Research Journal of Chemical Sciences E-ISSN 2231-606X
Vol. **6(7),** 65-72, July **(2016)** *Res. J. Chem. Sci.*

Review Paper

Thin Film Coating through Sol-Gel Technique

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Available online at: www.isca.in, www.isca.me
Received 31st March 2016, revised 2nd May 2016, accepted 30th June 2016

Abstract

Thin film coatings are a much explored domain, since films are well suited for the studies of physical, particularly optical properties and have numerous scientific, technological, and commercial applications. For depositing thin films, a large number of techniques have been used which involves different types of precursors. This review will highlight coating technology utilizing the sol-gel mediated precursor, which delivers high homogeneity, low temperature processing and various other advantages. Besides this, thin film depositing techniques like spin coating, dip coating have also been discussed with their various applications.

Keywords: Sol-gel, Thin film, Coatings, Applications.

Introduction

Sol gel: Sol-gel process is an amalgamation of a number of methods for synthesizing materials from solutions, which involves gel formation as one of its stages of processing. Most popular type of the sol-gel synthesis is based on controlled hydrolysis of compounds, usually alkoxides[1] $M(OR)_x$ (M = Ti, Si, V, Zr, V, Mo, Al, Sn, W, Zn, Ge, etc.) or corresponding chlorides[2], in an organic or aqueous medium. This method of synthesizing materials is based on the phase conversion of a sol obtained from metallic organometallic or alkoxides precursors. The obtained sol which is a solution of particles in suspension gets polymerized at low temperature, eventually forming wet gel[3]. The solvent is eliminated by exposure to standard heating to form the dry gel[4].

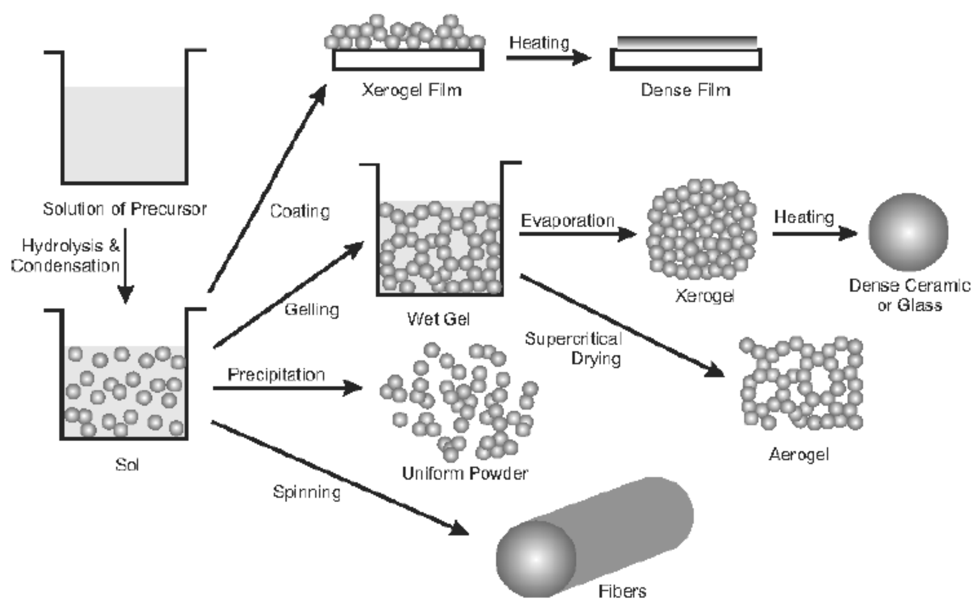

Figure-1
Steps involved in controlling the absolute morphology of the desired material[5]

At the initial stage of this process the polycondensation and hydrolysis reactions directs to the development of a colloidal solution, commonly known as sol, of hydroxide particles of size in nano regime. Modulating, primarily increase in the mass of the desired material or any significant changes in the outer surroundings like that of substitution of solvent, potential of hydrogen (pH), solvent substitution, etc. results in excessive contact formation between dispersed material and thus monolithic gel is formed[6], which have a flexible and very stable three-dimensional grid of hydroxides which encloses the solvent. Purification of sols thus formed after gelation can be achieved by extraction, dialysis (electrodialysis), ultrafiltration and evaporation of the corresponding sols at relatively lower temperatures.

One of the crucial roles in this method is ruled by different techniques of solvent elimination after gel formation. Various products (xerogels[7], ambigels[8], cryogels[9], aerogels[10]) can be obtained depending on the route of synthesis, whose applications can be done in accordance with their differing range of properties. The preservation of the size in nano regime of the product and exceptionally high surface to volume ratio (hundreds of m^2/g) is the common regularity that has been obtained from all these processes, even though bulk mass of the precursor can be different by thousands of times. A wide range of products of this method are brought into play as the starting material for obtaining ceramics and nanopowder oxides. With a pronounced quasi-one-dimensional arrangement xerogels can also be synthesized via this process[11]. For example, vanadium oxide nanotubes can be synthesized using $V_2O_5 \cdot nH_2O$ xerogel as the[12].

Polymer to gel process is also included in this method, which involves gel development by the Pechini method (citrate gel)[13] or by evaporation of the solution of the water soluble in the initial solution. Methods like supercritical drying or freeze-drying gels via treatment of consequent heat in an inert ambience is used for the fabrication of carbon aerogels and cryogels. One of the importance of these coatings is that these can be deposited at a low temperature, and thus allowing the coating of substrates in polymeric form. Furthermore, low temperature coating has very less impact on the concluding properties of the surface so, specific functional properties can be obtained that were previously not a part of the conventional processes.

Sol-gel technique has wide range of applications. One such application is the formation of thin film coatings through sol-gel which involves metal-organic or inorganic compounds as precursors[14]. Mostly metal alkoxides are used as metal-organic precursors because they lead to a solid amorphous metal by reacting with water through condensation and hydrolysis reactions. For either metal-organic or inorganic precursors, the modification in the structure of polymers or oligomeros relates directly to the hydrolysis extent and the functionality of the metal or preferred coordination number. In the scheme including metal organic precursor, the rate of hydrolysis is controlled by the hydrolysis ratio, whereas in inorganic precursors, this rate is often controlled by the pH[15]. The formation of thin films is done by centrifugal of gravitational exhausting, escorted with vigorous stirring and then drying which leads to the establishment of the shape of fluid outline, magnitude of the forces exerted on the solid phase and timescale of the deposition process.

In late 1980s and 1990s, various technical fields also started exploiting this technique, such as biomedical applications[17]. In 1989, sol-gel expertise for coating and powder purposes came into existence in Australia. This development is credited to the scientists from University of NSW, ANSTO, University of Technology, Monash University, DSTO and Silicon Technologies Pt. Ltd. A number of research papers were published covering wide a range of ceramics from ceramic superconductors, titanates, calcium phosphate, single and mixed oxides[18].

History: The sol-gel process through a suspension of colloidal particles came into existence with the origin of chemistry. This technique in 1846 was applied leading to the emergence of a new technology, when a scientist, Ebelmen observed the polycondensation and hydrolysis of tetraethoxysilane which is also known as tetraethylorthosilicate or TEOS. In 1939, the first patent for sol-gel was published which inculcates the synthesis and characteristics of SiO_2 and TiO_2 for optical applications[19]. The possibility of this technique in the production of high purity glasses which was unfeasible with established ceramic processing route was acknowledged in 1955[20]. Consequently, the first details on the relevance of this condensation technology to produce consistent multi-component glasses came into existence.

Seventy-six years ago Berger and Geffcken reported the sol-gel[19] and synthesized single oxide coatings. Later, Schroeder[21] formulized thin film coatings by using layers of many mixed oxide and single oxide. In 1953, the appearance of first thin film product took place in the market and by the end of 1959 considerable making of rear-view mirrors of automobiles (titanium and silicon oxides) started. With the progress in research works all around the world, antireflection coatings in 1964[22] and sunshield in 1969 made their way into the blooming market[23]. It was in 1969 when Hinz and Dislich[24] explained the chemistry of the synthesis of multi-component oxides, process technology and the fundamental standard of the chemical reactions was known. In 1969, applications for patent were filed[25] which was granted in the countries undergoing industrial development, with the details being published. Concurrently and autonomously, a comparable type of scheme was applied taken by Thomas and Levene and was filed as well[26]. From then it has been identified that this sol-gel process can be worn to synthesize any kind of multi-component oxide using various elements like any crystalline substance such as a glass or a ceramic of glass in their alkoxide form. For the same time it has also been known that the synthesis process following these routes leads to the formation of exceedingly pure and extremely homogeneous modified multicomponent oxide. During that time there was a very modest knowledge about the particulars of the steps involved and mainly about the central sol-gel reaction. Major changes have taken place till now in the reaction process. A substantial number of parameters should be distinctively known and ought to be regulated within close limits to certify uniformity in the desired material. After all this chronological observation, we must give some deliberation to the contemporary feature. Glass layer being one such example and it is the first invention in the market[27].

Advantages of sol-gel technique: For the preparation of thin films a number of methods have been employed including chemical vapour deposition, e beam evaporation, sol-gel process and sputtering. The conventional sol-gel scheme involves continuous condensation of the particles formed initially due to the hydrolysis of the alkoxide precursor and finally forming gel which is commonly known as hydrolytic route. For two main reasons, the sol-gel technique is predominantly advantageous for the development of thin coatings of oxides. Firstly, coating of the complex shapes became significantly easier utilizing the dipping which is thought to be the major drawback of the coatings via vapour deposition. Secondly, very small quantities of precursor are required and making the process economic, thus, the price of metal organic raw material is not of much significance. Regardless of large shrinkages in the drying process, thin oxide coatings actually do not fracture when the surface arrangements are fine, as rather than shrinking laterally the gel film would shrink in the width direction[28].

Room temperature is the appropriate temperature for carrying out this procedure and the desirable morphology can be monitored by controlling the reaction conditions. The liquid raw material can be easily functionalized on a base by spraying or spinning, heat treated at lower temperatures and dipping therefore, sol-gel process route is very much attractive scaling-up of synthesized oxide thin film. In case of non planar structures and on semiconductor chips, spray-coating practice offers the benefit of even film deposition.

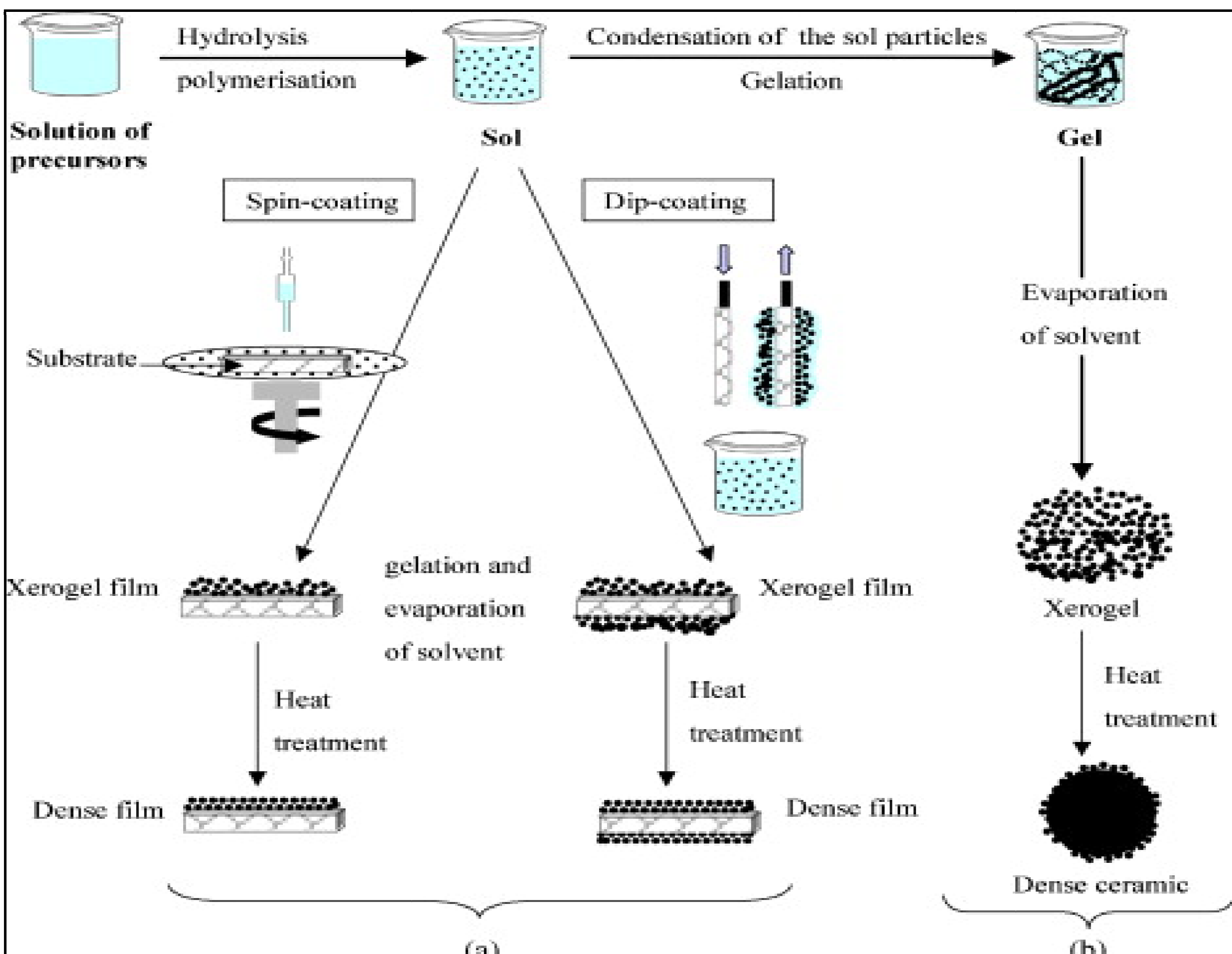

Figure-2
Steps for preparation of thin films and powder by the sol–gel process[16]

Moreover, the sol-gel process maintains the option of synthesizing a large area and small area coating of thin oxide films at an econmical technological applications[29].

Role of the thin film coating may be to provide one or more of a number of functions: (i) Chemical protection (e.g. corrosion protection)[30] (ii) Mechanical protection (e.g. abrasion resistance)[31] (iii) Optical properties (e.g. anti-reflective, optoelectronic)[32] (iv) Electronic properties (e.g. ferroelectric, conductive)[7,23] (v) Catalytic activity (usually associated with high surface area)[33].

Many different industries are gaining profit from adopting sol-gel because of its flexibility in fabricating a wide range of materials with desirable characteristics. Today, a lot of examples are found in the automotive, biomedical sectors, construction, communications, and electronics. Glasses and ceramics fabricated by sol-gel have identical material properties as that of those synthesized by the other conventional routes. The advantages of using sol-gel processing route as an alternative of high temperature processing methods are low synthesis temperature[34,35], high purity[36], high homogeneity[37], better yield[38], novel materials[39], low capital cost[34,35].

Disadvantages: Apart from being a great synthesis route, the sol-gel technique also has some serious drawbacks. The foremost ones being the drying of gel and the extreme volume shrinkage at the time of gelation, the elimination of the unwanted residuals (hydroxyls and organics) and the occurrence of large amount of pores. Perhaps, deficient technical and precise knowledge about the sol-gel process is the main disadvantage that creates wide range of complexities in the process [40].

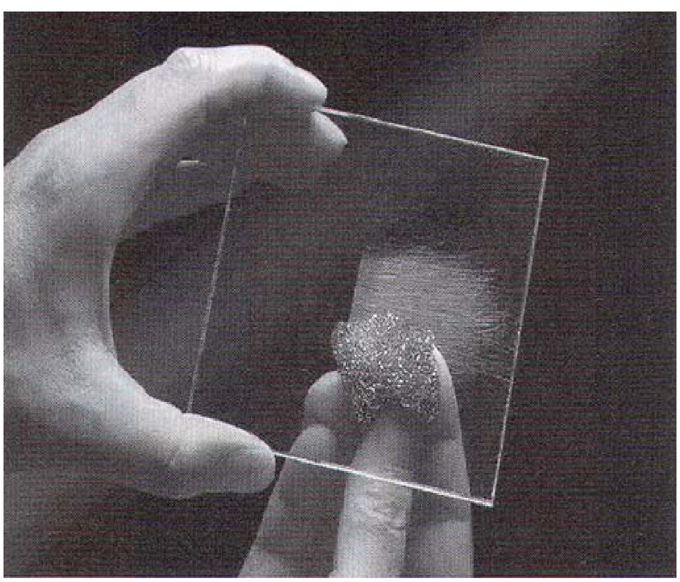

Figure-3
Scratch resistant coating (left half of slide coated, right half uncoated)[41]

Sol-gel thin film Coatings

Thin coatings are remarkably thin layers of raw materials (SiO_2, TiO_2, MgF_2, Au, Al etc.), that can be functionalized to the substrate like metal, glass or crystals, ceramics to effect a modification in its opto-electrical properties. Properties such as refraction, conductivity, reflection and anti-reflection can be shaped and tailored by specialist calibration of material selection, the relevant thicknesses of each thin layer and the number of layers. All these parameters are in relation to the incidental wavelengths of light. Application of thin films over different materials is done to improve and achieve brilliant properties that give superior advantages and applications of the materials which was not possible otherwise.

Thin films of variable thicknesses ranging from micrometre to nanometre can be synthesized according to our need. The utility of thin oxide films is greatly increased as it shows different applications and properties which involves light emitting diodes (electrical devices), computer memory applications, interference and electrochromic filter, magnetic films (data storage), solar cells, anti-reflective liquid crystal devices films, compact discs (optical storage devices) and electroluminescent devices[42]. The function of an optical coating is to alter the reflectance and transmittance of the material (substrate) on which they are functionalized. Classifications of the coatings on the basis of their application are as follows:

Antireflection coating: It is used for the inhibition of unnecessary reflections, usually occurring at *the* boundary between the two different substrates. Example: boundary between glass and air.

High reflection coating: In contrary to the antireflection coatings, reflectivity of a surface can be increased by mirror coatings.

Partial reflection coating: Beam splitters transmit a particular ratio of the entering light and return the rest of it. They are frequently used at nonzero angles of incidence.

Polarization coating: Using polarisers, the incident light can be separated into components that are orthogonally, characteristically reflecting one and transmitting the other.

Filter coating: These can be used to of the preceding functions and the selectivity is based on wavelength; for example, reflecting one wavelength and highly transmitting the other.

Dip Coating: It is the easiest method of thin film synthesis from chemical solutions at a fast rate with the maximum degree of control, making it appropriate for Research & Development and productions at small scale. In specific high technology cases this method can be used for deposition of coatings of large surfaces. The principle being a simple one, simply withdrawing the substrate at a constant speed which is initially dipped in a solution. At this stage of dipping process, solution homogeneously and naturally stretch on the plane of the material (substrate) by the mutual effect of capillary rise and viscous pull. Then solidification of the final coating takes place by natural or forced evaporation. A fine adjustment of the evaporation conditions (relative vapour pressure and temperature) and withdrawal speed is necessary to perfectly control the characteristics of the film which includes the thickness of te film and the inner structure. Amid all accessible methods used for this function, dip coating provides the exceptional prospect to precisely direct the vital parameters.

In comparison to the other conservative thin film formation processes such as forced or air evaporation, sputtering, chemical vapour deposition (CVD), sol-gel dip coating is potentially economical and requires less equipments. Nevertheless, the most imperative benefit of sol-gel technique over usual thin film coating processes is the capability to mould the micro-arrangement of the films to be formed.

Spin coating: The main difference between spin and dip coating is that in spin coating the film being deposited thins by evaporation and centrifugal draining. Spin coating can be divided into 4 stages: deposition, evaporation, spin off and spin-up, even though in case of sol-gel technique for thin film coating, usually evaporation overshadows the former stages of stages. During the deposition stage, surplus amount fluid is expelled on the surface of substrate. Now, in the spin-up stage, due to the centrifugal force, the outward radial flow of liquid start. Further in the spin-off stage, excess liquid flows to the edge and leaves as droplets. There is a greater resistance to flow as the film thins so there is a decrease in the rate of removal of excess liquid by the spin-off process, which can further be justified by the increase in viscosity due to the increase in non-volatile component. In the concluding stage, the primary mechanism of thinning is taken over by evaporation[44]. The plus point of spin-coating is that during the spin-off process, the uniformity that is attained tends to remain that way until there is any variation in the viscosity because of different substrate and is independent on shear force. This affinity is because of the resonance between the two main forces: and viscous force (acts radially inward) and centrifugal force (acts radially outward).

Applications

Optical Coating: Thin films are known for their distinctive optical properties that can be applied in electronic devices, data communication, ultra fast optical data storage, and so forth. Nanoscale platinum, gold, silver, etc bipyramids, triangular shapes, cubes, and spheres all display diverse colours because they absorb or scatter light of different frequencies as the electrons in the conduction band oscillates collectively at different resonance frequencies for different shapes. The intensity and frequency of Surface Plasmon Resonance (SPR) are dependent on the charge distribution at the nanoscale, which in turn is shape dependent[45]. Thin films offers an important number of applications such as blue laser diodes, white light emitting diodes (LEDs) and optically controlled switches[46].

Electronic films: As we move from bulk to nano scale, the surface to volume ratio changes drastically, inculcating some exceptional properties including quantum confinement (Q-dots, observed in semiconductors), confined surface plasmon resonance, catalytic (electrocatalytic properties) and super-paramagnetism (observed in some nanocomposites and metal oxide nanoparticles). All these new and exceptional properties have been productively applied to bio-imaging probes, biosensors, memory devices and optoelectronic devices. The production of these nanomaterials can be done through top-down or bottom-up approach. Once the nanomaterial has been synthesized, it can be deposited as coatings, or can be used as any other form by manipulation of the colloidal solution[47].

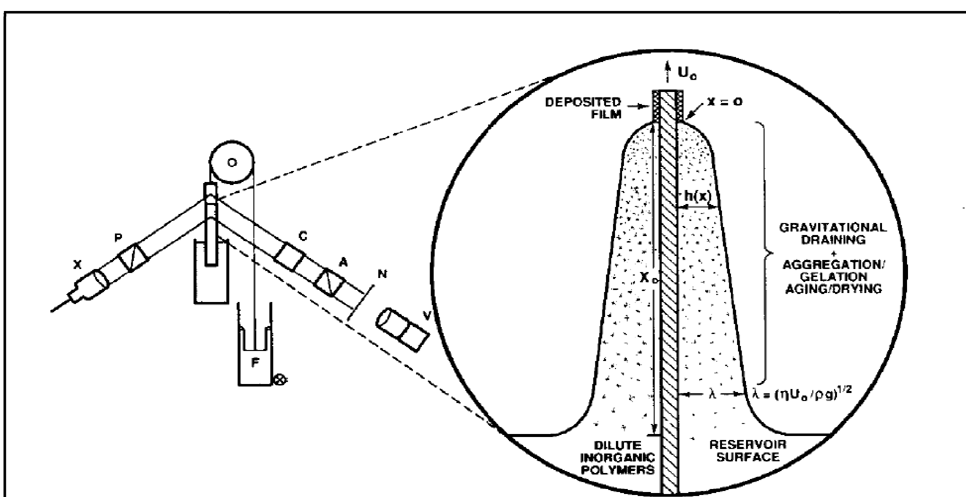

Figure-4
Schematic of dip coating technique[43]

Protective Films: To protect metals from corrosion organic coating are being used in wide range of industries. Ceramic coatings with good thermal and electrical properties and higher resistance to oxidation are attracting the mass as these can be worn at high temperature environments. In a wide range of field, TiO_2 coatings based on photo-induced charge transfer are being applied such as, pollutant degradation, solar cells or super hydrophilic materials. Its application as cathodic protection of metals (under UV illumination) is also being applied. Pure TiO_2 coating cannot be used under dark conditions (charge recombination problem), that can be overcome by using Fe doped TiO_2 layer under a TiO_2 coating by coupling another semiconductor having different energy level which could reduce the charge recombination[48].

Porous Films: Porous films are nowadays uses in various fields because of their unexpectedly high surface area. They are used in solar cells, many surface reactions, sensors, etc. For gas and chemical sensing, metal oxide materials have been used, which include gases like H_2, CO, Cl_2, CO_2, NO_x, CH_4, NH_3, SO_2, etc.[49]. In a solar cell, dye-sensitized mesoporous semiconductor film electrode is used as a sensor. For the metal oxide sensors, the performance is regulated with the particle size, shape, necking structure, porosity and film thickness[50]. For the application of surface reactions, porous TiO_2 thin films are desirable because of ultra high surface and thus many scientists have reported on its synthesis[51].

Conclusion

The sol-gel technique is one of the easiest techniques for the preparation of thin films, powder, xerogel, aerogels and glasses. Various parameters involved in the sol-gel technique i.e. concentration and composition of the corresponding metal alkoxide or chloride, synthesis temperature, solvents, sequence of the added precursors, can be modulated desirably to get the type of material required and hence, thin films having desirable properties and applications can be deposited. Different depositing techniques like dip coating and spin coating can be easily exploited to obtain the desired thickness of the film. A great variety of sol-gel derived films like optical, porous, protective and electronic have been synthesized for different applications.

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