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Hydrophobic silica thin films by sol-gel processing and spin coating technique at low temperature

Nurul Huda Abu Bakar, Karim Deraman*, R. Hussin, W. Nurulhuda W. Shamsuri, Faizal Mansor, Zuhairi Ibrahim, Bakar Ismail

Phosphor Materials Research Group, Department of Physics, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor

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ABSTRACT

Hydrophobic silica thin films were prepared by sol-gel processing and self-assembly by chemical vapor reaction with Trimethylchlorosilane (TMCS) at low temperature. The sols were divided into Sol A with ethanol, Polyethylene glycol (PEG) and water (H_2O) while Sol B were contain precursor of silica Tetraethylorthosilicate (TEOS) hydrolyze with ethanol which was stirred for 15 minutes. HCl was added into the mixture and stirred for another 10 minutes. After deposition on 1 x 1 cm corning glass using spin coating technique (two-step timer), the films were heated at 60˚C for 10 minutes and finally annealed at 150°C for 1 hour. The films were characterized by using Rudolph/Auto EL Ellipsometer, Shimadzu Spectrophotometer, Perkin Elmer Fourier Transform Infrared (FTIR) and Atomic Force Microscope (AFM). The results showed that the films thickness and refractive index were in the range of 105.2 to 112.4 nm and 1.35 to 1.38, respectively. The films were transmitted 70-80% of light (in visible range) with various bondings of C-H, Si-O-Si, Si-C and Si-OH. Surface roughness of the films was increased from 30.6 nm (silica thin film) to 140.5 nm (hydrophobic silica thin films) after modification have been done on the films by using TMCS (heated at 40˚C). It was found that the water contact angles increased when time of reaction increased from 109° to 124°.

| self-cleaning | self-assembled | sol-gel |

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1. INTRODUCTION

Hydrophobicity is a physical property of a molecule that is repelled from a mass of water. It can be easily translated any surfaces that are extremely difficult to wet. Because of these special properties, it becomes one's interest for self-cleaning and anti-corrosion phenomenon. Many techniques have been carried out to prepare hydrophobic coatings including plasma etching and polymerization [1], layer by layer film formation [2,3], electro-spinning [4], carbon nanotube modification [5,6] and chemical vapor deposition (CVD) [7]. However, the sol-gel processing is a promising method to produce films with a great variety of composition and structure.

The sol-gel method is a novel procedure among solution reactions which is based on the preparation of macromolecular network through the typical hydrolysis of metal alkoxide groups followed by the condensation of the silanols [8]. Nadargi *et al.* [9] were successfully prepared transparent silica thin films by single-step sol-gel processing followed by dip coating technique. In this work, the transparent silica thin films are prepared using $_x$single-step sol-gel processing followed by spin coating technique (two-step timer). The most important process parameters for spin coating are relative time of reaction to gel time, temperature and also spinning speed. If the sols are too viscous, the resulting films are rather thick. As a result, the films are easy to crack. On the other hand, if the sol contains too much solvent, the films often cannot cover the whole substrate [10]. So that in this work, uniform and defect-free films are made by applying two-step timer with high spin speed and using PEG as water binder and for reducing gel time.

Xiaoyan Song *et al.* [11] modified the surface of the films by chemical vapour deposition of $(CH_3(CH_2)7Si(OCH_30_2CH_3)$ (MODMS) and fluorooctylmethyldimethoxysilane (FODMS) and Hefeng Hou *et al.* [12] modified the surface chemistry with self-assembly monolayer using TMCS chemical vapour deposition in an oven maintain at 140˚C for 5 h for the hydrophobic properties. In order to improve this work, the self-assembly monolayer using TMCS are carried out at low temperature for various reaction times of surface modification. The water contact angles of the silica films have been calculated.

2. EXPERIMENTAL

2.1 Materials

The chemicals used were tetraethylorthosilicate (TEOS, reagent grade), and trimethylchlorosilane (TMCS, reagent grade), purchased from Sigma-Aldrich Chemie, Germany. Other reagents were ethanol (EtOH) (GCE reagent grade),

*Corresponding author at:
E-mail addresses: drkarimderaman@yahoo.com, huda_bakar@yahoo.com

polyethylene glycol (PEG) (Fluka Chemie, Switzerland) and hydrochloric acid (HCl) (QRëC, reagent grade). Distilled water was also used in this preparation.

2.2 Sample preparation

In order to study the effect of time reaction or self-assembled time towards water contact angle, the silica films were synthesized by the sol-gel method. Two sols were prepared which referred as sol A and B. Ethanol was used as solvent [13]. All the reagents and substrates were used as received. The whole preparation was carried out by the procedure described earlier [14]. The hydrolysis of TEOS was done under acidic catalyst condition. Figure 1 summarized the procedure of making the silica sols.

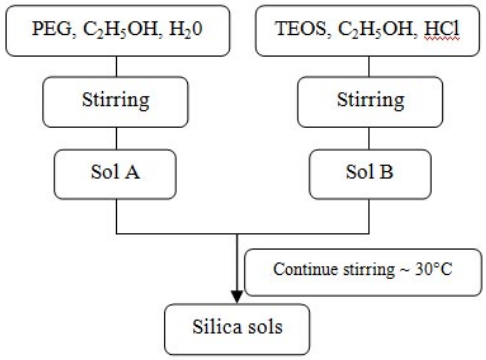

Fig. 1 The summarized procedure of preparation of silica sols

Then the silica sols were dropped on 1 x 1 cm glass substrates. The glass substrates were spin-deposited using a commercial spin coater (Chemat Technology, KW4A Spin coater) at room temperature (~27 ˚C). The spin coating time was set at 600 rpm for 15 s and 2000 rpm for another 30 s. To remove excessive of solvent, the spin-deposited films were heated under the same temperature at 60 ˚C for 10 minutes and finally annealing at 150 ℃ for 1 hour. These films were named hydrophobic silica thin films when their surface chemistry were modified using TMCS solution by simple chemical vapour reaction as formation of self-assembled films. Because of TMCS is easily evaporated, the temperature remain as low as 40˚C and the self-assembled time was varied in time range between 5 to 25 minutes, respectively.

2.2 Characterization

The thicknesses and refractive indices of the prepared silica thin film and hydrophobic silica thin film were measured using Rudolph/Auto EL Ellipsometer at 800nm. The transmission spectra were evaluated by a UV-VIS spectrophotometer (UV310PC Shimadzu) while the surface chemical modification of the hydrophobic silica thin film was evaluated by FTIR spectroscopy (Perkin-Elmer instruments), which gave the information about the various chemical bonds such as C-H, Si-O-Si, Si-C and O-H. The surface morphology of the films was also measured using AFM to determine the surface roughness.

To quantify the degree of hydrophobicity, the contact angle (θ) of water droplet placed on the hydrophobic surface was measure by hemisphere method [15]. From the photograph of water droplet, the highness (h) and radius (r) of water droplet is calculated. Then contact angle of water droplet (θ) is calculated by Eq. (1).

$$\sin\theta = \frac{2h}{\left(h^2 + r^2\right)} \quad or \quad \tan\frac{\theta}{2} = \frac{h}{r} \tag{1}$$

The calculated contact angles of water were plotted in Figure 4.

3. RESULTS AND DISCUSSION

3.1 Thickness and refractive index

The difference between thickness and refractive index of acid-catalyzed of prepared silica thin film and hydrophobic silica thin film are shown in Table 1. The refractive index of the coating film increased from 1.35 to 1.38 when it went through surface modification using TMCS. The value is in range with previous study reported by Ye at *al*. (2011) that the refractive indices increase from 1.25 to 1.42 continuously as the acid-catalyzed silica increases from 20% to 80%. This phenomenon can be explained by the filling model with an acidic catalyst as shown in Figure 2. From the figure it shows that the growth of silica sol tends to form linear chains and the pore volume of the formed film is extremely low causing the film with high refractive index [16]. The difference between thicknesses of the films caused by spontaneous and reversible surface modification where it build up more units of Si-CH_3.

3.2 Optical transmission

Figure 3 showed the optical transmittance spectra of the prepared silica thin film and hydrophobic silica thin film. Both of the films are transparent enough because they do not absorb visible light. It shows about 70-80% transmittance for light in visible wavelength range for the hydrophobic silica thin film.

3.3 FTIR analysis

The structural of the silica thin film was investigated by the FT-IR spectroscopy using the KBr method in transmission mode and was shown in Figure 4. Several characteristic absorption peaks were observed in the range 600-4000 cm^{-1} indicating the presence of methyl groups in the sample. The strong band around 3400 cm^{-1}, 1260 cm^{-1}, 1030 cm^{-1} and 821 cm^{-1} were observed.

The most important stretching band located at about 1000 cm^{-1} where it can determine the stoichiometry of the silica films. From the figure, both prepared silica film and hydrophobic silica film existed Si-O-Si band at 1030 cm^{-1} and hydrogen-bonded Si-OH band at 3400 cm^{-1}. The presence of absorption band at 1030 cm^{-1} confirms the formation network structure inside the film [17]. This absorption bands become broadened and actually shifted to lower wavenumbers. Because of annealing, the Si-O-Si band at 821 cm^{-1} also appeared [18].

By comparing both spectra between prepared silica thin film and hydrophobic silica thin film, new absorption band is observed at 1260 cm^{-1} respectively. This strong absorption band is attributed to Si-C stretching vibration [16]. It confirmed that the surface was modified by TMCS at self-assembled temperature as low as 40°C. In addition, the development of absorption band around 1400 cm^{-1} is corresponding to symmetric deformation vibration of C-H bonds, represents methyl groups are attached to silicon atoms [19].

Table 1 Difference between thickness and refractive index of prepared silica thin film and hydrophobic silica thin film

Sample	Thickness (nm)	Refractive Index (n)
Silica thin film	105.23	1.35
Hydrophobic Silica thin film	112.40	1.38

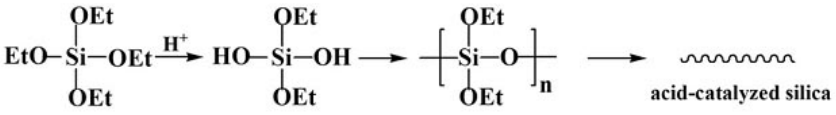

Fig. 2 Schematic representation the reaction process of acid-catalyzed silica

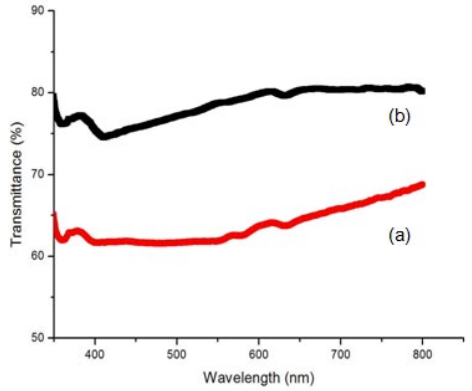

Fig. 3 Optical transmission spectra of the (a) silica thin film and (b) hydrophobic silica thin film.

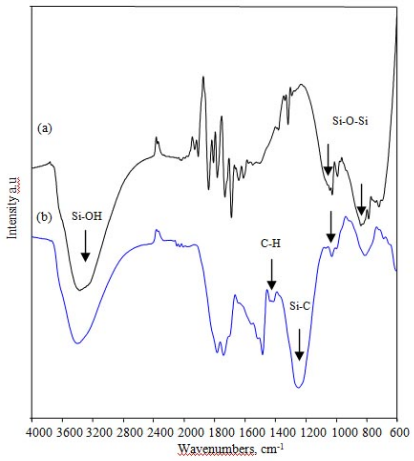

Fig. 4 FTIR spectra of (a) silica thin film and (b) hydrophobic silica thin film

3.4 Atomic Force Microscopy

In order to determined the relationship between water contact angle and surface roughness of the silica thin film and modified silica thin film, surface morphology was measured using AFM. From the AFM images shown in Figure 5(a) and 5(b), the surface roughness were increased. The rms values for prepared silica thin film is 30.6 nm while hydrophobic silica thin film exhibits roughness of 140.5 nm. Figure 5(a) represents the low roughness shows smooth and crater-like surface. Figure 5(b) shows rough but continuous hill-like structures surface where the water contact angle of the film is promoted greatly to 124°.

Although water contact angle of hydrophobic silica thin film is quite high, but the roll off angle is quite high as water droplet is not easily rolls and the droplet trend to stick to the surface. This is because large hysteresis is existed in this state. This hydrophobic equilibrium state is the Wenzel state [20] which water penetrates into the rough surface cavities. This can be reduced by increasing time or temperature during heat treatment of silica films formation. Another state is Cassie equilibrium state [20] where water droplet sits on the asperities of the surface while the air is entrapped in the structure below them. This state makes the droplet easily roll off.

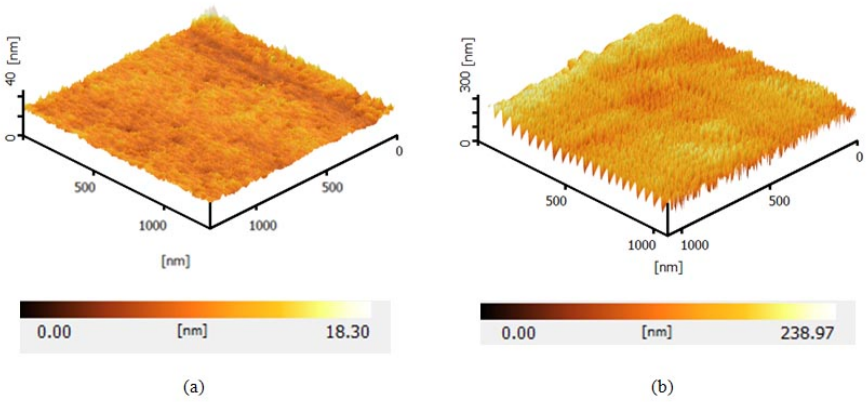

Fig. 5 Atomic force microscope images (a) on the prepared silica film and (b) on the hydrophobic silica film prepared at self-assembled time of 25 minutes. The horizontal scales of the images shows where the low area are dark coloured and high area are light coloured.

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3.6 Water contact angle

Contact angle measurements on the hydrophobic silica thin films with their self-assembled time are plotted in Figure 6. It shows that water contact angles increases with increasing time of reaction. The reason was that the TMCS react with hydroxyl group of prepared films to form a covalent bond of CH_3 group onto the surface of the films and then the hydrophobic films were obtained.

From the figure, it can be seen that the time of reaction or self-assembled time is directly proportional to the water contact angle.

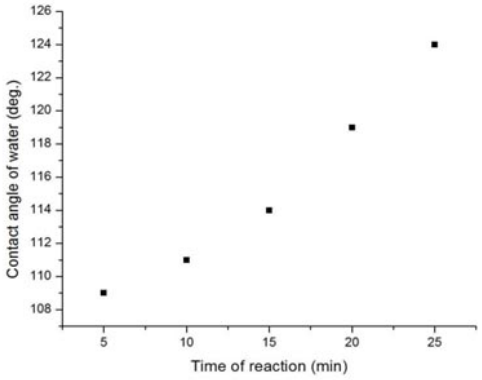

Fig. 6 Water contact angle (°) vs different time of reaction (min)

Apart from that, in this experiment proper amount of PEG have been used and the excess of water increase the hydrolysis rate and decrease the gel time. Thus the representative film surface exhibit uniform but thinner films during spin-deposited. The image of water droplet on the hydrophobic silica thin film prepared at self-assembled time of 25 minutes is shown in Figure 7.

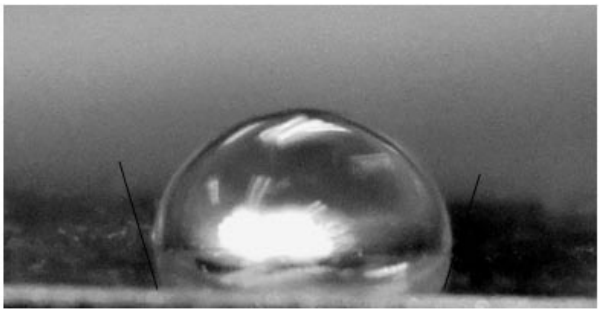

Fig. 7 Water droplet on hydrophobic silica thin film with self-assembled time of 25minutes.

4. CONCLUSION

Based on the experiment and results presented above, the following conclusions can be drawn:

1. The silica sol can be prepared by single-step acid catalyst with addition of PEG to increase hydrolysis rate and longer the aging time (sol not easily crystallize).
2. Film thickness and refractive index can be conveniently related with the self-assembled process and also from two-step timer spin coating which gives uniform but thinner films.
3. Hydrophobic silica thin films can be obtained by self-assembled using TMCS at temperature as low as 40˚C. And the water contact angle (CA) increased when time of reaction with TMCS increased.

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