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Sol-Gel Deposited Porogen Based Porous Low-k Thin Films for Interlayer Dielectric Application in ULSI Circuits

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Porous SiO_2 low-k thin films with low dielectric constant were successfully deposited by sol-gel spin-coating technique. The films were deposited by using Tertaethylorthosilicate (TEOS) as a precursor solution and HF was used as an acid catalyst solution. The Tween80 with different volumetric concentrations i.e. 0.0 ml, 0.5 ml and 0.7 ml was used as a pore generator to lower the dielectric constant of the films by introducing the porosity in the films matrix. The thickness and refractive index (RI) of low-k thin films have been measured by Ellipsometer. The refractive index and thickness of the films observed to be decreasing with increase in Tween80 concentration. The chemical bonding structures of films were analyzed by using Fourier transform infrared spectroscopy (FT-IR) spectroscopy and the stretching, bending and rocking peaks appear at 1077 cm^{-1}, 967 cm^{-1}, 447 cm^{-1} respectively confirm the formation of Si-O-Si network. The RIs of the films deposited at 0 ml, 0.5 ml and at 0.7 ml of Tween80 concentration are found to be 1.34, 1.26, and 1.20 respectively. Based on RI values of the films, the porosity percentage, density and dielectric constant have been calculated by standard formulation method. The increase in porosity percentage of films from 3 % to 55 % with increase in Tween80 concentration reveals that, the most of the hydroxyl group and porogen get evaporated and form more voids in the films. This increase in porosity percentage causes to lower the dielectric constant of films and was found to be 2.26 at the 0.7 ml of Tween80 concentration. Such porogen based low dialectic constant thin films can be suitable for interlayer dielectric (ILD) applications in ULSI circuits.

Keywords: Sol-gel, Tween80, Porosity, FT-IR, Low-k.

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1. INTRODUCTION

The continuous reduction in device size resulted in the improvement of device speed in Ultra Large Scale Integration (ULSI) technology. But the reduction in feature device size generates serious technological problems related to interconnect in back-end of line (BEOL). This shrinking in metal size leads to a significant increase in resistance (R) and interconnect capacitance (C), causing higher RC delay and cross-talk. Further increase in resistance results to increase in power consumption [1]. These interconnect problems affects on the overall performance of ULSI circuits. The introduction of copper (Cu) as a metal layers and low-k interlayer dielectric (ILD) material has incrementally improve the performance of device as compared to Al/SiO_2 technology. But still, the demand for new materials with low dielectric constant (k) as insulating interlayer dielectrics (ILD) is incessant. As per the recent International Technology Road map for Semiconductor (ITRS) the ILD materials with dielectric constant $k < 2.5$ are required beyond 45 nm technology [2]. The low-k thin films being deposited most prominently by using Sol-Gel (spin-on) as well as by chemical vapor deposition (CVD). The sol-gel technique have an advantage over CVD to deposit low-k thin films, because of its ability to introduce a high degree of porosity in the films by tailoring the chemical composition and the microstructure of the deposited films and decrease k values as low as 2.0-1.3 [3]. The dielectric constant of the material can be reduced by lowering the films density or introducing lower polarized bonds in the material. The reduction of density or introducing porosity in films has the strongest impact to lower the dielectric constant because air having the dielectric constant ~ 1. There are several ways to introduce the porosity in the low-k thin films such as evaporization of solvent by annealing films by using supercritical drying method. But, this process is reported to be very energy intensive, often dangerous and not easily adoptable to continuous thin film forming operation [4]. The easy and most adopted process for deposition of highly porous low-k thin films is the addition of sacrificial pore generator (porogen) in the precursor mixture solution. The selections of porogen have been based on chemical compatibility to the matrix solution. Fig. 1 enlightens the process for the deposition of porous low-k by using the porogen based method. In pore generator based method, initially the porogen adds in precursor mixture solution and then finally during annealing steps the decomposition of porogen leaves behind the voids and reduces the density of the films. The porosity and pore size is directly related to amount of porogen added in precursor solution and size of sacrificial particle. Hence, the pore size and porosity can be control by proper selection of porogen and amount of porogen addition in precursor solution [5]. There are several porogen such as cyclodextrin (CD), Brij-56, Tween80, and Pluronic P123 etc. are used to lower the dielectric constant of the films by introducing the porosity in the films matrix [6, 7].

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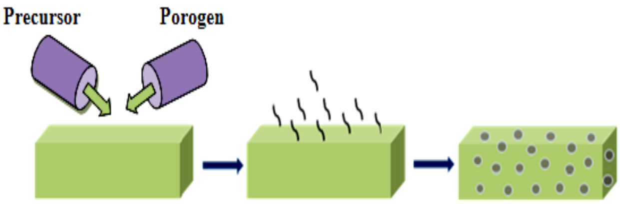

Fig. 1 – Deposition of porous low-k films using Porogen

In present work, the porous low dielectric constant thin films have been deposited by using porogen based sol-gel spin-on method. The Tween80 added in precursor mixture solution, was used as pore generator. The detailed study of effect of porogen addition on low-k thin films parameters such as porosity, density and dielectric constant was carried out. This manuscript is divided in four sections; experimental details are given in section 2 of the paper. The results and discussion is presented in third section and the fourth section concludes the paper.

2. EXPERIMENTAL

The porous low-k films were prepared by using spin-on sol-gel method. For the deposition of low-k thin films a sol was made by mixture of solution containing Tertaethylorthosilicate (TESO) as a precursor solution, Ethanol as a solvent and HF as an acid catalyst. The composition ratio of mixture solution TEOS: Ethanol: H_2O was kept as 1:2:4 with HF as an acid catalyst of 0.01 molar concentrations. Further the porogen Tween80 was added in a mixture solution with different volumetric concentration i.e. 0.5 ml and 0.7 ml. The prepared mixture solution was then stirred for 1 hr at constant speed. The sol before reaching the gel point was spin coated on pre-cleaned silicon wafer by using spin coating at a 3500 rpm for 30 sec. The deposited films were baked at 800 for 30 min and finally the films were annealed at 3000 C for 1 hr in closed furnace. Further the deposited films were characterized by using Ellipsometer (SD-Philips 1010) for thickness and refractive index measurement and Fourier Transform Infrared Spectroscopy (FTIR- Nicolet 380) was used for chemical bonding analysis.

3. RESULTS AND DISCUSSION

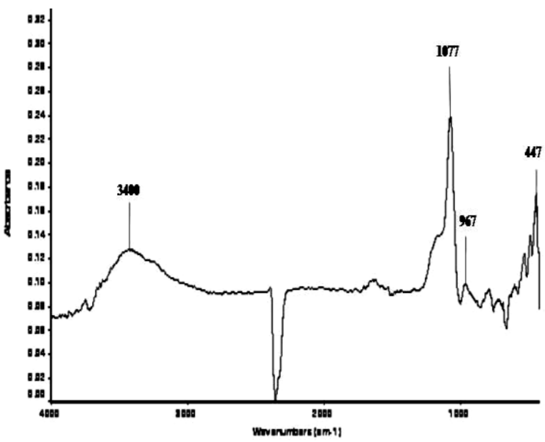

Fig. 2 – FTIR spectra of deposited low-k thin film

The chemical bonding of deposited low-k films shown in Fig. 2 was collected by using Nicolet 380 FT-IR spectroscopy in the range of 400 – 4000 cm^{-1} with resolution 4 cm^{-1} and scan rate of 128. The appearance of stretching, bending and rocking peaks at 1077, 967, 447 cm^{-1} respectively confirms the formation of Si-O-Si network [8].

The thickness and refractive index of deposited films have been determined by using Ellipsometer (SD-Philips 1010) having He-Ne laser of wavelength 632.8 nm. The Fig. 2 depicts the effect of Tween80 concentration on Refractive Index (RI) of the low-k films. From Fig. 2 it is observed that, the RI decreases continuously with increase of Tween80 concentration and it is lowered to 1.20 at 0.7 ml Tween80 concentration. Fig. 3 shows the effect of Tween80 concentration on films thickness. The thickness of the deposited low-k films observed to be decreasing from 160 nm to 119 nm.

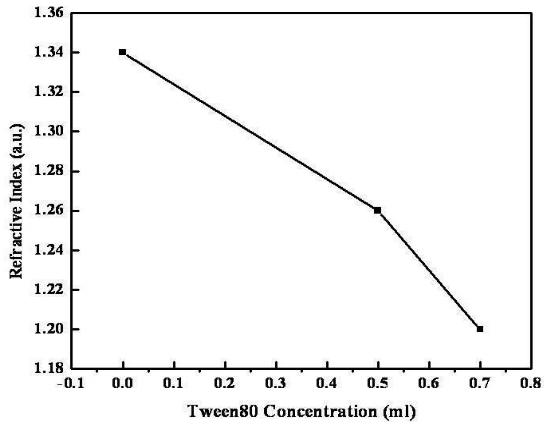

Fig. 3 – Effect of Tween 80 concentration on refractive index

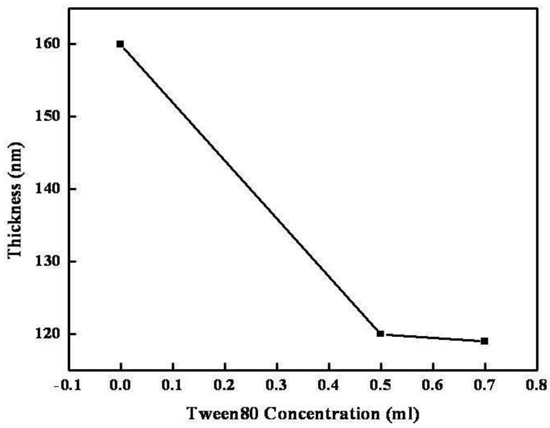

Fig. 4 – Effect of Tween 80 concentration variation on thickness

From the measured refractive index, the films density (ρ) and percentage of porosity (Π) has been calculated by using equation 1 and 2 respectively [9].

$$\rho = n - 1/0.202, \tag{1}$$

$$\Pi = 1 - \rho/\rho_s \tag{2}$$

Where, ρ_s is the density of a thermally grown conventional SiO_2 thin film (2.27 gm/cm^3).

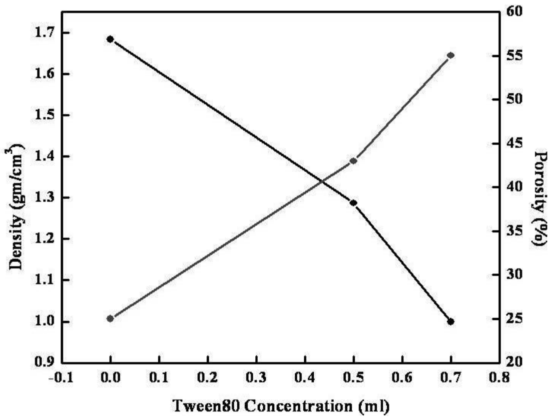

Fig. 5 – Effect of Tween80 concentration variation on Porosity and density of low-k films

Fig. 5 shows the calculated percentage of porosity and density of low-k films as a function of Tween80 concentration in precursor solution. From Fig. 4 it is observed that the film deposited without Tween80 (i.e. 0 ml of Tween80) show the density of 2.27 cm/gm^3, while after addition of Tween80 the density of films decrease with increase in Tween80 concentration and it lowered to 0.99 gm/cm^3 at 0.7 ml of Tween80 concentration. The decrease in density of the films with increase in Tween80 concentration due to the removal of – OH groups from Si-OH and decomposition of porogen into small fragment during the thermal curing and finally this fragment diffuse through surrounding matrix leaving behind the pores in the films [10, 11]. Simultaneously, percentage of films porosity observed to be increasing from 3 % to 55 % with increase in Tween80 concentration.

The dielectric constant of the films as a function of Tween80 concentration is shown in Fig. 6. Dielectric constant of the films was determined from refractive index value by using equation 3.

$$k = 1 + 6.33(n - 1) \qquad (3)$$

From Fig. 6 it is observed that the dielectric constant decreases with increase in concentration of Tween80. The films prepared without Tween80 show the higher dielectric constant, and it found to be 3.15. This higher dielectric constant of the film may be due to the presence of the higher polarized hydroxyl group (-OH) in the film matrix as depicted from FT-IR spectra peak observed at 3400 cm^{-1}.

However after the addition of Tween80 in the precursor solution it is observed that, the dielectric constant of the films decreases with increase in Tween80 concentration and the lower dielectric constant is found to be of 2.26 at 0.7 ml of Tween80 concentration. This decrease in dielectric constant of the film may due to increase in porosity percentage imply the less polarizibiity sites in the SiO_2 film network due to decrease in films density [12, 13].

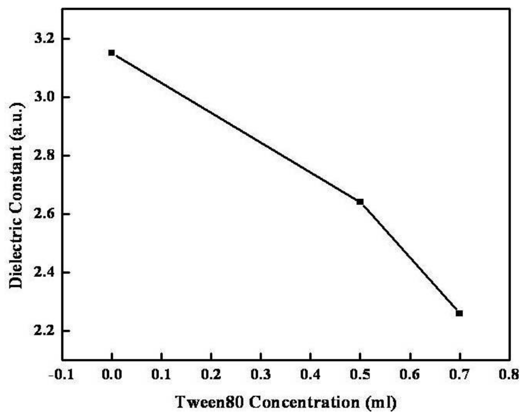

Fig. 5 – Effect of Tween80 concentration variation on dielectric constant

4. CONCLUSION

Porous low dielectric constant SiO_2 thin films were deposited by using sol-gel process with the addition of Tween80 as a pore generator. The porosity, density and dielectric constant properties of porous low-k films as a function of porogen Tween80 concentration were investigated. The result shows the porogen Tween80 has great impact on films properties. With increasing in Tween80 concentration it's observed that the percentage of porosity has been observed to be increased, while dielectric constant and refractive index have been found to be decreases. The percentage of porosity at 0.7 ml of Tween80 concentration found to be of 55 % which results in attaining the films lowest dielectric constant of 2.26. Such resultant porous low-k thin films can be suitable for interlayer dielectric in ULSI circuits.

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