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# The Effect of Annealing Temperature and Time on the Optical Properties of SnS Thin Films Prepared by Chemical Bath Deposition

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**Abstract**

*A research on the deposition and Characterization of SnS Thin Films by Chemical Bath Deposition Technique using Ammonia (NH3) as a complexing agent. Thin film of Tin (II) sulphide (SnS) is deposited onto glass substrates using chemical bath deposition (CBD) at room temperature for 3hours and 1hour. The optical properties of the film were measured using Double Beam UV- Spectrophotometer with serial number UV061514, Energy dispersive X-ray florescence (EDXRF) determines the compositions together with Rutherford Back Scattering (RBS) analysis revealed that thin films have percentage compositions of the elements (Sn/S, 50.1/49.9 for 3hours and Sn/S, 50.4/49.6 for 1hour) and their thicknesses are 100nm for 3hours and 150nm for 1hour. It was found that SnS thin film exhibits p-type conduction. Optical band gap values of direct and indirect transitions are estimated to be 1.98eV to 2.01eV and 1.82eV to 1.98eV for the two samples respectively. The other optical properties calculated from transmittance using appropriate equations are absorbance, reflectance, band gap , absorption coefficient, optical conductivity, refractive index and extinction coefficient.*

## Introduction

Rapid advances in renewable energy technology and implementation will be needed in the next several decades in order to ensure a stable electricity which will lead to smooth transition away from fossil fuels and nuclear energy, which comprised about 93% of the world's energy budget with a negligible contribution from solar energy. And also demand for development of smaller and smaller devices with higher speed and performance which is applicable in the world of technology called *Nanotechnology*[1]. Among these possible materials is Tin (II) Sulfide (SnS), a non-toxic, abundant, p-type absorber well matched for solar absorption with high absorption coefficient. In recent years, thin films of SnS have attracted much attention for the photovoltaic applications due to the high absorption coefficient and high conductivity[1,2]. Tin (II) sulphide thin films attracted extensive interest due to their photoconductivity properties for solar energy conversion.

SnS thin films can be generated by many methods such as thermal evaporation[3], pulse electron deposition[4], spray pyrolysis[5], SILAR[6], chemical bath deposition[7]. The film in this study is grown by chemical bath deposition (CBD) which creates a thin film on a solid substrate via a reaction in a liquid solution. The CBD method is inexpensive, easy to prepare and its necessary vessels can be found in an ordinary

chemistry laboratory. Therefore, this method has many advantages over others used to grow semiconductor thin films.

The direct and indirect band gaps of SnS thin film vary depending on the method of preparation and fabrication but some results agree with the literature values between 1.0eV-1.2eV and 1.2eV-1.5eV respectively. SnS thin has been used as an absorption layer in the manufacture of heterojunction solar cell due to its narrow band gap[8,9].

## Experiment

In the present work SnS thin films were prepared by chemical bath deposition on microscope glass substrate kept at room temperature with varying other compounds. To make 50ml solution, 0.5M solution of $SnCl_2$ which is the source of $Sn^{+2}$ was made to react with 3M of 99% Ammonia as complexing agent Subsequently with 1M solution of Thiourea which is the source of $S^{-2}$. 1M of Sodium hydroxide was added create an alkaline environment for deposition to take place and deionized water added to make-up to 50ml in a glass beaker. Cleaned glass substrates were immersed into the solution and were allowed between 60 to 180 minutes after which the substrates were removed and rinsed in de-ionized water and were allowed to dry in air . Different samples of SnS thin films with A and B chosen as representative samples. The samples were subjected to annealing temperatures and time of 250 °C for 3hours for A and 200 °C for 1hour for B respectively.Table 1 shows the various combinations adopted in the deposition processes.

***Table: 1 Experimental Summary***

| **Exp.** | **Volume of 0.5M of $SnCl_2$ (ml)** | **Volume of 1M o Thiourea (ml)** | **Volume of 3M of Ammonia ($NH_3$) (ml)** | **Volume of 1M o NaOH (ml)** | **Volume of Water (ml)** |
|---|---|---|---|---|---|
| A | 20 | 10 | 7.5 | 5 | 7.5 |
| B | 20 | 11 | 4 | 5 | 10 |
| C | 20 | 16 | 4 | 4 | 6 |
| D | 25 | 10 | 7 | - | 8 |
| E | 15 | 10 | 10 | 6 | 9 |
| F | 23 | 10 | 6.5 | 5 | 5.5 |

## Reaction Mechanism

$$SnCl_{2(aq)} + 4NH_{3(aq)} \rightarrow [Sn(NH_3)_4]^{2+} + 2Cl^-_{(aq)}$$

$$[Sn(NH_3)_4]^{2+}_{(aq)} + CS(NH_2)_{2(aq)} \rightarrow SnS_{(s)} + CS(NH_2)_{2(aq)} + 4NH_{3(aq)}$$

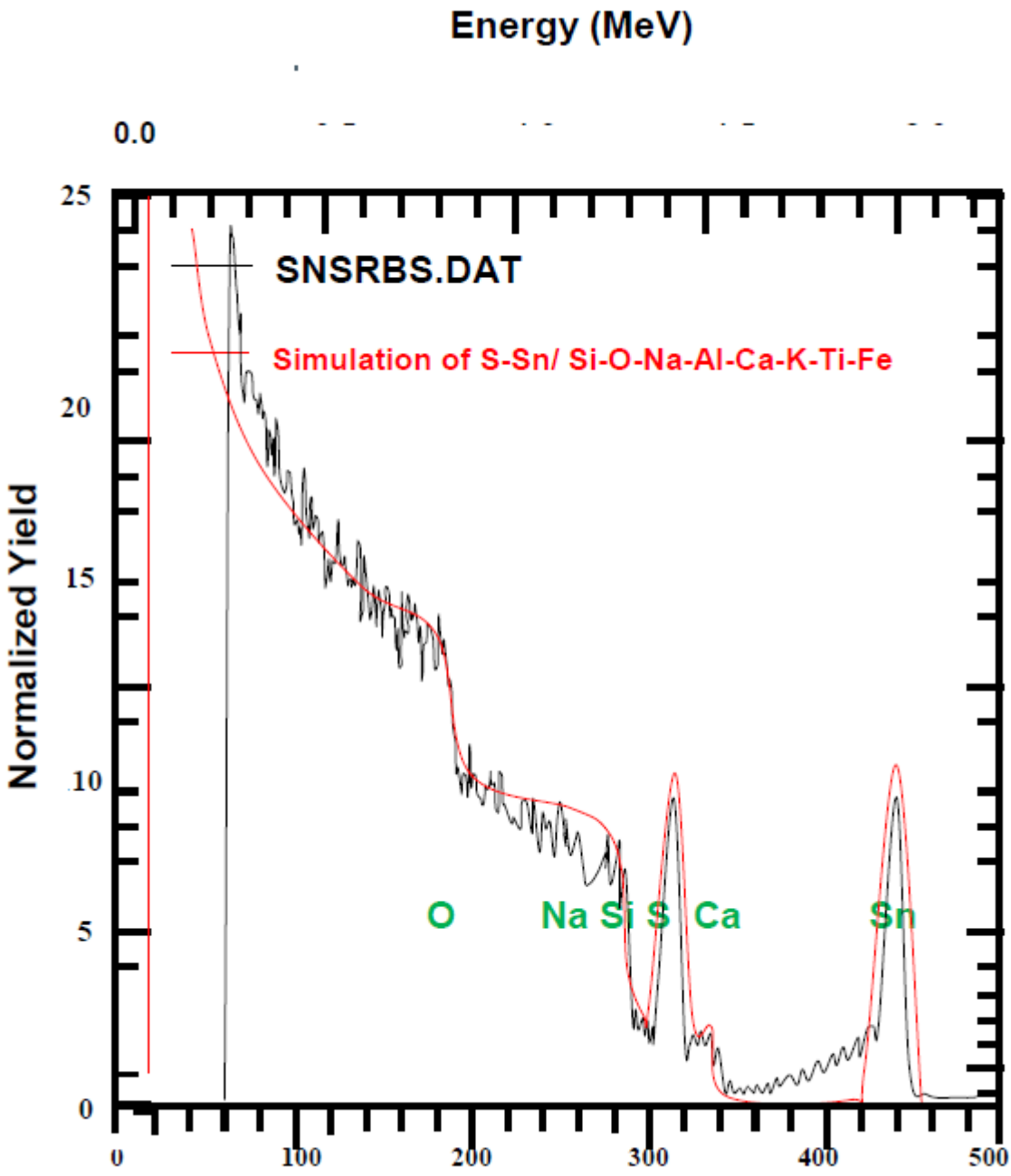
## Results and Discursion

In the deposition processes, deposition time, annealing temperatures, pH of solution and annealing time were considered, and changes in the properties of the films were observed. Many samples were deposited under varying conditions. Two samples A and B were chosen as representative samples. They were deposited at room temperature, with pH value of 8.8. Samples A and B were subjected to annealing temperatures of 250$^o$C and 200$^o$C and annealing time of 3hours and 1hour respectively. Thickness is measured by optical method using Rutherford Backscattering (RBS) equipment. The films were subjected to optical measurements using double beam UV- Spectrophotometer with wavelength ranging from 200-1100nm.

## Composition Analysis

***Table 2. EDXRF of the Deposited samples***

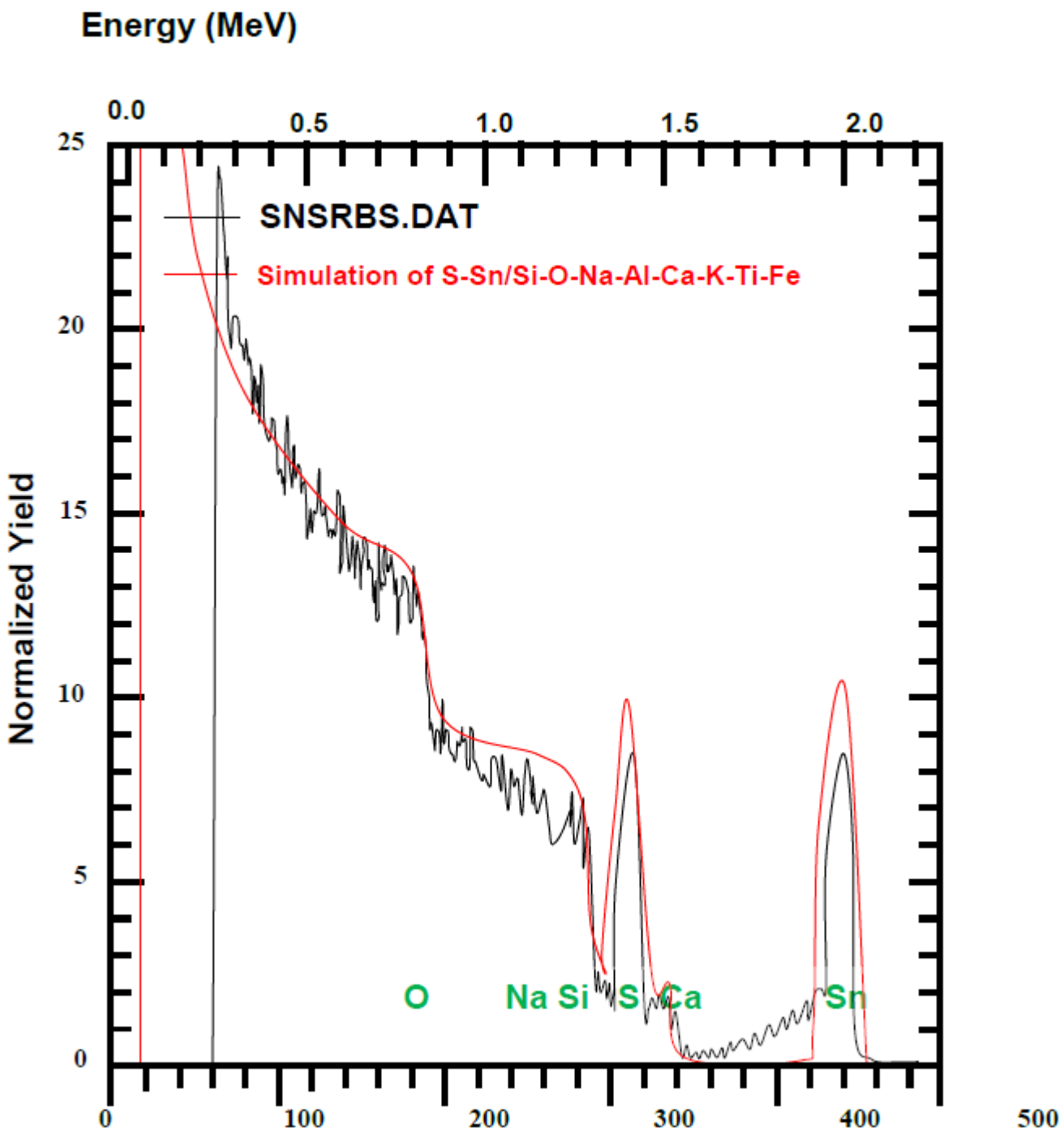
| **Elements** | **Concentration (3hours)** | **Concentration (1hour)** |
|---|---|---|
| S | < 2.383 | < 2.394 |
| Cl | 1.566 ± 0.423 %w | 1.566 ± 0.423 %w |
| K | 1.410 ± 0.298 %w | 1.410 ± 0.298 %w |
| Ca | 6.969 ± 0.857 %w | 6.969 ± 0.857 %w |
| Ti | 149.948 ± 32.524 ppm | 149.948 ± 32.524 ppm |
| Mn | 20.529 ± 2.637 ppm | 20.529 ± 2.637 ppm |
| Fe | 242.414 ± 25.468 ppm | 242.414 ± 25.468 ppm |
| Ni | 15.797 ± 2.822 ppm | 15.797 ± 2.822 ppm |
| Cu | 33.608 ± 8.163 ppm | 33.608 ± 8.163 ppm |
| Zn | 89.276 ± 19.390 ppm | 89.276 ± 19.390 ppm |
| Sn | 7550.161 ± 1247.832 ppm | 7561.161 ± 1248.822 ppm |




**LAYER Thickness Sublayers Channel Composition …**

**1 100.00 nm auto Sn 0.501 S 0.499**

***Fig. 1 Rutherford Back Scattering Analysis of Sample A Annealed at 250$^{o}$ C for 3 hours.***




| LAYER | Thickness | Sublayers | Composition … |
|---|---|---|---|
| 1 | 150.00 nm | auto | Sn 0.504 S 0.496 |

The thickness of the films are 100.00nm for 3hours and 150.00nm for 1hour and the percentage compositions of Tin (Sn) is 50.1% and Sulphur (S) is 49.9 % for 3hours and Tin (Sn) is 50.4% and Sulphur (S) is 49.6% for 1hour sample.

Optical Properties

The values of optical transmittance, T were obtained from a Double Beam UV- Spectrophotometer in the range from 200-1100nm. In order to estimate the optical band gap, the equation connecting the photon energy a nd optical absorption is used:

$(\alpha h\upsilon) \ \alpha \ (h\upsilon - Eg)^n$

$\mathbf{(\alpha h\upsilon) = f(h\upsilon - Eg)^n}$

where *E*g is the energy band gap, α is the absorption coefficient, f is the constant which depends on the film, *n* is a coefficient having the value 1/2 or 2 depending on the nature of electronic transitions and *h* is Planck constant. *n* has the value 1/2 for allowed direct transition, and 2 for allowed indirect transition. Figure 3 shows the optical transmission spectrum of the SnS thin films.

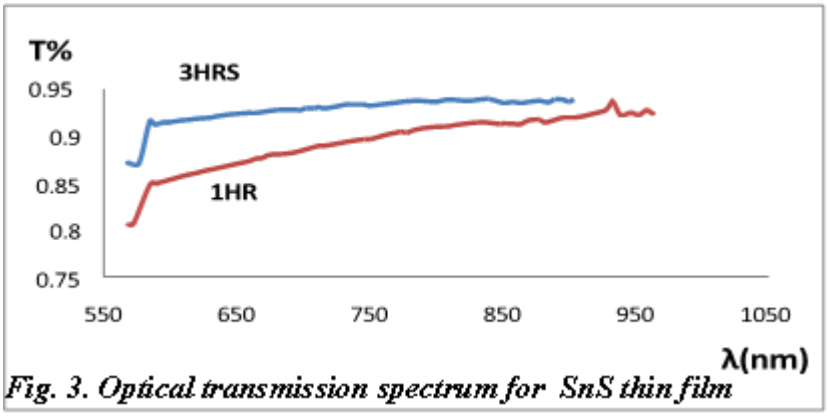



*Fig. 3. Optical transmission spectrum for SnS thin film*

The point where the linear part of $(\alpha hv)^2$ against $(hv)$ graph intersects the *hv axis* gives the forbidden band value for allowed direct transitions; on the other hand, the point where linear part of $(\alpha hv)^{1/2}$ against $(hv)$ graph intersects the *hv* axis gives us the forbidden band value for allowed indirect transitions. The two graphs of direct and indirect band gap are given in Fig. 4. and Fig. 5 respectively.

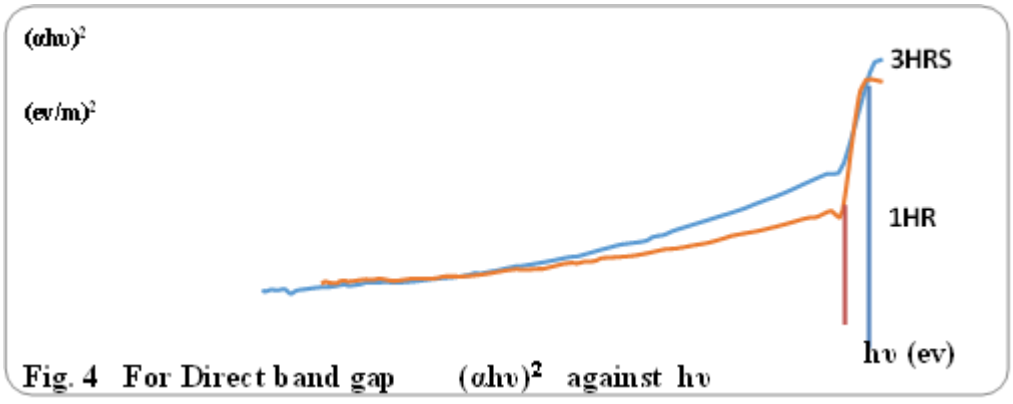



Fig. 4 For Direct band gap $(\alpha h\upsilon)^2$ against $h\upsilon$

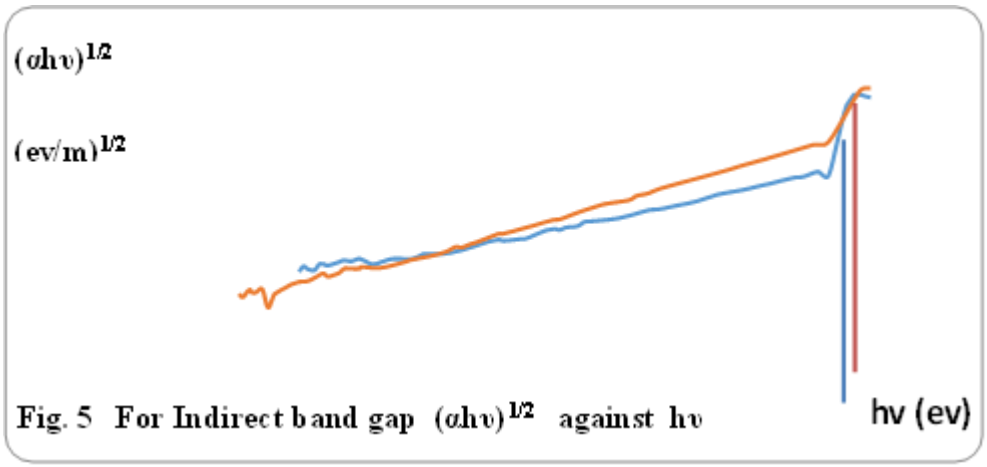



Fig. 5 For Indirect band gap $(\alpha h\upsilon)^{1/2}$ against hυ

The direct band gap of the two samples are estimated to be ***1.98eV*** and ***2.01eV*** for the samples annealed for 3hours and 1hour respectively.

The indirect band gap of the two samples were estimated to be ***1.82eV*** and ***1.98eV*** for the samples annealed for 3hours and 1hour respectively.

## Conclusion

In summary, SnS thin film was successfully deposited onto glass substrates by chemical bath deposition technique at room temperature for 3hours and 1hour. Energy dispersive X-ray florescence (ED-XRF) shows there is a presence of SnS on the slide. According to Rutherford Backscattering (RBS), the thickness of the two samples were measured to be 100nm and 150nm for 3hours and 1hour respectively, also the composition of the thin film on the substrates shows that there is a presence of Sn and S. Optical studies reveal that the film has high transmittance and high optical conductivity which will absorb photons faster. The direct band gaps of the two samples were found to be ***1.98eV*** and ***2.01eV*** for the samples annealed for 3hours and 1hour respectively. The indirect band gaps of the two samples were found to be ***1.82eV*** and ***1.98eV*** for the samples annealed for 3hours and 1hour respectively. Due to the suitable direct band gap value for an absorbing layer for efficient light absorption. Finally, SnS thin films can be used as absorber layer in solar cells.

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