Journal of the Taiwan Institute of Chemical Engineers 43 (2012) 971–979

Contents lists available at SciVerse ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

# Crystallinity control of zeolite nanoparticles for the preparation of mesoporous low-*k* films through a fast hydrothermal process

Hsin-Yan Lu, Chien-Hao Kung, Ben-Zu Wan *

*Department of Chemical Engineering, National Taiwan University, Taipei 106, Taiwan*

ARTICLE INFO

*Article history:*
Received 25 January 2012
Received in revised form 3 June 2012
Accepted 24 July 2012
Available online 25 September 2012

*Keywords:*
Low-*k* films
Zeolite
MFI structure
Hydrothermal process
Mechanical strength

ABSTRACT

A fast hydrothermal process for making coating solution containing MFI-type zeolite nanoparticles for the preparation of the mesoporous low-*k* films has been developed. The ratio of optical density (or particle crystallinity) of the nanoparticles in the films is a key factor influencing the electronic and mechanical properties. As the ratio is higher than 10%, the cracks are formed in the films, causing the decrease of the mechanical strength and the increase of the *k* values. Therefore, the ratio should be controlled less than 10% by using short hydrothermal time (less than 48 h). With the ratio of <10%, the films prepared from the coating solutions with the hydrothermal times of 36 and 42 h possess *k* values of less than 2, hardness of >1 GPa, elastic modulus of >10 GPa, and leakage current densities in the order of $10^{-8}$ A/cm$^2$, those all reach the requirements for the application in the future integrated circuits.


## 1. Introduction

The mesoporous low dielectric constant (*k* value) film, a combination of solid phase (silica or pure-silica–zeolite (PSZ) nanoparticles) and mesopores filled with air, is a potential candidate for the application as an interlevel dielectric (ILD). It can solve the problem of the resistive-capacitive time delay (RC delay) caused by parasitic resistance and parasitic capacitance. Moreover, the *k* values of the film can be controlled through adjusting the pore volume. According to the report established by ITRS in 2010, the required *k* value should be lower than 2 for the application in the integrated circuit (IC) industry in the near future [1]. Several previous studies have produced the mesoporous silica low *k* value (low-*k*) films by surfactant-template method to approach the goal of *k* value of <2 [2–12]. However, the mechanical strength of the films is not strong enough to withstand the stress suffered during the process of chemical–mechanical-polishing (CMP) in standard IC manufacturing processes [8,12]. The requirements of mechanical strength for the industrial applications are that the elastic modulus should be higher than 10 GPa and that the hardness should be higher than 1 GPa [12].

Since 2001, it has been claimed that the low-*k* films with pure-silica–zeolite (PSZ, a microporous crystalline material) of MFI type can possess strong mechanical strength [13–16]. Wang *et al.* have prepared low-*k* films with PSZ MFI-type nanoparticles and claimed that the films possessed strong mechanical strength (an elastic modulus of between 16 and 18 GPa) and a *k* value of 2.1 [13,14]. Li *et al.* in 2004 also reported a PSZ MFI-type low-*k* film with a *k* value as low as 1.6 and an elastic modulus of 1.6 GPa [16]. The low-*k* films presented above seem to meet all the requirements in the future IC industry. However, Eslava *et al.* repeated the experiment conducted by Wang *et al.* and obtained the results that would be fatal for the use of this kind of low-*k* films in the IC industry [17,18]. They observed that large voids (larger than 5 nm) were formed in the films, and the voids would cause a sealing problem that Cu metal would diffuse into the pores of low-*k* films in the later IC manufacturing processes, resulting in electrical degradation of electronic devices. They also demonstrated that the surface morphology and the mechanical strength of the low-*k* films would become worse with the increasing of the nanoparticle size. The same result was reported by Johnson *et al.* who synthesized zeolite low-*k* films from coating solutions containing nanoparticles of another type PSZ (MEL type) [19]. Furthermore, Hata *et al.* in 2008 observed that the surface of low-*k* film spin-coated from a coating solution containing only PSZ MFI nanoparticles was too rough to obtain useful data through spectroscopic ellipsometry [20]. The same observation was also reported in our previous research from optical microscopy images of the films [21]. The problem of rough surface morphology can be solved after the addition of surfactant (Tween 80, P123 or L44) [20–24] into the coating solutions, and the stable electronic and mechanical strength properties of the films would be obtained.

In our previous research [21], it was found that with the addition of surfactant Tween 80 in the coating solution containing

* Corresponding author.
*E-mail address:* benzuwan@ntu.edu.tw (B.-Z. Wan).

1876-1070/$ – see front matter © 2012 Taiwan Institute of Chemical Engineers. Published by Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jtice.2012.07.006

PSZ MFI-type nanoparticles, synthesized through a two-stage hydrothermal process, the mesoporous low-*k* films which possessed *k* values of <2 and high mechanical strength (hardness of >1 GPa and elastic modulus of >10 GPa) can be obtained. However, the time consumed for the preparation of coating solution was more than 156 h, which was too long and very uneconomic. Therefore, in this research, a much faster and more economic process for preparing the films with the nanoparticles has been developed. The effects of process parameters have been explored. The particles in different coating solutions have been characterized by using X-ray diffraction, FTIR analysis, $^{29}$Si MAS solid-state NMR, dynamic light scattering analyzer, and pore size distribution measurement. The ratio of optical density (or the crystallinity) of the particles has been defined and that of each sample has been calculated from the measurements. Moreover, the spin-coated films have been characterized by using SEM and the electronic and mechanical properties of those have been measured. The attempts have been made to find which process for making the coating solution and which property of the particles influence the film the most, by controlling which the mesoporous silica low-*k* film with high mechanical strength and low *k* value can be made.

## 2. Experimental

### 2.1. Preparation of coating solutions and mesoporous low-k films

The coating solutions containing silica particles and surfactant were synthesized through the following steps. First, TEOS (tetraethyl orthosilicate, >99 wt%, Merck), EtOH (ethanol, Acros Organics), TPAOH (tetrapropylammonium hydroxide, 25 wt%, Acros Organics), and DI water (deionized water) were mixed in a molar composition ratio of 1TEOS/5.6EtOH/0.36TPAOH/12.2$H_2O$ to form a precursor solution, and was stirred at 30 °C for 3 h. It was then heated to 100 °C and held for 36, 42, or 48 h for the hydrothermal process. The resulting solution was mixed with surfactant Tween 80 (polyoxyethylene(20)sorbitan monooleate, Acros Organics) with a weight ratio of Tween 80/TEOS of 0.41 to form the coating solution. The centrifuge was applied, if it was required to. The resulting coating solution was then spin-coated on a pre-cleaned 4-in. P-type (1 0 0) silicon wafer (Siltronic AG) at 2600 rpm for 30 s, using an SSP-01A spinner (King Polytechnic Engineering Co.). The pre-cleaned process for wafer was firstly cleaning with HF (48–51 vol%, Acros organic) and DI water with a volume ratio of 1HF/10$H_2O$ for 5 min, then immersed it in a mixture of $H_2O_2$ (35 wt%, Acros organics), $NH_4OH$ (28–30 wt%, Acros organics), and DI water, with a volume ratio of 1$H_2O_2$/1$NH_4OH$/50$H_2O$, for 20 min. After the spin coating process for loading film, the wafer was baked at 150 °C for 1 h and calcined at 450 °C for 5 h in air. Finally, after the film cooled down to 110 °C, it was immersed into a mixture of hexamethyldisilazane (Acros Organics) and toluene (Acros Organics) at 80 °C for 1.5 h to modify the surface to a hydrophobic state.

### 2.2. Characterization

In order to measure the pore size distribution and the crystallinity of each sample, the coating solution was dried at 60 °C for 3 h and then 90 °C for 3 h to obtain dried samples, and finally calcined at 550 °C for 5 h to obtain powder samples. The dried samples were characterized by using a Bruker DSX500 NMR spectrometer to obtain solid-state $^{29}$Si spectra. The spectra collected was used for calculating intensity ratios between the $Q^4$ and $Q^3$ lines ($Q^4 = Si(OSi)_4$, $Q^3 = Si(OSi)_3(OH)$), which can determine the amount of the surface silanol groups on the particles [25,26]. The sample was also characterized through nitrogen adsorption/desorption measurements at 77 K using a TriStar 3000 (Micromeritics) apparatus, to determine the pore volume and pore size distribution, and analyzed using X-ray powder diffraction (X'Pert PRO (PANalytical)) and FTIR (Spectrum 100, PerkinElmer) measurements to determine the particle crystallinity. Moreover, the particle size and particle size distribution were measured by using a dynamic light scattering analyzer, ZetaSizer Nano ZS (Malvern), with a laser wavelength of 633 nm. Before the measurement, 0.1 g of the coating solutions was diluted a hundredfold with DI water, then was placed into a transparent glass vial, and was thermal equilibrated at 25 °C. Each sample was measured 12–15 times in a round within 3–5 min. Generally three rounds were carried out.

The surface morphology and the thickness of the films were obtained using a FE-SEM (LEO 1530). For electronic and mechanical properties, the capacitance was measured using a Keithley model 82 CV meter. The frequency and the oscillation level were 1 MHz and 100 mV, respectively. The dielectric constant was calculated on the basis of the capacitance in the accumulation region of the capacitance–voltage curve, the film thickness, and the area of the electrode (0.0052 $cm^2$). The leakage current density of the film was determined from the current–voltage characteristics, measured using a HP4156 semiconductor parameter analyzer with an electric field of 1 MV/cm. The hardness and the elastic modulus of the film were measured using a Nano Indenter XP (MTS) system. The elastic modulus and hardness were measured by indenting the films with indention depth close to the film thicknesses through the continuous stiffness measurement (CSM) technique [27], and the Poisson ratio of the film was taken as 0.25 [12]. The data at the range of about 1/10 thickness was taken for comparison. The average values and the standard deviations of elastic modulus and hardness were calculated, based on six measurements at six different locations on the film.

## 3. Results and discussion

### 3.1. Characterizations of particle crystallinity and size of MFI-type PSZ nanoparticles

Figs. 1 and 2 present the X-ray diffraction (XRD) and Fourier transform infrared (FTIR) characterizations, respectively, of the powder samples from the coating solutions after a drying process. In both figures, BC in the symbols of 48BC, 42BC, and 36BC represents that the powder samples made from the coating solutions after addition of Tween 80 and before being centrifuged, the number in the symbols indicate the hydrothermal time; on the other hand, AC in the symbols 48AC, 42AC, and 36AC represent those BC samples after being centrifuged. As shown in the XRD results of Fig. 1, the crystallinity of the powder sample increases with the increase of the hydrothermal time, no matter the coating solutions are centrifuged or not. It suggests that more nanoparticles with higher crystallinity are formed in the solution with longer hydrothermal time. The crystal phases of all the samples are identified as those of MFI-type zeolite (PSZ nanoparticles) [21,28]. For the samples prepared from the same hydrothermal time, those made from centrifuged coating solutions (samples 36AC, 42AC, and 48AC) possess lower crystallinity than those without being centrifuged (samples 36BC, 42BC, and 48BC). It is apparent that the nanoparticles with high crystallinity can be removed from the solution by using centrifuge process. To quantitatively define the crystallinity of each powder sample, the ratio of optical density was calculated from FTIR spectra shown in Fig. 2. It is the ratio of band intensity at 550 $cm^{-1}$ to that at 450 $cm^{-1}$. The band at 550 $cm^{-1}$ represents the pentasil framework vibration of MFI-type zeolite structure, and that at 450 $cm^{-1}$ represents the vibration intensity from all the $SiO_2$ units [29]. The ratios measured of optical