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Characterization of FeS_2 Thin Film Prepared by Spray Pyrolysis Method for Optoelectronic Applications

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Abstract

In this work, the physical properties of iron sulfide (FeS_2) thin films deposited by the chemical spray-pyrolysis (CSP) technique were studied. The thin films are deposited on glass substrates at 200ºC, using $FeCl_3$ salt with thiourea $(NH_2)_2CS$ as precursors. Structural analysis of X-Ray diffraction manifested that the thin films contain two phases: Marcasite and Pyrite in planes (110), (111) at angles 2θ =26.3°, 2θ =28.3° respectively. Optical properties analysis showed that the prepared iron sulfide thin-films were highly absorbing in the UV-Visible range and the absorption coefficient was in the range of $1.6x10^5$ cm-1 with a relatively low resistivity of about 0.49 (Ω.cm). The calculated activation energy (Ea) was 0.024 eV and the bandgap value was 2.45 eV. Moreover, the FeS2 thin films were also deposited on (CdO) to fabricate a heterojunction photocell. In conclusion, there is the feasibility of preparing low-cost and highly absorbing iron sulfide (FeS_2) thin films for optoelectronic applications with acceptable homogeneity using the spray-pyrolysis technique.

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1. Introduction

Since the 1970s, attention has been paid to renewable energy sources due to the increasing depletion of global energy sources and the urgent need for alternative energy sources [1], So interest has been given to iron sulfide (pyrite) compounds because of their abundance in the earth's crust, the cheapness of the raw materials from which they can be prepared and is non-toxic. Moreover, FeS_2 is convenient to be used in photovoltaic applications due to its unique optical bandgap range compatible with the energy of the solar spectrum. Furthermore, it has a high absorption coefficient in the order of (10^5 cm^{-1}), which is a thousand times greater than the absorption of silicon. Pyrite has a wide range of electrical resistivity that extends from 100 to 800 Ω cm. Based on these properties, FeS_2 has the potential for inexpensive generation of photovoltaic (PV) energy allowing for the absorbing layer to be as thin as 100 nm. This makes pyrite a very interesting material to be studied for PV applications [2,3]. In 2013, Sean et al prepared cubic FeS_2 thin films with large-grain size using acetylacetonate molecular ink and high temperature (550 ºC) in air, H2S, and sulfur gases [4]. In 2014, Uhlig et al. synthesized undoped and Co and Se-doped FeS_2 films by mechanical alloying and studied their thermo-electric properties for temperatures in the range 300-600 K. They observed that the undoped FeS_2 samples showed higher electrical conductivity with decreasing particle size [5]. In 2014, Liu et al. synthesized a nano-gap pyrite crystal photodetector with promising detection ability in the visible UV regions. This work also demonstrated an easy route to synthesize high-quality FeS_2 Nano-materials and their potential for photovoltaic applications [6]. In 2020, Rahman et al discussed the state of the art of FeS_2 solar cells. They suggested some causes for the poor open-circuit voltage in the FeS_2 solar cell such as surface inversion, Fermi level pinning, ionization of bulk donor states, and photocarrier losses [7]. In (2021), Zebarjad et al prepared Sn doped FeS_2 by the electro-deposition method. The FeS_2 films were deposited on fluorine tin oxide (FTO) substrates. They concluded that tin-doped FeS_2 with minimum Sn concentration revealed a powerful response of about 20-fold enhancement in the spectral region of visible light [8]. CSP has several advantages. (1) It extremely easy way to dope films with virtually any element in any proportion. (2) Unlike closed vapour deposition methods, CSP does not require high-quality targets and/or substrates nor does it require vacuum at any stage. (3) The deposition rate and the thickness of the films can be easily controlled. (4) Operating at moderate temperature (100-500°C) [9]. In this work, the feasibility of preparing FeS_2 thin film is studied to fabricate low-cost photocell by spray pyrolysis technique [10, 11]. The angle of the nozzle in our CSP system is set at 45° to decrease the defects and to obtain smooth and more homogenous thin films [12]. Many research articles showed important applications of semiconducting thin films prepared by CSP in heterojunction devices [13-15]

2. Experimental Procedure

Iron pyrite FeS_2 thin films were deposited by the spray pyrolysis technique, using iron chloride $FeCl_3$ (purity, 99.9%) from (RbL) and thiourea Soda-lime glass substrate was washed with double distilled water and ethanol, then it was ultrasonically cleaned. $FeCl_3$ and thiourea (C.S $(NH_2)_2$) (purity, 99%) from (Merck) with molar concentration of 0.04 M and 1M. The precursor solution was mixed on a magnetic stirrer at a rotation rate of 300 rpm for 15 minutes. Nozzle to substrate distance was set at 35 cm and the spray angle was 45°. The solution flow rate was kept at 5 ml/min and carrier gas pressure was constant at 4 bar. The substrate temperature was about 200 °C. In the same way, cadmium oxide was prepared from cadmium nitrate salts $Cd(NO_3)_2$ (purity, 99%) from (PHD) with a concentration of 0.3 M. The CdO was doped with 6% copper nitrate $Cu(NO_3)_2$ (purity, 99%) from (PHD). The deposition was done on glass substrates at 350 °C, and then iron sulphide was deposited on cadmium oxide at a substrate temperature of 200°C.

3. Results and Discussion

3.1. X-ray Diffraction

Figure 1 shows the XRD diffraction pattern by (Xrd Philips xpert) of FeS_2 films prepared at 200°C. The pattern has only two peaks which belong to the iron sulfide compound with a cubic crystalline structure.

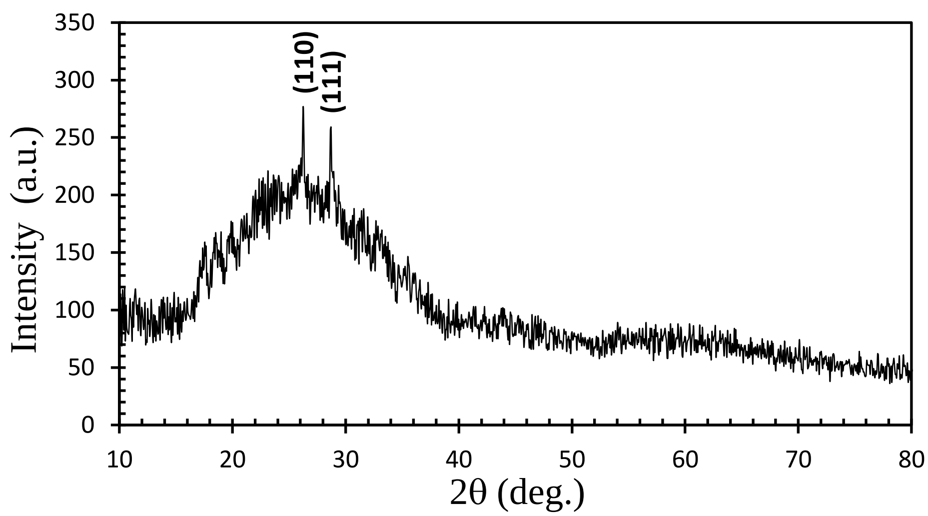

Figure 1: The XRD pattern of the thin film iron sulfide was obtained at 200 °C showing a marcasite and pyrite phase.

The orientation of the first peak is (110) and Brag's angle is 2θ=26.3°. This peak belongs to the marcasite phase as indicated by the diffraction card (JCPDS 00-037-0475). The second peak has the orientation (111) which corresponds Brag's angle 2θ=28.3° and belongs to the pyrite phase. This is matching the diffraction card (JCPDS JCPDS00-042- 1340). The X-ray diffraction pattern of FeS_2 thin film agrees well with the references [16, 17]. Table 1 displays the data extracted from XRD analysis namely Miller's indices The crystallite size, density of defects, and FWHM for FeS2 thin films synthesized at 200°C. The Scherrer formula was used to calculate the crystallite size (D) [18].

$$D\ (nm)=0.9\lambda(nm)/\beta\cos\theta \qquad (1)$$

where λ is the wavelength of X-ray (0.1541 nm), β is another symbol for full width at half maximum (FWHM), and θ is the Brag's angle.

Table 1: Miller's indices, crystallite size, the position of diffraction peaks (2ϴ), FWHM, density of defects, thin films synthesized at 200°C.

Samples	Miller indices	2θ (deg.)	FWHM (deg)	D (nm)	δ (x10^{10}) cm^2
Iron sulfide	(111)	28.8	0.23616	34.7	8.2
	(110)	26.1	0.70848	11.5	75.3

3.2. Morphological Investigation
Figure 2 shows the analysis of SEM (Tescan, Mira3) that the films of iron sulfide have particle-like shapes and this is consistent with the reference [19].

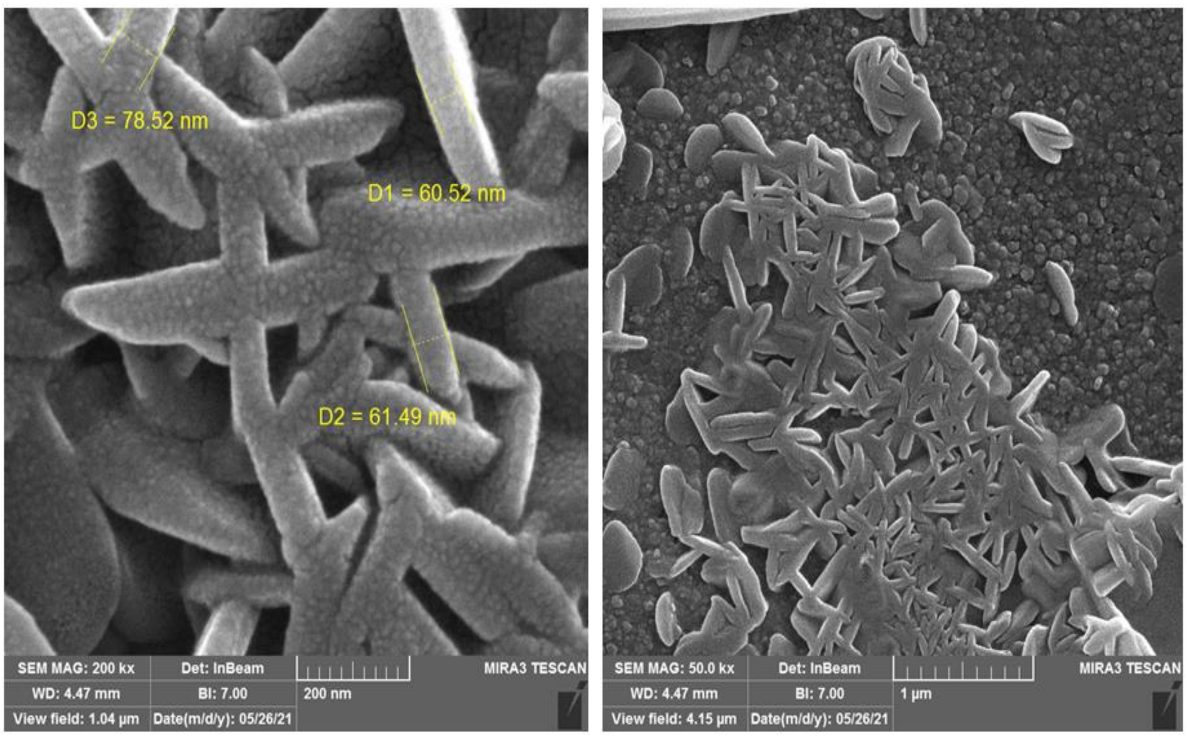

Figure 2: FESEM images of iron sulfide thin films prepared at 200 °C that it has particle-like shapes.

3.3. Optical Properties
Figure 3 shows the analysis of (UV-1800, Shimadzu) that FeS_2 thin films prepared by CSP have two energy gaps (Eg_1=1.3 eV, Eg_2=2.45). For example, the absorption coefficient is about 1.6x10^5 at a wavelength 400 nm. The calculated bandgap of iron sulfide prepared at substrate temperature of 200 ºC was 2.45 eV and this value has a good agreement with [20].

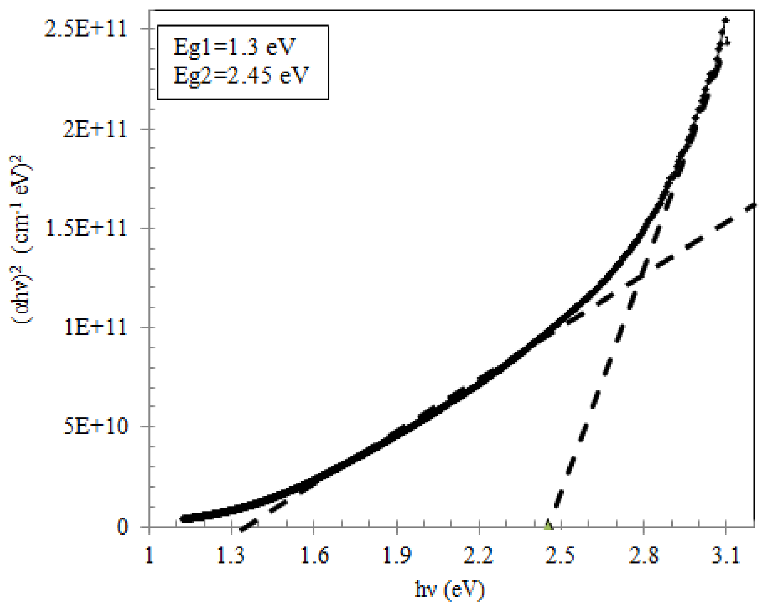

Figure 3: $(\alpha h\nu)^2$ calculated as a function of energy hν for FeS_2.

Figure 4 depicts the transmittance as unction of wavelength for FeS_2 prepared by CPS. The thickness of the sample (410 nm) is calculated from the cross-section view of the FESEM images. The thin film is highly absorbing in the visible region therefore it has very low transmittance (lower than 10%) as shown in Figure 4.

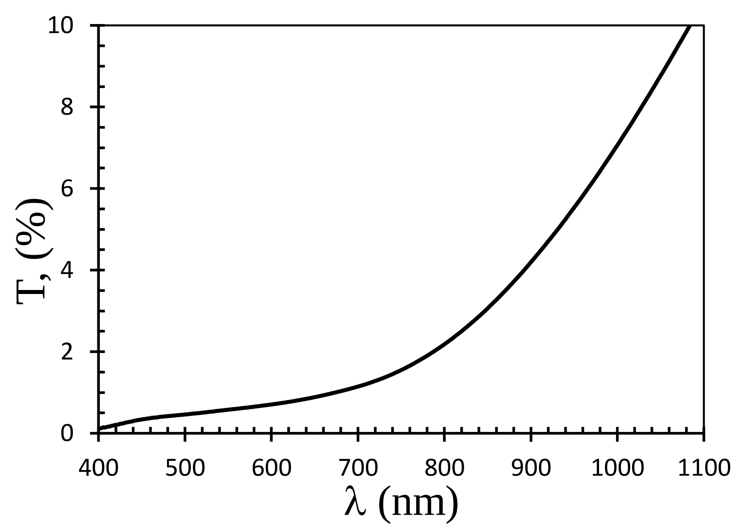

Figure 4: Transmittance spectrum of the FeS_2 at substrate temperature 200°C.

3.4. Electrical Characteristics

3.4.1. D-C Conductivity

Many factors determine the type of conductivity in FeS_2. In general, if the vacancies are from iron atoms and interstitial from sulfur atoms then the thin film is p-type and if the vacancies are from sulfur atoms and interstitial from iron atoms the thin film is n-type. Moreover, the mobility and resistance of the charge carriers are affected by inverse temperature [16]. Figure 5 shows that the thin film exhibits semiconducting behaviour where the conductivity increases with increasing temperature [21].

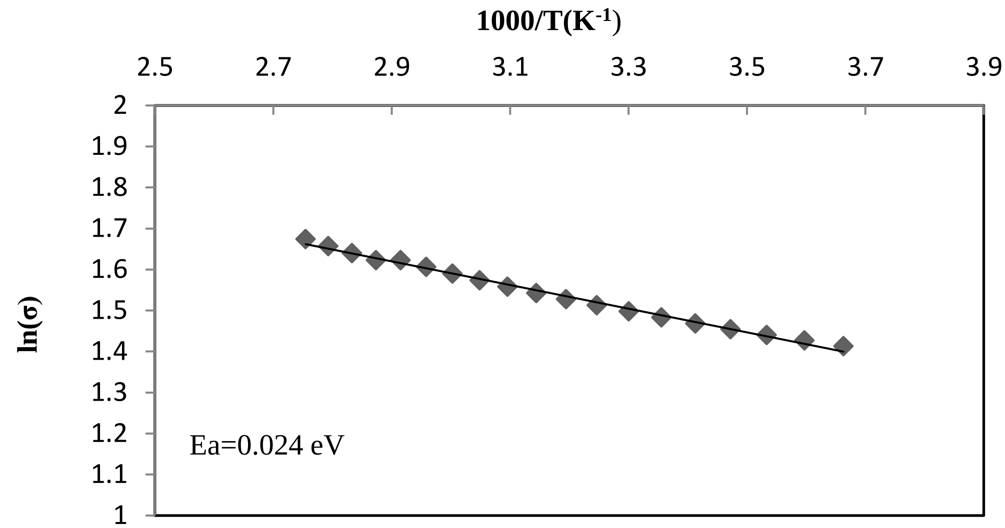

Figure 5: Natural logarithm of conductivity against (1000 / T) for temperatures in the range 273-363 K.

3.4.2. Seebeck Effect

The Seebeck test is one of the most important tests that indicate the type of semiconductor conductivity. Figure 6 shows that iron sulfide thin film prepared CPS p-type conductivity, i.e., the majority of charge carriers are the holes. The voltage difference increases with increasing temperature due to the movement of the holes from the hot to the cold side.

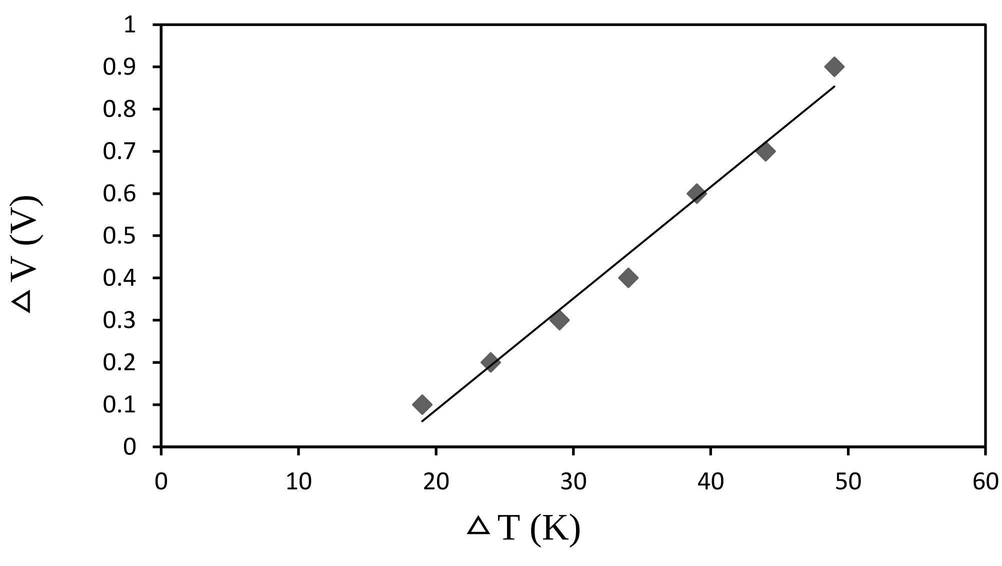

Figure 6: The thermovoltage, ΔV, against the temperature difference, ΔT.

3.5. Current-Voltage Characteristics of FeS_2/CdO Heterojunction

After studying the structural, optical, and electrical properties of iron sulphide film, FeS_2 thin film was deposited on 6% Cu doped cadmium oxide film, and the properties of a current-voltage diagram were drawn to figure out I-V characteristics in the forward and reverse biases, Figure 7 shows the behaviour of heterojunction with an obvious response to the white light and the photo-current in the forward direction is higher than that for the reverse bias. These two features qualify the junction of FeS_2/CdO for optoelectronic applications. Although the response of this cell is weak, however, this can be considered the first step to fabricating the low-cost solar cell.

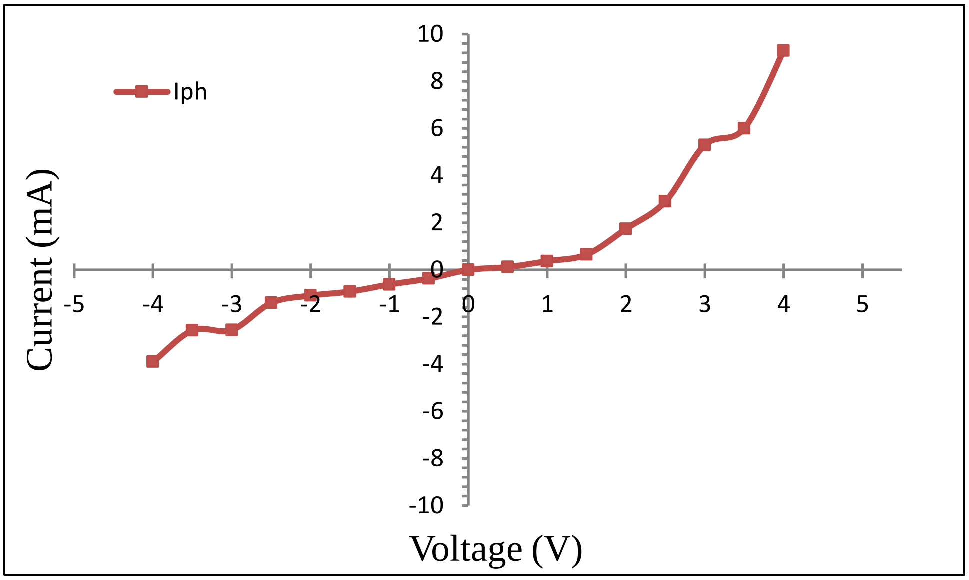

Figure 7: shows I-V characteristics for FeS_2/CdO photocell.

4. Conclusions

The structural, optical, and electrical properties of iron sulphide prepared by CSP are studied. In conclusion, there is a feasibility of preparing FeS_2 thin films with simple and low-cost CSP method. The films showed poor polycrystalline structure. FeS_2 thin films prepared by the CSP technique have a small direct bandgap and have high absorption coefficient which is preferred for optoelectronic application. A photocell can be fabricated from the deposition of FeS_2 by CPS on CdO to form a heterojunction photocell. A lower deposition rate can result in smoother and more homogenous layers of FeS_2 on CdO with a minimized number of defects and recombination losses.

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Conflict of Interest

The authors have no conflict of interest to declare.

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