Chapter I

Introduction

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1.1 General

In recent years, the metal oxide semiconductor materials have received much attention owing to their potential applications in optoelectronic and photovoltaic devices. High transparency as well as good electrical conductivity can be achieved by selecting wide band gap metal oxides. A review of research work on luminescent materials shows that oxide materials with a wide energy band gap demonstrate a high quantum efficiency of luminescence [1-4]. In this context, oxide materials can be used as host materials for doping by rare-earth elements. The doped oxide thin films can be applied in electro- and cathodoluminescent displays as emitting medium with highly-effective emission. Cadmium oxide is a promising candidate for development of short wavelength optical devices as well as for applications in optics and optoelectronics such as transparent conducting electrodes for flat panel displays and solar cells .The spray pyrolysis technique has the advantage of low cost, easy to use, safe and can be implemented in a standard laboratory. The layered films are prepared by only spray pyrolysis technique. The properties of deposited material can be varied and controlled by proper optimization of spraying conditions easily. Cadmium compounds are used in the metal plating and battery industry. Cadmium metal is alloyed with copper in the production of automobile radiators. Cadmium chloride is used in the dyeing and printing of fabrics, in electronics component manufacture and in photography. Cadmium oxide (CdO) is used in electroplating, in semiconductors, and in glass and ceramic glazes. Cadmium sulfide is used in the electronics industry for photocells and light emitting diodes. It is also used as a curing agent in tires.

1.2 Literature survey

1.2.1 Literature survey of cadmium oxide thin films:

Cadmium oxide is one of the main cadmium compounds. It crystallizes in a cubic lattice like sodium chloride, with octahedral cation and anion centers.

1	Chemical Formula	CdO
2	Crystal structure	Cubic
3	Molar mass	128.41 g mol^{-1}
4	Density	8.150 g cm^{-3} (Crystalline form), 6.95 g cm^{-3} (amorphous form)
5	Melting point	1427 °C
6	Direct band gap	2.5 eV
7	Thermal conductivity	0.7 W m^{-1} K^{-1}
8	Specific gravity	6.5
10	Lattice parameters	a = 4.6958 Å

CdO thin film is not a popular TCO material due to its low optical band gap. However, CdO is a particularly interesting material because it is one of the semiconducting oxides with high carrier mobility, and has great potential for using in optoelectronic devices [5-13]. CdO has great technological interest due to their high quality electrical and optical properties such as photovoltaic devices [14-15], gas sensors [16], phototransistors and diodes [17] etc. R.J. Deokate et al. synthesized the device quality F:CdO thin films with n-type conductivity. The shift of the direct band gap energy to higher values has been observed with increase in F doping concentration [18]. Dewei Ma et al. have successfully prepared absolutely (200) preferential-oriented CdO crystal thin films on Si and glass substrates by dc reactive magnetron sputtering technique. He found that the film grown on Si substrate has better crystallinity than that on glass substrate. The photoluminescence (PL) measurement shows that the pure CdO film has no luminescence behavior, but it can form alloy with ZnO to realize its applications in luminescent devices [19]. J. Herrero et al. have prepared thin film materials, commonly used as window layers in polycrystalline thin film solar cells by chemical bath deposition method [20]. The refractive index of cadmium oxide thin films by spray pyrolysis method was measured by Gurumurugan et al. [21]. Structural characterization of spray deposited cadmium oxide thin film was made by K. Gurumurugan [22]. O. Vigil et al. have deposited mixed thin film oxides of cadmium and zinc with different compositions on glass substrates by spray pyrolysis. The effect of the various parameters on the growth and on the film properties was presented. He found that the band-gap values changes between those of pure CdO and those of ZnO [23]. An experimental study was made on a Se-CdO photovoltaic cell of conventional Structure to optimize the conditions during the dc reactive sputtering of the CdO layer by C.H. Champness et al. A laboratory-fabricated Se-CdO photovoltaic cell with an optimized CdO window layer was found to yield a conversion efficiency of about 2.5% under 100 mW cm^{-2} of solar irradiance and about 5% under fluorescent room light of irradiance 0.13 $mWcm^{-2}$. For a standard commercial selenium photometry cell the corresponding efficiency values were 0.3% and 3% respectively [24]. Y. Dou et al have developed a method for measuring the band gap shrinkage in degenerately doped oxide semiconductors and have applied this technique to CdO. The influence of n-type doping CdO with In or Y has been investigated by high-resolution ultraviolet and x-ray photoemission spectroscopy. It is found that core levels and valence band features suffer a shift to high binding energy due to doping. However, this shift is less than the change in the width of the occupied conduction band. This provides a direct measurement of band gap shrinkage as a result of doping in an oxide semiconductor [25].

1.2.2 Literature survey of Al doped cadmium oxide thin films

Due to stability of spray method for doping, most of the workers have studied doping effect of different materials to improve the conductivity of CdO films for solar cell application [26]. Efforts have been made, to study, the effect of dopants such as indium (In) [27], aluminum (Al) [28] etc on the structural, electrical, optical properties of CdO thin films sol- gel method. R.K.Gupta et al deposited highly conducting and transparent aluminum doped CdO thin films using pulsed laser deposition technique. The effect of growth temperature on structural, electrical, and optical properties was studied. It is observed that the film orientation changes from preferred (111) plane to (200) plane [29]. B. Saha et al were prepared CdO thin films with Al doping by RF magnetron sputtering on glass substrates at a fixed temperature of 573K and pressure of 0.1mbar in argon+oxygen atmosphere. Good crystallinity with proper cubic structure was revealed from the XRD study. XPS study for the compositional analysis shows nonstoichiometric CdO films with O/Cd ratio of 0.75. The electrical conductivity is found to increase with increase of Al concentration first, and then the conductivity decreases with higher Al concentration [30]. R.Maity has deposited Aluminum-doped cadmium oxide thin films on glass substrates by sol–gel and dip-coating method. The XRD pattern reveals the good crystallinity of CdO thin films, and also a proper cubic phase formation. SEM micrograph showed the well-faceted structure. Optical study shows the 40–85% transparency in the visible region, with a bandgap value lying in the range 2.76–2.52 eV, depending upon the Al content in the films. Room temperature electrical conductivity varies from 1.91×10^{3}

to 2.81×10^{3} Ω^{-1} cm^{-1}, with Al concentrations [31].Al-doped CdO thin films were deposited by R.K.Gupta et al. using pulsed laser deposition technique on quartz substrate. The effect of oxygen pressure on optoelectrical properties was studied. It is observed that the electrical properties of these films strongly depend on the oxygen pressure .Low resistivity (2.27×10^{-5} Ω cm) and high mobility (79 cm^{2} V^{-1} s^{-1}) is observed for the film grown under oxygen pressure of 1×10^{-3} mbar [32].

1.3 Statement of the problem

The thin films materials play an important role in many technological applications such as in microelectronic devices, magnetic storage media and surface coatings. Varity of thin film deposition techniques have been developed to get good quality thin films like Chemical bath depositions, solution growth, sol–gel technique, spray pyrolysis, dc reactive magnetron sputtering, pulsed laser deposition, and MOCVD. Amongst all the deposition techniques, spray pyrolysis is a simple, an economical method for large-area deposition of thin films. Spray pyrolysis is an effective production method lead to short production time, homogeneous particle composition, and one-step production method. A plethora of deposition techniques viz. dc magnetron sputtering, reactive evaporation, sol–gel, chemical bath and spray pyrolysis have been employed to make thin layers of CdO. Spray pyrolysis has been evolved as one of the potential technique to deposit CdO thin films.

The present work can broadly be divided into (a) preparation of thin films of cadmium oxide from aqueous and non aqueous medium by spray pyrolysis technique. (b) Preparation of thin films of aluminum doped cadmium oxide. (c) Their characterizations by various methods. CdO films will be deposited on microslide glass substrates at different temperatures using aqueous solvent by spray pyrolysis technique. The preparative parameters such as deposition temperature, concentration of the solution, thickness of film, etc. will be optimized to get good quality films of CdO and Al doped CdO. The thickness of the films will be measured using the gravimetric weight difference method using the bulk density of CdO. The X-ray diffraction (XRD) technique will be used for the structure identification and crystallite size determination. The surface morphology of the films will be studied using scanning electron microscopy (SEM). The optical properties will be studied in the visible range of spectrum using spectrophotometer. The electrical properties of oxide films will be studied by van der pauw method using silver paste ohmic contact. Then CdO films will be deposited on microslide glass substrates using nonaqueous solvent by spray pyrolysis technique. Effect of nonaqueous solvent on the properties of CdO thin films will be studied by different characterization techniques.

An attempt will be made to decrease the resistance of CdO thin films by proper doping. Aluminum will be selected as doping material. Al doped CdO thin films will be deposited at different atomic percents of aluminum by spray pyrolysis technique and characterized by different techniques.

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