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A Study of Electrical and Optical Properties of Mercury Doped Cadmium Oxide Thin Films by Spray Pyrolisis Method

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Abstract: Thin film is a two dimensional solid layer which is developed by the process of deposition of atoms or molecules or ionic species on substrate. There are different methods to deposit thin films in which one of the simplest methods is the spray pyrolysis technique. However, all basic researches on thin films by different methods are generally confined to a limited range of thickness. i.e between few A^0 and 10μm. Since, the thin film investigations are in the form of active devices and passive devices. Power supply, rectification, Amplification, sensor elements, storage of solar energy, magnetic memories.etc. SEM is used to study the surface morphology.
Keywords : Cadmium Oxide, Mercury. Thinfilm. Spray Pyrolysis, SEM.

Introduction

An extensive survey on preparation conditions for a wide variety of thin film materials is presented. The preparation of these thin films[1] and their physico-chemical properties are discussed. Thin film formation by spray pyrolysis technique is the deposition process in which a precursor solution is pulverised by means of a neutral gas so that it arrives at the substrate in the form of very fine droplets. The constituents react to form a chemical compound onto the substrate. The chemical reactants are selected such that the products other than the desired compound are volatile at the temperature of deposition. The spraying system mainly consists of spray nozzle, precursor solution, substrate heater, temperature controller and air compressor or gas propellant.

To measure precursor solution and air, liquid and gas meters are used. A vertical and slanted spray deposition arrangement with stationary spray nozzle is frequently used in this technique. To achieve uniform deposition the moving arrangements either nozzle or substrates or both have been used. Sometimes the spray assembly is mounted on a moving table and is restored across the substrates using stepping motors. The properties of the film depend upon the anion to cation ratio, spray rate, substrate temperature, ambient atmosphere, carrier gas, droplet size and also the cooling rate after deposition. The film thickness depends upon the distance between the spray nozzle and substrate, substrate temperature, the concentration of the precursor solution and the quantity of the precursor solution sprayed. The film formation depends on the process of droplet landing, reaction and solvent evaporation, which are related to droplet size and momentum. An ideal deposition condition is when the droplet approaches the substrate just as the solvent is completely removed and depending on droplet velocity and direction, a droplet will be along the surface or hover motionless[2].

Film thickness measurement

(i) Mass method (Microbalance technique)

This method depends on the increase in weight of a film due to its increase in mass. So, from the knowledge of density and the deposited area, film thickness can be evaluated from the relation[3]

$$t = \frac{W}{\rho A}$$

Where,
w = weight difference of film
ρ = density of film
A = deposited area.

The microbalance is made up of quartz material and a pan is suspended from one end of a beam by means of quartz fiber. The other end of a pan carries counterpoise. A pointer or a mirror is attached to the beam of the balance. With the increase of weight of film, the pointer moves and its displacement with reference to a fixed point can be measured with a telescope. In case of mirror, its displacement can be measured with telescope and scale arrangement.

The measurement by movement of pointer can be standardized against known weights. A deflection of the pointer will correspond to increase in weight of deposit and thus thickness is measured from the above equation. In this method, the weights of substrate and film with substrate in air and water are measured and thus area of the film and substrate are calculated from graph.

(ii) Optical method (Interferometry)

This is an important optical method by forming fringes to calculate the thickness of the film. If a monochromatic light is allowed to incident on the film normally, the interference of light occurs due to interactions of multiple reflected beams in air gap. The interference pattern is viewed through microscope[4]. The distance between the fringes of lines depends on the air gap as well as the wavelength of monochromatic light. This principle is adopted and suitably modified for the multiple beam interferometer method of measurement of film thickness[5].

The film thickness can be determined by the relation $t = \frac{b\lambda}{2a}$

Where, b = Displacement of fringes at step
λ = Wavelength of light
a = distance between consecutive fringes

These fringes displacements, which are in the form of parallel lines, occur at film edge. Film thickness can also be estimated from its absorption properties of radiation such as light, α -rays, β-rays, electron beam etc.

Resistance measurement

Four probe method

In order to measure the sheet resistance, a rectangular sample of film is to be prepared. A four terminal method is used for the resistance measurement[6]. (i.e) The number of squares between the voltage terminals is counted and R =V/I is used. It is advisable to make the voltage terminals as narrow as possible at their points of intersection with the film in order to reduce any uncertainty in counting the number of squares lying between them. The most common form of four-point probe is used.

When the probes are placed on a material of semi-infinite volume, the resistivity is given by,

$$\rho = \frac{V}{I} = \frac{2\pi}{\frac{1}{S_1} + \frac{1}{S_2} - \frac{1}{S_1 + S_2} - \frac{1}{S_2 + S_3}}$$

When,

$S_1 = S_2 = S_3 = S$

$$\rho = \frac{V}{I} \times 2\pi S$$

If the material on which the probes are placed in an infinitely thin slice resting or insulating support, the above equation becomes,

$$\rho = \frac{V}{I} \times \frac{2\pi S}{\ln^2}$$

$$\frac{\rho}{d} = R_s = 4.532 \frac{V}{I}$$

Knowing the values of V&I, the sheet resistance R_s can be calculated.

Optical absorbance measurement

The absorbing characteristics of thin film are measured using spectrophotometer in the visible range[7]. It consists of

1. Strong light source (Tungsten lamp)
2. Collimator
3. The photo cell

The photocell is placed very close to the sample holder. The whole set up however enclosed in a light proof case. In the present studies, an optical absorption of coated films for different wavelengths is studied using computer controlled Elico make spectrophotometer[8,9]. The graphs are drawn between wavelengths and absorbance along x-axis and y-axis for different mercury doped cadmium oxide films. The energy band gap is calculated by drawing tangents to the curve in the graphs.

Thin film surface study

Scanning Electron Microscope (SEM)

SEM provides a pictorial representation of the surface, to understand the nature of the surface film. Surface Morphology shows the SEM micrographs of CdO thin films deposited with different solvent volumes. The surfaces of the films are homogeneous (with no voids) and densely packed. Well-defined grains show the crystalline nature of the samples. The films deposited from solution having lesser solvent volume (30ml) has grains fused together.

The SEM image of the film coated with 40ml solvent volume depicts densely packed patches of small sized grains fused together. For the film coated with 50 ml solvent volume, circularly shaped grains having different sizes are found scattered throughout the substrate surface. Traces of few grains fused together appear on the film surface. No fused grains appear for the film coated with 60ml solvent volume. Spherical grains with well define boundaries and with almost equal size found scattered throughout the surface, confirming the improved crystalline of the film. Film morphology thus changes with solvent volume. The grain size of the films estimated from the SEM

Results and Discussion

1. Thickness Measurement

The thickness of the mercury doped cadmium oxide films of varying doping levels of mercury are measured by loss of weight method and are presented in the Table below.

Film	Molarity Ratio	Thickness μm
CdO : Hg	0.01M:0.001	3.8
CdO : Hg	0.01M:0.0025	6.8
CdO : Hg	0.01M:0.005	10.0
CdO : Hg	0.01M:0.0075	12.2

2. Resistance Measurement

Film resistance at room temperature is determined using computer controlled Keithley electro meter and four-probe set up. It is evident from the table 6.2 that the resistance of thin film formed increasing with increasing level of mercury doping.

Film	Molarity Ratio	Resistance
CdO: Hg	0.01M: 0.001	261Ω
CdO: Hg	0.01M: 0.0025	590Ω
CdO: Hg	0.01M: 0.005	1.8kΩ
CdO: Hg	0.01M: 0.0075	508kΩ

3. Optical results

The optical absorption study of the film for wavelength range 380-1000nm is done using Elico make spectro photometer. To determine direct and indirect transition , a graph $(\alpha h\gamma)^2$Vs hγ & $(\alpha h\gamma)^{3/2}$ Vs hγ are plotted respectively. The direct and indirect band gaps of the coated films are presented in the Table below

Film	Molarity ratio	Energy band gap in eV	
		$(\alpha h\gamma)^2$	$(\alpha h\gamma)^{3/2}$
CdO:Hg	0.01: 0.001	1.5	1.9
CdO:Hg	0.01: 0.0025	1.7	2.0
CdO:Hg	0.01: 0.005	1.85	2.075
CdO:Hg	0.01 : 0.0075	1.9	2.1

SEM images analysis

SEM images.

The SEM image of magnification (x 1000) of the specimen in the absence and presence of coated film are shown in fig.(a),(b). The SEM micrographs in fig.(a) as the smooth surface of the metal. This shows the absence of any products formed on the surface. The SEM micrographs of metal coated surface fig.(b) indicates that in the presence of surface film the surface coverage increases which in turn results in the formation of insoluble complex on the surface of the metal and the surface is covered by a thin layer

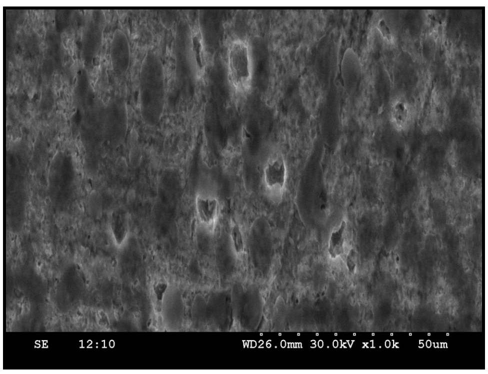

fig. (a)

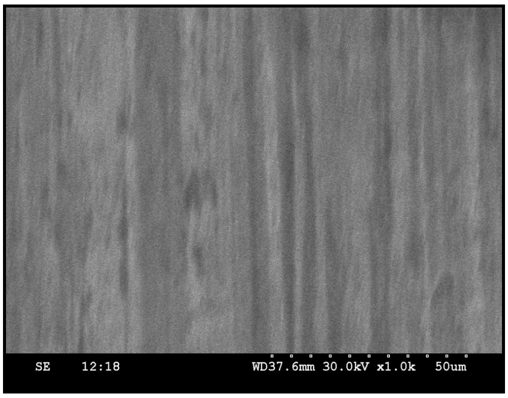

fig. (b)

Conclusion

Thin film of mercury doped cadmium oxide on glass substrate is prepared by model of Spray Pyrolisis method. Its thickness, Electrical resistance at room temperature and optical energy band gap are studied.

It has been found that as mercury concentration in cadmium oxide film increases, Electrical resistance and Energy band gap also increases. Also, the film prepared by this method is adherent with glass substrate.

The SEM images confirm the formation of thin film on the metal surface.

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