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THIN FILM FABRICATION USING SPRAY PYROLYSIS TECHNIQUE

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ABSTRACT:

The field of material science and engineering community's ability to conceive the novel materials with extraordinary combination of chemical, physical and mechanical properties has changed the modern society. There is an increasing technological progress. Modern technology requires thin films for different applications. Thin film technology is the basic of astounding development in solid state electronics. The usefulness of the optical properties of metal films, and scientific curiosity about the behavior of two-dimensional solids has been responsible for the immense interest in the study science and technology of the thin films. Thin film studies have directly or indirectly advanced many new areas of research in solid state physics and chemistry which are based on phenomena uniquely characteristic of the thickness, geometry, and structure of the film. Thin films are becoming common in optical coating applications. This article describes the fabrication of SnO₂ thin film using spray pyrolysis method.

Keywords: SnO₂, Thin Film, Spray Pyrolysis

1. INTRODUCTION

During the last thirty to forty years, the dominant TCOs have been tin oxide (SnO_2) , indium oxide (In_2O_3) , indium tin oxide (ITO), and zinc oxide (ZnO). All of these materials have been mass-produced in very large volumes over a long period of time and we assert that no new TCOs have been developed until about the last 5 years. During this time, there has been substantial coordinated activity in Japan, with Minami being particularly active. Huge number of publications devoted to optimization of TCO film deposition. It must also be recognized that there is a significant difference in the performance of the best material produced in research laboratories and those produced by manufacturing companies. Although efforts have been made elsewhere to develop new TCOs with the potential for improved performance, with the exception of a modest program at NREL from about 1985 onwards, a brief program at AT&T Lucent Technologies in the mid-1990s, and a recent start-up program at Northwestern University, there have been very few concerted efforts in the United States. A TCO is a wide band-gap semiconductor that has a relatively high concentration of free electrons in its conduction band. These arise either from defects in the material or from extrinsic dopants, the impurity levels of which lie near the conduction band edge. The high-electron-carrier concentration (the materials will be assumed to be n-type unless otherwise specified) causes absorption of electromagnetic radiation in both the visible and infrared portions of the spectrum. For the present purposes, it is the former that is the more important. Because a TCO must necessarily represent a compromise between electrical conductivity and optical transmittance, a careful balance between the properties is required. Reduction of the resistivity involves either an increase in the carrier concentration or in the mobility. Increasing the former also leads to an increase in the visible absorption. Increasing the mobility, however, has no deleterious effect and is probably the best direction to follow. To achieve high-carrier mobility will necessarily improve the optical properties. In present day, thin-film solar cells, both high- and low-resistivity materials are required to achieve maximum efficiencies. The role of the high-resistivity layer may be less obvious, but it appears that it is needed to prevent shunts of the junction leading to loss in voltage and fill factor. Optimization of the properties of TCOs generally requires an elevated temperature at some point in their fabrication. For example, some materials are deposited onto very hot substrates, which are compatible with glass manufacture, but some must be deposited onto heat-sensitive substrates such as plastics. For the latter, the upper limit on deposition or annealing temperature is probably less than 200°C. In addition, in the CIGS substrate cell, zinc oxide is the last layer deposited, and its deposition temperature must be compatible with the semiconductor layers already deposited. If the TCO deposition temperature increases much above 250°C, then inter diffusion of layers can occur, thereby ruining the device performance.

Volume 2, Issue 1, January 2014 International Journal of Research in Advent Technology Available Online at: http://www.ijrat.org

2. THIN FILM DEPOSITION TECHNIQUE

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 represents a very simple and relatively cost-effective processing method (especially with regard to equipment costs). It offers an extremely easy technique for preparing films of any composition. Spray pyrolysis does not require 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 versatile technique.



Fig1. Spray pyrolysis system.

3. INFLUENCE OF DEPOSITION PARAMETERS ON THIN FILM PROPERTIES

Thin-film deposition, using the spray pyrolysis technique, involves spraying a metal salt solution onto a heated substrate. 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.

3.1. Influence of Temperature

Spray pyrolysis involves many processes occurring either simultaneously or sequentially. The most important of these are aerosol generation and transport, solvent evaporation, droplet impact with consecutive spreading, and precursor decomposition. The deposition temperature is involved in all mentioned processes, except in the aerosol generation. Consequently, the substrate surface temperature is the main parameter that determines the film morphology and properties. By increasing the temperature, the film morphology can change from a cracked to a porous microstructure. In many studies the deposition temperature was reported indeed as the most important spray pyrolysis parameter. The properties of deposited films can be varied and thus controlled by changing the deposition temperature, for instance, it influences optical and electrical properties of zinc oxide films with the lowest electrical resistivity were deposited using an aqueous solution of zinc acetate at 490°C resulting in improved crystallinity, while films prepared at 420°C and 490°C showed high transmission (90–95%) in the visible range.

Volume 2, Issue 1, January 2014 International Journal of Research in Advent Technology

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Fig2. Schematic diagram of Spray pyrolysis system

3.2. Aerosol Transport

In an aerosol the droplet is transported and eventually evaporates. During transportation it is important that as many droplets as possible are transported to the hydrochloric acid substrate without forming powder or salt particles. Sears et al. investigated the mechanism of SnO_2 film growth. The influence of forces which determine both the trajectory of the droplets and evaporation were examined and a film growth model was proposed. Gravitational, electric, thermophoretic and Stokes forces were taken into account. The thermophoretic force pushes the droplets away from a hot



surface, because the gas molecules from the hotter side of the droplet rebound with higher kinetic energy than those from the cooler side.

In the spray pyrolysis process it is desired that the most droplets strike the substrate and spread. Siefert described the transport processes in corona spray pyrolysis. Here the droplets enter a corona discharge and are transported in an electric field to the substrate. The following forces were taken into account: gravitational, Stokes, thermophoretic, electric, and dielectric forces. The author has calculated that only droplets, with a radius larger than 5 μ m, will contribute to film formation at a substrate temperature of 430°C. This value depends on the composition of the solution, the applied voltage and the deposition temperature. The solvent is entirely vaporized in the smaller droplets that will consequently lead to powder formation. However, the authors have not considered formation of hollow particles during the transportation. The aerosol droplets experience evaporation of the solvent during the transport to the substrate. This leads to a size reduction of the droplet and to the development of a concentration gradient within the droplet. The precursor precipitates on the surface of the droplet, when the surface concentration exceeds the solubility limit. Precipitation occurs due to rapid solvent evaporation and slow solute diffusion. This results in the formation of a porous crust and subsequently hollow particles, which are not desired because they increase the film roughness.



Volume 2, Issue 1, January 2014 **International Journal of Research in Advent Technology** Available Online at: <u>http://www.ijrat.org</u>

3.3. Decomposition of Precursor

Many processes occur simultaneously when a droplet hits the surface of the substrate: evaporation of residual solvent, spreading of the droplet, and salt decomposition. In the lowest temperature regime (process A) the droplets plashes onto the substrate and decomposes. At higher temperatures (process B) the solvent evaporates completely during the flight of the droplet and dry precipitate hits the substrate, where decomposition occurs. At even higher temperatures (process C) the solvent also evaporates before the droplet reaches the substrate. Then the solid precipitate melts and vaporizes without decomposition and the vapour diffuses to the substrate to undergo a CVD process. At the increasing substrate temperature highest temperatures (process D) the precursor vaporizes before it reaches the substrate, and consequently the solid particles are formed after the chemical reaction in the vapor phase.



The quality and properties of the films depend largely on the process parameters. The most important parameter is the substrate surface temperature. The higher the substrate temperature, the rougher and more porous are the films. If the temperatures are too low the films are cracked. The deposition temperature also influences the crystallinity, texture, and other physical properties of the deposited films. The precursor solution is the other important spray parameter, which affects the morphology and the properties of the deposited films. In addition, the film morphology and properties can be drastically changed by using various additives in the precursor solution.

4. CONCLUSION

In this study, we showed how thin films could be successfully deposited by the low-cost chemical spray pyrolysis method in air. Spray pyrolysis technique is a cheap and easy method to prepare thin films.

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Volume 2, Issue 1, January 2014 International Journal of Research in Advent Technology Available Online at: http://www.ijrat.org

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