Research Article

A facile synthesis of Iron Sulfide thin films by Chemical Bath Deposition Method

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Abstract:

The study on iron chalcogenides are of particular interest because of their interesting magnetic, semiconducting, and structural properties. In this study, we investigated the facile chemical bath deposition of the monophasic FeS thin films. Layer by layer and continuous deposition method of synthesis of thin film to form a homogenous and uniform film has been employed. The XRD structural analysis confirmed the formation of FeS films with a tetragonal (mackinawite) structure. Optical band gap analysis revealed that the as-synthesised FeS thin films possess light harvesting capacity in the visible region of the solar spectrum.

Keywords: Metal chalcogenides, FeS Thin film, CBD method

INTRODUCTION

The wide growing demands of thin film solar cell and photovoltaic applications are demanding cost effective, inexpensive, non-toxic and earth abundant materials as an alternative to conventional materials (Ramasamy, 2012). Most of the materials widespreadly used for thin film based applications, namely cadmium, lead, indium and selenium are either toxic or non-abundant. The fast growing exploitation of non-renewable energy as solar energy applications therefore demands environmental friendly materials. Thin film solar cells based on copper, tin and iron have geared significant progress in the last few years either in metal oxides or sulfides (Zhang,2004); (Liu,2017); (Chen,2016); (Rondiya,2017); (Ge,2016). The hybrids and heterostructures based on these materials absorb the most of the visible solar spectrum. These materials are also proved to be a powerful candidate in thermoelectric, magnetic semiconductors, superconductors and sensors. Iron and copper chalcogenides are of particular interest because of their interesting magnetic, semiconducting, and structural properties. From the large family of iron sulfide phases, iron sulfide (FeS) is showing great interest because of its electronic, magnetic, and optical properties with applications that include solar cells and lithium ion batteries. They are also found potential applications in the biomedical applications, including protein immobilization and separation, magnetic targeting and drug delivery, cancer hyperthermia, magnetic resonance imaging (MRI) and many more. Xu *et al.* demonstrated interconnected porous FeS/C composite using FeS nanoparticles embedded in carbon nanosheets for its use in anode for LIBs. A new nanocomposite formulation using FeS and graphene oxide anode for lithium-ion batteries is proposed by Fei *et al.* via facile direct-precipitation approach. (Huang,2016); (Lu,2013); (Wei,2015); (Xu,206); (Fei,2013). Iron sulfides nanoparticles are considered to be advanced inorganic material with non-conventional applications, such as high-energy density batteries, precursors for the synthesis of superconductors and materials for photoelectrolysis. Therefore, the study of nonmaterial and thin film based on iron sulfide (FeS) with particle size and morphological changes is of great interest in the field of materials science. Various deposition and synthesis techniques have been experimented to deposit thin

films of iron sulfide (FeS) including chemical vapor deposition, electro-deposition, hydrothermal method, sputtering and chemical bath deposition (CBD) (Dutta, 2012); (Kim, 2011) (Fei, 2013); (Beal, 2012); (Min, 2009); (Sines,2012). The CBD is always found to be the simple, low temperature and cost effective method to deposit high quality thin films of FeS. The formation of different phases of FeS is always related to many factors, including temperature, solution pH, and aging time. Herein, we report a reproducible method for the deposition of nanocrystalline monophase of FeS thin films and are expected to be a general method for the preparation of other metal sulfide.

MATERIALS AND METHODS

Experimental Details

Materials

All the reagents used in the experiment, iron chloride tetra-hydrate ($FeCl_2$), thioacetamide (CH_3CSNH_2) and urea ($CO(NH_2)_2$) were purchased from Sigma Aldrich and used without purifying it further. HCl was used to manage the pH of the solution and Distilled water was used as solvent in all experimental procedure.

Synthesis of FeS Thin Films

The monophasic FeS thin films were grown onto glass substrates of dimension ($2 \times 5\ cm^2$) from the acidic bath as shown in figure 1 a. The required molarity of the solution is 0.15M iron chloride tetra-hydrate ($FeCl_2$), 1M urea and 2M thioacetamide. For that 180 ml of distilled water is kept in a beaker on a heat bath. When the temperature of the distilled water is raised above 50° C, 1.7292gm $FeCl_2$ is added and vigorously stirred using a magnetic stirrer which is attached to the heating unit. When $FeCl_2$ is dissolved completely in water, 3.6gm of urea and 9.0gm of thioacetamide was added to the solution under stirring. When all the reagents were dissolved completely, almost transparent solution is formed (figure 1b). The temperature is maintained at 85± 5°centigrade. Then 0.5M HCl is added drop by drop to the solution to adjust the pH to 3. After 10 min of reaction at fixed temperature under stirring, the color of solution

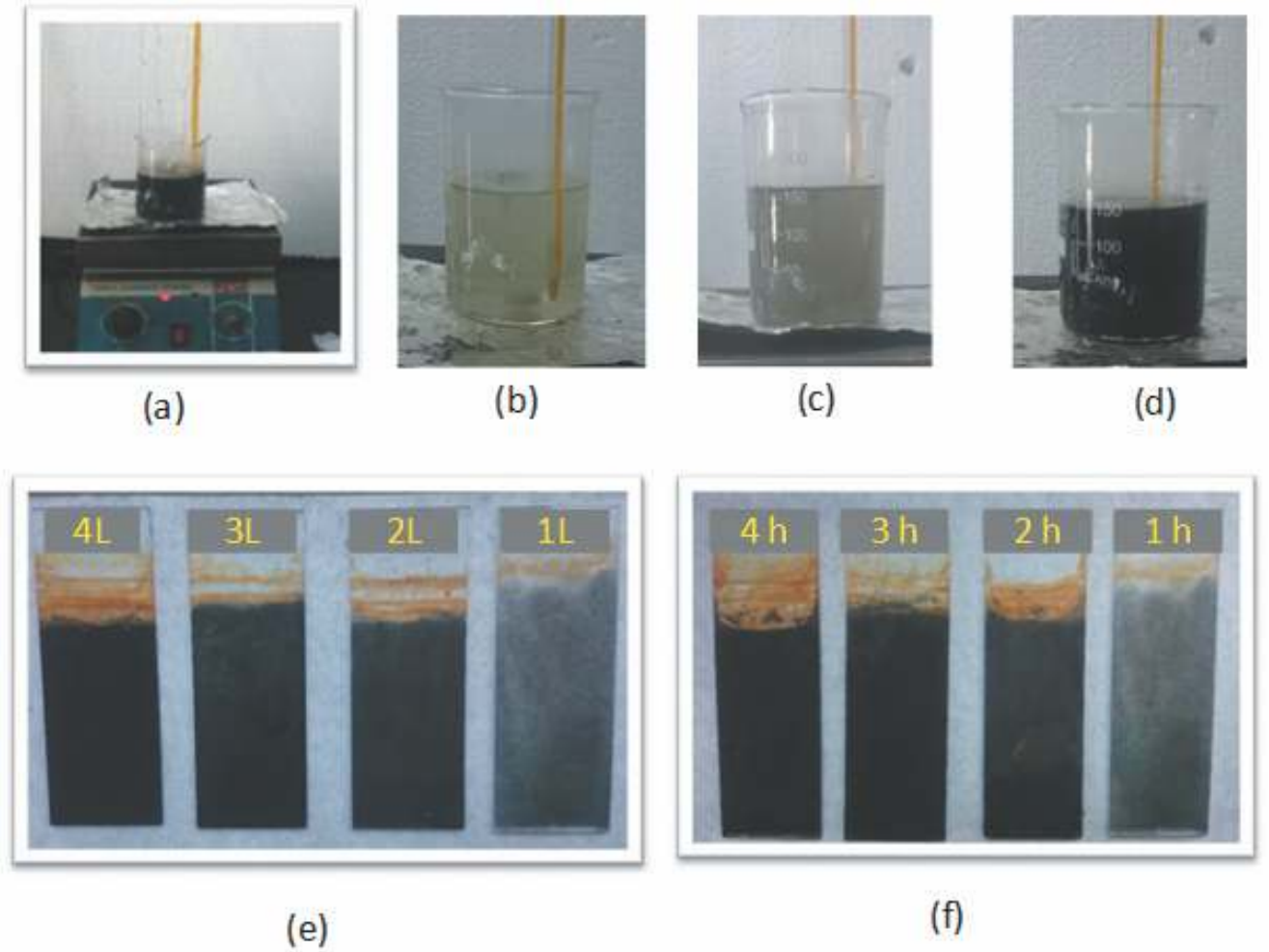

Fig. 1. (a) Experimental set up for chemical bath deposition of films, (b-d) progress of the reaction and confirmation of homogeneous bath, (e) layer by layer deposition and (f) continuous bath deposition.

changes to grey (figure 1c). Glass substrates were then immersed vertically in the chemical bath. After 20 min the solution turns to thick black contrast (figure 1d). The speed of stirring is reduced to very slow. A continues deposition method and layer by layer deposition method was employed for obtaining uniform films of FeS. To check the time dependent effect on the deposition of film, glass slides were removed from the reaction mixture after an interval of 1 hour. For the layer by layer deposition, the samples were removed at regular intervals, washed, dried and immersed back into the reaction mixture. The process was continued till the formation of uniform film. The images of typical such FeS films deposited is shown in figure 1(e) and (f).

All the films were washed with methanol and acetone to remove surface contaminants and chemical residues and post annealed at 70^0C for 1 hour before testing for any characterizations.

Peel test was performed for all the prepared samples using a commercially available adhesive tape for analyzing the adhesion between films and their substrates (Hull, 1987). The crystal structure and phase constitution of FeS thin film was characterized by X-ray diffraction (XRD) (D2 phaser BRUKER, $\lambda_{Cu\text{-}K\alpha}$=0.15418 nm). The UV absorption spectra of the sample were performed on a UV-VIS spectrophotometer (Shimadzu UV 3600, Japan) to check the optical band gap of the films. Hot probe analysis was used to test the conductivity of the sample. van der Pauw method of electrical resistivity measurement was done for selected samples.

RESULTS AND DISCUSSION

A thin film formed by precipitation using a controlled chemical reaction is employed in chemical bath deposition (CBD). During the reaction the slow release of the sulfur ion and iron ions and condensation of these ions on the substrate surface takes place to form homogeneous FeS films (Brien,1998). In a controlled hydrolysis reaction of iron salt ($FeCl_2$) and thioacetamide (CH_3CSNH_2) salt in the acidic media, Fe^{2+} and S^{2-} ions re released. The role of urea in the reaction mixture is to act as a chelating agent. Hydroxide ions via hydrolysis released in the mixture provide ammonia for the formation of complex ion with Fe^{2+}. These complex ions react with S^{2-} ions to form FeS. The reaction mechanism is explained briefly by following equations (Akhtar, 2015).

$$FeCl_2 \rightarrow Fe^{2+} + 2Cl^- \quad (1)$$

$$CH_3SCNH_2 + H_2O \leftrightarrow S^{2-} + CH_3SCONH_2 + 2H^+ \quad (2)$$

$$CO(NH_2)_2 + H_2O \leftrightarrow S^{2-} + 2NH_3 + CO_2 \quad (3)$$

$$Fe^{2+} + HO + 5NH_3 \leftrightarrow [Fe(NH_3)4]^{2+} \quad (4)$$

$$[Fe(NH_3)_4]^{2+} + S^{2-} \leftrightarrow FeS + 4NH_3 \quad (5)$$

$$[Fe(NH_3)_5]^{2+} + CH_3SCCNH_2 + H_2O \rightarrow FeS + 4NH_3 + CH_3SCONH_2 + 2H^+ \quad (6)$$

The XRD pattern shown in figure 2 of the typical FeS thin film is in good agreement with that of iron sulfide ((PDF No. 86-0389). It should be noted that the strongest peak oriented along (001) in the pattern can be well indexed as the mackinawite phase (P4/nmm space group) of FeS. The presence of single and intense peak reveals the growth of FeS crystallites along c-axis. Thus, it is suggested that nanocrystalline FeS is formed as the broadness of the peaks, intensity and positions are well matched with previously reported data for nanocrystalline mackinawite (Xing, 2015); (Hajja, 2013); (Lennie, 1995). The formation of monophasic mackinawite phase of FeS is further confirmed from the diffraction as the pattern does not show any extra peaks. The crystalline size of the particle and micro strain has been calculated from the X-Ray diffraction pattern using scherer's formula:

$$t = \frac{kl}{b\cos q} \quad (7)$$

$$e = \frac{b2q\cos q}{4} \quad (8)$$

where t is the grain size, ε is the micro strain, k is a constant taken to be 0.9, β is the full width half maximum(FWHM) and λ is the wave length of X-Rays. The obtained particle size and micro strain values are tabulated in table 1.

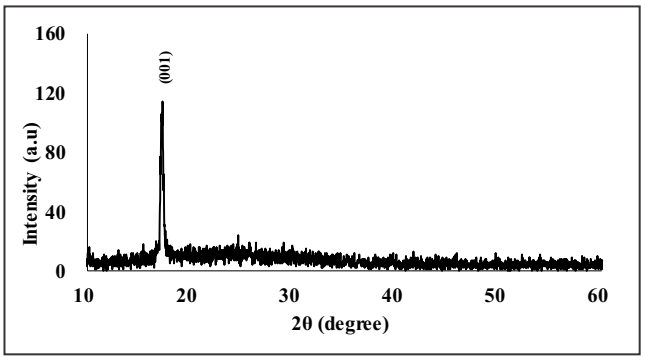

Fig. 2. Typical p-XRD pattern of FeS thin film deposited on a glass substrate

It is inferred that the crystallite size of the particle is increasing with increase the deposition time and number of layers. This data, verifies that the crystalline size of particles in thin films increases with the increase of the film thickness synthesized by acidic bath method. It is also found that the quality of the film

Table 1. Calculated values of grain size and micro strain from the XRD diffraction data

FeS Thin films	Duration / Layer	FWHM (Degree)	Grain Size (nm)	Micro strain
Layer by layer deposition	1 Layer	0.475	17.68	0.0134
	2 Layer	0.298	28.18	0.0084
	3 Layer	0.223	37.67	0.0063
	4 Layer	0.150	56.00	0.0042
Continuous depostion	1 Hour	0.475	17.68	0.0134
	2 Hour	0.253	33.20	0.0071
	3 Hour	0.161	52.18	0.0045
	4 Hour	0.128	65.63	0.0036

improves and shows crystallinity of the film as deposition time increases.

The absorption fitting method of calculating the band gap was employed (figure 3) and the values are tabulated in table 2. The band gap range of the films

Table 2. Optical band gap calculated from the absorption spectra

FeS Thin films	Duration / Layer	Band gap (eV)
Layer by layer deposition	1 Layer	1.98
	2 Layer	1.86
	3 Layer	1.86
	4 Layer	1.94
Continuous depostion	1 Hour	2.00
	2 Hour	1.82
	3 Hour	1.86
	4 Hour	2.06

revealed that the deposited films of FeS falls in the visible range region of the solar spectrum (Ghobadi, 2013).

Standard hot probe analysis was carried out to understand the carrier type of FeS thin films. A couple of cold probe and hot probe are attached to the semiconductor surface. The hot probe is connected to the positive terminal of the multimeter while the cold probe is connected to the negative terminal. If the

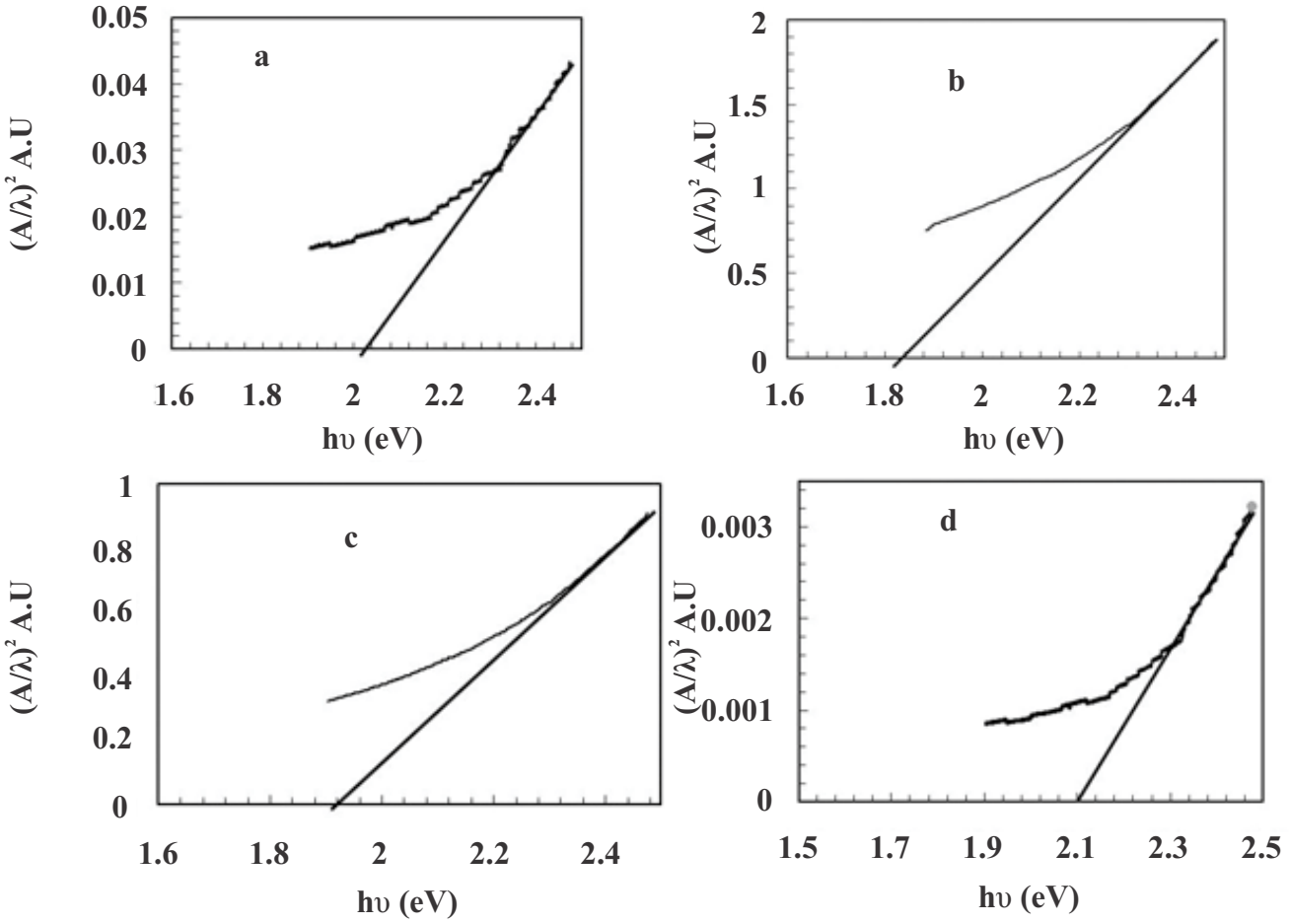

Fig. 3. Typical Band gap calculation from absorption fitting method of FeS thin films (a) 1hour, (b) 2 hour, (c) 3 hour and (d) 4 hour

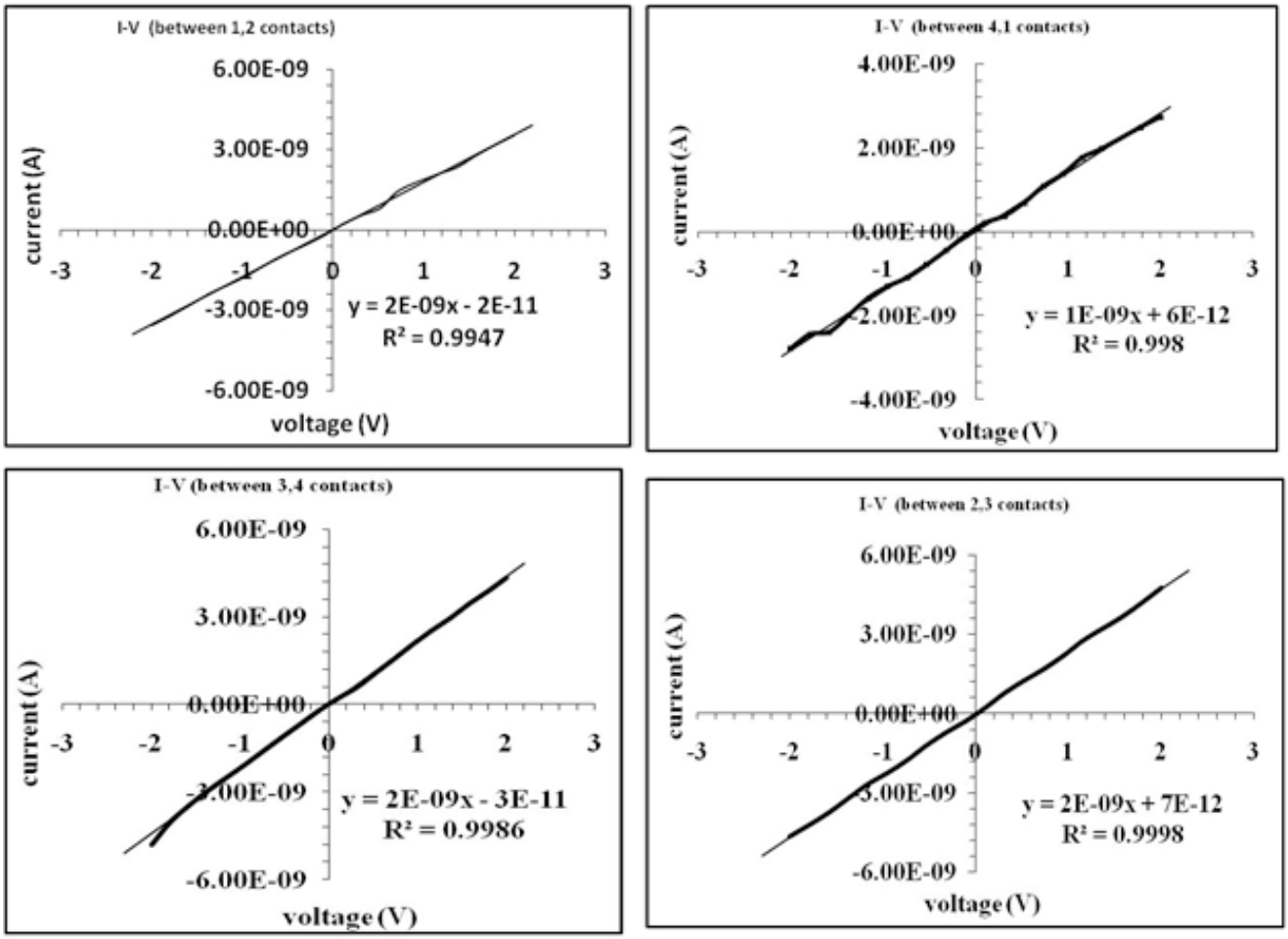

Fig.4. I-V analysis via e van der Pauw connections of as-deposited FeS thin films

semiconductor is n-type, then positive voltage is obtained across the meter. By this method, it is verified that the formed FeS is a n-type semiconductor.

The van der Pauw method of calculation of resistivity was employed to check the electrical conductivity measurements. The following conditions that must be satisfied to use electrical analysis: (a) The sample must have a flat shape of uniform thickness, (b) The sample must not have any isolated holes, (c) The sample must be homogeneous and isotropic, (d) All four contacts must be located at the edges of the sample, and (e). The area of contact of any individual contact should be at least an order of magnitude smaller than the area of the entire sample. The as synthesized FeS films were tested for electrical conductivity measurements.

The contacts were named (1,2) (2,3) (3,4) (4,1) and current, voltage analysis was done for all the four set of contacts as shown in the figure 4. The linearity of the graphs shows that the contacts made are good ohmic contacts and shows uniform conductivity across all the terminals. The average resistance across two points is calculated as ~ 1.75×10^9 ohms.

CONCLUSION

In summary, we have synthesized FeS thin films by chemical bath deposition method. Tape test was passed for the adhesion FeS films on glass substrate. Structural analysis verified that the formed FeS thin film is of Mackinawite structure. The crystalline size of the particle increases with the increase of deposit hours and as the increase of the number of layers. The strain size is decreasing correspondingly as the increase of crystalline size. Optical analysis shows the absorption of FeS is in the visible region of the optical spectra. The as-deposited FeS thin film is found to be n-type semiconductor in nature. Electrical conductivity analysis of the film shows high resistivity nature of the film.

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