Review on importance of intermittent spray for SPTD and its automation

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In thin film technology the Spray Pyrolysis Thin film Deposition (SPTD) method of thin film preparation being considered in research to prepare thin and thick films, ceramic coatings, and powders [1] for many decades. It's a versatile and effective technique to deposit metal oxide films and even multilayered films. Thin films are used in different applications like Solar cells, optoelectronics, sensors etc. It is a very simple and relatively cost-effective processing method (especially with regard to equipment costs). In this paper the importance of intermittent spray and its economic automation using microcontroller are discussed in detail. This in turn helps to prepare good thin film materials for various applications.

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1. Introduction

The SPTD is essentially the same film processing technique as so-called pyrosol technique, in which a source solution is sprayed on a heated substrate to be deposited as films. Here, a source solution is atomized, small droplets splash and vaporize on the substrate, and leave dry precipitates in which thermal decomposition occurs [1]. The SPTD has the advantage that thin film and the multilayer thin film formation are possible. This simple SPTD may be used to fabricate good quality thin films. The quality (better crystallinity, decrease in grain size, decrease in resistivity and lower defect density) and properties of the films depend largely on the process parameters [1,15]. The most important parameter is the substrate surface temperature [1]. This temperature maintenance is achieved with the help of intermittent spray [1,5]. In this paper the importance of intermittent spray [1,5] and its automation are discussed in detail.

2. Review on importance of intermittent spray

In spray pyrolysis thin film deposition technique a spray of compressed air is released from its nozzle. Then, the carrier gas carrying the precursors is heated when it is passing through the high temperature zone and reaches the substrate. In spite of prefixed high temperature in the substrate and also at the atmosphere surrounding it, the sprayed solution in the form of mist along with carrier gas mainly decreases the temperature of the substrate. It also decreases the temperature of the surroundings region where the aerosols travel through to reach the substrate. The rate of fall of temperature occurs high, when a continuous spray is done. Hence, in some of the reported research papers it has been stated that an intermittent spray was preferred in the spray coating process for getting a good thin film material formation [4,6,7,8,9,10,11,12]. In the time gap between the two sucessesive sprays of a series of sprays the substrate temperature (T_s) and the air medium above the substrate are restored to its initial levels of preferred temperature.

Some of the main improvements noticed in thin film quality in intermittent spray with respect to continuous spray are in terms of better crystallinity (XRD analysis) [19], Higher values of texture coefficient (TC), decrease in grain size, decrease in resistivity and lower defect density [4],[1],[2], [3].

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 [30]. For a taken chemical solution as the source material for spray pyrolysis the resulting thin films especially for optoelectronics applications can be improved by implementing an optimized intermittent spray.

In the research work of C. M. Mahajan, M. G. Takwale [4], they have made an attempt to maintain substrate temperature constant by obstructing the spray after regular interval of 2 minutes. The aluminum blade fan was used below the spray nozzle to obstruct the spray. The effect of continuous and intermittent spray on structural and optoelectronic properties of ZnO films was studied using different characterization techniques viz. X-ray diffraction (XRD), four probe method, UV–VIS spectroscopy, Scanning Electron Microscopy (SEM) etc.

In their work spray was paused after regular interval in order to reduce the drop down in temperature during continuous spray. The deposition temperature (450 ^{o}C) was kept constant by obstructing the spray for 60, 120 seconds duration, after regular intervals of 2 minutes. After the Completion of deposition process films were kept on the heater at the deposition temperature for 15 min in order to provide sufficient time and temperature for recrystallization.

From the low angle XRD of ZnO films prepared by continuous and intermittent stages showed that all films are polycrystalline in nature having hexagonal wurtzite structure with most preferred orientation along c-axis (0 0 2) plane according to ASTM standards [28]. As a result of increase in spray obstruction time the width of (0 0 2) peak increases and grain size decreases (band gap energy increases). Higher values of texture coefficient (TC) (0 0 2) for films synthesized by intermittent spray indicates an improvement in the structural order. This improvement was being attributed to better crystallinity and lower defect density because of steady deposition temperature during intermittent spray [29]. The lowest resistivity was reported for the obstruction period of 60 seconds duration.

In the research paper by Anca Duta et al synthesis of the nano structured TiO_2 layers that can be used for solid state solar cells is described. Spray Pyrolysis Deposition is used for obtaining the layers and the cell. They have reported that the best response was for the solar cell with TiO_2 thin films deposited with 20 numbers of sprayed sequences and subsequent annealing. It showed that a record of more number of sprayed sequences is needed to get a desired result.

E. Elangovan et al [6] had prepared a $SnO_{2:}$ F thin film from $SnCl_2$ $5H_2O$ as source material. The author has reported that there was an improvement in the thin film transparency and lower resistance value due to the shorter spray duration and longer spray interval employed in his study. This has resulted in complete decomposition of the precursor and hence continuous, dense and pore free films were achieved [6]. A similar explanation was also reported by B. Elidrissi & et al [7]. That is improvement can be attributed to better crystallinity and lower defect density because of steady deposition temperature during intermittent spray [7]. Elidrissi et al had studied SnO_2 films deposited at the spraying times t = 60s and t =240s were characterized by the authors. The respective thicknesses were 612 nm and 980 nm. The deposition time barely changed the direct optical band gap, whereas the deposition time changed the optical constants (refractive index, extinction coefficients, dielectric constants and optical conductivity), and Urbach energy values of the films. The (E_d) dispersion energy of the amorphous films was determined for the deposited films and reported as increasing with increasing deposition time. The M_{-1} and M_{-3} optical moments of the amorphous SnO_2 thin films increased with increasing deposition time [8].

By increasing the spraying time, there was an effect on the variation of optical constants. This variation was discussed in terms of defects present in the composition. During the film formation some defects may form, so, such defects produce localized states in the band gap of films. The presence of high concentration of localized states in the band structure is responsible for the variation of all optical parameters.

Hence, the properties or requirements of a Transparent and conducting oxide (TCO) thin films by spray pyrolysis with necessary optical parameters for different applications may be attempted by optimizing the time of spray. The developed low cost almost automatic microcontroller assisted thin film coating has adjustable intermittent spray time. Hence, such thin film coating becomes hassle free operation for a required number of intermittent sprays.

Masayuki Okuya & et al [9] had made the Dye-Sensitised solar cells by spray pyrolysis deposition technique. Layers of thin films were coated by SPTD method. In that an intermittent spray deposition was reported for making SnO_2:F thin film as the transparent conducting oxide (window) layer. It was prepared from di-n-butyltin (IV) diacetate ethanol solution with ammonium fluoride as an additive. It was reported that the sprayed mist cooled down the substrate hence, an intermittent spray was done to restore the substrate temperature.

Dwight R. Acosta et al [12] had studied the Titanium dioxide thin films. In that they have studied the effect of the preparation method in their photocatalytic properties. In their experiment A solution of alcoholic titanium (IV) oxide acetyl acetonate of 0.08 M concentration was prepared and sprayed onto the heated substrates (300, 350, 400, and 500 ºC). The spraying period of 1 second was followed by an interruption of 30 seconds to avoid excessive cooling of the substrate during the spray. Anatase structures of TiO_2 were reported for the films deposited at 400 and 450 ºC. Amorphous nature was present in the films deposited at substrate temperatures below 350 ºC.

The understandings out of the above mentioned research works shows that, it requires very close monitoring of the duration of spray, number of sprays, rate of chemical sprayed, temperature of the substrate and motion of the substrate if required. In a SPTD temperature of the substrate is fixed and a thermostat circuit maintains a constant temperature of the substrate. A thermocouple senses the temperature of the substrate and according to the temperature changes the corresponding current is fed to the heating coil to maintain constant heating to the substrate. This is independently does its job. An intermittent spray helps to ensure that the thin film growth happens in the user defined substrate temperature. It also helps to make the sprayed mist to pass through the necessary temperature zone above the substrate, so that the sprayed mist can under go vaporization and get deposited on the substrate. There is an optimized setting of above said parameters is needed in SPTD for the sprayed mist to undergo transitions in-between the fixed spray nozzle & substrate.

The intermittent spray helps all along the coating process to repeat this process for reproducibility of the thin film formation. That is the continuous spray alters the thermal layer zones inside the chamber. Since the continuous spray makes reduction of heat in the chamber and on the substrate quickly. Hence, intermittent spray helps to restore the temperature zone optimum for the next batch of spray mist to undergo the same deposition treatment. It is understood in detail in the reported research work by Eui-KyungOh and Sun-Geon Kim [10]. They have [10] studied the flow and temperature fields of the fluid phase in the region between the nozzle and substrate which were calculated numerically. Particle trajectories and particle evaporation were also simulated numerically by them. The evaporation of the aerosol particles occurred so abruptly that the aerosol-existing region has a clear boundary. The extent of the region was found to be a determining factor in the film deposition, which characterizes the process of the chemical aerosol deposition. Hence, optimum ventilation helps to avoid air turbulence above the substrate and helps to make good thin film deposition. Due to this a ventilator is incorporated in this project.

Eui-KyungOh et al [10] had studied experimentally and theoretically the formation of an inorganic film by chemical aerosol deposition. Carrier gas flow rate, nozzle-to-substrate distance and substrate temperature were chosen as major process variables. The experimental work has been carried out to find their effect on the deposition efficiency, film thickness and its distribution. Both the deposition efficiency and film thickness increased with the carrier gas flow rate and substrate temperature but decreased with the nozzle-to-substrate distance. They have used a spray time of 2 min. The carrier gas flow rate increases the rate of deposition [10] but by continuously doing so the quality of the thin film formation is not to its full potential [10]. It can be improved by intermittent spray even at higher gas flow rate.

3. Necessity of an adjustable timer device for intermittent spray

The rate of release of spray solution and solvent used (easily vaporizable or not) for dissolving precursor for each material can vary the rate of cooling of the substrate temperature. As per the requirement the intermittent spray time should be user defined for different types of thin film preparations. Hence, a fixed timer device won’t serve the purpose. In this scenario a microcontroller allows to go for preferred time of spray, pause of spray for a required number of coatings. It replaces use of a computer aided device at a low price. At the same time the out put of this microcontroller is synchronized with other operations involving with SPTD that can enhance the coating process, viz. Ventilator, constant speed motor for moving the substrate. That is at the time of spray the ventilator (exhaust) sends out the blown out carrier gas. Ventilation is giving room for the fresh aerosols to target the substrate. It avoids air turbulence above the substrate. If, ventilation happens only at the time of spray it will help to make good thin film coating by the way of avoiding air turbulence. When, an intermittent spray is done during the break time (pause spray) the ventilator is stopped, in turn it helps to build a stationary air medium to get heated. This gives the required thermal energy for the aerosols to absorb and gradually vaporize before it splashes the substrate [10].

4. Role of computer and microcontroller in SPTD

In a research work by M. O. Abou-Helal and W. T. Seeber [11] a novel spray pyrolysis setup was designed and assembled to fabricate TiO_2 thin films in the nanometer range thickness. The system developed by them was almost totally computerized, to control all the experimental parameters and to ensure the reproducibility. The computer controlled substrate movement was also provided to fabricate homogeneous and large area films. Most of these are controlled by a computer. Using micro controller the substrate movement is also done using a stepper motor [11].

5. Automation of intermittent spray in pyrolysis:

Instead of using a dedicated computer for spray control and for controlling the moving substrates for making homogeneous or nano thickness [11] thin film, this novel microcontroller aided SPTD itself can do the job. A microcontroller is designed in this regard and used successfully for making thin films for Dye Sensitised Solar Cell (This will paper will be published elsewhere). A novel inclined substrate holder [15,13], its rotation [14] and ventilation of coating chamber were incorporated

6. Conclusion

In spray pyrolysis thin film deposition technique the intermittent spray has advantages over the continuous spray process. It has been conclusively proven in the discussed review of research papers. Thus the optimized intermittent spray will yield good quality thin films for various applications. The automation of this using an economic microcontroller makes it an easy option to do research for the fabrication of good thin films. Small scale productions of thin films for different devices are possible by using this automated intermittent spray device.

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