SOL-GEL: A simple method of Thin film deposition and Nano-particle growth

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Abstract

Recent trend of miniaturization has emphasized the importance of thin films. This has led to development of various methods of thin film deposition. In this paper, Sol-Gel method of thin film deposition is discussed. It is a chemical method and does not require heavy or expensive equipments for thin films deposition. Moreover, it provides easy compositional control and modification, excellent control of stoichiometry, room temperature deposition with relatively low annealing temperature and possibility of film deposition on large area substrates. Interestingly, sol-gel method is being extensively used in preparing nano-particles of various compounds. Thin films, nano-particles, ceramics prepared by this method find industrial applications.

1 Introduction

Historically, sol-gel processing started with studies on silica gel way back in mid-1800s [1, 2]. This method had been widely used to prepare glass and poly-crystalline ceramics both as pellets and fibres. This method was also used to deposit films such as ITO (Indium Tin Oxide) and other similar compositions deposited on glass panes for insulation [3, 4]. The trend toward thin films began, in earnest, during 1970's but has recently accelerated, partly because newer techniques for producing high quality films have been developed and also because of a wide variety of applications of thin films. Thin films of different materials have some important advantages, such as, large capacitance, low switching voltage and the possibility of forming films directly on integrated semiconductor driving circuits [5, 6].

A detailed discussion of one of the fabrication method, namely, sol-gel technique, is presented here. Easy composition control and requirement of simple equipment makes it attractive for thin films fabrication. Recently, nano-particles of various materials have also been successfully prepared by this method. This method has been widely used to prepare oxide films of various materials for various applications like memory devices, optical sensors, gas sensors, etc. [7].

The objective of this paper is to describe various steps of sol-gel process.

2 Fabrication Techniques

The various techniques used for thin film fabrication can broadly be classified into two categories: [5, 8]

1. Physical methods
2. Chemical methods

- Various Physical methods are:
    1. Thermal evaporation
    2. Sputtering : which can be high electric field (DC) sputtering, radio-frequency field (rf) sputtering and Magnetron sputtering
    3. Pulsed Laser Deposition (PLD)
    4. Molecular Beam Epitaxy (MBE)
- Various Chemical methods are
    1. Spray Pyrolysis
    2. Chemical vapour deposition (CVD). Some variations of this are Metal-Organic chemical vapour deposition (MOCVD) and Plasma enhanced metal-organic chemical vapour deposition (PE-MOCVD).

With the exception of sputtering method, all other fabrication techniques generally produce polycrystalline films which have properties more similar to ceramics than to single crystal.

Sol-Gel process has some important advantages which makes it quite attractive for thin film deposition as well as for forming powders for pellet or ceramic formation.These are :
(i)The excellent control of stoichiometry,
(ii) ease of compositional modifications,
(iii) relatively low annealing temperature,
(iv) possibility of film deposition on large area substrates
(v) simple and inexpensive equipments are required to deposit films on different substrates. The sol-gel method would allow the coating of more complex shapes and forms.
(vi) powders can easily be formed by drying the gel at suitable temperature which can then be pressed into ceramics. This can be accomplished at a lower temperature as compared to traditional ceramic processing methods and glass melting processes.
However, there are some disadvantages also such as substrate sensitive crystallization of films and difficulty of producing high quality films with thickness greater than $1\mu m$ or less than 100nm [9].

Now, we discuss the various steps of sol-gel process.

3 Sol-Gel Process

Let's first define a few terms used in this process, namely, Colloid, Sol and Gel. **Colloids** are solid particles that range in size from 1 to 100 nanometers. Colloidal particle are dispersed in the solvent to form **Sol**. **Gel** represents a colloidal or polymeric solid containing fluid component which has internal network structure such that both the solid and the liquid components are highly dispersed. [10, 11]

Three methods are generally used to make sol-gel monoliths: (a) gelation of a colloidal powder solution, (b) hydrolysis and polycondensation of metal-nitrate or metal-alkoxide precursors solution. And then the gel is dried, (c) hydrolysis and polycondensation of a solution of metal-alkoxide precursor [10]. The solution is then aged and dried at an ambient condition.

3.1 Brief outline of steps

In the sol-gel technique, synthesis of an inorganic network is carried out by a chemical reaction of precursors in solvent and the solution so formed, at a comparatively lower temperature. The sol-gel process includes several steps [12], [10, 13] as given below:

(i) **Solution preparation** : In the first step, the solutes are dissolved in a suitable solvent to make a solution. The solutes may be inorganic nitrates, inorganic chlorides or a wide variety of metal-organic molecular compounds. The solvent can be water, a short chain aliphatic-alcohol, or an organic acid. For a multi-component composition, this step allows easy composition control.

(ii) **Formation of the sol** : When the solution is allowed to stand for some time sol is formed. Viscosity of the sol is more than that of a clear solution. If colloidal powders are available, they can be dissolved at a suitable pH which prevents precipitation so that a sol is formed directly as in the case of Silica gel [14, 15]. A solution of metal-alkoxide precursors is subjected to hydrolysis and condensation reactions in the solution. These then result in the formation of sufficient number of interconnected bonds which then behave as colloidal particles or sol.

(iii) **Gelation of the sol** :When the sol is allowed to stand for sufficient time, hydrolysis and condensation reactions continue resulting in the formation of gel. This process is called aging. An inorganic network can be formed by these reactions. The extent of cross-linking and the size of the particles affect the physical characteristics of the gel network. Viscosity increases sharply at gelation. Precipitation occurs when the size of the gel network is sufficiently large.

(iv) **Shaping of the gel**: Final gel shapes include spheres, fibres, powders, cubes, thin films etc. The gel can be given different shapes by controlling the time-dependent variation of the viscosity of the sol [16]. It has been shown that fibres can be drawn from a sol only for a range of viscosity greater than 1 Pa-sec [17, 18]. Films can be deposited only when the viscosity is much lower [4, 17, 18] . This is the key step in the sol-gel process.

(v) **Drying and firing of the gel**: The process of removing the solvent phase from the gel is called drying. The liquid in the pores are removed by evaporation. This results in shrinkage. The gel is dried by removing the physically adsorbed solvent. Firing refers to the conversion of the gel to a dense ceramic through pyrolysis. Powders can be formed at this stage which can be pressed to form ceramics. The resulting inorganic solid usually has an amorphous structure.

(vi) **Densification**: A post fired heat treatment of the gel results in further removal of the pores. This is required for further densification, grain growth and to obtain crystalline structure. In the case of thin films, annealing at higher temperatures results in the formation of crystallized films.

Now we discuss the steps enumerated in Section 3.1 a little extensively.

3.2 Solution Preparation

The starting chemicals which are compounds of the relevant components, acting as solutes in the sol-gel process are called precursors. The common compounds such as metal- chlorides, nitrates, acetates, acrylates, amines, hydroxides, if soluble in a solvent like water, aliphatic alcohols like methanol, ethanol, isopropanol, 2-methoxyethanol, etc., can be used as precursors. The requirement of sol-gel precursor is that they are soluble in the solvent and reactive enough to participate in the gel formation process [19].

Now, depending on the nature of the precursors, there are several preparation techniques available for the synthesis of materials by sol-gel processing technique. Some of the techniques are listed below [19].

3.2.1 All Metal Alkoxide Method

Metal alkoxides are regarded as the best precursors for sol-gel processing technique [19, 20, 21, 22]. Almost all metals form alkoxides, which have the general formula: $M(OR)_x$, where M is the metal, R is the alkyl group of the relevant alcohol and x is the valence state of the metal. Alkoxides are very reactive and readily hydrolyze to the corresponding hydroxides or oxides. The steps of hydrolysis can be represented as follows:

$$M(OR)_x + xH_2O \rightarrow M(OH)_x + xROH \quad (1)$$

Usually the product of hydrolysis is a polymeric gel which is formed through hydrolysis and condensation. Once the hydroxides are formed, condensation reaction may start through dehydration and dealcoholisation:

$$M(OH)_x + M(OH)_x \rightarrow M_2O_x + H_2O \quad (2)$$

$$M(OR)_x + M(OH)_x \rightarrow M_2O_x + xROH \quad (3)$$

However, all the above reactions tend to occur simultaneously, so that it is impossible to describe the process by separate and independent hydrolysis and condensation reactions. The subsequent gelation can be achieved through a cross linking of M_2O_x of the polymer specimen thereby increasing the viscosity, either by removal of the solvent, or aging of the solution [12]. There is also a limited class of compounds known as double alkoxides. These contain two different metals in the same compound and have the general formula : $M'_x M''_y (OR)_z$. M'_x and M''_y are metals, R is an alkyl group and x, y, z are integers. The physical properties of the metal alkoxides can be varied by changing the alkyl group and for most metals, soluble products which can in some cases even be liquid, can be obtained. In addition, many alkoxides are volatile and therefore can easily be purified by distillation to get very pure products. Double alkoxides have the added advantage of not only being volatile but maintaining the exact molecular stoichiometry within the metals [12]. The fabrication of a multicomponent system involves the preparation of a solution using all the metal components as the precursors in a suitable organic solvent and then reacting with water to form the oxide complex. The reaction can be represented for a three component system as follows [23, 3, 4]:

$$\begin{aligned} M(OR)_a + M'(OR)_b + M''(OR)_c \rightarrow \\ MO_{a/2} + M'O_{b/2} + M''O_{c/2} + yROH \end{aligned} \tag{4}$$

As the number of components increases, the mechanism of the hydrolysis and condensation reactions become more complex.

3.2.2 Alkoxide-Salt Method

Alkoxides of some metals are not commercially available due to some preparation problems. In these cases, the metal salts provide an alternative as they can be readily converted to the oxide by thermal or oxidative decomposition and are perfectly soluble in organic solvents. Thomas et.al.[19] found that some metal-acetates react with some metal-alkoxides to form metallometaloxane derivatives with the liberation of alkyl acetate:

$$\begin{aligned} M(OR)_n + M'(OAc)_m \rightarrow (OR)_{n-1}M- \\ O - M'(OAc)_{m-1} + ROAc \end{aligned} \tag{5}$$

where Ac represents the group $-COCH_3$. The reaction then continues with further reaction of acetate and alkoxide groups resulting in an increase molecular weight of the product[24].

Sol-gel technique involving salts are usually more complex than those with only alkoxides because the hydrolysis of the alkoxides is more easily accomplished than the thermal or oxidative degradation required of the metal salts[24].

Rate of hydrolysis and condensation reactions can be controlled by addition of various catalysts. Generally catalysts used are acid, base and acid-base catalysts [25, 26, 27, 28, 29, 30, 31, 32] .

3.3 Shaping of the gel

The gel formed can be used in various forms. Thin films are usually formed by spin coating onto various substrates. The smoothness of the film is controlled by the spin rate and the viscosity of the solution. Thin films can also be formed by dip coating of the gel. At an appropriate viscosity of the solution, the uniformity and the thickness of the film are maintained by controlling the rate at which the film is pulled out of the gel. The gel can also be dried and formed into powders which can be shaped into ceramic discs.

3.4 Thin film Deposition

Spin coating is one of the most commonly used method of sol-gel film deposition. This method is used in deposition of nano-scale or micro-scale thickness films on various substrates like glass, quartz, single crystal substrates, Silicon, Platinized silicon, etc. using a Spinner. It's widely used in photolithography to deposit one-micrometre-thick layers of photoresist and planar photonic structures of polymers [30].

Using a nozzle or a dropper, a little amount of the solution is poured onto the substrate. At this point, an extra amount of coating solution must be put over the substrate in comparison to the final amount of solution necessary for coating, so that the solution completely wets the surface and the substrate is fully covered. The substrate is then spun at speeds up to $10,000$ rpm with a spinner to disperse the coating material by centrifugal force. Thickness of the film is dependent on the concentration and viscosity of the solution as well as on the speed of rotation of the spinner. Thinner films are obtained at a higher speed. As the rotational speed of the substrate is increased from zero to the final required speed, the rotational motion causes aggressive fluid expulsion from the substrate. Spiral vortices can occur briefly as a result of the twisting motion generated by the inertia exerted by the top of the fluid layer as the substrate beneath rotates faster and faster. The fluid eventually thins out to the point where it can entirely co-rotate with the wafer, and any sign of a fluid thickness difference vanishes. The substrate eventually reaches the appropriate speed, and the fluid is thin enough that the rotating accelerations are perfectly balanced by the viscous shear drag. Fluid viscous forces dominate fluid thinning behaviour when the substrate spins at a constant pace, which is slow and generally uniform. Interference colours spinning off can be visible at this point in solutions containing volatile liquids. Since the fluid flows uniformly outward it must form droplets at the edge to be tossed off, and edge effects are also visible at this stage. When the substrate is rotating at a steady speed after this stage, solvent evaporation takes precedence over coating thinning. The evaporation of any volatile solvent becomes the dominating process in the coating at this time. The coating effectively gels at this point because the residual solution's viscosity rises as the solvents are withdrawn, thus freezing the film in place. The coating thickness is dependent on the rate of spinning, viscosity of the solution [33].

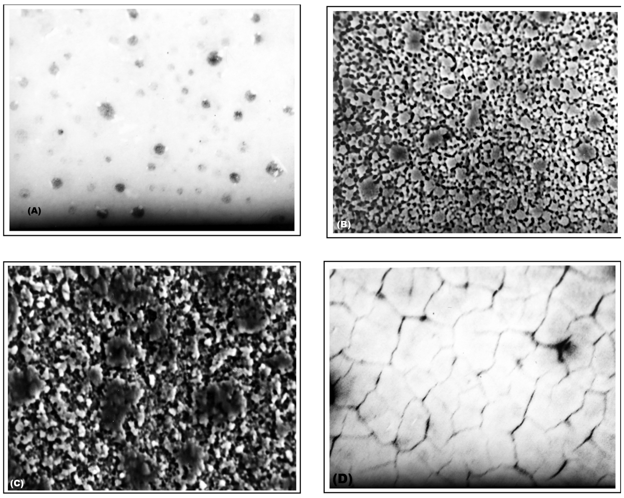

Figure 1: Scanning electron micrographs of Barium-Strontium Titanate $Ba_{0.4}Sr_{0.6}TiO_3$ films (A) amorphous (B) annealed at 700°C, (C) annealed at 800°C, (D) cracked films, deposited by sol-gel method on Pt/Si substrate.

The consistency of the film thickness is an important advantage of spin coating thin films. Thickness does not change by more than 1 % due to self-levelling. However while coating thicker sols of polymers or photoresist films,large edge beads can be formed.

Figure 1 shows the scanning electron micrographs (SEM) of the Barium-Strontium Titanate $Ba_{0.4}Sr_{0.6}TiO_3$ films deposited by sol-gel method on Platinized-Silicon (Pt/Si) substrate [34]. Films shown in figure 1(A), (B),(C) had a thickness of 50nm. Figure 1(A) shows that the as-deposited/as-fired films were amorphous in nature. Crystalline films were obtained by annealing the films at higher temperature. Figure 1(B),(C) show films annealed at 700°C and 800°C respectively. Well formed grains can be seen in both these cases.

3.4.1 Cracking behaviour of Sol-Gel films

A major problem in the sol-gel process is cracking and delamination of films during drying [35]. Cracking occurs mainly due to large shrinkages which occur during drying. And, the shrinkage can occur in two dimension only since the films must attach to the substrate.Viscosity of the solution and thickness of the films are other major factors resulting in cracking. Multiple coating followed by firing of films is done to avoid cracking. Figure 1(D) shows cracked film. The film was $1.2\mu m$ thick.

3.5 Synthesis of Nano-particles by Sol-Gel Method

Sol-gel method is one of the industrial methods of preparing nano-particles. When the sol is allowed to stand for sufficient time, a gel is formed. This is also called wet-gel.Depending on the drying conditions of the wet-gel two types of dried-gels can be obtained, namely aerogel and xerogel [36]. If the pore-liquid is removed from the wet gel under special drying conditions, a highly porous and a low density gel is formed called aerogel [10] [36]. Aerogels have nano-meter scale pores, high internal area and very low density [37] [25]. Drying of wet gel to form areogels is generally done by supercritical method, subcritical method or by sublimation process [25]. In super-critical method the wet gel is dried under critical temperature and pressure to remove the solvent from the system as gas. This process can also be carried out at low temperature or at high temperature. When the process is carried out at low temperature the pore-liquid is first replaced with a liquid such as CO_2 which is then removed at an ambient temperature and pressure [38]. In case of high temperature super-critical drying the solvent is directly removed from the wet-gel at critical temperature and pressure. The pressure and temperature are adjusted in such a way that the network does not collapse and the structure is maintained. Chemical additives like glycerol, formaldehyde, oxalic acid, tetramethylammonium hydroxide are used to control the drying process. In the sublimation or freeze drying method, the liquid inside the gel is first frozen and then dried by sublimation. Drying at ambient pressure is generally used on an industrial scale [36]. Xerogels are formed by drying the gels under normal conditions. The main difference between aerogel and xerogel are in the size and number of the cavities. Aerogels have very low thermal conductivity due to highly porous structure of these nano-materials. Nano-scale powders are formed by this method. Usually the powders so formed are amorphous in nature which can be crystallized by annealing or sintering them at higher temperature.

Wet chemical method has long been used to prepare mixed ferrites. Recently, the method has been specifically used to prepare nano-particles of mixed ferrites. The method is also called co-precipitation method. The method, in brief, involves the preparation of solutions of different metal salts such as sulphates, chlorides, nitrates, etc., in appropriate ratios, which are then mixed to form a solution. An alkali solution of sodium hydroxide or potassium hydroxide or a base like ammonia is prepared in appropriate concentration. For simultaneous or co-precipitation of metal-hydroxides, the prepared metal solution is added dropwise to the alkaline solution.The suspension of metal hydroxides, so obtained, is usually heated to a temperature of $60-80°C$ and oxygen gas is bubbled through the suspension along with mechanical stirring to convert ferrous iron into ferric state. The precipitate is filtered, washed repeatedly and dried at 130°C. The dried material is sintered at approximately 700°C to obtain the desired mixed ferrites. The nano scale powders of ferrites can be obtained by this method [39, 40, 31, 41, 42, 43]. Jadhav et.al. [39, 40] made a detailed study of the ferrite nano-materials so prepared. A series of substituted ferrites of composition $Co_{1-x}Zn_xFe_2O_4$ with x varying from 0.0 to 0.7 was prepared by them by wet chemical or co-precipitation method. the samples were characterized by X-ray diffraction and magnetization studies. Results revealed nano size of the ferrites prepared. Jadhav et.al.[26] also reported ferrite nano-particles prepared by sol-gel autocombustion method in which nitrates of suitable metal ions and a suitable chelating agent or fuel, such as citric acid, urea, glycine, etc., were used as starting material. Ammonium hydroxide was added to the aqueous solution of metal nitrates and the chelating agent. Detailed preparation method is given by Shirsath et.al.[26] Singh et.al.[31]. Particle size, magnetic properties depends on the chelating agent to nitrate ratio and type of chelating agent used [26, 44]. Nanoparticles of mixed and simple ferrites were prepared and studied by this method.

3.6 Applications of Sol-Gel Deposited films and nano-particles

Historically sol-gel method was used to make silica gel glasses [1, 2]. Indium TinOxide (ITO) films deposited by sol-gel method were used as anti-reflection coatings [3, 4].

This method has been extensively used to deposit dielectric and ferroelectric films. Those films have found a wide range of applications using the ferroelectric, piezoelectric, pyroelectric, electro-optic properties of these materials [6]. Ferroelectric films in the paraelectric phase at room temperature have been used in large capacitors for DRAM (Dynamic random access memory) and the films in the ferroelectric phase as memory capacitors [6, 5, 45]. These films have applications in tunable phase shifters, integrated microwave devices, optical applications, infra-red detectors, gas sensors, light sensors as photodiode, solar cells, glucose sensors[46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56]. Materials like alumina prepared by sol-gel method has been used in medical field as carriers for drug delivery [57, 58, 59]. Recently Barium-Strontium-titanate films have been used as glucose-sensor [53].

Recent interest in nano particles makes sol-gel attractive as the particle size is generally in the nano-meter range. Ease of composition control and variation makes sol-gel an attractive method for uniform and ultra-fine ceramic powders. These nano-scale sized particle find applications in biomedical and dental applications, herbicides, agrochemicals, powder abrasives for finishing operations [60]. Also ease of assimilation of various particles makes it easy to incorporate nano-particles in the material modifying the characteristics of the material.

Sol-gel method is used to fabricate various ceramic membranes for microfiltration, nanofiltration, ultrafiltration, reverse osmosis. By drying the gel under suitable condition it is possible to obtain porous solid matrices which can be used as membranes. In 1950's sol-gel process was used to make radioactive powders of UO_2 and ThO_2 for nuclear fuels.

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