Self-Assembled Process for the Preparation of Ultra-thin Zeolite Films

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(Received January 9, 1998; CL-980018)

A simple and effective process of preparing ultra-thin zeolite films on a silicon substrate is described. The starting material was a stable colloidal dispersion of TS-1 zeolite particles with a size of 50 - 100 nm. The silicon wafer is placed in a 20 mM solution of hexanoic acid in water at pH = 3. When the colloidal dispersion is added, the adsorption of the hexanoic acid molecules onto the zeolite particles causes them to deposit on the silicon wafer to form a thin layer with a thickness of about 103 nm.

Zeolites are an important class of porous inorganic oxides that have wide applications in industry for separation and catalysis. Thin films of zeolites can be used as highly selective membranes, chemical sensors, electrodes, and optoelectronic devices. There are a variety of techniques to fabricating zeolite films, including dip-coating, spin coating, sputtering, and laser ablation.[1] Recently, Yan and Bein successfully used self-assembled thiol-silane monolayers to fabricate zeolite Y on gold surface for application as chemical sensor.[2] In addition, after first introduction by Decher, self-assembly techniques using electrostatic interaction between colloidal nanoparticles and adsorbed polyelectrolytes in the fabrication of ceramic thin films have been intensively investigated by J. Sterte, T. E. Mallouk, etc.[3] Although their methods were successful in preparing ceramic films, the investigation for a new method using a van der waals interaction for the fabricating ceramic thin films may be plausible to extend the known self-assembly techniques.

We have found that hexanoic acid can be adsorbed by inorganic oxides to form self-assembled arrays at the substrate-water interface.[4] When hexanoic acid is adsorbed on the surface of a substrate as well as that of dispersed zeolite particles, the hydrophobic interaction in an aqueous medium may be sufficient to cause the zeolite particles to deposit on the substrate to form a thin film on its surface. Here we describe a simple and effective process to prepare ultra-thin zeolite films by depositing zeolite nanoparticles from a colloidal dispersion onto a substrate *via* self-assembled arrays of hexanoic acid on the solid surfaces (Figure 1).

The zeolite system used in our work is TS-1 zeolite, which can be prepared as stable colloidal dispersions of nanoparticles usually from 50 to 100 nm in size with 95% crystallinity.[5] When the TS-1 zeolite particles were redispersed in deionized water, no precipitation was observed due to the Brownian motions of the nanoparticles.

IR-transmittable Si wafers were used as the substrate for fabricating the TS-1 zeolite films. They were cut to 1 cm x 1 cm squares, cleaned by sonicating in hot water, then methanol, and finally 1 : 1 methanol/toluene, followed by rinsing with deionized water. The cleaned silicon wafer plates were kept in deionized water. The fabrication of TS-1 zeolite thin films on the silicon wafer involves following steps: (i) immersion of a silicon wafer into a 2 m*l* aqueous solution of 20 mM hexanoic acid[5] for 30 min at a constant temperature ranging from 25 to 70 ℃; (ii) addition of 0.02 wt% of TS-1 zeolite colloidal solution (3 m*l*), keeping the system at the same temperature for 6 more hours (the dispersed nanoparticles coagulated and ultimately settled out of solution after 5 h); (iii) gentle washing of the plates by soaking with slowly stirred deionized water for 20 sec; (iv) drying at 70 ℃ in air for 1 h. The resulting ultra-thin TS-1 films deposited on Si wafers were characterized FT-IR, SEM, XRD, and AFM.

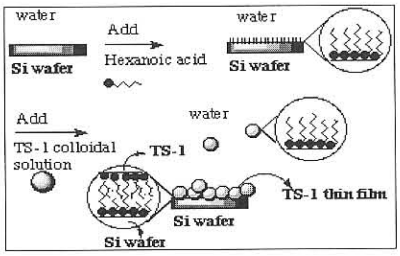

Figure 1. A schematic representation of the method for the formation of an ultrathin film TS-1 zeolite films on a Si wafer.

There are two essential features in our process of forming ultra-thin layers of zeolite particles on a silicon substrate. The first is the use of the colloidal dispersion of TS-1 zeolite nanoparticles, which have the shape of spheres with an average size of 50-100 nm,[6] and the second is the formation of self-assembled arrays of hexanoic acid molecules on the surface of these particles as well as the silicon wafer. To confirm the critical role of hexanoic acid in this process, we carried out the experiment under various conditions (Table 1). Without hexanoic acid, no coagulation and film formation of TS-1 zeolite were observed. In the presence of hexanoic acid, coagulation and film formation were observed only at pH < 5. The results are explained in the following.

The adsorption of hexanoic acid from an aqueous solution onto the surface of an inorganic oxide is highly dependent on pH. It obeys the Langmuir equation and is a chemisorption process.[7] Usually, monolayers of hexanoic acid molecules are formed on the oxide surface, although bilayers may be present under special conditions.[4] At pH > 6, the solid surfaces are negatively charged; hexanoic acid (pKa = 4.88) is largely dissociated and would not be well adsorbed on the surface. At lower pH, the hexanoic acid molecules can be adsorbed onto the the zeolite TS-1 nanoparticles to form monolayers. The

Table 1. Conditions for the coagulation and deposition of TS-1 zeolite nanoparticles onto a silicon substrate[a]

Hexanoic Acid (mM)	TS-1 zeolite (wt%)[b]	pH[c]	Temp.(℃)	Rxn. hour	Coagul -ation	Film formation
20	0.02	3	70	6	O	O
20	0.02	6	70	6	X	X
20	0.02	9	70	6	X	X
20	0.04	3	70	6	O	O
20	0.2	3	50	10	O	O
20	0.2	3	25	48	O	O
0	0.2	3	70	48	X	X
0	0.2	6	70	48	X	X

[a]The final volume of all samples was about 5 m*l* [b]TS-1 particle (g)/ H_2O (g) x 100.

[c]pH levels were adjusted using 6 M of both HCl and KOH solutions.

surfaces of the silicon substrate is covered with -OH groups and can adsorb hexanoic acid molecules to form a monolayer as well. Because the hydrophobic nature of the surfaces reduces the stability of the colloidal dispersion, the nanoparticles would slowly deposit on the surface of the substrate, and would also coagulate into larger particles and settle out of the aqueous phase. Since the hexanoic acid molecules adsorbed on the substrate probably form an extensive monolayer, the first layer of TS-1 zeolite particles deposited on the substrate would cover the surface rather uniformly. However, subsequent layers would be less uniform due to the different sizes and shapes of the TS-1 zeolite particles (Figure. 2 and 3).

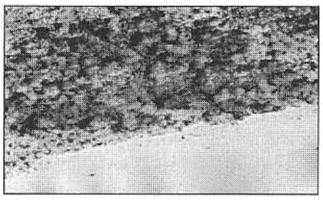

Figure 2. The optical microscopy (x 500) image in the interface region of TS-1 zeolite thin films and bare Si wafer.

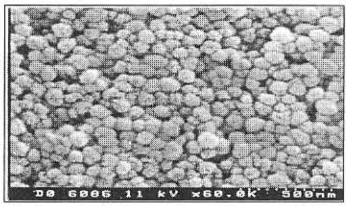

Figure 3. The scanning electron microscopy (SEM) surface image of a deposited TS-1 zeolite film

The approach of using a colloidal dispersion to facilitate the adsorption of ceramic nanoparticles to an oppositely charged surface has been reported by many groups.[3] In their work, a delicate balance of the adsorption and desorption equilibria between nanoparticles and adsorbed polyelectrolytes was kept to minimize their desorption on rinsing.[3] Our process does not have the problem of desorption on rinsing because the hexanoioc acid molecules adsorbed on the surfaces of the zeolite particles and the substrate have fairly strong interaction with the solid surfaces. The TS-1 zeolite particles are held on to the substrate surface and to one another by bilayers of hexanoic acid molecules, one layer on each side. However, the adhesion is not strong, and the deposited film can be removed with a Scotch tape. To overcome this problem, the sintering process at 750 ℃ is under investigation by us to increase the adhesion.

The FT-IR spectra and X-ray diffraction (XRD) results of the films are identical to the TS-1 powders. In the FT-IR spectra, two peaks characteristic for TS-1 zeolite appear at 950 cm^{-1} and 800 cm^{-1} for both the films and powders. The XRD pattern of TS-1 zeolite films is identical to the TS-1 zeolite particles but the intensity of peaks is weaker. XRD results show that the TS-1 zeolite film has the MFI-type structure with an orthorhombic symmetry, which is the same as that reported previously.[6] The thickness of the films was determined by routine AFM scanning at the interface between one part with a deposited film and another part from which the film was removed (Figure 4). From a slice with a 30 μm x 30 μm cross section, the thickness was found to be about 103 nm for the deposited TS-1 films.

Our results show that ultra-thin and dense zeolite films with the thickness of several nanoparticles can be formed on a silicon substrate through the process of self-assembly of hexanoic acid molecules on the two kinds of surfaces. This technique is simple and inexpensive. Large poreless, smooth, thin films can be produced. The thickness of the film can be increased by repeating the film deposition process, and further control of the film thickness by varying the experimental condition is being studied. It is hoped that this method would become valuable in the preparation of chemical sensors as well as other systems requiring thin ceramic films.

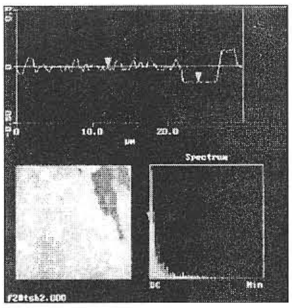

Figure 4. AFM topography (30 *u*m x 30 *u*m) of a TS-1 zeolite film deposited on a Si wafer with a cross-sectional analysis in the interface region.

This work was supported by a grant from Korea Sience and Engineering Foundation (971-1104-023-1,1997).

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