Evaporated iron disulfide thin films with sulfurated annealing treatments

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FeS₂ thin films were grown on a glass substrate using a physical vapor deposition technique at room temperature. Subsequently, the thin films were annealed in two different atmospheres: vacuum and vacuum-sulfur. In the vacuum-sulfur atmosphere a graphite box was used as sulfur container and the films were sulfurated successfully at 200–350 °C. It was found that annealing in a vacuum-sulfur atmosphere was indispensable in order to obtain polycrystalline FeS₂ thin films. The polycrystalline nature and pure phase were determined by XRD and Raman techniques and the electrical properties by the Hall effect. Using the sulfurating technique, the n-type semiconductor was prepared at 200–350 °C and a p-type at 500 °C. The carrier concentrations were between 1.19 × 10¹⁹ and 2.1 × 10²⁰ cm⁻³. The mobility was 9.96–5.25 cm² V⁻¹ s⁻¹ and the resistivity was 6.31 × 10⁻² to 1.089 × 10⁻¹ Ω cm. The results obtained from EDS showed that the films prepared in the vacuum-sulfur atmosphere were close to stoichiometric and that the indirect band gap varied between 1.03 and 0.945 eV.

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1. Introduction

Elements in Group 16 of the periodic table (oxygen, sulfur, selenium, tellurium, and polonium) react with transition metals, which results in compounds called chalcogenides. Metal chalcogenides are a group of semiconductor materials that are currently being extensively studied for their properties and potential applications. Polonium is not economically viable and is also very harmful to human health (radioactive). Chalcogen sulfides have recently drawn attention because of their allotropic properties. They can be formed from binary to quaternary compounds with relative ease. In addition, they are abundant in the earth crust and generate non-toxic compounds. Recently, iron disulfide or iron pyrite (FeS₂) has been used as the principal semiconductor material for photovoltaic applications among 23 inorganic photovoltaic single junction materials due to its low cost and wide availability [1].

The iron sulfide system (Fe₅S₈) is known to have seven different stable phases: (1) trolite (FeS) with a hexagonal phase and P63/mmc space group; (2) mackinawite (FeS) with a hexagonal phase and P4/mmm space group; (3) greigite (Fe₃S₄) with a cubic phase and Fd-3m space group; (4) smythite (Fe₄S₅) with a trigonal phase and R3(-)m space group; (5) pyrrhotite (Fe₁₋ₓS) with a primitive hexagonal phase and four phases: two (Fe₅S₈) one trigonal, P3(1) 21 and another monoclinic-beta, F2/d. In addition, two are FeS with a hexagonal phase and both with P6(3)/mmc space group; (6) marcasite (Fe₅S₈) with orthorhombic phase and Pnmm space group; and (7) pyrite (FeS₂) with a cubic phase and Pna-3 space group. The most studied are the marcasite and pyrite phases. In nature, as minerals, pyrite and marcasite are the most prevalent iron sulfide compounds. Marcasite is present in minerals of pyrite as an impurity phase. It is less stable than pyrite, and it oxidizes frequently, freeing sulfur, which forms sulfhydric acid in the presence of humidity and continued oxidation of the compound [2]. This phenomenon might explain why pyrite used in thin films in solar cells does not exceed 3% efficiency. This could be due to phase impurities and point defects, among other optical properties (marcasite E₈ =0.3 eV) [3].

The following properties are known about iron disulfide or pyrite: optical band gap (Eₘ =0.95–1.7 eV), absorption coefficient α ≈ 5 × 10⁴ cm⁻¹, high current mobility ≈ 120–360 cm² V⁻¹ s⁻¹, carrier concentration 10¹⁴–10²⁰ cm⁻³, and electrical resistivity 0.1–1.9 Ω cm [4–20]. Iron disulfide thin films have been grown using a large number of chemistry and physics techniques, including chemical bath deposition, sol-gel, electrophoretic deposition, electrodeposition spray pyrolysis, one pot hydrothermal synthesis, molecular ink, metal organic chemical vapor deposition [7–10], sulfurization of metallic iron or iron oxide films, sputtering,
pulsed electron ablation, sequential evaporation, and thermal evaporation [17–20]. The latter is a rapid and economical technique used to obtain iron thin films of high quality. Currently, the challenge remains to obtain high quality pyrite thin films, produced using simple processing, which eliminates the intrinsic defects of the material itself, as mentioned above. The aim of this study was to obtain iron sulfide thin films, grown by a rapid thermal evaporation technique and subsequent annealing in two different atmospheres: vacuum and sulfurization. By varying a closed-space sublimation technique, iron sulfide films in phase pyrite with good optical, electrical, and structural properties were obtained at relatively low sulfurizing temperatures (250–350 °C) over short time periods (40 min), and using small amounts of sulfur (20 mg).

2. Experimental methods

The thin films of iron disulfide (ID) were deposited on corning glass substrates by using evaporation technique from Iron (II) sulfide powder (99.99%). The ID substrate films were grown at room temperature under a vacuum of 5x10⁻⁵ mbar. The distance between source and substrate was kept constant, at 16 cm. The current applied to the source was 200 Amperes, the source-substrate and current were optimized with calibration graphs, varying the distance of 5–25 cm and currents to 150–230 A in steps of 10 A. This was done in order to obtain films adherent to the substrate, homogeneous and free of pinholes. The coated slides were annealed in two atmospheres (vacuum and sulfurizing) at different temperatures (200 °C to 350 °C in 50 °C increments) every 40 min. The sulfurized process was performed as follows: Close Space Sublimation equipment (CSS) was utilized with modifications. A graphite box was fabricated with 3.5:8.5:10 dimensions (width:length:height). The sulfur powder was placed inside of the box and current were optimized with calibration graphs, varying the distance of 5–25 cm and currents to 150–230 A in steps of 10 A. The temperature was controlled by solid state relays and commercial drivers assembled in the laboratory. The control was performed by independent k type thermocouples at lower and upper source. The thermocouples were calibrated under the AMS 2750E, BAC 5621K standards. Measurement results were traceable to standards maintained at the NIST. Test methods are per ASTM E220-13, ASTM E230/E230M-12, through certification report P.O. # 3146.

The characterizations of the ID thin films were carried out by ultraviolet-visible (UV-vis) spectra and the films were measured on a Genesys 10S spectrophotometer. The XRD measurements were performed with a RIGAKU Ultima IV diffractometer with a copper wavelength of (1.54 Å). Elemental analysis was conducted on a QUANTAX EDS Bruker system. For the SEM images a NanoSEM, FEI microscope. For the Raman measurements a Dilor Labram II microRaman Bruker system. The thickness was measured on a Sloan Dektak II profilometer, AFM Dimension on a 3100 Nanoscope VEECO.

3. Results and discussion

The thickness of the films without the annealing treatment was 1812 ± 5 nm. The average thicknesses of the films with the annealing treatment in the vacuum atmosphere were 1181.5 ± 3, 944 ± 1, 925.7 ± 4, and 880 ± 3 nm for 200, 250, 300, and 350 °C annealing temperatures, respectively. In the vacuum-sulfurized atmosphere, the annealing treatment gave average film thicknesses of 1707 ± 2, 1451 ± 6, 879.5 ± 3, and 815.7 ± 3 nm for 200, 250, 300, and 350 °C annealing temperatures, respectively. Fig. 1 shows the X-ray diffraction (XRD) patterns of the films: Fig. 1a shows the results of annealed films at different temperatures in vacuo, and Fig. 1b shows the results of annealing in a sulfurizing atmosphere. At the bottom of each figure is located the diffraction pattern corresponding to the pyrite with cubic structure and spatial group Pa-3(205) PDF#42-1340 pattern.

The ID films with annealing in the vacuum atmosphere (Fig. 1a) at 200 and 250 °C did not show peaks that could be associated with any crystalline system. Following annealing at 300 and 350 °C

Fig. 1. XRD patterns of iron disulfide annealed in (a) vacuum and (b) vacuum-sulfurized atmospheres at different temperatures.
the films showed small peaks that could be associated with the pyrite phase. At higher temperatures (> 350 ºC) the films presented holes and were very thin (≈ 220 nm for 400 ºC). For the films obtained by annealing in the vacuum-sulfurized atmosphere at 250–350 ºC, diffraction peaks appeared at 2θ = 28.55, 33.11, 37.14, 40.82, 47.64, 56.37, and 61.56 degrees, which correspond to (111), (200), (210), (211), (220), (311), and (222) planes, respectively. This correlates well with the pyrite PDF#42-1340 pattern. In the vacuum-sulfurizing atmosphere at 250 ºC the pyrite phase began to form at a relatively low temperature. Others authors have also observed the improvement in the crystalline properties of thin films with annealing [21–22].

From the XRD results of the ID films annealed in sulfurizing atmospheres, the crystal size and the strain (η) were calculated from the full width at half maximum (FWHM) and using the Williamson–Hall equation. Fig. 2a shows the results of crystal size and Fig. 2b shows the results for the strain, which both increased with temperature, varying between 46 and 73 nm and between 0.010 and 0.034, respectively. This could be due to a stage or plateau that diminished the strain, thereby improving the crystallinity. Microstrain increases with increasing grain size. This means that the imperfection in the ID compound increased, while
the grain size increased from 46 to 73 nm, and for the temperature range 300 to 350 °C the dislocation density remained almost unchanged. This stress was related to defects in the films. The tensile stress could be a result of sulfur vacancies that are very common in chalcogenide materials [23–26].

In Figs. 3a and b the results of Raman spectroscopy at the two different annealing treatments are shown for vacuum and vacuum-sulfur atmospheres, respectively. Three peaks can be seen at 333.99, 372.579, and 429.413 cm⁻¹, which correspond to pyrite in its cubic phase. The pyrite system presents six vibrational modes in Raman spectroscopy: Γ = A₃ + E₃ + 3T₃ + 2A₁ + 2E₂ + 3T₂. The T₃ modes are active in the infrared, while A₁g, E₂g, and T₂g are all active in the Raman spectrum of the first order. The A₁g, E₂g, and T₂g modes are optically inactive. The mode at 333.99 cm⁻¹ (E₂g) corresponds to the vibration of S₂, 372.579 cm⁻¹ (A₁g) is for the stretch of the dimer S–S, and 429.413 cm⁻¹ corresponds to the T₂g mode, which results in the release, stretch, or the combination of both modes.

Additionally, in Fig. 3 the films with thermal annealing in the vacuum-sulfur atmosphere had better crystalline quality. The pyrite film with thermal annealing at 350 °C had more defined peaks that showed more intensely. These peaks correspond to the vibrational modes of E₂g and A₁g. There is no evidence of any mixture of phases. Otherwise, the Raman spectra of vacuum and vacuum-sulfur annealing treatments showed no sign of marcasite (323 cm⁻¹). These results are in accordance with the XRD results. The Raman spectra closely match the vibrational modes corresponding to pyrite, except for the peak marked with an asterisk (*) at 486 cm⁻¹, which suggests the presence of polysulfides. Elemental sulfur has intense Raman active modes at 400–500 cm⁻¹ and minor vibrational modes at 200–300 cm⁻¹ [27–29]. Fig. 3a and b show that peaks do not appear below 300 cm⁻¹, which confirms that there is no elemental sulfur.

Figs. 4a and b show 3D topographical results from atomic force microscopy (AFM) measurements for annealing in vacuum and vacuum-sulfur atmospheres, respectively. The measured area was 800 × 800 nm and 1000 × 1000 nm for annealing in vacuum and vacuum-sulfur atmospheres, respectively. Both the aggregate size and the roughness increased with increase in temperature. The aggregates have a spherical shape. The smooth part at 200 °C (both atmospheres) corresponds to a sulfur concentration of 64% on the films (from energy-dispersive x-ray spectroscopy (EDS)). For the films annealed in a vacuum atmosphere, there was an increase in the roughness as the annealing temperature increased. This increase could be attributed to loss of sulfur as the heat temperature treatment increased (64–32 at%), which is performed by EDS analysis. In contrast to the films annealed in the vacuum-sulfur atmosphere, the size, shape, and roughness of the aggregate were all different. Therefore the aggregate could be considered a sulfide-content product, which increases as the temperature of sulfurizing increases (64.5–67.3 at%) when performed using EDS analysis.

Fig. 5 shows scanning electron microscopy (SEM) images of the ID thin films annealed in a vacuum-sulfur atmosphere at (a) 200, (b) 250, (c) 300, and (d) 350 °C with both the surface and cross sections shown. For all of the samples, the grains are small and increase in size as a function of annealing temperature, except for the ID thin film with thermal treatment at 350 °C which is seen as forming new grains, framed more densely, and with columnar growth. For temperatures below 350 °C the growth is non-lamellar. It was confirmed that the aggregate was spherical, and the sulfidation temperature favored the growth of dense, uniform ID pyrite films free of pinholes. This was confirmed by XRD, Raman, and EDS. All of the films were uniform and free of holes.

Fig. 6 shows the results of EDS for ID films annealed in two different atmospheres, Fig. 6a in vacuum and Fig. 6b in vacuum-sulfur atmospheres. The EDS results for the vacuum atmosphere showed that the sulfur content varied between 64% and 32% in atomic percentage and decreased as the temperature of thermal annealing increased. The [S]/[Fe] ratio gradually increased with increasing temperature of the thermal treatment. It ranged from 1.8 to 0.47 for 200 °C and 350 °C, respectively. Otherwise, the deviation of the films from their stoichiometry (losing sulfur) increased as the temperature of thermal annealing in the vacuum atmosphere increased. For the EDS results for the vacuum-sulfur atmosphere (Fig. 6b), the sulfur content varied between 64.5% and 67.2% in atomic percentage and increased as the temperature of thermal annealing increased. The [S]/[Fe] ratio increased gradually with increasing temperature of the thermal treatment. The ratios were 1.82, 1.94, 1.99, and 2.0 for 200, 250, 300, and 350 °C, respectively. On the other hand, the films close to their stoichiometry (not losing sulfur) increased the temperature of thermal annealing in the vacuum-sulfur atmosphere. For a thermal annealing treatment at 300 and 350 °C in a vacuum-sulfur atmosphere, the ID thin films were in their stoichiometric ratios of 1.99 and 2, respectively.

Fig. 7 shows the results for the electronic properties of the films
obtained from experiments on the Hall effect. Fig. 7a shows the carrier concentration \( (n/cm^3) \), Fig. 7b the mobility \( (\mu/cm^2 V^{-1} s^{-1}) \), and Fig. 7c the resistivity \( (\rho/\Omega m) \). All of the ID thin films showed p-type conductivity. The ID thin films with annealed in either a vacuum (squares) or vacuum-sulfur (spheres) atmosphere. The carrier concentration in the vacuum atmosphere decreased as the annealing temperature increased \( (3.011 \times 10^{20} \text{ to } 6.28 \times 10^{12} \text{ cm}^{-3}) \); the decrease in the number of carriers could be associated with loss of sulfur as the thermal annealing temperature increased, forming sulfur vacancies as point defects in the lattice. The films annealed in a vacuum-sulfur atmosphere demonstrated differing properties, and the carrier concentration increasing as the temperature increased \( (5.92 \times 10^{19} \text{ to } 3.3 \times 10^{20} \text{ cm}^{-3}) \).

The mobility in the vacuum atmosphere decreased as the annealing temperature increased \( (6.44 \text{ to } 0.21 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}) \). This trend was not maintained at 350 °C where the mobility increased slightly \( (0.4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}) \). The mobility in the vacuum-sulfur atmosphere was also observed to have the same trend in the annealing treatment, but the mobility values for the first two temperatures were lower \( (4.46 \text{ and } 2.91 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}) \), respectively and for the last two temperatures were higher \( (0.73 \text{ and } 2.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}) \), respectively. The resistivity values in the vacuum atmosphere increased as the annealing temperature increased \( (7.97 \times 10^{-3} \text{ to } 3.36 \times 10^5 \text{ } \Omega \text{ cm}) \). For ID thin films annealed in the vacuum-sulfur atmosphere, the resistivity values increased as the temperature increased from 200 to 300 °C \( (1.5 \times 10^{-2} \text{ to } 1.13 \times 10^{-2} \text{ } \Omega \text{ cm}) \), but for 250 °C the resistivity increased slightly \( (1.8 \times 10^{-2} \text{ } \Omega \text{ cm}) \). The ID thin films annealed in a vacuum-sulfur atmosphere maintained a value of resistivity close to \( 10^{-2} \text{ } \Omega \text{ cm} \). Samples annealed in a vacuum-sulfur atmosphere at 500 and 550 °C have n-type conductivity and a carrier concentration \( (1.19 \times 10^{20} \text{ and } 2.01 \times 10^{20} \text{ cm}^{-3}) \), respectively, mobility of \( 9.96 \text{ and } 5.25 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \), respectively, and resistivity of \( 6.314 \times 10^{-2} \text{ and } 1.089 \times 10^{-2} \text{ } \Omega \text{ cm} \), respectively.

For samples thermally treated in a vacuum, the carrier concentration lapses by seven orders of magnitude. This may be due to an increase in sulfur vacancies that is favored by the temperature and the atmosphere in the thermal treatment. The mobility decreases by two orders of magnitude for both 300 and 350 °C. This is due to increase in the resistivity. It is well known that mobility is inversely proportional to resistivity and also depends on the ionized impurities present and lattice scattering processes. For the vacuum-sulfur atmosphere, the carrier concentration...

Fig. 5. SEM images of iron disulfide annealed in a vacuum-sulfur atmosphere at different temperatures, surfaces, and cross sections.

Fig. 6. EDS results of iron disulfide annealed in (a) vacuum and (b) vacuum-sulfur atmospheres at different temperatures.
increased as a function of annealing temperature, the mobility decreased at 300 ºC, causing a reduction in agglomerate grains, and the resistivity remained almost constant due to the higher quality of polycrystalline films.

The band gap results were obtained by absorbance measurements of the thin films with the two different thermal annealing experiments. The indirect band gap was calculated from the plots of $(\alpha h \nu)^{1/2}$ as a function of $(h \nu)$. Subsequently, the linear portion was extrapolated on the graph and the intercept with the energy axis $(\alpha h \nu)^{1/2} = 0$ was the band gap. Fig. 8 shows the indirect band gap values as a function of annealing temperature in the two different atmospheres, vacuum (black squares) and vacuum-sulfur (black spheres).

For the samples annealed in the vacuum-sulfur atmosphere, the band gap increased as the annealing temperature increased (0.98 to 1.025 eV). On the other hand, for the samples annealed in the vacuum atmosphere, the band gap decreased as the annealing temperature increased (1.03–0.945 eV). The change in the band gap with carrier concentration is attributed to the Moss-Burstein effect [23]. In related studies, similar results have been obtained at different annealing temperatures [18,30–32].

Fig. 9 shows room temperature photoluminescence spectra of the films thermally treated in a vacuum-sulfur atmosphere, where the annealing temperature was varied between 200 and 350 ºC in 50 ºC increments, and at 500 ºC. All of the samples presented photoluminescence at room temperature at energies lower than 1.3 eV and all of the samples showed three peaks at 1.82, 2.35, and 2.96 eV. The peaks shifted to higher energies with increase in annealing temperature. The shift of a photoluminescence peak is habitually provoked by band structure deformation from lattice distortion [33,34]. The FWHM decreased with increase in the annealing temperature, which is shown in Fig. 9: as the temperature...
of sulfurization increased, the peaks shifted to higher energies. This is consistent with the band gap results, which increased as the sulfurization temperature increased. The intensity of photoluminescence increased as the sulfurization temperature increased due to an improvement in the crystallinity of the ID films caused by the effect of the temperature change.

4. Conclusions

FeS$_2$ thin films were grown on glass substrates using a physical vapor deposition technique and were subsequently annealed in two different atmospheres, vacuum and vacuum-sulfur. It was found that heat treatment was indispensable in a vacuum-sulfur atmosphere in order to obtain FeS$_2$. The vacuum-sulfur annealed films were found to be pure phase pyrite, within the detection limit of the instruments at low temperature (250–350 °C). Additionally, the films were polycrystalline in nature, as determined by XRD and Raman spectroscopy, and the crystal size varied between 46 and 73 nm. EDS confirmed that the [Fe]/[S] ratio approached that of the stoichiometric compound. The carrier concentration ranged from $1.19 \times 10^{17}$ to $2.1 \times 10^{20}$ cm$^{-3}$. The mobility was $9.96–5.25$ cm$^2$ V$^{-1}$ s$^{-1}$ and the resistivity varied between $6.31 \times 10^{-2}$ and $1.089 \times 10^{-2}$ Ω cm. In addition, the indirect band gap was found to be between 1.03 and 0.945 eV.

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