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Growth and characterization of porous SiO_2 thin films for interlayer dielectrics applications in ULSI

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The HF acid has been used as a catalyst with TEOS, ethanol and water, to deposit porous SiO_2 dielectric thin films by spin coating technique. The effects of HF catalyst concentration on properties of deposited thin films have been studied using different characterization techniques. The films have been characterized with the FTIR spectrometer, the stretching Si-O-Si peak at 1074 cm^{-1} and the other vibrational peak positions of the absorption spectrum confirms the deposition of SiO_2 thin film. The FWHM of the Si-O-Si stretching peak found to be increasing with corresponding increase in broadness in Si-O-Si peak ensures the presence of porosity in the film. The refracive index (RI) of a deposited film measured using ellipsometer is 1.33 and the thickness of film is of 2500 A^0. The porosity calculated from the RI is 27.4 % and dielectric constant determined to be of 3.1. The presence of nanopores in the films have been revealed from SEM image. The presence of such nanopores lead to diminishing of the dielectric constant, that makes these films suitable to be used as an interlayer dielectric in ULSI applications.

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1. Introduction

For microelectronics industry, the growth of the integrated circuits IC technology is primarily based on continued scaling. As device dimensions are scaling into deep submicron region the billions of transistors interconnected on a ULSI (Ultra Large Scale Integrated circuits) chip to give desired functions and imposes strong demand on new backend of line (BEOL) interconnect structures [1]. With shrinking in device size the complexity of interconnects structure increases requiring multilevel interconnections to realize high performance and high functionality integrated circuits. However, the use of multilevel interconnections increases signal propagation delay and cross talk in devices using conventional metal (Al) interconnects and silicon dioxide (SiO_2) as the Interlayer Dielectrics (ILD). The performance and reliability of ULSI devices are presently dominated by the propagation delay (RC delay), crosstalk noise, and power dissipation. To reduce these factors, new materials for their use as metal lines and Inter Layer Dielectrics (ILD) are being developed. The low dielectric constant (k) materials are in the great demand as they are being used as ILD due to their capability of reducing parasitic capacitance and power dissipation in ULSI devices [2-5]. The low –k materials are prepared by forming the less polarizable bonds in the material and with the introduction of porosity the lowering of the density of material is achieved [6]. Hence, we had used HF and TEOS to reduce the polarizability as they introduce hydrogen, carbon, fluorine and non-polar C-C bonds having k value of 2.6-2.8 [7] and achieved a low dielectric porous SiO_2. The problem with organic polymers is their thermal instability, softness, low resistance to plasma processes and incompatibility with traditional technological processes [4]. However, it is difficult to reduce the dielectric constant (k) of these hybrid materials below 2.5 with fully dense materials, hence in order to achieve very low-k values (about 2.0 or less), it is essential to introduce porosity to such materials [8]. It is known that the low-k porous silica films prepared by means of sol-gel coating have the high thermal stability compared to all other candidates under investigation and exhibit good planarization and gap-filling capabilities [9].

As the dielectric constant of porous low-k films is mainly dependent on the porosity of the films, raising the porosity with closed pores and its uniform distribution in the film has become the most important factor in porous low-k films preparation [10]. The description of porosity in solids is complicated by the existence of different shapes of pores, connections between the pores, and the distribution in size of pores. According to the IUPAC definition micropores have diameters smaller than 2nm, while mesopores have diameters between 2 to 50 nm and macropores have diameters larger than 50 nm [11]. The introduction of voids into the network of the material degrades other material properties such as mechanical strength, the chemical structure etc. Hence, the compromise porous network of the material must be carefully designed to achieve sufficient thermo mechanical stability [3]. For the use of porous material as ILD in ULSI, the pore sizes need to be significantly smaller than the smallest feature size, the pore size distribution must be

narrow to maintain good uniformity of the electrical and mechanical properties, and the pores ideally should not be interconnected to limit moisture absorption and environmental contamination. In this regard the work is carried out to form nanopores in SiO_2 thin films using the sol gel (Spin coating) technique with HF catalyst that gives good planarization. It is expected that, the weak acidity of HF acid effectively controls the formation speed of nucleus during gelation and produces micro porous films that are more suitable for interlayer applications. The second section of this paper contains the experimental procedure used for the deposition of thin films. The results are discussed in third section and fourth section concludes the paper.

2. Experimental

In our earlier work [12], the porous SiO_2 xerogel films were deposited by spin coating technique with the dielectric constant of 3.65 using Tetraethylorthosilicate (TEOS) as a source of Si, solvent ethanol and water with HCl as acid catalyst for hydrolysis. These films have been deposited by spin coating technique on precleaned p-type (100) Si substrates having resistivity ~10-20 ohm.cm. The TEOS+ Ethanol+ Water+ HF acid have been used with optimized molar ratio 1:3:2:0.1 as sol for the present study. This sol, just before its gel point, was spun on precleaned Si substrates by a spin coater in the optimized viscosity range with the spin rate of 2000 rpm for 30 seconds. Further, the deposited films were dried at 200 ^{0}C temperature in an oven to remove undesired water molecules. The beaker containing solution was covered during the period to avoid loss of solvent. The effect of HF concentration variation on properties of SiO_2 films has been studied in this paper. It has been observed during experimental work that, the time required for gel formation (gelation time) decreases with increase in HF concentration as shown in Fig. 1. These films have been characterized further using the Ellipsometer, FTIR, and SEM for measurement of refractive index, chemical composition and surface morphology of the films, respectively. It reveals from characterization results that, the dielectric constant of the films deposited using HF acid as a catalyst, observed to be lowered as compared to the dielectric constant of the films deposited by using HCl acid as catalyst. The FTIR Spectra show the absorption peaks at energy 133.33 meV, 56.701 meV, 99.575 meV corresponding to stretching, rocking, and bending vibrations of Si-O-Si bond, respectively, that confirms the presence of SiO_2 thin film. The SEM image shows the porous surface of the films. The porosity present in the film reduces the overall dielectric constant of the deposited film, such porous films are observed to be suitable for ULSI applications as ILD due to their low dielectric constant and good mechanical strength.

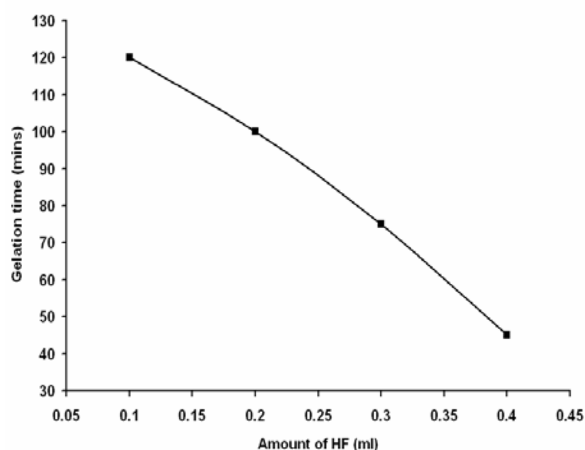

Fig. 1. Effect of addition of HF on gelation time.

3. Results and discussion

The FTIR analysis was carried out to obtain information about chemical bonding characteristics using the Nicolet 380 FTIR spectrometer. The Fig. 2 shows the Absorbance spectra of the deposited porous SiO_2 thin films using the catalyst HF acid with variations from 0.1 to 0.4ml. The spectra were recorded in range 400-4000 cm^{-1} with 4 cm^{-1} resolution & 128 scans for both sample and background. The absorption spectra show the Si-O-Si stretching peaks at 1074.9, 1074.92, 1075.22, and 1076.67 cm^{-1} with increase in HF concentration from 0.1 to 0.4 ml respectively. For the thin film with 0.1ml HF concentration, the important vibrational peaks have been observed in the recorded FTIR spectra shown in Fig. 3 are at 452.2 cm^{-1}, 802.75 $cm^{-1}$and 1074.9 cm^{-1} corresponding to rocking, bending and stretching motions of Si-O-Si bond respectively. The occurrence of peak at 3284.4 cm^{-1} and 963.65 cm^{-1} shows the presence of –OH bond in film. The Si-O-Si stretching peak at 1074.9cm^{-1} is associated with the transverse optical mode whereas, the presence of broadness in absorption peak is indicative of largely non stiochiometric and porous SiO_2. The broad Si-O-Si stretching peak shows shoulder at higher wave number side and this extends up to 1300 cm^{-1}. Chon and Lee [13] suggested that the shoulder peak (the LO mode at, 1225 cm^{-1}) is related to the porosity of a silicon dioxide film. The presence of LO mode in film is attributed to the presence of porosity. The inset picture in Fig. 3 (b) in range 1025-1250 cm^{-1} shows the deconvolution spectra of Si-O-Si stretching peak taken using Fourier self deconvolution (FSD) facility available with the Ominc software. It clearly shows the three peaks concealed in the main stretching peak. These peaks located at 1070 cm^{-1} and 1151cm^{-1} correspond to Si-O symmetric and Si-O asymmetric stretching [14]. The one more peak present in

deconvoluted spectra at 1225 cm^{-1} is related to porosity [15]. As acid concentration increases, the broadness of the Si-O-Si stretching peak is observed to be increasing, it is due to the incorporation of the electronegative fluorine atom, which terminates the Si–O–Si network that makes Si–O–Si bond angle larger and the network becomes less polarizable, which also contributes a great deal to the decrease in the dielectric constant (k) value of the film.

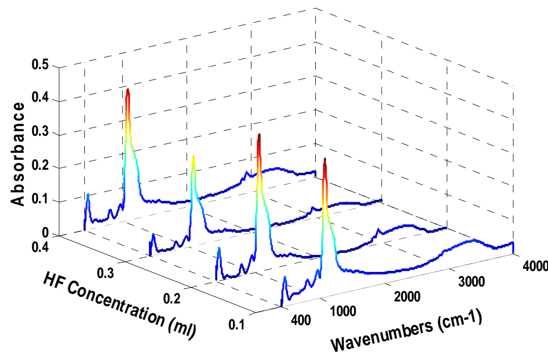

Fig. 2. FTIR absorption spectra of deposited porous SiO_2 thin films at different HF concentrations.

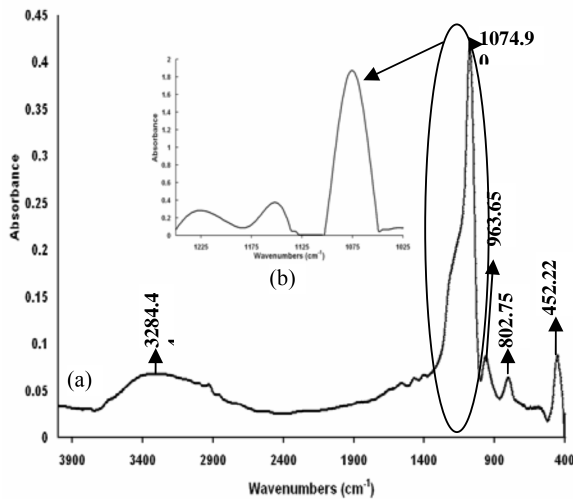

Fig. 3 (a) FTIR Absorption spectrum of deposited porous SiO_2 thin film.(b) Deconvoluted spectrum of Si-O-Si stretching peak.

After increasing the HF concentration in the sol from 0.1 ml to 0.4 ml, the main asymmetric Si-O-Si stretching peak in the films found to be shifting towards the higher wave number side and bond angle is observed to be increasing as shown in Fig. 4 reveals the less polarizable network due to incorporation of fluorine [16]. The nonlinear increase in the bond angle with the increase in the HF concentration is attributed to the higher acidic nature of the catalyst.

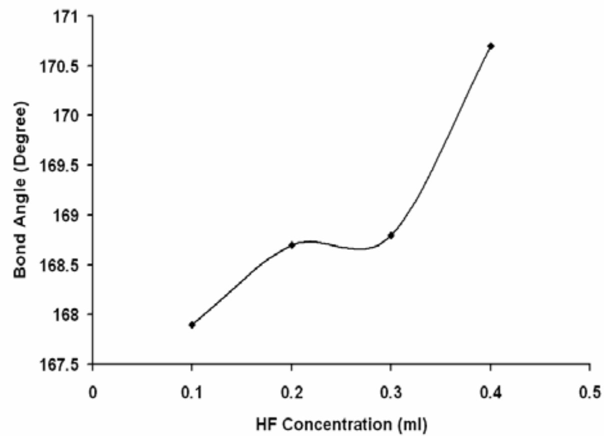

Fig. 4. Effect of concentration of HF on bond angle.

The values of FWHM and peak area of Si-O-Si stretching peak is calculated using the Omnic/TQ Analyst Software provided with Nicolet 380 FTIR spectrometer is presented in Fig. 5. The increase in FWHM is due to the presence of porosity in the films. The calculation of peak area is based on FWHM and intensity of absorption. The variations observed in peak area are because of stress formation on the deposited film due to increase in HF concentration.

The refractive index (RI) of the deposited film have been measured using the Ellipsometer (Philips SD-1000) at the visible wavelength of 632.8 nm is 1.3332, which is less than the RI of SiO_2 xerogel thin film deposited using the HCl as catalyst. The decrease in RI is due to the presence of nanopores created by F incorporation in oxide network.

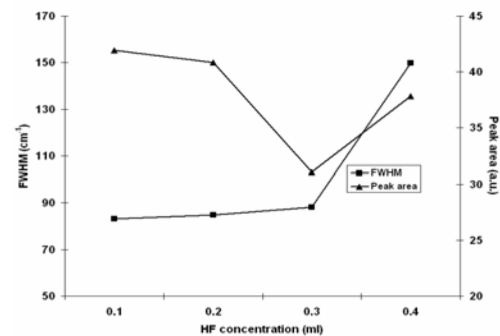

Fig. 5. Effect of concentration of HF on FWHM and peak area.

The dielectric constant is frequency dependent property associated to electronic, ionic and orientation polarization.

$$\varepsilon_{total} = \varepsilon_{ele} + \varepsilon_{ion} + \varepsilon_{or} \tag{1}$$

The electronic polarization falls in visible range hence dielectric constant due to electronic polarization [16] is

$$\varepsilon_{ele} = \eta^2 \quad (2)$$

From equation (1) and (2) the electronic contribution in total dielectric constant reduces to 1.777 that is less than that of SiO_2 (2.1316). Thus, the calculated dielectric constant is 3.1, which is reduced because of reduction in electronic contribution [2]. The percentage of porosity in the film calculated from RI is 27.4%. As concentration of HF increases the stress on film increases and hence it is difficult to measure the RI of other films.

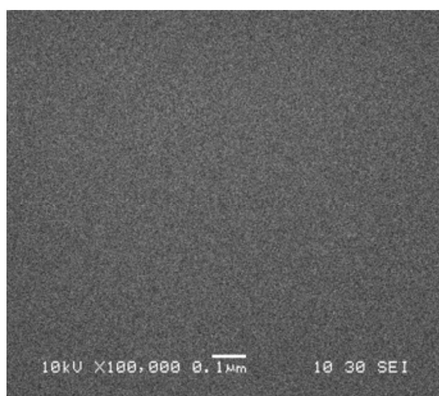

Fig. 6. SEM image of the sample.

In Fig. 6 high resolution of 0.1 μm SEM image of deposited porous SiO_2 thin film (Sample at 0.1 ml HF concentration) is shown. This SEM image provides a visual confirmation of high compositional and porosity uniformity of the deposited film. On analyzing the SEM image, it appears that, the average pore size is in the range between 10 and 20 nm. This estimated pore size reflects only those pores that are visible in the images. For determination of actual pore size and its distribution, adsorption study would be required.

4. Conclusions

The porous SiO_2 thin films have been deposited successfully by the spin coating technique using HF as catalyst. The presence of porosity lowers the dielectric constant of the film down to 3.1, which is less than that of the dielectric constant of conventional SiO_2 thin film. From the FTIR study it reveals that, the shift in Si-O-Si stretching peak to higher wave number side is due to incorporation of F in deposited film that helps to increase the porosity and lowers the polarizability, which in turn lowers the dielectric constant of the film. The presence of porosity has been confirmed from the calculated dielectric constant based on the measured RI of the deposited film. The SEM image confirms the presence of nanopores in the film that were expected with use of HF catalyst. Such porous SiO_2 thin films with low dielectric constant can be used as ILD in ULSI devices.

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