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Investigating the effect of pH on the structural and optoelectronic properties of iron disulfide (FeS_2) nanostructures synthesized by the electrodeposition method

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Extended Abstract

Introduction

Iron disulfide (FeS_2), commonly known as pyrite, is a promising semiconductor for photovoltaic and optoelectronic applications due to the abundance and low cost of its constituent elements, suitable chemical stability, and favorable optical properties. In particular, FeS_2 exhibits a high optical absorption coefficient in the visible and near-infrared regions, making it a potentially attractive material for solar cells and optical detectors. However, the practical performance of FeS_2-based devices is strongly influenced by structural defects, secondary phases, crystallinity, and the synthesis conditions. Pyrite and marcasite are the two principal polymorphs of FeS_2, and their formation is highly dependent on parameters such as temperature, chemical composition, and the chemical environment during synthesis.

Among the available fabrication techniques, electrodeposition is an attractive approach for producing FeS_2 thin films because of its simplicity, low cost, scalability, and ability to control the growth conditions. Parameters such as deposition potential, deposition time, bath composition, and particularly the pH of the electrolyte can significantly influence the chemical composition, crystalline structure, morphology, and electrical and optical properties of the deposited films. Although several studies have investigated FeS_2 thin films synthesized through solution-based methods, systematic investigations into the effect of the electrodeposition bath pH on the structural and optoelectronic characteristics of FeS_2 thin films remain limited. Therefore, the objective of the present study was to investigate the effect of electrolyte pH on the structural, morphological, optical, and electrical properties of FeS_2 nanostructured thin films fabricated by electrodeposition. The films were deposited at different pH values and subsequently sulfurized to promote the formation and stabilization of the pyrite phase. The influence of pH on crystallinity, surface morphology, optical emission, carrier concentration, and flat-band potential was systematically evaluated.

2. Materials and Methods

FeS_2 thin films were deposited on fluorine-doped tin oxide (FTO) substrates using a three-electrode electrochemical cell consisting of an FTO working electrode, a platinum counter electrode, and a saturated calomel reference electrode. To investigate the influence of pH, three aqueous electrolyte solutions were prepared under otherwise identical conditions. The electrolyte contained 50 mM ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) and 100 mM sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$) dissolved in 100 mL of deionized water. The initial pH of the solution was 4, while the other two solutions were adjusted to pH values of 3 and 5 using sulfuric acid and sodium hydroxide. Prior

to deposition, the FTO substrates were carefully cleaned through a multistep ultrasonic cleaning procedure. Electrodeposition was performed at room temperature for 15 min using an applied potential of −1.65 V between the reference and working electrodes. After deposition, the films were washed with ethanol and dried under ambient conditions. To obtain the desired FeS_2 phase, the deposited films were sulfurized in a horizontal tube furnace under vacuum in the presence of sulfur powder at 250 °C for 1 h and at a pressure of 10 Torr. The samples prepared at pH values of 3, 4, and 5 were designated P(3), P(4), and P(5), respectively. The structural and physical characteristics of the fabricated films were investigated using several complementary characterization techniques. X-ray diffraction (XRD) was employed to determine the crystalline structure and phase composition. Field-emission scanning electron microscopy (FESEM) was used to examine surface morphology, while energy-dispersive X-ray spectroscopy (EDX) was applied to determine the elemental composition. Raman spectroscopy was used to evaluate phase purity and crystalline quality, and photoluminescence (PL) spectroscopy was employed to investigate the optical characteristics and estimate the bandgap energy. The electrical properties were evaluated using Mott–Schottky analysis to determine the conductivity type, carrier concentration, and flat-band potential.

3. Results and Discussion

The XRD results confirmed that all synthesized samples exhibited the cubic pyrite structure of FeS_2 after sulfurization. No significant impurity phases associated with other sulfides, iron oxides, or tin compounds were detected, indicating a high degree of phase purity. A clear dependence of the diffraction characteristics on pH was observed. Reducing the electrolyte pH from 5 to 3 increased the intensity of the diffraction peaks and reduced the interplanar spacing and peak width. The enhancement in diffraction intensity at lower pH was attributed to the increased concentration of hydrogen ions in the acidic electrolyte, which promotes ion mobility and improves crystallization. The acidic environment can also remove amorphous surface layers and oxide impurities, thereby reducing lattice defects and promoting crystal growth. The crystallite size and lattice strain were further evaluated using the Scherrer and Williamson–Hall approaches. Both methods demonstrated that decreasing the pH resulted in an increase in crystallite size accompanied by a reduction in crystalline strain. According to the Scherrer analysis, the crystallite sizes were approximately 66.85 nm, 54.11 nm, and 43.37 nm for P(3), P(4), and P(5), respectively. The corresponding Williamson–Hall results also confirmed the improvement in crystallinity at lower pH. These findings demonstrate that a more acidic deposition environment favors the formation of larger and more structurally ordered FeS_2 crystallites.

FESEM observations revealed substantial changes in the surface morphology as a function of pH. The P(3) sample exhibited relatively larger particles, a denser structure, layered surface features, and clearly defined grain boundaries, indicating enhanced particle growth and structural cohesion. At pH 4, the particles were relatively spherical and nanoscale, with a relatively uniform distribution, although some aggregation and surface irregularities were observed. In contrast, the P(5) sample displayed a heterogeneous morphology with a broad particle-size distribution, including both fine and coarse particles, together with greater porosity and reduced surface uniformity. Therefore, the pH of the electrolyte plays an important role in controlling particle growth, aggregation, surface uniformity, and microstructural characteristics. EDX analysis confirmed the presence of Fe and S in all samples without detectable additional elements, further supporting the high purity of the deposited films. The atomic Fe ratios for P(3), P(4), and P(5) were approximately 2.32, 2.01, and 2.39, respectively. The reduction in pH decreased the sulfur-to-iron ratio and caused the chemical composition of the P(3) sample to approach the ideal stoichiometric Fe ratio of 1:2. This result indicates that the more acidic deposition condition is favorable for obtaining a composition closer to stoichiometric FeS_2 .

Raman spectroscopy further confirmed the formation and phase purity of pyrite FeS_2 . The main Raman bands located at approximately 335 and 368 cm^{-1} were assigned to the characteristic Eg bending mode and Ag symmetric stretching mode of the S–S bonds, respectively. No Raman peaks associated with marcasite, troilite, iron oxides, or other sulfide phases were observed. Moreover, reducing the pH from 5 to 3 increased the intensity of the characteristic Raman peaks, indicating improved crystallinity and a reduction in lattice defects. The Raman results were therefore consistent with the XRD observations and confirmed that the lower-pH environment promotes higher structural quality in the synthesized films. The optical properties were investigated through PL spectroscopy. Emission bands in the 400–570 nm wavelength range were associated with defect-related energy levels within the pyrite structure. As the pH decreased, the intensity of these defect-related emission bands decreased and a blue shift toward shorter wavelengths was observed. The reduction in emission intensity indicates a decrease in structural defect centers and, consequently, a reduction in radiative recombination processes. All samples also exhibited an emission band near 766 nm, which

was attributed to near-band-edge emission. The intensity of this band decreased with decreasing pH, suggesting a reduction in carrier recombination and an increase in carrier density. The bandgap energy estimated from PL measurements was approximately 1.62 eV for the FeS_2 nanostructures. The electrical behavior of the FeS_2 films was evaluated by Mott–Schottky analysis using Au/FeS_2 /FTO structures. The negative slopes of the Mott–Schottky plots demonstrated that all samples exhibited p-type semiconductor behavior, with holes acting as the majority carriers. The results showed that decreasing the electrolyte pH increased both the carrier concentration and flat-band potential. The highest values were obtained for the P(3) sample, indicating improved charge separation and electrical characteristics under the most acidic deposition condition. The measured carrier concentrations for P(3), P(4), and P(5) were approximately 58.75×10^{12}, 24.39×10^{12}, and 5.82×10^{12} cm^{-3}, respectively, while the corresponding flat-band potentials were approximately 0.19, 0.15, and 0.10 V.

4. Conclusions

In this study, FeS_2 nanostructured thin films were successfully fabricated on FTO substrates by an electrodeposition process using aqueous, low-cost, and relatively environmentally friendly precursors. The influence of electrolyte pH on the structural, morphological, optical, and electrical properties of the deposited films was systematically investigated. XRD and Raman analyses confirmed the formation of the cubic pyrite phase and the absence of significant secondary phases. The results demonstrated that decreasing the electrolyte pH from 5 to 3 significantly improved the crystalline quality of the films. The crystallite size increased, while the lattice strain decreased, indicating a more ordered crystal structure. FESEM observations also confirmed that pH strongly affects particle size, aggregation, porosity, and surface uniformity. The P(3) sample exhibited a denser and more coherent morphology compared with the samples synthesized at higher pH values. Furthermore, EDX analysis showed that the composition of the P(3) sample was closer to the ideal Fe stoichiometric ratio of FeS_2 .

The optical and electrical results further demonstrated the beneficial effect of reducing pH. The decrease in defect-related PL intensity indicated a reduction in structural defects and carrier recombination, while the bandgap energy was determined to be approximately 1.62 eV. Mott–Schottky measurements confirmed p-type conductivity for all samples, and the carrier concentration increased significantly with decreasing pH, reaching approximately 58.75×10^{12} cm^{-3} for the P(3) sample. Overall, the findings indicate that controlling the pH of the electrodeposition bath provides an effective means of tailoring the structural and optoelectronic properties of FeS_2 nanostructures. The combination of low-cost electrodeposition, improved crystallinity, favorable optical absorption, p-type conductivity, and enhanced carrier concentration demonstrates the potential of these FeS_2 thin films for photovoltaic and high-performance optoelectronic applications.

Keywords: FeS_2 nanostructures, Pyrite, Electrodeposition, Mott-Schottky analysis, Optoelectronic properties, Flat band voltage.

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