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Role of Ammonia on Structural, Electrical, FTIR and Optical Studies of Fes$_2$ Films Formed by CBD

Vedavathi A[1], Ramakrishna Reddy K T[2] and Munikrishna Reddy Y[3*]

[1]*Department of Physics, Sri Sathya Sai Institute of Higher Learning, Anantapuramu-515001*
[2]*Department of Physics, S. V. University, Tirupati-517502 (A P)*
[3]*Department of Physics, S S B N Degree & PG College, Ananthapuramu-515001(A P)*

Abstract: - Thin films of iron pyrite (FeS_2) had been grown by chemical bath deposition method (CBD) using iron sulphate and thiourea as precursors. Ammonia and Ethylene Diamine Tetraacetic Acid (EDTA) were used as the complexing agents. The films were deposited using different ammonia concentrations (AC) that vary from 10M to 14M, keeping the other growth parameters constant. The structural, optical and electrical properties of the films had been investigated using appropriate techniques. The increase of AC had a significant effect on the crystalline phase of FeS_2 films. The X- ray diffraction spectra revealed a dominant (110) plane with marcasite phase at AC=10 M that changed into pure pyrite phase with increase of AC to 14 M. The later phase had a strong (200) plane as the preferred orientation. All the grown films had homogeneous and uniform surface morphology. The Fourier transform infra-red spectra (FTIR) indicated the –OH, C-H and S-O stretching vibration modes. The films exhibited two optical band gaps i.e. an indirect band gap in the range, 0.99 – 0.96 eV and a direct band gap varying from 1.28 eV to 1.14 eV with increase of AC from 10 M to 14 M. The resistivity of the polycrystalline films was observed to be varied from 0.02Ω-cm to 0.005Ω-cm with the ammonia concentration which was much higher than that of the Si and CdS thin films.

Keywords: - *Chemical Bath Deposition, FTIR, Iron pyrite thin films, SEM, XRD*

I. INTRODUCTION

In recent years, iron pyrite films have attracted much attention as an absorber material for photoelectrochemical and photovoltaic applications [1, 2]. It has favorable band gap (Eg=0.95 eV) which is very close to Si (Eg=1.1eV)[3,4]. It consists of earth abundant and cheap elements that are safe to handle for large scale production. Its large scale applications will never be exhausted because of the availability of its constituent elements. Generally, the two naturally occurring phases of FeS_2 are Pyrite and marcasite. Marcasite has an orthorhombic crystal structure with a narrow band gap 0f 0.34 eV that makes it unsuitable for photovoltaic cell fabrication [5,6]. The pyrite phase exhibits cubic structure with a high optical absorption coefficient of 10^5 cm^{-1} [4], direct band gap of 1.38 eV and indirect band gap of 0.95 eV [7,8]. FeS_2 thin films have been prepared by variety of methods such as flash evaporation, metal organic chemical vapor deposition [13,15**]**, thermal evaporation, sputtering, chemical vapour deposition, electrodeposition, molecular beam deposition, spray pyrolysis and chemical bath deposition (CBD). CBD is simple and inexpensive wet chemical process useful for large area film deposition with less material usage and reproducible properties. Further, it is easy to dope the materials in this method and use simple precursor deposition. It is based on the reaction between different ions in water solution and in acidic medium. Triethanolamine (TEA) and Ethylene Diamine Tetra Acetic Acid (EDTA) are generally used as complexing agents that avoid precipitation by slowing down the release of the metallic ions thereby forming a solid film on the substrate surface. In this work, ammonia had been used as the complexing agent along with EDTA instead of TEA for the first time to prepare FeS_2 films. The effect of ammonia concentration on the structural and optical properties of the grown films is reported.

II. EXPERIMENTAL

Iron sulphate ($FeSO_4.7H_2O$) and Thiourea ($CS(NH_2)_2$) were used as precursors with NH_3 and EDTA as complexing agents. Three sets of films were prepared by varying the AC from 10.0 M to 14.0 M. Sodalime glass plates were used as substrates. Non-uniformity and poor adhesion of the films were the common notified problems in CBD. In order to obtain good films, the substrates were cleaned in the following procedure: The substrates were thoroughly cleaned with ordinary water, soap solution and distilled water sequentially. The socleaned substrates were dipped in potassium dichromate solution for 5-6 hours. Just prior to the deposition, the films were rinsed with distilled water and placed in beaker. Solutions with the required 1 M, 1 M and 0.1 M concentrations for $FeSO_4.7H_2O$, $CS(NH_2)_2$ and EDTA respectively were prepared by standard techniques. The ammonia concentration varied from 10.0 M to 14.0 M. 20 ml of distilled water is added to the bath and stirred well. The deposition time (t_d) 60 minutes and bath temperature (t_b) 70^0 C were maintained for all the concentrations. The as-deposited films were removed from the beaker and dried. Structural analysis of the films were carried out by using Siefert X-ray diffractometer (model: 3003 TT) with Cu-Kα radiation source (wavelength, λ = 1.542 A°) and Raman spectrometer. Surface morphology and chemical composition of the films were carried out using Carl Zeiss SEM (EVO MA 15) attached with Oxford instruments (Inca Penta FET x3) X-ray energy analyzer. Optical absorption studies were carried out using Perkin-Elmer Lambda 950 UV-Vis-NIR spectrophotometer. FTIR measurements were carried out with Nicolet Model 400D Spectrometer operating in the wavenumber range 4000–1500cm^{-1}. Electrical properties were measured using Four Probe arrangement.

III. RESULTS AND DISCUSSION

The as-grown FeS_2 films were dark reddish brown in color. X-ray diffraction is a powerful tool for the structural determination of bulk films, unknown material identification, determination of the orientation of the single crystals and preferred orientation of the polycrystals etc. The purity and phases of the films were analyzed by XRD. Typical XRD patterns of the Iron sulfide films deposited at different concentration of ammonia were shown in the Fig. 1.

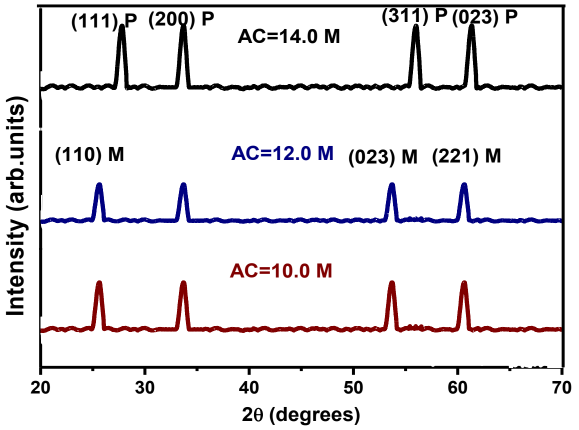


Fig. 1. XRD patterns of the deposited pyrite films at different ammonia concentrations.

(In the figure, M- represents marcasite and P- represents pyrite phases of FeS_2)

From the spectra, it was clear that the films were polycrystalline in nature. The narrow and sharp peaks indicated that the films were well crystallized. When the concentration of ammonia was 10.0 M, the phases mainly composed of marcasite and a small amount of pyrite. Four peaks of (110), (200), (311) and (023) [6, 18] planes were observed corresponding to both marcasite and pyrite phases of FeS_2. Average cystalllite size had been obtained from the broadening of the (200) diffraction peak by using the Scherrer formula given by:

$$t = \frac{0.9\lambda}{B\cos\theta} \qquad 1$$

Where t is the crystallite size, λ is the wavelength of the X-rays; B is the full width at half maximum (FWHM) and θ is the diffraction angle. After correcting by the instrumental broadening of the diffraction lines as measured with FeS_2 pyrite powder pattern, the FWHM was measured and the crystallite size was calculated. The variation of the crystallite size and FWMH with concentration of ammonia at (200) plane was shown in Fig.2.

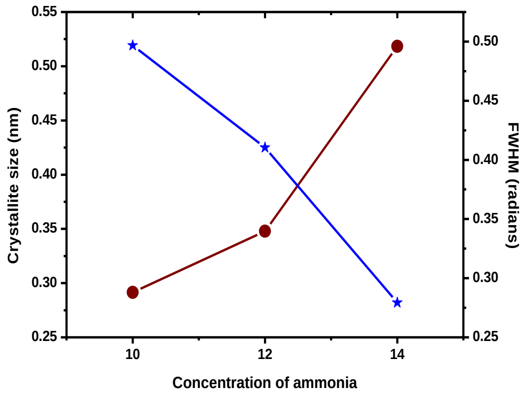
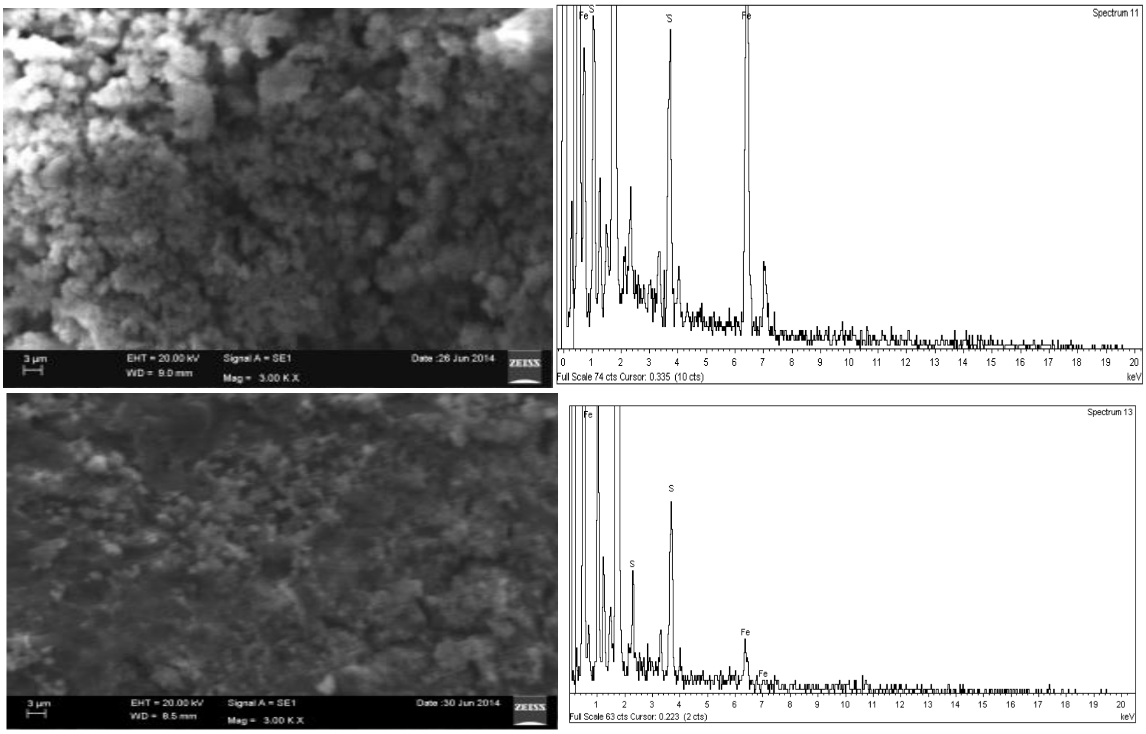


Fig. 2. Variation of crystallite size and FWHM with AC at (200) plane.

From the fig, it was noticed that the crystallite size does not depend on the concentration of the complexing agent. However, it may be a function of the amount of heat applied to the films [11]. As the AC of the bath was increased to 12.0 M, the intensity of the peaks corresponding to marcasite decreased without any phase conversion. However, at 14.0 M AC, all the peaks corresponding to marcasite were converted into pure pyrite phase of FeS_2 with the planes corresponding to (111), (200), (311) and (023) (Cubic, JCPDS 42-1340) **[**19]. This may be due to the ammonia concentration which was sufficient to help the Fe ion precursor to release necessary Fe^{2+} ions for the pyrite formation. Further increment in the concentration resulted in poor adhesion of the material on the substrate.

The scanning electron microscopy is the most commonly used technique to study the surface morphology and microstructure of the films. The SEM micrographs of the films deposited at different AC were shown in Fig.3.



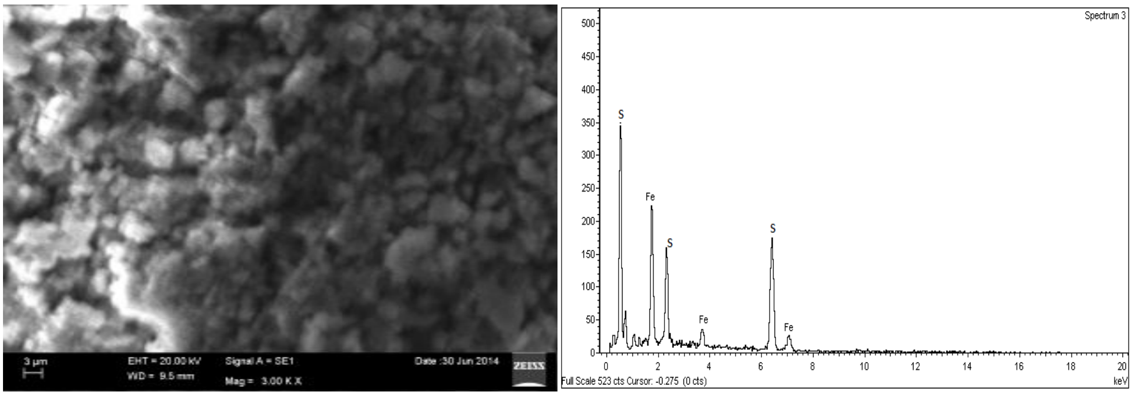


Fig. 3. SEM images and EDAX spectra of deposited FeS$_2$ films at different AC.

Form the SEM images it was observed that films deposited at 10 M of AC had an inhomogeneous distribution of grains on the substrate with small grain size. However, at 14 M a regular distribution of large grains over the substrate surface was observed. Energy dispersive analysis of X-rays (EDAX) is one of the analytical techniques used for the elemental analysis or chemical characterization of the sample. This technique is sometimes referred to as EDS (Energy dispersive spectroscopy) and is used for identifying the elemental composition of the specimen in the area of interest. EDAX works as an integrated feature of SEM and cannot be operated without it. The EDAX analysis revealed the presence of intense peaks related to Fe and S in addition to few small peaks corresponding to impurity elements like Si, Mg, and Na. The later peaks are mainly from the glass substrate as the grown layers were very thin (~ 100 nm). Stoichiometric ratio of S/Fe=2.00 is given to the reference pyrite [10, 16]. Spectra from different zones of that pyrite prove that its stoichiometry can be found to be 2.00±0.02.

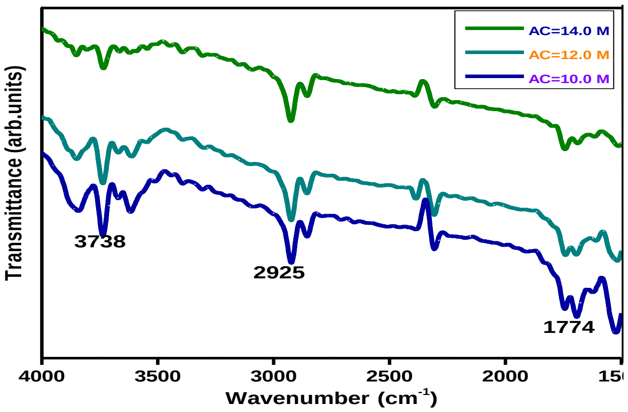


Fig.4. FTIR spectra of the pyrite films at different ammonia concentration.

For the determination of the surface properties of the films FTIR is found be one of the most popular techniques which are commonly used. Fig. 4 represents the FTIR data of FeS$_2$ films grown in this work. The spectra exhibit a small peak around 3738 cm^{-1} due to -OH stretching modes. Another band at 2925 cm^{-1} was also observed, which could be assigned to the C-H stretching modes. In addition, the band appeared at 1774 cm^{-1} [11, 13] represents the asymmetric S-O mode corresponding to the sulphate ion.

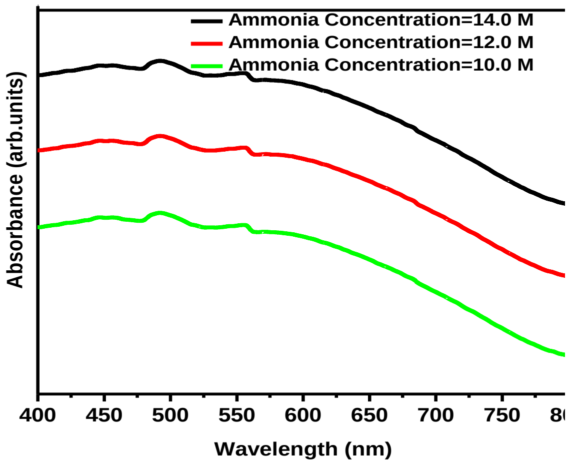


Fig. 5. Optical absorbance spectra of the deposited pyrite films.

The optical studies showed good optical absorption in the wavelength range of 400-800 nm (Fig 5). The optical absorbance of the films was very high throughout the visible and near infra-red regions. This made pyrite FeS$_2$ an important material for solar cell absorbers. Another important property of the films for photovoltaic applications is band gap. The optical absorbance of the material was evaluated by using Stern's relation which is given by:

$$\alpha = \frac{[k(h\upsilon - E_g)^{\frac{n}{2}}]}{[h\upsilon]} \qquad 2$$

Where υ is the frequency, h is the Plank's constant; k equals a constant while n has the values of either 1 or 4. The value of n is 1 for direct transition and 4 for indirect transition. The band gap of the material was calculated by extrapolating the $(\alpha h\nu)^{1/2}$ vs hν and $(\alpha h\nu)^2$ vs hν plots. The films exhibited two optical band gaps i.e. an indirect band gap in the range, 0.95 – 0.98 eV and a direct band gap varying from 1.28 eV to 1.14 eV with the increase of AC from 10 M to 14 M. These band gap values are comparable with values reported in the literature [12, 13].

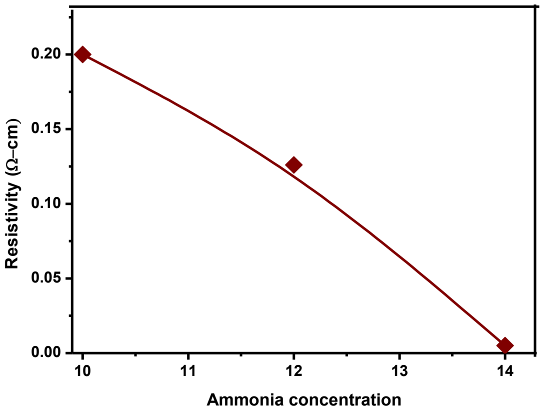


Fig. 6. Variation of electrical resistivity of FeS$_2$ films with AC.

Four probe method is one of the most common methods for measuring resistivity of compound semiconducting thin films and is especially suitable for measurements in the low resistivity regime. The resistivity of films decreases from 0.02 Ω cm at AC=10.0 M to 0.005 Ω cm [14, 17] at AC=14.0 M, as shown in

Fig. 6. The decrease of electrical resistivity with increase of ammonia concentration could be attributed to the increased mobility of the charge carriers along with the increase of grain size. As the grain size increases, the conductivity of the material increases which indicate the semiconducting nature of the grown films.

IV. CONCLUSION

The iron pyrite thin films were chemically deposited by using aqueous solutions of Iron sulphate and Thiourea. The film deposited at AC < 14 M concentration showed pyrite as well as marcasite phases while the films that were grown at 14 M had only pyrite phase with cubic structure. The later films showed uniform and better surface morphology compared to the films formed at concentrations lower than 14 M. The EDAX analysis revealed the presence of Fe and S with some impure elements. The FTIR spectrum exhibited peaks related to –OH, C-H and S-O stretching modes. The optical studies indicated a decrease of direct band gap from 1.28 eV to 1.14 eV as AC increased from 10 M to 14 M.

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