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DEPOSITION AND SURFACE MODIFICATION OF LOW-K THIN FILMS FOR ILD APPLICATION IN ULSI CIRCUITS

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The low-k thin films have been deposited successfully by sol gel technique using tetraethylorthosilicate (TEOS) precursor and the surface of deposited thin films have been modified by wet chemical treatment using trimethylcholorsilane (TMCS) and hexane solution with 15 % *volume ratio to remove the hydroxyl groups from the surface of deposited low-k thin films. The characterization of the as deposited and surface modified low-k thin films has been carried out by Ellipsometer, Fourier transform infrared (FTIR) spectrometer, and contact angle meter. For the determination of the dielectric constant of the deposited thin film the metal – insulator-semiconductor (MIS) structure was formed by depositing the Aluminium (Al) metal on the low-k thin film. Further the capacitance-voltage curve of the MIS structure has been obtained at* 1 *MHz frequency. The dielectric constant of the as deposited thin film is found to be* 2.15. *The lowering of O-H peaks and appearance of* CH_3 *peaks in FTIR spectra confirms the surface modification of* SiO_2 *films. The contact angle of the deposited thin film is changed from* 83.3° *to* 104° *after surface modification that validates the transformation of thin film surface from hydrophilic to hydrophobic after the surface modification treatment.*

Keywords: *LOW-K, TMCS, SURFACE MODIFICATION, HYDROPHOBIC, CV, CONTACT ANGLE.*

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1. INTRODUCTION

The introduction of the advanced fabrication processes causes the new revolution in the technology that helps in scaling the device size towards the nanoregime. The scaling in the device size towards the nanoregime results in high speed and reliable devices. But this miniaturization of devices in ultra large scale (ULSI) integrated circuits with conventional materials limits their speed due to the properties of materials like resistivity, mechanical strength etc. Thus, an Al metal in ULSI is replaced with Copper (Cu) for backend of line (BEOL) application due to the low resistivity of Cu interconnect which minimizes the resistance (R) in RC (C-capacitance) delay of interconnect. The reduction in interconnect capacitance has also got significant attention alongwith lowering in interconnect resistance in order to lower the RC delay. To lower the interconnect capacitance it is essential to minimize the dielectric constant of insulator between interconnects used as interlayer dielectric (ILD) in ULSI circuits. As per the recent ITRS the dielectric constant for the 32 nm technology should be less than 2.5. The dielectric constant can be reduced by lowering the density of the materials (by introducing the porosity) or by introducing lower polarized bonds. But by introducing the lower polarized bonds it is difficult to achieve the ultra low-k value of thin films. Thus, the another option to lower the density of the materials is to incorporate porosity in the film [1-3].

Two important techniques being used to deposit the low-k thin film are the PECVD and the sol gel out of which, the sol-gel is the best method because of its ability to introduce the high porosity with controlled pore size [4-5]. The sol-gel deposited low-k thin films contains the large number of hydrophilic groups (–OH bonds) on its surface that may detoriate the dielectric constant of the film. Such hydrophilic groups can not be fully eliminated during the annealing processes. Thus to prevent change in dielectric constant of the porous thin film the surface should be modified from hydrophilic to hydrophobic [6].

From the literature survey it is observed that wet chemical treatment, Plasma treatment and UV treatment are mostly used to enhance the properties of the porous low-k thin film [7-10].

In present work, the wet chemical treatment method has been used for the surface modification of low-k thin films. The surface modifications were carried out by using TMCS / Hexane as a modifying agent. During the surface modification processes hydroxyl groups present on surface of films gets replaced by trimethylsilyl (TMS) groups from the TMCS preventing silica condensation reactions during drying. These low-k thin film have been characterized by Ellipsometer, FTIR and contact angle measurement setup and Capacitance-voltage analyzer before and after surface modification process.

The second section of this paper explains the experimental part, in the third section the results are discussed and fourth section concludes the paper.

2. EXPERIMENTAL DETAILS

The precursor solution was prepared by mixing TEOS with ethanol, deionised water and acid catalyst at room temperature for deposition of porous SiO_2 low-k thin films with a molar ratio of 1:4:2:0.1 of TEOS: Ethanol: H_2O: HF respectively. The mixture solution was stirred for 1 hour at ambient temperature. The prepared sol was then dispensed on p-type Si ⟨100⟩ substrate before the gel point is reached and spun by spin coater. The spin coated, thin films were then heated at 100° C at room temperature. Then, the films were modified by chemical treatment method using the TMCS ($(CH)_3$ SiCl) as a sylinating agent with 15 % in hexane for 5 hours. The surface modified films were dried on hot plate at 80 °C for 30 minute and then finally annealed in a closed furnace at 300 °C for an hour. The films were characterized before and after the surface modification using by Ellipsometer (Philips SD 1000) for thickness measurement, FTIR (Nicolet 380) for chemical bonding analysis and contact angle meter (GBX make) for confirmation of hydrophobic surface. The dielectric constant of deposited film was determined by forming MIS structure using C-V analyzer.

3. RESULTS AND DISCUSSION

The as-deposited and surface modified SiO_2 thin films have been characterized by Ellipsometer having He-Ne laser of wavelength 632.8 nm. The average thickness of all the films is about 200 nm. The FTIR characterization of deposited and surface modified thin films have been carried out in the range of 400 - 4000 cm^{-1} with resolution of 4 cm^{-1} and scan rate of 128 to obtain information about surface bonding characteristics and evidence of surface modification. The FTIR absorption spectra of as deposited and surface modified films are presented in figure 1. The peaks at 441 and 805 cm^{-1} are identified as the rocking and bending vibration modes of Si-O-Si respectively and the peak at 1077.9 cm^{-1} corresponds to the Si-O-Si stretching vibration, which confirms the formation of Si-O-Si network in the films. The broad peak at 3416.9 cm^{-1} is due to O-H stretching vibration appeared in as deposited film just before the surface modification illustrates the hydrophilic nature of the film. After the surface modification of the deposited film using 15 % of TMCS solution in hexane the peak at 3416.9 cm^{-1} due to hydroxyl group gets diminished in FTIR spectra. The appearance of carbon peak in FTIR spectra of the surface modified film is due to replacement of -OH group by -CH group from TMCS [11]. The peak at 2960 and 2921 cm^{-1} corresponds to the asymmetric and symmetric stretching of CH_3 group respectively, while the peak at 2855 cm^{-1} represents the symmetric stretching of C-H in CH_2 group [12]. The intense peak at 1259 cm^{-1} is attributed to the Si-C bond [6]. This incorporation of carbon group into the modified film indicates the formation of hydrophobic nature of the film.

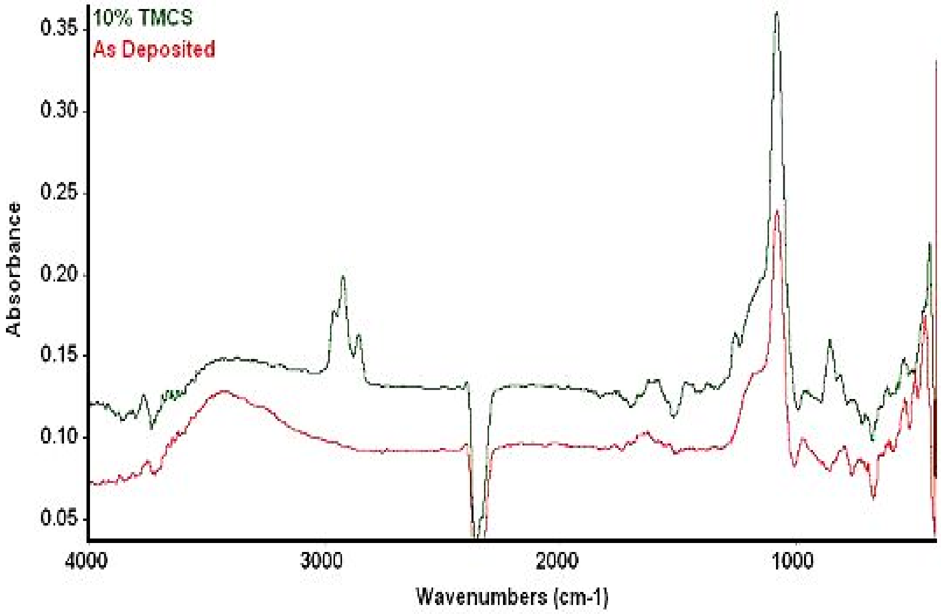

Fig. 1 *– FTIR spectra of as deposited and surface modified thin film*

The dielectric constant of the as deposited thin film has been carried out by forming MIS capacitor by depositing Al metal on deposited thin film as a gate electrode and on lower side of the Si substrate for formation of second contact. The top contact area of the metal film was 2.48×10^{-2} cm^2. The capacitance – voltage characteristics has been carried out at 1 MHz frequency at IIT Mumbai. The dielectric constant of the deposited film is determined from the equation 1 [13] using the accumulation capacitance of C-V curve as shown in Figure 2. The *k* value of the film before surface modification is determined to be 2.15.

$$k = \frac{C_{ap} \cdot t}{\varepsilon_o \cdot A}, \tag{1}$$

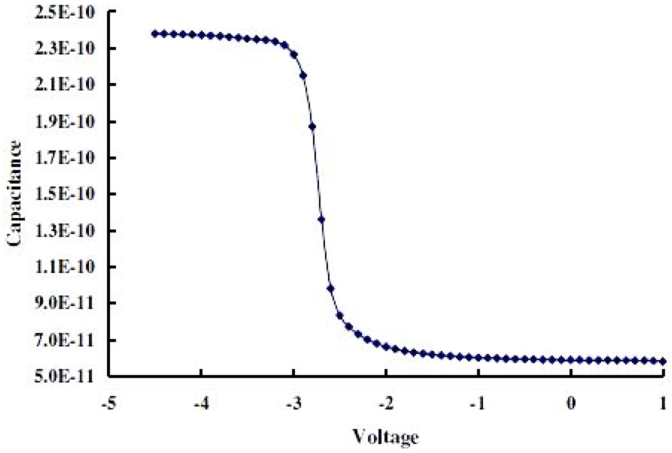

Fig. 2 *– Capacitance Voltage curve at* 1 *MHz frequency*

The hydrophobic nature of the surface modified low-k thin film has been determined by the contact angle measurement of the water droplet on the surface of the low-k thin film using contact angle meter. In this process, the drop of water is added on top surface of the film and the water droplet is photographed. The contact angle has been calculated directly from software by using young's equation. The contact angle of as deposited and surface modified film is shown in Figure 3a and b respectively. The contact angle of as deposited and surface modified film is observed to be 83.3° and 104° respectively. From the measured contact angle value it confirms that the hydrophilic surface of the film has became hydrophobic after wet chemical treatment, as the contact angle after modification is more than 90° [14].

a b

Fig. 3 *– Contact angle figure (a) hydrophilic surface ($\theta = 83.3°$), (b) hydrophobic surface ($\theta = 104°$)*

4. CONCLUSIONS

The SiO_2 low-k thin films of 200 nm thickness have been deposited successfully by sol gel spin coating technique using tetraethylorthosilicate (TEOS) as a source of Si. The hydrophilic nature of the film has been improved by silylation method. The silylation of the low-k thin film have been carried out by using TMCS/Hexane as surface modifying agent. The FTIR peaks of the surface modified low-k thin film appearing at 852 cm^{-1} and 2959 cm^{-1} confirms the replacement of the hydrophilic groups. The contact angle of 104° confirms the surface modification of the low-k thin film from hydrophilic to hydrophobic by TMCS silylation. Such hydrophobic thin films with low dielectric constant of 2.15 are suitable for ILD applications in ULSI circuits.

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