Studies on CdIn_2O_4 derived from CdIn_2S_4 prepared by flux method

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MS received 22 January 2007; revised 14 March 2007

Abstract. Stoichiometric and nonstoichiometric powders of cadmium indium oxide were derived from calcination of cadmium indium sulphide prepared by flux method. The materials were confirmed by XRD. Thick films of above prepared powders were prepared on glass substrates using screen printing technique. The thick films were characterized by SEM and EDAX. The electrical conductivity of CdIn_2O_4 thick films was calculated. The gas sensing performance of stoichiometric thick films of CdIn_2O_4 was tested for various gases. The films showed good response to LPG.

Keywords. Flux method; CdIn_2S_4 ; calcination; CdIn_2O_4 ; thick films; gas sensing.

1. Introduction

Cadmium indium oxide (CIO) belongs to a group of broad-band-gap semiconductors. It exhibits *fcc* spinel structure and is a *n*-type semiconductor because of the existence of specific point defects (Xiangfeng *et al* 1999a). CIO has been extensively studied due to its remarkable properties such as a low metal-like electrical resistivity, a high transmissivity in the visible range of the light spectrum and a good reflectivity in the near-IR (Haacke 1976; Miyata 1980; Budzynska *et al* 1985; Pisarkiewicz *et al* 1987). Attention being paid to transparent conductive coatings give their wide range of applications, e.g. in optoelectronics (Sihvonen and Boyd 1960; Mehta and Vogel 1972) and in solar energy conversion technology (Fan and Bachner 1976; Manifacier *et al* 1979; Frank *et al* 1982; Lampert 1982). These films can be used as transparent electroheaters, antistatic layers or transparent electrodes in solar cells. CIO also finds applications in the field of gas sensing. Szklarski *et al* (1989) reported that CIO thin films made by sputtering were sensitive to CO. Xiangfeng (2003) found that CIO thick films prepared by co-precipitation method are highly sensitive to chlorine gas. Dong *et al* (2000) found that pure CIO and Pt-activated CIO films prepared by rf reactive sputtering were sensitive to ethanol.

CIO have been prepared by different methods such as d.c. reactive sputtering (Budzynska *et al* 1985), rf sputtering (Wang *et al* 1992), chemical co-precipitation method (Xiangfeng *et al* 1999b), vacuum deposition methods (such as conventional sputtering) (Fraser and Cook 1972; Lehmann and Widmer 1975), chemical vapour deposition (Kane *et al* 1975; Major *et al* 1983), pyrosol process

(Spitz and Viguie 1970) (which is a chemical vapour deposition-related technique). It is found that there has been no report on the preparation of CIO by flux method. Hence, efforts have been made to prepare CIO powders by flux method. Flux method is a simple technique to synthesize high quality homogeneous solid solutions with a potential of up-scaling. It permits the synthesis of solid solution well below the melting point of the material (Bidnaya *et al* 1962; Scheel 1974; Patil *et al* 1998). Doping with suitable elements can be easily achieved. Non-stoichiometric and stoichiometric forms of solid solutions are obtainable. Equipments required are simple and within the financial scope of most laboratories. Screen printing is a viable and economical method to produce thick films of various materials which has been used to produce varistors, actuators, solar cells etc (Rincon *et al* 1999).

In the present study, initially we synthesize stoichiometric and nonstoichiometric CdIn_2S_4 (CIS) powders by flux method with varying proportions of cadmium precursor. As prepared powders were calcinated at 1000°C for 12 h in air in order to replace sulphur by oxygen so as to obtain finally CIO product. The effects of change in proportion of cadmium in CIS as well as CIO on the structural and electrical properties have been investigated. Also the gas sensing performance of stoichiometric CIO has been studied and reported here.

2. Experimental

2.1 Synthesis of CdIn_2O_4 powders by flux method

For the synthesis of CIO, first we prepared the stoichiometric and nonstoichiometric CIS powders by flux method using sodium polysulphide (Na_2S_x) as a flux. Na_2S_x solvents are reported as suitable fluxes to synthesize metal-

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lic sulphides. Patil and Wani (2001) reported the growth of CdS crystals using Na_2S_x as a flux. The advantages of Na_2S_x solvents are the presence of common anion and insignificant incorporation of sodium into the material to be synthesized. Na_2S_x are soluble in cold water and can be easily separated from the final product.

AR grade powders of indium sulphate, cadmium sulphide, sulphur and sodium sulphide were mixed in appropriate proportion so as to obtain stoichiometric CIS product. The mixture was ball-milled for 2 h and then transferred into 50 ml platinum crucible. The crucible was placed in kanthal wound muffle furnace having temperature control of $\pm 2^\circ\text{C}$. The furnace temperature was increased to 600°C with a heating rate of $60^\circ\text{C}/\text{h}$. This temperature was then maintained for 1 h. The Cr–Al thermocouple was used to sense the temperature of the furnace. During heating, excess sulphur got evaporated and it combined with oxygen of air and water in sodium sulphide to form SO_2 and H_2S , respectively. The furnace was then switched off to allow it to cool down to room temperature overnight. The product in the crucible was washed several times with double distilled water. Sodium polysulphide got dissolved in water and separated out easily. Final product was dried.

By using the above procedure and varying the proportion of cadmium source (CdS), two different nonstoichiometric powders were prepared.

To obtain CIO from CIS, the above prepared powders were calcinated at 1000°C for 12 h in air in order to replace sulphur by oxygen so as to obtain finally CIO required products.

2.2 Preparation of CdIn_2S_4 and CdIn_2O_4 thick films

Thick films of each composition were prepared by screen printing technique as follows:

- (i) The powder was thoroughly ground in an agate pestle-mortar using double distilled acetone to ensure a sufficiently fine particle size.
- (ii) The thixotropic paste was formulated by mixing the fine sample powder with solution of ethyl cellulose (a temporary binder) in a mixture of organic solvents such as butyl cellosolve, butyl carbitol acetate, terpineol etc. Fluidity of the paste depends upon the extent of organic part

which goes in its formulation (i.e. solid to liquid ratio) (Setty 1979). The ratio of inorganic part to organic part was kept as 75:25 in formulating paste. This particular ratio for the paste formulation was found to be thixotropic in nature and gave good line definition of the prints.

(iii) The paste was screen printed using a 160 mesh size screen and a flexible squeegee onto glass substrates in the desired patterns. The wet films were dried under IR radiation. The screen printed films were uniform and well adherent to the substrates.

(iv) The screen printed films were fired at 500°C for 30 min to remove organic binder. This high temperature firing also matures the thick film elements and bounds them integrally to the substrates.

2.3 Characterization

The structural properties of powders were studied with X-ray diffractogram (Philips PW 1730) (XRD) using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) with Ni filter in a scanning angle of range 20–80 degrees. Scanning electron microscope (JEOL JSM-6360A) (SEM) was used to examine the surface morphology of the films. Quantitative elemental analysis of the films was carried out by computer controlled energy dispersive X-ray analyser (EDAX) attached to the scanning electron microscope. The electrical conductivity of the films was measured by a two-probe method. The gas response was studied by using a static gas sensor system which is indigenous.

3. Results and discussion

3.1 Elemental composition

The at.% of Cd, In and S for CIS thick films were obtained by EDAX at three different locations on the surface of each film and average of the three is represented in table 1. Similar procedure was applied for CIO thick films and results are tabulated in table 2.

It is clear from tables 1 and 2 that samples S2 and SO2 are stoichiometric while S1 and SO1, cadmium deficient and S3 and SO3 are cadmium excess. The S1, S3, SO1 and SO3 thick films are nonstoichiometric.

Table 1. Elemental composition of CdIn_2S_4 thick films.

Sample number	At.% of elements in film					Remarks
	Cd	In	S	Cd/In	Cd/S	
S1	8.95	34.54	56.52	0.259	0.158	NS
S2	14.26	28.98	56.76	0.492	0.251	S
S3	19.12	24.71	56.17	0.774	0.340	NS

S: Stoichiometric; NS: nonstoichiometric.

Table 2. Elemental composition of CdIn_2O_4 thick films.

Sample number	At.% of elements in film					Remarks
	Cd	In	O	Cd/In	Cd/O	
SO1	8.62	33.74	54.64	0.255	0.150	NS
SO2	14.08	29.35	56.57	0.480	0.249	S
SO3	19.04	24.33	56.63	0.783	0.336	NS

Figure 1. XRD patterns of CdIn_2S_4 powders: (a) S1, (b) S2 and (c) S3.

3.2 XRD analysis

3.2a XRD analysis of CdIn_2S_4 : Figure 1 shows XRD patterns of CIS powders prepared by flux method. It is

seen in all samples that most of the peaks are corresponding to cubic spinel CIS phase (ASTM data file no. 31-229). Few additional peaks of $\beta\text{In}_2\text{S}_3$ phase (ASTM data file no. 32-456) are also present. All the samples are polycrystalline in nature.

Figure 2. XRD patterns of CdIn₂O₄ powders: (a) SO1, (b) SO2 and (c) SO3.

3.2b XRD analysis of CdIn₂O₄: Figure 2 shows XRD patterns of CIO powders prepared by calcinating CIS powders. It is clear from figure 2 that all the samples contained major peaks of CIO cubic phase (ASTM data file no. 29-258) with additional peaks of In₂O₃ cubic phase (ASTM data file no. 6-416). Only sample SO3 shows one more additional peak of CdO (ASTM data file no. 5-640). All samples are polycrystalline in nature.

3.3 Surface morphology

The SEM pictures of the samples are shown in figure 3. From the figure it can be seen that the average length of

crystals for samples SO1, SO2 and SO3 are 2.8, 6.2 and 8.2 μm, respectively. Also, it can be seen that there are some void spaces. The surface morphology of the film changes with change in Cd/In ratios. The stoichiometric film (SO2) consists of few regular shaped needle-like microcrystals indicating initiation of preferential growth along C direction. Large number of irregular shaped and some having regular shaped crystals are associated with SEM image (SO3) as shown in figure 3(c). Almost all grains having needle shapes would be due to the highest Cd/In ratio. Needle shaped microcrystals could be attributed to the optimum or above optimum concentration of cadmium in CIO.

3.4 Electrical conductivity

The electrical conductivity of CIO thick films was measured as a function of temperature in the range 250–450°C. Figure 4 shows variation of logarithm of conductivity with reciprocal of temperature. The conductivity increases

with increase in temperature indicating the semiconductor behaviour of CIO. All the films are found to be of *n*-type as observed from thermoelectric power (TEP) measurement.

3.5 Gas sensing performance

3.5a Sensing characteristics: Gas response, selectivity, response time and recovery time are the important characteristics in gas sensing.

(i) *Gas response:* Gas response is defined as the ratio of change in conductance of a sample on exposure to a test gas to the conductance in air

$$S = (G_g - G_a)/G_a = \Delta G/G_a,$$

where G_g and G_a are the conductances in the presence and absence of the test gas, and ΔG is the change in conductance.

(ii) *Selectivity:* The ability of the sensor to respond to a certain gas in the presence of other gases is known as selectivity.

Figure 3. SEM micrographs of CdIn_2O_4 thick films: (a) SO1, (b) SO2 and (c) SO3.

Figure 4. Variation of electrical conductivity with temperature.

Figure 5. Variation of gas response with operating temperature.

(iii) *Response time and recovery time*: The time taken for the sensor to attain 80% of maximum change in conductance upon exposure to gas is the response time. The time taken by the sensor to get back 80% of the original conductance is the recovery time.

3.5b Response of CIO thick films: Figure 5 shows variation of gas response of stoichiometric CIO thick films (sample SO₂) to some reducing gases with operating temperature. It is clear from figure 5 that the gas response to LPG is apparently higher than those of other gases tested. At 400°C, the gas response to 1000 ppm LPG is 415, response and recovery times are 5 and 8 s, respectively. But selectivity is poor. Selectivity could be increased by surface modification (Wagh *et al* 2006).

The response mechanism depends on the surface reaction between chemisorbed oxygen and reducing gases. The adsorption of oxygen on the film surface has two forms: physisorption and chemisorption. At elevated temperature, chemisorption is dominant. The transition from physisorption to chemisorption needs activation energy, which can be accomplished by increasing operating temperature (Dong *et al* 2000). It has been reported that the amount of oxygen adsorbed on the sensor surface goes on increasing with an increase in temperature, reaches to maximum and then decreases with further increase in operating temperature. The response to gas to be tested follows the same behaviour. When reducing gas comes into contact with the sensor surface, it gets oxidized. The rate of oxidation would be the function of the amount of adsorbed oxygen on the surface and the type of gas to be tested. The larger the rate of oxidation, the larger would be the number of electrons released, and in turn the larger would be the gas response.

4. Conclusions

Stoichiometric and nonstoichiometric CIO powders can be obtained by calcination of CIS prepared by flux method. The prepared CIO materials are of polycrystalline and *n*-type semiconductor. Surface morphology of the samples depends upon the at.% of cadmium. Stoichiometric CIO shows higher response to LPG. Moreover, the response and recovery times are faster.

Acknowledgements

Authors are grateful to Prof. S A Patil, Physics Department and Dr S R Chaudhari, Principal, Pratap College, Amal-

ner, for providing laboratory facilities. One of the authors (MDM) sincerely thanks the University Grants Commission, Govt. of India, for sanctioning a teacher fellowship. He also acknowledges Prof. A A Patil, Principal, Z.B. Patil College, Dhule, for encouragement and constant support to carry out this research work.

References

- Bidnaya D S, Obukhovskii Y A and Sysoev L A 1962 *J. Inorg. Chem.* **7** 1391
- Budzynska K, Leja E and Skrzypek S 1985 *Sol. Energy Mater.* **12** 57
- Dong Y F, Wang W L and Liao K J 2000 *Sensors & Actuators* **B67** 254
- Fan J C C and Bachner F J 1976 *Appl. Opt.* **15** 1012
- Frank G, Kauer E, Kostlin H and Schmitte F J 1982 *Proc. SPIE* **324** 58
- Fraser D B and Cook M D 1972 *J. Electrochem. Soc.* **119** 1368
- Haacke G 1976 *Appl. Phys. Lett.* **28** 622
- Kane J, Schweizer H P and Kern W 1975 *Thin Solid Films* **29** 155
- Lampert C M 1982 *Proc. SPIE* **324** 1
- Lehmann H W and Widmer R 1975 *Thin Solid Films* **27** 359
- Major S, Banerjee A and Chopra K L 1983 *Thin Solid Films* **108** 333
- Manificier J C, Szepessy L, Bresse J F, Perotin M and Stuck R 1979 *Mater. Res. Bull.* **14** 163
- Mehta R R and Vogel S F 1972 *J. Electrochem. Soc.* **119** 752
- Miyata N 1980 *J. Electrochem. Soc.* **127** 918
- Patil L A and Wani P A 2001 *Cryst. Res. Technol.* **36** 371
- Patil L A, Wani P A, Saraf K B and Wagh M S 1998 *Cryst. Res. Technol.* **33** 233
- Pisarkiewicz T, Zakrzewska K and Leja E 1987 *Thin Solid Films* **153** 479
- Rincon M E *et al* 1999 *Semicond. Sci. Technol.* **14** 390
- Scheel H J 1974 *J. Cryst. Growth* **24/25** 669
- Setty M S 1979 *Indian J. Pure & Appl. Phys.* **17** 283
- Sihvonen Y T and Boyd D R 1960 *Rev. Sci. Instrum.* **31** 992
- Spitz J and Viguie J C 1970 Fr. Patent 7,038,371
- Szklarski T, Zakrzewska K and Rekas M 1989 *Thin Solid Films* **174** 269
- Wagh M S, Jain G H, Patil D R, Patil S A and Patil L A 2006 *Sensors & Actuators* **B115** 128
- Wang W L, Gao J Y, Lao K J, Peng D L and Jiang S R 1992 *Mater. Letts* **13** 342
- Xiangfeng Chu 2003 *Mater. Res. Bull.* **38** 1705
- Xiangfeng Chu, Xingqin Liu and Guangyao Meng 1999a *Mater. Res. Bull.* **34** 693
- Xiangfeng Chu, Xingqin Liu, Yanchun Song and Guangyao Meng 1999b *Sensors & Actuators* **B61** 19