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Gas Sensing Properties of Nanocrystalline Fiber like Structure of CdS thin films for H_2S gas detection

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Abstract : In this work, growth, characterization and gas sensing performance of fiber like structure thin films of CdS by chemical bath deposition (CBD) technique using the reaction between cadmium sulphate, thiourea and NH_3 in an aqueous solution has been reported. The films of were deposited at different pH (9, 9.5, and 10) onto glass substrate at 65 ^oC. Characterization includes a different analytical technique such as, X-ray diffaractogram (XRD), Field emission scanning electron microscope (FE-SEM) and energy dispersive X-ray analysis (EDAX). The films deposited for pH =10 was observed to be most sensitive (S = 79) to H_2S for 5 ppm at 50 ^oC. The response and recovery time is 7 sec, 12 sec respectively.
The results are discussed and interpreted.
Keywords: fibre like structure, CdS thin films, chemical bath deposition technique, gas sensor system, response and recovery time.

1. Introduction

Thin films of cadmium sulphide (CdS) films have been used in industries predominantly in solar cells [1]. The best solar cells based on Cu(InGa)Se2 (CIGS) absorbers are achieved by using a very thin (50 nm) CdS buffer layer deposited by chemical bath deposition (CBD).

Cadmium sulhide has useful properties of optoelectronics, being used in both photosensitive and photovoltaic devices. Direct band-gap CdS thin films have been the subject of intensive research because of its intermediate band-gap, high-absorption coefficient, electron affinity, low resistivity, easy ohmic contact and finally the structure. CdS thin films can be grown with α and β phase depending on the deposition conditions [2]. It is well known that α - CdS invariably grows with columar structure along the *c*-axis perpendicular to the substrate [3]. This means that there are no grain boundaries parallel to the junction which would impede the flow of photogenerated excess carriers to the grid. Reasonable conversion efficiency, stability and availability of low-cost deposition technique attracts the usage of CdS as window electrode in solar cell structure [4].

In recent years there has been growing interest in developing techniques for preparing semiconductor nanoparticles and thin films because the properties in nano form differ significantly from those of their bulk counter parts. Therefore there is much interest in physical properties of nanometer size (20-80 nm) semiconductor materials due to their novelties; their properties are different and often superior to those coarse grained polycrystalline materials and also amorphous alloys of same composition [5, 6]. In addition to increased strength, hardness, enhanced diffusivity, improved quality, roughness, reduced elastic modulus, higher thermal exapansion coefficient, lower thermal conductivity and superior soft magnetic properties [7]. Much effort has been made to control the size, morphology and crystallinity of CdS thin film.

Among various techniques that can be used for the preparation of thin CdS films such as thermal evaporation, chemical spray, electro deposition and sputtering, CBD is a simple which is also used to deposit the semiconductor for gas sensor properties. The CBD method appears suitable for large area industrial process because it is the least expensive and a low temperature method. Another advantage of the CBD technique is its ability to deposit very thin films (50 nm) in a conformal manner on a rough substrate surface. The rate of growth in CBD is controllable by pH, temperature, time of deposition and the relative concentrations of the reactants in the bath solution. The alkaline bath solution (pH > 9) normally consists of a cadmium salt, thiourea [$SC(NH_2)_2$], NH_4OH and a complexing agent such as NH_4Cl and TEA[8]

Gas sensors are important in environments monitoring, home safety and chemical controlling. Gas sensors can be manufactured using different materials, technologies and phenomena. Sensing devices should be smaller and cheaper hence research regarding sensitivity, selectivity, response-recovery time, reproducibility, cost, portability, deposition techniques, fabrication of devices, operating temperatures and gas concentration for different materials [9].

Hydrogen Sulphide (H_2S) is a Toxic and Inflammable gas, produced in sewage plants, coal mines, oil and natural gas industries. It is used in large amounts in various chemical industries, research and as process gas in production of heavy water, Therefore it is required to detect H_2S gas. The aim of this work is to present a structural, microstructure, electrical and gas sensing properties of fiber like structure CdS thin films prepared by chemical bath deposition method and demonstrates for sensing different gases and were observed to be most sensitive to H_2S at 50 ^{O}C. Phase purity and grain sizes were examined using X-ray diffraction and field emission scanning electron microscope (FESEM).

2. Experimental Details

This method allows the deposition of very thin films, of the order of a few nanometers and it is an easy and inexpensive chemical bath deposition technique. The physical properties of the chemical deposition of CdS films are dependent upon the growth parameters such as the bath temperature, the relative concentrations of the various reactants in the solution the pH value and the type of substrate [10]. The chemical bath deposition technique was used to deposit the thin films of cadmium sulphate on glass substrate. The starting materials used were cadmium sulphate and thiourea (Made: Sd-fine 99.99% purified). Triethanolamine (TEA) was used as a complexing agent. Ammonia solutions were used to optimized pH of the reaction mixture. In order to obtain good quality of thin films, following parameter were optimized such as deposition time, temperature of deposition. pH of the solution is varied (9 to 10) by addition of liquid ammonia drop in the prepared solution. The optimum value of time, temperature and pH were tabulated in Table 1.as the prepared CdS thin films samples were annealed at 200 ^{o}C for 10 min

Table 1. Optimum parameter to obtain CdS thin films

Deposition parameter	Optimum value / item
Deposition time	80 min.
pH	S1=9 , S2= 9.5, and S3=10
Concentration of precursor Cadmium sulphate, Thiourea	0.1 M
Solvent	Deionized water
Deposition temperature	65 ^{o}C

3. Characteirization and Results

3.1. Structural properties

3.1.1. X-ray diffraction:

X-ray diffraction technique (Miniflex Model, Rigaku, Japan) has been employed to identify the crystalline property of CdS thin film. Figure 1 shows the XRD pattern of as-deposited CdS thin film. The

characteristics peak of as-deposited CdS film of 2θ value corresponding to CdS planes (100), (002), (101),(102),(110) and (103) with preferential orientation plane indicated the formation of CdS.

The average crystallite size of CdS thin film samples were calculated by using the Scherrer formula,

$D = 0.9\lambda/\beta\cos\theta$ ---------- (1)
Where, D = Average crystallite size
λ = X-ray wavelength (1·542 Å)
β = FWHM of the peak
θ= Diffraction peak position.

The average crystallite size was found to be 31 nm.

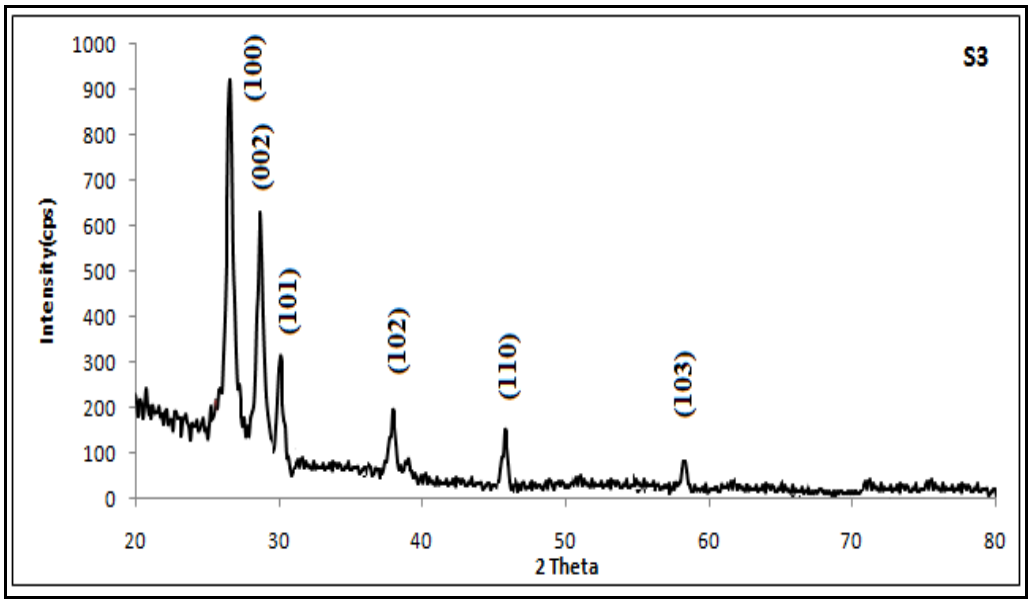

Fig. 1: X-ray diffractogram of CdS thin films.

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3.2 Surface morphology study using FESEM

The surface morphology and quantitative elemental analysis of CdS thin films were studied using field emission scanning electron microscopy (FE-SEM) coupled with EDAX (JEOL JSM – 6360 A).

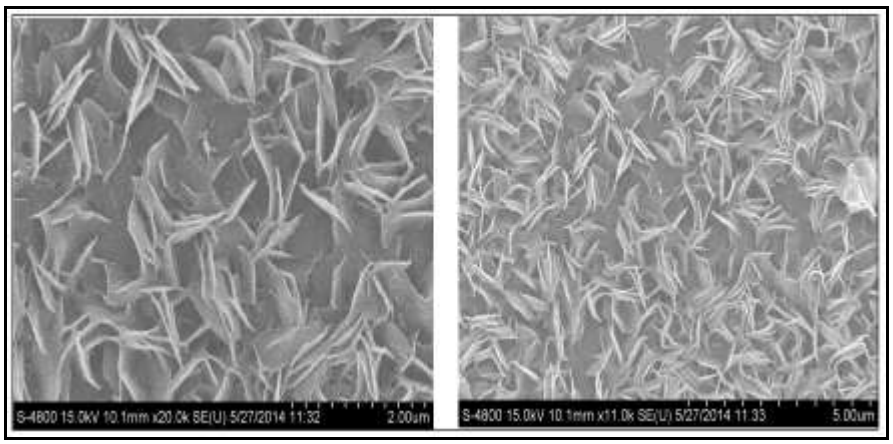

Fig.2. FESEM images of CdS thin film

FESEM imaged of CdS thin films at different magnification were represented in Fig.2.It shows the fibre like structure formation of CdS thin film. Grain size was observed to be 720 nm.

3.3 Quantitative elemental analysis (EDAX)

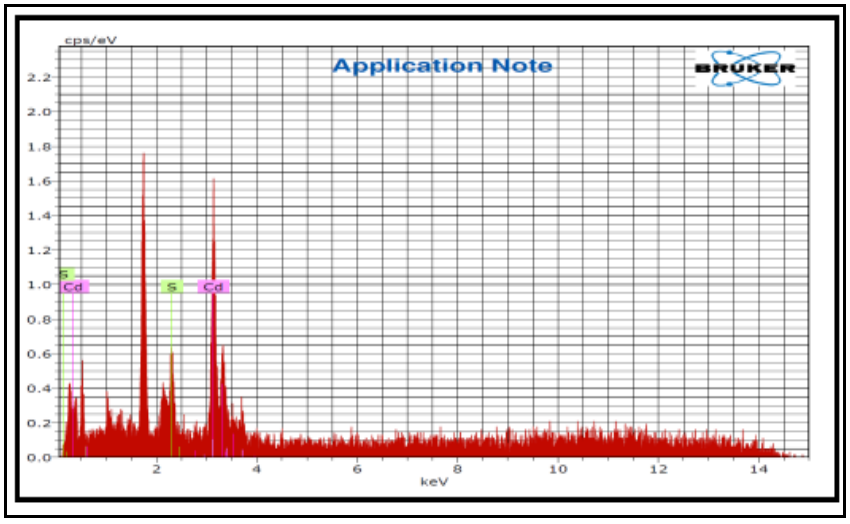

Fig. 3. EDAX of CdS thin film

The quantative elemental composition of CdS thin film was analyzed using an energy dispersive spectrometer was shown in Fig.3.

Table 2. Quantative elemental analysis as prepared CdS thin films

Element	Observed	
	wt %	at %
S	33.60	40.56
Cd	66.40	59.44
Total	100.00	100.00

Table 2 indicate that the formation of CdS thin films. We conclude that as prepared CdS thin film was nonstoichiometric in nature.

3.4. Electrical properties

3.4. 1. I-V Characteristics:

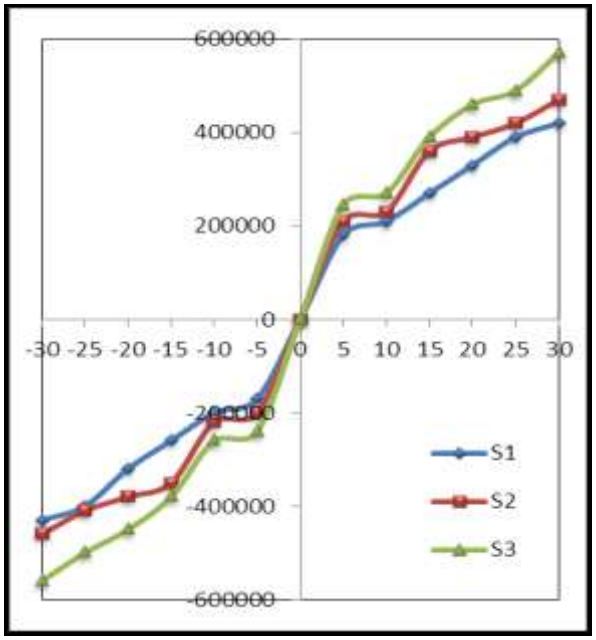

Fig. 4: I–V characteristics of thin film sensors: samples S1, S2, S3

Fig. 4 shows the I–V characteristics of samples S1, S2, and S3 observed to be nearly symmetrical in nature indicating ohmic nature of contacts. The non-linear I–V characteristics may be due to semiconducting nature of the films [11].

3.4.2. Electrical conductivity profile

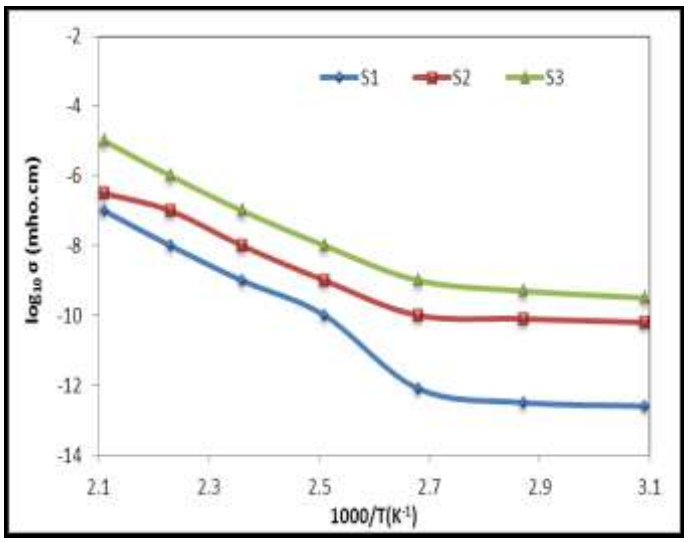

Fig. 5: Variation of log (σ) with operating temperature (◦C)

Fig.5 shows the variation of log *(σ)* with operating temperature. The conductivity of each sample is observed to be increasing with an increase in temperature. The increase in conductivity with increase in temperature could be attributed to negative temperature coefficient of resistance and semiconducting nature of CdS thin films [12].

4. Gas sensing performance of CdS thin films

4.1 Sensitivity

Fig. 6 depicts the variation of gas response to 5 ppm H_2S gas with operating temperature of a pure CdS thin film. The response to H_2S goes on with increasing the operating temperature, reaches to the maximum at 50 ^oC and decreases with further increasing the operating temperature.

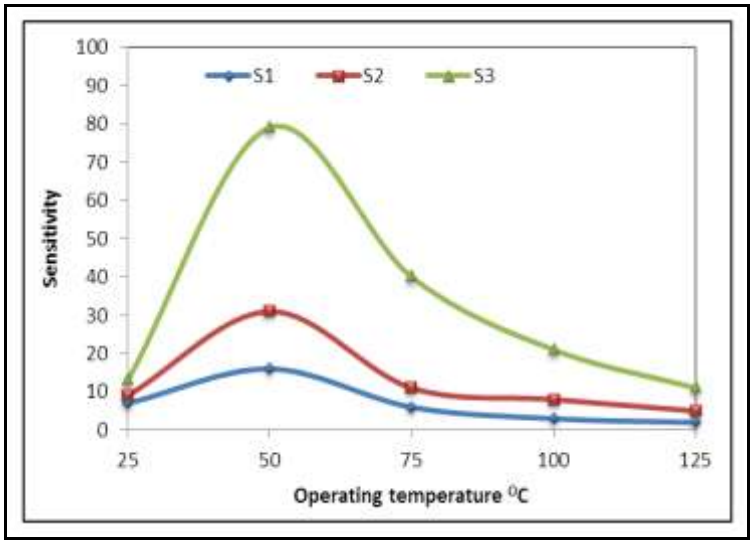

Fig. 6: Gas response of nanostructured CdS thin films with operating temperature

Response to a gas is related generally to the number of oxygen ions adsorbed on the surface of the film. If surface chemistry of the film was favorable for adsorption, response and selectivity would be enhanced [13].

4.2 Selectivity

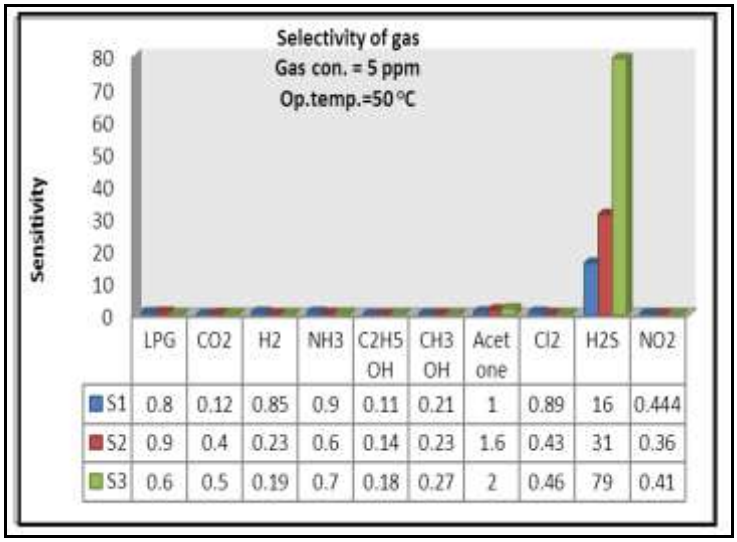

Fig. 7: Selectivity of CdS thin films for different gases

Selectivity can be defined as the ability of a sensor to respond to a certain gas in the presence of different gases [14]. Fig.7 shows the histogram of gas response for different gases The detector showed the high selectivity for H_2S gas, amongs the gases: LPG, CO2, H_2, NH_3, C_2H_5OH, Cl_2, H_2S and NO_2.

4.3 Effect of gas concentration in ppm on sensitivity

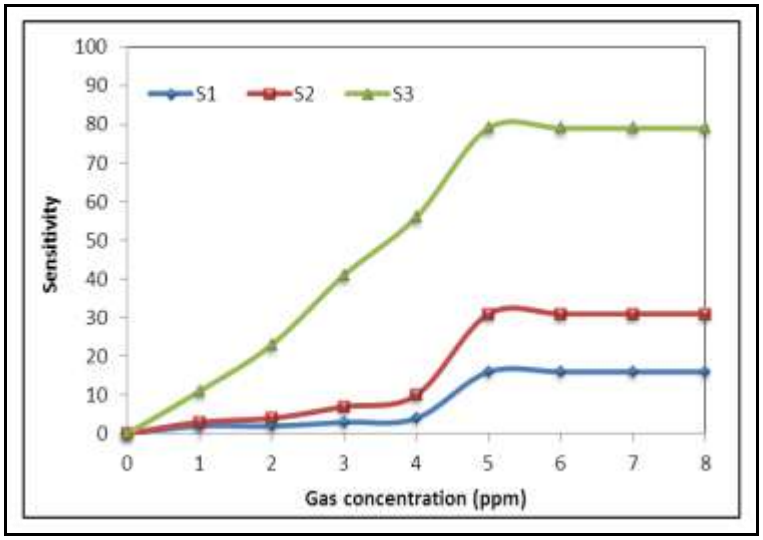

Fig. 8: Measurement profile of nanostructured thin films at different concentration

Figure 8 exhibits response to H_2S gas for various gas concentrations ranging from 1ppm to 8 ppm at 50^oC operating temperature. The response increases continuously with increasing the gas concentration. The sensor can detect the H_2S gas below its occupational exposure limit of 5 ppm.

4.4 Response and recovery of the sensor

The response and recovery time is an important parameter used for characterizing a sensor. It is defined as the time required to reach 90 % of the final change in current, when the gas is turned on and off respectively. The sensor response vs. time is shown in Fig. 9 for 5 ppm of H2S. From the plot, it is seen that the response time is 7 sec and the recovery time is 12 sec.

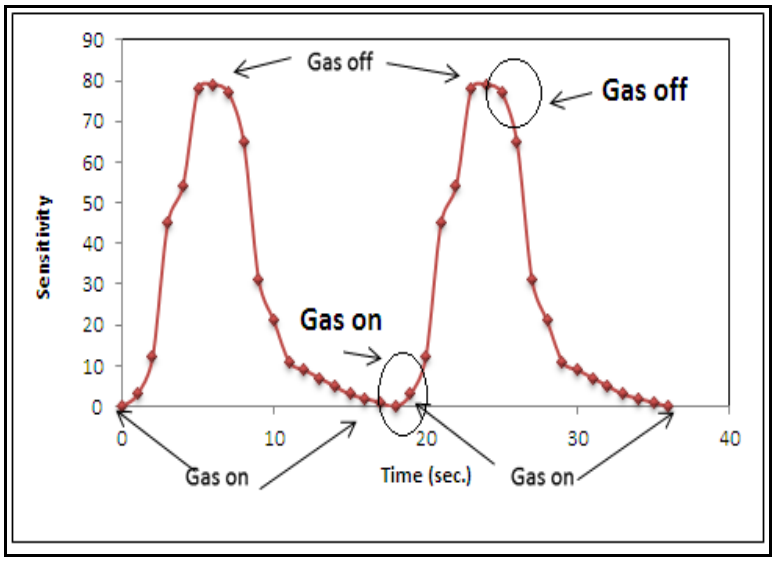

Fig. 9: Response and recovery of the sensor for most sensitive sample (S3).

This may be due to the presence of sufficient gas molecules at the interface for reaction to occur. From the same graph, it is found that for higher concentrations of H2S, the recovery time was long. This may be due to the reaction products are not leaving from the interface immediately after the reaction [15].

4.4 Stability of the sensor

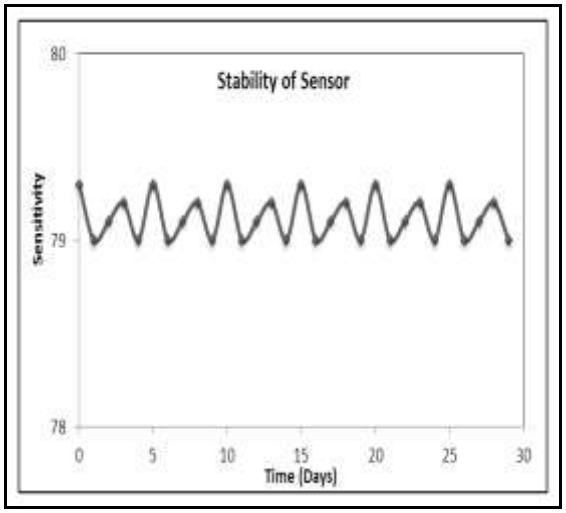

Fig. 10: Stability profile of the sensor

The stability of the CdS sensor was measured by repeating the test many times (30 days). During the test, no significant variation was observed as shown in Fig. 10. The H_2S gas sensor had prominent long term stability in atmosphere for about 30 days. The obtained results show that both H_2S gas response and electrical conductance were reproducible [11].

5. Discussion

5.1 Gas sensing mechanism

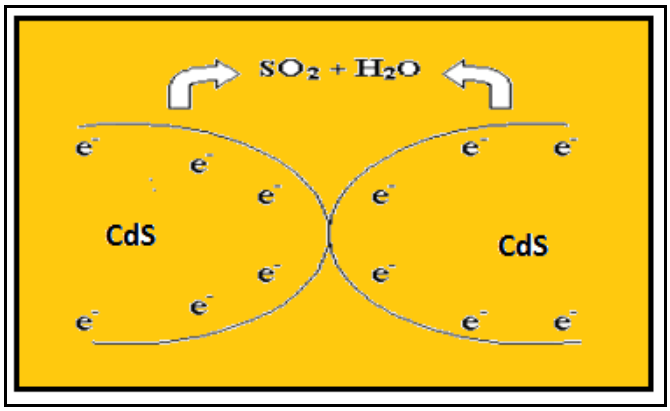

Fig. 11. H_2S gas sensing mechanism.

The gas-sensing mechanism of fibre like structure of CdS 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 CdS based sensors as shown in Fig. 11.

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

O_2 (gas) $\longrightarrow$ O_2 (ads) ------- (2)

O_2 (ads) + e^- $\longrightarrow$ O_2^- (ads) ------- (3)

$O^- + e^-$ $\longrightarrow$ O^{2-}(ads) ------- (4)

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

$$H_2S + 3\,O \longrightarrow H_2O + SO_2 + 6e \text{ ---------- (5)}$$

CdS thin film when exposed to H_2S gas, conductivity would be very low in air and very high on exposure of H_2S gas and therefore, the gas response would be highest for CdS thin film. For the CdS thin film, the low gas response at low operating temperature can be attributed to the low thermal energy of the gas molecules, which is not enough to react with the surface adsorbed oxygen species. As a result, the reaction rate between them is essentially low and low gas response is observed. On the other hand, the reduction in response after the optimum operating temperature may be due to the difficulty in exothermic gas adsorption at higher temperature as a result, the initial resistance of the thin film would be decreases and the overall change in resistance on the exposure to gas would be smaller leading to lower response to the target gas [16]. Uniform and optimum dispersion of an additive dominates the depletion of electrons from semiconductor. Oxygen adsorbing on additive (misfits) removes electrons from the additive and additive in turn removes the electron from the nearby surface region of the semiconductor and could control the conductivity.

6. Conclusions

The deposition conditions are optimized to obtain CdS thin films. The structural investigation using XRD reveals that formation of CdS thin films. XRD study confirms the formation of nano-crystalline CdS thin film. Surface morphology study reveals the formation of fiber like structure. The elemental analysis conferred that as prepared CdS thin films were nonstoichiometric in nature. Electrical conductivity increases with increase temperature of the CdS thin films, indicating semiconducting nature. The fiber like structure of CdS thin film of (Sample S3) was most sensitive to H_2S gas and exhibit the response of S= 79 % to the gas concentration as 5 ppm at the temperature of 50 ^{0}C.The sensor has good selectivity to H_2S against LPG, CO_2, H_2, NH_3, ethanol, methanol and Cl_2. The fiber like structure of CdS thin films exhibit rapid response–recovery with long term stability of sensor. Low operating temperature, highly selective and rapid response–recovery are the main features of this sensor.

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References

1. B. S. Bhadoria, Rama Shanker Yadav and Akanksha Srivastava, Optical Study of Cadmium Sulphide Thin Film Prepared by Chemical Bath Deposition, J. Pure Appl. & Ind. Phys. Vol.1 (3), 200-205 (2011)
2. E.P. Warekois, M.C. Lavine, A.N. Mariano, H.C. Gatos, J. Appl. Phys. 33 (1962) 690.
3. T.J. Coutts, Thin Solid Films 90 (1982) 451.
4. G. Morris, Proceedings of the workshop on Low Cost Electronic Materials and Solar Cells, Columbu, Srilanka, 1997, p. 35.
5. Henglein A., Small partical research; physicochemical properties of extremely small colloidal metal and semiconductor partials, *Chem.Rev.*, 89, 1861-1873 (1989)
6. Fukuka A., Sakamoto Y., Guan S., Ingaki S., Sugimoto N., Fukushima Y., Hirahara K., Lijima S. and KIkawa M., Novel templating synthesis of neckless-shaped mono and bimetallic nanowire in hybrid organic-inorganic mesoporous material, *J. Amer. Chem.Soc.*, 123, 3373-3374 (2001)
7. Lokhande C.D., Sangpal B.R., Pathan H.M., Giersig M., Tributch H., Structural studies on successive ionic layer adsorption (SILAR)-deposited CdS thin films, Appl. Surf.Sci., 181, 277 (2001)
8. A. E. Rakhshani and A S Al-Azab, *J. Phys.: Condense. Matter* 12, 8745–8755 (2000).

9. S.M.A. Durrani, E.E. Khawaja, M.F. Al-Kuhaili CO-sensing properties of undoped and doped tin oxide thin films prepared by electron beam evaporation Talanta 65 (2005) 1162–1167.
10. V. B. Sanap, B. H. Pawar, *Chalcogenide Letters*, 2009,6, 415.
11. R. H. Bari, S. B. Patil, Room temperature cigarette smoking sensing performance of nanostructured SnO_2 thin films, International Journal of ChemTech Research, Vol.8, No.3, pp 1189-1202, 2015
12. R. H. Bari, S. B. Patil, Improved NO_2 sensing performance of nanostructured Zn doped SnO_2 thin films, International Journal of TechnoChem Research, Vol.01, No.02, pp 86-96, 2015
13. R. H. Bari, S. B. Patil, Low temperature NO_2 sensing performance of nanostructured SnO_2 thin films, Archives of Physics Research, 2014, 5 (6):1-11
14. L.A. Patil, A.R. Bari, M.D. Shinde, Vinita Deo, Sensors and Actuators B: Chemical, 2010,149, 79.
15. L.A. Patil, A.R. Bari, M.D. Shinde, Vinita Deo, Sensor Review, 2010, 30, 290.
16. R. H. Bari, P. P. Patil, S. B. Patil, A. R. Bari, , Detection of H_2S gas at lower operating temperature using sprayed nanostructured In_2O_3 thin films, Bull. Mater. Sci., Vol. 36, No. 6, November 2013, pp. 967–972.

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