Nanoporous Silica Thin Films Synthesis by Sol-Gel Process

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Abstract

Synthesis of thin films of nanoporous silica on glass substrate is very delicate process in sol-gel synthesis technique. Homogeneity of the film prepared and its continuity affected by the conditions of the reaction. It was found that the physical and optical properties of mesoporous thin films prepared through surfactant templating as pore size, pore volume, pore size distribution, and ordering depend on the concentration of the surfactant used. Physical properties of thin film characterized by Nitrogen adsorption   isotherm, HRTEM-ED, and Photoacoustic Spectroscopy (PAS).

Key words: thin films, nanoporous, glass substrate, Homogeneity, pore size, pore volume, pore size distribution, ordering, Nitrogen adsorption isotherm, HRTEM-ED, PAS.

1. Introduction

Ordered mesoporous materials synthesized through surfactant templating exhibit high porosity with channel or interconnected pore structures of amorphous silicate framework, uniform apertures in the range of 2 nm diameter and large surface area of $\leq 1000\,\mathrm{m}^2/\mathrm{g}$ [1, 2]. They have expanded the pore size related applications of zeolite molecular sieves from microporous to nanoporous. Their intra-channel and intra-pore voids provide the confined

space to accommodate nanostructured molecules and clusters [3, 4], and the reactive surface hydroxyl groups on the intra-channel and intra-pore surface can be chemically modified through silynation [5]. In addition to the original 2D-hexagonal MCM-41 (*P6mm*) and 3D-bicontinuous cubic MCM-48 (*Ia3d*) phases of ordered mesoporous materials, several other structures such as lamellar, 3D- hexagonal (*P63/mmc*), 3D-cubic (*Im3m*, *Pm3m* or *Pm3n*) etc. with their surfactant liquid crystal counterparts also become available. Most of the mesoporous materials reported are based on either silica or aluminosilicate [6, 7]. Some attempts were made to either incorporate Ti, Zr,V, Nb, B, Ga, Fe... etc. into the silicate framework or fabricate mesoporous structures out of transition metal oxides [8,9]. Formation of ordered mesoporous materials takes place under alkaline, acidic or neutral conditions via the cooperative interaction of organic surfactants and inorganic species through electrostatic attraction or hydrogen bonding [10,11]. The morphological variability achievable covers powder, fiber, film, hard sphere, hollow, rod and monolith [12–13]. Besides powder, thin film has attracted the most attention because of their potential uses in chemical sensors, membrane separation, optical devices and electronic devices [6,16–24]. Continuous thin films of surfactant-templated mesoporous silica were detected growing either in self-support form [25] or on top of porous or dense support [26]. Preparation methods including sol–gel coating and hydrothermal synthesis since first being reported in 1996 were reviewed recently [27–29]. Synthesis of such thin films is preferably under acidic condition and has the growth from a homogeneous solution of reactants as well as being induced by rapid solvent evaporation from a sol precursor coated on a solid support. Through an epitaxial-like growth, the mesochannels can be aligned under a controlled reactant flow [30] or on a modified anisotropic surface of a glass substrate [31] or on a specific crystalline plane i.e. (110) plane of a silicon wafer [32]. With a bulk alignment of mesochannels in a continuous thin film, guest molecules and clusters can be incorporated and aligned in confined directions, and thus create orientation dependent optical, electronic, optoelectronic or magnetic properties and applications. However, the epitaxial-like growth takes more time than the solvent evaporation methods. In the latter, the sol solution usually consists of soluble silica and surfactant in ethanolic and aqueous solution with an initial concentration of surfactant much less than the critical micelle concentration (CMC). The silicate species in the precursor sol undergo hydrolysis and condensation to form a gel. During and after the coating process, the surfactant concentration increases through the evaporation of solvent. When the concentration of surfactants reaches CMC, surfactant ions or molecules will form micelles and thus enhance the growth of organic-inorganic hybrid mesostructures. The

degree of condensation of silicate moieties and the rate of solvent evaporation play critical roles during self-assembly and thus affecting the ordering of the final mesostructure. Sol–gel based dip- or spin-coating and aerosol-associated deposition is usually employed to rapidly produce continuous mesoporous films on substrates in large area and controlled thickness [33, 23]. Interfacial bonding between the coated film and the substrate can take place through hydroxyl condensation by heat treatment, and the resulting film will attach itself to the substrate firmly. Grosso et al. [34] recently reported that the final mesostructure and texture of silica and titania films are controlled by the specific chemical and processing parameters. They suggested that the mechanism of self-assembly is through concentration gradients as well as the film's composition in quasi-equilibrium with its environment. Mechanical strength and stability of mesoporous films are important prerequisites for their optical and electronic applications, and good mechanical properties can, in turn, be achieved through well-organized film texture [35, 36]. Furthermore, the scope of applications of mesoporous films is closely associated with their pore properties such as pore size, porosity and pore structure [37–39]. Mesoporous silica films, with their dielectric constant as a function of porosity and reasonable mechanical strength derived from the ordered pore structure [23, 37], are considered as one of the most promising low- dielectric materials for ultra-large-scale integration (ULSI) device. Gas transport of these films was found to be somewhat affected by the randomness of the ordered domains in the mesoporous membrane [38]. Furthermore, the uniform thickness and proper density of the nanoporous coating play a key role in the film's anti-reflection of light [39]. Since the pore structure and film texture of supported thin films were found to be affected by substrate, and such films are usually used together with its substrate in applications, it is desirable to perform the characterization using on-substrate techniques for supported thin films instead of the characterization of films detached from their substrates, where removing thin films from its substrates is so difficult, especially if the substrate is silica [42].

2. Experimental

2.1 Synthesis

The deposition of mesoporous silica films was performed by evaporation- induced self-assembly in a spin-coating process. Mesoporous silica thin films were synthesized using cetyltrimethylammonium bromide (CTABr) as a surfactant and tetraethylorthosilicate (TEOS) as a silica source. The molar composition of the reaction mixture was x CTABr : 1

TEOS : 2.5 HCl : 125 H_2O, where x was 0.13 and 0.2 for the films A and B respectively. Synthesis was performed as follows: the surfactant, distilled water, and hydrochloric acid were mixed to give a clear solution, which was allowed to react at desired temperatures prior to the addition of TEOS. A desired amount of TEOS was added to the reaction mixture immediately while the mixture was being vigorously stirred. The mixture was stirred for 10 min and then allowed to react at various temperatures under static or stirring conditions for desired times. The pH was lower than 2 for all of the conditions tested here. The substrates used were carefully cleaned glass slides. The coating was performed at 4000 rpm spin coating and the films dried at 100 ^{o}C overnight. Surfactant removal was achieved by solvent extraction by Soxhlet system in HCl / Ethanol mixture several times to facilitate template removing, then calcination in air under static conditions at 550 ^{o}C for 6 h.

2.2 Characterization

Nanoporous silica materials were evaluated by High Resolution Transmission Electron Microscopy-Electron Diffraction (HRTEM-ED) Philips using an accelerating voltage of 200 kV and EMS software for electron diffraction analysis and TEM image simulation by using Bloch wave method was used to perform the morphology of the samples. The Brunauer–Emmett–Teller (BET) surface area was measured at 60 ^{O}C on Nitrogen adsorption isotherm apparatus USA. The samples were outgassed for 12 hrs. at 300 ^{O}C. Photo Acoustic Spectroscopy has been used to characterize the ordering of the structure in different depth in the thin films prepared.

3. Results and Discussion

3.1 Nitrogen Adsorption-Desorption Isotherms

Table 1 shows the results obtained from Nitrogen adsorption isotherms at 77 K to estimate the porosity of mesoporous films; due to its ability in reducing uncertainty related to equipment dead volume. Total surface areas of the films were measured by Kilven equation without any corrections. Films were crushed and but inside the instrument after calculating weight of mesoporous silica thin film separately. Powders samples with the same molar ratios have synthesized with the same molar ratios of thin films and measured as a

reference samples. The average pore size of the first film is wider than the second one and also, the average pore volume of the first film is bigger than the second film as listed in Table 1 . Figure 1 shows Nitrogen isotherms of the two films indicate mesoporous structures with type *IV* isotherm and H2 Hysteresis. Type H2 was attributed to a difference between condensation and evaporation processes occurring in pores with the narrow necks and wide bodies (often referred to as "ink-bottle" pores).

Pore sizes distribution (PSD) calculated of the two films were according to BJH method, and the results are two sharp peaks of distribution of the two films at pores sizes 4, and 3 nm for the first and second film, respectively as shown in (Fig. 2).
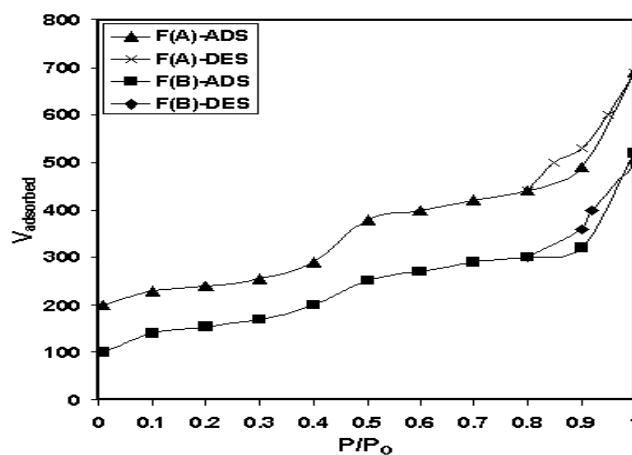

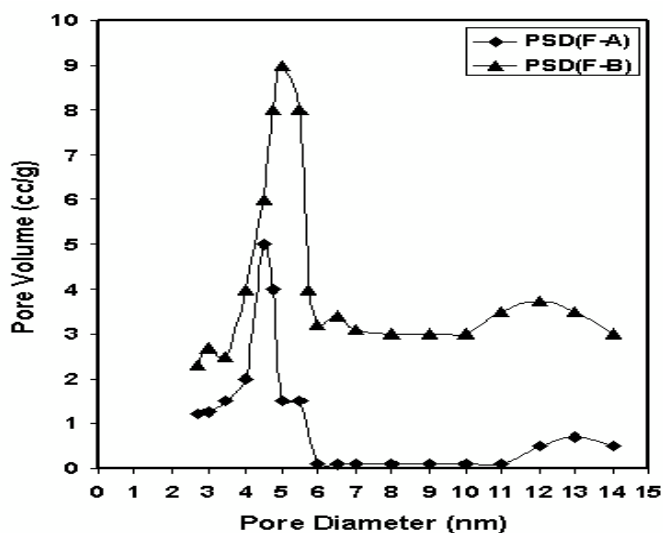**Figure 1**. N2 adsorption-desorption isotherms of Films (A) and (B)

Figure 2. Pore size distributions (PSD) of Films (A) and (B)

Table 1. N_2 adsorption isotherms of the two thin films samples

Average Pore Volume (V_p) (cc/g)	Average Pore Diameter (D_p) (nm)	Total Surface Area (S_{BET}) (m^2/g)	Sample No.
0.9	4	800	1
0.8	3	670	2

3.2 High Resolution Transmission Electron Microscopy (HRTEM)

High Resolution Transmission electron microscope of the films A, and B are shown in (Figs. 3 and 4) respectively. It is obvious that the first film is more ordered than the second one, and that means the increasing in surfactant concentration affected on the thin film produced, where increasing surfactant concentration helps in changing the assembly processes and gelation times.
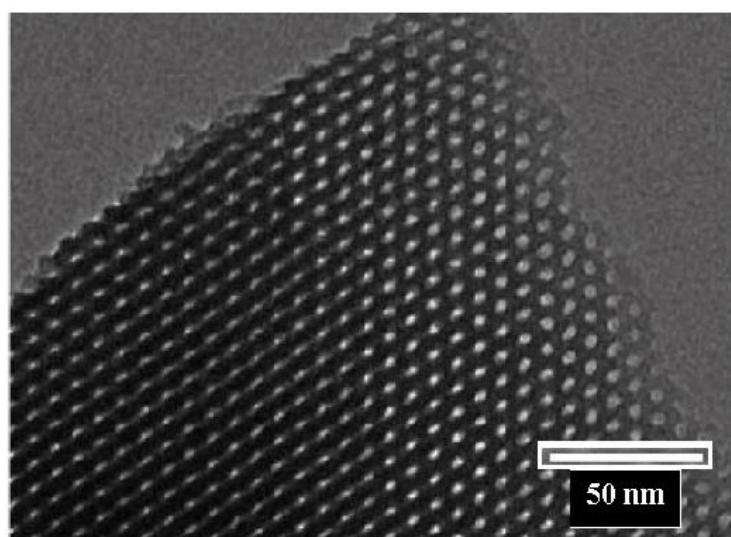

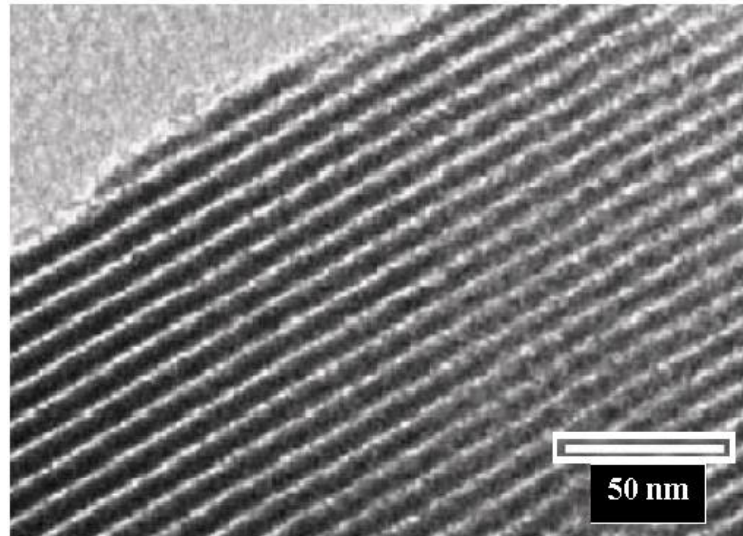**Figure 3**. HRTEM of Film (A) with surfactant concentration X = 0.13

Figure 4. HRTEM of Film (B) with surfactant concentration X = 0.2

3.3 Photoacoustic Spectroscopy (FT-IR (PAS))

Measuring FT-IR spectra as a function of depth is desirable for analysis of layered and gradient composition samples. PAS provide variable sampling depths but often cannot measure as deep as is desired, are susceptible to spectral interferences and do not directly provide layer-by- layer spectra. Microtoming of samples to get layer-by-layer depth information has been a useful method for avoiding these limitations but requires handling of extremely delicate slices and expensive equipment. Microtoming is also only applicable to materials that can be sliced. The MTEC MicroLap System provides a cost-effective alternative   to microtoming that avoids   handling   of   slices,   provides layer-by-layer spectra with depth resolution on a micrometer scale, and is applicable to nearly all planar materials. FT-IR spectra are measured layer-by-layer prior to abrasive removal of each successive layer of material. Measurements   are   made   by attaching the sample to a lapping puck, zeroing a micro-gage, measuring a spectrum of the top layer by PAS, removing several micrometers of material with the micro-lapper, and repeating the cycle. MicroLap can be used to depth profile materials that are difficult to microtome such as coatings on paper. Figure 5 shows typical MicroLap FT-IR PAS spectra of the 2 thin films layers to create the profile plots. The spectra were measured at $8\ cm^{-1}$ resolution and 20 kHz mirror velocity. The plot shows that a and b for the first and second film respectively at two different depths in the two films are very similar, and that indicates the ordering of the structures in the two films.
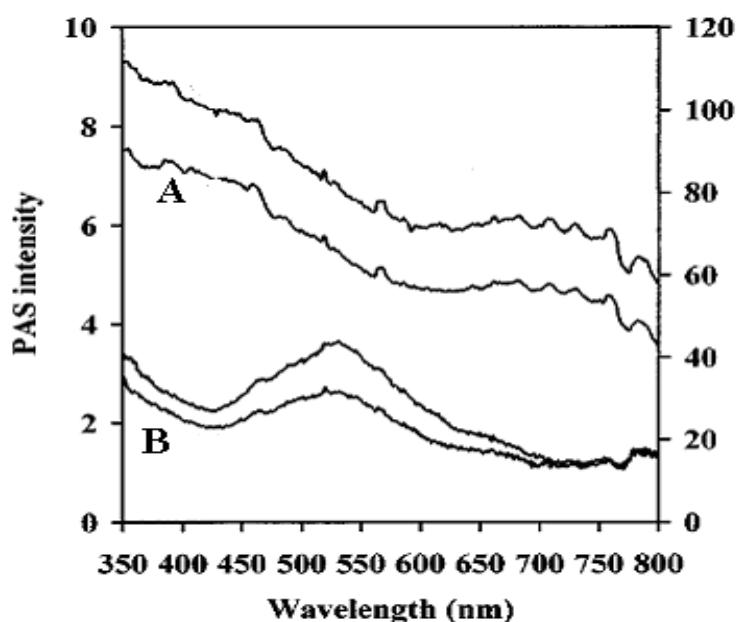
Figure 5. FT-IR PAS spectra of 2 Thin Films layers of Mesoporous silica on glass substrates, (A) for the first Film in 2 different depth; and (B) for the second Film in 2 different depth

4. Conclusion

Mesoporous silica thin films synthesized by using TEOS as a silica source and CTABr as a cationic template. The thin films produced characterized by XRD, Nitrogenadsorption-desorption isotherm, HRTEM, two thin films (A) with 2D structure, and (B) with 3D structure with the same molar ratios but different surfactant concentrations have been prepared, where, the pore sizes of the two thin films were 3 and 4 nm, respectively. Photoacoustic technique was used to determine the ordering of the structures, and the structuring order was very obvious in the two thin films prepared.

Acknowledgments

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