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Gas sensing performance of chemically deposited nanocrystalline Cu_2S thin films

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Abstract: In this work, nanocrystalline Cu_2S thin films have been prepared by spray pyrolysis technique. These films were characterized by different analytical instruments such as XRD, FE-SEM and EDAX to known crystal structure, surface morphology and elemental composition. Gas sensing performance of the prepared thin films was conducted using static gas sensing system and it was observed that prepared thin film sample S3 shows maximum gas response (S=560) to the H_2S gas at operating temperature 150 ^{0}C with rapid response (4 s) and fast recovery (9 s) of the sensor. The results are discussed and interpreted.
Keywords: Nanocrystalline d Cu_2S thin films, spray pyrolysis, H_2S gas sensor.

1.0 Introduction

In the past few decades, there has been an increasing investigation in semiconducting chalcogenide thin films, which have been due to their wide applications in various fields of science and technology. The study of nanocrystalline Cu_xS thin films has received much attention due to numerous technological applications in achievement of solar cells, in photochemical conversion of solar energy as solar absorber coating, as selective radiation filters on architectural windows for solar control in the warm climates, as electroconductive coatings deposited on organic polymers [1, 2].

So far, Cu_xS thin films have been prepared by various deposition techniques viz. modified chemical bath deposition (CBD), photo chemical deposition, metal organic chemical vapour deposition (MOCVD) and spray pyrolysis deposition [3,4]. Spray pyrolysis technique for preparation of thin films from aqueous solution is a promising technique because of its simplicity; by this method a large area of thin film can be deposited without sophisticated equipment.

The sensors are required basically for monitoring of trace gases in environment. Presently the atmospheric pollution has become a global burning issue. Gases from automobiles and industrial exhausts are polluting the environment. In order to detect measure and control these gases; one should know the amount and type of gases present in the environment. Thus the need to monitor and control these gases has led to the research and development of a wide variety of sensors using different materials and technologies [5].

Apart from sensitivity, selectivity is a critical issue regarding semiconductor gas sensors. It has been shown that by modulating the sensor working temperature and characterizing its transient response, it is possible to extract new parameters, which are of significant importance for the sensor and the investigated gases. This method required a very simple measurement system and improves the selectivity and sensitivity of sensors as each gas characteristic conductance verses temperature profile for type of sensor [6].

In this way, measuring the response of one sensor at n different temperatures is similar to having an array of n sensors working at fixed temperature. In particular semiconductor metal oxide is promising material for detection of various gases, e.g. LPG, H_2, CO_2, NH_3, C_2H_5OH, CH_3OH, Cl_2 and H_2S. Furthermore, nanocrystalline materials present new opportunities for enhancing the properties and performance of gas sensors and are recognized as essential for achieving high gas sensitivity.

In this work spray pyrolysis technique competes with the others due to its low cost, suitable properties and process well suited to large-scale production. It has several advantages in producing nanostructured thin films suitable for the gas sensors, such as, relatively homogeneous composition, easy control of film thickness and fine and porous microstructure. In this work, nanocrystalline Cu_2S thin films with different spraying time of the solution were prepared by spray pyrolysis technique. Crystal structure, elements of the constituents and grain sizes were studied from X-ray diffraction (XRD), Energy dispersive X-ray diffraction (EDAX) and Field emission scanning electron microscopy (FE- SEM). These nanostructured Cu_2S thin films were tested for sensing different gases and were observed to be most sensitive to H_2S at 150 ^oC.

2. Experimental Details

2.1 Preparation of nanocrystalline thin films

We have deposit the thin films on glass substrate. The deposition was carried out using glass substrate of the dimension 75mm*25mm*2mm. These substrate were first washed with water and then boiled in chromic acid and again boiled in distilled water, finally the substrates were washed with distilled water.

The preparation of nanocrystallie Cu_2S by using spray pyrolysis technique. The solution was prepared by dissolving equal volume percentage (1:1) of Cupper chloride dehydrate ($CuCl_2.2H_2O$) and Thiourea (CH_4N_2S) in deionized water so as to get desired solution concentration (0.05 M). The spray produced by nozzle was sprayed onto the glass substrates heated at 300 ^oC. Various parameters such as 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 thin films. The films with different spraying time of the solutions: 5 min, 10 min, 15 min., and 20 min. were obtained and were referred to as S1, S2, S3 and S4 respectively. Optimized parameters were tabulated in Table 1. As synthesized nanocrystalline Cu_2S thin films were annealed in air at 300 ^oC for 10 min.

Table 1: Process parameters for the spray deposition of nanocrystalline Cu_2S thin films

Spray parameter	Optimum value / item
Nozzle	Glass
Nozzle to substrate distance	30 cm
Concentration of Cupper chloride dehydrate ($CuCl_2.2H_2O$) and Thiourea (CH_4N_2S)	0.05M
Spray deposition time	5 min., 10 min., 15 min., and 20 min.,
Solvent	Deionised water
Solution flow rate	7 ml/ min.
Carrier gas	Nitrogen gas
Substrate temperature	300 ^OC

3. Characterization of thin films

3.1 Determination of film thickness

Film thickness was measured by using a weight difference method [7] (considering the density of the bulk Cu_2S). 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 Cu_2S. Measuring the surface area of the deposited film, taking account of Cu_2S 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 Cu_2S
ρ is the specific weight of Cu_2S
The values of the film thickness are given in Table 2.

Table 2: Measurement of spray deposition time and film thickness.

Sample No.	Spray time (min.)	Thickness (nm)
S1	5	142
S2	10	169
S3	15	187
S4	20	199

The thickness of the film was varied from 142 to 199 nm. From table 2 it was found that, the thickness of the film increases with increase in spray deposition time of the sprayed solution.

3.2 X-Ray Diffraction

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). Fig.1 shows the X-ray diffractogram of nanocrystalline Cu_2S thin film sample S3. The observed peaks are matching well with the standard JCPDS data of Cu_2S [8]. The XRD pattern reveal that Cu_2S thin film is crystalline in nature, average crystalline size is calculated from Scherre'r formula [7] and it was observer to be 22 nm.

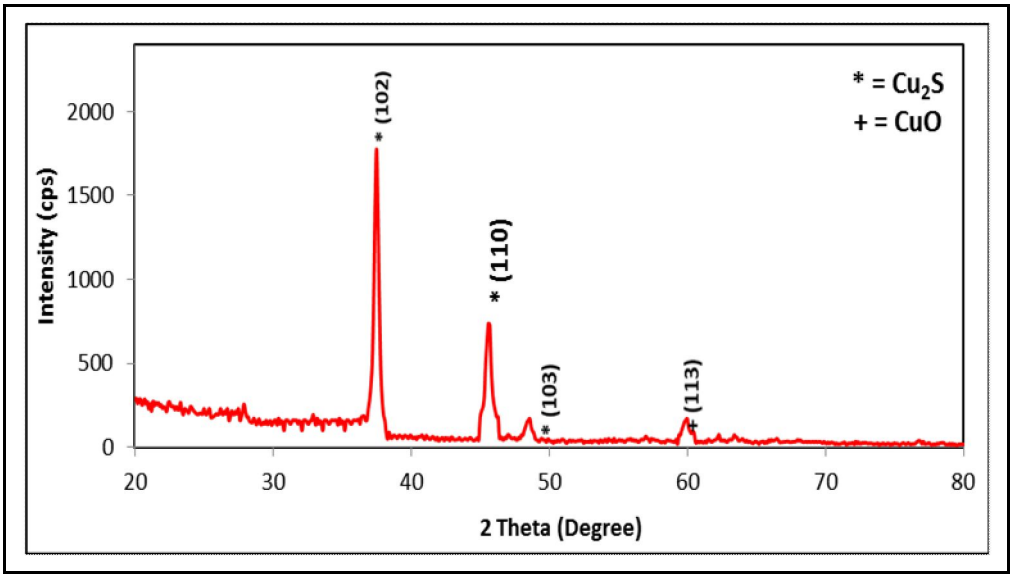


Figure 1: X-ray diffractogram of most sensitive thin film (Sample =S3)

3.3 Surface morphology using FE-SEM

The surface morphology and quantitative elemental analyses of nanocrystalline Cu_2S thin films were studied using Field Emission Scanning Electron Microscopy (FE-SEM) coupled with EDAX (JEOL JSM – 6360 A).

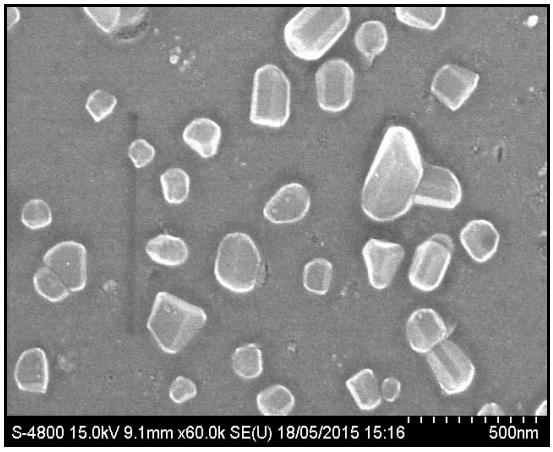


Figure 2: FE-SEM images most sensitive thin film sensor (S3)

Fig. 2 shows the FE-SEM image of most sensitive nanostructured Cu_2S thin film sample S3. FE-SEM micrograph is showing topography of the film surface. The morphology of the grains was mixed grains of cubical and tetragonal shape with different size. The grain size was observed to be 40 nm.

3.4 Elemental analysis using EDAX

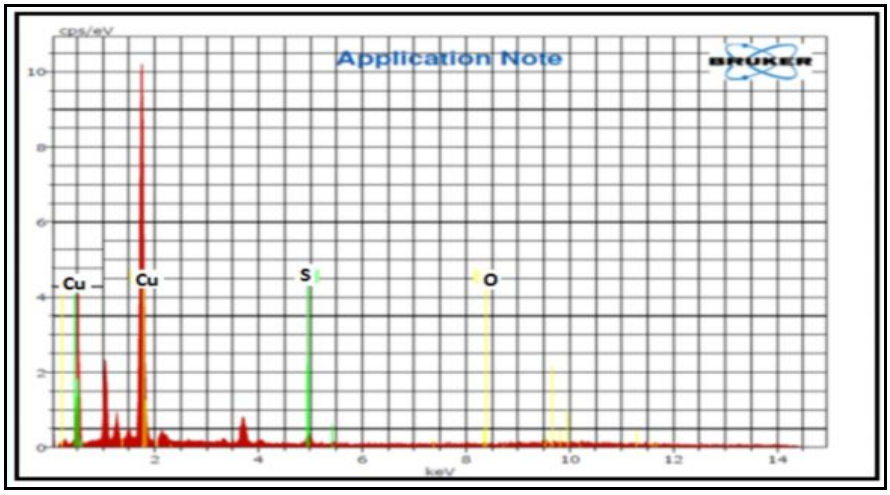


Figure 3: Elemental analysis of nanocrystalline Cu_2S thin film sample (S3)

The quantative elemental composition of the nanostructured Cu_2S thin film (sample S3) was analyzed using an energy dispersive spectrometer shown in Figure 3.

Table 3: Elemental compositions of nanocrystalline Cu_2S thin films.

Elements	Observed	
	at %	wt %
Cu	64.42	32.89
S	35.58	63.11
Total	100	100

The quantitative elemental composition of the thin films and the amounts of Cu_2S analyzed using an energy dispersive spectrometer is represented in Table 6. Stoichiometric at % of Cu and S are 50 and 50, respectively. The observed compositions of sample was nonstoichiometric proportion.

4. Gas sensing performance of the thin films

The gas sensing performance were carried out using a static gas chamber to sense H_2S gas in air ambient and the experimental set up is described elsewhere [9]. The nanocrystalline Cu_2S thin films were used as the sensing elements. 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 ports of the base plate. The air was allowed to pass into the glass chamber before start of every new gas exposure cycle. Gas concentration (50 ppm) inside the static system is achieved by injecting a known volume of test gas in gas injecting syringe. The conductance of the sensor in dry air was measured by means of conventional circuitary by applying constant voltage (5V) and measuring the current by picoammeter. The conductance was measured both in the presence and absence of test gas.

4.1. Gas response with operating temperature

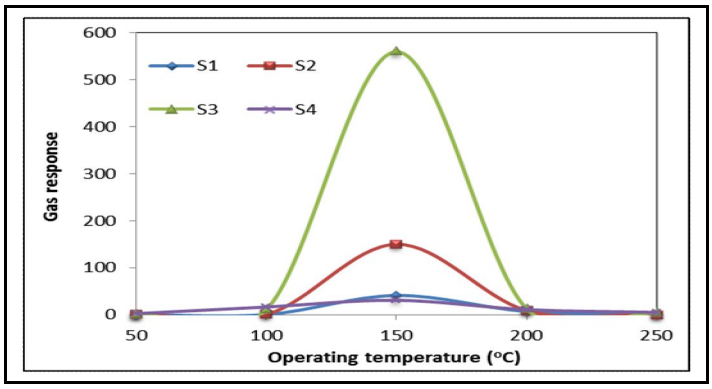
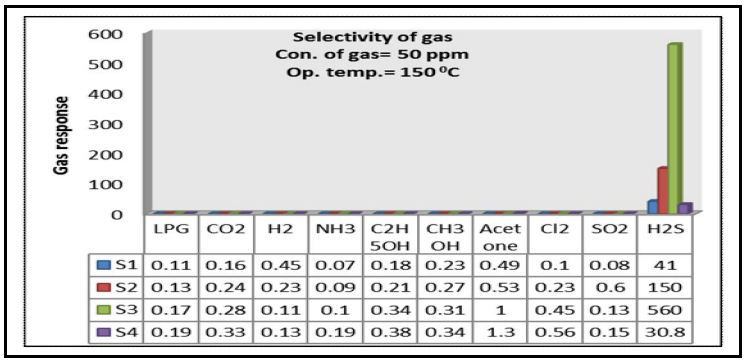


Figure 4: Gas response of nanocrystalline Cu_2S thin films with operating temperature.

Fig.4 shows variation of gas response with operating temperature of nanocrystalline Cu_2S thin film samples S1, S2, S3 and S4 on exposure of 50 ppm H_2S. It is clear from Fig.4, that the H_2S response of sample S3 is higher at 150 ^oC as compared to those of sample S1, S2, and S4. Due to the greater surface area of nanostructured materials, its interaction with the adsorbed gases is stronger, leading to higher gas response [10].

4.2. Selectivity



	LPG	CO2	H2	NH3	C2H5OH	CH3OH	Acetone	Cl2	SO2	H2S
S1	0.11	0.16	0.45	0.07	0.18	0.23	0.49	0.1	0.08	41
S2	0.13	0.24	0.23	0.09	0.21	0.27	0.53	0.23	0.6	150
S3	0.17	0.28	0.11	0.1	0.34	0.31	1	0.45	0.13	560
S4	0.19	0.33	0.13	0.19	0.38	0.34	1.3	0.56	0.15	30.8

Figure 5: Selectivity of nanocrystalline H_2S thin films for different gases.

Selectivity or specificity is defined as the ability of the sensor to respond to certain gas in the presence of the other gases. Fig. 5 depicts the bar diagram to indicate H_2S selective ability of the sensor as compared to other conventional gases.

4.3. Response and recovery of the sensor

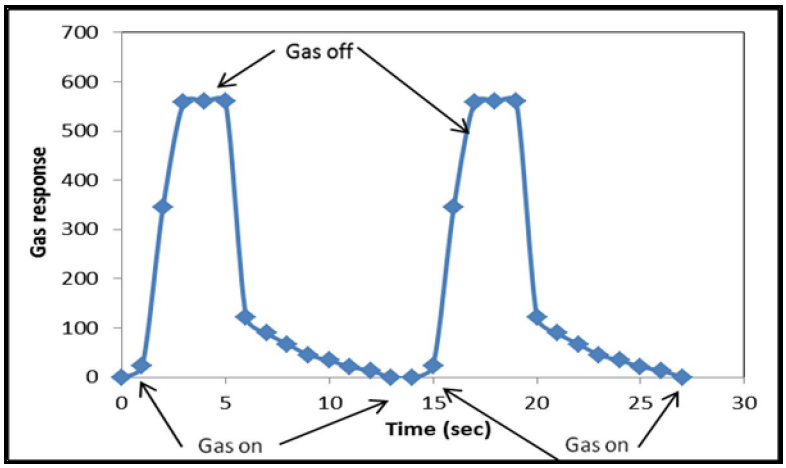


Figure 6: Response and recovery of the sensor.

The response and recovery of the nanocrystalline Cu_2S thin film (sample S3) sensor on exposure of 50 ppm of H_2S at 350^oC are represented in Fig. 6. The response is quick (4 s) and recovery is fast (9 s). The negligible quantity of the surface reaction products and their high volatility explain the quick response and fast recovery to H_2S gas [9].

4.4. Stability performance of the sensor

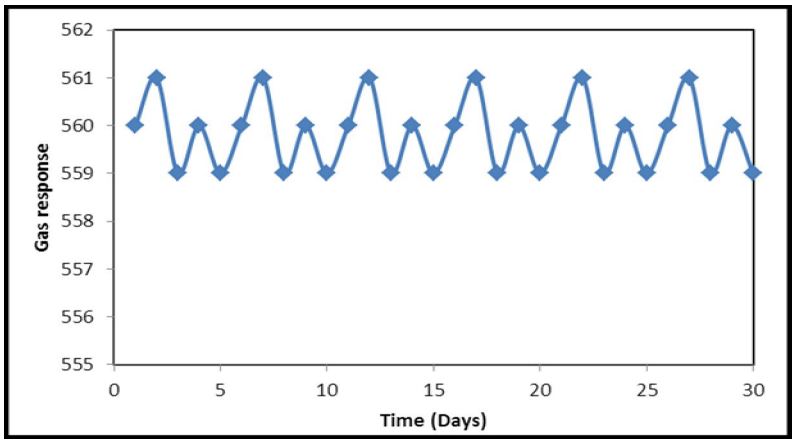


Figure 7: Stability profile of the sensor

The stability of the nanocrystalline Cu_2S sensor were measured by repeating the test many times (30 days). During the test, no significant variation was observed as shown in Fig. 7. The H_2S is selective gas sensor had prominent long term stability in atmosphere for about 30 days. The obtained results show that both H_2S response and electrical conductance were reproducible.

5. Discussion

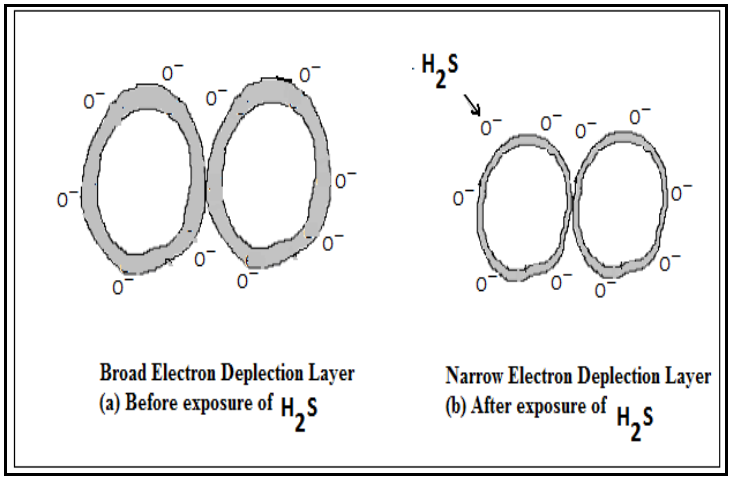


Figure 8: Gas sensing mechanism

Gas sensing mechanism is generally explained in terms of change in conductance due to the interaction of test gases with the semiconducting surface. The change of conductance is either by adsorption of atmospheric oxygen on the surface and/or by direct reaction of lattice oxygen or interstitial oxygen with the test gases. In case of former, the atmospheric oxygen adsorbs on the surface by extracting an electron from the conduction band, in the form of super oxides or peroxide, which are mainly responsible for the detection of the test gases. Before exposure of H_2S, Cu_2S nanoparticles are depleted of electrons from the conduction band by oxygen species (O_2^-, O^- and O^{2-}) adsorbed on particle surface [10], forming an electron depletion layer on particle surface which increases the sensor resistance.

Fig. 8 shows the H_2S sensing mechanism (Fig. (a) before exposure of H_2S and (b) after exposure of H_2S) of Cu_2S thin films, When the oxidation reaction rate of nitrogen dioxide is much higher than the rates of adsorption and desorption of the reactants, the steady state oxygen coverage depends critically on the relative oxygen and H_2S concentrations in the gas phase. To allow for fast surface reactions the temperature has to be high enough, although not too high, to prevent bulk-surface interactions which can cause long time variations in the sensor parameters [11].

6. Conclusions

1. Nanocrystalline Cu_2S thin film were prepared by simple and inexpensive spray pyrolysis technique.
2. The structural, surface morpholohy properties confirm that the as-prepared Cu_2S thin films are nanostructured in nature with cubic grains.
3. Elemental analysis shows that as prepared thin films was nonstoichiometric in nature.
4. Nanocrystalline Cu_2S thin film sensor shows a high response to H_2S at low operating temperature 150 ^oC.
5. The sensor showed good selectivity to H_2S gas against other conventional gases.
6. The Nanocrystalline Cu_2S thin film exhibits rapid response–recovery which is one of the main features of this sensor.
7. Nanocrystalline exhibits long term stability sensing performance.

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