VERSATILIY OF SPRAY PYROLYSIS TECHNIQUE FOR THE DEPOSITION OF CARBON THIN FILMS

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ABSTRACT: In this paper we briefly review, the spray pyrolysis technique and the applications in production of thin films, ceramic powders, and fibers. Spray pyrolysis has been applied to deposit a wide variety of thin films. The processes involved in the spray pyrolysis technique are also discussed in this review paper. These films were used in various devices such as solar cells, carbon solar cells, sensors, and solid oxide fuel cells, etc. It is observed that often the properties of deposited thin films depend on the preparation conditions. An extensive review of the effects of spray parameters on film quality is given to demonstrate the importance of the process of optimization. The substrate surface temperature is the most critical parameter as it influences film roughness, cracking, crystallinity, etc.

Keywords: SPT, Thin films, Deposition Techniques, Parameters, Conditions, Properties of deposited films, ets.

I. INTRODUCTION

In the last few decades, the thin films technology has played vital role in the development of electronics, optoelectronics and PV solar cells applications. There are a numerous advantages and application of thin films technology. Thus, the thin films are applicable in industrial purpose research field, AR coatings, mirror coating, interference filters, sun glasses, decorative coating in plastics, textile industry, in fabrication of solar cells, electric and electronic circuits, etc. Hence, the thin films technology is also the backbone of microelectronics. In early 20th century, thin film technologies were developed to make various gadgets using small quantity of material, thus, reduced the cost. Hence, one of the most promising ways to reduce the cost of PV solar cell is thin film technology. Thin film solar cells also allow the use of a given optimum efficiency. It is found that the physical, chemical, optical, electrical and magnetic properties exhibited by thin films are different than that of its bulk counterpart. Thin film can be defined as a low dimensional material (1000 nm), created by one-by-one condensing the atomic (molecular/ionic species of matter onto a substrate. There are many techniques to deposit the films, e.g.-CVD, PVD, ion plating, sputtering, electroplating, ECD, etc. However, all these techniques require sophisticated instrumentation and high vacuum system. Thermal flash evaporation technique on the other hand can be used to deposit thin film at relatively less vacuum level. The deposition unit is also very simple and thin film can be prepared in few minutes. The advantages of films are high deposition rate, clearer environment for the thin film preparation and growth (i.e. better vacuum and general applicability to all classes of materials for the deposition of thin films). The thin films are classified into three categories: according to its thickness as–ultra-thin films, thin-films, and thick-films, etc. Thin films of semiconducting materials are currently one of the intensively studied topics in the materials research. It is not only because of their extreme properties very interesting for applications, but also due to an enormous potential for the basic scientific research. The extreme properties triggered enormous research activity in developing of new technologies which would allow depositing material with tailored properties for various applications. Although, films and coatings are used mainly to fabricate electronic, solar cells, metallurgical components and to protect the substrates from corrosion, reaction and surface damage for various applications. A variety of thin films and coatings of metals, oxides, carbides, nitrides, carbon materials etc. are produced by various techniques. Thus, the thin films are produced by various techniques. The selection of techniques depends upon the type of materials to be used for making thin film. The broad classification of thin film deposition techniques can be made as (i) Chemical and (ii) Physical (iii) Electrochemical.

For either of these process, typical steps in making thin films are:
(a) Emission of particles from source (heat, high voltage, etc.)
(b) Transport of particles to substrate and
(c) Condensation of particles on substrate
Among all the techniques mentioned above, the thermal flash evaporation technique has been of interest particularly in R&D applications where low installation cost and inexpensive, disposable vaporate containers

are required. By this technique carbon thin films have been synthesized from poly Vinyl Alcohol (PVA), camphor, clove oil, turpene and different plant derived precursors. The band gap (E_g) of thin films obtained by using this process with different precursors is shown in table-[1].

Table :1. Carbon Thin Films obtained by Thermal Flash Evaporation Technique and their corresponding band gaps.

Name of Precursors	Band-Gap (E_g) in eV
Camphor	**1.40**
Turpene	**1.34**
Kerosene	**2.58**
Clove Oil	**1.33**
Poly Vinyl Alcohol	**1.65**
Poly Ethylene Glycol	**4.02**

II. THIN FILM AND ITS FORMATION

Thin film is a low dimensional material (~ 1000nm) , created by one-by-one condensing the atomic / ionic species of matter onto a substrate. The thin film is basicallly two dimensional phenomema in condensed phase, implying a physical matter having one dimensional extremely small as compared with the remaining two dimensions.

Thin film can be classified accordingly to their thickness as-

1. Ultra thin films(UTF)-

2. Thin films (TF)-

3. Thick films(TcF)-

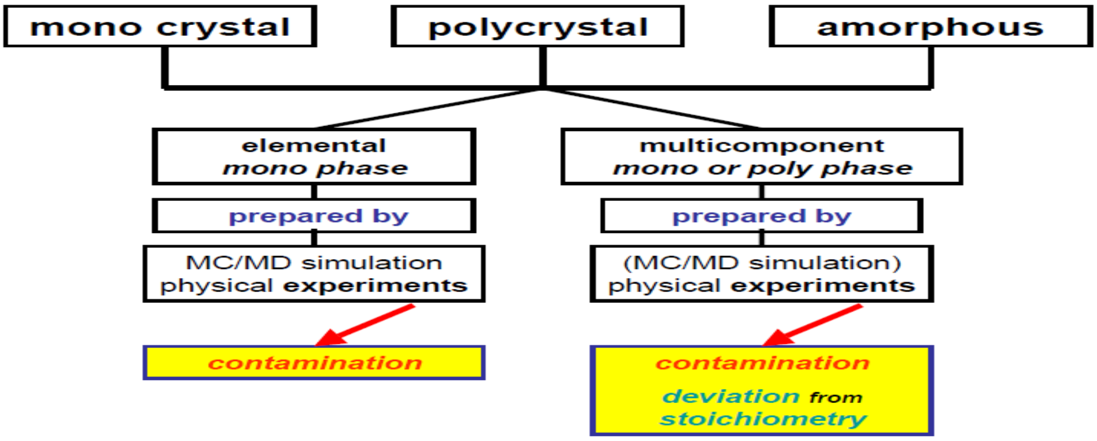
There is no clear-cut distinction among them, but on an average for ultra thin films- the thickness is of the order of few (10^{-10}m =10^{-1} nm) to few ten A^0 thin films, the thickness ranges from few hundred A^0 to few thousandA^0. But for thick films, the thickness of range is greater than few tens of micron. The thin film prepared from PLD process are small droplets (typical size 0.2µm - 3µm), and large irregular-shaped out growths (diameter more than 10µm).

It has been obserbed that the physical, chemical, optical, electrical, magnetic, etc., properties exhibited by the thin films are different than that of its bulk counterpart. Hence, because of the novel and unique superior properties thin film have been used in a number of application.

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 solid-state physics, electronics devices, and industries. etc.

The coating and thin films are used mainly to fabricate electronic, metallurgical components and to protect the substacte from corrosion, reaction, and surface damage for various applications. The deposition processes include evaporation, chemical vapour deposition, physical vapour deposion, sputtering, electroplating, dipping, spraying, etc. A variety of thin films and coatings of metals, oxides, carbides, nitriate silicides, borides and corbon precusors, etc, are successfully deposited by the CVD process for many different applications, such as electronic devices, passivation, solar cells, etc. The latest research is directed toward achieving defect-free uniform films and coatings on different substrates with high deposition rate for low-cost and mass-scale production. The thin films having various poential technical value, and numerous materials have been prepared in the form of thin films over a century also due to scientifc curiousity in their properties. They have wide range of applications ans extends from microelectronics to coatings of several square meters on window-glasses.

Table 2: Types of Thin Films and Preparation Modes



The quality and properties of thin films depend largely on the preparation conditions, anion to cation ratio, spray rate, substrate distance, substrate temprature, ambient atmosphere, carries gas, droplets size, and also the cooling rate after deposition. The thin films thickness depends upon the distance between the spray-nozzle and substrate, substrate temprature, concentration of the precursor solution and the quality and quantity of the precursor solution sprayed. The thin film formation depends upon the process of droplets landing, reaction and solvent evaporation, which are related to droplets size and momentum. An ideal deposition condition is when the droplets approaches the substrate just as the solvent is completely removed.

Recently emphasis given to two aspects:

(i) An atomization techniques to control the droplets size and their distribution more precisely.

(ii) An use of starting compound such as organotin to obtain highly oriented thin films seems more promising.

The quality of the diposited thin films above all, determined by the crystallinity of the lattice and surface smoothness. The thin film have great technological importance owing to their potential application in photoelectrochemical cells (PECs), solar cells decorative coatings, electronics, optoelectonic devices, and thermo-elecrtric cooler, etc.

III. VERSATILITY OF SPRAY PYROLYSIS TECHNIQUES(SPT)

A number of techniques have been investigated and examined, during the last three decades, in search for the most reliable and cheapest method to producing the thin films. But due to the simplicity of apparatus and good productivity the chemical - spray paralysis technique (SPT), is one of the major and fascinating techniques to deposit a wide variety of materials in thin film form. This technique on a large scale offered a most attractive way for the preparation of thin films of noble metals, metal oxides, spinal oxides, chalcogenides and superconducting compounds, etc. The sp technique is very useful for the preparation of thin films of simple oxides, mixed-oxides and group, I-VI, II-VI, III-VI, IV-VII, V-VI, VIII-VI elements. The pioneering work has been done by Chamberlin and Skarman in 1966 on CdS films for solar cells. Recently, SP technique has been successfully employed for the preparation of super-conducting oxide thin films. The thin films of such metal oxide and metallic spinal oxide materials prepared by sp technique have matching properties for wide variety of potential application. Chalcogenide semiconductor compounds of group II-VI and V-VI have applications in precise temperature control of laser diodes, optical recording systems, electrochemical devices, strain gauges and thermoelectric devices. These thin films have greater technological importance owing to their potential applications in solar selective and decorative coatings, optoelectronic devices, thermoelectric devices, photo-electrochemical cells etc. Pamplin has presented a review of transparent conductors and a bibliography in a conference on spray paralysis. Viguie and Spitz have classified chemical spray deposition process according to the type of reaction. Moreover Mooney and Radding reviewed the SPT and its control in relation to CdS thin films and devices application. Krishna Kumar et al. reviewed thin film preparation by sp technique for solar cells. Kern and Tracy have reported on a high-speed production spray paralysis process for titanium dioxide antireflection coating for silicon solar cells. This topic explained, the chemical versatility of SPT and also demonstrated by reviewing the relevant literature on transition metal oxides, metallic spinal type oxides, binary, ternary, and quaternary chalcogenides and superconducting on thin film materials prepared by sp- techniques is presented.

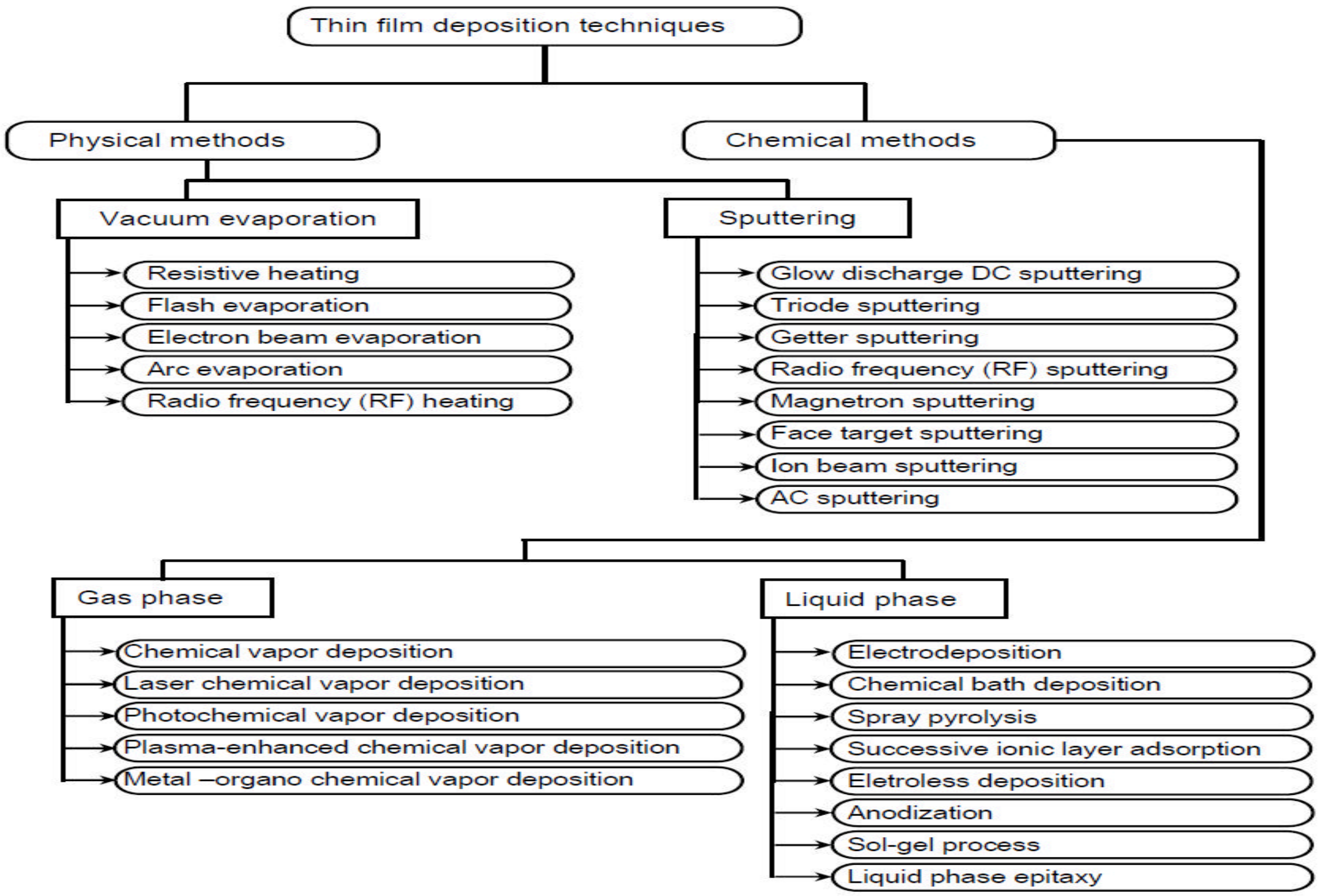
IV. THE PREPARATION OF VARIOUS THIN FILMS BY SPT

The breaking of part of complex molecule into simple units by the use of heat is *called paralysis*. Since, this process is concerned with organ metallic compound in an aqueous form. So, the paralysis technique has been used to prepare thin films of various materials. In the spray paralysis technique, the materials whose solution/slurry, when sprayed over a substrate at high temperature, get decomposed to give a thin film of the material. The precursor (material) solution is pulverized by means of a neutral gas (i.e. Nitrogen) so that it arrives at near the substrate in the form of very fine and extremely small droplets. The constituents react to form a chemical compound onto the substrate. The chemical reactants are selected such that the products other than the desired compound are volatile at the temperature of deposition. The quality and properties of the thin films obtained depend upon the anion to cation ratio, spray rate, substrate temperature, ambient atmosphere, carrier gas, droplet size and also the coating rate after deposition. The film thickness depends upon the distance between the spray nozzle and the substrate, the substrate temperature, the concentration of the precursor solution and the quantity of the precursor solution sprayed. The film formation depends on the process of droplet landing on the substrate, reaction and solvent evaporation; which are related to the droplet size and momentum also. An ideal deposition condition is when the droplet approaches the substrate just as the solvent is completely removed. Lampkin showed that, depending on the droplet velocity and flow direction, a droplet will either flatten, skip along the surface or hover motionless.

V. THIN FILMS DEPOSITION TECHNIQUE

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 in Table 13, as

Table 3 : Broad classification of thin film deposition techniques



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 pyrolysis) method is most popular today because large number of conducting and semiconducting materials can 49 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 pyrolysis processing and preparation of thin films, since

the pioneering work done by Chamberlin and Skarman in 1966, on cadium sulphide (CdS) films for solar cells. Thereafter, 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 superconductiong 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.

VI. Advantages of SPT

- **It offers an xtremely easy way to dope films with virtually any element in any proportion, by merely adding it in some form to the spraysolution.**
- **Unlike closed vapor deposition method, spray pyrolysis 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.**
- **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.**
- **Operating at moderate temperatures (100-500°C), spray pyrolysis can produce films on less robust materials.**
- **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.**
- **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.**
- **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 pyrolysis offers such an opportunity.**

VII. SPRAY PYROLYSIS TECHNIQUE(SPT)

Spray pyrolysis technique consists of a thermally stimulated chemical reaction between clusters of liquid or vapour 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 pyrolytic (endothermic) decomposition and forms a single crystalline or cluster of crystallites as a product. The other volatile byproducts and solvent escape in the vapour 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. The schematic diagram of the spray pyrolysis 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 and (f) air tight metallic chamber.

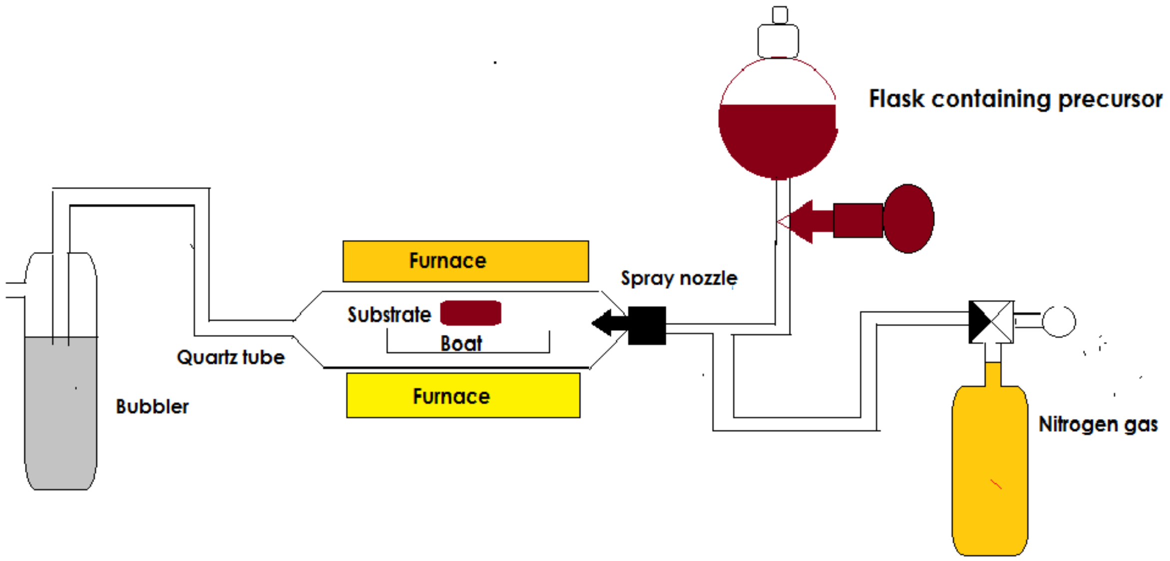


Figure 1: Schematic Diagram of Spray Pyrolysis Technique

VIII. CONCLUSIONS

The spray pyrolysis technique is a new emerging wonderful method in material science. It possesses many advantages, such as low processing temperature, high homogeneity and purity of products, and, 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: (1) atomization techniques to manage the drop size and their distribution a lot of exactly, and (2) 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 pyrolysis technique. The key challenges of spray pyrolysis are control over the morphology and composition of product particles. Spray pyrolysis technique is a versatile and effective technique to deposit carbon thin films. 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. It is often suggested that a modified CVD process occurs close to the surface of the substrate. However many observations contradict the involvement of a model with a CVD character. Further efforts are necessary to clarify the model for film deposition.

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