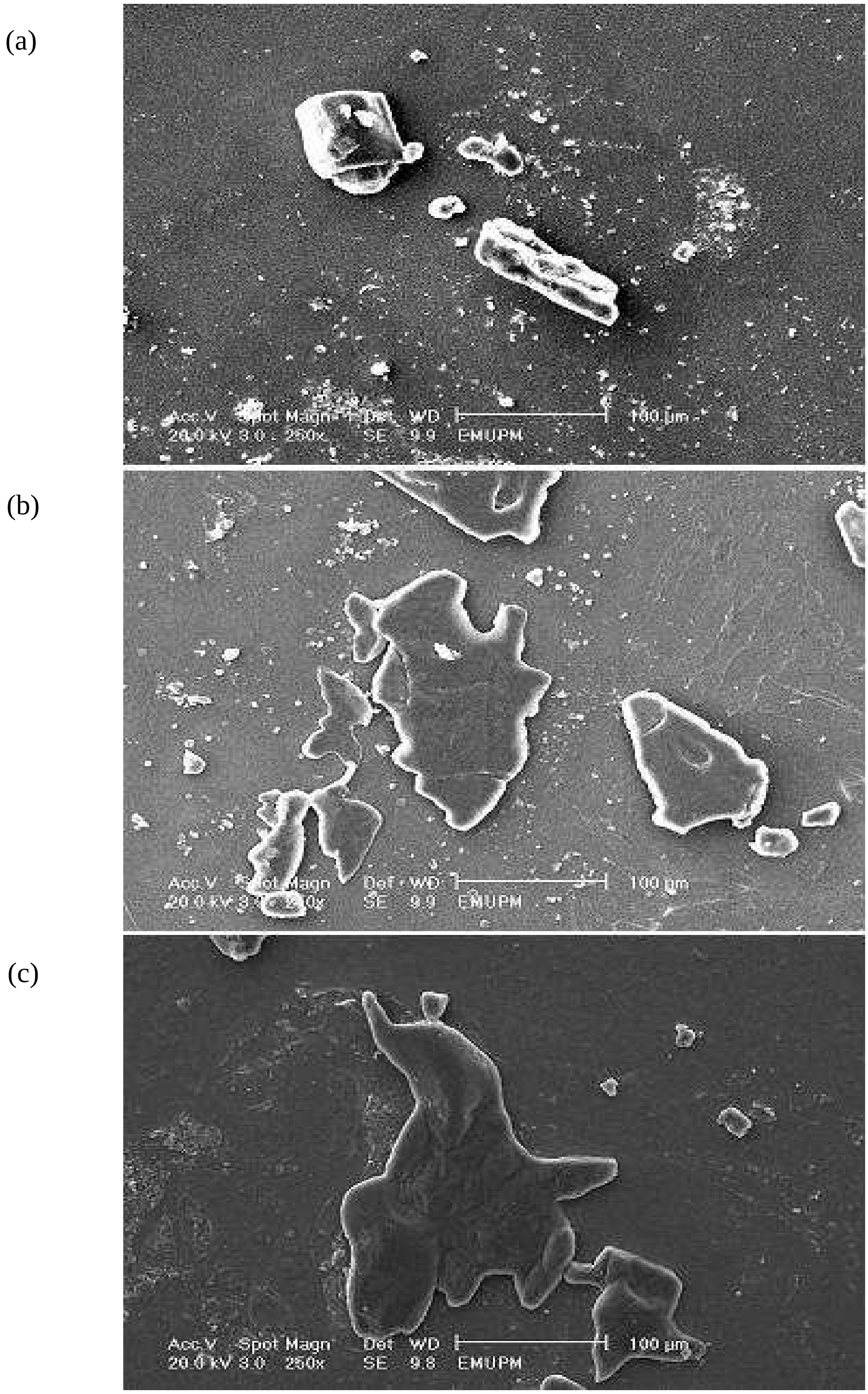


Fig. 2 SEM micrograph of FeS_2 thin films deposited at different deposition periods (a) 30 min (b) 60 min (c) 90 min

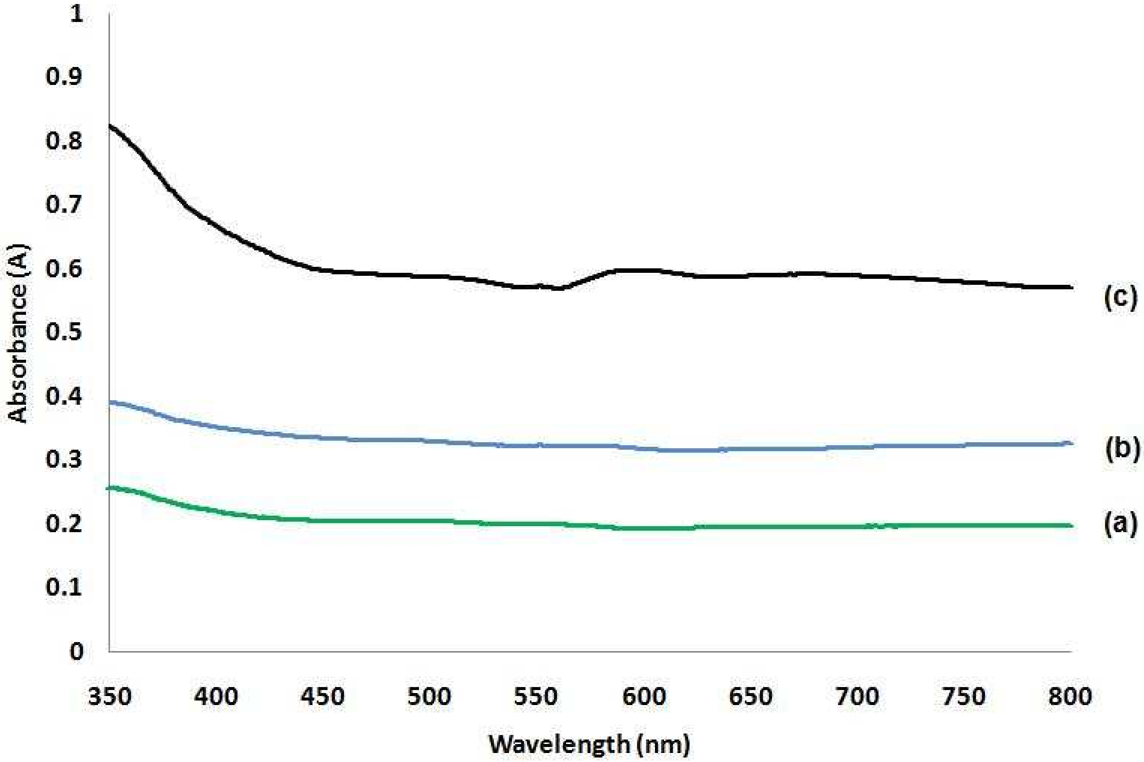
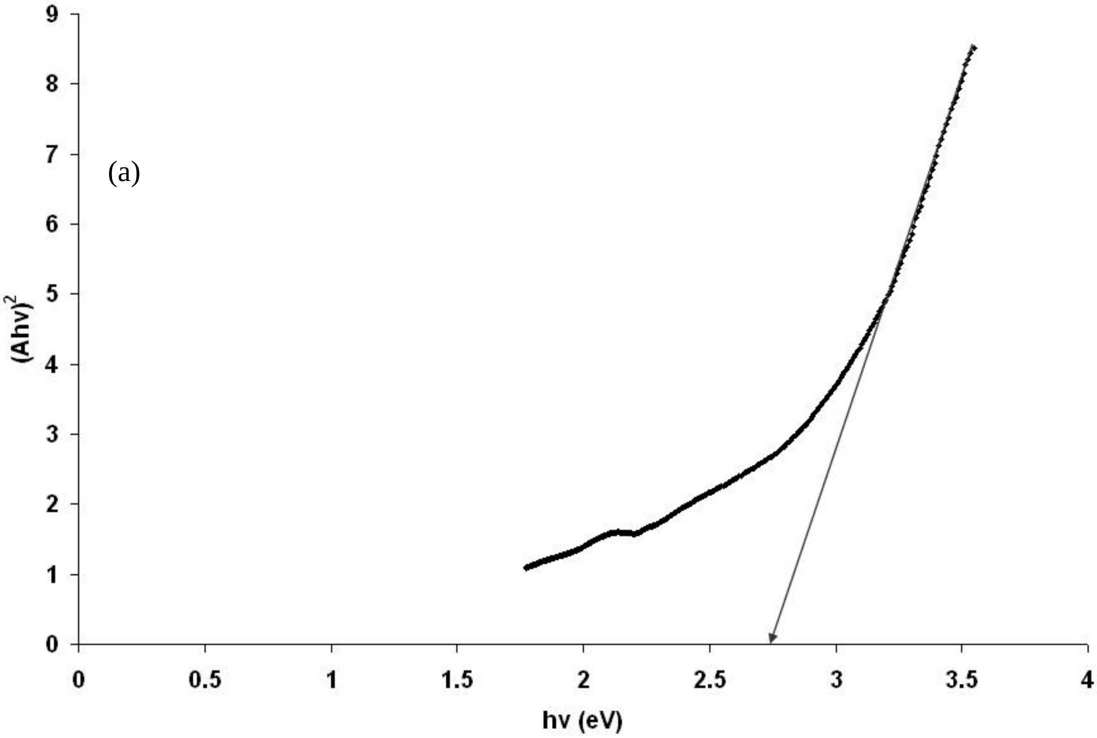


Fig. 3 Absorbance versus wavelength spectra of FeS_2 thin films deposited at different deposition periods (a) 30 min (b) 60 min (c) 90 min



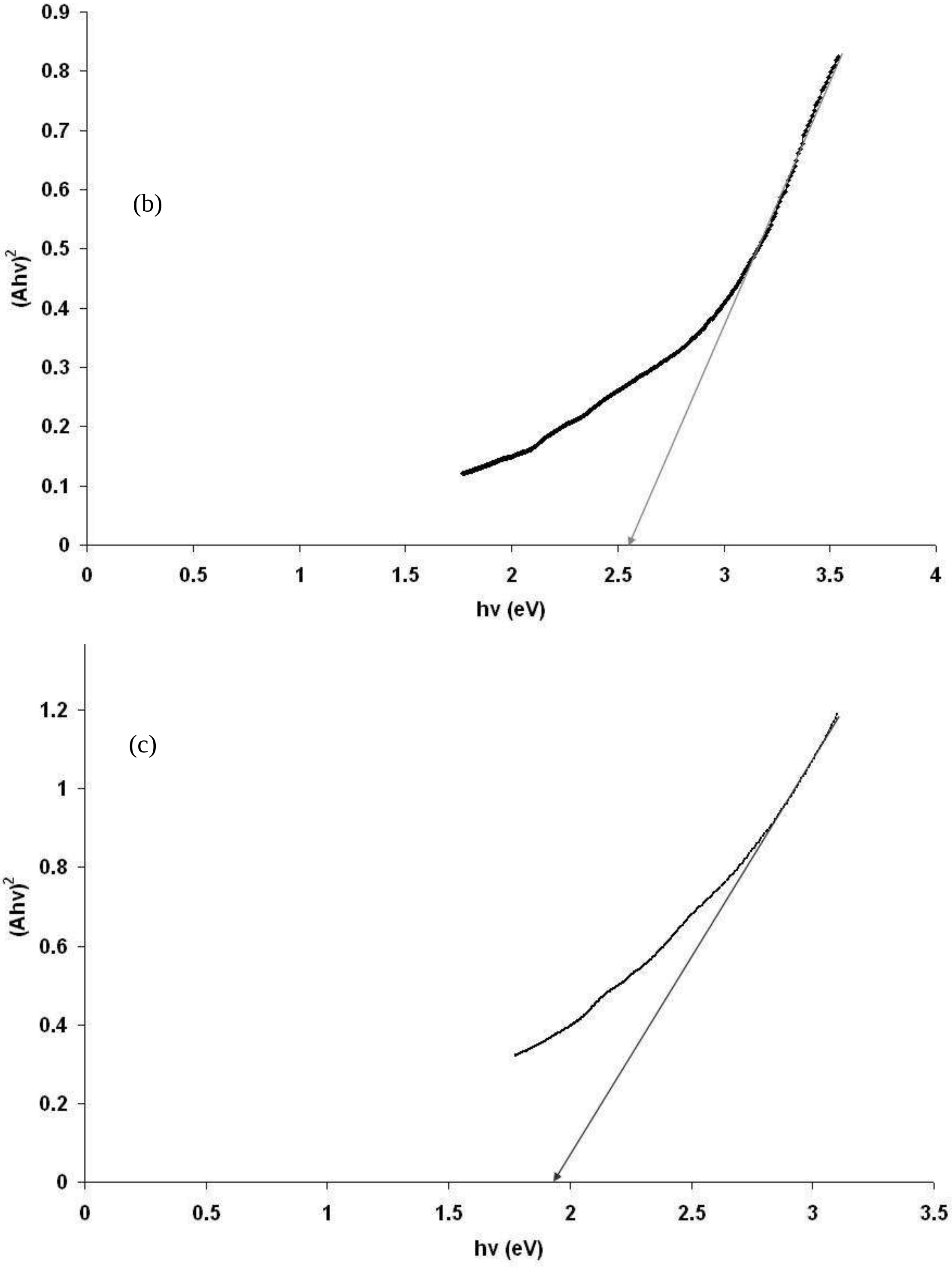


Fig. 4 Plot of $(Ahv)^2$ versus hv band gap of FeS_2 thin films deposited at different deposition periods (a) 30 min (b) 60 min (c) 90 min