

Article

Impact of Iron Pyrite Nanoparticles Sizes in Photovoltaic Performance

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Abstract: With rising energy demand and depleted traditional fuels, solar cells offer a sustainable and clean option. In recent years, and due to its acceptable band gap, high absorption coefficient, and inexpensive cost, iron pyrite (FeS₂) is a popular material for solar cells. Earth abundance and nontoxicity further boost its photovoltaic possibilities. The current study examined the influence of sulfurization at 350–400 °C on iron pyrite layers fabricated using spray pyrolysis. The morphology and size from TEM confirmed the XRD results of synthesizing a pyrite FeS₂ with an average particle size of 10–23 nm at 350–400 °C, respectively. The direct band gap calculated by DFT as a function of temperature was found to be consistent with the experimental findings, 0.87 eV (0.87) and 0.90 eV (0.95) at 350 °C and 400 °C, respectively. We found high-performing photovoltaic cells on ITO/ZnO/FeS₂/MoO₃/Au/Ag, obtained with an excellent quality of nanoparticles and nanostructures of FeS₂ pyrite, which improved with the method of preparation and growth parameters.

Keywords: iron pyrite; band energy; organic photovoltaic cells



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1. Introduction

In the last decades, transition metals experienced a renewal of interest due to their excellent electrical, transport, magnetic, and optical properties [1–3]. In general, FeS₂ pyrite is an ideal material for the fabrication of solar cells and photovoltaic devices [4–9] due to its high absorption coefficient ($\alpha > 10^5 \text{ cm}^{-1}$ for $h\nu > 1.3 - 1.4 \text{ eV}$) [5], its small band gap (about 0.95 eV) [10], high photocurrent quantum efficiency (> 90%) [6], and low material cost [4–11].

FeS₂ pyrite was one of the first crystal structures that resulted from Bragg, in 1914 [12], with his XRD system. It has a simple cubic structure similar to that of rock salt.

FeS₂ pyrite is a good option for thin film photovoltaic. Considering its potential and current importance [4–9], many experimental [4–9,13–40] and theoretical works [41–60] have been interested to FeS₂. Schlegel et al. [33] determined the transition and reflectivity spectrum of a single crystal of FeS₂. They showed that FeS₂ pyrite has an empty 3d e_g band at 300 K, a completely filled 3d t_{2g}, and an indirect band gap equal to 0.95 eV. Kou et al. [25] found a band gap at 297 K of about 0.84 eV. Karguppikar et al. [40] reported that pyrite can be an indirect semiconductor from its conductivity properties, Hall effect data, and optical gap of 0.92 eV. Sun et al. [37] determined an FeS₂ pyrite thin film by sulfurizing oxide precursor films. From their UV-vis absorbance spectroscopy and X-ray photoelectron spectroscopy (XPS), they showed a direct band gap of about 0.75 eV, an indirect band gap of about 1.19 eV, and a high absorption efficiency ($\alpha > 10^5 \text{ cm}^{-1}$). Yu et al. [39] used the chemical bath deposition (CBD) method. They reported that the band gap of FeS₂ can be increased from 0.86 to 1.31 eV when doped by Mn.

Many other preparation methods, such as spray pyrolysis, metal organic chemical vapor deposition (MOCVD), and ion beam sputtering have been declared for the synthesis of nanocrystals, nanowires, and crystallites of FeS₂.

Mostly all experiments found a band gap between 0.84 and 1.03 eV. For theoretical study, Bullet [42] used the first principle local density approximation (LDA) calculation to investigate the optical properties of iron pyrite. He found an indirect band gap of 0.4 eV for marcasite and 0.7 eV for pyrite. This value is smaller by 0.25 eV when compared to the experimental indirect band gap (0.95 eV). Zhao et al. [59] performed the self-consistent linear combination of atomic orbital (LCAO) formalism to determine the electronic properties of iron pyrite. Their smallest theoretical direct band gap was about 0.64 eV, and they found an indirect band gap of 0.59 eV. Additionally, Opahlele et al. [53,54] determined the electronic properties of FeS₂ utilizing an LDA potential parameterized by the Perdew-Zunger (LDA-PZ). Their calculated band gap was about 0.85 eV. Muscat et al. [52] employed the periodic LCAO method with the CRYSTAL 98 package and pseudopotential technique with CASTEP Software package.

Wadia et al. [61,62] showed a complete research study a few years ago and investigated 23 potential materials for photovoltaics and found that FeS₂ pyrite was the best one, beating all materials in terms of cost. It was confirmed that the extraction cost of silicon was 57 times more than that of FeS₂ (USD 1.7 for silicon compared to USD 0.03 for FeS₂). Additionally, the silicon energy output for extractions was 12 times bigger than that of FeS₂ (24 KWh kg^{−1} vs. 2 KWh kg^{−1} for 24 KWh kg^{−1}). Rahman et al. [62] showed that FeS₂ is much more cost-effective than silicon if they are produced with taxation and the same regulations in the same country. All these beneficial and interesting features make FeS₂ an excellent candidate for photovoltaic performance.

We included the prepared structure to show the real effect of the structure on band gap for devices that are not photovoltaic. The biggest dilemma for iron pyrite is attributed to the structure of pyrite, for which we completely studied to include the impact of the nanoparticles of iron pyrite on photovoltaic performance. This work aimed to improve a new progress in the use of iron pyrite in photovoltaics.

2. Experimental

2.1. Materials and Method

We used spray pyrolysis for the fabrication of our sample. Amorphous iron oxide films were placed on normal glass substrates by spray pyrolysis. Then, the found films were heated under a sulphur atmosphere. We started by cleaning the glass substrates. The process was as follows: first, we put the films in an acidic solution for 3 h. After that, they were kept in a detergent solution and washed with distilled water. Then, they were kept in a solution of methanol and washed utilizing an ultrasonic cleaner for 15 min. Finally, the substrate was cleaned with distilled water and dried under a stream of nitrogen. In the second procedure, we chose to spray FeCl₃·6H₂O (0.05M) for 5 min in an aqueous-based solution onto glass substrates. After we dissolved FeCl₃·6H₂O in deionized water (ionization reaction: 2H₂O → H₃O⁺ + OH[−]), a dark amorphous iron oxide layer was obtained. The jet flow rate and the distance nozzle-substrate were about 7 mL/min and 45 cm. Carrier gas was used by compressed air. We obtained dark layers. Then, it was heated under a sulphur atmosphere (~10^{−6} torr) at two sulfurization temperature (350 °C–400 °C). However, we succeeded in obtaining FeS₂ pyrite via spray pyrolysis.

2.2. Characterization

The crystal structure of the FeS₂ pyrite was analyzed by powder X-ray diffraction (XRD) using a Siemens D500 diffractometer (Siemens Bruker, Germany) (CuK α radiation λ = 1.54201 Å). The parameter lattice and crystal structure were obtained using the Reitveld method by utilizing the PDXL program. Raman spectra were determined to further study the phase evolution with increasing temperature. The morphology and size of nanocrystals were recorded using transmission electron microscopy (TEM) using JEOL

2010 (200 KV) microscopy. Optical absorption was investigated using a SHIMADZU 3100s spectrophotometer (SHIMADZU, Columbia, MD, USA).

2.2.1. X-ray Diffraction:

XRD patterns of the FeS_2 pyrite sample are shown in Figure 1. Typical diffraction peaks at $2\theta = 28.71^\circ, 33.43^\circ, 37.25^\circ, 40^\circ, 57.79^\circ, 59.98^\circ, 61.89^\circ$, and 64.31° are attributed respectively to plan (111), (200), (210), (211), (220), (311), (222), (230), and (321), corresponding with the norm diffraction data of the FeS_2 (JCPDS card n°028-0076; space group $\text{Pa}\bar{3}$). No other impurities, such as marcasite, pyrrhotite, or greigite compounds, were detected in the XRD patterns, confirming the high purity of the obtained sample. Powder XRD patterns appeared in a cube of crystalline in a pyrite structure, where the disulfide ions localized in octahedral, coordinated with Fe metal ions within a space group symmetry of T_h^6 ($\text{Pa}\bar{3}$). The significant effect of temperature can be observed on the position of sulfur (S). The sulfur position changed when the temperature increased. The X-ray diffraction (XRD) patterns of two samples exhibit a notable degree of similarity, with minor discrepancies observed in the intensity of diffraction peaks. This resemblance is primarily attributed to the identical material composition of both samples, namely, iron pyrite. Moreover, it is imperative to note that the XRD patterns for these two samples share congruent structural characteristics, resulting in the consistent norm of diffraction data as specified in the ASTM file.

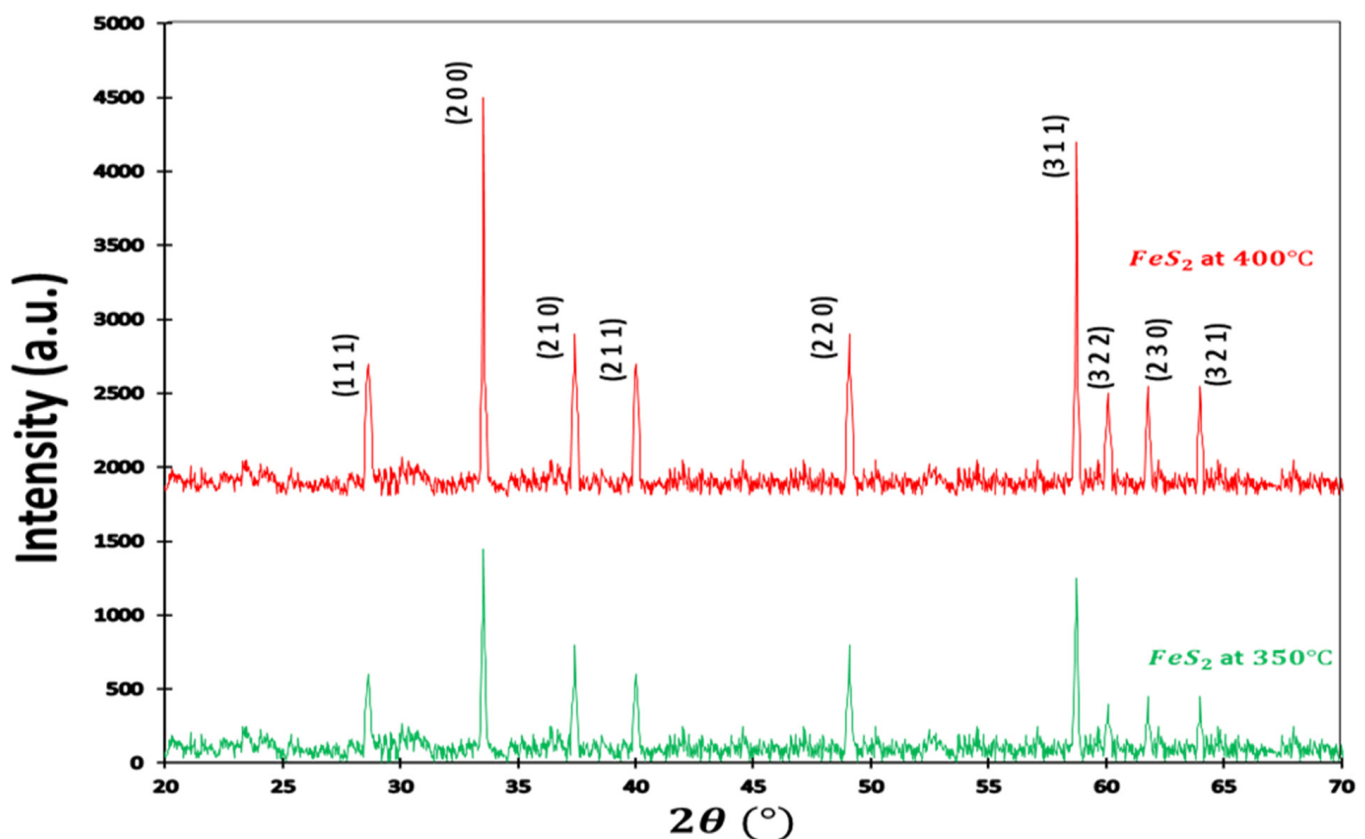


Figure 1. XRD pattern of FeS_2 pyrite. The X-ray diffraction (XRD) patterns of two samples exhibit a notable degree of similarity, with minor discrepancies observed in the intensity of diffraction peaks. This resemblance is primarily attributed to the identical material composition of both samples, namely, iron pyrite. Moreover, it is imperative to note that the XRD patterns for these two samples share congruent structural characteristics, resulting in the consistent norm of diffraction data as specified in the ASTM file.

The output parameters are listed in Table 1.

Table 1. Cells parameters.

Tempurature	350 °C	400 °C
Cubic lattice a	5.409 Å	5.417 Å
ν (Position paramater)	0.113	0.111
u (Suffer position)	0.387	0.389

2.2.2. Raman Spectra

The Raman spectra of the FeS₂ pyrite are presented in Figure 2. As shown, sulfurization was conducted at different times and temperatures (350 °C and 400 °C). We identified that the increase of the sulfurization time and temperature reduced the perfection of formation of other phases, and this resulted in a pure pyrite structure. We observed two strong typical Raman peaks at 342 cm⁻¹ and 403 cm⁻¹, corresponding to E^{low} and E^{High} modes and generated by Fe-Fe and S-S vibrations, respectively. We used long sulfurization times for two temperatures to find the growth condition for high throughput and low-cost processing. In the past literature, time sulfurization ranged between 90 and 120 min [63,64] and was still considered short sulfurization between 3 h and 8 h [65,66].

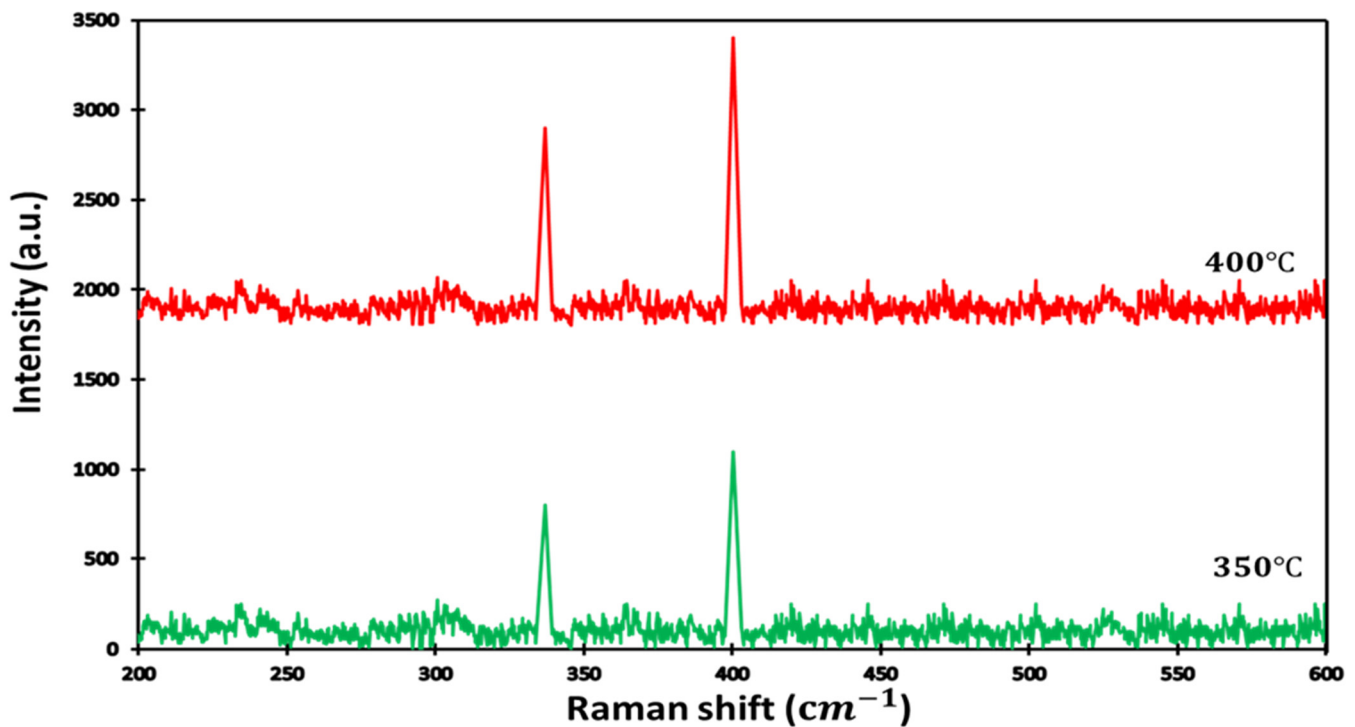


Figure 2. Raman spectra for thin film obtained after sulfurization for time = 14 h and at two sulfurization temperatures.

From our Raman analyses, we calculated the intensity ratio of E^{low} and E^{High}, which are related to sulfur distribution versus the crystallinity of the FeS₂ sample. Table 2 presents the difference in the contribution of sulfurization at different temperatures. It can be noticed that sulfurization increased with temperature, and the increase of the band gap highlights the influence of the sulfur position on the formation of intermediate levels in the band gap of the MS₂ transition metal.

Table 2. The intensity of the E^{low} mode and the intensity ratio of ($E^{\text{low}}/E^{\text{High}}$) modes of the FeS_2 sample at different temperatures.

Temperature ($^{\circ}\text{C}$)	350 $^{\circ}\text{C}$	400 $^{\circ}\text{C}$
$I(E^{\text{low}})$	0.66	0.79
$I(E^{\text{low}})/I(E^{\text{low}})$	0.73	0.83

2.2.3. Transmission Electron Microscopy

Besides the variation nanoparticle size conforming to the results from transmission electron microscopy (TEM), as in Figure 3, the nature of sulfurization using this method affects the morphology of the resulting FeS_2 pyrite. For logical statistics, around 100 particles of a representative sample section were studied. Particle diameters were calculated, assuming an ideal spherical particle shape based on the measured area. In case of FeS_2 pyrite at 400 $^{\circ}\text{C}$ Figure 3a–c, the smallest particles in the range of 7–15 nm. Overall, average particle sizes were between 10 nm and 23 nm, and highest size was 39 nm. However, for FeS_2 pyrite at 350 $^{\circ}\text{C}$ (Figure 3d,e), we obtained only particles between 10 nm and 23 nm.

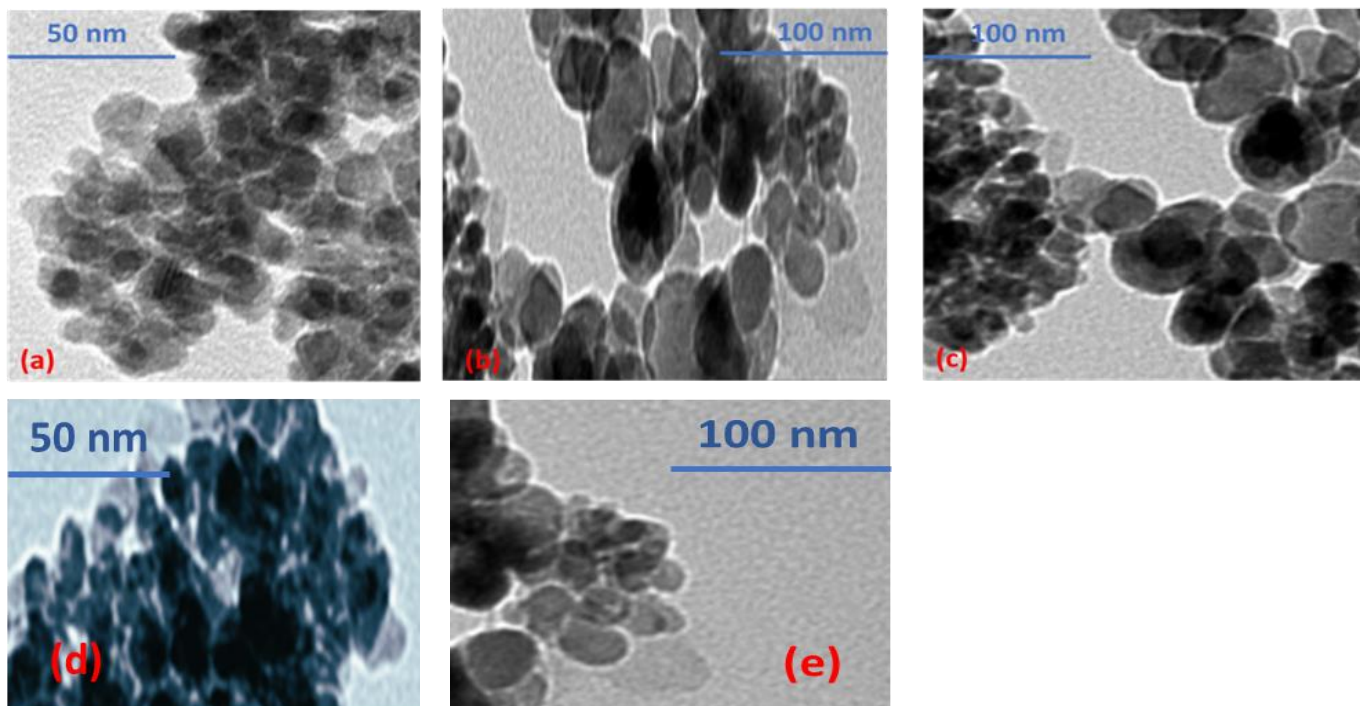


Figure 3. (a–c): TEM image of FeS_2 at 400 $^{\circ}\text{C}$. (d,e): TEM image of FeS_2 at 350 $^{\circ}\text{C}$.

At higher magnification (Figure 3b,c), the surface of layers appeared granular with different grain sizes, and this enabled us to confirm the good crystallinity, showing its photovoltaic performance.

2.2.4. Optical Properties:

The mathematical equation for the optical band gap was given by Tauc et al. [67], and we used it in these studies as well [68,69]:

$$\alpha h\nu = A(h\nu - E_g)^n$$

$$\text{where } \begin{cases} n = 2 \rightarrow \text{for an indirect transition} \\ n = \frac{1}{2} \rightarrow \text{for an direct transition} \end{cases}$$

where α is the absorbance coefficient, A is a constant, and $h\nu$ is the photon energy. The variation $(\alpha h\nu)^{\frac{1}{2}}$ vs. photon energy $h\nu$ suggest an indirect band gap and for $(\alpha h\nu)^2$ vs. photon energy $h\nu$, depicting a direct experimental transition. Notice that pyrite may have an indirect or direct transition [70,71]. The question is: will the band gap of our sample be indirect or direct? In fact, if iron pyrite layers have a direct band gap, it is very important for them to apply multispectral photovoltaic cells, because a direct band gap means a direct transition.

$(\alpha h\nu)^{\frac{n}{2}}$ were plotted as functions of photon energy $h\nu$, with $n = 4$ and $n = 1$, and it is presented in Figure 4a–c. Only the plot of $(\alpha h\nu)^2$ vs. $h\nu$ has a straight line, indicating that FeS₂ pyrite film has a direct band gap energy for different temperatures of fabrication. Table 3 gives the acquired values of the band gap of FeS₂ pyrite film according to the two temperatures. FeS₂ pyrite had a low band gap when heat treated at 350 °C. Figure 4d shows the absorption coefficients, which were always high, and they were greater than $1.2 \times 10^5 \text{ cm}^{-1}$.

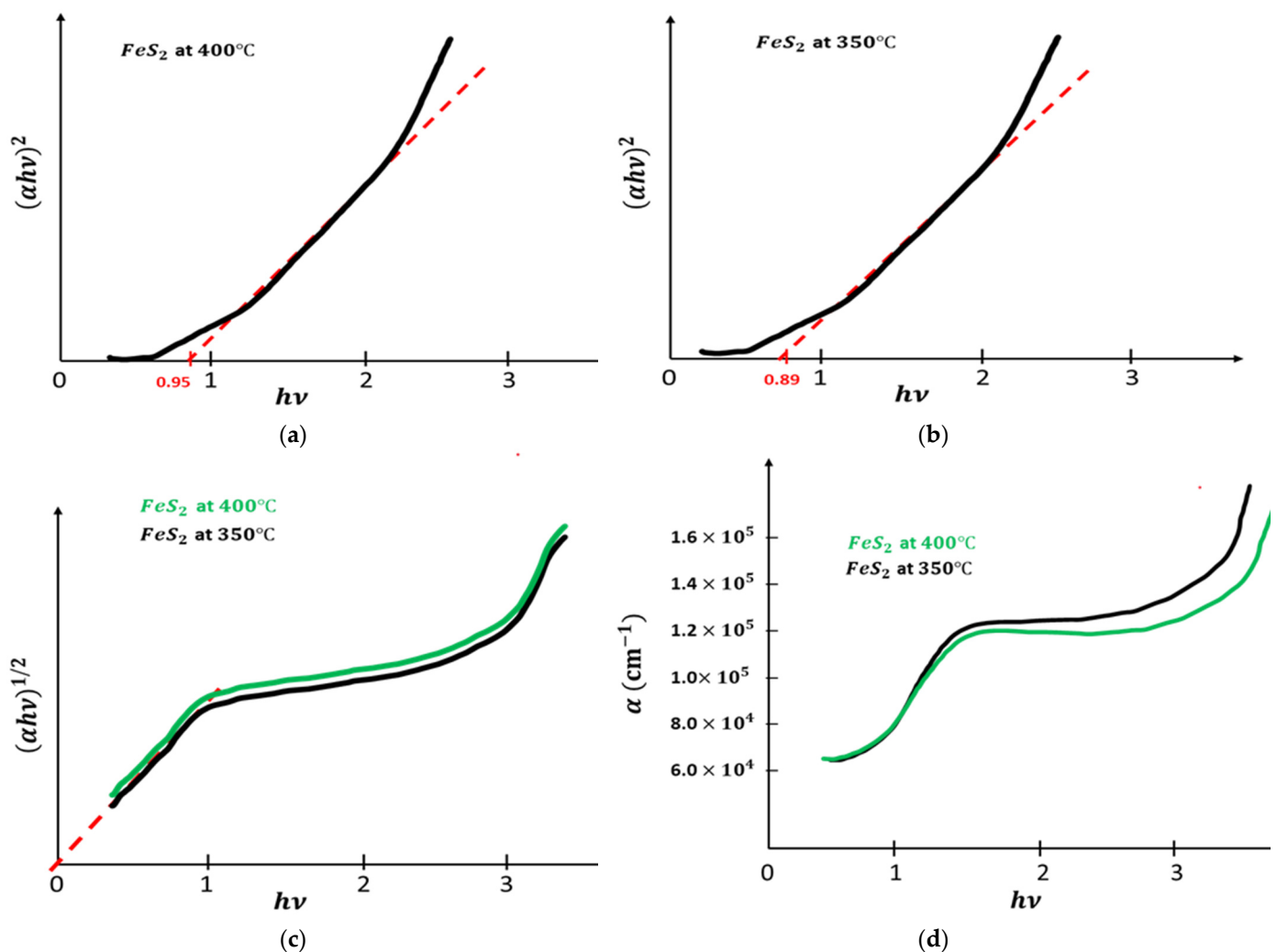


Figure 4. (a): $(\alpha h\nu)^2$ vs. $h\nu$. (b): $(\alpha h\nu)^2$ vs. $h\nu$. (c): $(\alpha h\nu)^{1/2}$ vs. $h\nu$. (d): α vs. $h\nu$.

Table 3. Experimental band gap.

Temperature	350 °C	400 °C
Band gap (eV)	0.89	0.95

3. Band Structure

3.1. Computational Details

Density-Functional Theory [72,73] was used within the linear muffin-tin orbital method in the atomic-sphere approximation (LMTO-ASA). The LMTO ASA method was explained in detail in several reports [74–76]. In our calculations, we employed the self-consistent band calculations because they are the first principles of calculations utilizing density functional theory (see [72]), utilizing the local density approximation (see [77]), and utilizing numerical techniques based on the treatment of electron ion interaction in the pseudopotential approximation [78]. Moreover, the Hamiltonian Atomic Spheres Approximation is totally specified by the potential parameters. It generates moments from the eigenvectors of the Hamiltonian. Regarding specified potential, there is an individual correspondence between the energy E_v of the wave function φ and the logarithmic derivative D_v at the sphere radius. In essence, it is possible to specify either one. The potential P becomes simple because [79,80]:

$$P(\varepsilon) = \text{const} \frac{D(\varepsilon) + 1 + 1}{D(\varepsilon) - 1} \approx \left(\frac{\Delta_l}{\varepsilon - C_1} + \gamma_1 \right)^{-1}$$

where γ_1 , Δ_l , and C_1 are the “potential parameters” that parameterize P . C_1 defines the band “center of gravity”, Δ_l is the “band width” parameter, which correlates with the bandwidth of l channel if it were uncoupled from the other channels, and γ_1 is the “band distortion parameter”, which describes the deformations relative to a universal shape. Generally, small parameterization is a perfect method to study band structure.

First, we obtained the potential parameters for all atomic spheres. The muffin-tin potential constant V_{MTZ} was the crossing point of muffin-tin potential around Fe and S, and it is listed in Table 4. We had 24 symmetry operations. The initial sphere packing was equal to 82.2%, and it was scaled to 92.9%. The role of these empty spheres is to reduce the number of iterations in this system and to reduce the overlap between the spheres centered at Fe and S.

Table 4. The muffin-tin potential constant.

Temperature	350 °C	400 °C
V_{MTZ}	−0.679772	−0.737209

3.2. Pyrite Crystal Structure

FeS_2 pyrite has a cubic crystal structure and the space group number 205 (with space-group T_h^6 (Pa3)). In these structure, there are eight S atoms located in eight positions and four Fe atoms in four positions. The lattice parameters for FeS_2 pyrite are listed in Table 5.

Table 5. Pyrite cell parameters.

Temperature	350 °C	400 °C
space group	T_h^6	T_h^6
cubic lattice	5.409 Å	5.417 Å
v position parameter	0.113	0.111
sulfur position	0.387	0.389
Bond length $d_{\text{S-S}}$	2.117 Å	2.083 Å
Bond length $d_{\text{Fe-S}}$	2.264 Å	2.259 Å
Bond angle Fe – S – Fe	115.21°	114.88°
Bond angle Fe – S – S	102.82°	103.28°
Bond angle S – Fe – S	100.09°	100.13°

In FeS_2 pyrite, each S atom is coordinated with three Fe atoms, for which the dimer pairs S_S are in tetrahedral sites, and each Fe atom is coordinated with six S atoms in octahedral sites.

Moreover, these structures contain pairs of sulfur S_2 molecules, contrary to individual S atoms presented in the Figure 5a image of the overlapped unit cell of FeS_2 pyrite. To study the deviation from tetrahedral and octahedral geometries, we describe the correlation of the S-S bond length and cubic lattice. The relationships between our cell parameters are presented in Table 5. The structure ν of the pyrite is between 0.10 and 0.13 [81]. Our work demonstrated that the value of ν ranges between 0.111 and 0.113, showing significant effects of increased temperature conditioning FeS_2 pyrite. We noticed that the Fe sites had a small trigonal distortion, for which the S-Fe-S bond angles were 100.09° at 350°C and 100.13° at 400°C , and the three Fe-S-Fe bonds were between 114.88° and 115.21° , for which the S sites were distorted from tetrahedral symmetry.

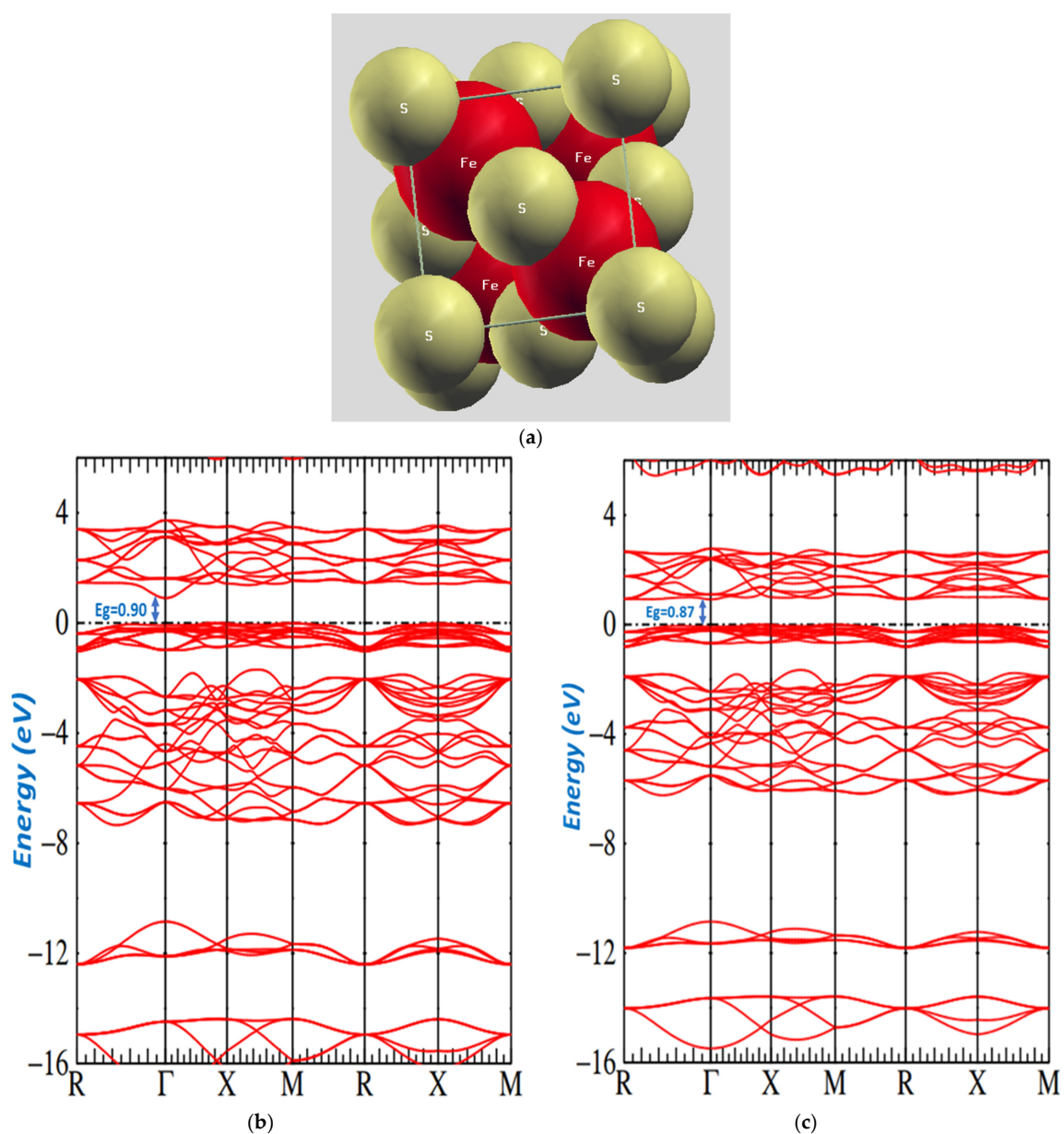


Figure 5. (a): Image of overlap of FeS_2 pyrite. (b): Band structure of FeS_2 pyrite. (c): Band structure of FeS_2 pyrite at the temperature 350°C and at the temperature 400°C .

3.3. Energy Bands of FeS₂ Pyrite

The DFT energy bands for samples at different temperatures are shown in Figure 5b,c. The two figures provide the band structure on a form of energy that shows a general electronic structure. These figures present the region around the Fermi energy, which clearly depicts the details of a low conduction band and the highest valence band.

However, our band structure indicates that FeS₂ has a band gap semiconductor. We had four FeS₂ units in each unit cell and accommodated 40 occupied valence bands. The minimum conduction band was in Γ , and the maximum valence band was at Γ . The direct transition was observed at Γ and had the values of 0.87 eV and 0.90 eV.

Our obtained results are different than those of Zhou et al. [59] and Temmerman [58], who found 0.59 eV and 0.64 eV. Their gap was smaller than the experimental gap of 0.95 eV. Moreover, we were successful because our obtained gaps were significantly consistent with our optical gaps.

The calculated gap, optical gap, minimum band conduction $CB_{\max}$, maximum valence band $VB_{\max}$, and Fermi energy are summarized in Table 6. The bands are relative to bonding and antibonding pairs of S₂ orbitals. In the range between -14 and 8 eV corresponding S3s, the structure of sulfur and these S3 states are predominant. The S 3p state is presented with a small addition of an Fe 3d function, starting at approximately -6 eV. Basically, these bands have Fe t_{2g} hybridized with p orbitals, and they are below the Fermi energy. The lowest conduction band contained a combination of Fe e_g orbitals. They were above Fermi energy. S3p Fe 3d is a preminent character on the conduction band.

Table 6. Band structure of FeS₂ Parameters.

Temperature	350 °C	400 °C
Calculated gap E_g	0.064 Ry = 0.87040 eV	0.06550 Ry = 0.90508 eV
optical gap E_g	0.89 eV	0.95 eV
minimum band conduction $CCB_{\min}$	-0.052792 Ry	0.066017 Ry
maximum band valence $VB_{\max}$	-0.116791 Ry	-0.000533
Fermi enrgy E_f	-0.116791 Ry	-0.000533

Figure 6a,b presents the density of the states calculated, and it shows the states above and below the Fermi level of iron pyrite. It discloses the importance of hybridization between Fe and S states and the effect of temperature on the fabrication of pyrite.

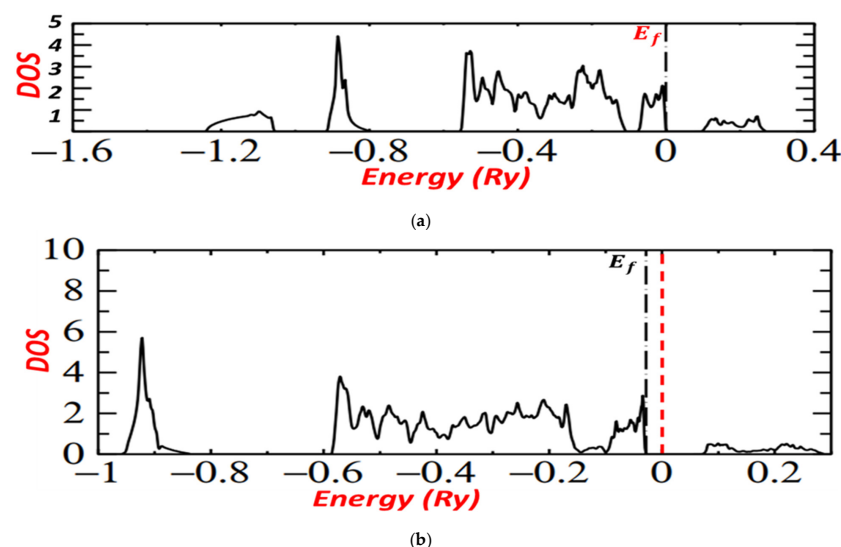


Figure 6. (a): DOS for FeS₂ pyrite at the temperature 400 °C. (b): DOS for FeS₂ pyrite at the temperature 350 °C.

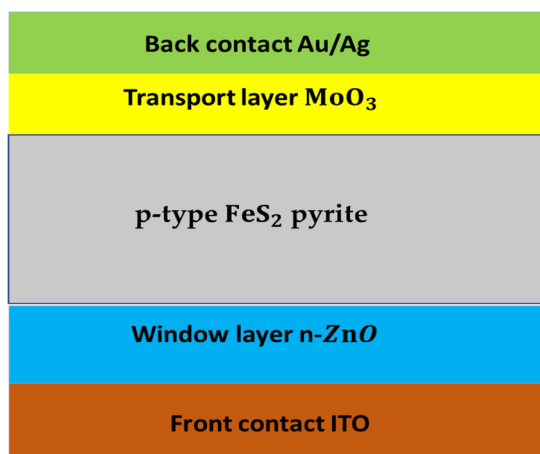
For the two graphs, level t_{2g} lies between -0.1 Ry and 0, below the Fermi level, but for FeS_2 pyrite prepared at 400°C , it is near 0 and near Fermi level, which implies the good crystallite and electronic properties of iron pyrite prepared at 400°C .

For both graphs, we noted that the conduction band was made entirely of Fe eg with Sp, marking that the conduction band was pure Sp while the valence bands were completely derived from the Fe t_{2g} .

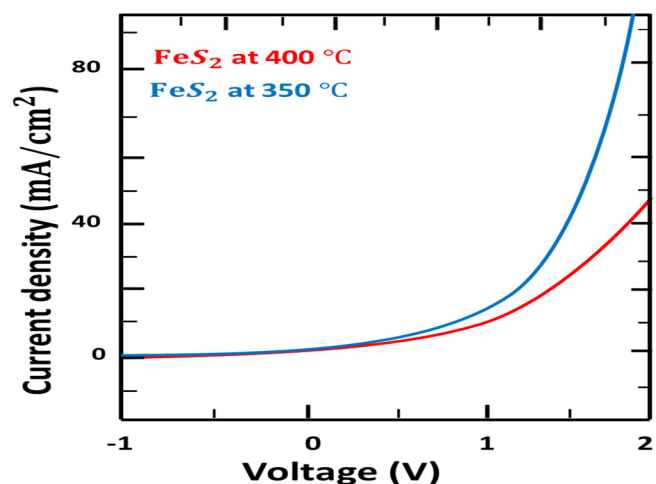
4. Pyrite in Photovoltaics: Modeling the ITO/ZnO/FeS₂/ MoO₃/Au/Ag Device

The synthesized FeS_2 pyrite samples were evaluated for the application of photodetector devices. We modeled ITO/ZnO/FeS₂/MoO₃/Au/Ag to study the improvement in solar cell characteristics realized by the increase of temperature in two cases of preparation of FeS_2 pyrite. We chose this application because it holds numerous benefits due its ability to be prepared at mild conditions, its low cost of chemicals, its mechanical flexibility, its better tuning, and due to it being a suitable alternative to silicone-based solar cells [82,83].

The device structure is presented in Figure 7a. ITO film was cut mechanically to obtain a $2.5\text{ cm} \times 2.5\text{ cm}$ substrate. All substrates were cleaned in isopropanol, water, and soap for 15 min. For layer parameters, a washed indium tin oxide (ITO) glass substrate was managed by ultraviolet-ozone for 15 min. The ZnO layers were spin coated with 60 mg ml^{-1} ZnO/ CHCl_3 solution annealed at 250°C for 15 min in the air to form a ZnO layer of 100 nm. The MoO₃ (20 nm) Au (30 nm) Ag (90 nm) layers were placed successively by thermal evaporation.



(a)



(b)

Figure 7. (a): Device structure of ITO/ZnO/FeS₂/ MoO₃/Au/Ag. (b): Current density versus voltage (J–V) characteristics of fabricated solid solar cells.

In recent years, ZnO has become the prime candidate for organic photovoltaic cells [84] since its efficient improvement in stability. Here, we used the n-p layer heterojunction p-type FeS_2 pyrite solar cell using an n-type window layer. Additionally, MoO₃ thin film can react as an effective electron-blocking layer or hole transporting to reduce the recombination of holes and electrons [85].

The schematic illustration characterization by exercising voltage from -1 to 2 V under a dark current using the modeled ITO/ZnO/FeS₂/MoO₃/Au/Ag structure, as presented in Figure 7b. The reported I–V characteristics and calculations for p-type FeS_2 pyrite at 350°C were similar [86], principally below the onset voltage and the I–V curves above 1.5 V . However, the I–V curves for p-type FeS_2 pyrite at 400°C showed a large difference above 1.4 V , for which the onset voltage was around 1.3 eV . This result corresponds well with the

fabrication of FeS₂ pyrite, indicating that the nanostructures composed of FeS₂ pyrite at 400 °C are excellent in building n-p junction ZnO/FeS₂ pyrite.

We concluded that, to obtain high-performing photovoltaic cells on ITO/ZnO/FeS₂/MoO₃/Au/Ag, it is necessary to focus on the quality of nanoparticles and nanostructures of FeS₂ pyrite, which improved by increasing the temperature of preparation (400 °C). We also mentioned to the effect of sulfur position, distance sulfur–sulfur, and temperature to band gap of FeS₂ pyrite.

5. Conclusions

This work was an inclusive study of FeS₂ pyrite. Our study reported on the increase of temperature of preparation, characterization, and calculation of band gap of FeS₂ pyrite. Our experiment demonstrated the effect of temperature of preparation on the favorable optical and electrical properties of FeS₂ pyrite. Our results confirmed that p-type FeS₂ pyrite is a good choice for fabricating solar cells. We also found the gap energy and sulfur-sulfur distance for samples with different temperatures of preparation, which were prepared by spray pyrolysis. We proved the correlation between growth parameters and the calculated band structure. The optical gap energy obtained in this work is in good agreement with the gap energy calculated by the LMTO-ASA method.

Our findings proved a significant powerful dependency between gap energy and distance sulfur–sulfur. Moreover, we concluded that the excellent crystallinity, nanoparticles, and nanostructures of FeS₂ pyrite confirm a more efficient photovoltaic application.

Finally, it is important to note that the high-performing photovoltaic cells on ITO/ZnO/FeS₂/MoO₃/Au/Ag positively improved the quality of nanoparticles and nanostructures of FeS₂ pyrite.

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