ANALYSIS OF VARIATION OF ACID CATALYST CONCENTRATION ON PROPERTIES OF LOW-K THIN FILMS

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ABSTRACT
The paper presents the analysis of acid catalyst concentration on dielectric constant of silicon dioxide. The dielectric constant of deposited film is lowered up to 3.51 with 13% porosity for 0.75 ml acid concentration. The compositional properties of films were analyzed by Fourier transform infrared (FTIR) spectrophotometer and the rocking, bending and stretching peaks at 447.56cm-1, 798.31cm-1 and 1070.68cm-1 respectively confirms formation of Si-O network. The full width half maxima (FWHM), peak area, bond number and bond density reveals the lowering in dielectric constant. The lower values of strain of these films calculated from Si-O-Si stretching peak makes them suitable for ILD application in ULSI circuits that controls extrusion of metal. The SEM/EDAX characterizations show the uniform surface morphology of deposited films.

Keywords: Sol gel, HCl catalyst, dielectric constant, FTIR

I. INTRODUCTION

With scaling down of design rules for Ultra Large Scale Integrated (ULSI) chips beyond 45 nm node [1], attempting to fulfill with the stringent performance specifications demanded by the microelectronics industry [2, 3]. In this ULSI technology low-k films use for the interlayer dielectric (ILD) application to minimize the problems of resistance-capacitance (RC) delay [4] and crosstalk noise to improves the speed of the device and reduces the power consumption [5, 6]. The low-k materials can be deposited by Sol-Gel (spin-on) as well as by chemical vapor deposition (CVD). However, sol-gel technique have an imperative advantage over CVD, because of it has an ability to introduce a high degree of porosity in the films and decrease k values as low as 2.0-1.3 [7, 8]. From the literature survey it observe that various precursors have been used to deposit the low-k SiO_2 dielectric thin films by sol gel such as methylsilesquioxane (MSQ), Methyltriethoxysilane (MTES), tetraethylorthosilicate (TEOS), tetramethylorthosilicate (TMOS), etc [9-11]. The TEOS, TMOS are alkoxides, where the sol–gel process of these alkoxides involves two specific reactions termed as hydrolysis and condensation that occurs simultaneously. In hydrolysis, alkoxides produces Si-(OH)4 entities in presence of acid or base, which on controlled condensation converts to sol. Acidic catalyst enhances hydrolysis rate than condensation with increasing number of silanol (Si-OH) groups that gives siloxane (Si-O-Si) linkage during condensation. The process of condensation can be accelerated by addition of base catalyst [12, 13]. The proportion of acid and base catalyst affects on the final viscosity of sol. At 10-40 cP viscosity [14] the sol is dispensed that undergoes a sharp increase in viscosity and get converted into a ‘‘gel’’. This gel is dried thermally at a moderate temperature to remove the original solvents and the film undergoes a major weight and volume loss up to 50%. The gels prepared by sol gel technique can be distinguished depending on drying techniques as xerogel and aerogel. Xerogels are formed through conventional drying by evaporation whereas; aerogels use supercritical

drying of solvents [2].The microstructure of films can be easily modified by controlling the sol gel process parameters. The acid concentration in sol was varied to observe its effect on the microstructure and dielectric properties of deposited thin films. The optimization of process parameters has been carried out to lower the dielectric constant of the thin film. This manuscript has four sections; second section describes the experimental approach used for the deposition of SiO_2 thin film. The results and discussion is presented in third section and the fourth section is of conclusion in which we had given significance of acid concentration on the dielectric constant and other properties of SiO_2 thin films.

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II. METHODS AND MATERIAL

The porous silica thin films were synthesized by sol gel technique, in which films were deposited by spin-coating on p-type (100) Silicon (Si) wafers, with resistivity ~10-20 ohm-cm. The sol was prepared by a two step acid-base catalyst process. In first step TEOS, ethanol and water was mixed with the composition ratio of TEOS: Water: Ethanol as 1:2:3.8. To this solution HCl were added separately in three different concentrations from 0.25 -0.75 m.mol/l to accelerate the hydrolysis reactions.

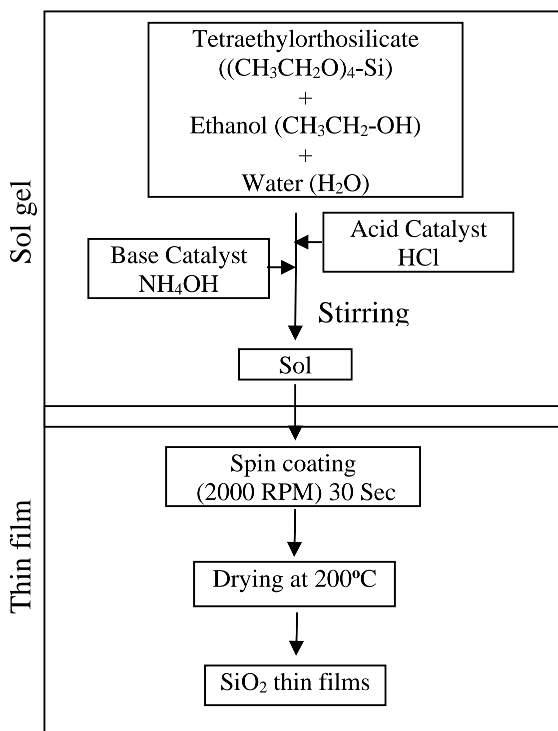

Figure 1: Experimental steps for deposition of SiO2 thin films.

In the second step, NH4OH (0.1M) were added to the 1ml of aforementioned solution and stirred constantly for 15 minutes, this base addition enhances the condensation rate. The prepared solution, just before its gel point, was spun on pre cleaned Si substrates by a spin coater in the optimized viscosity range with the spin rate of 2000 rpm for 30 seconds. The deposited films were dried at 200 0C in furnace for 10 minutes to remove residual solvent. The experimental flow is schematically illustrated in Figure 1. Further, the characterizations of deposited films were done by ellipsometer (SD-Philips 1010), Fourier Transform Infrared (FTIR) spectrometer (Nicolet 380) and Scanning Electron Microscope/ Energy dispersive spectroscopy (SEM/EDAX). The effect of variation of the HCl concentration and aging time on the properties of SiO_2 films deposited by spin coating has been discussed in next section.

III. RESULTS AND DISCUSSION

Figure 2 elaborates the FTIR spectra of deposited film at 6 hours aging time with variation in acid concentration **.**The spectra obtained in the range of 400-4000cm^{-1} with resolution 4cm^{-1} and 128 scan rate.

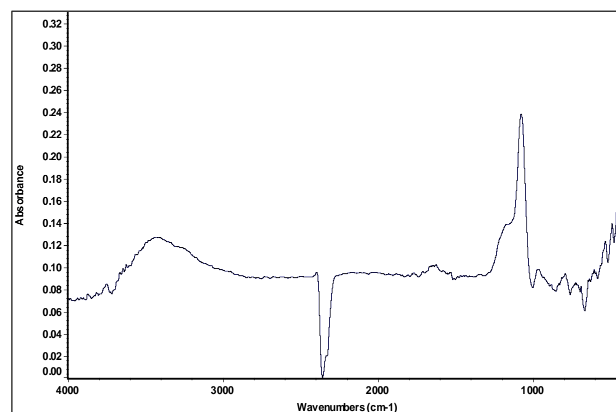

Figure 2: FTIR spectra

The FTIR spectrum (a) show the bondings of Si-O-Si rocking, Si-O-Si bending, Si-OH, Si-O-Si stretching, Si-H and –OH bonds at 447.56cm^{-1}, 798.31cm^{-1}, 950 cm^{-1}, 1070.68cm^{-1}, 2358.13cm^{-1} and 3400cm^{-1} respectively confirms the formation of Si-O-Si network. Other samples also have near about same peaks due to similar bondings with slight shift in wave numbers. The strong Si-O bonds exhibited in the spectra indicate that the SiO_4 tetrahedron structure is the backbone of films.

The detail study of FTIR results is carried out through keen observations of FWHM and peak area of Si-O-Si peak determined using the TQ analyst/Omnic based software provided with Nicolet 380 FTIR spectrophotometer. The figure 3a shows the increase in FWHM of the films deposited at two aging times with increase in acid concentration. The values of FWHM observed to be increasing exponentially for 4 hours aging of gel. The gel with 6 hours aging time shows linear nature this may be due to saturation in viscosity at higher aging time. The increase in FWHM value at higher acid concentration shows that the stretching bond is increased. The rise in FWHM with increase in acid concentration for both aging times supports the presence of porosity in film. Figure 3b represents the effect of acid concentration variation on bond number and bond density determined from details of Si-O-Si peak obtained through FTIR.

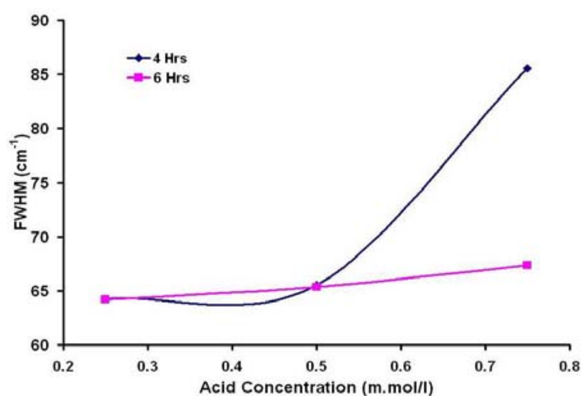

Figure 3a: Effect of acid concentration variation on FWHM of Si-O-Si peak.

The bond number determined from FWHM and peak area of Si-O-Si shows decrease with increase in acid concentration. The bond density is the ratio of bond number to thickness of film and the profile also shows decreasing trend similar to bond number. The lowering in bond number and bond density supports lowering in the overall density of film consequently increases in porosity.

The influence of acid catalyst on Si-O-Si peak area and strain is shown in table 1 is observed to be less on films of 6hrs aging than that of 4 hrs aging films. The peak area increase in peak area with increase in acid concentration supports the presence of porosity. The microscopic strain on film is determined from the important stretching vibration wavenumber of Si-O-Si bond [15]. The strain values are observed to be very low which is advantageous for extrusion control.

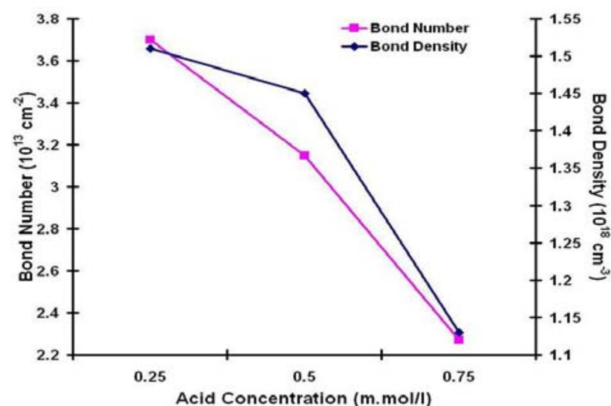

Figure3b: Bond number and bond density dependence on Acid concentration variation

The thickness and refractive index of the deposited SiO_2 thin films have been characterized by Ellipsometer having wavelength of 632.8 nm. Figure 4a depicts the effect of acid concentration on Refractive Index (R.I.) with aging time of 4 hours and 6 hours. It can be observed that the R. I. decreases continuously with the increase of the acid concentration and it is lowered to 1.39 for 0.75 ml acid concentration at 6 hrs aging time. This result matches with the result of Pawel Karasinski [16].

Table 1 Acid concentration effect on Si-O-Si peak area and strain

Sr. No.	Acid concentration (m.mol/l)	Si-O-Si Peak area (6hrs)	Strain (6hrs)
1	0.25	10.26	0.007304
2	0.5	10.98	0.007407
3	0.75	11.62	0.008783

The inset picture in figure 4a shows the lowering in thickness of film up to 2005 Å with rise in acid concentration for 6 hours aging time. The thickness of films deposited at 4 hrs is lowered by 445 Å for 6 hrs aging time, the reason is the increase in hydrolysis rate with acid concentration that lowers the viscosity of sol and ultimately lowers the films thickness.

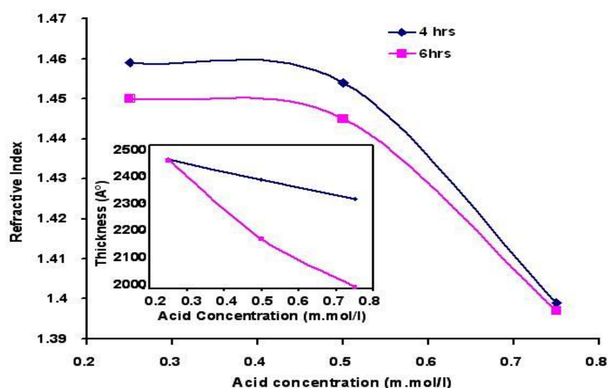

Figure 4a: Effect on acid concentration variation on refractive index at 4 hours and 6 hours aging time. Inset picture shows the effect of acid concentration on thickness of films.

The dielectric constant of the film can be reduced by introducing the porosity; hence the study of density and porosity of films deposited by sol gel that gives inherent porous film has been carried out. The profiles of density and porosity of deposited films at 6 hours aging time due to its lower R.I. with variation in acid concentration is presented in figure 4b.

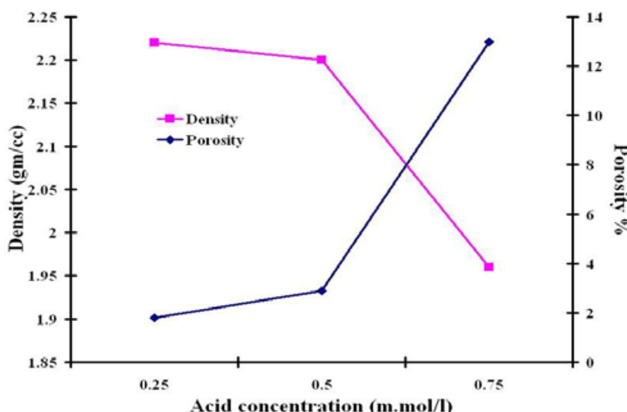

Figure 4b: Dependence of density and porosity on acid concentration

The density decreases rapidly with increase in acid concentration due to weight loss of more –OH groups from Si-OH during drying and shrinking in thickness due to the deletion of organic component from the film resulted in leaving behind the pore in the film. Simultaneously, the porosity of the film is observed to be increased from 1.8 % to 13 %, implying that the decrease of the dielectric constant resulted from the increase of porosity with variation in acid concentration from 0.25 ml to 0.75 ml.

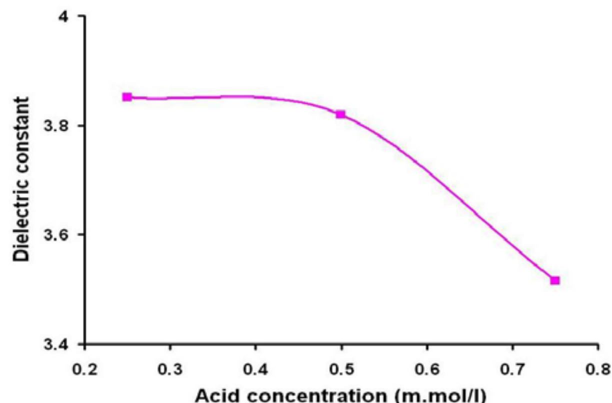

Figure 4c: Acid concentration variation effect on dielectric constant.

The figure 4c shows the lowering in dielectric constant with increase of acid concentration. The dielectric constant is calculated from formula [17] which is based on measured refractive index is 3.51. The dielectric constant of films is observed to be decreasing with increase in hydrolysis rate that retains more –OH groups which evaporates during annealing making the film less thick and more porous.

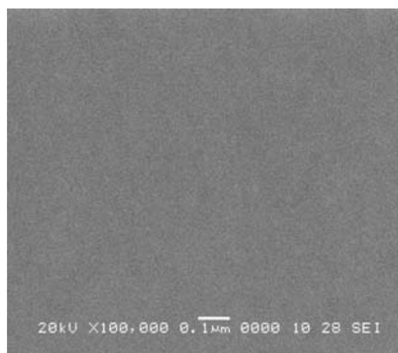

Figure 5a: SEM of sample having acid concentration 0.5 ml.

In Figure 5a high resolution of 0.1µm SEM (JSM- 6360) image of deposited SiO_2 thin film (Sample of 0.5ml acid concentration) is shown. This SEM image provides a visual confirmation of high compositional uniformity of the deposited film. EDAX measurements of deposited SiO_2 thin film were taken for elemental analysis is shown in Figure 5b. The presence of Oxygen and Silicon is confirmed by the peaks appeared at 0.525 and 1.739 keV respectively.

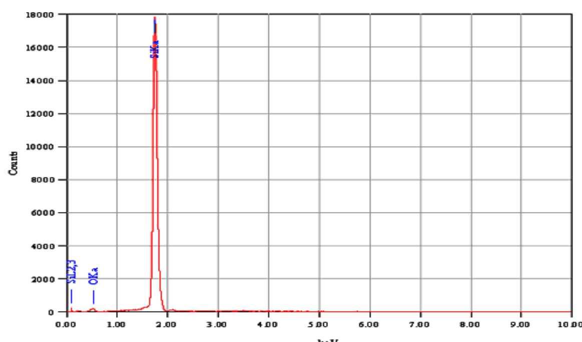

Figure 5b: EDAX of sample having acid concentration 0.5 ml.

IV. CONCLUSION

The effect of acid catalyst concentration variation on dielectric constant is studied by deposition of SiO2 thin films by sol gel spin coating techniques. For 6 hours aging time the dielectric constant is lowered upto 3.51 with 13% porosity compare to 3.9 of SiO2 where, acid concentration were 0.75 ml. The peaks due to Si-O-Si rocking, Si-O-Si bending and Si-O-Si stretching is present in FTIR spectra confirms the deposition of SiO2 thin films. The broadness in Si-O-Si peak confirms the presence of porosity in film whereas the lowering of bond number and bond density with increase in acid concentration also supports the appearance of porosity. The SEM/ EDAX show uniform surface morphology of film and presence of Si, and O element in it. The lower strain is advantageous part of these films that controls extrusion of metal during its application for ILD in ULSI circuits. Such porous thin films having low dielectric constant and refractive index are observed to be suitable for interlayer dielectrics and optical interconnects application in advanced integrated circuits.

V. ACKNOWLEDGEMENT

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VI. REFERENCES

[1] Takenobu Yoshino, Nobuhiro Hata,Jun Kawahara,Takamaro Kikkawa, Applied Physics Letters 90, 182111 (2007)
[2] K.Maex, M. R .Baklanov, D. Shamiryan, F. Iacopi, S. H. Brongersma, Z. S. Yanovitskaya, J. Appl. Phys 93 (11), 8793 (2003)
[3] K. C. Aw, N. T. Salim, W. Gao , Z. Li,J Mater Sci: Mater Electron 17, 607 (2006)
[4] Chi-Tong Chen, Bi-Shiou Chiou, J Mater Sci: Mater Electron 15, 139 (2004)
[5] In Seob Bae, Sang Jin Cho, Seong Hun Jeong, Hyung Jun Cho. Byungyon Hong, Jin Hyo Boo, Plasma Processes and Polymers, 4, 5812 (2007)
[6] V. N. Sekhar, T. C. Chai, S. Balakumar, Lu Shen, S. K. Sinha, A. A. O. Tay, Seung Wook Yoon, J Mater Sci: Mater Electron, 20, 74 (2009)
[7] Richard F. Reidy, Future Fab International 23, 95 (2008)
[8] Woei Chang Ee, Kuan Yew Cheong, Physica B 403, 611 (2008)
[9] Kwang Hun Kim, Dong Jun Lee Hee Woo Rhee, Journal of Korean Physical Society, 39 (1), 119 (2001)
[10] David S. Jacob and Aharon Gedanken, Journal of the American Ceramic Society, 91 (9), 3024 (2008)
[11] Chernev G ,Samuneva B, Djambaski P, European Journal of Glass Science and Technology Part A, 46 (2), 175 (2005)
[12] P.K. Jal, S. Patel, B.K. Mishra, Talanta ,62 ,1005 (2004)
[13] Chien-Tsung Wang , Chun-Lung Wu, Thin Solid Films 496, 658 (2006)
[14] E.Anulekha Manjari, A. Subrahmanyam, N. DasGupta, A. DasGupta, Applied Physics Letters, 80(10),1800 (2002)
[15] Fen Chen, Baozhen Li Timothy, D. Sullivan, Claral Gonzalez, Chrishtopher D. Muzzy, H.K. Lee, Mark D. Levy, Michael W. Dashiell, James Kolodzey, Journal of Vacuum Science and Technology, B618(6),2826 (2000)
[16] Pawel Karasinski, Optica applicata 35(1), 117 (2005)
[17] Bhavana N. Joshi, A. M. Mahajan, Journal of Optoelectronics and Advanced Materials 10(2), 422 (2008)