OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 4, No. 9, September 2010, p. 1304 - 1306

Surface modification of porous SiO_2 thin film by chemical treatment

B. N. JOSHI, Y. S. MHAISAGAR, A. M. MAHAJAN*
Department of Electronics, North Maharashtra University, Jalgaon – 425001 (M.S.), India

Surface modification of porous SiO_2 thin film deposited by sol-gel technique has been examined in detail. The surface modification of porous films using hexamethyldisilazine (HMDS) has been carried out successfully to remove silanol (Si-OH) groups and thereby achieved a lower dielectric constant (k) of the deposited thin films. Surface profile, thickness and refractive index of low-k thin films have been analyzed through Ellipsometer. The deposited films are observed to be having low-k and good uniformity before and after modification. The chemical bondings of porous SiO_2 films have been realized by using Fourier transform infrared spectroscopy (FTIR). The increase of carbon peak in film with increase in HMDS proportion reveals that, the most of the hydroxyl (–OH) groups get converted to methyl groups which makes hydrophobic surface of the film.

(Received July 30, 2010; accepted September 15, 2010)

Keywords: Low- k, HMDS, Surface modification

1. Introduction

Meso and micro porous materials are in great demand because of its potential applications as low dielectric thin films, chemical and biological sensor membranes, catalyst supports and gas separation membranes [1]. Particularly, low-k interlayer dielectric (ILD) materials are in great demand in Ultra Large Scale Integrated Circuits (ULSI) as these materials minimizes the resistance – capacitance (RC) delay, crosstalk and power consumption. In last few years many low-k materials including inorganic, organic, hybrid and porous [2-4] have been developed. The inorganic and hybrid materials have their limitations to lower the dielectric constant. However, the organic materials are having dielectric constant 2.6-2.8 but their thermal instability, softness, low resistance to plasma processes make them incompatible with traditional technological processes [5]. Therefore, the porous materials with ultra low dielectric constant are attracting more attention for ILD applications [6]. Based on the literature study it has been observed that, the pores on the surface of film remain open and interconnected thus, the number of gases, chemicals, and water easily penetrate in porous structure during different processes like etching, resist removal, Chemical mechanical polishing (CMP) etc. which significantly affects to the properties of the material [7]. For example, unreacted Si-OH groups present on the porous surface of film easily adsorb water during various process of IC fabrication, and due to high polarizability of the water that may drastically increases the dielectric constant of the film. Thus, it is of great concern to achieve stabilized electrical properties of the film to increase it's reliability for integration in IC.

For the purpose of film's stability, it is important to modify the surface of thin films, a better solution to this is to prepare hydrophobic surface of the film and seal the pores present on the surface. Here, we have surveyed different techniques for surface modification. Some of the techniques are plasma treatments, UV treatments and chemical treatment. The chemical treatment or liquid environment treatment is cost effective and simple in which the deposited film is kept in the trimethylchlorosilane (TMCS) or HMDS liquid, such surface treatment is also referred as 'Silylation' [8]. TMCS and HMDS both chemicals replaces surface silanol groups with less polar methyl groups. However, TMCS contains chlorine produces hydrochloric acid during processing that may corrode metal used for interconnects whereas HMDS doesn't contain any chlorine [9]. In present work, the porous films were deposited and modified further using the hexane and HMDS solution. Ellipsometer and FTIR characterizations have been employed for refractive index determination and chemical analysis respectively. The experimental work carried out to study surface modification is described in second part of paper. Third part of paper has results and discussion, the fourth part concludes the paper.

2. Experimental

The porous SiO_2 thin films have been deposited on precleaned p type Si (100) substrates using the Tetraethylorthosilicate (TEOS) as source of Silicon. The TEOS to water ratio was kept at 1:2, ethanol used as solvent and HF as catalyst. Further, the deposited films were baked in an oven at 200 ^{0}C and then the films were chemically treated by soaking them for 1 hour in the solution of hexane, hexane and HMDS with different proportion ratios. The proportion of HMDS was varied from 0, 20, and 40 % with hexane. The samples named as a, b, c, d for as deposited, 0% HMDS, 20 %HMDS, and 40 %HMDS respectively. In surface modification the surface silanol groups get replaced by methyl groups of HMDS as shown in reaction-

$$2\ Si_s{-}OH + (CH_3)_3\text{-}Si\text{-}NH\text{-}Si\text{-}(CH_3)_3 \rightarrow 2\ Si_s\text{-}O\text{-}Si\text{-}(CH_3)_3 + NH_3$$

This step is necessary because porous films contain a large amount of silanol groups at the pore surfaces, they will readily absorb moisture from atmosphere, which increases dielectric constant and causes hole poisoning and other integration problems. Further, Ellipsometer and FTIR characterizations were used to study different properties of the deposited thin films.

3. Results and discussion

The deposited films were characterized by the Nicolet 380 FTIR spectrometer in range 400-4000 cm^{-1} with 4 cm^{-1} resolution & 128 scans for both sample and background (Reference) and the spectra in absorbance mode is as shown in Fig. 1. The Fig. 1(a) shows the as deposited film spectrum, while in Fig. 1(b) the spectrum of 0%HMDS i.e. film is soaked in hexane only. The figure 1(c) and 1(d) are spectra of films soaked in 20% and 40 % HMDS/ Hexane solution. The most intense absorption peak of Si-O-Si bond at 1075-1082 cm^{-1} occurs due to asymmetric stretching which confirms the formation of SiO_2 network. It is clearly revealed from spectra that the as HMDS% increases the peak at 3400 cm^{-1} and 960 cm^{-1} decreases, due to higher concentration of –OH group. Further, it has been observed that the Si-C and C-H peak at 850 cm^{-1} and 2930 cm^{-1} [10] respectively appears in samples c and d and this confirms that, the increase in HMDS converts most of –OH bonds to methyl groups and makes the film surface hydrophobic [11].

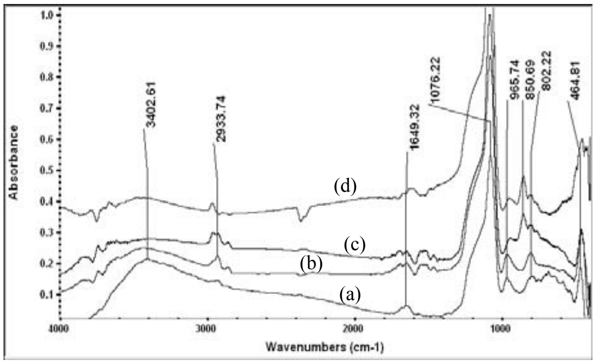


Fig. 1. FTIR spectra of porous SiO_2 films (a) Without modified (b) modified in hexane at 0%HMDS (c) modified in hexane at 20%HMDS (d) modified in hexane at 40%HMDS.

The Fig. 2 represents the FTIR spectra of sample d wherein, spectrum (a) was taken just after modification and (b) after 5 days of modification. Thus no moisture absorption occurs even after 5 days it reveals that, the hydrophobic surface remains stable in atmospheric conditions. From Fig. 3 it is observed that, the Si-O-Si stretching wavenumber increases with the increase in HMDS proportion from 1076 cm^{-1} to 1083 cm^{-1}. This increase in stretching wavenumber of deposited films is due to the incorporation of carbon. The carbon combines with silicon and oxygen to make a Si-O-C chain. This bonding of carbon with oxygen reduces the dielectric constant of the spin on deposited thin films.

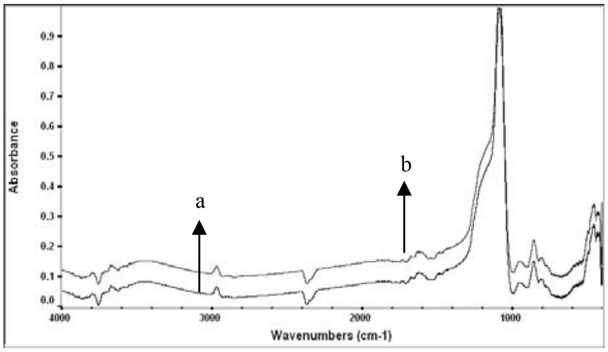


Fig. 2. FTIR spectra of porous SiO_2 films modified in hexane at 40%HMDS Just modified (b) after 5 days of modification.

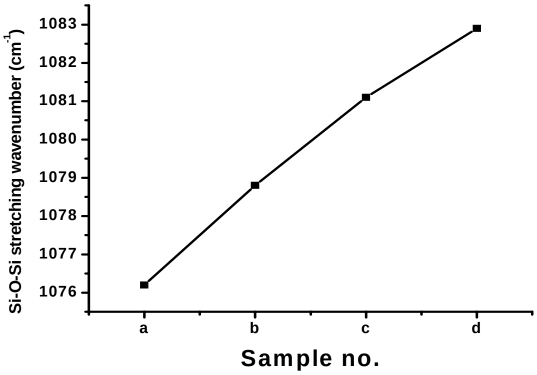


Fig. 3. Si-O-Si stretching wavenumber with as deposited and various surface modified.

The surface modification is much needed for the protection of the thin films from the environmental moisture and other impurities during different layer deposition process on the low-k deposited thin films. Therefore, we have carried out the surface modification of porous low dielectric films to achieve hydrophobic surface. Here, we have used HMDS with different proportion to realize the surface modification variation. It is observed that, the surface modification affects to the peak area of Si-OH and C-H bond where the Silanol groups get replaced by C-H groups from HMDS with increase in HMDS proportion from 0 to 40% as depicted in Fig. 4.

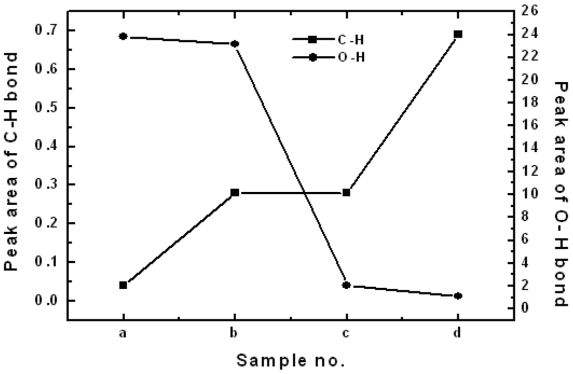
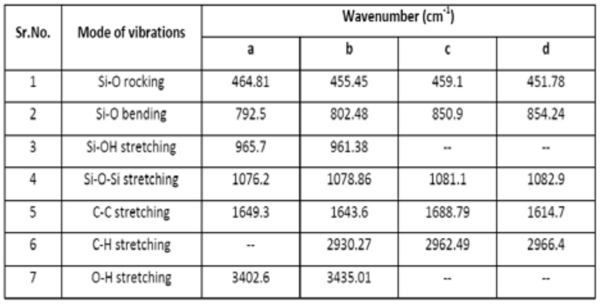


Fig. 4. Peak area of C-H and O-H bonds with as deposited and various surface modified films.

The Table 1 shows the different chemical bondings present in film with its corresponding wavenumbers. The presence of C-H bond in sample c and d shows surface modification of films. The as deposited and surface modified films were also characterized by ellipsometer (Philips SD-1000). From Table 2 it is clear that the refractive index, thickness and dielectric constant of surface modified film are observed to be increasing slightly that may be due to the sealing of pores with methyl group but, the dielectric constant is yet low compare to that of conventional SiO_2. The dielectric constant is determined from the refractive index through the formula given by Jung-Kyun Hong et al [12].

Table 1. Chemical bonds present in as deposited film and films soaked in HMDS with variation 0% to 40%.



Sr.No.	Mode of vibrations	Wavenumber (cm^{-1})			
		a	b	c	d
1	Si-O rocking	464.81	455.45	459.1	451.78
2	Si-O bending	792.5	802.48	850.9	854.24
3	Si-OH stretching	965.7	961.38	--	--
4	Si-O-Si stretching	1076.2	1078.86	1081.1	1082.9
5	C-C stretching	1649.3	1643.6	1688.79	1614.7
6	C-H stretching	--	2930.27	2962.49	2966.4
7	O-H stretching	3402.6	3435.01	--	--

Table 2. Ellipsometric characterization of as deposited and surface modified thin film.

Sr. No	Characteristics of porous SiO_2 thin films	Sample a	Sample d
1	Refractive index	1.17	1.28
2	Density (gm/cc)	0.841	1.386
3	Dielectric constant	2.07	2.77
4	Thickness (A^o)	2534	3548

4. Conclusions

The surface modification of deposited porous thin films has been carried out successfully. The increase of C-H group with increase in HMDS concentration confirms the surface modification of deposited porous film. The dielectric constant of surface modified film is 2.77 which is very much less than that of conventional SiO_2. Such surface modified porous films are suitable for interlayer applications in ULSI circuits.

Acknowledgement

Authors would like to acknowledge the Council of Scientific and Industrial Research, New Delhi for providing financial assistance for this work (vide no. 03(1127)/08/EmR-II).

References

[1] Moonhor Ree, Jinhwan Yoon, Kyuyoung Heo, J. Mater. Chem, **16**, 685 (2006).
[2] Michael Morgen, E. Todd Ryan, Jie-Hua Zhao, Chuan Hu, Taiheui Cho, Paul S. Ho, Annu. Rev. Mater. Sci. **30**, 645 (2000).
[3] Hisao Nagai, Masaru Hori, Toshio Goto, Toshiaki Fuji, Mineo Hiramatsu, Jpn. J. Appl. Phys. **42**, 2775 (2003).
[4] B. N. Joshi, A. M. Mahajan, Optoelectron. Adv. Mater.– Rapid Comm. **1**(12), 659 (2007).
[5] K. Maex, M. R. Baklanov, D. Shamiryan, F. Iacopi, S. H. Brongersma, Z. S. Yanovitskaya, J. Appl. Phys **93**(11), 8793 (2003).
[6] Bhavana N. Joshi, A. M. Mahajan, J. Optoelectron. Adv. Mater. **10**(2), 422 (2008).
[7] S. Altshuler**,** Y. Chakk, A. Rozenblat, A. Cohen, Microelectronic Engineering, **80**, 42 (2005).
[8] S. V. Nitta, V. Pisupatti, A. Jain, P. C. Wayner Jr., W. N. Gill, J. L. Plawsky, J. Vac. Sci. Technol. B **17** (1), 205 (1999).
[9] A. Kumar, H. Bakhru, J. B. Fortin, G. R. Yang, T. M. Lu, C. Jin, W. W. Lee Thin Solid Films, **396**, 5(2001).
[10] Pradip B. Sarawade, Jong-Kil Kim, Ho-Kun Kim, Hee-Taek Kim, Applied Surface Science **254**, 574 (2007).
[11] Suzhu Yu, Terence K. S. Wong, J. Sol-Gel Sci. and Tech., **29**, 57 (2004).
[12] Jung-Kyun Hong, Hee-Sun Yang, Moon-Ho Jo, Hyung-Ho Park, Se-Young Choi, Thin Solid Films **495**, 308 (1997).

---

[*] Corresponding author: ashokmm7719@rediffmail.com