International Journal of
Scientific Research in Science and Technology (IJSRST)
Print ISSN : 2395-6011, Online ISSN : 2395-602X
International Conference on Advanced Materials
Held on 14, 15 December 2017, Organized by Department of Physics,
St. Joseph's College, Trichy, Tamilnadu, India

Characterisation of Spray Deposited MnO_2 Thin Films

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Abstract

Manganese dioxide is a low band gap, high optical constant semiconductor that exhibits ferroelectric properties. This material has in recent years had a variety of applications, particularly as an electrode, in electrochemical and electrochromic batteries, in fuel cells as well as in energy efficient device applications. Like most of the pure oxide crystals, undoped MnO_2 is normally an electrical, insulator. Manganese dioxide is prepared by spray pyrolysis technique due to simple, inexpensive and reproducible property. Complementary investigation such as X-Ray Diffraction, SEM are used to study structural and morphology of MnO_2 thin film Microstructural studies indicate that powders were crystalline in nature. It was found that grain size for the preferential orientation is in the order of nanometer.

Keywords: Electrochemical, Morphology, XRD, Thin Film.

1. Introduction

Thin films have received intensive applications after Second World War due to various technological applications. The beginning of "Thin Film Science" can possibly be traced to the observations of Grove [1] who noted that metal film formed by sputtering of cathodes with high-energy positive ions. Rapid developments in thin film technology have been spurred by the growing importance of microelectronics. "A thin film may be scientifically defined as a solid material having one of its dimension in the order of few Å to micron formed by the process of condensation of atomic, molecular or ionic species either by physical or chemical and or electro chemical process on a solid support (substrate)"

1.1. Aim of the work

The aim of the present work is to prepare MnO_2 thin film on glass substrate by spray pyrolysis method and to study its structural, optical and morphological properties.

1.2. Need of Thin Films

Different materials in the forms of thick or thin films, powder or pellet and gels are being prepared by many methods for various needs. Devices or components made in thin film form have advantages over the bulk materials because of

1. Extreme compactness and corresponding reduction in size and weight.
2. Superior performance and high reliability coupled with the low cost of production
3. Low power consumption etc.

Hence material in thin film forms are preferred much in the field of space science, solar energy utilization, high memory computer elements, sensors, micro batteries and hybrid circuits. Also transition from bulk to the thin film state may even cause a drastic change in its properties, arises because of their thickness, large surface to volume ratio, and preparative factors such as rate of deposition, substrate temperature, environmental conditions, residual gas pressure in the system, purity of the material to the deposited, inclusion of foreign matter, in homogeneity of the film, structural and compositional variations of films.

1.3. Application of Thin Films

Thin films are deposited onto bulk materials (called as substrate) to achieve properties unattainable or not easily attainable in the substrate alone. The following table divides the properties required into six basic categories and gives examples of typical application with each category.

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Examination of below table shows that the range of thin film applications is very broad in deed. Often, multiple properties are obtainable simultaneously.

S. No.	Thin Film property	Typical application
1.	Optical	Reflective /antireflective coating Interference filters Decoration (colour, luster) Memory disc (CDs) Wave guide
2.	Electrical	Insulation Conduction Semiconductor devices Piezo electric devices
3.	Magnetic	Memory disc
4.	Chemical	Barriers to diffusion against oxidation or corrosion Gas / Liquid sensor
5.	Mechanical	Tribological (wear resistant coatings) Hardness Adhesion Micro mechanics
6.	Thermal	Barrier layers Heat sinks

For, example Cr coating used on plastic parts for automobiles impart hardness, metallic cluster, and protection against ultraviolet light. The Cr coating on a plastic part achieves the functionality of the same part made from bulk metal, but at significant savings in cost and weight.

2. Preparation Techniques

Variety of thin film materials such as metals, semiconductors, insulators or dielectric etc, are prepared and for this purpose various preparative techniques have been developed [11-12]. Newer methods are also being evolved to improve the quality of the deposits with maximum reproducible properties. Any thin film deposition process involves three main steps.

1. Production of the appropriate atomic, molecular, or ionic species
2. Their transport to the substrate and
3. Condensation on the substrate either directly or chemical and or electro chemical reaction to form a solid deposit.

The techniques of thin film deposition can be classified as below.

I. Vapour phase deposition
II. Liquid phase / solution deposition

2.1. Spray Pyrolysis Technique

A large number of metallic salt solutions when sprayed onto a hot substrate decompose to yield oxide films. It was used as early as 1910 to obtain transparent oxide films. In 1960s Chamberlin et al.,extended the technique to produce sulphide and selenide films. The technique involves a thermally stimulated reaction between clusters of liquid / vapour atoms of different chemical species. Spray pyrolysis method lies some where in the regime between a thin film and a thick film technique, depending on the atom cluster size. The following are the physical, chemical aspects and growth kinetics of spray pyrolysis technique.

2.1.1. Physical Aspects

The spray pyrolysis technique involves different stages like spraying a solution, usually aqueous, containing soluble salts of the constituent atoms of the desired compound onto a substrate maintained at elevated temperatures. The sprayed droplet reaching the hot substrate surface undergoes pyrolytic (endothermic) decomposition and forms a single crystalline or a cluster of crystallites of the product. The other volatile by-products and the excess solvent escape in the vapor phase. The substrate provides the thermal energy for the thermal decomposition and subsequent recombination of the constituent species followed

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by sintering and recrystallization of the clusters of crystallites giving rise to a coherent film.

2.1.2. Chemical Aspects

The chemicals used for spray pyrolysis have to satisfy the following condition i) on thermal decomposition the chemicals in solution form must provide the species/complexes that will undergo a thermally activated chemical reaction to yield the desired thin film material and ii) the remainder of the constituents of the chemicals, including the carrier liquid should be volatile at the spray temperature. For a given thin film materials, the above conditions can be met by a number of combinations of chemicals. However, different deposition parameters are required to obtain comparable quality films.

2.2. Features of the Spray Pyrolysis Process

2.2.1. Growth Rate

The chemical nature, temperature of the substrate, and concentration of the spray solution, its additives, and the spray parameters largely determine the growth rate. The growth rates can be as large as 100 Å min^{-1} for oxide films and 50 Å min^{-1} for sulphide films.

2.2.2. Substrate Effects

In general the spray pyrolysis process affects the substrate surface. When it is not desirable for the substrate to take part in the pyrolytic reactions, neutral substrates such as glass, quartz, ceramics or appropriate oxide/carbide coated substrates are employed. In the case of certain oxide films on Si some desirable etching takes place during deposition. Metallic substrate have not been found suitable for this process.

Generally, at lower substrate temperature foggy and diffusely scattering films are obtained. High substrate temperature yields thinner, continuous, hard and spectrally scattering films. Moreover, at higher temperatures, re-evaporation of anionic species may occur, leading to metal-rich deposits.

2.2.3. Properties of Spray deposited films

In general, spray deposited films are strongly adherent, mechanically hard, pinhole-free and stable with time and temperature. The surface topography of the films is rough and the roughness depends on the spray conditions and the substrate temperature. The microstructure ranges from amorphous to microcrystalline depending on the droplet mobility and chemical reactivity of various constituents.

2.2.4. Preparation of Manganese Dioxide Thin Films

Manganese dioxide thin films have been deposited on glass substrate by spray pyrolysis technique using Analar grade salts. The salt used to prepare MnO_2 films were: manganese acetate [$Mn(CH_3COO)_2.4H_2O$], of 0.1M dissolved in 50ml of deionized water. A home made spraying system shown in figure (a) has been developed to obtain high quality thin films. It consists of i) spray gun ii) plate heater with thermostat and iii) glass chamber with exhaust system. Spray gun is made up of two co-axial glass nozzles of length 15cm.

The solution was sprayed at an angle of 45˚ onto preheated glass substrate kept at a distance of 50cm from the spray gun. Prior to deposition, the substrate were chemically cleaned. Compressed dry air at a pressure of 2 kg/cm^2 from an air compressor via an air filter-cum regulator was used as the carrier gas and spray rate of the solution was maintained at 3 ml/min. To avoid excessive cooling of substrates, successive spraying process was used

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with time period of 15 seconds between successive bursts. Substrate temperature was controlled by a chrome-nickel thermocouple fed to a temperature controller with an accuracy of ±2˚C. The temperature on top side of the substrate is measured by placing thermocouple on a reference glass substrate kept nearer to the coating substrate so as to measure the exact temperature.

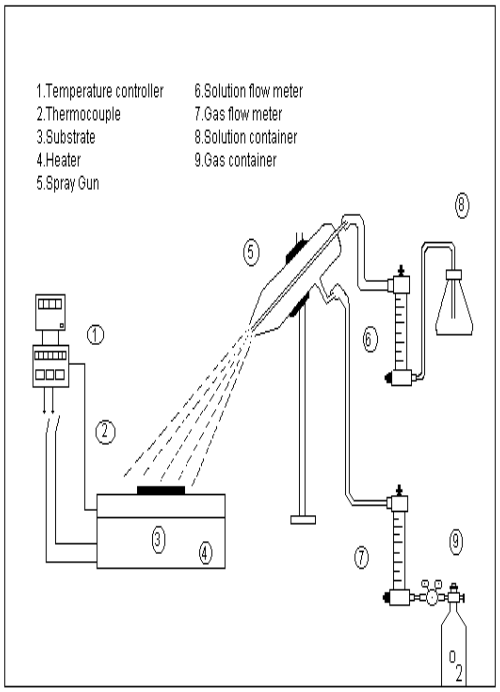

Figure 1(a). Experimental setup of Spray Pyrolysis Unit

3. Analysis Technique

3.1. X-ray Diffraction Characterization

English physicists Sir W.H. Bragg and his son Sir W.L. Bragg developed a relationship in 1913 to explain why the cleavage faces of crystals appear to reflect X-ray beams at certain angles of incidence. This observation is an example of X-ray wave interference commonly known as X-ray diffraction (XRD), and was direct evidence for the periodic atomic structure of crystals postulated for several centuries. The Braggs were awarded the Nobel Prize in physics in 1915 for their work in determining crystal structures beginning with NaCl, ZnS and diamond. Although Bragg's law was used to explain the interference pattern of X-rays scattered by crystals, diffraction has been developed to study the structure of all states of matter with any beam, e.g., ions, electrons, neutrons, and protons, with a wavelength similar to the distance between the atomic or molecular structures of interest.

3.2. Optical absorption measurements

The optical study of a solid concerns not only with the physical phenomena such as refraction, reflection, transmission, absorption, polarization and interference of light but also the interaction of photon energy with matter and the consequent changes in the electronic states. Absorption of light by different materials can induce various types of transitions such as band to band, between sub-bands, between impurity levels and bands, transitions of free carriers within a band and also resonance due to vibrational state of lattice and impurities. Absorption of light by an semiconductor or insulator takes place broadly by two process, namely, i) by raising the electrons from the valence band to conduction band ii) by exciting the lattice vibrations of the material. The later process provides information regarding the bond length of the lattice, the effective charge of the lattice atoms and the characteristic lattice vibration frequency.

The optical method provides a very simple way of finding the band gap as compared to the method using thermal excitation, which is less reliable.

3.3. Scanning Electron Microscope (SEM) studies

This is one of the most useful and versatile instruments for the investigation of surface topography, grain size, microstructural feature, etc.

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It provides a pictorial display of the surface layer with a high depth of focus greater than that possible in an electron microscope. The principle involved in imaging is to make use of the scattered secondary electrons when a finely focused electron beam impinges on the surface of the film. The secondary electron are formed by the interaction of the primary electron beam with the loosely bound electrons of the surface atoms and their emission is very much sensitive to the incident beam direction and the topography of the surface atoms. The more oblique is the surface, the greater will be the surface area from which secondary electron can emit.

The surface morphology of the films is studied using HITACHI S-3000H model shown in fig (d). It consists of an electron source, a series of lens system to produce a finely focused electron beam on the film surface and two pairs of deflection coils at right angles to each other. The emitted secondary electrons are collected in a collector, which is amplified and then fed to a CRT. As the electron beam scans the film surface there will be a change in the secondary electron emission according to the surface texture. The scanning picture observed on the CRT represents the image of the surface.

4. Results and Discussion

Large numbers of MnO_2 thin films were prepared to optimize preparation conditions. The as grown films were subjected to study further characterization. Film thickness was estimated by weighing method and verified with cross sectional view of SEM image. To investigate the microstructural detail of the film, PANalytical X-ray diffractometer (Model D/MAX ULTIMA III) using Ni-filtered CuKα X-radiation (λ = 1.54056Å), was employed with generator setting of 30mA and 40kV. Continuous scanning was applied with a speed of 10˚/min. A range of 2θ from 10˚ to 100˚ was scanned from a fixed slit type, so that all possible diffraction peaks could be detected. X-ray line broadening technique is adopted to determine microstructural details. Optical studies were carried out using Elico SL 159 spectrophotometer in the wavelength range 300 -1100nm.

4.1. Structural Analysis

Pos. [°2Th.]	FWHM [°2Th.]	h k l
22.61	0.99	1 1 0
37.12	0.84	2 0 1
52.85	0.76	5 1 0
63.17	0.72	5 1 1

Figure 1(b) shows the XRD pattern of MnO_2 films prepared at 250°C on glass substrate. The precursor salt concentration is fixed to 0.05M. The film is of polycrystalline nature and peaks match with standard JCPDS card no. 2-2169. The planes are indexed to (110), (201), (510) and (511) with cubic crystal structure. XRD lines shows broadened in their shape when compared with standard JCPDS line. The prepared MnO_2 film shows polycrystalline in nature, and hence large number of grains with various relative positions and orientations cause variations in the phase difference between the wave scattered by one grain and the others. On the other hand, lattice strain broadening is caused by varying displacement of the atoms with respect to their reference-lattice positions. A uniform compressive or tensile strain (macrostrain) results in peak shift [3] of X-ray diffraction lines, whereas a non-uniform of both tensile and compressive strain results in broadening of diffraction lines (microstrain). Thus grain size and microstrain effects are interconnected in the line broadening of peaks, which makes it difficult to separate.

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θ rad	β rad	Interplanar spacing (10^{-10}m) d=nλ/2sinθ	Microstrain (arb. Unit) S=d/(D*sqrt(12))
0.197209	0.008635	3.92	0.007
0.323769	0.007327	2.42	0.003
0.460969	0.006629	1.73	0.002
0.550983	0.00628	1.47	0.001

θ rad	β rad	Grain Size (nm) D=κλ/βCOSθ	Dislocation density (10^{15} lines/m) ρ=1/D²
0.197209	0.008635	16.1	3.81
0.323769	0.007327	19.7	2.56
0.460969	0.006629	23.0	1.87
0.550983	0.00628	25.6	1.52

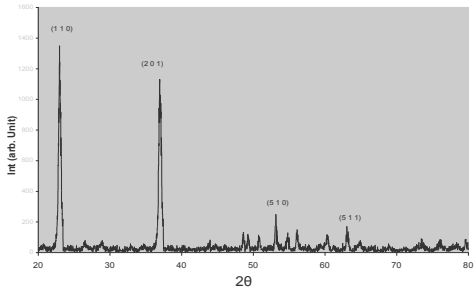

Figure 1(b). XRD pattern of spray deposited MnO_2 thin film

It is observed that as deposition temperature increases grain size of preferential orientation peaks increases from 30 to 60nm due to coalescence of grains Also microstrain found to decreases from 0.00034 to 0.00021 as deposition temperature increases. This is attributed due to decreases in defect and perfect crystalline nature.

4.2. Optical and Morphology studies

Figure 1(c) and (d) show the optical transmittance and surface morphology of the film. The smooth increase in optical transmittance indicates the good crystalline nature of the film. Also the morphology show well connected spherical shape grains.

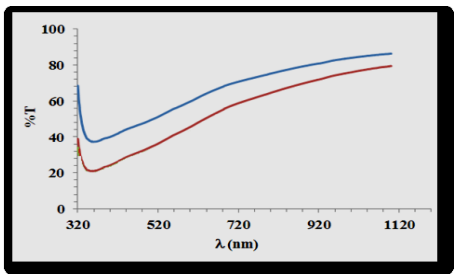

Figure 1(c). Optical transmittance of MnO_2 films annealed at two different temperature (Blue line – 350°C and Red line – 250°C)

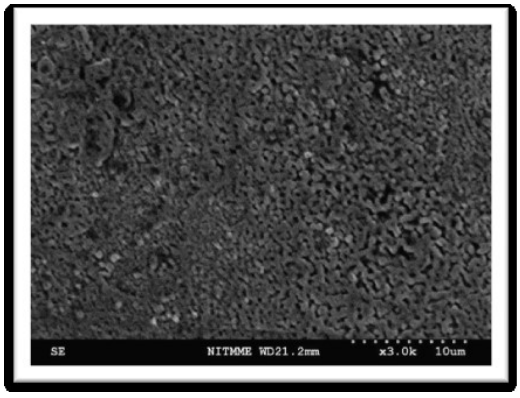

Figure 1(d). Surface morphology of spray deposited MnO_2 thin film

Conclusion

MnO_2 thin films were prepared by home built spray pyrolysis unit on glass substrate. Microstructural studies indicate that films were polycrystalline in nature. The preferential orientation is along (110) plane. X-ray line broadening technique is adopted to correct instrumental broadening effect. It was found that grain size for the preferential orientation is in the order of nanometer. Also X-ray pattern indicate a small shift in 2theta value as compared with standard value. This result is due to strain created between tin oxide nanoparticles during growth stages. Optical transparency found to be nearly 75% in the entire visible region. Scanning electron micrograph confirms the presence of grains on the

surface with size of nanometer range. Further work has to done to still minimize the grain size either by chemical or physical route.

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