Chemical Concepts

International Journal of Chemical Concepts
ISSN:2395-4256 www.chemconsai.com
Vol.02, No.02, pp 88-95, 2016

"Synthesis, characterization and gas sensing performance of spray pyrolysed nanostructured $CuInS_2$ thin films"

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Abstract : Spray pyrolysis technique was employed to deposit nanostructured $CuInS_2$ thin films on to the glass substrates heated at 300 ^oC. The structural, surface morphology were studied using X-ray diffraction (XRD), Field emission scanning electron microscopy (FE-SEM). Elemental composition was conducted using EDAX. The gas sensing performance of the films was tested for various hazardous gases. The sensor (10 min) showed high gas response (S = 890 at 100 ^oC) on exposure of 50 ppm of H_2S and high selectivity against other gases. Its response time was short (7 s) and recovery was also fast (11 s). The results are discussed and interpreted.
Keywords: Nanostructured $CuInS_2$, H_2S gas sensing, response and recovery time

1.0 Introduction

Chemical and biological sensors have a profound influence in the areas of personal safety, public security, medical diagnosis, detection of environmental toxins, semiconductor processing, agriculture, and the automotive and aerospace industries. The past few decades has seen the development of a multitude of simple, robust, solid-state sensors whose operation is based on the transduction of the binding of an analyte at the active surface of the sensor to a measurable signal that most often is a change in the resistance, capacitance, or temperature of the active element [1].

$CuInS_2$ thin film is one of the most promising absorber material with absorption co-efficient ($10^5 cm^{-1}$), exceptional insensitivity to radiation damage or impurity and optimum band gap of 1.5eV which is perfectly matches with solar spectrum. $CuInS_2$ thin film offers the outlook of low production cost with few microns of thickness can absorb majority of the incident light energy higher than the band gap of the material. Furthermore, it does not contain any toxic constituents as Se or Ga atoms. It was found that increase in the efficiency of solar cells based on chalcopyrite semiconducting materials was mainly attributed by post annealing treatment in air or oxygen [2].

Hydrogen sulfide (H_2S) the most dangerous manure gas. It is produced from the anaerobic decomposition of organic materials, it chemically interacts quickly with blood hemoglobin and blocks oxygen from being carried to body's tissues and organs [3]. At higher concentration exceed TLV value, cause instant paralysis and death. Therefore for security and monitoring of H_2S is very important in petrochemical, coal manufacturing industries and every sector of life [4]. Measurements and detection is the focus of study.

Various deposition techniques have been use for the fabrication of $CuInS_2$ thin film such as aerosol jet deposition[5], chemical bath deposition[6], chemical vapour deposition[7], co-evaporation[8], electrodeposition [9], paste coating method1[10], SILAR method[11]. Among these techniques, spray pyrolysis is an attractive method for the deposition of thin film in large area production which is useful for gas sensor application.

In this work, nanostructured $CuInS_2$ thin films with different spraying time of the solution were prepared by spray pyrolysis technique. Phase purity, constituents of the elements and surface morphology were studied from X-ray diffraction (XRD), Energy dispersive X-ray diffraction (EDAX) and Field emission scanning electron microscopy (FE- SEM). These nanostructured $CuInS_2$ thin films were tested for sensing different gases and were observed to be most sensitive to H_2S at 100 ^oC.

2.0 Experimental details

2.1 Preparation of nanostructured $CuInS_2$ thin films

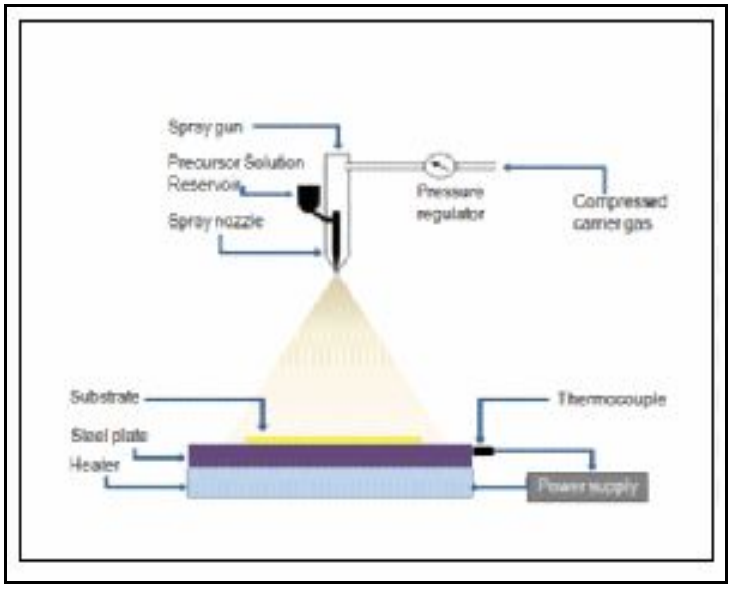


Figure 1: Spray Pyrolysis System

Fig. 1 shows the experimental set of $CuInS_2$ by using spray pyrolysis technique. $CuInS_2$ thin films of various thicknesses were deposited by varying spraying time of solution between 5 to 15 minutes.$CuInS_2$ (CIS) thin film was deposited on a glass substrate by an aqueous solution of Cupper chloride dehydrate ($CuCl_2.2H_2O$), Indium trichloride ($InCl_3$), and Thiourea (CH_4N_2S) so as to get desired solution concentration (0.05 M).

In the present study, the copper/indium molar ratio in the solution was Cu/In=0.50 and sulfur/copper ratio ration in the solution S/Cu=8.0. The surplus amount of thiourea was required in the final solution since it avoids the precipitation of metallic hydroxides and sulfides because it forms complexes with copper and Indium ions. The spray produced by nozzle was sprayed onto the glass substrates heated at 300 ^oC. Nitrogen gas is use as carrier gas. Various parameters such solution concentration (0.05 M), spray rate (7 mL/ min), nozzle to and fro frequency (14 cycles/ min), nozzle to substrate distance (30 cm), etc. were optimized to obtain good quality films. The films with different spraying time of the solutions: 5 min, 10 min, and 15 min., were obtained and were referred to as S1, S2, and S3 respectively. Process parameters to obtain nanostructured $CuInS_2$ thin films were tabulated in Table 1.

Table.1. Process parameters for the spray deposition of nanostructure $CuInS_2$ thin films

Spray parameter	Optimum value / item
Nozzle	Glass
Nozzle to substrate distance	30 cm
Concentration of Cupper chloride dehydrate ($CuCl_2.2H_2O$), Indium trichloride ($InCl_3$), and Thiourea (CH_4N_2S)	0.05M
Spray deposition time	5 min., 10 min., and 15 min.,
Solvent	Deionised water
Solution flow rate	7 ml/ min.
Carrier gas	Nitrogen gas
Substrate temperature	300 ^OC

2.2. Annealing of samples

As synthesized $CuInS_2$ thin films were annealed in air at 300 ^oC for 10 min.

3. Characterization of thin films

Film thickness was measured by using a weight difference method. The crystal structure of films was analyzed with X-ray diffractometer (Miniflex Model, Rigaku, Japan, Advanced D8) by using Cu-Kα lines (λ= 1.542Å). The surface morphology and quantitative elemental analysis of nanostructure $CuInS_2$ thin films were studied using Field Emission Scanning Electron Microscopy (FE-SEM) coupled with EDAX (JEOL JSM – 6360 A). The gas sensing performance of the thin films were tested using static gas sensing system.

3. 1 Determination of film thickness

Film thickness was measured by well-known a weight difference method [12] (considering the density of the bulk $CuInS_2$). The films were deposited on clean glass slides whose mass was previously measured. After the deposition the substrate was again weighted, determining the quantity of deposited $CuInS_2$. Measuring the surface area of the deposited film, taking account of $CuInS_2$ specific weight of the film, thickness was determined using the relation:

$T = M/A.\rho$ ----------(1)
Where,
A is the surface area of the film [cm^2]
M is the quantity of the deposited tin oxide
ρ is the specific weight of $CuInS_2$
The measured thickness of the thin film samples S1, S2 and S3 were given in Table 2.

Table 2: Measurement of spray deposition time with film thickness

Sample No.	Spray time (min.)	Thickness (nm)
S1	5	144
S2	10	169
S3	15	189

The thickness of the film was varied from 144 to 189 nm. It was found that the thickness of the film increases with increase in spray deposition time of the solution.

Fig. 2 shows the X-ray diffractogram of nanostructured $CuInS_2$ thin film sample S2. The broad peaks of the XRD pattern corresponding to $CuInS_2$ material are observed to be nanocrystalline in nature. The characteristics peak of as-deposited CIS film corresponding to different planes (112), (004), (200), (204) and (220) with preferential orientation along (112) plane indicated the formation of $CuInS_2$. The observed peaks are matching well with the standard JCPDS data of $CuInS_2$ (JCPDS card no.75-0106) and Cu_2S (JCPDS card no.26-1116). The XRD pattern reveal that $CuInS_2$ thin film is crystalline in nature, average crystalline size is obtained from Scherer's formula was observer to be 31 nm.

$D = 0{\cdot}9\lambda/\beta\cos\theta$ ----------(2)
Where, D = Average crystallite size
λ = X-ray wavelength (1·5418 Å)
β = FWHM of the peak
θ= Diffraction peak position.

3.2 X-Ray Diffraction

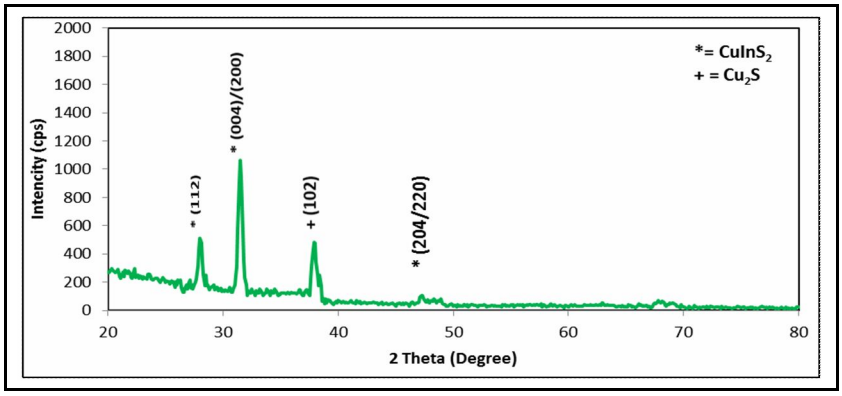


Figure 2: X-ray diffractogram of most sensitive thin film (Sample =S2)

3.3 Surface morphology properties using FE-SEM

Fig. 3 shows the FE-SEM image of most sensitive nanostructured $CuInS_2$ thin film sample S2. FE-SEM micrograph is showing topography of the film surface. The morphology of the grains was spherical in shape. The grain size was observed to be 35 nm.

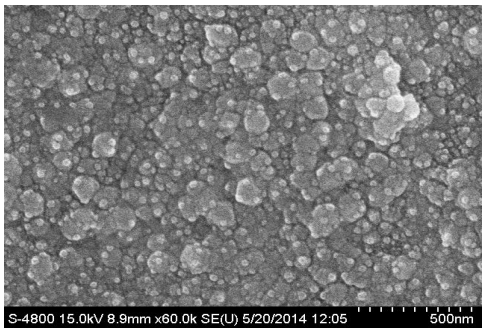


Figure 3: FE-SEM images most sensitive thin film sensor (S2)

3.4. Elemental analysis using EDAX

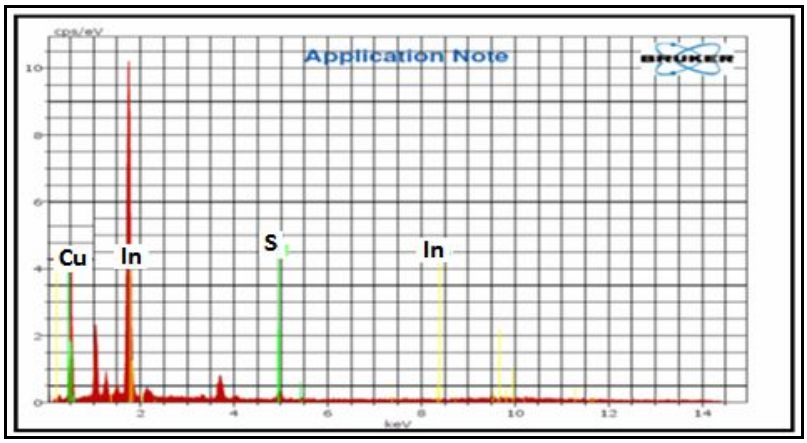


Figure 4: Elemental analysis of nanostructured $CuInS_2$ thin film sample (S2)

The quantative elemental composition of the nanostructured $CuInS_2$ thin film (sample S2) was analyzed using an energy dispersive spectrometer shown in Fig. 4. The EDAX spectrum (Figure 4) showed the intense peak of Cu, In, S indicating the composition of Cu, In and S were present in the CIS film.

Table 3. Elemental compositions of nanostructured $CuInS_2$ thin films.

Elements	Observed	
	at %	wt %
Cu	25.20	40.60
In	23.34	38.62
S	51.46	20.78
Total	100	100

The quantitative elemental composition of the thin films and the amounts of $CuInS_2$ analyzed using an energy dispersive spectrometer is represented in Table 3. Stoichiometric at % compositions of Cu, In and S are 25, 25 and 50, respectively. The observed compositions of sample was nonstoichiometric proportion.

4. Gas sensing performance of the thin films

4.1 Details of gas sensing system

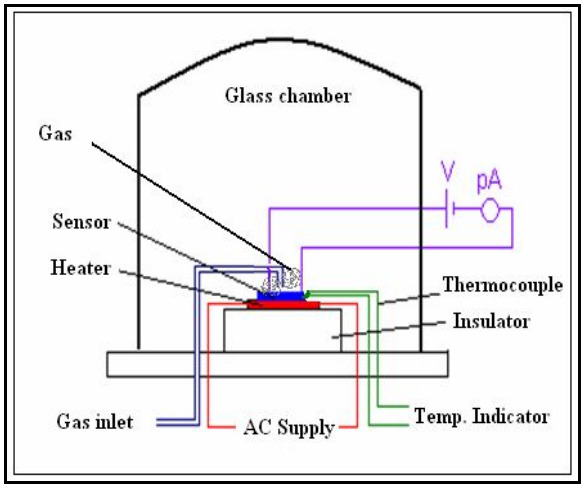


Figure 5: Block diagram of the static gas system

The sensing performance of the sensors was examined using static gas sensing system. The static system is built in our laboratory (Fig.5), which consists sensor element, heating element, gas inject unit, temperature-measuring unit, Pico-ammeter, glass dome and steel base plate are major components of static gas system. There are electrical feeds through on the base plate. Heating unit is fixed on base plate. It provides the desired temperature to sensor for its proper functioning. Sample under test can be mounted on the heater. Cr-Al thermocouple is mounted to measure the temperature. The output of thermocouple is connected to temperature indicator. Gas inlet valve fitted at one of the part base plate. Gas concentration (50 ppm) inside the static system is achieved by injecting a known volume of test gas. 5 V dc voltage is applied to the sensor element constantly and current meter can measure current.

4.2. Gas response with operating temperature

Fig. 6 shows variation of gas response with operating temperature of nanostructured $CuInS_2$ thin film samples S1, S2 and S3 on exposure of 50 ppm H_2S. It is clear from Fig.6, that the H_2S response of sample S2 is higher at 100 ^oC as compared to those of S1, S2 and S3. Due to the greater surface area of nanostructured materials, its interaction with the adsorbed gases is stronger, leading to higher gas response [13].

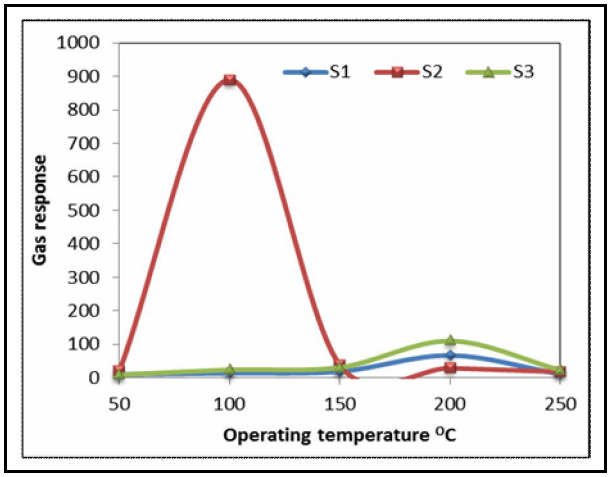
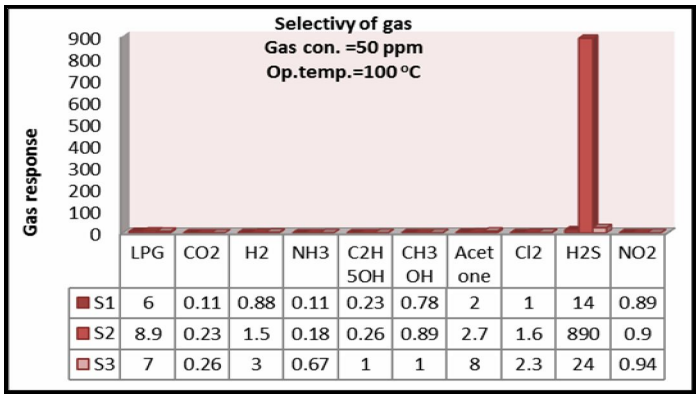


Figure 6: Gas response of pure nanostructured $CuInS_2$ thin films with operating temperature

4.3. Selectivity



	LPG	CO2	H2	NH3	C2H 5OH	CH3 OH	Acet one	Cl2	H2S	NO2
S1	6	0.11	0.88	0.11	0.23	0.78	2	1	14	0.89
S2	8.9	0.23	1.5	0.18	0.26	0.89	2.7	1.6	890	0.9
S3	7	0.26	3	0.67	1	1	8	2.3	24	0.94

Figure 7: Selectivity of H_2S thin films for different gases

Fig. 7 shows the variation of gas responses of nanostructured $CuInS_2$ to thin films to H_2S (50 ppm) among the mixture of gases. It is clear from the Fig.7 that the nanostructured $CuInS_2$ samples show the enhanced and selective response to H_2S at 100 ^oC among all other gases. The film surface chemistry would have been favorable to oxidize the H_2S easily than other gases, giving larger response to H_2S and smaller to others [14].

4.4. Response and recovery of the sensor

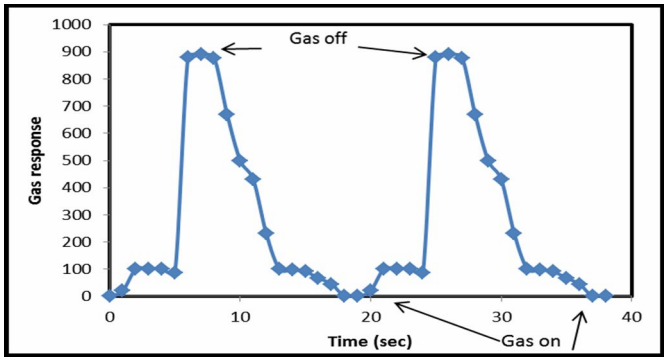


Figure 8: Response and recovery of the sensor

The response and recovery of the nanostructured $CuInS_2$ thin film (sample S2) sensor on exposure of 50 ppm of H_2S at 100 ^oC are represented in Fig. 8. The very short response time (7 s) and recovery time (11 s) are

the important features of the nanostructured $CuInS_2$ thin film sensor. The negligible quantity of the surface reaction products and their high volatility may be reason of the quick response to H_2S and fast recovery to its initial chemical status [12].

5. Discussion

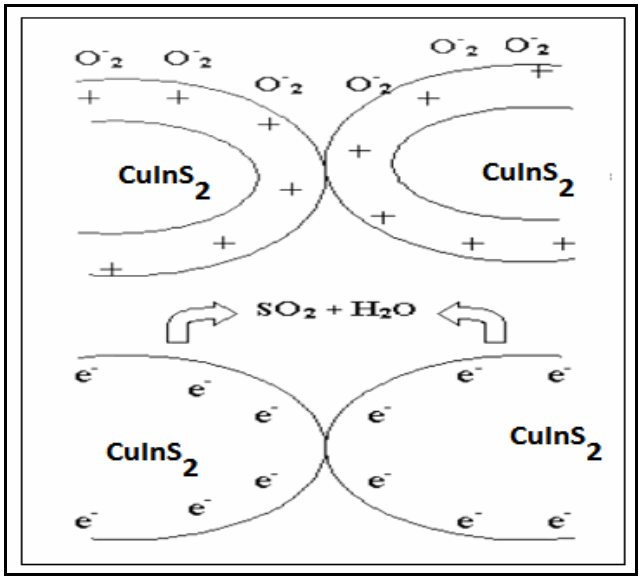


Figure 9: Gas sensing mechanism

The gas-sensing mechanism of $CuInS_2$-based thin films belongs to the surface controlled type, which is based on the change in conductance of the semiconductor. The oxygen adsorbed on the surface directly influences the conductance of the $CuInS_2$ based sensors as shown in Fig. 9.

The amount of oxygen adsorbed on thin film surface depends on the operating temperature, particle size and specific surface area of sensor [15]. The state of oxygen on the surface of $CuInS_2$ thin film undergoes the following reaction,

O_2 (gas) $\longrightarrow$ O_2 (ads) -------- (3)

O_2 (ads) + e^- $\longrightarrow$ O_2^- (ads) -------- (4)

O^- + e^- $\longrightarrow$ O^{2-}(ads) --------- (5)

The oxygen species capture electrons from the material, which results in the concentration changes of holes or electrons in the $CuInS_2$ semiconductor. When the $CuInS_2$ thin film is exposed to H_2S gas, the reductive gas reacts with the oxygen adsorbed on the thin film surface[11-15]. Then the electrons are released back in to the semiconductor, resulting in the change in the electrical conductance of $CuInS_2$ thin films. It can be expressed in the following reaction:

$H_2S + 3\,O \longrightarrow H_2O + SO_2 + 6e$ ----- (6)

6. Conclusions

1. Nanostructured $CuInS_2$ thin films could be prepared by simple and inexpensive spray pyrolysis technique.
2. Thickness of the films was observed to increase from 144 to 189 nm with increase in spray time of solution.
3. XRD, surface morphology and elemental composition studies reveals the formation of mixed phase of $CuInS_2$ with spherical grains and nonstoichiometric nature of the film which is found to be important for obtaining enhanced response characteristics.

4. Nanostructured $CuInS_2$ thin film thin film based sensor structure have been designed for the trace level (50 ppm) detection of H_2S gas at low operating temperatures (<100 ^oC) and exhibit the response of S= 890.
5. The sensor has good selectivity to H_2S against different gases.
6. The nanostructured $CuInS_2$ thin films exhibit rapid response–recovery which is one of the main features of this sensor.

Acknowledgements

The authors are thankful to the University Grants Commission, New Delhi for providing financial support. Thanks to Principal, G. D. M. Arts, K. R. N. Commerce and M.D. Science College, Jamner, for providing laboratory facilities for this work.

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