

Sol-gel Spin Coating method for thin film deposition

Nishant Kumar^{1*} and Anu Katiyar²

¹Department of Physics, School of Science,

Maharishi University of Information Technology, Lucknow, UP, India

²Department of Physics, University of Lucknow, Lucknow, UP, India

*E-mail:nishant1986lu@gmail.com

Abstract:

Any sample with one of its dimensions very much less than other two may be called a thin film [1]. They are thin layers of material ranging from fractions of nanometers to several micrometers. Thin films are benefiting the electronic semiconductor devices, photonic devices and optical coatings etc. Thin film properties are strongly dependent on the method of deposition, substrate material, the rate and angle of deposition and the ambient atmosphere. The specific applications demand specific film properties such as high optical transmission/reflection, adhesion, hardness, porosity, high resistivity or conductivity, chemical inertness towards corrosive environments and stability with respect to temperature, stoichiometry and orientation in single and polycrystalline films. Amorphous films are also found to be useful e.g. in optical sensors [2-4], lasing materials [5] etc.

Deposition of thin films

Obtaining a thin film of any material on a substrate surface with proper adherence is thin film deposition. Deposition techniques can be broadly classified as physical and chemical deposition methods.

The deposition process of a film can be divided into three basic phases:

1. Preparation of the film forming particles (atoms, molecules, cluster)
2. Transport of the particles from the source to the substrate
3. Adsorption of the particles on the substrate and film growth

Physical Deposition Methods

Physical deposition methods require maintenance of vacuum of 10^{-6} Torr or more. They include several methods such as sputtering, thermal evaporation, pulsed laser deposition, cathodic arc deposition etc. Besides these, other methods like reactive sputtering, molecular beam epitaxy, atomic layer deposition, liquid phase epitaxy etc. are also used for obtaining improved quality of films by precisely controlling the deposition parameters. Rate of deposition, substrate

temperature, ambient conditions, residual gas pressure in the system, purity of the material to be deposited, in homogeneity in the films, structural or compositional varieties of the films in localized or wider areas determine the electrical, optical, magnetic and surface properties of the deposited films [6].

Chemical Deposition Methods

Chemical deposition methods include electroplating, chemical vapour deposition, plasma enhanced chemical vapour deposition, organometallic solutions etc. A non-vacuum technique, for producing thin optical films, is the use of organometallic solutions that are applied to a substrate's surface either by dipping or by spinning or by spraying. The film is then dried and baked in the furnace. Thermal decomposition takes place and the film is converted to pure oxide while the organic constituents evaporate. Thickness control is achieved by adjusting the temperature, viscosity and other properties of the solution. This technique besides being continuously used in materials related research has been used successfully to coat high power laser optical components with antireflection design that have extremely high damage thresholds. In the present chapter we will discuss sol-gel spin coating using organometallic solutions. The thickness of the films obtained from sol-gel spin coating; lie in the range of few hundreds of nanometers. There are several methods for producing ZnO based films e.g. chemical vapor deposition, spray pyrolysis, dip coating, sol-gel, etc. Out of these methods sol-gel is simpler besides producing good quality films.

Sol-gel process

In chemical deposition process, sol-gel process is widely used for the deposition of thin films, nanostructures, nanorods etc. The sol-gel preparation of any metal oxide involves combining reactants and the subsequent solidification of the resultant solution into an amorphous oxide gel [7]. The porous oxide is then heated to give densified glasses and polycrystalline solids [8]. Incorporation of dopant and formation of composites is easy [9]. The sol-gel method is an alternative to vacuum deposition techniques. Use of solution based process to form metal oxide semiconductor films for optoelectronic and microelectronics devices may improve the mass production throughput and reduce cost, since it enables maskless processes including micro contact printing, inkjet printing, and roll printing technology etc. [10].

Sol-gel process consists essentially of three steps [11]-

- a. Formation of low viscosity solutions of suitable precursors i.e. metal derivatives (organic/inorganic) which could finally yield the oxides or metal oxides themselves. Low viscosity ensures homogenation.
- b. Formation of a uniform sol and causing it to gel to endow chemical homogeneity on the ceramic product during desiccation.
- c. Shaping during or after gelation into the final form fibers, surface coating etc. before annealing.

The temperature, pH of the medium and anions/complexing agents present in the solution are the main factors [12] affecting the sol-gel process. The sol-gel process is used in developing thin film transistors [13,14], excitonic devices working at high temperatures [15], antireflection coatings, solar reflecting glass, transparent conducting films [16], magnetic films [17], protective coatings, films for sensors [4] etc.

Sol and precursors

The starting chemicals are called 'precursors' which are compounds of relevant components acting as solutes in sol-gel process [18] and they should be able to form reactive inorganic monomers or oligomers. Precursors should be soluble in the reaction media and should be reactive enough to participate in the gel forming process. The reactivity of precursor depends on its chemical nature and applied reaction conditions.

In the sol-gel method the metal oxides or metal hydroxides generally remain in the solution rendering it directly coatable on the substrates. The thickness of the film can be adjusted by changing the concentration or viscosity of the solution. When metal is not available in a soluble form, its organic compound can be taken as a precursor in a suitable solvent and then is made to undergo slow and controlled hydrolysis till it provides a metal-oxygen-metal network in a sol state maintaining most of the time the solubility and transparency of the solution.

In case of metal oxide precursors, the product can be easily freed [19] from the carbonaceous residue. Alkoxides [11] of group I and II metals are non-volatile solids and often depict low solubility in organic solvents. As an alternative [11], metal salts - which are soluble in organic solvents and can be converted easily to the oxide by thermal or oxidative decomposition are used.

Gelation:

The transformation of fluid sols to solidified gel [20] depends on the rheology of the sols [6]. Gelation reduces the distance between the colloidal particles and bonds are formed. The transformation [21] of the solution into a semi-rigid wet gel can be done by

- a. by water evaporation or extraction using tray drying, spray drying or dispersion in an immiscible fluid.
- b. by removal or neutralization of anions or
- c. by polymerization of organometallic compounds.

The network forming components, monomers or colloids react into active form after the preparation of a solution or homogeneous colloidal sol [18]. For stable colloids the neutralization of surface charges, aggregation and further condensation by reactive surface groups leads to gelation.

To deposit thin film, sol or precursor state is used while for fabricating fibers gel-state is used. Gels allow for a high degree of control of the crystallization and formation of different porous and dense microstructures [22].

Sol-gel spin coating

Sol-gel spin coating is a simple cost-effective and useful process for film deposition using solution type reagents. In this process the substrate is made to spin around an axis perpendicular to the coating area. The method includes four distinct stages.

- i. In the first step a controlled amount of the precursor is poured over the substrate which wets substrate uniformly. If needed, sub-micron filter is also used to eliminate larger particles from the precursor.
- ii. The second step involves spinning of substrate with desired rotation speed to remove the excess fluid. The top of the fluid layer exerts inertia while the substrate rotates at a faster speed. These two forces result in twisting motion which may lead to formation of spiral vortices. But in normal cases the precursor is thin enough so that it keeps co-rotating with the substrate and any evidence of thickness difference is absent. Ultimately the substrate reaches its desired speed and the viscous shear drag is exactly balanced by the rotational acceleration.

- iii. In the third stage viscous forces dominate the thinning behavior of the fluid. The fluid thinning tends to formation of uniform films. However, in few cases edge effects are also seen. The fluid which is rotating flows uniformly outside. If the fluid is in excess, then the drops must be formed at the edges so that they may fling off. Thus the thickness at the ends may be slightly greater than that at the central portion of the substrate leading to edge effect.
- iv. In the fourth step and final stage fluid starts evaporating and dominates its own thinning behavior. It is the step in which the solvent phase gets removed and the sol is converted to dense ceramic. As the fluid rotates at a high speed, its temperature rises and leads to evaporation of the fluid. Thus the viscosity of the remaining solution increases leading to the 'gel-state' of the coating. The resulting film usually has an amorphous structure. Although the third and fourth stages i.e. viscous flow and evaporation occur simultaneously, the viscous flow effect dominates initially and evaporation dominates later.

The sol should be kept in an air tight flask to maintain its viscosity otherwise it gets converted into gel and cannot be used for the deposition of films.

The film thickness can be controlled by adjusting the solution viscosity and other coating conditions like rotation rate, annealing temperature and time duration of coating etc. [10, 23]. The sol gel spin coating method has been extensively used for the deposition of oxide films [24, 25-28, 10, 13-16, 30, 31].

The advantages of sol-gel process are

- Ultra homogenation due to atomic scale mixing,
- High degree of uniformity,
- Control of thickness,
- Possibility of multilayer coating,
- Control over the microstructure of the film i.e. pore volume, refractive index, pore size, surface area etc. and
- No restriction on shape and size of the substrate.
- Also the substrate can be simultaneously coated on both sides.

References

1. Joy George, 'Preparation of Thin Films' Pub. Marcel Dekker NY(1992).
2. S. Dixit, A. Srivastava, A. Srivastava and R. K. Shukla, J. Appl. Phys. 102. 113114 (2007).

3. S. K. Shukla, G. K. Parashar, A. P. Mishra, P. Misra, B. C. Yadav, R. K. Shukla, A. Srivastava, A. Srivastava, F. Deba, G. C. Dubey, *Chemical Sensors*, 20, Supplement B 546 (2004).
4. S. Dixit, A. Srivastava, A. Srivastava, R. K. Shukla, *Jpn. J. of Appl. Phys.* 47(7A) 5613 (2008).
5. H. Dong, D. Wang, K. Chen, J. Huang, H. Sun, W. Li, J. Xu, and Z. Ma, *Appl. Phys. Lett.* 94, 161101(2009).
6. Ph.D. Thesis, “Structural and Optical Properties of Zinc Oxide and Barium Titanate Based Thin Films” by Kamakhya Prakash Misra, University of Lucknow, 2010.
7. J. D. Mackenzie and D. R. Ulrich, *Proc. of SPIE Conf. on Sol-gel Optics*, 1328 (1999) 2-13.
8. B. D. Fabes et al, *Proc. of SPIE conf. on Sol-gel Optics*, 1328 (1990) 319-328.
9. J. D. Mackenzie, *Proc. of SPIE conf. on Sol-gel Optics*, 878 (1988)128.
10. C. Y. Tsay, H. C. Cheng, C. Y. Chen, K. J. Yang and C. K. Lin, *Thin Solid Films* 518, (2009) 1603.
11. R. C. Mehrotra, *History of Precursors*, *Proc. of the Winter School on Glasses and Ceramics from Gels*; Sao Carlos (SP) Barzil 14-19 Aug 1989, Ed. M. A. Aegerter, M. Jafelicci Jr, D. F. Souza and E. D. Zanotto, Utopia Press, Singapore pp. 1-12.
12. E. Matijevic, *Accounts of Chem. Res.* 14 (1981) pp. 22.
13. H. C. Cheng, C. F. Chen, C. Y. Tsay, *Appl. Phys. Lett.* 90, 012113 (2007).
14. W. J. Park, H. S. Shin, B. D. Ahn, G. H. Kim, S. M. Lee, K. H. Kim and H. J. Kim, *Appl. Phys. Lett.* 93, 083508(2008).
15. Y. Zhang, B. Lin, X. Sun, and Z. Fu, *Appl. Phys. Lett* 86, 131910(2005).
16. A. Jain, P. Sagar and R. M. Mehra, *Materials Science-Poland*, 25, 233(2007).
17. S. -Y. Bae, C. -S. Kim and Y. -J. Oh, *J. of App. Phy.* 85(8) 5226(1999).
18. Helmut Schmidt, ‘Chemical Processing up to Gelation’ *Proc. of The Winter School on Glasses and Ceramics from Gels*; Sao Carlos (SP) Barzil 14-19 Aug 1989, Ed. M. A. Aegerter, M. Jafelicci Jr, D. F. Souza and E. D. Zanotto, Utopia Press, Singapore pp. 62.
19. I. Thomas, US Patent 3, 799, 754, March 26, 1974; I. Thomas, ‘Multicomponent Glasses from the Sol-gel Process’ in *Sol-gel Technology for Thin Films, Fibers, Preforms*

- Electronics and Speciality Shapes, Ed. L. C. Klein, Noyes Publications, New Jersey, **1988**.
20. Sumio Sakka, Rheology of Sols in the sol-gel processing, Proc. of the Winter School on Glasses and Ceramics from Gels; Sao Carlos (SP) Barzil 14-19 Aug **1989**, Ed. M. A. Aegerter, M. Jafelicci Jr, D. F. Souza and E. D. Zanotto, Utopia Press, Singapore pp. 76.
 21. Jerzy Zarzycki, New Methods in Sol-gel Synthesis, Proc. of the Winter School on Glasses and Ceramics from Gels; Sao Carlos (SP) Barzil 14-19 Aug **1989**, Ed. M. A. Aegerter, M. Jafelicci Jr, D. F. Souza and E. D. Zanotto, Utopia Press, Singapore pp. 257-269.
 22. G. Westin, M. Wijk and A. Pohl, J. of Sol-gel Sci. and Tech. 31, 283 (**2004**).
 23. Sumio Sakka, Rheology of Sols in the sol-gel processing, Proc. of the Winter School on Glasses and Ceramics from Gels; Sao Carlos (SP) Barzil 14-19 Aug **1989**, Ed. M. A. Aegerter, M. Jafelicci Jr., D. F. Souza and E. D. Zanotto, Utopia Press, Singapore pp. 346-374.
 24. N. Kumar, A. Srivastava, Journal of Alloys and Compounds 706, (**2017**) 438-446
 25. K. P. Misra, R. K. Shukla, A. Srivastava, A. Srivastava, Appl. Phys. Lett. 95 (**2009**) 031901.
 26. A. Srivastava, N. Kumar, K. P. Misra, S. Khare, Mater. Sci. Semicond. Process. 26(**2014**)259–266
 27. R. K. Shukla, A. Srivastava, A. Srivastava, and K. C. Dubey, J. Cryst. Growth 294 (**2006**) 427-431.
 28. Nishant Kumar, A. Srivastava, Opto-Electronics Review 26 (**2018**) 1–10.
 29. A. Srivastava, N. Kumar, and S. Khare, Opto–Electron. Rev. 22(**2014**) 68-76.
 30. Y Natsume, H Sakata, Thin Solid Films, 372 (**2000**) 30–36.
 31. Y. Cao, L. Miao, S. Tanemura, M. Tanemura, Y. Kuno, Y. Hayashi, Appl. Phys. Lett. 88, (**2006**) 251116.