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Review Article

An Overview to Current Trends in Metal Oxide Thin Film Preparation Methods

Cemre AVŞAR[1*]

[1]*Toros Agri Industry and Trade Co. Inc. R & D Center, Mersin / Turkey*

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*****Corresponding author e-mail: cemre.avsar@toros.com.tr

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ABSTRACT

Thin film preparation and coatings technology has been gaining attention as there is an increasing demand to the functionalized novel materials. Surface design through catalytically active materials such as metal oxides or zeolites as thin films and application through coating provides unique properties to the substance and result novel materials physically and chemically differing from their bulk form. Design technologies allow the preparation of structurally ordered thin films and coatings. Currently, designed thin film materials and coatings have a wide application range such as catalysis, sensing, anti- reflective surfaces, photovoltaics, or specialty design for targeted applications. This study provides a brief overview to the preparation methods of catalytically active coatings and thin film substances, which might be of industrial relevance in the case of the design for targeted applications.

Keywords: Thin film, coatings, functional material design, activated surface

1. INTRODUCTION

Design and synthesis of thin films and functionalized surfaces is a specialty area, in which sequential procedures are required. Catalytically active surfaces and functionalized thin films should have highly oriented structure with homogenously distributed morphology and uniform composition through the surface. Prior to synthesis, thin film substrates are pretreated, followed by coating step. Some cases require a multi-layer coating step, allowing a more stable surface with high adhesion property. Current applications of thin films and coatings have a wide range of application areas such as electrochemical applications, membrane synthesis, separation processes, functionalized surfaces such as antibacterial or photocatalytic coatings. [1-7]

Specialty designed thin films and coatings are prepared by synthetic procedures via physicochemical, electrochemical, thermal or mechanical methods to obtain a desired property. The basic approach in thin film preparation is the chemical reaction taking place at the interface of two materials.[8] For this reason, it is important to adjust and control the parameters affecting thin film growth.

2. Thin Film Synthesis and Coatings Technology

2.1. Substrate pre-treatment

Adhesion between the thin film coating and substrate is of importance to satisfy the stability and durability requirements. In this manner, high surface area with high roughness and porosity is desired to achieve an efficient adhesion. Prior to thin film synthesis, substrates are generally chemically pre-treated to remove the impurities on the coating surface. Pre-treatment procedure is generally treatment with acidic, alkali or oxide agents to obtain a cleaned surface with some etching to prepare for coating.[9-11] Anodic oxidation is an appropriate method to prepare porous metal oxide layers of alumina, silica or stainless steel on various substrates.[12] Thermal oxidation is commonly applied to obtain porous layers of iron and silica.[13] Surface oxidation is basically similar to chemical

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treatment techniques, mostly acidic or alkali treatments are performed for surface oxidation. However, oxidation agents differ according to substrate type, alumina substrates are generally treated with acidic media, whereas silica or titania substrates require alkali media for surface oxidation.[14]

2.2. Deposition Methods for Preparation of Metal Oxide Surfaces

2.2.1. Sol-gel coating

Sol gel method is basically defined as the utilization of a sol precursor, which is further hydrolyzed and gelled, resulting *in situ* deposition on the substrate surface. Metal oxide coatings are generally prepared by sol-gel method. Once the substrate is immersed into the sol solution, it is essential to provide appropriate time to allow the formation of sol into gel on the substrate surface.[15-18] Generally, sol particles are hydrolyzed via acidic media and hydrolysis rate should be controlled by the substrate.

In some cases, sol-gel coating is co-operated with dip coating method to obtain functionalized coated surfaces.[19] The mechanism of this hybrid synthesis technique can be basically defined as the sol-gel thin film formation via dipping. In this manner, thin film material precursors and substrate surface are adhered to each other, followed by withdrawal, and drying.[20] Although sol-gel dip coating method is also a straightforward method, operating parameters should be optimized for specific cases as preparation methods can adversely affect the catalytic performance of resulting thin films.

Metal oxide thin films with adequate porosity can be produced by sol-gel method with an adequate adhesion between coated metal oxide and substrate surfaces. Sol-gel media, hydrolysis agent and the stabilizer type can affect the catalytic properties of the coating and the thickness and uniformity of the thin film. Physical properties of the sol solution, such as viscosity, aging time or pH can also affect the adhesion rate on the surface.[21-22] The mechanism of during sol-gel coating method is affected by various parameters, thus it is essential to optimize the physico-chemical behavior of the coating media.

Alternative methods have been emerged to sol-gel method such as spray or spin coating and electrostatic spray deposition methods, in this manner the rheology of the synthesis solution plays an important role to bear the shear rate during coating process.[23-25] Coating efficiency in terms of coating thickness in spin and spray coating is affected by the viscosity of the sol and shear rate upon spin speed. Electrostatic spray deposition differs from spin and spray coating methods, in which heated substrate surface is coated with charged aerosol sprayed on.

2.2.2. Dip coating

Dip coating method is a straightforward method to obtain catalytic surfaces on substrates, and mostly preferred for the coating of high-surface area substrates**.** Coating media is an important parameter to obtain stability on coatings, mostly active components are preferred in the coating media.[26-27] Particle size is an important parameter affecting the dip coating mechanism. Smaller particle size allows the formation of more adherent layers on the substrate surface. Viscosity modifiers, binders and additives are utilized to obtain a desired viscosity range in the coating solution. Cellulose type agents such as ethyl cellulose[28], hydroxyethyl cellulose [29], propyl cellulose [30] or acidic agents such as polyacrylic acid[31] are utilized for viscosity adjustment.

Desired viscosity would result efficient adhesion. In the case of viscosity modifiers are utilized, it is essential to remove the residues after coating and drying process by calcination. Monolithic substrates are the most inappropriate for dip coating process as they have high surface area.[32] The ease of application of dip coating process to monolithic surfaces have led a wide application area for catalytic applications.

2.2.3. Electrochemical routes

Electrochemical route for preparation of thin film coatings involves electrodeposition or electroplating methods. This route can be explained by the deposition of metal oxide on a substrate in the presence of an ionic solution. Deposition can be achieved by the application of an electric current.[33] Applied electric current allows the movement of ions in the deposition solution, which further deposit on the surface of the charged substrate.
Electrophoretic deposition method is the deposition of a material present in a charged suspension solution through an electric current to obtain a coating.[34,35] Another electrochemical route is the autocatalytic plating, in which the fundamental of redox chemistry is utilized.[36] Electrochemical routes are straightforward and efficient methods to obtain metal oxide coatings with cost effective approach.

2.2.4. Vapor deposition routes

Vapor deposition routes are basically classified as chemical vapor deposition (CVD) and plasma-assisted chemical vapor deposition (PACVD) methods. CVD method utilizes a volatile precursor to be deposited on the substrate in a deposition chamber. The operating conditions for CVD method is preferred to be under low pressure and high temperatures to favor the deposition

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rate.[37] PACVD method allows the deposition at relatively lower temperatures with the presence of plasma and result high deposition rates.[38] CVD and PACVD methods are efficient deposition methods for nanoscale materials. Physical vapor deposition (PVD) method is the utilization of vapor generated for thermal coating on the substrate.

PVD had increased attention on electrochemical routes as it highly provides accuracy- uniform deposition, high adhesion with wide range of applicable substrates. PVD method is also efficient at low thickness thin film coatings.[39] Classifications of PVD method can be performed as cathodic sputtering or evaporation. Cathodic sputtering method utilizes a plasma generated in vacuum, and the substrate is operated as the anode. Plasma generated allows the coating on the substrate.[40] Atomic layer deposition (ALD) method is basically similar to CVD in terms of volatile precursor utilization, which is separated by purge of an inert gas. Film thickness control is highly versatile in ALD method with the help of pulses.[41] This method also has a high potential for nanoscale deposition as it favors the sub-nanoscale thickness control.

Pulsed laser ablation (PLA) deposition is the ablation of metal oxide particles on the substrate at low pressure and high temperature conditions.[42] Increase in the laser pulse increases the film thickness; thus, it can be said that the film thickness is controlled by the number of pulses.

Thermal vapor deposition is the deposition of vapor phase precursor onto the substrate surface via contact with each other and form thin film on the surface. Vapor phase transport techniques are highly applicable for thin film preparation as control of film thickness is highly adjustable and structural changes in the film can be obtained.[43] Solvent evaporation induced self-assembly is another thermal vapor deposition method, in which heat is also utilized for deposition and suitable for nanoscale coatings. Flame vapor deposition (FVD) is basically defined as the decomposition of the precursor to the air and the contact with the substrate to form a coating.[44,45]

3.General Comparison of Deposition Methods

CVD and PVD methods generally result thin film coatings of fine thickness with low surface area. Relatively low surface area obtained via CVD and PVD methods result low catalytic activity of the resulting films. Sputtering methods are preferred when catalytic activity is of importance. Higher thickness films can be obtained via FVD method. FVD method has the advantage since it does not require operation conditions at low pressures. On the contrary, CVD and PVD methods require deposition chambers. Sol-gel coatings might be structurally unstable and highly brittle upon thermal treatments. Among all of those methods discussed, it is essential to prefer the appropriate substrate- metal oxide type and the deposition method for a particular application.

4. CONCLUSIONS

This study provides a brief review of current technologies in synthetic thin film and coating synthesis. Synthesis routes are mainly classified into four main groups as sol gel, dip coating, electrochemical synthesis, and vapor deposition synthesis routes. Basic definitions and highlighted features of each synthesis route are given, advantages and disadvantages are discussed with general comparison of deposition methods. Substrate and synthesis route selection for targeted application is also given. This review might be useful as a summary of the current technologies in thin film synthesis and coating preparation methods.

4.1.List of Abbreviations

CVD	chemical vapor deposition
PACVD	plasma-assisted chemical vapor deposition
PVD	physical vapor deposition
ALD	atomic layer deposition
PLA	pulsed laser ablation
FVD	flame vapor deposition

Conflict of interest

Author declares that there is no a conflict of interest with any person, institute, company, etc.

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