Tin Sulfide Nanoparticles as a p-Type Semiconductor Material: Synthesis and Characterization

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Abstract

In this paper, the synthesis and characterization of tin sulfide as a p-type semiconductor material are reported. The low-cost, straightforward uses of transparent conductive tin sulfide technique of chemical bath deposition. The pH levels (7, 8, 9, and 10) were changed while maintaining a fixed bath temperature to create the tin sulfide nanoparticles. XRD, FTIR, and UV-visible have all been used to determine the structural and optical characteristics of tin sulfide nanoparticles in this study. Created via chemical bath deposition at various pH values to examine how pH affects the characteristics of the nanoparticles. Tin Sulfide's structural analysis and crystalline size are revealed by its X-ray diffraction pattern, and both are shown to be affected by changes in pH. Correspondingly, for pH 7, pH 8, pH 9, and pH 10. A Tauc plot was used to determine the SnS nanoparticles' optical bandgap energies. From pH 7 to pH 10, it was noticed that the size of the SnS nanoparticle crystallite decreased. It was shown that the quantum confinement effect causes the band gap energy of SnS nanoparticles to grow when crystallite sizes decrease. Sulfur (S) and tin (Sn) atoms' dominating bond stretching is confirmed by FTIR spectra. The SnS nanoparticles generated with enhanced optical characteristics might be employed as an absorber layer in the development of SnS-based heterojunction solar cells, according to optical characterization, which demonstrates that the direct energy band gap (Eg), which is seen to rise with increasing pH value, is increasing with pH values.

Keywords: Band gap, Chemical bath deposition, Absorbance.

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Introduction

A variety of binary semiconductors, particularly those in the (iv-vi) groups of the periodic table, have been researched over the past 10 years because of their narrow energy gap and potential for usage in solar cells [1-2]. The (iv-vi) semiconductors have been proven to be very beneficial in solar cells and other far-IR-operating optoelectronic devices, such as thermoelectric transducers. Many attempts have been made by various researchers to measure the electrical and optical characteristics of SnS, SnSe, and SnTe thin films. Tin sulfide has narrow band-gap semiconductor characteristics and has been applied to numerous electronic gadgets [3-5]. Tin sulfide, which has various binary compounds such as SnS, Sn_2S3, Sn_3S_4, Sn_4S_5, and SnS_2 has sparked substantial attention due to its structural diversity. Tin monosulfide (SnS) and tin disulfide (SnS_2) are the most prominent of these compounds, attracting a lot of research due to their fascinating characteristics and prospective applications [6-7]. Because of its physical and chemical characteristics, SnS is a good contender for photovoltaic applications. SnS thin films have been grown using various deposition techniques, including vacuum techniques such as thermal evaporation [8], radio frequency (RF) sputtering [9], electron beam evaporation [10], chemical vapor deposition [11], atomic layer deposition [ALD] [12], and non-vacuum techniques such as chemical spray pyrolysis [13], successive ionic layer deposition [14], and chemical bath deposition (CBD) [15]. When compared to physical procedures, CBD as a non-vacuum technology is more straightforward and requires less energy. Material characteristics and growth rate can be regulated and varied using this process by modifying deposition parameters (temperature, pH, precursor concentration, and so on) [16, 17]. According to reports, chemical bath deposition (CBD) is a growing alternative technique. Due to its ease of use, low cost, and potential for capturing large-area films. When the ionic product exceeds the solubility product, a film begins to develop in CBD. To prevent superfluous perception, material loss during the deposition process, and

the emergence of an undesired secondary phase of tin sulfide, growth parameters must be optimized, such as deposition duration and solution concentration [18-19]. It is obvious that the methods described above for the creation of SnS thin films and nanomaterials have certain limitations. For instance, they need specialized equipment, hazardous chemicals, an organotin precursor, surfactants, or certain reaction conditions such as a high temperature and an atmosphere devoid of oxygen and water. Therefore, greater focus should be given to the creation of straightforward, affordable, and environmentally friendly SnS production techniques [7]. Tin sulfide (SnS) has received a lot of study attention recently in order to better understand its chemical, structural, electrical, and optical properties for use in optical devices. Light-emitting diodes (LED), optical switches, photovoltaic technology, and optical sensors are only a few examples of the applications [20-21]. This study examines the effects of the structural, electrical, and optical characteristics of tin sulfide thin films at a fixed bath temperature (70 °C) and a range of pH values (pH 7, pH 8, pH 9, and pH 10). The films were applied (by CBD) to glass substrates at a constant temperature of 70 °C and with various pH values (pH 7, pH 8, pH 9, and pH 10), which had an impact on the film's characteristics. Experimental characterization of the films, presentation, and discussion of the results [22].

Experimental

1. Chemicals

The chemicals used to synthesize the SnS nanoparticles such as Stannous Chloride ($SnCl_2.2H_2O$) and Thiourea $(NH_2)_2CS$) were used as precursor source of Sn and S, respectively and pH maintain used Sodium hydroxide (NaOH). All these chemicals were used without further purification. Used deionized water (DI) as solvents.

2. *Synthesis of SnS nanoparticle*

Chemical bath deposition was employed to create SnS nanoparticles. Keeping the other parameters (temperature and concentration) fixed while varying the pH values from 7 to 10. Two 100ml borosilicate beakers were utilized for the preparation, and they were rinsed in soapy water (at room temperature), acetone, and deionized (DI) water SnS nanoparticles were created by adding 40 ml of DI to 40 ml of Thiourea (0.25M) solution in a 100 ml beaker after 30 minutes of continuous magnetic stirring to create the solution. A homogeneous solution was created after 45 minutes of continuous, vigorous stirring of the solution. The solution was then given a color change with the addition of NaOH (1M), and the amount of the NaOH solution was varied from 6 to 9 ml to assess the impact of the various pH levels (7, 8, 9, and 10) on the SnS nanoparticles. After this solution was placed in a chemical bath for two hours, the bath solution was already prepared for deposition. The treatment was finished after two hours at a steady temperature of 70 °C. The solution was filtered through filter paper, and the nanoparticle was repeatedly rinsed with DI water to remove unreacted ions before being allowed to air dry for four days and then being collected for further characterization. [17].

Result and Discussion

1. Structural analysis

SnS nanoparticle X-ray diffraction pattern with a Chemical Bath Deposition duration of 2 hours (70 °C) with various pH values of 7, 8, 9, and 10. All samples were scanned in the range 10–70º with a scan speed of 2.5º/min. The crystal planes of (210), (400), (211), (401), (302), and (512) are shown to correlate to the specified diffraction peaks based on the SnS nanoparticles XRD pattern (Fig.1). In the finished product, only the unique XRD peaks of the hexagonal phase SnS (JCPDS card No. 65-2610) are discernible. There are two distinct peaks at 26.63º and 29.93º for all pH-values nanoparticles. Other, weaker peaks may be seen at 33.34º, 37.28º, 47.88º, 50.18º, and 57.62º [23].

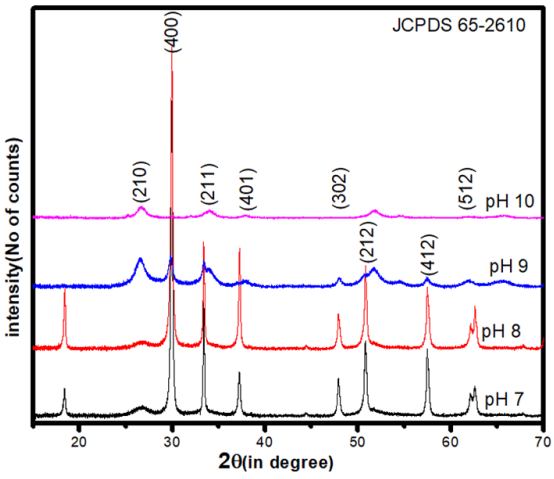

Figure 1: X-Ray diffraction patterns of SnS nanoparticles

The intensity of the diffraction peaks decreased as the pH value rose. This may be the result of the material's reduced crystallinity. A SnS nanoparticle's structure is stiffer at pH of 7 or 8 compared to pHs of 9 or 10. Using Scherrer's formula, we may calculate the size of the crystallites **(D)** along the main crystallographic direction (400).

$$D = \frac{0.9\lambda}{\beta Cos\theta}$$

Where K (0.9) is a determining factor, λ is the wavelength of the x-ray source that corresponds to the lines in copper, θ is the angle of Bragg reflection, and β is the breadth of the

diffraction peak at half maximum in radians [17,24-27].

Table 1: SnS nanoparticles prepared by CBD and their calculated crystalline size

Sample	pH	D(nm)
SnS 1	7	30.54
SnS 2	8	19.67
SnS 3	9	10.15
SnS 4	10	05.38

We can see that the crystallite size reduced as the pH rose. Tin Sulphide structural makeup and crystalline size are revealed by its X-ray diffraction pattern, and it is found that these properties get smaller as the pH rises. Crystallite sizes are 30.54 nm, 19.67 nm, 10.15 nm, and 05.38 nm for pH 7, pH 8, pH 9, and pH 10, respectively [28].

2. UV- Visible Spectroscopy

Spectroscopy in the ultraviolet-visible spectrum is either absorption or reflectance. In order to detect a molecule's absorbance in the 200–400 nm wavelength range, UV spectroscopy, a subset of absorbance spectroscopy, requires a chemical reaction. UV radiation is absorbed, which causes electrons to be excited into a higher energy state. It is used to research semiconductors, metals, and insulators that are present in bulk, thin-film, colloid, and nanostructured forms. As seen in Fig. 2, the SnS nanoparticles absorbance spectra between 400 and 800 nm were recorded as they were being deposited. After closely examining the spectra, it was discovered that there was a large absorption edge in the region of wavelengths from UV to visible.

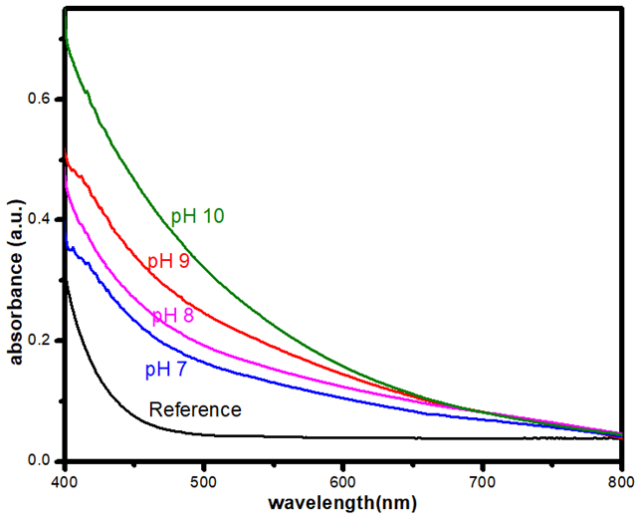

Figure 2: UV-Vis Absorption Spectra of SnS nanoparticles

The band gap of SnS nanoparticles at various pH values is determined using the tauc plot and the equation shown below.

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

For SnS nanoparticles produced at various pH values, see Fig. 3 for the Tauc-plot. As the pH increased, there was no discernible change in the band gap, although it varied depending on the sample. The band gap decreased as became more acidic [29].

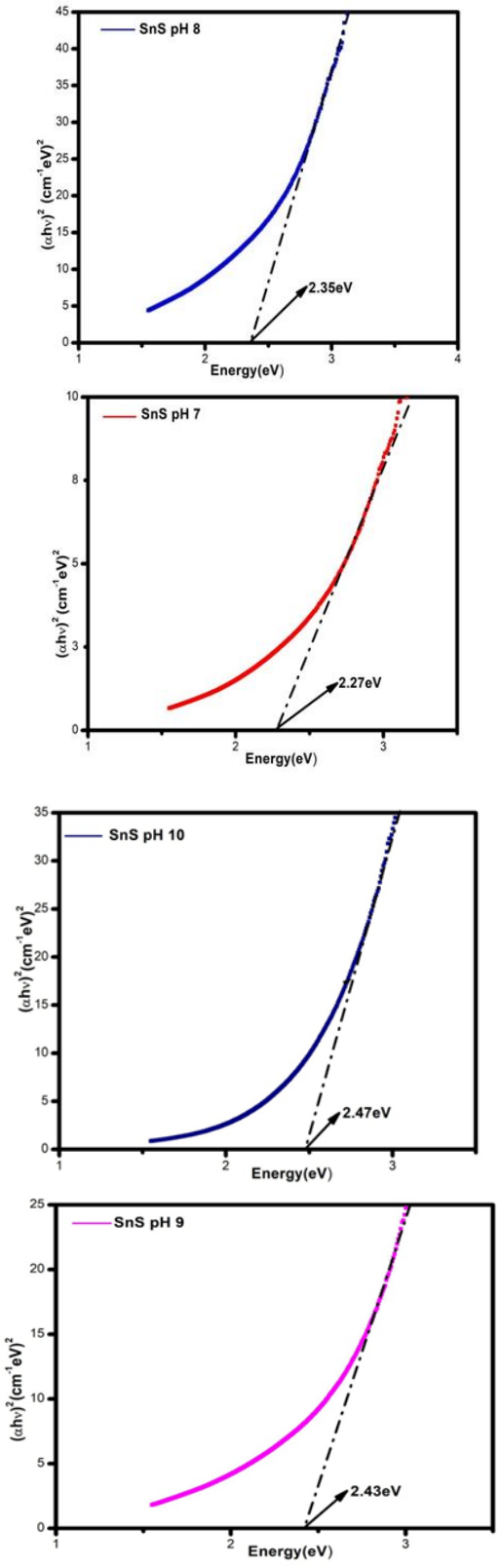

Figure 3: Tauc Plot of SnS nanoparticles synthesized at different pH value

Table 2: Bandgap of SnS nanoparticles with different pH value

Sample	pH	Bandgap (eV)
SnS 1	7	2.27
SnS 2	8	2.35
SnS 3	9	2.43
SnS 4	10	2.47

SnS nanoparticles' band gaps were 2.27eV, 2.35eV, 2.43eV, and 2.47eV at pH 7, 8, 9, and 10. With smaller crystal sizes, the band gap grew wider. By changing the band gap in semiconductors, new materials can be created for effective optoelectronic device applications [23-24, 30].

3 FTIR analysis

The infrared absorption peak is referred to as the fingerprint of the sample when it matches the vibrational frequencies between the bonds in the sample. A specific chemical bond in the sample vibrates at a specific frequency when light of various energies impacts it. This vibration is brought on by the vibrational energy of bonds. Figure 4 shows the FTIR spectrum of pure SnS nanocomposites produced using the chemical bath deposition approach. The results of the FTIR examination demonstrated the properties of high-purity nanoparticle production [22].

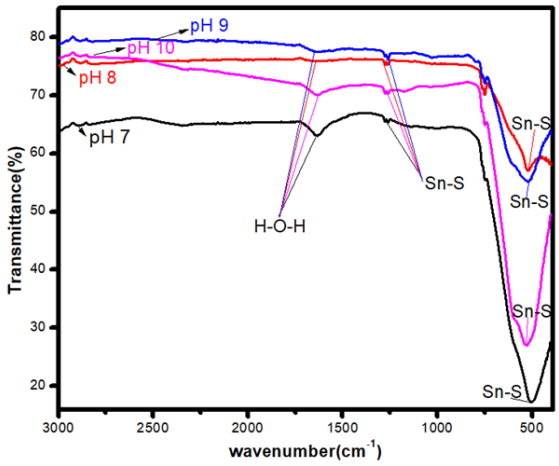

Figure 4: FTIR spectra of SnS nanoparticles at different pH value

Its observed band is at 1641 cm^{-1}, 1650 cm^{-1}, 1655 cm^{-1}, and 1610 $cm^{-1}$for pH 7, 8, 9, and 10. This band is connected to the stretching O-H vibrations of water adsorbed on nanoparticles. At pH levels 7, 8, 9, and 10 and at 500 cm^{-1}, 513 cm^{-1}, 521 cm^{-1}, and 531 cm^{-1}, respectively, distinct SnS 25 bands can be detected. Both the presence of water and the stretching vibration of SnS are blamed for these [31].

Conclusions

SnS nanoparticles were prepared by used chemical bath deposition method. The characteristics of the nanoparticles altered when the pH was adjusted to 7, 8, 9, or 10. The X-ray diffraction pattern displays the structural analysis and crystalline size of tin sulfide. The crystallite sizes for pH 7, pH 8, pH 9, and pH 10 are 30.54 nm, 19.67 nm, 10.15 nm, and 05.38 nm, respectively. We noticed that when pH increased, crystallite size and peak strength decreased, implying that crystallinity decreased as well. We calculated optical band gap values that were related to various pH values. A Tauc plot was used to calculate the optical bandgap energies of the SnS nanoparticles. 2.27 eV, 2.35 eV, 2.43 eV, and 2.47 eV were the results. The size of SnS nanoparticle crystallites decreased as pH values climbed from pH 7 to pH 10. Because of the quantum confinement effect, the band gap energy of SnS nanoparticles rises with smaller crystallite sizes.

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