THIN FILM DEPOSITION BY SPRAY PYROLYSIS TECHNIQUES

DR. VINAY KUMAR SINGH
Department of Physics, Raja Singh College, Siwan, Bihar, India, Pin-841226.

ABSTRACT: *In this research paper an intensive reviews of thin film and spray paralysis techniques has been studied. A thin film is a layer of material ranging from fractions of a nanometer (monolayer) to several micrometers in thickness. The prime requisite for getting sensible quality thin film is that the optimization of propaedeutic conditions viz. substrate temperature, spray rate, concentration of solution etc. This is often the foremost crucial parameter because it permits management over the scale of the droplets and their distribution over the preheated substrates. The consequences of precursor, dopants, substrate temperature, post tempering treatments, concentration etc., on the physico-chemical properties of those films are given likewise. The properties of the thin film will be simply tailored by adjusting or optimizing these conditions that successively are appropriate for a specific application. The key challenges of spray paralysis are control over the morphology and composition of product particles. It has been widely applied in the past few years.*

Keywords: Thin films, CVD, PVD, SPT, Deposition, Parameters, Conditions, Substrate, Applications, etc.

I. INTRODUCTION

The spray paralysis technique is a wonderful method in material science. A simple and inexpensive method of preparing thin and thick films, ceramic coatings, and metal and metal oxide powders in large scale is spray paralysis. Any element can be easily doped in the required ratio via solution medium in this method. It is a simple and cost-effective processing method in which different types of materials can be deposited into thin film form. Spray paralysis is a thermally stimulated reaction. The main components of spray paralysis equipment are an atomizer, precursor solution, substrate heater and a temperature controller. The atomizer may be an air blast in which liquid is exposed to a stream of air or ultrasonic frequencies which produce short wavelengths or electrostatic in which liquid is exposed to a high electric field. In spray paralysis, the aqueous solution containing soluble salts of the ingredient atoms of the needed compound is sprayed on to the heated surface of the substrate in which endothermic decomposition takes place and results in single crystallite or a cluster of crystallites of the necessary compound is formed. Initially, the necessary chemical reactants are selected carefully so that when they, in solution form are sprayed on the heated surface, the other undesired chemical products and the excess solvent should be volatile at the temperature of deposition. The thermal energy needed for the thermal decomposition and also the recombination of the species taking part in the combination after sintering and recrystallization of the crystal clusters, is supplied by the heated substrate. In spray paralysis, the aqueous solution containing soluble salts of the ingredient atoms of the needed compound is sprayed on to the heated surface of the substrate in which endothermic decomposition takes place and results in single crystallite or a cluster of crystallites of the necessary compound is formed. Initially, the necessary chemical reactants are selected carefully so that when they, in solution form are sprayed on the heated surface, the other undesired chemical products and the excess solvent should be volatile at the temperature of deposition. The thermal energy needed for the thermal decomposition and also the recombination of the species taking part in the combination after sintering and recrystallization of the crystal clusters, is supplied by the heated substrate.

II. SPRAY PYROLYSIS TECHNIQUE

The paralysis means the decomposition of chemical compounds or solutions under the action of heat at very high temperature. Actually, paralysis word is originated from *pyro* means (heat) and *lysis* means (breaking). Thus, *pyrolysis* means change under the action of heat. The breaking of part of complex molecule into simple units by the use of heat is called paralysis. It possesses many advantages, such as low processing temperature, high homogeneity and purity of products, and so on. The chemical spray paralysis technique (SPT) has been, throughout last three decades, one amongst the most important techniques to deposit a large type of materials in thin film kind. It possesses many advantages, such as low processing

temperature, high homogeneity and purity of products, and so on. The paralysis is a particular type of CVD that takes place by thermal decomposition of volatile components on the substrate. In the thermal decomposition, the substrate is normally heated above the decomposition temperature and reactant gases flow over the hot substrate, decomposition into films or coatings. The spray process involves spraying of solutions or natural oils or carbon precursors as a oils of various constituents atoms of desired compounds, elements, on the heated substrate that is maintain at elevated temperature. The spray of very fine droplets of solution filled in the spray-gun is achieved by the spray- nozzle with the help of carrier-gas. A schematic block diagram of a spray paralysis arrangement is shown in Figure 2.

In short, spray paralysis needs the following steps:

- **Transforming liquid precursor or solution of precursor in to micro sized droplets**
- **Making solvent to evaporate**
- **Allowing solute to condense**
- **Making the solute to decompose and react**
- **Sintering the solid particles**

III. TYPES OF SPRAY PYROLYSIS TECHNIQUES

Some new and modified advanced spray atomization, Spray Paralysis technique are given below

(i) Electrostatic spray paralysis.
(ii) Corona sprays paralysis.
(iii) Microprocessors based spray paralysis.
(iv) Ultrasonic nebulizer atomization.
(v) Improved spray hydrolysis.

IV. DEPOSITION TECHNIQUE OF SPRAY PYROLYSIS

A number of techniques have been examined in search for the most cheapest and reliable method of producing the thin films. An owing to their reliability, simplicity, and an inexpensiveness, chemical techniques has been studied more extensively for the preparation of thin films. Moreover, they facilate materials to be designed on a molecular level. But spray paralysis technique is supposed to be one of the cheaper and less expensive technique or methods for the preparation of thin films. Modern day technology requires thin films for variety of applications. There are various techniques by which one can deposit thin films. Thin film deposition techniques can be broadly classified as follows; The choice of the particular method depends on several factors like material to be deposited, nature of substrate, required film thickness, structure of the film, application of the film etc. Among the methods mentioned above, solution spraying on hot substrate (spray paralysis) method is most popular today because large number of conducting and semiconducting materials can be prepared by this technique. Compounds in the thin film form, on a variety of substrates (glass, ceramic or metallic), have been prepared by this technique. Many studies have been conducted over about three decades on spray paralysis processing and preparation of thin films. Thus, the SPT due to the simplicity of the apparatus and the good productivity of this technique on a large scale, it offered a most attractive way for the formation of thin films of metal oxides, metallic spinel type oxides, binary chalcogenides, ternary chalcogenides, superconducting oxides, etc. It is a simple and low cost technique and has capability to produce large area of high quality adherent films of uniform thickness. Spray paralysis technique consists of a thermally stimulated chemical reaction between clusters of liquid or vapor atoms of different chemical species. It involves spraying of a solution usually aqueous containing soluble salts of the containing atoms of the desired compound on to preheated substrates. Every sprayed droplet reaching the surface of the hot substrate undergoes paralytic (endothermic) decomposition and forms a single crystalline or cluster of crystallites as a product. The other volatile byproducts and solvent escape in the vapor phase. The substrates provide thermal energy for the thermal decomposition and subsequent recombination of the constituent species, followed by sintering and crystallization of the clusters of crystallites and thereby resulting in coherent film. The atomization of the spray solution into a spray of fine droplets also depends on the geometry of the spraying nozzle and pressure of a carrier gas.

V. DESCRIPTION OF SPT EQIPTMENTS

The schematic diagram of the spray paralysis technique is shown in Fig.1. It consists of mainly, (a) spray nozzle, (b) rotor for spray nozzle with speed controller, (c) liquid level monitor, (d) hot plate with temperature controlling arrangement, (e) gas regulator valve (f) air tight metallic chamber (g) substrate, etc.

(a) Spray Nozzle: **It is made up of a glass and consists of the inner solution tube surrounded by the gas tube through which carrier gas flows. With the application of pressure to the carrier gas, a vacuum is created at the tip of the nozzle and the solution is automatically sucked and the spray starts.**

(b) Rotor for Spray Nozzle: An electric car wiper (12V, 2A) is used to rotate the spray nozzle along with a speed controller.

(c) Liquid Level Monitor: The spray rate, at a fixed pressure, depends on the height of the solution, measured with reference to the tip of the nozzle and the arrangement for the change in height of the solution, forms liquid level monitor.

(d) Hot Plate: The iron disc, with diameter 16 cm and thickness 0.7 cm, was supported on the electric heater. Maximum temperature up to 600°C can be obtained with this arrangement. Chromel-alumel thermo-couple was used to measure the temperature of the substrates and is fixed at the center of the iron disc. The temperature of the hot plate was monitored with temperature controller.

(e) Gas Regulator Valve: The gas regulator valve was used to control the pressure of the gas. A coming glass tube of length 25cm and a diameter of 1.5cm were converted into a gas flow meter.

(f) Air Tight Metallic Chamber: Since number of toxic gases is evolved during the spray, it is necessary to fix the spraying unit in an air tight metallic chamber. An outlet of the chamber was fitted to exhaust to remove the gases evolved during spray deposition

[g] Substrates: The substrate is made of quartz or silica (SiO_2) material. It is chosen as the substrate and it is act as a plate, so it is called quartz-plate. Substrate is a passive component in the device and is required to be mechanically stable, matching thermal expansion coefficient with deposited layers and inert during the device fabrication. The flexible or rigid, metal or insulator used for deposition of different layers (contact, such versatility allows tailoring and engineering of the layers in order to improve device performance. This substrate is kept in a boat which is made of ceramics material which melting point is 3000℃. But substrate is always kept in fixed position, for this substrate holder is used which is made of iron or steel.

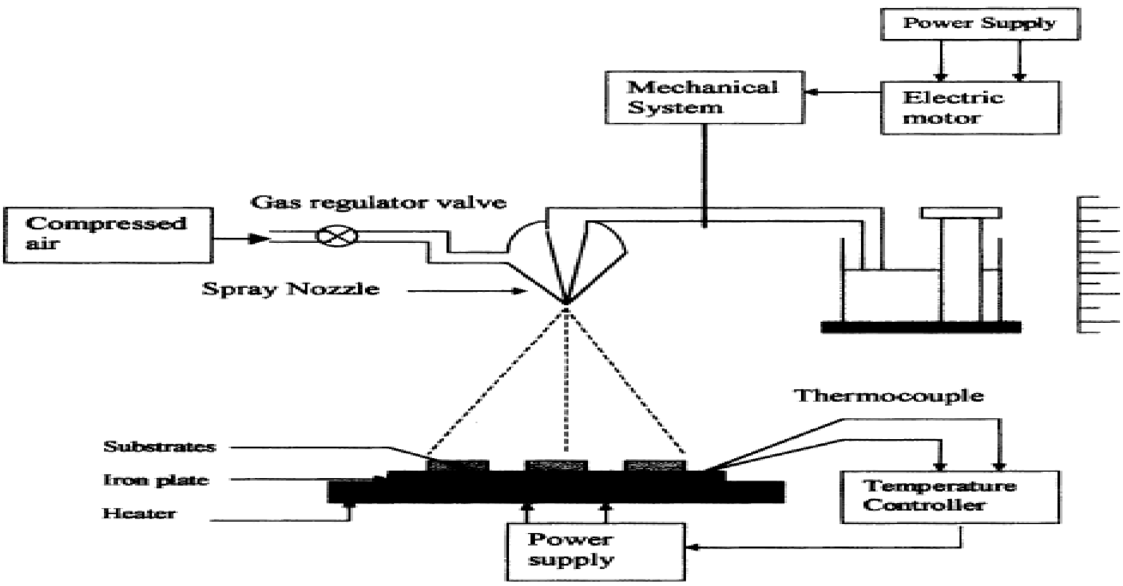

Figure 1: Schematic diagram of spray pyrolysis system.

VI. FORMATION OF THIN FILMS DROPLETS DURING SPT PROCESS

In spray paralysis, precursor solution is atomized through a nozzle. The nozzle converts the solution into small droplets, known as aerosols. These aerosols are allowed to incident onto the preheated substrates. The paralytic decomposition of the aerosols depends on substrate temperature. The formations of thin films with desired properties are possible only at optimum substrate temperature. Various steps during paralysis of aerosols are summarized as:

[1] In the first step, an aqueous precursor solution is converted into aerosols by spray nozzle.
[2] Solvent evaporation takes place in the second step.
[3] In this step, vaporization of the solvent leads to precipitate formation as the droplets / aerosol approaches the substrate.
[4] Pyrolysis of the precipitate occurs in succession before the precipitate reaches the substrate; this constitutes step 4.
[5] In step 5, when the precipitate reaches the substrate, nucleation and growth of metal oxide thin films
[6] Finally, growth of the nuclei leads to the formation of continuous thin layer of metal oxide (step 6).

VII. CHEMICAL SPRAY PYROLYSIS (CSP)

A Chemical spray paralysis (CSP) is used for depositing a wide variety of thin films, which are used in devices like solar cells, sensors, solid oxide fuel cells etc. It has evolved into an important thin film deposition technique and is classified under chemical methods of deposition. This method offers a number of advantages over other deposition processes, the main ones being scalability of the process, cost-effectiveness with regard to equipment costs and energy needs, easiness of doping, operation at moderate temperatures (100-500˚C) which opens the possibility of wide variety of substrates, control of thickness, variation of film composition along the thickness and possibility of multilayer deposition. CSP technique involves spraying a solution, usually aqueous, containing soluble salts of the constituents of the desired compound onto a heated substrate. Typical CSP equipment consists of an atomizer, a substrate heater, temperature controller and a solution container. Additional features like solution flow rate control, improvement of atomization by electrostatic spray or ultrasonic nebulization can be incorporated into this basic system to improve the quality of the films. To achieve uniform large area deposition, moving arrangements are used where either nozzle or substrate or both are moved. There are too many processes that occur sequentially or simultaneously during the film formation by CSP. These include atomization of precursor solution, droplet transport, evaporation, spreading on the substrate, drying and decomposition. Understanding these processes will help to improve film quality. Deposition process in CSP has three main steps: atomization of precursor solutions, transportation of the resultant aerosol and decomposition of the precursor on the substrate.

VIII. CRITICAL SPRAY PARAMETERS OF SPT

[1] Substrate Temperature: **The substrate temperature is the most important deposition parameter. At temperatures below 2000C, the droplets deposited are still rich in solvent. This large amount of unreacted precursor solution on the glass plate results in powdery deposit. Quick drying of this layer results in stresses and subsequent cracking. At very high temperatures (>3500℃), the deposited spray droplets have a very high chance of re-evaporation. Therefore discrete particles are formed on the surface due to slow spreading which gives rise to porous films. This increases the surface roughness. The number of particles on the surface increases with increasing deposition temperature.**

[2] Spray Rate: **Spray rate is another important parameter which influences the property of films formed. It has been reported that properties like crystallinity, surface morphology, resistivity and thickness are affected by changes in spray rate. It is generally observed that smaller spray rate favors formation of better crystalline films. Smaller spray rate requires higher deposition time obtaining films of the same thickness prepared to higher spray rate. Surface morphology of the films varies with the spray rate. Higher spray rate results in rough films. Also, it is reported that films deposited at smaller spray rates are thinner due to the higher re-evaporation rate.**

[3] Precursor Solutions: **Precursor solution plays a vital role in the formation of thin films of various compounds. The true solutions, colloidal dispersions, emulsions and sols can be used as aerosol precursors. Aqueous solutions are usually used due to ease of handling safety, low cost and availability of a wide range of water soluble metal salts. The solute must have high solubility, which increases the yield of the process.**

[4] Nature of Precursor Solution: Precursors used for spraying is also very important and it affects the film properties to a great extent. Solvent, type of salt, concentration and additives or dopants influence the physical and chemical properties of the films. Usually, de-ionized water which is ideal for a low cost process is used as solvent. The concentration of the precursor solution determines the duration of spraying needed to obtain a uniform film deposition. A low concentration means lengthy spray duration. Higher concentration requires comparatively less spray time, but it can lead to rough and grainy films. Usually the concentration ranges from 0.001 M to 0.1M and it is seen that smooth films are obtained at low concentrations.

[5] Angle and height of spray head: This parameter is also important because it can also influence the properties of deposited films. Each nozzle has a spraying angle. Therefore, the nozzle-substrate distance determines the area coated and deposition rate. Smaller the distance of the atomizer to the substrate, higher the deposition rate and smaller the coated area. Different types of spray heads with different angles produce different spray patterns. The height and angle of spray head should ensure maximum uniformity and large area of coverage. In the pressurized spray pyrolisys set up, where the precursor solution is atomized using an air stream there are also other limitations. In this case the minimal nozzle-substrate distance is not limited by the substrate size, but by the cooling effect of air flow. At small distances pronounced cooling of the substrate occurs. Simultaneously, more heat is required from the heating plate, because the droplet mass flow density increases with decreasing distance. A pressure, or air blast, atomizer uses high speed air in order to generate an aerosol from a precursor solution. Increasing the air pressure causes a direct decrease in the generated mean droplet diameter. Inversely, increasing the liquid pressure causes a direct increase in the mean droplet diameter. Perednis showed that all droplets sprayed from an air blast atomizer are contained within a 70° angle spray cone angle, while half are within a narrower 12° angle. It was also determined that the flow rate has a very small influence on the spray characteristics, which can be mostly ignored for modeling.

IX. PRECURSORS (LIQUIDS) ATOMIZATION

The atomization procedure is the first step in the spray paralysis deposition system. The idea is to generate droplets from a spray solution and send them, with some initial velocity, towards the substrate surface. Spray paralysis normally uses air blast, ultrasonic, or electrostatic techniques. The atomizers differ in resulting droplet size, rate of atomization, and the initial velocity of the droplets. It has been shown that the size of the generated droplet is not related to any fluid property of the precursor solution and depends solely on the fluid charge density level qe as shown in

$$r^2 = \left(\frac{-\alpha'}{\beta'}\right)\frac{3\,\varepsilon_0}{q\,\rho_e} \qquad (1)$$

Where ε_0, the permittivity, q is is the elementary charge, and α/β is a constant value equal to 1.0 10^{-17} J. The mass of a droplet, assuming a spherical shape depends on its density,

$$m = \frac{4\,\pi}{3}\,\rho_{q\,r^3} \qquad (2)$$

Where, r is the droplet radius and q is the droplet density. The initial leaving velocity of the droplet is an important parameter as it determines the rate at which the droplets reach the substrate surface, the heating rate of the droplet, and the amount of time the droplet remains in transport Due to its ease of production, many companies chose to use pressure atomizers instead of the ultrasonic atomizers. A pressure, or air blast, atomizer uses high speed air in order to generate an aerosol from a precursor solution. Increasing the air pressure causes a direct decrease in the generated mean droplet diameter. Inversely, increasing the liquid pressure causes a direct increase in the mean droplet diameter. Perednis showed that all droplets sprayed from an air blast atomizer are contained within a 70^0 spray cone angle, while half are within a narrower12^0. It was also determined that the flow rate has a very small influence on the spray

characteristics, which can be mostly ignored for modeling. The general simplified schematic diagram for spray paralysis deposition is shown in Fig. 2, where three processing steps can be viewed and analyzed:

1. Atomization of the precursor solution.
2. Aerosol transport of the droplet.
3. Decomposition of the precursor to initiate film growth

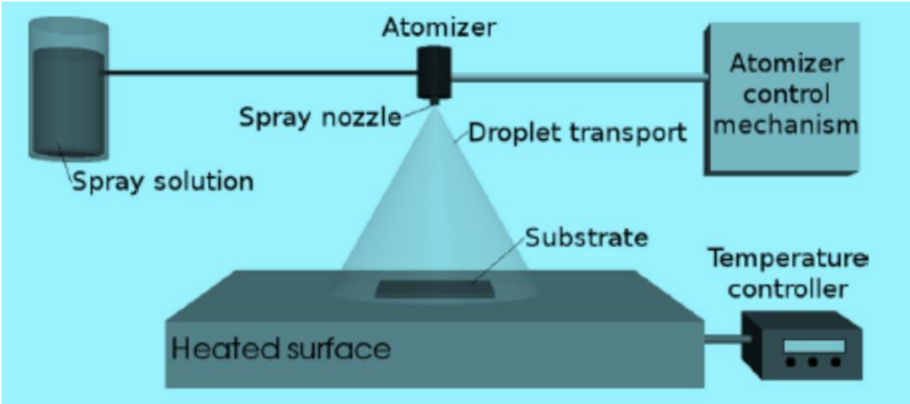

Fig. 2: General schematic of a spray pyrolisys deposition process.

X. FACTORS GOVERNING SPRAY PYROLYSIS TECHNIQUE (SPT)

Thin film formation by using SPT depends upon a various parameters. SPT consists of a thermally stimulated chemical reaction between clusters of liquid or vapor atoms of different chemical species. Every sprayed droplet reaching the surface of the hot substrate undergoes paralytic decomposition and forms a single crystallite or cluster of crystallites as a product on the substrate. The substrates provide thermal energy for the thermal decomposition and subsequent recombination of the constituent species, followed by sintering and crystallization of the clusters of crystallites and thereby resulting in coherent film. The number of factors governing the film formation mechanism depends on,

1. The automation of the spray solution into a spray of fine droplets which depends on the geometry of the spraying nozzle and pressure of a carrier gas.
2. The properties of thin films depend upon the anion to cation ratio, spray rate, substrate temperature, ambient atmosphere, carrier gas, droplet size and also on the cooling rate after deposition.
3. The film thickness depends on the distance between the nozzle and substrate, solution concentration, quantity and substrate temperature.
4. The film formation depends upon the process of droplet landing, reaction and solvent evaporation which are related to droplet size and its moment. An ideal deposition condition is that when a droplet approaches the substrate just as the solvent is completely removed. Lampkin showed that depending on droplet velocity and flow direction, a droplet would be either flattens, skip along the surface.

XI. SUBSTRATE CLEANING

Substrate cleaning is the process of breaking bonds between substrate and contaminant without damaging the substrates. In thin film deposition process substrate cleaning is an important factor to get reproducible films as it affects the smoothness uniformity, adherence and porosity of the films. The substrate cleaning process depends upon the nature of substrate; degree of cleanliness required and nature of contaminates to be removed. The common contaminates are grease, adsorbed water, air borne dust, lint, oil particles etc. The micro slides supplied by Blue Star of dimensions 7.5 cm x 2.2 cm x 0.1 cm have been used as substrates. The following process has been adopted for cleaning of substrates:

[1] The substrates were washed with detergent solution 'Labolene' and then with water.
[2] These substrates were boiled in chromic acid for five minutes.
[3] Substrates were cleaned with double distilled water.
[4] These substrates were kept in NaOH solution to remove the acidic contaminations.

[5] The substrates were again washed with distilled water and cleaned ultrasonically.
[6] Finally substrates were dried in alcohol vapors.

XII. ADVANTAGES AND DISADVANTAGES

Apart from its simplicity, spray paralysis technique has a number of advantages. Spray-paralysis is a simple and low cost technique for the preparation of semiconductor thin films. It offers an extremely easy way to dope films with virtually any elements in proportion, by merely adding it in some form to the spray solution. It has a capability to produce large area, high quality adherent films of uniform thickness. Spray paralysis does not require high quality targets nor does it require vacuum at any stage, which is great advantage if the technique is to be scaled up for industrial applications. The deposition rate and thickness of the films can be easily controlled over a wide range by changing spray parameters.

The Majors Advantages of Thin Films are:

[1] It offers an extremely easy way to dope films with virtually any element in any proportion, by merely adding it in some form to the spray solution.
[2] Unlike closed vapor deposition method, spray paralysis does not require high quality targets and / or substrates nor do it require vacuum at any stage, which is a great advantage if the technique is to be scaled up for industrial applications.
[3] The deposition rate and the thickness of the films can be easily controlled over a wide range by changing the spray parameters, thus eliminating the major drawbacks of chemical methods such as sol-gel which produce films of limited thickness.
[4] Operating at moderate temperatures (100-500°C), spray paralysis can produce films on less robust materials.
[5] Unlike high-power methods such as radio frequency magnetron sputtering (RFMS), it does not cause local over-heating that can be detrimental for materials to be deposited. There are virtually no restrictions on substrate material, dimension or its surface profile.
[6] By changing composition of the spray solution during the spray process, it can be used to make layered films and films having composition gradients throughout the thickness.
[7] It is believed that reliable fundamental kinetic data are more likely to be obtained on particularly well-characterized film surfaces, provided the films are quite compact, uniform and that no side effects from the substrates occur. Spray paralysis offers such an opportunity.
[8] A major advantage of this method is operating at moderate temperature (100-5000^0 C), and can produce films on less robust materials. By changing composition of the spray solution during the spray process, it can be used to make layered films and films having composition gradients throughout the thickness.

Disadvantages of thin films

[i] Non-uniformity of film with larger grain size due to uncontrollable spray droplet size
[ii] Wastage of solution i.e. the low ratio of atoms effectively deposited to those supplied
[iii] Low deposition rate.

XIII. CONCLUSIONS

In the last few decades thin films: Science and technology are became new branch of material science and has played vital role in the development of solar cells, solid-state physics, electronics devices, and industries, etc. A survey on obtainable literature on chemical SP technique reveals that it so offers a beautiful methodology to arrange large choice of thin film materials for numerous industrial applications. The standard and properties of thin films rely for the most part on the preparation conditions. Recently, stress given to two aspects: First atomization techniques to manage the drop size and their distribution a lot of exactly, and Second use of beginning compounds like organotin to get extremely homeward thin films looks brighter. Any efforts are necessary to couple these two aspects to get prime quality thin films by spray paralysis technique. Therefore, spray pyrolisys deposition represents a versatile technique, allowing the development of large area thin films for solar energy conversion devices. The paper reviews the parameters that have significant influence on the crystalline structure and morphology, with a focus on the most

important output properties for opto-electronic devices. A case study is detailed for the new generation of photovoltaic, particularly, on the solid state solar cells. Deposition and annealing temperatures, spraying geometry and sequences, the precursor concentration and solvent(s) are discussed and the importance of the additives is outlined as important tools in tuning the precursors' stability/reactivity, thus the nucleation and growth processes.

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REFERENCES:

[1] R.R. Chamberlin, J.S. Skarman, J. Electrochem. Soc. 113 (2000), 86.
[2] K.L. Chopra and I.J. Kaur, *Thin film Device applications*, Plenum Press, New York, 1983.
[3] K.L. Chopra and S.R. Das, *Thin Film Solar Cells*, Plenum Press, New York, 1983.
[4] R.R. Chamberlin, J.S. Skarman, *J, Electrochem. Soc.*, 113(1966), 86.
[5] M. Fujimoto, T. Urano, S. Murai and Y. Nishi, *Jpn. J. Appl. Phys.*, 28(1989), 2587.
[6] I. Yagi, K. Kakizawa, K. Murakami and S. Kaneko, *J. Ceram.Soc.Jpn.*, 102(1994), 296.
[7] C.H. Lee, L.Y. Lin, *Appl. Surf. Sci.*, 92(1996) , 163.
[8] A. Aoki, G. Nogami, *J. Electrochem. Soc.*, 143(1996) L 191.
[9] P.S. Patil and P.R. Patil, *Tr. J. Phys.*, 18(1994) 1330.
[10] D. Craigen, A. Mackintosh, J. Hickman, K. Colbow, *J. Electrochem. Soc.*, 133(1986), 1529.
[11] P.S. Patil and R.S. Patil, *Bull. Mater. Sci.*, 18(1995), 911.
[12] L.D. Kadam, C.H. Bhosale and P.S. Patil, *Tr. J. Phys.*, 21(1997), 1037.
[13] P.S. Patil, E.A. Ennaoui, C.D. Lokhande, M. Muller, M. Giersig, K, Diesner and H. Tributsch, *Thin Solid Films*, 310(1997) 57.
[14] C.H. Chen, A.A.J. Buysman, E.M. Kelder, J. Scnoonman, *Solid State Ionics*, 80(1995)
[15] R.N. Singh, J.F. Koenig, G. Poillerat, P. Chartier, *J.Electroanal. Chem.*, 314(1991)241.
[16] B. Lefez, P. Nkeng, J: Lopitaux, *Mater. Res. Bull.*, 31(1996), 1263.
[17] C.S. Huang, C.S. Tao, C.H.Lee, *J. Electrochem. Soc.*, 144(1997), 3556.
[18] A.G. Valyomana, S. Mathew, K.P. Vijaykumar, C. Purushottam, *Bull. Mater. Sei.*, 16(1993), 55
[19] J.P. Mangalhara, R. Thangraj, O.P. Agnihotri, *Bull. Mater. Sci.*, 10(1988) 333.
[20] J.De Merchant and M.Cocivera, *J. Electrochem. Soc.*, 143(1996) 4054.
[21] K. Y. Rajpure, A.M. Patil, C.D. Lokhande and C.H. Bhosale, *Thin Solid Films*.
[22] V.V. Killedar, C.D. Lokhande and C.H. Bhosale, *Thin Solid Films*, 289(1996) 14.
[23] S. Lopez, S. Granados, A.Ortiz, *Semiconductor Sci. Technol.*, 11(1996)
[24] W.A.S.A. Ghafor, N.A. Awad, N.S. Othman, *Ind J.Pure and Appl.Phys.*, 31(1993) 123.
[25] Y.D. Tembhurkar and J.P. Hirde, *Bull.Mater.Sci.*, 17(1994) 465.
[26] S.P.S. Arya and H.E. Hinterman, *Thin solid Films*, 193(1990) 841.
[27] S. Kumari, A.K. Singh and O.N. Srivastava, *Supercond, Sci. and Technol.*, 9(1996) 405.
[28] S.H. Pawar and P.N. Pawaskar, *Mater.Res.Bull.*, 30 (1995) 277.
[29] K. Badeker, Ann. Phys. (Berlin) 22 (1907) 749.
[30] K. L. Chopra, S. Major, D. K. Pandya,*Thin Solid Films*, 102 (1983)
[31] H. Hosono, T. Kamiya, M. Hirano, *Bull. Chem. Soc. Jpn*. 79 (2006)
[32] H. Kawazoe, K. Ueda, *J. Am. Ceram. Soc*, 82/12 (1999) 3330.
[33] T. Minami, Semicond. *Sci.Technol.* 20 (2005) S35.
[34] D. S. Ginley, J.D. Perkins, H. Kawazoe, D.M. Newns, A.B. Kozyrev, *Proceedings of the Materials Research Society, Materials Research Society*, (2001) 433.
[35] D. C. Paine, H.-Y.Yeom, B. Yaglioglu, in: G.P. Crawford (Ed.), Flexible Flat Panel Displays, *WileyInterscience*, JohnWiley and Sons (2005) 79.
[36] R. Ayouchi, D. Leinen, F. Martin, M. Gabas, E. Dalchiele and J. R. Ramos Barrodo, *Thin Sold Films* 426 (2003) 68.
[37] H. L Hartnagel, A. L Dawar, A. K Jain, C. Jagadish, *Semiconducting Transparent Thin Films* (Philadelphia, PA: Institute of Physics Publishing) (1995).
[38] T. Minami, *MRS Bull.*25 (2000) 38.

[39] A. J. Freeman, K R Poeppelmeier, T O Mason, R P H Channg, T J Marks, *MRS Bull.* 25.

[40] R. G. Gordon, *MRS Bull.* 25 (2000) 52.

[41] J.C Viguiě, J. Spitz, *J. Electrochem. Soc: Solid State Science and Technology.* 122(4) (1975).

[42] T. Minami, H Nanto, S Takata Japan. *J. Appl. Phys.*23 (1984) L280.

[43] T. J. Minami. *Vac. Sci. Technol.* A 17 (1999) 1765.

[44] L. Holland, *Vacuum Deposition of Thin Films.* Wiley, New York (1958).

[45] J. L.Vossen, *Phys. Thin films*, 9 (1977) 1.

[46] T.H. Sajeesh et al., *MRSI-AGM*, New Delhi (2007).

[47] J. C. Manifacier, *Thin Solid Films* 90 (1982) 297.

[48] J.B. Mooney, S.B. Radding, *Annu. Rev. Mater. Sci.* 12 (1982) 81.

[49] Ratheesh Kumar P.M., Ph.D Thesis, Cochin University of Science and Technology.

[50] Teny Theresa John, Ph.D Thesis, Cochin University of Science and Technology, India

[51] Lampkin C.M., *Prog. Cryst. Growth Characterization of Materials.* 1(4) (1979) 405.

[52] S.P.S Arya, H.E.Hintermann, *Thin Solid Films.* 193 (1990) 841.

[53] J. Zeleny, *Phys. Rev.* 3(2) (1914) 69.

[54] J.M. Grace, J.C.M. Marijnissen, *J. Aerosol Sci.* 25 (6) (1994) 1005.

[55] T. Sebastian, R. Jayakrishnan, C. SudhaKartha, K.P.Vijaya kumar, *The Open Surface Science Journal.* 1 (2009).

[56] G. Dong, M. Zhang, X. Zhao, H. Yan, C. Tian and Y. *Ren Applied Surface Science* 256.

[57] Duminica, F.D.; Maury, F.; Abisset, S. Pyrosol deposition of anatase TiO2 thin films starting from Ti(OPr)4/acetilacetone solutions. *Thin Solid Films*, 2007, *515*, 7732-7739.

[58] Perednis, D.; Gauckler, L.J. Thin Film Deposition Using Spray Paralysis. *Journal of Electroceramics*, 2005, 14, 103-111.

[59] V.K. Singh, M. K. Sharan, & K.P. Srivastava, Amorphous Semiconducting Carbon Thin Films from Castor Oil. *Material Science Research India*, Vol. 03, No. (2a), 2006, pp (263-266).

[60] V.K. Singh, M. K. Sharan, & K.P. Srivastava, Amorphous Semiconducting Carbon Thin Films for Carbon PV-Cells, *Acta Ciencia Indica of Chemistry*, Vol. XXXIVC, No. 1, 27, (2008), pp (127-132).

[61] V.K. Singh, M. K. Sharan, & K.P. Srivastava, Spray Paralyzed Semi-Conducting Carbon Thin Films from Turpentine Oil, *International Journal of Chemical Sciences*, Vol. 4(3): 2006, pp (660-664).

[62] V. K. Singh & H. N. Sah, Review of Carbonaceous Materials in Castor Oil for Thin Films Deposition, *Journal of Emerging Technologies and Innovative Research*, Vol. 4, Issue 7, July 2017, pp 205-211.

[63] V. K. Singh & H. N. Sah, Versatility of Spray Paralysis Technique for the Deposition of Carbon Thin Films, *Journal of Emerging Technologies and Innovative Research*, Volume 4, Issue 8, August 2017, pp 312- 318.

[64] V. K. Singh, Solar Electricity from Solar Energy and Future Applications, *Journal of Emerging Technologies and Innovative Research*, Volume 4, Issue 9, September 2017, pp 511-518.

[65] V. K. Singh, Versatility of Thin Film and Thin Film Deposition Techniques and Parameters, JETIR , Volume 4, Issue 10, October 2017, pp 585-591.