



## Research Article

### SnS:Cu Thin film a green solar absorber: a method to reduce oxygen in sprayed SnS:Cu

Gisa Grace Ninan\*, C. Sudha Kartha and K.P. Vijayakumar

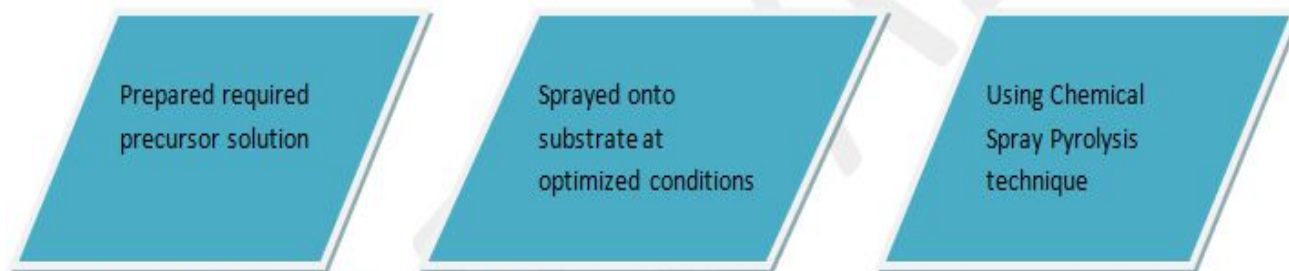
Department of Physics, Cochin University of Science and Technology, Cochin-682022

\*Corresponding author: [gisagrace@gmail.com](mailto:gisagrace@gmail.com)

Accepted: 23 June 2017, Available online: 27 September 2017

**Objective:** Recent research on thin film solar cells emphasizes on synthesizing earth-abundant, non-toxic, cost-effective materials for large scale production of solar cells. We are optimizing an absorber material for solar cell fabrication which satisfies all the above criteria.

#### Methodology:



**Duration taken for the research:** 2 weeks

**Conclusion:** We were able to confirm the possibility of preparing SnS:Cu thin films with reduced Oxygen, even using ambient oxygen preparation technique. This in turn is a good milestone for the fabrication of absorber layer to use in solar device.

## Abstract

In the present work, we report effect of variation of sulfur concentration, keeping the concentrations of Cu and tin constant for all the samples. The ratio of sulfur is varied as (Sn:S) 1:2, 1:4 and 1:6. Structural, Electrical and Optical properties of SnS:Cu films are studied using X-ray diffraction, Raman analysis, Hall measurements and UV-Vis-NIR spectroscopy. From X-ray photoelectron spectra (XPS) analysis, we could prove that even the most inevitable oxygen content present in spray pyrolysis method can be

**Research Article**

SnS:Cu Thin film a green solar absorber: A method to reduce oxygen in sprayed SnS:Cu

Ninan *et al.*

controlled just by adjusting the precursor ratio and hence can be used for preparing quality SnS:Cu thin films.

**Keywords:** Spray techniques, Optical properties, Electrical properties, Thin films

**Introduction**

In the face of recent research thin film solar cells emphasizes on synthesizing earth-abundant, non-toxic, cost-effective materials for large scale production of solar cells. Being an absorber layer, the material should be inexpensive and abundant along with appropriate opto-electronic properties. Considering these, SnS:Cu is a potential candidate (tin, sulfur and copper being abundant in nature and non-toxic). More over the doped binary compound (SnS:Cu) has simpler chemistry than many of the well established absorber materials with multi components. In this regard physical and electronic properties of Tin Sulfide attract special attention. Problems like lattice mismatch, defect density, high resistivity inhibits from attaining the estimated theoretical conversion efficiency about 24% (Loferski *et al.*, 1956). Synthesis of n-type and p-type SnS to fabricate homojunction can reduce the lattice mismatch to a great extend. The polarity of SnS can be easily controlled by temperature treatment or by changing tin and sulfur concentration (Sajeesh *et al.*, 2010). In our earlier papers, we have successfully reduced the resistivity by Cu doping and also succeeded in synthesising n-type and p-type SnS (Ninan *et al.*, 2014, <sup>a</sup>Ninan *et al.*, 2016). In this paper an attempt has been made to prepare SnS:Cu films with low oxygen content just by adjusting precursor ratio. Through this simple process, we could reduce oxygen to a very negligible order giving a different insight for the usual comment that for “sprayed films” Oxygen is a must!

**Materials and Methodology**

Using chemical spray pyrolysis (CSP) method SnS:Cu films are prepared on to a glass substrates. The precursors used are aqueous solution of stannous chloride ( $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ ), thiourea ( $\text{CS}(\text{NH}_2)_2$ ) and cuprous chloride ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ). 4% of the tin concentration in the precursor solution is optimized as doping percentage for Cu (Ninan *et al.*, 2014). Molarity of thiourea precursor has been varied in the ratio of tin and sulphur as 1:2, 1:4 and 1:6. Substrate temperature is kept at 375°C and is sprayed at the rate of 2 ml/min. Compressed air (pressure~1.5 bar) is used as the carrier gas. Samples are named as S2, S4 and S6 respectively.

Structural analysis of the films are performed using Rigaku (D.Max.C) automated X-Ray diffractometer and filtered Cu K $\alpha$  ( $\lambda = 1.5405 \text{ \AA}$ ) radiation and Ni filter operated at 30 kV and 20 mA is used to record diffraction pattern. UV-VIS-NIR spectrophotometer (JASCO V 570 model) is used to measure band gap of the films. Horiba Jobin Yvon LabRAM micro spectrometer is used to carry out Raman analysis.

# Research Article

SnS:Cu Thin film a green solar absorber: A method to reduce oxygen in sprayed SnS:Cu

Ninan et al.

Electrical characterization is done through Hall measurement (Ecopia model No HMS-53000, magnetic field = 0.57 T and capable of current measurement in the range 1nA-20 mA). The compositional analysis and Oxygen percentage is obtained from XPS spectra using Kratos Analytical AMICUS spectrometer fitted with the Mg K $\alpha$ /Al K $\alpha$  dual anode X-ray source.

## Result and Discussion

X-ray diffractograms of Sulfur varied SnS:Cu samples are depicted in Figure 1. All the samples have SnS (111) plane and (002) corresponding to 2 $\theta$  value of 31.5 $^{\circ}$  and 15.84 $^{\circ}$  (JCPDS: 75-0925). It is seen that as the Sulfur concentration increases the plane intensity is getting decreased. Interestingly there are no Cu $_x$ S phases. There are reports emphasizing that the (111) plane as preferred orientation for PV applications (Reddy et al., 2006, <sup>b</sup>Ninan et al., 2016).

Raman analysis is carried out and is shown in Figure 2. The exciting radiation is 632.8nm. For SnS:Cu thin films the Raman bands are reported at 95cm $^{-1}$  and 224cm $^{-1}$  (<sup>a</sup>Ninan et al., 2016, <sup>b</sup>Ninan et al., 2016). In the present study Raman bands matches almost with the reported values. Also the Raman bands of SnS $_2$  at 315cm $^{-1}$ , 215 cm $^{-1}$  and Sn $_2$ S $_3$  at 307cm $^{-1}$ , 251cm $^{-1}$  are absent (Mathews et al., 2013).

Absorption measurements of SnS:Cu samples are (in the wavelength range of 190-2500 nm) shown in Figure 3 (the ( $\alpha$ h $\nu$ ) $^2$  versus energy (h $\nu$ ) graphs). Optical band gaps (which are direct in both cases) exhibit 1.38 eV. This band gap value is already reported and corresponds to SnS:Cu (Ninan et al., 2014, a Ninan et al., 2016, <sup>b</sup>Ninan et al., 2016).

Electrical properties of these samples are investigated through Hall measurement. Carrier concentration, resistivity, mobility and polarity are depicted in Table 1. The polarity of all the samples are confirmed to be n-type. The S2 sample is found to have minimum resistivity along with enhanced mobility.

Table 1: Electrical measurements done for samples				
Sample name	Carrier concentration (/cm $^3$ ) (*10 $^{18}$ )	Resistivity (ohm.cm)	Mobility (cm $^2$ /v.s)	Polarity
S2	4.2	1	1.3	n
S4	6.16	1.1	0.79	n
S6	4.1	3.7	0.4	n

Research Article

SnS:Cu Thin film a green solar absorber: A method to reduce oxygen in sprayed SnS:Cu

Ninan et al.

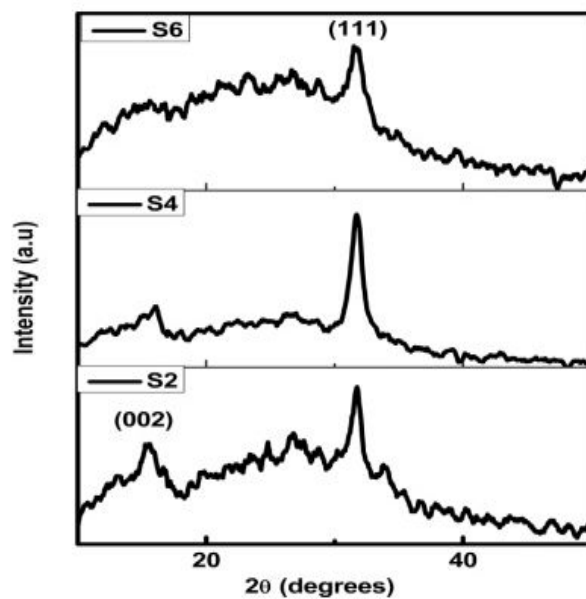


Figure 1: X-Ray diffractograms of Sulfur varied SnS:Cu samples.

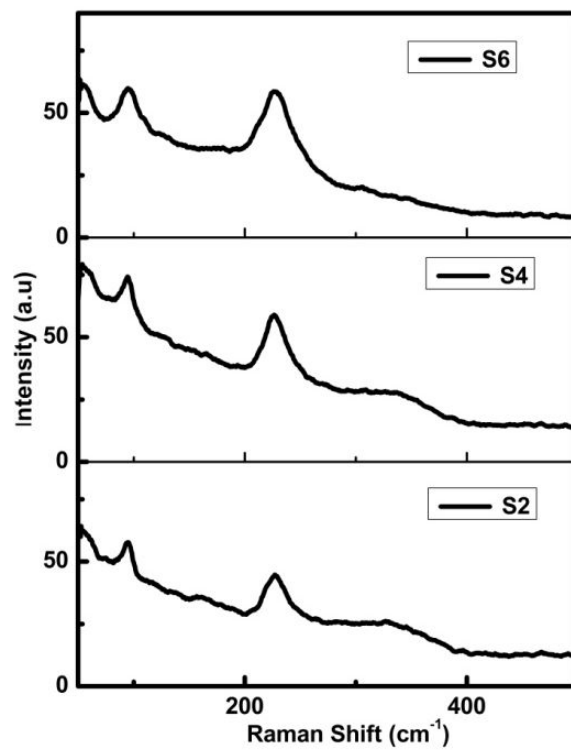


Figure 2: The Raman Spectra of Sulfur varied SnS:Cu samples.

Research Article

SnS:Cu Thin film a green solar absorber: A method to reduce oxygen in sprayed SnS:Cu

Ninan et al.

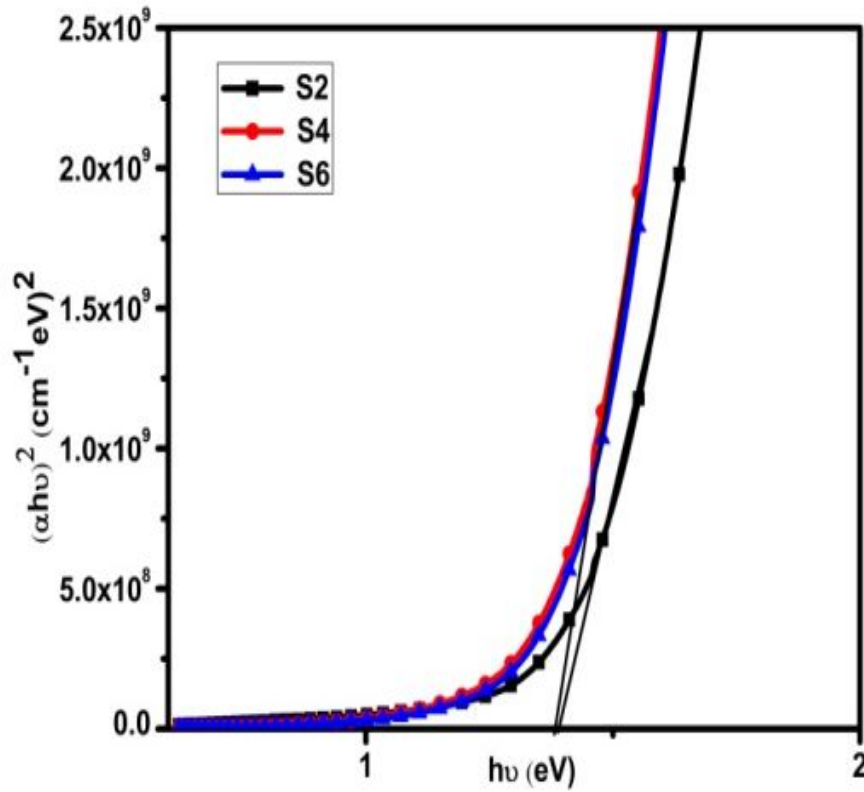


Figure 3: The Band gap obtained for Sulfur varied SnS:Cu samples.

Compositional analysis of the samples is carried out using XPS technique. Atomic concentration of each element is obtained and is shown in Table 2. It is already reported that in Spray pyrolysis presence of excess tin concentration leads to n-type conduction (<sup>a</sup>Ninan et al., 2016).

Table 2: Atomic Concentration of each element				
Sample name	O 1s	Sn 3d	S 2p	Cu 2p
S2	13.79	54.47	27.29	4.45
S4	11.9	54.19	30.75	3.16
S6	4.49	50.78	39.81	4.92

Thus the values of atomic concentration also confirms the possibility for n-type polarity in Cu:SnS.

Research Article

SnS:Cu Thin film a green solar absorber: A method to reduce oxygen in sprayed SnS:Cu

Ninan et al.

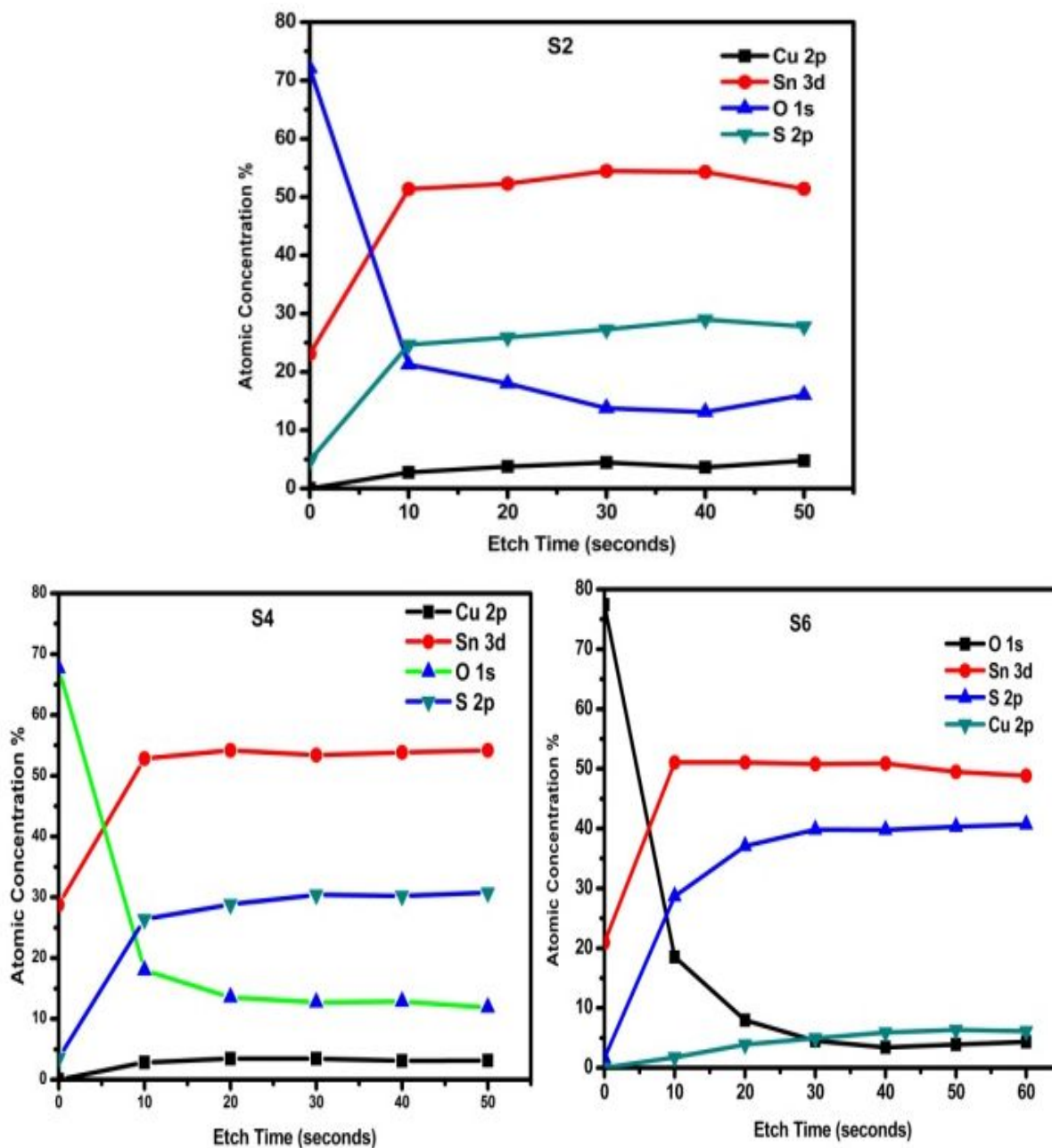


Figure 4: The XPS spectra of samples

From the Figure 4, it is clearly seen that the oxygen concentration decreases as the Sulfur concentration is increased. The percentage of copper doping remains almost constant in all the cases. Thus we have succeeded in synthesizing SnS:Cu films with very less oxygen concentration, which is a great success. Hence we fabricated oxygen reduced thin films using oxygen rich preparation technique.

**Research Article**

SnS:Cu Thin film a green solar absorber: A method to reduce oxygen in sprayed SnS:Cu

*Ninan et al.*

**Conclusions**

From the above characterization, we studied the structural, optical and compositional details of Sulfur varied SnS:Cu thin films. Most importantly we were able to confirm the possibility of preparing SnS:Cu thin films with reduced Oxygen, even using ambient oxygen preparation technique. This in turn is a good milestone for the fabrication of absorber layer to use in solar device.

**Social relevance and expected outcome**

We succeeded in synthesizing n-type SnS:Cu thin film which is very promising for photovoltaic application. We could fabricate homojunction Solar cells using both n-type and p-type SnS. This would reduce the lattice mismatch problem in SnS solar cells, which is considered as the main reason for low efficiency. All the elements used are non-toxic, abundant and is easily available.

**Acknowledgments**

One of the authors [G.G.N.] would like to thank the UGC for providing fellowship in the form of ‘Research Fellowships in Science for Meritorious Students’ (UGC – RFSMS). One of the authors (KPV) and (CSK) would like to thank CSIR and KSCSTE respectively for financial assistance under “Emeritus Scientist” Scheme.

**References**

1. JJ Loferski (1956), Theoretical Considerations Governing the Choice of the Optimum Semiconductor for Photovoltaic Solar Energy Conversion, J. Appl. Phys, 27: pp. 777.
2. TH Sajeesh, AR Warriar, CS Kartha and KP Vijayakumar (2010), Optimization of parameters of chemical spray pyrolysis technique to get n and p-type layers of SnS, Thin Solid Films, 518: pp. 4370– 4374.
3. GG Ninan, VG Rajeshmon, CS Kartha and KP Vijayakumar (2014), Cu doping: An effective method for improving optoelectronic properties of sprayed SnS thin films, AIP conference proceedings, 1591: pp.1440–1442.
4. <sup>a</sup>GG Ninan, CS Kartha and KP Vijayakumar (2016), Spray pyrolysed SnS thin films in n and p type: Optimization of deposition process and characterization of samples, J. Anal. Appl. Pyrolysis, 120: pp. 121–125.

**Research Article**

SnS:Cu Thin film a green solar absorber: A method to reduce oxygen in sprayed SnS:Cu

*Ninan et al.*

5. KT Ramakrishna Reddy, N Koteswara Reddy and RW Miles (2006), Photovoltaic properties of SnS based solar cells, Sol. Energy Mater. Sol. Cells, 90: pp. 3041–3046.
6. <sup>b</sup>GG Ninan, C Sudha Kartha and KP Vijayakumar (2016), On the preparation of n-type SnS:Cu using chemical spray pyrolysis for photovoltaic application: Effect of annealing, Sol. Energy Mater. Sol. Cells, 157: pp. 229–233.
7. NR Mathews, C Colín García and IZ Torres (2013), Effect of annealing on structural, optical and electrical properties of pulse electrodeposited tin sulfide films, Mater. Sci. Semicond. Process, 16: pp. 29–37.



This work is licensed under a [Creative Commons Attribution 4.0 International License](https://creativecommons.org/licenses/by/4.0/). Proper citation of this article is mandatory wherever it is required.