

Synthesis of sol-gel derived silica and titania silica films using spin coating method

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(Received: April 24, 2008; Accepted: June 02, 2008)

ABSTRACT

Sol-gel derived silica and titania doped silica films were fabricated by spin coating on silicon substrates. The work primarily deals with the influence of various sol-gel processing parameters such as addition of base catalyst, water to precursor ratio and sol pH on the gel times and consequently on the film thickness. The viscosity of the sol increases gradually with time and then attains a large value very rapidly for a given amount of base catalyst. Increase in the amount of base catalyst increase the gel time. As the molar ratio of water to precursor is increased the gel time initially decreases, however at large values of the ratio the gel time increase and the resulting films are thinner. Titania doped silica films were also fabricated. The thickness of silica films doped with 5.25 mol% titania decreases with spin speed.

Key words: Sol-gel, Silica films, spin coating, thickness of films.

INTRODUCTION

The sol-gel technique has been widely used in the preparation of transparent oxide glasses by hydrolysis and condensation of metal alkoxides since Ebelmen reported the first synthesis of silica from silicon alkoxide in 1844¹. In a strict sense, "sol-gel processing" is the synthesis of an oxide network via inorganic polymerization starting from molecular precursors in solution. This term frequently is extended to refer to the preparation of inorganic oxides by "wet chemistry". The sol-gel process provides a new approach to the preparation of glasses and ceramics with many advantages over conventional methods. Thin films formed using sol-gel techniques represent the oldest commercial application of sol-gel technology. Today, sol-gel thin film coating are being intensively studied for such diverse applications as protective and optical coatings, passivation and planarization layers, sensors, high or low dielectric constant films, inorganic membranes, electro-optic and non-linear

optical films, electro-chromics, semi-conducting anti-static coatings, superconducting films, strengthening layers and ferroelectric²⁻⁴. The sol-gel process has emerged as an effective route for the fabrication of optical waveguides and guided wave devices and circuits. In particular, it is possible to incorporate active dopants like neodymium, erbium and cesium for integrated optical active devices and circuits⁵. According to Iller⁶ the sol-gel polymerization occurs in three stages: polymerization of monomers to form particles, growth of particles and linking of particles into chains, then networks that extend through out the liquid medium thickening into a gel. With the context of these stages, many factors affect the resulting silica network, such as, pH, temperature and time of reaction, reagent concentrations, catalyst nature and concentration, H₂O/Si molar ratio (R), aging temperature and time, This paper investigates the effect of some of the above factors on the gel time and the thickness of the sol-gel derived silica films. The focus will be on the processing parameters.

The second stage of the present work explores the possibility of using sol-gel films as wave guiding layers. A key issue when producing wave guiding materials is the ability to precisely control the index of refraction, which must be higher than the index of the substrate⁷. For this titania doping of the sol-gel silica films was done by adding to the silica precursors a titania doping of the sol-gel silica films was done by adding to the silica precursors a titania precursor based on tetrapropylorthotitanate or TPOT.

EXPERIMENTAL

Tetraethylorthosilicate (TEOS) and tetrapropylorthotitanate (TPOT) were purchased from MERCK German. Silicon wafers were cleaned with deionised water and acetone. The sol-gel precursors used in this work have been previously described by Hyum *et al.*,⁸. In the first phase of the work thin films of silica were fabricated. Sol was prepared using tetraethylorthosilicate (TEOS), ethanol, water and HCl. The mixture was refluxed at 70°C for 2 hours. A certain amount of base catalyst (0.1 M NH_4OH) was added to 10ml of the previous solution. This solution was then used for spin coating. The spin time was kept at 60 sec throughout this work. The viscosity measurements were made using a viscometer. We have used spin coating unit fabricated by "Omicron Scientific Equipment Co". It has a 800-5000 RPM solid state continuous speed motor. The spun-on film was aged in a ethanol atmosphere for some time before taken out and dried. In the second stage of the work titania doping of the sol-gel silica firms was done by adding to the silica precursor a titania precursor based on tetrapropylorthotitanate or TPOT. The sol gel precursors used in this work are almost identical to those previously described. TEOS and TPOT were both obtained at 99.99% purity. The preparation of precursors is as follows: Both the precursors were dissolved in ethanol 1:1 ratio by volume. Additional HCl was added to the TEOS precursor for making $R=1$. This mixture was refluxed at 70°C for minutes. The TEOS and TPOT were mixed together to give the required silica-titania ratio. Ethanol and HCl were then added to take the water: precursor ratio to $R=2$ and the mixture was aged for 24 hours. Finally the mixture was diluted before the deposition of the film. After preparation of the precursors, the

silicon wafer to be coated was annealed a number of times to ash any organic surface contaminants and to remove moisture, this promotes adhesion of the sol-gel material to the substrate. It is possible to produce multi layer films in which each layer is spun on and dried before the next layer is deposited. This has been demonstrated by using relatively cheap manually operated equipment that employs a spinner. The film thickness was determined by white light interferometry. A thick film was then built up as a multilayer. At each iteration, the wafer light was spin coated with sol-gel material, annealed at a fixed temperature for a fixed time, then cooled. The cycle time is-3 min at normal work rates, using manual transfer of the wafer between the spinner and the annealer. At the dispensing step, the sol-gel material was filtered to 0.2 ppm and applied to the wafer by using a syringe. The wafer was then spun for 30 s at a speed in the broad range of 1000-5000 rpm.

RESULTS

For two different amounts of base addition 0.2 ml and 0.6ml, the viscosity of the sol first gradually increase with time and then faster to larger values and ultimately the solution loses fluidity. The initial work deals principally with the influence of various sol-gel processing parameters on film properties and the interdependence of these parameters. From the study, a gel time (t_{gel}) can be estimated as the time when the sol concentration probably reaches a maximum value. The viscosity also attains a maximum value. For two different amounts of the base catalyst (NH_4OH) 0.1 ml and 0.3ml, the gel time was estimated to be minutes and 5 minutes respectively. As the molar ratio of water to precursor (R) changed from values ranging from 1 to over 30, initially the gel time decreased however higher values of R resulted in longer gel times and thinner films. This effect is evident in fig. 1 which shows gel times as a function of R and the initial alcohol. TEOS molar ratio. Increasing the amount of base catalyst accelerated reaction rate and decreased the gel time. This is evident in Fig. 2.

The next phase of the present work explores the possibility of using sol-gel silica films as wave guiding layers. The variation of the thickness of single annealed layers with spin speed

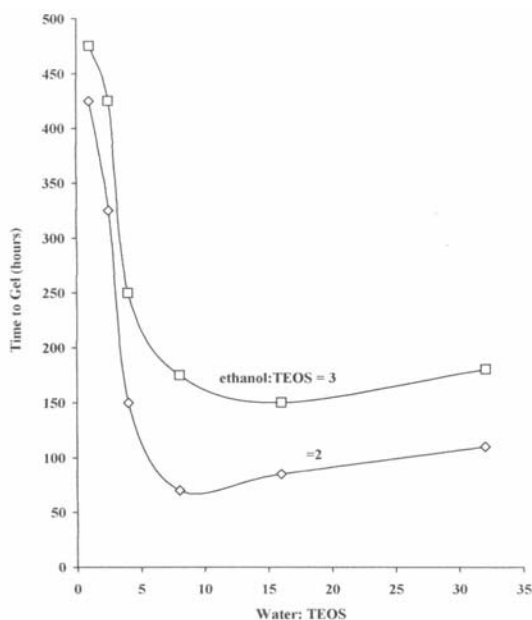


Fig. 1: Variation of gel time with different water: TEOS ratio for different ethanol: TEOS ratio

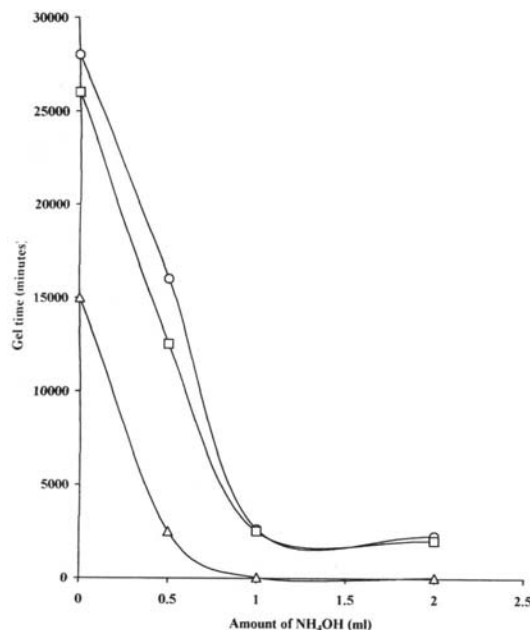


Fig. 2: Variation of gel time with different amount of base °---R=1, □--R=2, Δ--R=4

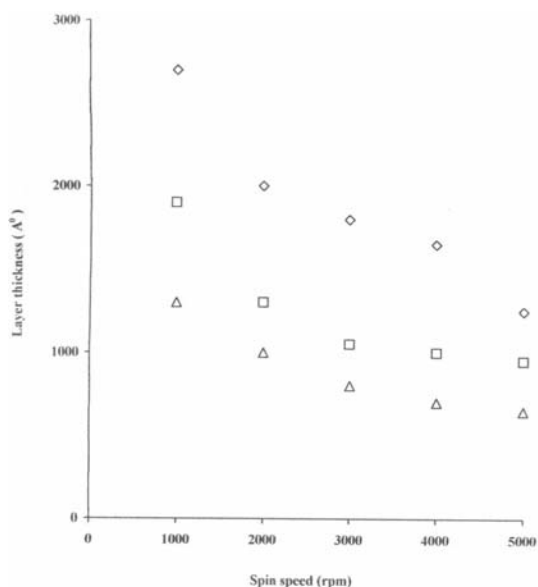


Fig. 3: Variation of single layer thickness with spin speed for silica doped with 6.25 mol% titania and diluted with different amounts of ethanol.

◇---1:1, □---2:1, Δ --- 3:1

is shown in Fig. 3 for silica doped with 6.25~mol.% titania and diluted with ethanol in the ratios of 1 part ethanol:1 part sol-gel, 2:1, and 3:1. The layer thickness obtained at a given spin speed decreases with the dilution and increases with the titania concentration.

DISCUSSION

Once ammonia was added to the solution, the polymerization reaction was accelerated and the solution viscosity increased accordingly due to either cross-linking, sol formation and/or solvent evaporation. The molar ratio of water to precursor ratio influences the structural evolution of sol-gel materials because of the role of water in the hydrolysis and condensation process. Theoretically, a water: TEOS ratio, R , of 2 is sufficient for complete hydrolysis and condensation process, by generally the reactions do not go to completion under these conditions because of the formation of intermediate species. As R is increased, the extra water promotes hydrolysis and is consumed. The more efficient hydrolysis at large R values and low pH decreases the gel time. Additionally, higher values of R caused more complete hydrolysis of monomers before

significant condensation occurs. Differing extents of monomer hydrolysis should affect the relative rates of the alcohol-or water-producing condensation reactions. Generally, with understoichiometric additions of water ($R < 2$), the alcohol producing-condensation mechanism is favored. Although increased values of R generally promote hydrolysis, when R is increased while maintaining a constant solvent: silicate ratio, the silicate concentration is reduced. This in turn reduces the hydrolysis and condensation rates, resulting in longer gel times and thinner films. As with hydrolysis, condensation can proceed without catalyst, however, their use in organosiloxanes is highly helpful. Increasing the amount of base catalyst accelerated the reaction rate and decreased the gel time. Generally speaking, the hydrolysis reaction, through the addition of water, replaces alkoxide groups (OR) with hydroxyl groups (OH). Subsequent condensation reactions involving the silanol groups (Si-OH) produce siloxane bonds (Si-O-Si) plus the by-products water to alcohol. Under most conditions, condensation commences before hydrolysis is complete. However, conditions such as, pH, H_2O/Si molar ratio (R), and catalyst can force completion of hydrolysis before condensation begins. Additionally, because water and alkoxides are immiscible, a mutual solvent such as an alcohol is utilized. With the presence of this homogenizing agent, alcohol,

hydrolysis is facilitate due to miscibility of the alkoxide and water. As the number of siloxane bonds increases, the individual molecules are bridged and jointly aggregate in the sol. When the sol particles aggregate, or inter-knit a network, a gel is formed. Upon drying, trapped volatiles (water, alcohol, etc) are driven off and the network shrinks as further condensation can occur.

CONCLUSION

The results derived in the present work lead to the following conclusions about the spin coating process of the silica films. The synthesis parameters such as water: precursor ratio, amount of base catalyst, sol pH have influence on gel time. The film properties are related to the various parameters of the fabrication process. This work will lead to better understanding of the sol-gel thin films which will lead to production of better quality of films.

ACKNOWLEDGMENTS

The authors would like to thank Dr. D.K. Shrivastava, Principal C.M.D. College of providing laboratory facilities. We are also thankful to UGC, CRO Bhopal for providing financial assistance for carrying out this work.

REFERENCES

1. Ebelmen, J.J., *C.R. Acad., Sci.*, **19**: 398 (1844).
2. Floch, H.G and Bellebille, P.F., *J. Sol-gel Sci. Tech.* **1**: 293 (1994).
3. MacCraith, B.D., *Sensors Actuators B* **11**: 29 (1993).
4. MacCraith, B.D., McDonagh, C.M., G, O'Kecffe, Keyes, E.T., J.G. Vos., O'Kelly B. and McGlip, J.F., *Analyst*, **118**: 385 (1993).
5. Selvarajan, A. and T. Srinivas, T., *IEEE Journal of Quantum Electronics.*, **37**: 9, 1117 (2001).
6. Iler, R.K., *The Chemistry of Silica.*, (Wiley: New York, 1979).
7. Melpodler S.M., West, A.W., Barnes C.L and Blanton T.N. *Journal of material Sciences.*, **26**(13): 3585-3592 (1991).
8. Hyen, S.H., Kim, J.J and Park H.H., *J. Am. Cheram. Soc.*, **83**: 3,533 (2000).