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# Effect of concentration of tetrapropylammonium hydroxide on silica suspensions for making spin-on porous low dielectric constant films

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#### A R T I C L E I N F O

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#### ABSTRACT

Porous silica low-dielectric-constant (low-*k*) films were prepared using coating solutions containing a surfactant and various kinds of silica nanoparticles synthesized using different concentrations of tetrapropylammonium hydroxide (TPAOH). The effect of the TPAOH concentrations (TPAOH/Si molar ratios, 0.15–0.36) on the properties of these silica nanoparticles and their corresponding porous films were investigated. Decreasing the TPAOH concentration increases particle size and decreases the number of silanol groups on silica particles. Therefore, the low-*k* film properties (*i.e.*, *k* value, leakage current density, porosity, surface morphology, hardness, and elastic modulus) of the resulting films differed. When making the low-*k* films, porosity increases as the TPAOH concentration decreases. Nevertheless, decreasing the TPAOH concentration leads to the formation of large aggregates of surfactant micelles, resulting in holes (observed by scanning electron microscopy) on a film. These large holes can cause extremely high leakage current densities and high *k* values. Additionally, a low TPAOH concentration produces films with low mechanical strength. Conversely, the film from silica nanoparticles prepared with a relatively higher TPAOH concentration possess a more uniform film surface, a lower *k* value, a lower leakage current density, a higher elastic modulus and a higher hardness.

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#### 1. Introduction

To reduce resistance–capacitance delay in electrical signals, introducing low dielectric constant (k value) materials into an integrated circuit (IC) is imperative. Although a porous silica film is a promising candidate with ultra-low k values ( $k \le 2$ ), the mechanical strength of the porous films is too weak to withstand stress encountered in integrated cycles such as chemical mechanical polishing processes and packing processes in the IC industry [1]. On the other hand, low-kfilms also have a low leakage current density because they also serve as an electric insulator in a device.

Pure-silica-zeolite (PSZ) MFI low-*k* films have been developed [2–5]. The PSZ MFI-type zeolite is a crystalline silica with a well-defined threedimensional framework with a micropore size of about 5.5 Å. Coating solutions containing PSZ MFI nanocrystals were prepared using tetrapropylammonium hydroxide (TPAOH) as a structure-directing agent in hydrothermal processes. Some films with a *k* value <2 and an elastic modulus >10 GPa (high mechanical strength) have been prepared. However, Eslava *et al.* [6] demonstrated that the surface morphology and mechanical strength of PSZ MFI low-*k* films would become worse as nanocrystal size increases. The same finding was reported by Johnson *et al.* who synthesized zeolite low-*k* films from coating

\* Corresponding author. *E-mail address:* benzuwan@ntu.edu.tw (B.-Z. Wan). solutions containing nanocrystals of another PSZ (the MEL type) [7]. On the other hand, the TPAOH concentration in precursor solutions is an important parameter for synthesis of MFI silica suspensions via a hydrothermal process [8,9]. As the TPAOH concentration increased, the size of MFI nanocrystal decreased, and the surface charges, which developed from ionization of surface hydroxyl groups on MFI nanocrystals, increased. Nevertheless, the effect of the TPAOH concentration on spin-on porous low-*k* films from the silica suspensions has not been reported in literature.

In a previous study [10], PSZ MFI nanocrystal suspensions were prepared using a two-stage hydrothermal process followed by a centrifuge process, based on the processes developed by Li et al. [5]. The surface morphologies of these PSZ MFI films were improved markedly by adding a surfactant to the coating solutions. In addition, the surfactant can be utilized to increase pore volume in the films. A much faster and more economical one-stage hydrothermal process for preparing a noncrystalline silica suspension was then developed [11]. By using the surfactant as a leveling agent and to generate pores, ultra-low-k porous films with high mechanical strength and low leakage current density can be created. Therefore, noncrystalline silica nanoparticles are a promising material for producing porous silica low-k films. In this work, porous silica low-k films were prepared from coating solutions composed of surfactant Tween 80 and various noncrystalline silica nanoparticles synthesized with different TPAOH concentrations. The effect of the TPAOH concentration on the properties of the silica nanoparticles and their corresponding porous silica films is investigated.





#### 2. Experimental section

#### 2.1. Sample preparation

The coating solutions containing noncrystalline silica nanoparticles and surfactant were synthesized using the following steps. First, tetraethyl orthosilicate (TEOS) (Merck), ethanol (EtOH) (Merck), TPAOH (25 wt.%) (Acros Organics), and deionized water were mixed as precursor solutions. The molar ratio of TEOS/EtOH/H<sub>2</sub>O was 1/5.6/12.2. To investigate the concentration effect of TPAOH, TPAOH/TEOS (TPAOH/Si) molar ratios were varied in the range of 0.15-0.36. The precursor solutions were stirred at 30 °C for 3 h and then heated to 100 °C for 24 h as a hydrothermal process for the synthesis of noncrystalline silica nanoparticles. The resulting solutions were diluted with an equal weight of ethanol, and mixed with surfactant Tween 80 (Polyoxyethylene(20)sorbitan monooleate; Acros Organics) with a weight ratio of Tween 80 to TEOS of 0.41:1 to form coating solutions.

The procedures for cleaning silicon wafers, the spin-coating processes, the film baking and calcination processes, and film surface modification using hexamethyldisilazane (HMDS) (Acros Organics) solution followed those in a previous study [11]. The resulting films were used later for characterization, electrical measurements, and mechanical measurements.

#### 2.2. Characterization

The chemical structure of the films was characterized by transmission Fourier transform infrared spectroscopy (FTIR) (PerkinElmer, Spectrum 100, USA) with nitrogen purging. The collected spectra were subtracted from background spectra and normalized by film thickness. The film thickness was determined using a cross-sectional fieldemission scanning electron microscope (FE-SEM) (LEO 1530). The film surface morphology was observed by a FE-SEM (JSM-7600F). To assess electronic properties, an array of aluminum dots, roughly 5000-Å thick, were formed on a film surface via condensation of aluminum vapor through an aluminum shadow mask. Capacitance was measured using a Keithley model 82 capacitance-voltage meter. The frequency and oscillation level were 1 MHz and 100 mV, respectively. The dielectric constant was calculated on the basis of capacitance in the accumulation region of the capacitance-voltage curve, film thickness, and area of the electrode (0.0052 cm<sup>2</sup>). The leakage current density of films was determined from current-voltage characteristics, and measured using a HP4156 semiconductor parameter analyzer. The elastic modulus and hardness of films were analyzed using a Nano Indenter XP (MTS) system. The indentation depth of each film is close to the film thickness when using the continuous stiffness measurement technique [12]. A standard Berkovich (three-sided pyramidal) diamond indenter probe was used in indentation experiments. The elastic modulus and hardness of films were extracted from each test point with an indentation depth of 10% of total film thickness. The reported values and standard deviations of the elastic modulus and hardness are averages of six measurements at six different locations on the film.

Average particle sizes of noncrystalline silica suspensions were determined with a dynamic light scattering (DLS) analyzer, a ZetaSizer Nano ZS (Malvern), with a laser wavelength of 633 nm. Typically, 0.1 g of each as-synthesized silica suspension was diluted a hundredfold with deionized water to obtain diluted samples for DLS experiments. The solid-state <sup>29</sup>Si magic angle spinning nuclear magnetic resonance (MAS NMR) spectra of dried powder samples were obtained using a Bruker AVIII 600 spectrometer (Bruker, Germany). The dried powder samples were prepared directly from as-synthesized silica suspensions by drying at 60 °C for 3 h and 90 °C for 3 h in air. The spectra collected were used to calculate  $Q^4/(Q^3 + Q^2)$  intensity ratios ( $Q^n = Si(OSi)_n(OH)_{4-n}$ ), which can determine the number of surface silanol groups on silica particles. Coating solutions were dried and then calcined at 550 °C for 5 h in air to acquire calcined powder samples. The pore volume and pore size distribution of calcined powder samples were characterized through nitrogen porosimetry at 77 K using a TriStar 3000 (Micromeritics) apparatus.

#### 3. Results and discussion

#### 3.1. Characterization of noncrystalline silica nanoparticles

Noncrystalline silica nanoparticle suspensions prepared with different TPAOH concentrations were characterized using the DLS analyzer to determine the average sizes of silica particles. Powder samples dried from suspensions were characterized by solid-state <sup>29</sup>Si MAS NMR. Table 1 shows the average sizes of silica particles as a function of TPAOH/TEOS molar ratios. The average sizes are all <10 nm and decrease as the TPAOH/TEOS molar ratio increases. These analytical results indicate that increasing TPAOH concentration in a solution with a constant silica precursor (i.e., from TEOS) concentration leads to an increased number of nuclei and a decreased silica concentration for crystal growth in a hydrothermal solution, thus producing small particles. Fig. 1 shows solid-state <sup>29</sup>Si MAS NMR spectra with signals at about -109, -98, and -88 ppm, which are attributed to  $Q^4$  [Si(OSi)<sub>4</sub>],  $Q^3$  $[Si(OSi)_3(OH)]$ , and  $O^2 [Si(OSi)_2(OH)_2]$  sites, respectively, in the framework. Notably,  $O^2$  and  $O^3$  represent defect sites with silanol groups. The  $O^4/(O^3 + O^2)$  ratios of samples can be determined after deconvolution analysis. These ratios are significantly influenced by the TPAOH concentration in a solution. The  $Q^4/(Q^3 + Q^2)$  ratios decrease as the TPAOH/ TEOS molar ratio increases, indicating that TPAOH limits condensation reactions. In other words, the number of silanol groups on the surface of noncrystalline silica nanoparticles increases when the TPAOH concentration increases. The more silanol groups are, the more hydrophilic surface of nanoparticles is. Therefore, noncrystalline silica nanoparticles prepared with a high TPAOH concentration have a stronger hydrophilic surface than those prepared with a lower TPAOH concentration.

#### 3.2. Transmission-FTIR measurements of film samples

Fig. 2a shows FTIR spectra of porous silica films before and after HMDS surface modification as a function of TPAOH concentration. The typical Si – O – Si vibration bands at 1000–1250 cm<sup>-1</sup> [13,14], indicate the formation of Si-O-Si networks in all films. Due to incomplete condensation of Si – OH bonds in a silica framework, Si – OH stretching vibration at around 960 cm<sup>-1</sup> [13] appears in spectra. After surface modification, the absorbance intensity around 960  $\text{cm}^{-1}$  decreases. Additional absorbance peaks at about 1260 cm<sup>-1</sup> (Si – CH<sub>3</sub> stretching) [14] can be observed in the films, and they are associated with the formation of trimethylsilyl groups from silvlation reaction of Si-OH groups by HMDS treatment. Fig. 2b shows the relative absorbance of Si-OH bands (at about 960 cm<sup>-1</sup>) versus Si-0-Si bands (1000-1250 cm<sup>-1</sup>) as a function of TPAOH/TEOS molar ratios. The absorbance of each band is determined from absorption area. The Si-OH/Si-O-Si ratio can quantitatively represent the number of silanol groups per unit surface of a film. The Si – OH/Si – O – Si ratios of films after surface modification are much less than those before surface modification (Fig. 2). The silanol groups remaining in films after surface modification are attributed to a limitation of silylation due to steric hindrance of the

es	of	silica	nanoparticle	suspension

Table 1

particle suspensions synthesized in solutions with different Properties of TPAOH concentrations.

TPAOH/TEOS (molar ratio)	Average size (nm)	$Q^4/(Q^3 + Q^2)$	Total pore volume (cm <sup>3</sup> /g)
0.15	6.7	1.04	0.540
0.25	5.8	0.89	0.396
0.36	4.5	0.67	0.357

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