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Increasing mechanical strength of mesoporous silica thin films by addition of tetrapropylammonium hydroxide and refluxing processes

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ABSTRACT

The incorporation of mesopores into silica films is an effective way to reduce the dielectric constant. However, the pores reduce the film mechanical strength. This study investigates two steps for preparing coating solution. One was the reflux of the silica colloid at 70 °C. The other was the addition of TPAOH (tetrapropylammonium hydroxide) into the colloid. The reflux step can increase the mechanical strength, reduce the flat band voltage and reduce the leakage current of the films. Nevertheless, the low-*k* value (*k* represents dielectric constant) increases as the porosity of the film falls. Adding a slight amount of TPAOH before the reflux process can recover both the porosity and the low *k* value, while maintaining the high mechanical strength and the low flat band voltage. Results of this study demonstrate that two more steps (the addition of TPAOH and the reflux) in the preparation of the coating solution can increase the film hardness and elastic modulus from 0.8 to 1.4 GPa and from 5.8 to 9.9 GPa respectively, while maintaining the low-*k* value close to 2.05.

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1. Introduction

Mesoporous silica films prepared by the surfactant-template method have been developed as low-*k* materials (*k* represents dielectric constant) [1–8]. The dielectric constant and the refractive are reduced simply by increasing the porosity of the films. The benefit of the surfactant-templated method is its capacity to generate different mesopores of controllable size and volume. A comparison with the high-pressure hydrothermal method for producing micropores in silica film [9] indicates that the normal pressure method for producing mesopores is simpler and requires less time for preparation. Over the last few years, mesoporous films with low dielectric constant and with high transmittance have been prepared [2–5,10]. However, our earlier works revealed that the leakage current density increased and the mechanical strength decreased as the porosity increased [3,11], perhaps because of the increase in the number of silanol sites in the more porous film as fewer condensation reactions occur between silanols during the preparation process. The mechanical properties are important to for chemical–mechanical-polishing in the integrated circuit industry [12]. Therefore, the mechanical strength of mesoporous silica low-*k* films must be improved for practical application in the future.

The mixture of tetraethylorthosilicate (TEOS), ethanol, deionized water, hydrochloric acid and surfactant (template) is typically adopted to prepare the coating solution by the surfactant-template method [2]. TEOS is the silica source; ethanol is the solvent; water is the reactant for the hydrolysis of TEOS and hydrochloric acid is the catalyst for the condensation reaction between silanol groups. The coating solution is stirred at room temperature for at least 3 h before the spin-coating process for making the film. This work studies two more steps to improve the mechanical properties of the film. One is the refluxing of the silica colloid at 70 °C to make larger silica particles before adding surfactant and before 3 h stirring of the colloid [5]. The other is the addition of TPAOH (tetrapropylammonium hydroxide) into the colloid before reflux. Following reflux and the addition of surfactant, the larger silica particles around the micelles form a thicker pore wall, increasing the mechanical strength of the film. Therefore, this work compares films from the coating solution with and without reflux; the low *k* value, mechanical properties, flat band voltage, leakage current density and porosity of the films were measured to characterize the effect of the reflux time. However, Das et al. noted that adding tetrapropylammonium cations to the colloid improves the hydrothermal stability of the resulting MCM-41 (mesoporous composite materials) mesoporous silica powders by thickening the pore wall [13]. Although the conditions for synthesizing MCM-41 powders differ substantially from those for synthesizing mesoporous silica low-*k* thin films — basic aqueous solution under high pressure hydrothermal conditions for making MCM-41 powders and acidic ethanol solution under normal pressure for making films, the attempt was made herein to improve the mechanical properties of the films by adding tetrapropylammonium hydroxide in the coating solution.

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2. Experimental details

2.1. Film preparation

Our earlier work studied the preparation of the coating solution without the reflux and without the addition of TPAOH [1–3]. The coating solution was a mixture of tetraethylorthosilicate (TEOS), deionized water (H_2O), ethanol (EtOH), hydrochloric acid (HCl) and Polyoxyethylene(20)sorbitan monooleate (Tween® 80). TEOS was from Merck, and the other chemicals were from Acros. A similar mixture was used herein. The molar ratio of TEOS/EtOH/H_2O/HCl was 1.0/8.6/4.2/0.03. When the effect of TPAOH (also from Acros) was studied, TPAOH at a molar ratio to TEOS of 0.003 or 0.01 was present in the solution. After the solution was refluxed at 70 °C for a certain period and cooled to room temperature, the surfactant (Tween® 80) was added in a surfactant/TEOS weight ratio of 0.41. It was then stirred at room temperature for 3 h. The resulting solution was spin-coated on a 4-inch P-type (1,0,0) silicon wafer at 2600 rpm for 30 s using an SSP-01A spinner (King Polytechnic Engineering Co.). After the spin coating, the film was baked at 106 °C for 1 h. Calcination was performed at 400 °C (at a rate of increase of temperature of 1 °C/min) for 0.5 h in air in a Type 48000 furnace (Barnstead Thermolyne). The film surface was modified to become hydrophobic by immersing it in a hexamethyldisilazane and toluene solution at 80 °C for 1.5 h.

2.2. Characterization

The details of the characterization have been presented elsewhere [3]. Nitrogen adsorption/desorption measurements were made at 77 K using a Micromeritics ASAP 2000 apparatus to characterize the pore of the films. The Barrett–Joyner–Halenda (BJH) method [14] was adopted to analyze the pore size distribution, by which the thickness of adsorbed nitrogen layer on the pore wall and the pore size relative to the adsorption pressure were obtained during the analysis. A software package from Micromeritics was used for the detailed calculation. For the total pore volume of the sample, it was estimated from the adsorbed nitrogen volume that accumulated from a vacuum to a relative pressure $P/P_0=0.95$, where P is the adsorption pressure and P_0 is the nitrogen-saturated vapor pressure, which is 1 atm at 77 K. The porosity of the films is defined as the ratio of pore volume to sample volume [3,11]. The density of silica, 2.2 g/cm^3, was used for the calculation of sample volume (= weight of sample divided by silica density). To measure various physical properties (dielectric constant, leakage current density, flat band voltage, hardness and Young's modulus), the films were applied directly to apparatuses. The capacitance measurements were made using a Keithley Model 82 CV meter. The frequency and the oscillation level were 1 M Hz and 100 mV, respectively. The dielectric constant was calculated from the capacitance in the accumulation region of the capacitance–voltage curve, the film thickness and the area of electrode (which was 0.0052 cm^2). The film thickness was measured using cross-sectional scanning by electron microscopy on an S-800 (Hitachi). The flat band voltage (at which the accumulation region switched to the depletion region) was obtained from the capacitance–voltage curve. The leakage current density of the film was determined from the current–voltage characteristics, measured using a HP4156 semiconductor parameter analyzer at an electric field of either 1 MV/cm or 1.9 MV/cm. The hardness and the Young's modulus of the film were measured using a Nano Indenter XP system. The value obtained near a film thickness of 1/10 was used for comparison. The Poisson ratio of the mesoporous silica film was taken as 0.25.

3. Results and discussion

3.1. Effect of coating-solution reflux time on properties of films

Various reflux times were used without the addition of TPAOH to prepare coating solutions, to prepare smooth films after spin-coating, baking, calcination and surface modification. For comparison, a film was prepared from the same mixture without any reflux. Table 1 presents the measurements of film thickness, dielectric constant, flat band voltage, leakage current density, hardness and elastic modulus. The reflux negatively affected the low-*k* values. The general trend is that a longer reflux time of the coating solution yielded films with higher *k* values. The *k* value of the solution refluxed for 24 h was 2.47 — increased from 2.05 for the film without any reflux. However, the reflux time did not affect the leakage current densities, and very positively affected the hardness and elastic modulus. As indicated in Table 1, the mechanical properties increased markedly with the reflux time of the coating solution. Even when just a short 1.5 h reflux time was used, the hardness of the film exceeded 1 GPa and the elastic modulus approached 10 GPa, which is in the range required for practical applications. Therefore, this work concludes that the reflux process at 70 °C for the coating solution can increase the mechanical strength of silica low-*k* films.

The mechanical strength and the flat band voltage listed in Table 1 are both increasing with the increase of reflux time. Notably, the flat band voltage is the voltage at which the accumulation region switches to the depletion region in a capacitance–voltage curve for a metal–insulator–semiconductor unit. The charges in a film or at the interface between the silicon wafer and the film influence the flat band voltage [15]. If more positive charges are present within the film or at the interface, then the flat band voltage should shift to a more negative value; if more negative charges are present, the flat band voltage should become more positive. Table 1 reveals that all of the flat band voltages are negative, and the values slowly approach zero as the reflux time increases, suggesting that the process for refluxing the coating solution reduces the positive charges within the film. The positive charge may be associated with the protons (H^+) of the residual –Si–O–H sites (silanol groups) [3,15]. The reflux process can promote the condensation reaction between –Si–O–H groups to produce more –Si–O–Si– in the silica particles. Accordingly, the resulting films can have fewer positive charges and stronger mechanical strength.

3.2. Effect of reflux time of coating-solution on nitrogen adsorption/desorption isotherms of films

The low-*k* values are strongly related to the porosity of the films. Therefore, the nitrogen adsorption/desorption isotherms and the porosity analyses are used to characterize the effect of reflux on the low-*k* values of the films. Fig. 1 shows the detailed isotherms of all the samples (except sample refluxed for 1.5 h) that are listed in Table 1. The isotherm of sample refluxed for 1.5 h can be represented by that of sample refluxed for 0.75 h, due to the similarity. All of the isotherms exhibit type IV adsorption [16], from which at least two apparent capillary condensations during adsorption in each film can be observed. One condensation is close to $P/P_0=0$, which occurs in micropores. The other is above $P/P_0=0.4$, which occurs in mesopores. Hysteresis above $P/P_0=0.4$ suggests the ink-bottle structure of the mesopores. The mesopore size distributions of all the samples can be calculated using the BJH method and the isotherm data, and are

Table 1
Effect of reflux time for the preparation of coating solution on various properties of the films

Reflux time (h)	Thickness (nm)	Dielectric constant	Flat band voltage (V)	Leakage current density (10^{-8} A/cm^2)	Hardness (GPa)	Elastic modulus (GPa)
0	510	2.05	−75	3.80	0.8	5.8
0.75	534	2.17	−57	3.26	1.0	6.9
1.5	527	2.28	−45	3.26	1.2	8.1
3	482	2.11	−41	3.54	1.2	8.2
24	499	2.47	−42	4.09	1.5	10.5

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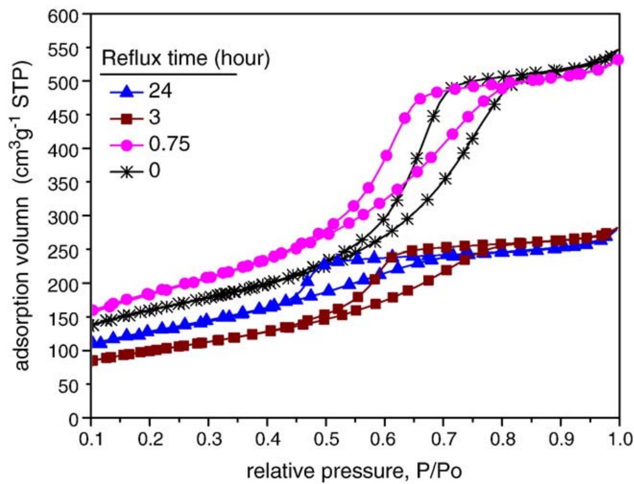

Fig. 1. Nitrogen adsorption/desorption isotherms of mesoporous silica films prepared from coating solutions refluxed for 0, 0.75, 3 and 24 h.

shown in Fig. 2. The mesopore sizes that correspond to the highest slope of adsorption volume to pore diameter all exceed 3 nm, and are dominated by the micelles formed from surfactant. Additionally, the *t*-plot of the adsorption isotherm at low P/P_0 yields the micropore volume (of pores smaller than 2 nm) of each film. Table 2 lists the data of total pore volume, micropore volume, porosity and mesopore size of each sample.

Table 2 reveals that the porosity, total pore volume and mesopore size of the films decrease as reflux time of the silica colloid increases, indicating that the increase in low-*k* values with the reflux time occurs mainly by the decrease in porosity in the films. The reflux process may increase the sizes of silica particles in the colloid, improving the mechanical strength of the porous films, as presented in the last section. Nevertheless, larger silica particles provide a smaller silica surface for forming pores, and fewer silanol groups for condensation reactions between the silica particles that surround the micelles (formed with surfactant) in the colloid. Restated, fewer bonds between particles make them less likely to resist the shrinkage of the mesopores and the reduction of pore volumes following the removal of surfactant during calcination. Therefore, the porosity of the film was lower after longer reflux in the preparation of silica colloid.

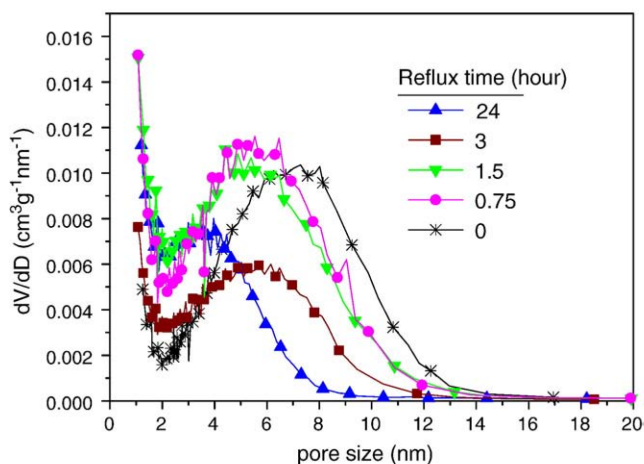

Fig. 2. Pore size distribution derived from the nitrogen adsorption isotherms of mesoporous silica films prepared from coating solutions refluxed for 0, 0.75, 1.5, 3 and 24 h.

Table 2
Mesopore size, total pore volume, micropore volume and porosity of porous silica films prepared from the solutions with different reflux times

Reflux time (h)	Mesopore size (nm)	Total pore volume (cm^3/g)	Micropore volume (cm^3/g)	Porosity
0	7.28	0.80	0.020	0.64
0.75	4.23	0.78	0.015	0.64
1.5	4.88	0.76	0.006	0.63
3	4.63	0.41	0.002	0.48
24	3.24	0.40	0.008	0.47

However, as presented in Table 2, the micropore volume decreases as the reflux time increases to 3 h. Nevertheless, it then increases as the reflux time increases to 24 h. The micropores are formed by the growth of the silica framework around the ethylene oxide (EO) chains of the micelles, as has been reported in the literature [11,17]. Accordingly, the decrease in micropore volume indicates that less growth around the EO chains is associated with larger silica particles. However, the beginning of the formation of more micropores at the longest reflux time (24 h) herein may suggest that various micropores may be formed from the void space among the large silica particles.

3.3. Effect of addition of tetrapropylammonium hydroxide on properties of films

TPAOH was added to the solution with a molar ratio to TEOS of 0.003 or 0.01. After reflux for 3 h, the addition of surfactant, and stirring at room temperature for 3 h, colloid solution for coating was obtained. The film properties (low-*k* value, leakage current, flat band voltage, mechanical strength) following calcinations and surface treatment were compared with those of the film prepared from the colloid without TPAOH addition and with a reflux time of 3 h, as shown in Table 3. The effect of adding TPAOH with a TPAOH/TEOS molar ratio of 0.003/1 on film properties is substantial. The resulting film has a lower *k* value and a lower flat band voltage and a higher mechanical strength than the film from the colloid without the addition of TPAOH. The lower flat band voltage and better mechanical properties indicate that the presence of TPAOH promotes the condensation reaction between –Si–O–H groups to form –Si–O–Si– in the silica particles during reflux. Nevertheless, as the TPAOH/TEOS ratio was increased to 0.01/1, the low-*k* value, shown in Table 3, increased and became slightly higher than that of the film that was prepared from the colloid without any TPAOH addition. The flat band voltage was also increased; however, it was still lower than that of the film without TPAOH addition. Moreover, the mechanical strengths were maintained close to those of the film with TPAOH addition at a TPAOH/TEOS molar ratio of 0.003/1. The results suggest that adding TPAOH at a TPAOH/TEOS molar ratio of as low as 0.003/1 effectively increases the mechanical strength and reduces the low-*k* value of the film that is prepared from the reflux process. In fact, the *k* value of the film can be close to the lowest *k* value in Table 1, which is that of the most porous film prepared from the colloid without adding TPAOH and without going through any reflux process.

Table 3
Effect of TPAOH addition to the coating solution on various properties of the films[a]

TPAOH/TEOS mole ratio	Film thickness (nm)	Dielectric constant	Flat band voltage (V)	Leakage current density (10^{-8} A/cm^2)	Hardness (GPa)	Elastic modulus (GPa)
0/1	482.0	2.11	−41	3.54	1.2	8.2
0.003/1	478.8	2.06	−28	11.9	1.4	9.9
0.01/1	513.0	2.16	−34	11.1	1.5	9.6

[a] All samples were refluxed for 3 h.

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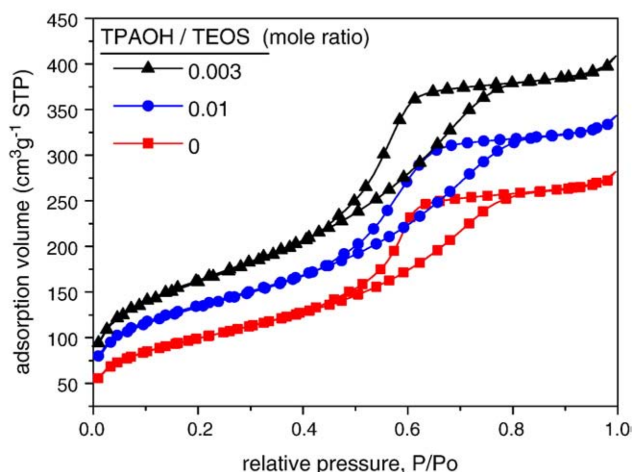

Fig. 3. Nitrogen adsorption/desorption isotherms of mesoporous silica films prepared from coating solutions refluxed for 3 h with mole ratios of TPAOH/TEOS of 0, 0.003, and 0.01.

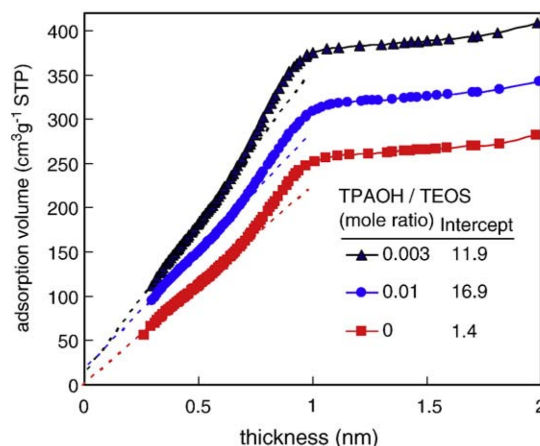

Fig. 5. *t*-plot of nitrogen adsorption isotherms of mesoporous silica films prepared from coating solutions refluxed for 3 h with mole ratios of TPAOH/TEOS of 0, 0.003, and 0.01.

3.4. Effect of addition of tetrapropylammonium hydroxide on nitrogen adsorption/desorption isotherms of the films

Fig. 3 displays the isotherms from the films prepared with TPAOH addition at TPAOH/TEOS ratios of 0/1, 0.003/1 and 0.01/1. All samples were refluxed for 3 h. All of the isotherms exhibit type IV adsorption. Sample from the colloid with TPAOH/TEOS ratio of 0.003 is the most porous film in Fig. 3. As the amount of TPAOH increased to a TPAOH/TEOS ratio of 0.01/1, the porosity decreased, but remained higher than that without any TPAOH addition.

Fig. 4 displays the mesopore size distributions. Fig. 5 presents *t*-plots of the adsorption isotherms in the low value range of P/P_0. Table 4 summarizes the total pore volume and porosity from Fig. 3, the mesopore size from Fig. 4 and the micropore volume from Fig. 5 for each sample. The micropore volume increases with the amount of TPAOH addition. TPAOH is a template for synthesizing microporous ZSM-5 zeolite. Accordingly, one of the roles of TPAOH in this work is as a template in the silica colloid. Calcination for removing the template produces micropores. Nevertheless, X-ray diffraction analysis revealed no crystalline structure of ZSM-5 zeolite, suggesting that either the crystals were too small to be detected, or only amorphous microporous materials were formed in the films. However, the mesoporous volume declines as the molar ratio of added TPAOH increases from 0.003 to 0.01, as shown in Fig. 4, although the same amount of surfactant was used to form the mesopores. In this work, a small amount of gel was generated when the colloid prepared with added TPAOH at a TPAOH/TEOS ratio of 0.01/1 was aged at room temperature for 17 h. However, a clear solution was maintained when colloid was prepared with added TPAOH at a TPAOH/TEOS ratio of 0.003/1. Therefore, the mesopore volume of sample from colloid with TPAOH/TEOS ratio of 0.01 is lower than that of sample from that with TPAOH/TEOS ratio of 0.003, perhaps because of the small amount of gel formed in the solution with the TPAOH/TEOS ratio of 0.01/1. The same reason may explain why the flat band voltage of sample from TPAOH/TEOS ratio of 0.01 is more negative than that of sample from the ratio of 0.003, as presented in Table 3.

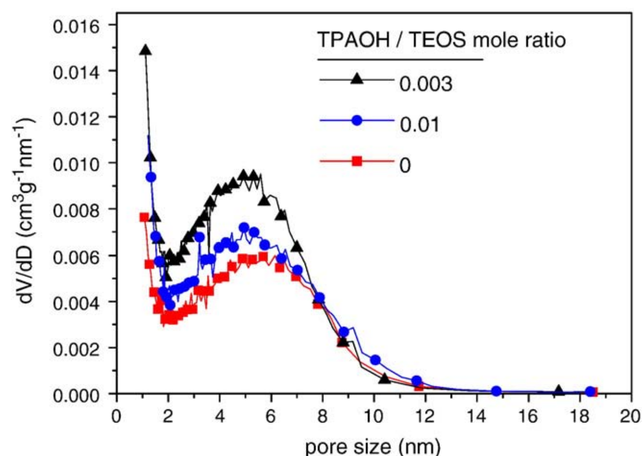

Fig. 4. Pore size distribution derived from the nitrogen adsorption isotherms of mesoporous silica films prepared from coating solutions refluxed for 3 h with mole ratios of TPAOH/TEOS of 0, 0.003, and 0.01.

4. Conclusions

A longer reflux of silica colloid from TEOS solution at 70 °C can cause a more extensive condensation reaction between silanols. The resulting films therefore have fewer positive charges, less negative flat band voltages, and greater mechanical strength (hardness and elastic modulus). Nevertheless, the lower porosity of the film makes the low-*k* value higher. When a small amount of TPAOH (TPAOH/TEOS molar ratio = 0.003/1) is added to the silica colloid and reflux is carried out, the mechanical strength of the film can be increased further and the flat band voltage becomes less negative than those of the film from the colloid without TPAOH addition, indicating that the presence of TPAOH promotes the condensation reaction between silanols in the colloid. Notably, the small amount of TPAOH in the reflux process generates a more porous film. Therefore, using two more steps (the addition of TPAOH and the reflux) in the preparation of coating solution can increase the film hardness and elastic modulus from 0.8 to 1.4 GPa and from 5.8 to 9.9 GPa respectively, with a low-*k* value of close to 2.05.

Table 4
Mesopore size, total pore volume, micropore volume and porosity of porous silica films prepared from the solutions with different TPAOH addition[a]

TPAOH/TEOS mole ratio	Mesopore size (nm)	Total pore volume (cm^3/g)	Micropore volume (cm^3/g)	Porosity
0/1	4.63	0.41	0.002	0.48
0.003/1	4.19	0.60	0.018	0.57
0.01/1	4.28	0.51	0.026	0.53

[a] All samples were refluxed for 3 h.

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