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Development of a Porous Silica Film by Sol-gel Process

Binay K. Dutta, Tayseir M. Abd Ellateif, and Saikat Maitra

Abstract**—**In the present work homogeneous silica film on silicon was fabricated by colloidal silica sol. The silica sol precursor with uniformly granular particle was derived by the alkaline hydrolysis of tetraethoxyorthosilicate (TEOS) in presence of glycerol template. The film was prepared by dip coating process. The templated hetero-structured silica film was annealed at elevated temperatures to generate nano- and meso porosity in the film. The film was subsequently annealed at different temperatures to make it defect free and abrasion resistant. The sol and the film were characterized by the measurement of particle size distribution, scanning electron microscopy, XRD, FTIR spectroscopy, transmission electron microscopy, atomic force microscopy, measurement of the refractive index, thermal conductivity and abrasion resistance. The porosity of the films decreased whereas refractive index and dielectric constant of it `increased with the increase in the annealing temperature. The thermal conductivity of the films increased with the increase in the film thickness. The developed porous silica film holds strong potential for use in different areas.

Keywords**—**Silica film, Nanoporous, Sol-gel, Templating, Dip coating.

I. Introduction

SO-GEL technique is widely used for fabrication of porous silica films [1-3]. These films possess many important technical properties like excellent heat insulation, relatively low dielectric value, continuously adjustable refractive index, high laser damage threshold etc. Therefore these films find applications in different important areas, like, photonics, optoelectronics, lightweight structural material based thermal insulation, optical coating etc. Nano porous silica films are extensively used in optical coatings, like anti-glaring and anti-reflecting coating in different optical applications. These include cathode ray tube, colour monitor tube, video display panel, lens in high power laser system etc. The special network structure of these films is also exploited in sound detector systems. Again, the excellent insulating property and the near perfect interface of these films on silicon play a crucial role in very large scale integrated devices (VLSI). These films are also used as adsorbents, scaffolds for composite material synthesis, in separation technology, molecular and bio-molecular engineering etc. Use of porous silica films can improve the efficiency of solar cell because of their lower scattering losses. [4-9]

Binay K Dutta is with the Chemical Engineering Department, The Petroleum Institute, Abu Dhabi, UAE (phone: +97126075246; fax: +97126075200; e-mail: bdutta@pi.ac.ae).

Tayseir M. Ellateif is a Ph.D. student in the Chemical Engineering Department, UTP, Malaysia

S. Maitra is with the College of Ceramic Technology, Calcutta 700 010, (e-mail: maitrasaikat@rediffmail.com).

Therefore, fabrication of both nano- and meso- porous silica films with uniform pore diameter of 50-300 nm have become an important area of research and many works have been done in this direction [10-13]. Silica sols formed under different conditions exhibit different microstructures, like particle size, shape, cluster formation tendency etc., and the microstructures along with processing temperature and thickness of these films strongly affect their optical, dielectric, thermal and mechanical properties. Therefore a systematic study is required to establish relationship between processing conditions and these parameters.

In the present investigation, nano- and meso-porous silica films have been fabricated by sol-gel process following base catalyzed hydrolysis of tetraethoxy orthosilicates (TEOS) in aqueous medium. Glycerol was used as template to control the growth of silica particles of colloidal silica sol. The dip coated silica films were annealed at different temperatures. The sol and the film was characterized by the measurement of particle size distribution, scanning electron microscopy, XRD, atomic force microscope, measurement of the refractive index and abrasion resistance to investigate the formation mechanism of the porous film.

II. Experimental

The silica sol was prepared by a two-stage process. In first stage TEOS, NH_4OH and C_2H_5OH were mixed at room temperature with a molar ratio 1:3:25. It was refluxed at 80^oC for 5 hours. In the second stage TEOS, water and glycerol with molar ratio 2:6: 1 was added to the formed sol at pH~9. The new sol was aged at 40^oC for 7 days. SiO_2 content in the sol was maintained as 5wt%. Particle size of the sol was measured with zetasizer (make: Malvern, model: ZEN 3600). The sol was also characterized by FESEM (make: Zeiss, model: SUPRA 55VP) and EDX study

The silica sol was dip coated on the surface of a silicon wafer of 0.5 mm thickness. The temperature and relative humidity during the coating process were maintained at 25^oC and 60% respectively. The dipping and lifting speed were maintained at 0.2-0.4 cm/s. The dip coated wafer was dried in an air oven at 80^oC for 2 hours. The dried coated wafer was heat treated in an electrically heated muffle furnace at different temperatures from 600 to 1000^oC with a soaking period of 40 minutes in each case. Surface morphology of the coated samples was measured by AFM (alpha 3000A, WITEC, GmbH, Germany) and FESEM. Refractive index of the film were measured an ellipsometer (PhE101M, Angstrom., US). Thermal conductivity of the films was measured following a method described by Tsuneyuki et al [14]. The measurements were performed in a vacuum (~10^{-5}

Torr). The abrasion resistance of the films was studied following a method described by Floch et al [15].

III. RESULTS AND DISCUSSION

In the present work silica sol was prepared by the alkaline hydrolysis of TEOS. Under basic conditions it is likely that water dissociates to produce nucleophilic hydroxyl anions in a rapid first step. The hydroxyl anion then attacks the silicon atom via S_N2 –Si mechanism in which OH^- displaces OR^- with inversion of the silicon tetrahedron. Some authors also proposed a mechanism involving a stable 5-coordinated intermediate [16]. The intermediate decays through a second transition state in which any of the surrounding ligands can acquire a partial negative charge. The active products of hydrolysis are easily polymerized into $Si_xO_y(OH)_z$. The active $Si_xO_y(OH)_z$ either participates in growth of silica particles or form new nuclear of silica particles based on reaction conditions. If concentration of the $Si_xO_y(OH)_z$ exceeds a critical value, silica particles grow through aggregation of the $Si_xO_y(OH)_z$ and form inhomogeneous silica particles, even a precipitated silica [17].

If the growth of silica particles is limited, new silica particles are formed. With glycerol in the sol-gel medium, $Si_xO_y(OH)_z$ remains wrapped up in glycerol, and its aggregation tendency is lowered. Therefore, new silica particles are formed rapidly in condensed, smaller and uniform form. Furthermore the higher pH makes the silica particles charged negatively and re-dissolved, which also prevents aggregation of silica particles.

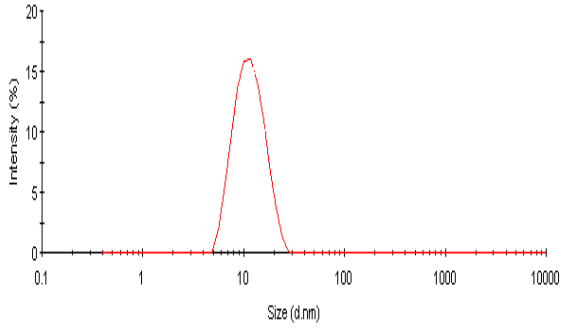

Fig. 1 Particle size distribution of silica sol

From the particle size distribution of the sol (Fig. 1) it was observed that the average size of the aggregates was 10 nm and all the particle aggregates of the sol were nanoscopic in dimension. The silica particles were amorphous according to XRD with peaks less than $2\theta = 10^o$ conforming to JCPDS file (79-1711) (Fig. 2). From the morphological analysis of the sol sample it has been observed that the sol contained spherical

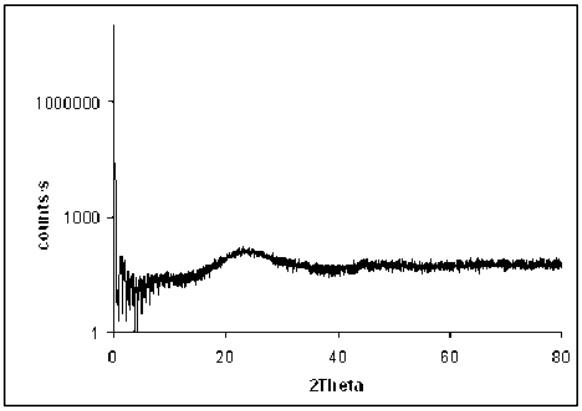

Fig. 2 XRD pattern of Silica Sol Particles

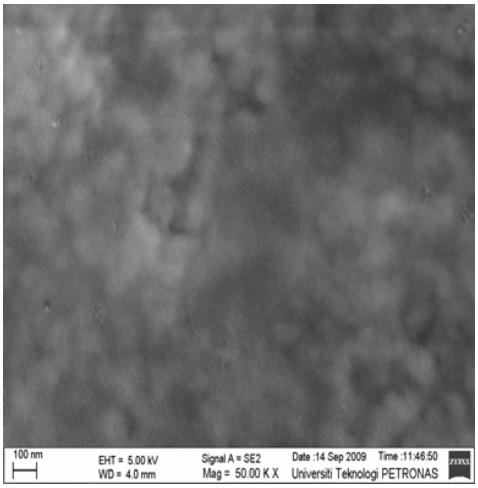

Fig. 3 SEM micrograph of silica sol

and agglomerated silica particles (Fig. 3). The purity of the sol system was ascertained from the EDX studies (Fig. 4)

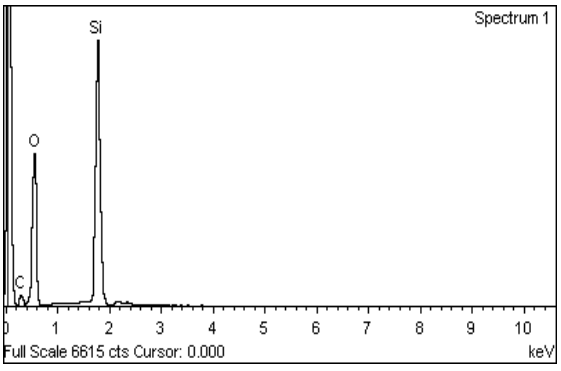

Fig. 4 EDX spectra of the Silica Sol Sample

which indicated the presence of silicon, oxygen and carbon as the elemental composition. The carbon present in the system originated from the alcohol used..

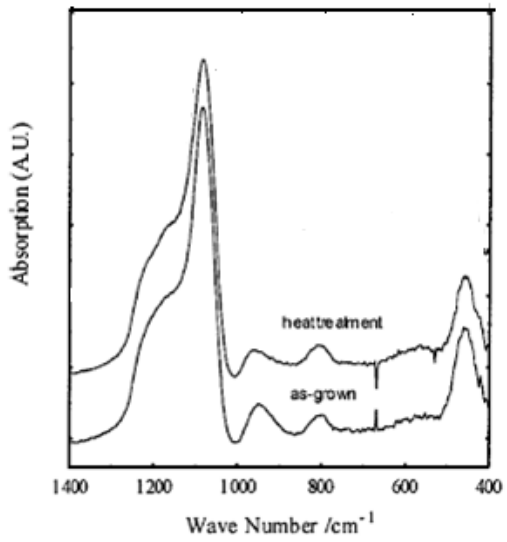

Fig. 5: FTIR Spectra of the silica samples before and after heat treatment

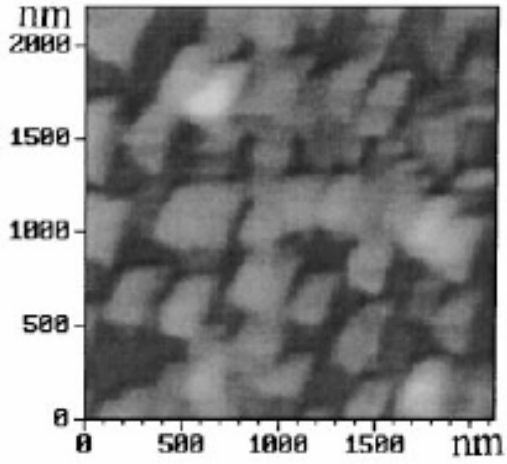

Fig. 6 AFM Photograph of the Silica Coating

Glycerol was used to control the growth as well as the state of existence of silica particles in the colloidal sol. Again, the presence of glycerol controlled the cracking tendency of the silica films during drying. The glycerol template remained trapped inside the silica films and was likely to form a modulated structure. Relaxation of this hetero-structure could reduce the thermal stress of the silica films during its annealing. Furthermore, the template could migrate to the surface of the silica film with the flow of solvent within the silica and accumulated at the surface as solvent was evaporated. This non-uniform distribution of the template could result in the formation of an elastic surface, which prevented the silica film from being cracked.

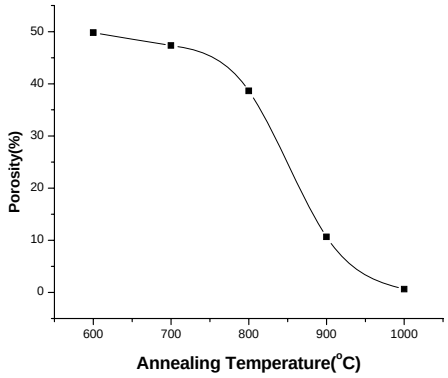

Fig. 7: Variation in porosity of the silica film with annealing temperature

In the FTIR spectra (Fig 5) of the silica film the 1080 cm^{-1} peak represents a pure stretching vibration of Si-O-Si bonds, the peak at 800 cm^{-1} is assigned to the vibration of Si-O-Si bonds, the peak at 460 cm^{-1} is attributed to a bending vibration of Si-O-Si bonds, and the peaks at 960cm^{-1} is assigned to a stretching vibration of Si-OH bonds (Fig.5). After the heat treatment at intermediate temperature a reduction in the relative intensity of the Si-OH stretching band at 960 cm^{-1} is observed which gradually disappeared after heat treatment at elevated temperature [16].

From the AFM pattern of the films it was also observed the surface of the films has been densified and smoothened as a result of heat treatment. It may be related to the strengthening of the silica gel network through cross-linking by more Si-O-Si bonds between silica particles due to the disappearance of OH group and in general, greatly correlated with increasing physical properties such as micro-hardness [17].

Refractive index (n_ρ) of the porous silica films is strongly related to porosity ρ of the films by the following relationship,

$$n_\rho^2 = (n^2 - 1)(1 - \rho) + 1 \quad (1)$$

where n_ρ and n are effective refractive index of the films, refractive index of the silica bulk, 1.457 at 632.8 nm respectively, ρ is the porosity of the films.

Porosity of the films was calculated from this equation. With the increasing in annealing temperature the porosity of the films continuously decreased and at annealing temperature of 1000°C, the film became virtually non-porous (Fig. 7). The relative density of the film therefore increased with the increase in the annealing temperature and at the annealing temperature of 1000°C, the relative density was almost 1 (Fig. 8). As a consequence the refractive index of the films continuously increased with the increase in the annealing temperature (Fig. 9). At the annealing temperature of 1000°C, the refractive index of the film was ~1.45. The dielectric constant (κ) of the film was calculated using the formula

$$\kappa = n^2 \quad (2)$$

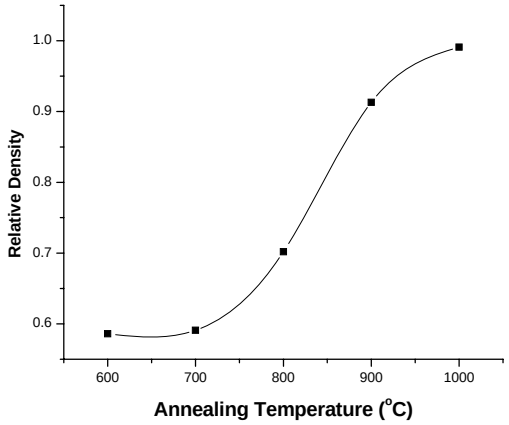

Fig. 8 Variation in relative density with annealing temperature for the silica film

The dielectric constant of the films also increased with the increase in the annealing temperature (Fig. 10). All these measurements were carried out 0.8μm thick film.

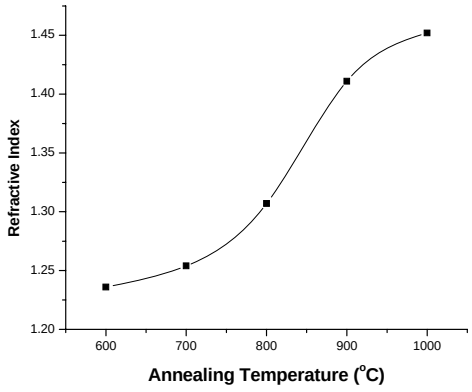

Fig. 9 Variation in refractive index with annealing temperature for the silica film

The thermal conductivity of the film was studied at different thickness of the film. The thermal conductivity of the films increased with the increase in the thickness. But the thermal conductivity values were less than intrinsic thermal conductivity of crystalline silica (1.47w/m/k).

The abrasion resistance of the films was found to be satisfactory. The hydrolysis and subsequent condensation reactions of residual and added TEOS resulted in the formation of randomly branched and/or entangled linear chains. Therefore, It is possible that network of the sols had a composite structure consisting of particles, randomly branched or/and entangled linear chains of silica. The strengthening of the film can be related to the this random branching and entanglement of the silica chains.

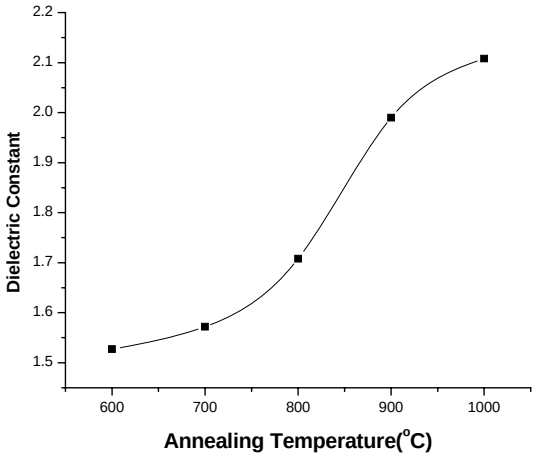

Fig. 10 Variation in dielectric constant with annealing temperature for the silica film

IV. Summary and Conclusions

Silica sol was prepared by the alkaline hydrolysis of TEOS by a two stage hydrolysis process in the presence of glycerol template. The sol resulted in the formation of nano sized spherical colloidal silica particle with narrow particle size distribution. The sol was used to fabricate dip coated silica film on Si wafer. At 1000°C with 40 minutes of annealing a virtually nonporous film was obtained. The refract tive index and dielectric constant of the film increased with the increase in the annealing temperature. The thermal conductivity of the film increased with the increased in the film thickness. The film possessed adequate abrasion resistance due to the random branching and entanglement of linear silica chains.

References

[1] S. Sakka, Current sol gel activities in Japan, J. Sol Gel Sc.Tech., (2006), 37(2), 135-140.
[2] M. Novotny and J. Matousek, Preparation of silver doped silica sol-gel layer, Ceramics-Silikaty, 52(2), 72-76(2008).
[3] M.A. Agerter, R. Almeida, A. Soutar, K. Tadanaga, H. Yang and T. Watanabe, Coatings made by sol-gel and chemical nanotechnology, J. Sol Gel Sci. Tech., (2008), 47(2), 203-236.
[4] H.J. Moon, H.P. Hyung, J.K. Domng, H.H. Sang, S.Y. Choi and J.T. Paik, "SiO_2 aerogel film as a novel intermetal dielectric", J. Appl. Phys.(1997), 82(3), 1299-1305.
[5] C. Avelino, "From microporous to mesoporous molecular sieve materials and their use in catalyst", Chem. Rev., (1997), 97, 2373-2381.
[6] S.A. Johnson, P.J. Ollivier and T.E. Mallock, "Ordered meso-porous polymers of tunable pore size from colloidal silica templates", Science, (1999), 283, 963-966.
[7] S. Nagarajan , M. Li , R. A. Pai , J. K. Bosworth , P. Busch , D.-M. Smilgies , C. K. Ober, T. P. Russell and J. J. Watkins, "An Efficient Route to Mesoporous Silica Films with Perpendicular Nanochannels" Adv. Mater., (2007), 29(2), 246-251.
[8] J. K. Kim, J. K. Park and H. K. Kim, Preparation of a nano-porous silica aerogel and its application to a bio-conversion process, Res. Proces.(2006),53, 3-5.
[9] W. Li, S. Seal, E. Megan, J. Ramsdell and K. Scammon, Physical and optical properties of sol-gel nanosilver doped silica film on glass substrate as a function of heat treatment temperature, J. App. Phys. (2003), 93(12), 9553-9561.

[10] M. Z. Yin, X. Yao and L. Y. Zhang, A novel fabrication of meso-porous silica film by sol-gel of TEOS, J Zhejiang Univ. SCI., (2004), 5(4), 422-427.
[11] D.Y.Zheng, J.G.Feng, Q.S.Huo, N.Melosh, G.H.Fredrickson, B.F.Chmelka, G.D.Stucky and T. Copolymer, Synthesis of meso-porous silica with periodic 50 to 300 angstrompores, Science, (1998), 279, 548-551.
[12] T.M.Parrill, Heat treatment of spun-on acid catalyzed sol-gel silica films, J. Mater. Res., (1994), 9, 723-728.
[13] J. Wang, G. Wu, J.Shen, T.Yang, Q.Zhang, B. Zhou and Z.Deng, Scratch resistant improvement of sol-gel derived nanoporous silica films, J. Sol Gel Sci Tech., (200), 18, 219-224.
[14] Y. Tsuneyuki, N.Nagai, S.Katayama and M.Todoki, Measurement of thermal conductivity of silicon dioxide thin film s using a 3ω method, J. Appl. Phys., (2002), 91(12), 9772-9779.
[15] H.G.Floch and P.F.Belleville, A scratch resistant single layer AR coating by a low temperature sol-gel route, Sol Gel Opt II–SPIE (1992), 1758, 135.
[16] C. J. Brinker and G. W. Scherrer, Sol Gel Science, The Physics and Chemistry of Sol Gel Processing, Academic Press Inc., New York) 1990, 97.
[17] R K Iler, The Chemistry of Silica, (Wiley, New York) 1979, 348.
[18] F.L.Galeener, Planar rings in vitreous silica, J. Non Cryst Solid, (1982), 49(1-3), 53-62.
[19] P.F.Belleville and H.G. Floch, Ammonia hardening of porous silica antireflective coatings, Sol Gel Opt. III-SPIE(1994), 2228, 25.