

Surface texture modification of spin-coated SiO₂ xerogel thin films by TMCS silylation

YOGESH S MHAISAGAR, BHAVANA N JOSHI and A M MAHAJAN*

Department of Electronics, North Maharashtra University, Jalgaon 425 001, India

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Abstract. The SiO₂ xerogel thin films were deposited successfully by sol–gel technique via the acid-catalyzed hydrolysis and condensation of tetraethylorthosilicate (TEOS) with ethanol as a solvent. Further, the deposited thin films were treated wet chemically by trimethylchlorosilane (TMCS) and hexane solution with 10% and 15% volume ratio to remove the hydroxyl groups from the surface of deposited SiO₂ thin films. These as deposited and surface-modified films were characterized by ellipsometer, Fourier transform infrared (FTIR) spectrometer and contact angle meter. The presence of 2900 and 850 cm⁻¹ peaks of CH₃ vibrations in FTIR spectra of surface-modified films confirms the hydrophobisation of SiO₂ surface. The maximum contact angle of 108.7° was observed for the surface-modified film at 10% TMCS.

Keywords. Low-k; TMCS; surface modification; hydrophobic; contact angle.

1. Introduction

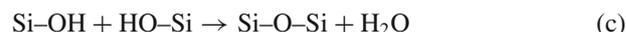
The porous nanostructured materials with high porosity, large surface area and very low bulk density are the potential candidates that are used in wide application areas such as heterogeneous catalysis, separation process, guest–host chemistry, adsorbents host for quantum structures, separation of large biological molecules, environmental pollution control etc (Naik and Ghosh 2009; Gurav *et al* 2010). Porous materials are classified into three types according to their size. The mesoporous materials have pores with diameter between 2 and 50 nm. Microporous materials have pore diameter of less than 2 nm and macroporous materials have pore diameter of greater than 50 nm. Sol–gel process is the best method used for the synthesis of porous silica because of its ability to introduce a high degree of porosity in the films. From the literature survey, it is observed that various precursors were used to deposit silica film by sol–gel such as methylsilsesquioxane (MSQ), methyltriethoxysilane (MTES), tetraethylorthosilicate (TEOS), tetramethylorthosilicate (TMOS) (Liu *et al* 2008; Naik and Ghosh 2009). The sol–gel process involves two specific reactions termed as hydrolysis and condensation that occur simultaneously in the formation of silica films. In the first step, precursor is first hydrolyzed by reacting with water (as shown in reaction (a)) in the presence of mutual solvent such as ethanol and the acid catalyst which is used to enhance the hydrolysis rate. In the condensation reaction (reactions (b) and (c)), water and alcohol product formed in the hydrolysis reaction

get polymerized and form siloxane bonds. The microstructure of the silica film can be easily modified by controlling the sol–gel process parameters.

Hydrolysis reaction:



Condensation reaction:



(Brinker and Scherrer 1990).

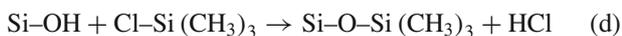
The synthesized porous silica films usually are hydrophilic nature which can absorb moisture under the atmospheric condition due to the presence of the polar OH radical on the surface that can easily absorb the hydrogen ions from the ambience and forms H₂O (Zhou *et al* 2008). The condensation of these water molecules into the pores of the material leads to capillary tensions, which destroy the structure of silica (Naik and Ghosh 2009). Therefore, there is need to change the silica surface from hydrophilic to hydrophobic to prevent the collapse of silica network by appropriate surface chemical modification method. This is done by replacing the hydrogen of the –OH radical of silica matrix with some organic groups via the nonhydrolyzable Si–C covalent bond that functions as network modifier. In general two methods are used for the surface modification of the gels. (i) Co-precursor method: in this method, the surface modifying agent is added to the silica sol itself before gelation. (ii) Surface derivatization method: in this method, the gel is obtained first and then kept in a bath containing a mixture of solvent and surface modifying agent. Different hydrophobic

* Author for correspondence (ammahajan@nmu.ac.in; ammahajan.ele@rediffmail.com)

agents can be used for this purpose such as hexamethyldisilazine (HMDS), trimethylchlorosilane (TMCS), and hexamethyldisiloxane (HMDSO) or combinations of HMDSO and HMDS or HMDS and TMCS or their mixture with hexane/toluene etc (Aravind *et al* 2010).

On hydrophobic surface, the water remains in droplet form, implying that cohesive forces associated with bulk water are greater than the forces associated with the interaction of water with the surface. The nature of the solid surface interacting with the liquid is measured by the contact angle of a liquid droplet on a solid substrate. If the contact angle of water is less than 30° , the surface is said to be hydrophilic. Surfaces with contact angles greater than 90° are designated as hydrophobic. The contact angle exceeding 150° are associated with superhydrophobicity and called as lotus effect.

In present work, TMCS with hexane was used for silylation process. The silylation process replaces surface hydroxyl groups with trimethylsilyl (TMS) groups from the TMCS preventing silica condensation reactions during drying. The structural changes on the surface of the SiO_2 thin film reacted with TMCS are shown as follows (Aravind *et al* 2010):



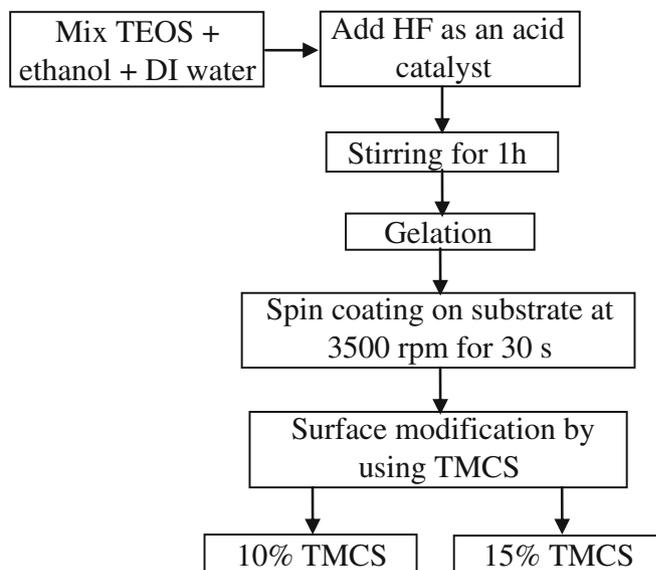
These as-deposited and surface-modified films were then characterized by ellipsometry, FTIR and contact angle measurement setup. The second section of this paper explains the experimental part, third section contains the results and discussion part and fourth section concludes the paper.

2. Experimental

The precursor solution was prepared by mixing TEOS with ethanol, de-ionized (DI) water and acid catalyst at room temperature for deposition of SiO_2 xerogel thin films. The composition of the sol was TEOS : ethanol : H_2O : HF in a 1 : 4 : 2 : 0.1 molar ratios. The mixture solutions were stirred for 1 h at ambient temperature. This sol was then deposited by spin on method on p-type $\text{Si} < 100 >$ substrates.

After the spin coating, the deposited thin films were heated at 100°C . Then, the films were modified by chemical treatment method using TMCS ($(\text{CH}_3)_3\text{SiCl}$) as a modifying agent in different volume concentrations i.e. 10% and 15% with hexane for 5 h. The experimental steps are presented in flow chart 1.

The surface-modified films were dried on a hot plate at 80°C for 30 min and then finally annealed in a closed furnace at 300°C for an hour. During the surface modification the silica surface becomes hydrophobic by replacing H from the surface Si-OH groups by hydrolytically stable $-\text{Si}-(\text{CH}_3)_3$ groups present in TMCS, according to the chemical reaction (d) (Lijiu and Shanyu 2009; Rao and Rao 2010). The surface modified xerogel SiO_2 thin films were further characterized by ellipsometer (Philips SD 1000) for thickness measurement, FTIR (Nicolet 380) for chemical bonding analysis and



Flow chart 1. Experimental steps.

contact angle meter (GBX) for confirmation of hydrophobic surface.

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 was about $200 \text{ nm} \pm 5 \text{ nm}$. The FTIR characterization of deposited and surface-modified thin films were carried out in the range of $400\text{--}4000 \text{ cm}^{-1}$ 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 444 and 817 cm^{-1} are identified as the rocking and bending vibration modes of Si-O-Si, respectively and the peak at 1078 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 3400 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. The development of intense peak at 1259 cm^{-1} , corresponds to the symmetric deformation vibration of C-H bonds represent the attachment of methyl group with Si (Orozco-Teran *et al* 2005; Aksenov *et al* 2009). Peaks appearing at 2960 and 2921 cm^{-1} are due 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 (Aksenov *et al* 2009). The table 1 shows the different chemical bondings present in the as-deposited and surface-modified films with their corresponding wavenumbers.

The Si-OH peak at 969 cm^{-1} appeared in as-deposited film due to the incomplete hydrolysis, which further gets

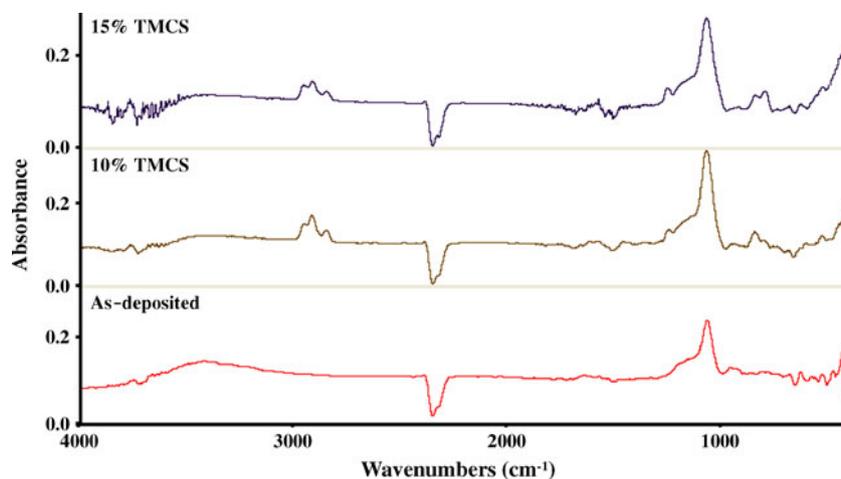


Figure 1. FTIR absorption spectra of as-deposited and surface-modified (10% and 15% TMCS) SiO₂ thin films.

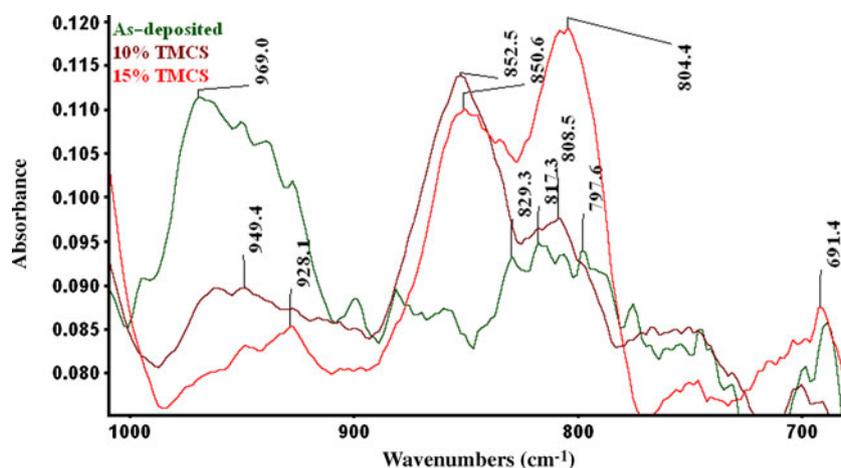


Figure 2. FTIR spectra showing removal of OH and addition of Si-C in the range 650–1000 cm⁻¹.

Table 1. Chemical bonds present in as-deposited and surface-modified films in 10% and 15% of TMCS.

Mode of vibrations	Wavenumbers (cm ⁻¹)		
	As-deposited	10% TMCS	15% TMCS
Si-OH stretching vibration	3423–3400	–	–
C-H asymmetric stretching, CH ₃	–	2959	2960
C-H symmetric stretching, CH ₃	–	2922.8	2921
C-H symmetric stretching, CH ₂	–	2855.5	2855
C-H asymmetric bending, CH ₃	–	1466	1454
C-H symmetric bending, CH ₃	–	1374	1364
Si-CH ₃ symmetric deformation	–	1254	1260
Si-O-Si symmetric stretching	1078	1079.3	1080
Si-OH stretching vibration	970	–	–
Si-C rocking vibration, CH ₃	–	852	850
Si-O-Si bending vibration	817	808	804
Si-O-Si rocking vibration	444	445	428

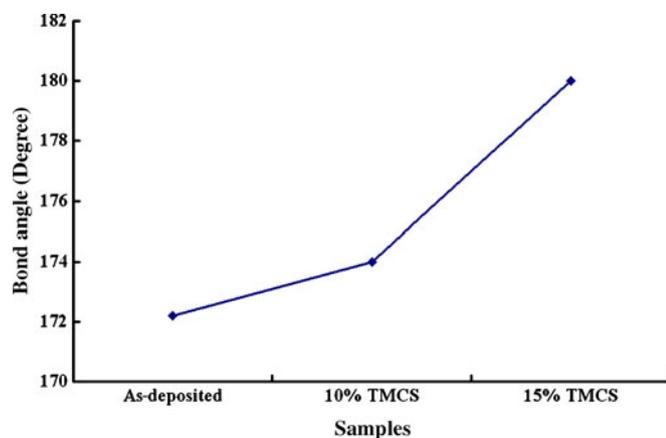


Figure 3. Bond angle of the Si–O–Si bond after surface modification.

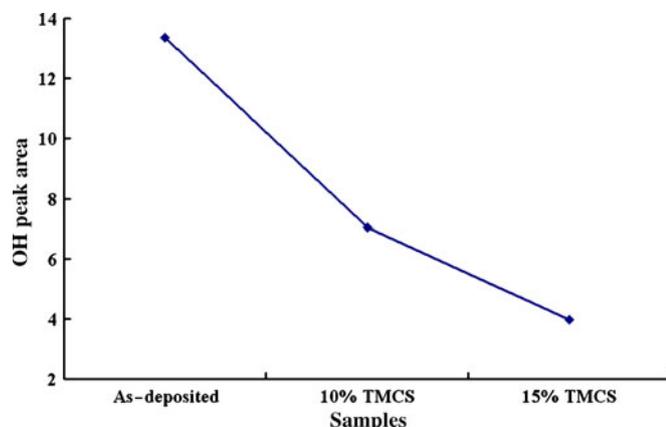


Figure 4. Peak area of –OH bond for different surface modifications.

diminished after the surface modification, giving rise to the new peak at 850 cm^{-1} corresponding to the rocking vibration of the Si–C bonds (Zhou *et al* 2008; Joshi *et al* 2010). Figure 2 shows the removal of –OH group and increase in Si–C bonds observed in the range $650\text{--}1000\text{ cm}^{-1}$. This incorporation of carbon group into the modified film indicates the formation of hydrophobic nature of the film.

The Si–O–Si bond angle was determined according to the central force model using Si–O–Si stretching wavenumber (Park *et al* 1996). Figure 3 shows that the Si–O–Si bond angle increases with surface modification and its value is greater than that of relaxed SiO_2 (bond angle = 144°). The bond angle depends on Si–O–Si stretching wavenumber which increases due to the linking of carbon with Si–O bond (Joshi *et al* 2010). Figure 4 shows that the OH peak area decreases from 13.5 to 3.97. This reduction in the –OH peak area with increase in TMCS is due to replacement of surface OH by CH_3 from TMCS. A detailed analysis of the CH_3 and Si–C peak areas were determined by using TQ analyst available with FTIR as shown in figure 5. The effect of the

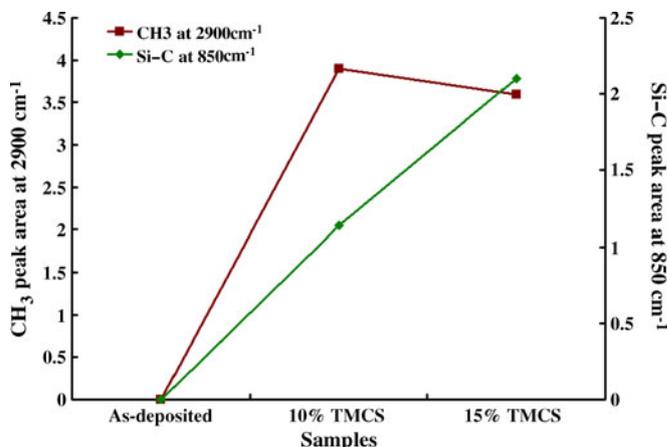


Figure 5. Peak area of CH_3 and Si–C group present in as-deposited and surface-modified film.

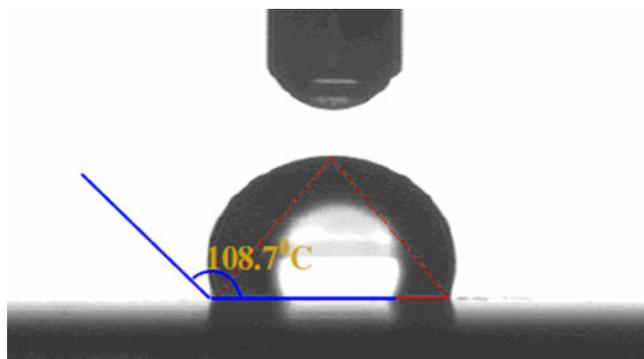


Figure 6. Water droplet on surface-modified thin film for contact angle measurement.

surface treatment with different TMCS concentrations show that after the surface modification the hydroxyl group ($3400\text{--}3600\text{ cm}^{-1}$) decreases. After the TMCS surface treatment, most of the hydroxyl group gets replaced by $-\text{CH}_3$ which articulates the change of hydrophilic texture of the film to the hydrophobic surface.

The hydrophobicity of the film after the TMCS surface treatment was determined by measuring the contact angles (θ) of the water droplet placed on the surface of the film. In this process, the drop of water is added on top surface of the film and the water droplet was photographed. The contact angle was calculated directly from the software by using Young's equation. The contact angle of as-deposited film was obtained to be 83.3° ($\theta < 90^\circ$) that shows the surface of the film is hydrophilic due to the presence of silanol (Si–OH) group as observed in FTIR spectrum. After the surface modification with 10% TMCS, the contact angle of the films increases to 108.7° as shown in figure 6. This confirms the modification of the hydrophilic surface of the film to the hydrophobic after the surface modification, as the contact angle $\theta > 90^\circ$ (Gurav *et al* 2009). The contact angle details of surface-modified films in 10% and 15% TMCS at different annealing temperature is shown in table 2.

Table 2. Contact angle at different processes.

Contact angle of as-deposited thin film	Surface modification at 10% TMCS			Surface modification at 15% TMCS		
	Without annealing	Annealed at 200°C	Annealed at 300°C	Without annealing	Annealing at 200°C	Annealed at 300°C
83.3	105.4	108.7	100.6	101.4	100.4	104

4. Conclusions

The SiO₂ thin films of 200 nm thickness were deposited successfully by sol-gel spin coating technique. The hydrophobic SiO₂ xerogels thin films were obtained by surface modification using TMCS/Hexane as surface modifying agent. The FTIR study shows the absorption of -CH₃ bonds on the surface of the film by the peaks appearing at 852 cm⁻¹ and 2959 cm⁻¹. The contact angles of 108.7° and 101.4° confirm the modification of the surface of the film from hydrophilic to hydrophobic by TMCS silylation.

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