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Thin films by Spray pyrolysis: A versatile technique

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ABSTRACT

In this article we have demonstrated how the spray pyrolysis technique is important for preparing thin films. Spray pyrolysis method is an easy and economical method for creating ceramic coatings, powders, and thin and thick films. Thin films containing noble metal nanoparticles [1] (MNPs) like Au, Ag, Pt etc. are a demanding field of current research due to their exotic functional properties. Spray pyrolysis is a simple and versatile method for the deposition of thin films. The spray pyrolysis method gives phase and material pure (Co_3O_4) films of controlled morphology.

Keywords: *MNPs, Thin films, spray pyrolysis*

1. INTRODUCTION

A thin film is a layer of material ranging from fraction of nanometer to several micrometers in thickness. Ideally thin film may be defined as a solid layer having a thickness varying from a few A^0 to about 11 μm or so. The basic research on thin films is confined to a limited range of thickness. This totally depends upon which property of the thin film is to be investigated. Say between a few Angstroms to about 5000 A0. Thin films have very interesting properties that are quite different from those of the bulk materials which they are made up of. This is because their properties depend on several interrelated parameters and on the technique employed for their fabrication. Ceramic thin films are also in wide use. The relatively high hardness and inertness of ceramic materials make this type of thin films coatings of interest of protection of substrate materials against corrosion, Oxidation, and wear.

There are some factors which determine the physical, electrical, optical, and other properties of thin films. Rate of deposition, substrate temperature, environmental conditions, and residual gas pressure in the system are the factors that determine these properties. There are some observed are purity of the material to be deposited, inclusion of foreign matter in the deposit, inhomogeneity of the film, structural and compositional variations of the film in localized or wider areas etc. When there is a transition from the bulk to the thin film state may cause a drastic change in its properties as illustrated by the behavior of alkali metals and noble metals. Thus, highly conducting sodium, potassium, rubidium, and gold, platinum etc. having positive temperature coefficient of resistance (TCR) in the bulk form show negative TCR when in thin film states thus behaving as semiconducting films. Bulk bismuth and antimony which are metallic in nature behave as semiconductors in the thin film states.

The films which are prepared by vacuum deposition or by any technique are invariably associated with some growth defects or imperfections. Like lattice defects, stacking faults, twinning, disorders in atomic arrangement, dislocations, grain boundaries, foreign atom inclusion, etc. Surface states of a film also play a dominant role in modifying electrical and other properties. Because of the high surface to volume ratio in a film, a freshly formed film surface becomes highly reactive. Further because of the unbalancing of forces near the surface region, new phenomena such as thermionic emission, adsorption of gases, catalysis, solid state reactions, etc. characteristic of a surface are more often observed in thin films rather than in bulk. It is, therefore, of utmost importance to study thin films not only because of technological importance but also because of our inadequate knowledge about their interactions with the electrical, magnetic, and electromagnetic fields. Sometimes new phenomenon is observed in the thin film state.

2. TYPES OF THIN FILMS

Thin films are classified in many ways, mainly according to the materials used for coatings, the damage threshold, the strength, and the characteristics etc. There are metallic coatings that always have a lot of absorption and only limited applications. The dielectric coatings have practically negligible levels of absorption. A dielectric coating consists of two or more thin layers of different transparent optical materials. Materials with thicknesses ranging from fractions of a nanometer to several micrometers are called thin films. Although thin films are frequently employed in the industrial sector for coatings, they can also be utilized to create sophisticated memory storage devices and convert light energy into electrical power. Thin films are employed in a wide range of technical applications due to their adaptability.

2.1. How Do Thin Films Come to Be?

Inorganic compounds, polymers, and ceramics are often utilized materials in the production of thin films. They can be applied to diverse surfaces via sputtering, chemical vapor deposition, and evaporation, among other deposition processes. Not only are thin films extremely adaptable in terms of their applications, but they also come in a wide variety of forms. The following six primary types of thin films have a variety of uses, ranging from optically clear coatings to hard titanium and everything in between.

1. Metallic Thin films

Special thin films known as mechanical thin films are usually made of materials that are resistant to wear, corrosion, and abrasion. Thin mechanical films can be used in coating applications to offer extra strength against abrasion and friction to almost any surface, including metals, plastics, glass, and so on. Additionally, they provide excellent anticorrosive protection, which makes them useful in a variety of fields and applications, including transportation logistics and aerospace engineering.

2. Optical Thin Films

Typically, materials are coated with optical thin films to give them the appropriate optical characteristics. They are among the developments in the solar energy industry that enable the creation of flexible, lightweight, and environmentally friendly solar panels. Depending on the underlying layer mix and film protection, these specialty coatings can improve performance, increase reflectivity, or change color. These special thin films have the potential to benefit any product that is exposed to sunshine since they provide protection against UV radiation and sun-induced fading.

3. Electronic Thin Films

In electrical or electronic applications, thin films, especially those made of aluminum, copper, and alloy offer greater versatility than their bulkier counterparts. Heat transfer is made possible by these thin films' superior insulation compared to thick film components. The thin coating minimizes power loss and boosts sensor sensitivity when applied to circuitry. Because of this feature, they work extremely well with a variety of surfaces, including semi, insulators, and integrated circuits.

4. Magnetic Thin Films

When using magnetic qualities in engineering and industrial applications, magnetic thin films offer an alternative to conventional materials. They are extremely thin, frequently having a width of less than one nanometer. They nevertheless retain all the characteristics of ordinary magnets, namely attraction and repulsion. They also have several benefits, like remarkable durability and resistance to outside interference. These characteristics make them perfect for lengthy life in consumer products or operation in difficult equipment. Various kinds of magnetic thin films find application in automation systems, sensing apparatus, memory disks, and other data storage devices.

5. Thermal Thin Films

Thermal thin films are also referred to as insulating thin films, thermal thin films help with electrical resistance, heat dissipation, and insulation in a variety of industries. The polymers used to create these films have high-performance thermal properties, and they also contain unique additives that strengthen the films' resilience to thermal cycling and other harsh environments. For more flexibility and quicker application periods, thermal thin films can also be applied without the use of textiles or adhesives. In comparison to other materials, thermal thin films produce insulating layers that provide superior airtight sealing while using less electricity. Their immense value for industrial applications stems from this.

6. Chemical Thin Film

Among the most intriguing and intricate materials used in contemporary manufacturing are chemical thin films. These films provide a variety of promising properties, such as electrical conductivity, optical activity, and corrosion-resistant coatings. Chemical thin films provide protection that can increase the durability of very basic products. One can create bespoke compositions that are specific to the circumstance by combining different components. Chemical thin films are offering engineers and manufacturers alike an endless array of creative opportunities as new research is being conducted on them every day.

3. FERRITE MATERIALS

A Ferrite is a type of ceramic compound of iron oxide (Fe_20_3) combined chemically with one or more additional metallic elements. They are ferromagnetic meaning they can be magnetized or attracted to a magnet and are electrically nonconductive. Ferrites can be divided into families based on their magnetic coercivity, their resistance to being demagnetized. Hard ferrites have high coercivity, they are difficult to demagnetize. They are used to make magnets for devices such as refrigerator magnets loudspeaker and small electric motors. Ferrites are usually non-conductive ferrimagnetic ceramic compounds derived from iron oxides such as hematite (Fe_2O_4) as well as oxides of other metals. Ferrites are like most of the other ceramics, hard and brittle.

Spinel ferrite: Any crystalline material, not necessarily an oxide that possesses the same crystal structure as this mineral. Many ferrites spinel's with the formula AB_2O_4. Where A and B represent various metal cations. Usually including iron Fe.

General formula: $A[B_2]O_4$

Where, A divalent metal ions Fe^{2+}, Mg^{2+}, Ni^{2+}

B trivalent metal ions Fe^{3+}, Cr^{3+}, Al^{3+}, Mn^{3+}

Cubic close packing of O^{2-} ions

4. EXPERIMENTAL DETAILS

The A.R. grade form nickel oxide (NiO), manganese oxide (MnO_2), and ferric oxide (Fe_2O_3) were mixed in stoichiometric proportions to prepare a series of polycrystalline spinel ferrite $Ni_{1+x}Mn_xFe_{2-2x}O_4$, where $0.0 \leq x \leq 0.6$, in the step of 0.1. The samples were prepared by using standard double sintered ceramic technique [8]. The stoichiometric calculations were carried out by using the equation,

$$(1+x)\,NiO + xMnO_2 + (1-x)\,Fe_2O_3 \rightarrow Ni_{1+x}Mn_xFe_{2-2x}O_4$$

Each sample was ground for 4 hours using agate mortar. The samples were pre-sintered in a muffle furnace at 950°C for 12 hours. The pre-sintered samples were reground and compressed into a disc shaped pellet form by using hydraulic press with a pressure of 6 ton per inch^2. These pellets were sintered at 1200°C in air for 24 hours and were slowly cooled to room temperature.

X-ray diffraction (XRD) patterns were recorded at room temperature in the 2θ range of 20^0 to 80^0 to confirm the formation of single-phase cubic spinel structure. The dielectric measurements such as dielectric constant (ε'), dielectric loss (ε'') and dielectric loss tangent (tan δ) were investigated in the frequency range 100Hz to 5MHz at room temperature using LCR-Q meter.

5. METHODS OF PREPARATION OF THIN FILMS

Thin film preparation techniques can be broadly categorized into two groups: chemical techniques (which include electrochemical techniques) and physical techniques. We will focus primarily on physical techniques because they produce films that are extremely pristine and well-defined. In actual use, they work with a wide variety of materials and thicknesses. However, initially, we will list the many processes that can be utilized to create thin films in the part that follows.

The most significant chemical and electrochemical processes include chemical vapor deposition, anodic oxidation, electrolytic deposition, and electrolysis deposition.

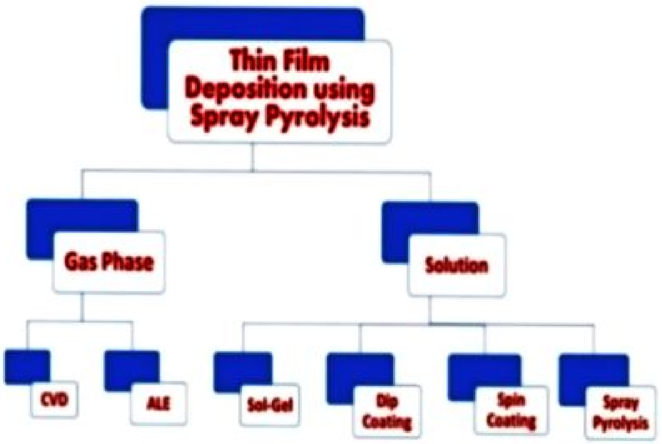
(a) The material (metal) to be deposited is present in a solution or melt in the form of ions during cathode electrolytic deposition. The positive ions of the metal will be drawn to the cathode where it would be deposited if two electrodes are inserted into the solution (or melted). The mass of the material deposited is directly correlated with the power consumed.

(b) The rate of deposition relies on the bath's temperature, and occasionally a catalyst is required to encourage the deposition. For instance, layers of nickel are formed on the surface of other metals using this deposition technique.

(c) The creation of films made of the oxides of specific metals, such as Al, Ta, Nb, Ti, and Zr, is the primary application of anode oxidation (anode electrolytic deposition). The metal that has been oxidized is an anode that has been dipped in the electrolyte, drawing oxygen ions to it. By means of diffusion driven by a powerful electric field, the ions traverse the pre-existing oxide film and amalgamate with the metallic atoms to generate oxide molecules. Because the strength of the film determines its growth rate exponentially.

6. TECHNIQUES FOR FABRICATING FERRITE THIN FILMS

There are various techniques for fabricating ferrite thin films. Out of which there are Sputtering technique, Ferrite plating, Dip coating process, Spray pyrolysis, Electro deposition or chemical bath deposition (CBD), Spin coating, Pulsed laser deposition, Sol-gel method etc.



Spray Pyrolysis Technique

Spray pyrolysis is a highly easy and economical method for creating ceramic coatings, powders, and thin and thick films is spray pyrolysis. Fig. 2 displays the spray pyrolysis scheme. An atomizer, precursor solution, substrate heater, and temperature controller make up the spray pyrolysis apparatus. In the spray pyrolysis process, an atomizer is utilized to create a stream of liquid that needs to be coated over the substrate. The atomization process determines the droplet size of the precursor solution. Whereas ultrasonic spraying creates smaller size droplets, aerosol spraying produces larger size droplets. For the coating, the substrate is heated above the hot plate. The two crucial variables to consider are the droplet size and the deposition temperature.

Spray pyrolysis method atomizes the solution into tiny droplets, which are then carried to the heated substrate by gas producing thin films. Because the smaller droplets are determined by ultrasonic spraying, the atomic cloud aerosol produces larger droplets. This affects the material's surface shape. Spray pyrolysis uses little equipment and is incredibly effective and economical. The resultant thin films have a substantial substrate coverage surface area, mass synthesis potential, and uniformity.

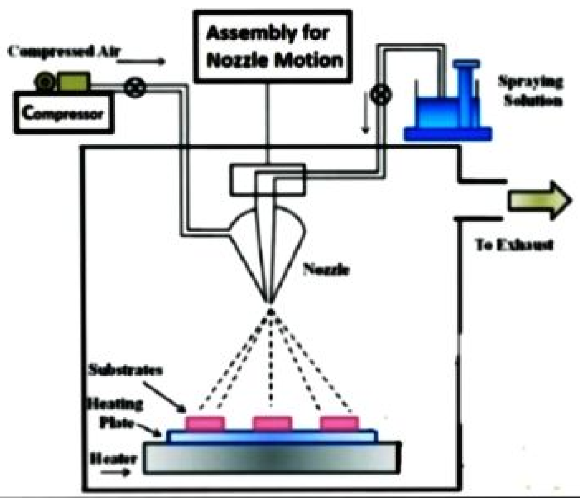


Fig.1: Spray pyrolysis method unit

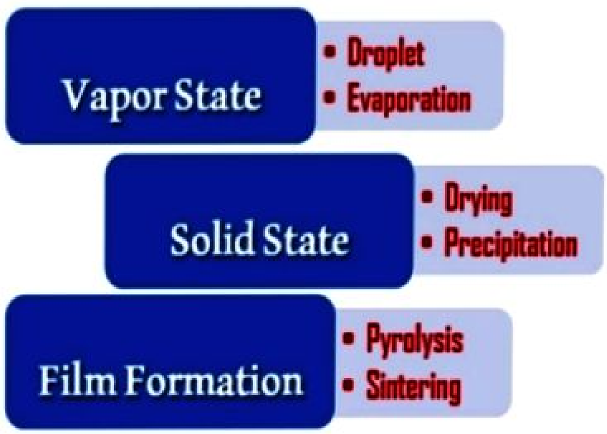


Fig.2: Stages in Spray Pyrolysis Method

Stages in Spray Pyrolysis Method

There are various stages in spray pyrolysis method such as vapor state, Solid State, and Film formation as shown in **Fig. 2.**

Technological applications

It is found that there was a rapid development in thin film technologies in nineteenth century when growing importance of micro-electronics including integrated circuits and hybrid circuits of thin films. Thin films' growth was found to be phenomenal due to their tremendous applications in space and military uses. There are many advantages of thin films over the bulk material due to low cost of production, extreme compactness, high reliability and corresponding reduction in sizes and weights, low power consumption, etc.

7. CONCLUSIONS

Applications for thin film coatings range from light absorption to equipment protection against abrasion. The optical, electrical, or electronic, magnetic, chemical, mechanical, and thermal films are the six primary types of thin films. There is a thin film solution that works for you, regardless of the application you have in mind because each variety has unique qualities and applications.

- The spray pyrolysis technique is a very simple, cheap, versatile method for the deposition of thin films because of having number of parameters for the optimization of properties and surface morphology of thin films as compared to the other methods.
- This technique is versatile technique to fabricate many M-S plasmonic thin films. The spray pyrolysis technique is amenable to large area deposition.
- Ferrite thin films with spinel structure are potentially interesting and scientifically promising for high frequency devices where low conductivity and high saturation magnetization are important aspects.

- Taking in view all the properties, application, and the importance of ferrite thin films it is very important to have a study of thin films. It is the need of time to study spinel ferrite thin films. The spray pyrolysis technique is a versatile method for the deposition of thin films.

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