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RESEARCH ARTICLE

SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF SnO_2 THIN FILMS PREPARED BY SPRAY PYROLYSIS TECHNIQUE

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Abstract

Tin dioxide (SnO_2) thin films belong to a special class of metal oxides that combine high electrical conductivity with optical transparency. Such Transparent Conducing Oxide (TCO) thin films thus constitute an important component for optoelectronic applications. Spray pyrolysis deposition is a simple and relatively cost effective technique for thin film preparation. This work consists of the synthesis of tin dioxide thin films using spray pyrolysis technique and its structural characterization. The films are prepared by automated spray pyrolysis technique. Tin oxide films were prepared for different concentrations of the precursor solution. The films formed were found to be transparent for low concentration of the precursor solution. Characterization of the prepared films using X-ray diffraction technique is presented and discussed. Spray deposited tin dioxide thin films finds a number of applications, markedly as electrode materials in solar cells.

1. Introduction

The application of thin films in modern technology is widespread. The methods employed for thin-film deposition can be divided into two groups based on the nature of the deposition process viz., physical or chemical. The physical methods include physical vapour deposition (PVD), laser ablation, molecular beam epitaxy, and sputtering. The chemical methods include gas-phase deposition methods and solution techniques. The gas-phase methods are chemical vapour deposition (CVD) and atomic layer epitaxy (ALE), while spray pyrolysis, sol-gel, spin and dip-coating methods employ precursor solutions. Spray pyrolysis is a processing technique being considered in research to prepare thin and thick films, ceramic coatings, and powders. Unlike many other film deposition techniques, spray pyrolysis is a very simple and relatively cost-effective processing method (especially when considering the equipment costs). It is an extremely easy technique for preparing films of any composition. Spray pyrolysis does not necessitate high-quality substrates or chemicals. The method has been employed for the deposition of dense films, porous films, and for powder production. Even multilayered films can be easily prepared using this flexible technique. Spray pyrolysis has been used for several decades in the glass industry and in solar cell production[1].

Liquid spray coating is probably the most versatile mechanical coating technique of the deposition techniques noted, and it is particularly well-suited for high-speed automated mass production. Deposition of very thin films is possible by judicious selection and optimization of spray machine parameters for forming “atomized” droplets and the reagent and solvent systems used to formulate the spray liquid[2].

In principle, spray pyrolysis is a simple technique where an ionic solution (prepared by starting materials in appropriate stoichiometric proportions) containing the constituent elements of the compound, is sprayed over a heated substrate
(around 300°C to 500°C). Generally the metals are in solution as their chlorides, nitrates or acetates[3,4]. Droplets impact on the substrate surface, spread into a disk shaped structure, and undergo thermal decomposition. The shape and size of the disk depends on the momentum and volume of the droplet, as well as the substrate temperature. Consequently, the film is usually composed of

overlapping disks of metal salt being converted into oxides on the heated substrate. Thin-film deposition using spray pyrolysis can be divided into three main steps: atomization of the precursor solution, transportation of the resultant aerosol, and decomposition of the precursor on the substrate[1].

The main spray pyrolysis parameters influencing the structure and properties of the deposited films are temperature of the substrate, concentration of the precursor, spray duration, spray rate etc. The substrate surface temperature is the most critical parameter as it influences film roughness, cracking, crystallinity, etc.

The wide variety of electronic and chemical properties of metal oxides makes them exciting materials for basic research and for technological applications alike. Oxides span a wide range of electrical properties from wide band-gap insulators to metallic and superconducting. Tin dioxide belongs to a class of materials called Transparent Conducting Oxides (TCO) which constitutes an important component for optoelectronic applications[5].

Tin oxide thin films have some very beneficial properties, such as transparency for visible light, reflectivity for infrared light, and a low electrical sheet resistance, making them suitable for a wide variety of applications as gas sensors, electrodes in solar cells, infrared reflectors for glass windows, transparent electrodes in electroluminescent lamps and displays etc. [6,3]. The important properties of tin oxide are high reflectivity for infrared light, high mechanical hardness, and good environmental stability.

Tin oxide has a tetragonal rutile structure. Tin Oxide (SnO_2) is a n-type semiconductor with wide energy band gap (3.7 eV)[7]. Its unit cell contains two tin and four oxygen atoms as is shown in figure 1. The tin atom is at the centre of six oxygen atoms placed at the corners of a regular octahedron. Every oxygen atom is surrounded by three tin atoms at the corners of an equilateral triangle. If tin oxide was completely stoichiometric, it would be an insulator. However, in practice, deposited tin oxide layers contain a reasonable number of oxygen vacancies, making electrons available for conduction. In applications such as solar cells, the tin oxide layers are chemically doped, for example, by fluorine or antimony, to further enhance the conductivity.[8,9,10]

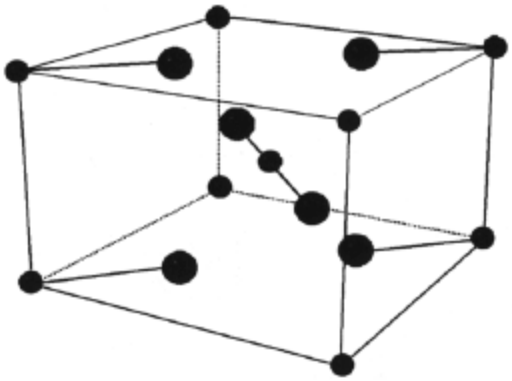

Figure 1. Unit cell of crystalline structure of SnO_2. Bigger circles represent oxygen atoms (from [9])

SnO_2 thin films have been deposited using different techniques, such as spray pyrolysis, sol-gel process, chemical vapour deposition, sputtering, and pulsed laser deposition. In the present investigation, the spray pyrolysis technique is used to prepare thin films of SnO_2 because the technique is simple and involves low-cost equipments and raw materials. Moreover, the deposition rate and the thickness of the films can be easily controlled over a wide range by changing the spray parameter[11]. The technique involves a simple technology in which an ionic solution (containing the constituent elements of a compound in the form of soluble salts) is sprayed over heated substrates. Though a number of tin salts are available for this purpose, the most suitable is one whose decomposition temperature is not very high, the decomposition reaction leading to the formation of SnO_2 is thermodynamically feasible, and no residue of the reactants is left behind in the deposited material. Keeping these in sight, an aqueous solution of $SnCl_4 \cdot 5H_2O$ as the precursor solution is used for spray pyrolysis in the present investigation. In this paper, the synthesis and characterization of tin oxide thin films is reported.

II. EXPERIMENTAL

SnO2 thin films were deposited by the CSP technique from aqueous solutions containing tin chloride pentahydrate as a precursor, using compressed air as a carrier gas. Automated spray pyrolysis equipment is used for the synthesis of thin film in this work. The schematic diagram of this setup is shown in figure 2.

Precursor solutions at different molarities (0.1M, 0.05M, 0.04M, 0.03M) are prepared. Glass slides cut in small pieces are used as a substrate on which films are grown. The films formed are of nanoparticle regime, so the substrate used should be completely dirt free. So these glass slides are cleaned using

ethanol, nitric acid and distilled water. Then these glass slides were ultrasonically cleaned. The substrates were then placed on the substrate heater of the spray equipment to provide proper heating with uniformity to films. The temperature for decomposition of tin oxide is 400 ˚C as obtained from literature. The temperature controller was set to 400 ˚C and left to heat.

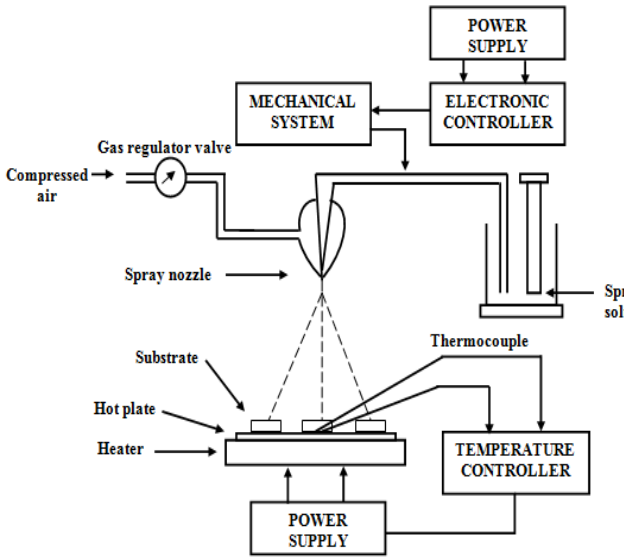

Figure 2. Schematic diagram of spray equipment

The x ray diffraction data were recorded on a Rigaku Mini-flex X ray diffractometer using CuKα radiation source (λ=1.5414 Å) at 2θ values between 20˚ and 80˚ at room temperature. The accelerating voltage of 30 KV, emission current of 20 mA and scanning rate of 0.05% were used. XRD pattern were obtained for various samples of SnO_2 prepared by changing the molarity. The XRD pattern of samples under the study can be indexed with that of SnO_2 (JCPDS-41-1445).

III. RESULTS AND DSICUSSION

Tin oxide thin films were prepared by chemical spray pyrolysis technique. The transparency of thin films so formed depends on parameters like substrate temperature and concentration of the precursor solution. Also other parameters such as spray duration, flow rate, pressure etc. also affect the features of the thin film. Transparency and thickness are two important features to be considered. Since the major application area is solar cells fabrication the thin films must possess high optical transparency and minimum thickness.

Samples of 0.1 M were prepared at 200 ˚C, 1 bar pressure and a flow rate of 2 cc/min. The spray duration was set to 1 minute. For this temperature, the films formed were thick and not transparent, since the decomposition temperature of tin oxide is about 400 ˚C. Also the pressure was too high that the substrates were not remaining stationary above the hot plate. Another set of samples were prepared at a temperature of 400 ˚C and the pressure was reduced to 0.5 bar. The films formed for these conditions were better than the first set of samples. For the next set of samples the flow rate and molarity was also reduced to 1 cc/min and 0.5 M respectively. Highly transparent films were obtained for molarities 0.5 M, 0.4 M and 0.3 M.

The XRD analysis shows peaks at 2θ values 26.6˚, 33.5˚ and 55.5˚ corresponding to the (110), (101) and (211) lattice planes. The variation in XRD with change in molarity of the precursor solution is shown in the following figure.

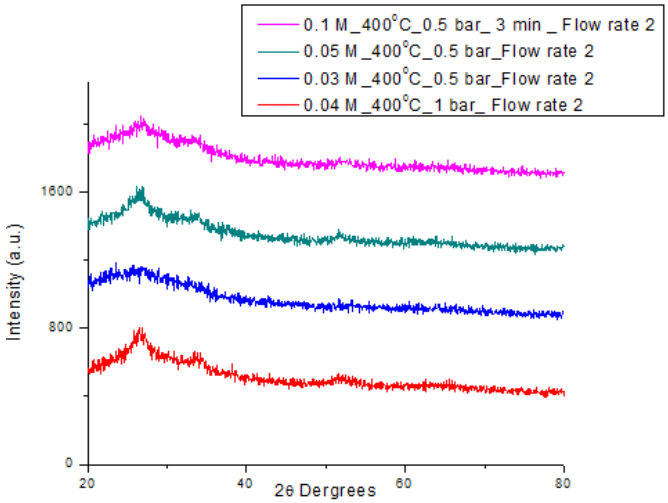

Figure 3. XRD pattern variation with different spray parameters of spray pyrolytically grown tin oxide thin films

From the above XRD patterns it is clear that molarity of the precursor solution strongly affects the structure of the film formed. With the decrease in the molarity the crystal growth is enhanced. The preferential orientation is (110) for films with molarities 0.1, 0.05 and 0.04. The intensity of the peak reflected from the plane (110) is maximum when the molarity is 0.04 M. The reflection from the plane (101) is maximum when the molarity is 0.04. The plane (211) is enhanced for the molarity 0.05. For the molarity of 0.3M there was no preferential orientation. Hence it is concluded that for molarities less than 0.3 the film formed was amorphous.

The inter planar spacing between the planes can be calculated from Bragg‘s equation,

$$2d\ sin\ \theta = n\lambda$$

$$\frac{1}{d^2} = \frac{4\ \sin^2\theta}{\lambda^2}$$

where d is the inter planar spacing, λ is the wavelength of Cu Kα radiation and θ is the diffraction angle.

The relation between lattice constants and inter planar distance for tetragonal system is,

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}$$

where h,k,l are the miller indices and a and c are the lattice constants.

The lattice constants calculated using the above equation for a molarity of 0.04 M is,

i) a= b= 4.70 Å

ii) c= 3.32 Å

CONCLUSION

Tin Oxide (SnO_2) thin films have been successfully deposited using chemical spray pyrolysis technique. The quality and properties of the films depend largely on the process parameters. Films were prepared by varying the concentration of the precursor solution. The structure of the films thus formed was found to be varying with the molarity variation.

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