

# Synthesis and analysis of low-k material for intermetal dielectric applications in VLSI

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The SiO<sub>2</sub> xerogel thin films have been deposited using the TEOS:Ethanol:Water:HCl with molar ratio of 1:2:3.8:0.005. This optimized molar ratio has been used to analyze the effect of aging time on properties of deposited thin films. We had achieved much success in reducing the dielectric constant with the incorporation of the porosity in films with corresponding increase in aging time. The FTIR characterization confirms the deposition of SiO<sub>2</sub> xerogel, the increase in FWHM and broadness in Si-O-Si peak, ensures the increase in porosity and clearly relates the presence of porosity in film. The image figure of spectrum prominently exhibits peaks of IR. The porous films with better low-k value of 3.63 were deposited at room temperature by optimizing the process parameters such as composition of chemicals, aging time etc. This porous SiO<sub>2</sub> thin films when introduced as an inter-metal between interconnect is useful to enhance the execution speed of a VLSI and to reduce the power consumption.

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## 1. Introduction

The phenomenal sustained growth of electronics industry in the last three decades is primarily due to the success of silicon integrated circuit technology. As compared to any other technology, complementary metal-oxide-silicon (CMOS) transistor based integrated circuits have dominated the field of semiconductor manufacturing. The growth of integrated circuit technology is mostly based on the continual scaling down of devices to ever smaller dimensions. The scaling down of devices to smaller size gives higher packing density as well as higher operating speeds which is main requisite of the modern VLSI technology. However, with higher device speed, parasitic capacitance between metal layers increases which in turn, enhances the interconnection delay as compared to gate delay. This interconnection delay drastically affects the device performance hence, it is necessary to minimize the parasitic capacitance and consequently the interconnection delay [1, 2]. Therefore, worldwide efforts are being put by the researchers to search new materials for their use as metal lines like Cu instead of Al due to its low resistivity and the use of low-k dielectric material in a place of current SiO<sub>2</sub> thin films as intermetal dielectrics (IMD) in between interconnects which improves switching speed and performance of devices [3].

Currently, the two main technological routes are in use to deposit the low-k dielectric materials: spin-on or plasma enhanced chemical vapour deposition (PECVD). The spin-on technique (or spin-coating, SOD) consists of the deposition of a solution by centrifugation followed by steps of baking and thermal treatments in order to eliminate solvents and consolidate the layer by crosslinking [4-6]. The investigated low-k films for interlayer applications in VLSI have categories like organic, inorganic and hybrid materials out of which

organic materials have more significant integration problems than inorganic materials such as poor adhesion, thermal instability, anisotropy of dielectric constant and low resistance to O<sub>2</sub> plasma. Whereas, the inorganic films overcome all of these problems but generally they have high-k and more serious moisture absorption hence it requires liner and capping layers. Hence, hybrids between organic and inorganic materials are very promising low-k material used in current technology [7]. Yet, many challenges are associated with the successful integration of these materials into on-chip interconnects because with low dielectric constant, the intra- and interlevel dielectric material must satisfy large number of requirements like high thermal and mechanical stability, good adhesion to the other interconnect materials, resistance to processing chemicals, low moisture absorption, etc.

The modern technology, has allowed to built millions of transistor on a very small chip, to achieve the better device performance close attention over the porous low dielectric constant (low-k) and ultralow dielectric constant (ultralow-k,  $k < 2$ ) materials are essential [8,9]. Among, the porous low-k and ultralow-k materials under study, the porous SiO<sub>2</sub> film prepared by sol gel becomes a promising material due to its excellent performance, such as good insulating and thermal expansion, smaller pore size (<2 nm) and the capacity of extending to ultralow-k from low-k. SiO<sub>2</sub> xerogel prepared by the ambient drying process and deposited using a sol gel (spin-coating) technique is one of the potential dielectric thin film has been emerged as an attractive alternative to conventional SiO<sub>2</sub> because of its high thermal stability and their ability to be rendering hydrophobic [7-11]. The sol-gel (Spin Coating) technique is popularly used in current technology in which films are deposited from organic precursors by low temperature polymerization reactions that, offers attractive advantages in terms of flexibility of composition and structure. The great potential of the low k dielectric

has forced us to focus in our present work of the deposition of SiO<sub>2</sub> xerogel by spin coating and the study of effect of aging time variation on porosity of the film. The optimization 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<sub>2</sub> xerogel 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 porosity in lowering the dielectric constant of SiO<sub>2</sub> xerogel thin film and applications of these SiO<sub>2</sub> low-k xerogel thin films for VLSI as Intermetal Dielectric (IMD).

### 2. Experimental

The p-type (100) Si Wafers, with resistivity ~10-20 ohm-cm, have been used as substrates. These substrates were cleaned using Trichloroethylene, Acetone and Methanol. The coating solution was prepared by a two step process involving acid-base catalyst reactions. In the first step, the precursor TEOS (Tetraethylortosilicate), which is non toxic and easy to handle compared to other precursors, was mixed with the solvent ethanol, then water was added and acid was used as catalyst with the composition ratio of TEOS: Water: Ethanol: Acid as 1:2:3.8:0.005. In the second step, NH<sub>4</sub>OH (0.1M) were added to the 1ml of aforementioned solution which forms complete gel after half an hour. The solution, just before its gel point, was spun on precleaned Si substrates by a home made photoresist spinner in the optimized viscosity range with the different spin rate from 1000 to 3000 rpm for 30 seconds.

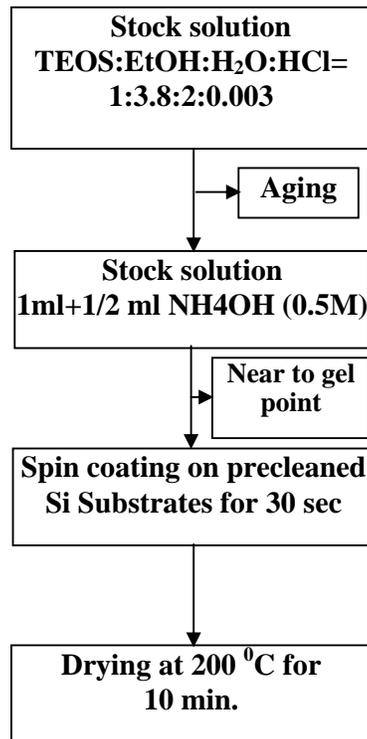


Fig. 1. Experimental flow of sample preparation

The deposited film was dried at 200 °C for 10 min in an oven. The beaker containing solution was covered during the period to avoid loss of solvent. The experimental flow is schematically illustrated in Fig. 1. Further, the deposited films were characterized for their optical properties. The effect of variation of the aging time on the properties of SiO<sub>2</sub> films deposited by spin coating has been discussed in results and conclusions section.

### 3. Results and discussion

The ellipsometer (Philips SD-1000) is used to measure the refractive index and thickness of the deposited films using the wavelength of 632.8 nm. It reveals from the Fig. 2 that, the refractive index decreases with increase in aging time, while corresponding thickness of the film is found to be increasing. Our results are in good agreement with the results reported by S.V. Nitta, et.al [4] implies that, as aging time increases the gel retains more of the porosity developed during gelation. The dielectric constant of film calculated based on the RI measured by ellipsometer found to be decreasing with increase in aging time as shown in inset picture of Fig. 2 which is due to increase in the porosity of the film.

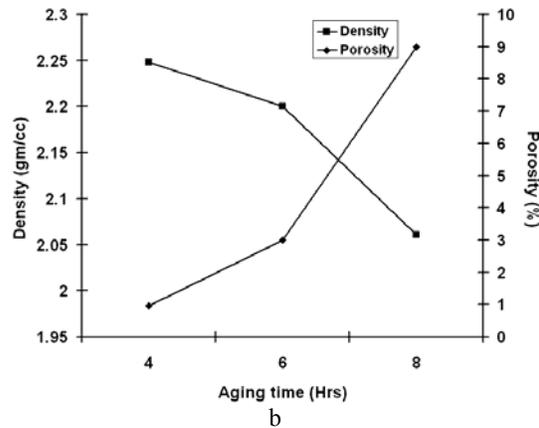
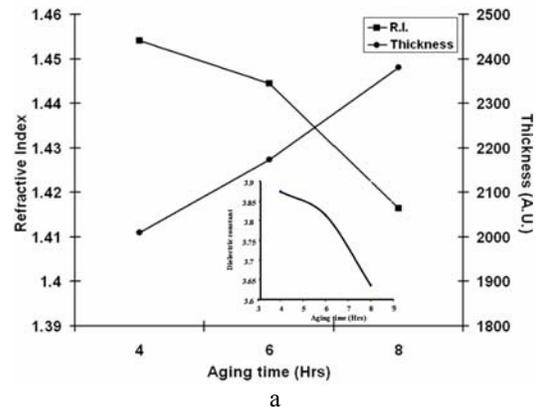


Fig. 2. (a), Effect of aging time on RI and thickness of deposited film and inset figure shows the effect on dielectric constant, (b), Effect of aging time on density and porosity.

The film density,  $\rho$ , has been determined from the measured refractive index ( $\eta$ ), using the relationship,  $\rho$  is proportional to  $(\eta - 1)$  for silica xerogel [1]. The dielectric constant ( $k$ ) and the porosity ( $\Pi$ ) of the films were calculated indirectly from the density. The film porosity was obtained from the relationship,

$$\Pi = 1 - \rho/\rho_s \quad (1)$$

where  $\rho_s$  (thermally grown conventional  $\text{SiO}_2$  film) =  $2.27 \text{ g/cm}^3$  and  $\rho$  is density of deposited film. Similarly, the dielectric constant of  $\text{SiO}_2$  xerogel film was determined from the relationship

$$\kappa = 1 + 1.28\rho \quad (2)$$

Fig. 2(a) shows the relationship between density and porosity of the deposited film with respect to aging time. It has been observed from Fig. 2(a) that, with increase in aging time the density of film decreases nonlinearly which is due to the incorporation of porosity in film and it is verified from calculations showing the increase in porosity in the film. The FTIR analysis was carried out to obtain information about chemical bonding characteristics using the Nicolet 380 FTIR spectrometer. The absorbance spectra of thermally treated (at  $200^\circ\text{C}$ )  $\text{SiO}_2$  xerogel films deposited with variation in aging time is as shown in Fig. 3(a), 3(b) and 3(c) for 4, 6 and 8 hours respectively. The image form of each spectrum is developed with the help of MATLAB software by using CSV file format of spectra obtained from the Omnic software provided with FTIR. The image is placed on upside of spectrum clearly elucidate the peaks in spectrum. The IR spectra were recorded with spectral resolution of  $4 \text{ cm}^{-1}$  using 128 scans for both sample and background (Reference). In the deposited thin film, the main vibrational peaks have been observed in the recorded IR spectra at  $447 \text{ cm}^{-1}$  and  $1065 \text{ cm}^{-1}$  corresponding to rocking and stretching modes of Si-O-Si bond respectively [9-11]. It reveals from the spectra as aging time increases the stretching peak shifts to higher wave number (blue shift) side which is due to decrease in density of the deposited film, whereas, there is not much variation in rocking wave numbers but the bending wave number is shifted to  $798 \text{ cm}^{-1}$  instead of  $808 \text{ cm}^{-1}$ . The occurrence of peak at  $3279.8 \text{ cm}^{-1}$  and  $960 \text{ cm}^{-1}$  shows the presence of -OH bond in film. The main stretching peak is associated with the transverse optical mode. The presences of broadness in absorption peaks as well as peak position are indicative of largely non stoichiometric and porous  $\text{SiO}_2$ . The broad Si-O-Si stretching peak shows shoulder at higher wave number side and this extends upto  $1300 \text{ cm}^{-1}$ . The image form of each figure shows the dark line on upside of the main Si-O-Si stretching bond the darkness of line corresponds to intensity of peak and the width of dark as well as the faint broad line on upside of peak relates to the broadness of the peak in spectrum. Chon and Lee [12] suggested that the shoulder peak (the LO mode at,  $1200 \text{ cm}^{-1}$ ) was related to the porosity of a silicon dioxide film. The LO mode was attributed to the Si-O-Si

stretching vibration in network structures with porosity [4, 11].

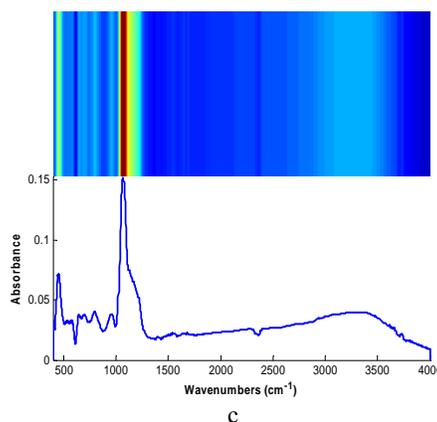
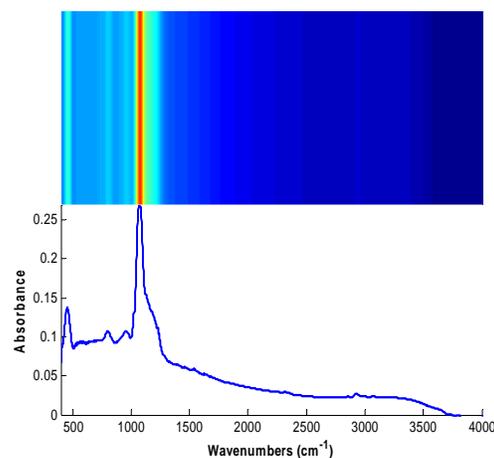
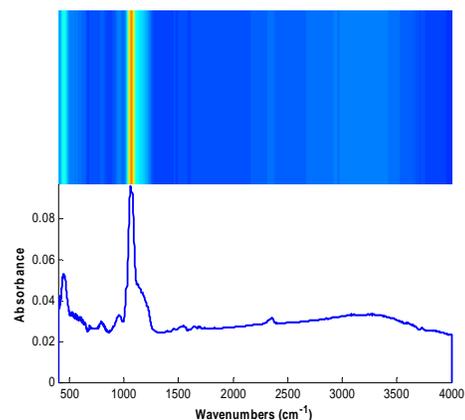


Fig. 3. (a), Absorbance FTIR Spectra of  $\text{SiO}_2$  xerogel thin films deposited at aging time of 4 hours,(b), Absorbance FTIR Spectra of  $\text{SiO}_2$  xerogel thin films deposited at aging time of 6 hours,(c), Absorbance FTIR Spectra of  $\text{SiO}_2$  xerogel thin films deposited at aging time of 6 hours.

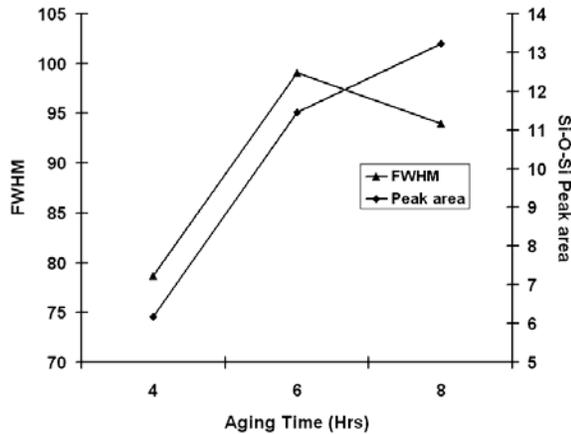


Fig. 4. Effect of aging time on FWHM and peak area.

It has been observed from the Fig. 4 that, the effect of variation of aging time on FWHM increases at 6 Hrs aging time and then decreases slightly may be due to defect or non uniformity. The values of FWHM of main Si-O-Si peak is calculated using the Omnic/TQ Analyst Software provided with Nicolet 380 FTIR spectrometer matches with the values of reported data [13]. The peak area under the main Si-O-Si asymmetric stretching peak is observed to be increasing with the increase in aging time is due to the presence of porosity that gives rise to increase in shoulder of Si-O-Si stretching peak. These results of increase in peak area are due to presence of porosity, contributing in lowering the dielectric constant of the deposited film.

The vital parameters like bond angle, bond number are calculated using different formulas, it is observed that bond angle increases with aging time due to increase in stretching wave number of Si-O-Si bond and the decrease in bond number is due to the lowering in density of the film, this relates the presence of porosity of the film as shown in Fig. 5.

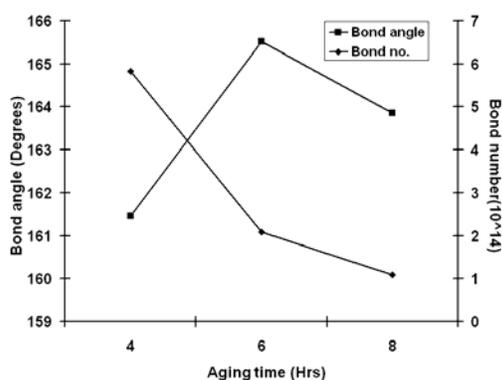


Fig. 5. Effect of aging time on bond angle and bond number.

Table 1. Wave number of mode of vibrations of different bonds.

Sr. No.	Modes of Vibrations	Peak Wave number (cm <sup>-1</sup> )			Reference
		Aging time			
		4 Hrs	6 Hrs	8 Hrs	
1	Si-O Rocking	447.9	459.1	449.6	-
2	Si-O Bending	794.3	798.5	798.3	14
3	Si-OH bond	956.1	954.7	960.0	14
4	Si-O Symmetric stretching	1065	1069	1065.6	-
5	Si-O Asymmetric stretching	1143.9	1148.3	1146.3	14

Table 2. FWHM and Peak Area of Symmetric and Asymmetric peaks of Si-O-Si vibration modes

Modes of vibrations		Aging time		
		4 Hrs	6 Hrs	8 Hrs
FWHM	Si-H Peak	37.43	34.31	19.72
	Si-OH	42.92	62.74	34.40
	Si-O Symmetric stretching Peak	33.65	35.0	34.87
	Si-O Asymmetric stretching Peak	26.19	29.87	26.94
Peak Area	Si-O Symmetric stretching Peak	11.02	24.36	19.05
	Si-O Asymmetric stretching Peak	3.63	6.33	5.49

The wave number values of different modes of vibrations of Si-O bond and other Si-OH bonds present in the films with the references are summarized in Table 1. The important parameters related to these bonds like FWHM and Peak area are presented in Table 2. It is observed from Table 2 the FWHM of Si-OH bond increases with increase in aging time. The deconvolution of Si-O stretching peak in symmetric and asymmetric mode is carried out with the help of Fourier Self Deconvolution tool present in the Omnic software provided with the FTIR. With these detailed FTIR based results it has been observed that the incorporation of porosity and its basic effects can be studied from the FTIR.

#### 4. Conclusions

The SiO<sub>2</sub> xerogel thin films have been deposited successfully using the spin coating technique. The porosity lowers the dielectric constant of the film upto 3.63, which is less than that of the dielectric constant of conventional SiO<sub>2</sub> thin film. The FTIR characterization of the films shows the blue shift in asymmetric stretching bond of Si-O-Si, which is due to lowering in density. The increase in bond angle, peak area and FWHM confirms the presence of porosity in the film. The images obtained through the MATLAB clears the expounding vision of the IR spectrum. The deposited low - dielectric thin films were

characterized using ellipsometer and FTIR to analyze the porosity of film and to realize the lowering of dielectric constant. These films are used as an intermetal dielectrics in VLSI for enhancing the performance of the VLSI circuits by reducing the interconnect delay.

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