
Chapter I

INTRODUCTION

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1.1	General	2
1.2	Literature Survey	3
1.3	Statement of the Problem	8
	References	10

INTRODUCTION

1.1 General

In recent decade, the improved transparent conducting oxides are very essential for various important applications such as thin film photovoltaics, flat panel displays, solar cells, transparent electrodes, spintronics etc. Both the photovoltaic panels and flat panel displays depend on the TCO having excellent optical transmittance across the visible range of wavelengths as well as electrical conductivity. To obtain the high conductance and transmittance, high mobility is required to minimize the free carrier absorption of near infrared radiation.

High transparency as well as good electrical conductivity is achieved by selecting wide band gap metal oxide. Transparent electrically conductive films have been prepared from a wide variety of materials such as CdO, ZnO, SnO₂ etc. From many oxides semiconductors, cadmium stannate is one of the best oxide semiconductors due to its high figure of merit, mobility and carrier absorption, conductivity, thermal and chemical stability. Cadmium compounds have widely used in the metal plating, battery industry, production of automobile radiators, dyeing and printing of fabrics, electronics component manufacturing, electronics industry for photocells, light emitting diodes, curing agent in tires and in photography.

Various deposition methods such as RF sputtering [1-2], DC reactive sputtering [3-4], DC Magnetron plasmatron sputtering [5], reactive Magnetron sputtering [6], atom beam sputtering [7], Spray pyrolysis, Electrodeposition and co-precipitation methods are employed to prepare cadmium stannate in thin film form.

We have strived to deposit the Cd₂SnO₄ films by using spray pyrolysis, but for cadmium stannate requires the high decomposition temperature (>600°C). For high temperatures we require high temperature resistant substrates, so as per limitation of

spray pyrolysis it is not feasible to achieve it. Therefore, we have easily achieved Cd_2SnO_4 phase in bulk form by controlling the preparative parameters. At present looking for new gas sensing materials and developing the properties of known gas sensing materials have become an active research field. Most of these materials are metal oxides. Oxides are advantages for detections of high sensitivity, simple design, low weight and cost. Pervoskites are mixed oxides with general formula being ABO_3 , among the Pervoskites type alkaline earth stannates, Cadmium stannate has been recently considered to be a new material for gas sensors, because of its high selectivity, sensitivity and stability towards ethanol gas. Also it shows quite attractive electrical and dielectrical properties. Among all this ^{the various} methods viz. sol-gel, spin coating, electrodeposition, co-precipitation etc, co-precipitation method offers various advantages over others such as,

1. Simple and rapid for preparation of samples
2. Required precursors are cheap and easily available
3. Easy to control of size of crystallites and chemical composition or stoichiometry
4. It is isotropically homogeneous
5. It does not require any costly instrumentation.
6. Various possibilities to modify the particle surface state and overall homogeneity

1.2 Survey of Literature

Cadmium Stannate

In 1960, low cost and ternary cadmium stannate oxide material was discovered by A.J. Smith [8]. Cadmium stannate have following physical properties.

Does chemical formula is Physical property?

1	Chemical Formula	Cd_2SnO_4
2	Crystal Structure	Spinnel Cubic, Orthorhombic
3	Direct band gap	3.06 eV
4	Density	6.014 gm/cm ³
5	Melting point	602 K
6	Lattice constant	9.19 Å

Cadmium stannate is a perspective metal oxide system for various photonic solid-state devices and electrochemistry applications. It was intensely investigated starting from early seventies. There are number of patents describing protocols of preparation of Cadmium Stannate bulk materials and films under different conditions. It has been observed that oxide structures in which Cd^{2+} , In^{3+} and Sn^{4+} are found in edge sharing octahedral are excellent TCO's that transmit visible light and conduct electricity [9]. Because of these physical properties Cadmium stannate is used in many applications such as,

1. Photovoltaics , Flat panel displays [9],
2. Gas sensors [10]
3. Photo galvanic cells [11]
4. Liquid crystal displays [12]
5. Heat mirrors [13], transparent electrodes [14]
6. CdTe/ CdS based solar cells [15]
7. Larger flat screen high definition televisions [HDTV's], the larger and portable computers electrochromic windows and photovoltaic thin films [16]
8. Optoelectronics [17]
9. Wear resistant applications [18]

10. Thin film resistors [19]

11. Spintronics, magnetic refrigeration, low thermal temperature systems []

Reference ?

Nozik et.al. [20] investigated the physical properties of the material and suggested that the conductivity of this material might be due to presence of vacancies in oxygen lattice. They prepared thin films of cadmium stannate by RF sputtering from a polycrystalline Cd_2SnO_4 target onto Quartz and Pyrex substrates. The Sputtering was carried out in a chamber in which target was horizontally suspended over a substrate platform. The sputtering atmosphere was either pure Ar or a mixture of Ar and O_2 depending upon the desired conductivity of Cd_2SnO_4 films. The pressure was usually maintained at $10 - 20\mu$. A target substrate distance of $\sim 21/2$ inch was used at a power level at 600 W. Deposition rate was $\sim 0.5 \mu/h$. Film stoichiometry was checked by determining Cd/Sn ratio from X- ray emission data. Cd_2SnO_4 was bright yellow with room temperature conductivity between 10^{-1} to $10^{-3} \Omega^{-1}cm^{-1}$. A large shift of fundamental optical absorption edge towards UV was observed.

Miyata et al [21] studied cadmium tin oxide (CTO) films by RF sputtering from $CdO-SnO_2$ target in an Ar or Ar- O_2 atmosphere. They observed highest resistivity of the films of about $6.5 \times 10^{-4} \Omega$ for the film having thickness in the 2500-15000 Å. The average transmittance was 90 % over the visible region. They observed mobility of $57 cm^2 V^{-1} s^{-1}$. X ray diffraction pattern for CTO films deposited in an Ar and Ar- O_2 atmosphere exhibit a broad Cd_2SnO_4 (130) peak. Armando et al. [22] deposited the thin films of Cd_2SnO_4 by spray pyrolysis Technique. The structural, optical and electrical properties were investigated. The films show high optical transparency and electrical conductivity up to $1.1 \times 10^2 \Omega^{-1}cm^{-1}$. The films were polycrystalline in nature with the face centered cubic structure and lattice constant 9.19 Å. Agnihotri et al. [23] prepared thin films of Cd_2SnO_4 by spray pyrolysis technique. Films exhibited interference colors

and very little scattering. They reported direct energy band gap of 2.8 e V and indirect energy band gap of 2.8 eV for Cd₂SnO₄

Metz et al [24] grown CdO-SnO₂ films on corning 1737 F glass at 365°C and carrier gas ratios were adjusted until the films with 2:1 Cd/Sn ratios were obtained. Films grown for 1.5 h exhibited thickness of 970 nm. As deposited films were highly crystalline with cubic spinel structure as determined by XRD. They obtained room temperature conductivity of 2170 Ω⁻¹ cm⁻¹ with n- type carriers from the sign of hall coefficient. The corresponding room temperature conductivity was 6.64 × 10²⁰ cm⁻³ and 20.3 cm² V⁻¹s⁻¹. Transmittance greater than 85% for the 970 nm thick film was observed over the most of the visible region. Ravindra et al [25] prepared thin films of cadmium stannate by electroless deposition technique. As deposited films have 75 % transmittance in the visible range, 48 % reflectance in the IR and band gap of 2.7 eV. Resistivity of the film was 10⁻¹ Ωcm. They annealed the films in vacuum and obtained 82 % transmittance in the visible range, 62 % reflectance in the IR and band gap of 3.1 eV. By annealing the films in presence of hydrogen 87 % transmittance in the visible range, 76 % reflectance in the IR and band gap of 3.2 eV was obtained. Resistivity of the films was lowered to 10⁻² to 10⁻³ Ωcm for vacuum and hydrogen annealed films respectively.

may be
Electrolysis
(pl. check).

Tang et.al [26] prepared CdSnO₃.H₂O nano cubes via ion exchange method. After thermal treatment they obtained cubic shape of CdSnO₃. The influences of reaction conditions such as ion exchange (ultrasonic treatment) duration, solvent constitutes, surfactant, and pH on the formation of CdSnO₃.3H₂O crystals were described. Valincius et.al [27] studied electrochemical properties of nano crystalline cadmium stannate films. Cadmium Tin Oxide films were prepared by a sol-gel method analogues to that described by Dislitch et al [14]. Films were found to be n- type

degenerate semiconductors with a charge carrier's level from 10^{19} to 10^{22} cm^{-3} depending upon thermal treatment. X ray diffraction was used to reveal the appearance of cubic cadmium stannate (Cd_2SnO_4) phase at annealing temperatures above 600°C and to indicate the extent of the dominant phase above 750°C . The flat band potential (E_{FB}) for Cd_2SnO_4 electrodes determined from the capacitance measurements was found to be around $+0.25$ V at pH 7.4. Electrochemical activity towards ten redox processes in the range -0.45 V $< E < 0.45$ V was investigated and Standard electron transfer rate constants were estimated from ac impedance measurements.

Krishna Kumar [28] et al. synthesized Cadmium stannate thin films by spray pyrolysis technique using cadmium acetate and tin (II) chloride as a precursors at substrate temperatures 450°C and 500°C . XRD pattern confirmed the formation of orthorhombic cadmium stannate phase for the film prepared at substrate temperature of 500°C , whereas, films prepared at 450°C were amorphous. Film formation did not occur at substrate temperature from below 375°C . SEM images reveal that the surface of the prepared Cd_2SnO_4 film is smooth. The average optical transmittance was about 86% for the film prepared at substrate temperature 500°C with the film thickness of 400 nm. The optical band gap value of the films varied from 2.7 to 2.94 eV. The film prepared at 500°C showed minimum resistivity about 35.6×10^{-4} Ω cm.

Cardile et al [29] prepared green and yellow forms of dicadmium stannate under oxidising and reducing conditions respectively. These two forms were crystallographically similar but they were different in electric and spectroscopic properties. The g values and peak widths of EPR conduction electron resonances and Cd NMR chemical shifts were systematically larger in green materials than yellow materials consistent with the higher concentration of the conduction electrons with the former. In contrast an electrical conductance was smaller in green samples than yellow

samples probably due to scattering by the high donor concentrations in the green materials. Dark green Cd_2SnO_4 was prepared by electrochemical treatment of yellow material. Spectroscopic properties similar to other green compounds were found.

Shen et. al [30] and Zhang et al [31] studied the effect of Cd/Sn ratio and calcining temperature on phase constituents in CdO-SnO₂ system. Hui et. al. [32] prepared CdSnO₃ powders by a chemical co-precipitation synthesis method. The preparation conditions were carefully controlled. Samples were further calcinated at 500° C for 6 hr. The phase and microstructure of the obtained powders were characterized by X-ray diffraction (XRD). The product corresponded to a small particle size of 1-3 μm and high surface area of about 60-65 cm²/gm. The electrical properties, sensitivity, synthetic conditions, operating temperatures and selectivity of CdSnO₃ sensors were investigated. It was found that the sensor has good sensitivity and selectivity to vapour of C₂H₅OH. Gas sensing mechanism was studied with the X-ray and infra red (IR). Shannon et al [33] obtained single crystals of Cd₂SnO₄ and CdSnO₃ either by a flux or a high pressure method. Ronconi et al [34] deposited thin films of Cd₂SnO₄ by metal organic decomposition technique. All the films prepared have cubic spinel structure [Fd3m]. They reported resistivity of 10⁻³Ω cm, thickness of 350 nm, optical transmittance greater than 92% and band gap of 3.06 eV. Miyata et al [35] have obtained Cd₂SnO₄ films on corning substrates by dc reactive sputtering from a Cd-Sn alloy target in an Ar-O₂ atmosphere. All the films prepared have orthorhombic Cd₂SnO₄. They observed the lowest resistivity about 2 x 10⁻⁴ Ωcm and transmittance 90% over the visible region for a 6% O₂ concentration in an Ar-O₂ atmosphere. Lloyed et al [36] deposited thin films of Cd₂SnO₄ by RF sputtering. They reported resistivity of 2 x 10⁻⁴ Ω cm. Films with the low resistance values find the application in current driven devices such as DC electroluminescent panels and electrochromic displays.

They are also suitable for low voltage demisting or defrosting coatings.

1.3 Statement of problem

The synthesis of inorganic nanostructures with well defined composition, crystallinity, microstructure etc has been a vigorous research area from last few years. It is due to the fact that materials show unique and special properties from those in bulk. So it finds large number of applications in the field of gas sensing, catalysis, photography, electronics, photonics, data storage, optoelectronics, biological labeling, imaging and biosensing. As per literature, lot of work had already been carried out on different aspects of material properties of Cd_2SnO_4 . Among all ternary complex oxides, cadmium stannate has been considered to be a promising candidate for gas sensors because of its high selectivity, sensitivity and stability towards some reducing gases for high temperatures. Cadmium stannate is wide band gap semiconductor and therefore can be applied to many other applications. So it is proposed to develop the cadmium stannate by chemical coprecipitation technique. The proposed work is broadly divided into

- A) Preparation of the cadmium stannate (Cd_2SnO_4) powder
- B) Preparation of the Pellets and
- C) Their physico-chemical characterization (viz. electrical resistivity, frequency dependent dielectrical properties, Electrical conductivity etc.)

Cd_2SnO_4 samples will be prepared by chemical co-precipitation method using AR grade equimolar (0.1M) stannic chloride pentahydrate ($SnCl_4 \cdot 5H_2O$) and cadmium chloride ($CdCl_2$) as precursors in 1:2 compositions by volume in solution. The preparative parameters such as solution pH estimated using the relation between pH and concentrations of the both the solutions will be adjusted to neutral by adding

aqueous ammonia to preserve the hydroxide phases of Cd and Sn. White gelatinous precipitate formed will be filtered, dried and sintered at different temperatures within 400-1200°C in an air atmosphere. These compositions will be further mixed with polyvinyl alcohol as a binder and pressed into pellets of 15 mm diameter and 2-3 mm thickness using a hydraulic press for the further characterization.

The pellets will be characterized by using X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) techniques. The DC electrical resistivity, activation energy will also be determined. Frequency dependent dielectrical properties and Electrical conductivity of these pellets will also be studied.

References

1. G. Haacke, Appl. Phys Lett. 30 (1977) 380
2. G. Haacke W.E. Mealmaker, L.A. Siegel, Thin Solid Films, 55 (1978) 67
3. N. Miyatta, K. Miyake, S. Nao, Thin Solid Films, 58 (1979) 385
4. N. Miyatta, K. Miyake, Y. Yamaguchi, Appl. Phys. Lett., 37 (1980)180
5. S. Schilller, G. Beister, E. Buedke, Thin Solid Film, 96 (1982) 113
6. J. Dudonis, A. Jotautis, R. Naujokaitis, Elektronika ir Electrotechnika, 5 (2003) 48
7. T. Nakazawa, K. Ito, J. Appl. Phys., 27 (1988) 1630
8. A.J. Smith, Acta. Crystollogra.13 (1960) 749
9. R.D. Shannon, J. L. Gillson, R.J. Bouchard, J. phys. chem. Solids, 38 (1977).877
10. Y.L. Liu, H.F. Xing, Z.M. Liu, G.L. Shen, R.Q. Yu, Anal. Chem. Act, 527 (2004) 21
11. D. Hall, J. Electrochem. Soc, 124 (1977) 804
12. S. Schilller, G. Beister, E. Buedke, Thin Solid Film, 96 (1982) 113
13. G. Haacke, Appl. Phys Lett., 30 (1977) 380
14. G. Haacke W.E. Mealmaker, L.A. Siegel, Thin Solid Films, 55 (1978) 67
15. X. Wu, P. Sheldon, T.J. Coutts, D.H. Rose, H. Moutinho, 26th IEEE Photovoltaic
specialist conference, Anaheim, Callifornia, Sept 29 -Oct 3, 1997
16. D.S. Ginley, C. Bright, MRS Bull, 24 (2000) 15
17. L.A. Goodman, RCA Rev, 35 (1974) 613
- 18 N. Jackson, J. Ford, Thin Solid Films, 77 (1981) 23
19. L. I. Maissel, R. Glang, Handbook of Thin Film Technology McGrawHill, New
York,
1970, chap.18
20. A.J. Nozik, Phys. Rev. B, 6 (1972) 453
21. N. Miyata, K. Miyake, T. Fukushima, K. Koga, Appl. Phys. Lett., 35 (1979) 542

22. A. Ortiz, J. Vac. Sci. Technol., 20 (1982) 7
23. O.P. Agnihotri, B.K. Gupta, A.K. Sharma, J. Appl. Phys., 49 (1978) 8
24. A.W. Metz, M.A. Lane, C.R. Kannewurf, K.R. Popplmeier, T.J. Marks, Chem
 Vap. Deposition, 10 (2004) 6
25. D. Ravindra, J.K. Sharma, J. Appl. Phys., 58 (1985) 2
26. Y. Tang, Y. Jiang, Z. Jia, L. Xu, Inorganic chemistry, 45 (2006) 26
27. G. Valincius, V. Reipa, V. Vilker, J.T. Woodward, M. Vaudin, J. Electro. Soc.
 148 (2001) E-341
28. V. Krishnakumar, J. Current Appl. Phys. 9 (2009) 467
29. C. M. Cardile, J. Phys. Chem. Solids, 48 (1987) 881-885
30. T. Zhang, Y. Shen, D. Qiang, F. Huajun, J. Mater. Sci Lett. 13 (1994) 1647
31. T. Zhang, Y. Shen, R. Zhang, Mater. Sci Lett. 23 (1995) 69
32. W. X. Hui, W.Y. De, L.Y. Fang, Z. Z. Lai, Mater. Chem. Phys. 77 (2002) 588
33. R.D. Shannon, J.L. Gillson, R.J. Boucahard, J. Phys. Chem. Solids, 38 (1977) 877
34. C. Ronconi, O. L. Alves, Mol. Cryst. Liq. Cryst. 374 (2002) 275
35. N. Miyata, K. Miyake, Y. Yamaguchi, Appl. Phys. Lett. 37 (1980) 18040
36. P. Lloyd, Thin Solid Films, 41 (1977) 113