

Evaporated iron disulfide thin films with sulfurated annealing treatments



D. Santos-Cruz^a, S.A. Mayén-Hernández^a, F. de Moure-Flores^a, J.S. Arias-Cerón^b,
J. Santos-Cruz^{a,*}

^a Facultad de Química, Materiales-Energía, Universidad Autónoma de Querétaro, Querétaro 76010, México

^b Departamento de Ingeniería Eléctrica, Sección de Estado Sólido, CINVESTAV-IPN, Apdo. Postal 14-740, México D.F. 07360, México

ARTICLE INFO

Article history:

Received 5 June 2015

Received in revised form

13 November 2015

Accepted 14 November 2015

Available online 25 November 2015

Keywords:

Thin film

Optical

Structural

Electrical properties

ABSTRACT

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 1.19×10^{20} and $2.1 \times 10^{20} \text{ cm}^{-3}$. The mobility was $9.96\text{--}5.25 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and the resistivity was 6.31×10^{-2} to $1.089 \times 10^{-2} \Omega \text{ cm}$. 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 (Fe_xS_y) is known to have seven different stable phases: (1) troilite (FeS) with a hexagonal phase and P63/mmc space group; (2) mackinawite (FeS) with a hexagonal phase and P4/nmm space group; (3) greigite (Fe₃S₄) with a cubic phase and Fd-3m space group; (4) smythite (Fe₃S₄) with a trigonal phase

and R3(-)m space group; (5) pyrrhotite (Fe_(1-x)S) with a primitive hexagonal phase and four phases: two (Fe₇S₈) 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 (FeS₂) with orthorhombic phase and Pnmm space group; and (7) pyrite (FeS₂) with a cubic phase and Pa-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 sulfhydrylic 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 $E_g=0.3 \text{ eV}$) [3].

The following properties are known about iron disulfide or pyrite: optical band gap ($E_g=0.95\text{--}1.7 \text{ eV}$), absorption coefficient $\alpha \approx 5 \times 10^5 \text{ cm}^{-1}$, high current mobility $\approx 120\text{--}360 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, carrier concentration $10^{14}\text{--}10^{20} \text{ cm}^{-3}$, and electrical resistivity $0.1\text{--}1.9 \Omega \text{ cm}$ [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 [7–16], sulfurization of metallic iron or iron oxide films, sputtering,

* Corresponding author.

E-mail address: jsantos@uaq.edu.mx (J. Santos-Cruz).

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 5×10^{-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 graphite box (20 mg). FeS₂ thin film were mounted on the open top of the box. The substrate was in contact with the upper source that supplied the temperature to the substrate. The temperature in the lower source was kept constant at 85 ± 2 °C to ensure that the sulfur powder remained in the gas phase throughout the entire heat treatment. The substrate temperature was increased from

200–350 °C in increments of 50 °C. The working vacuum chamber heat treatment was 5.4×10^{-4} Torr. 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 Nova NanoSEM, FEI microscope. For the Raman measurements a Dilor Labram II microRaman was employed. 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 1118.5 ± 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

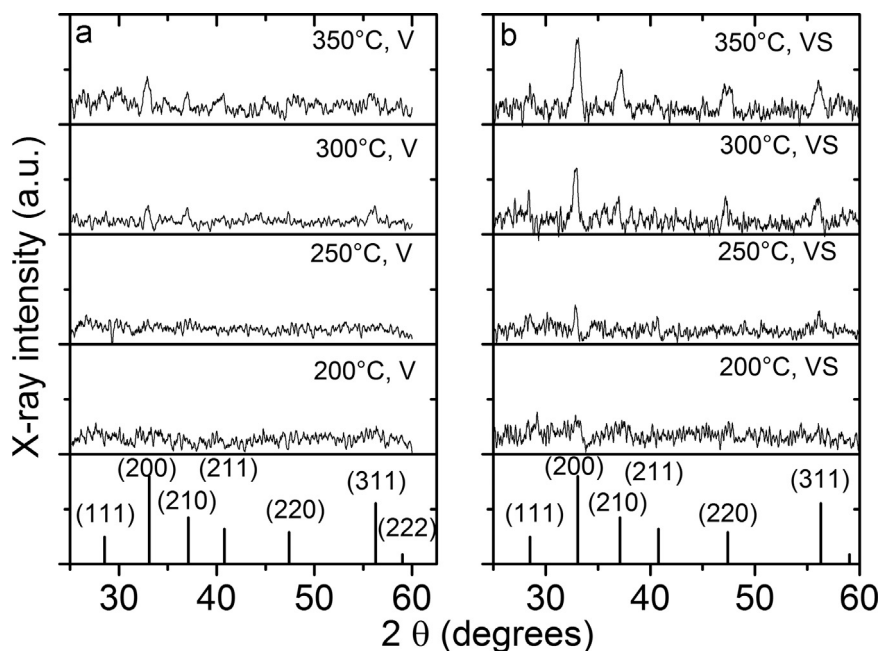


Fig. 1. XRD patterns of iron disulfide annealed in (a) vacuum and (b) vacuum-sulfurized atmospheres at different temperatures.

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