Ultra-thin zeolite films prepared by spin-coating Silicalite-1 precursor solutions

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Received 9 July 2003; in final form 15 September 2003

Abstract

A procedure has been developed to prepare ultra-thin zeolite films supported on Si(1 0 0). Films were prepared by spin-coating a solution of Silicalite-1 zeolite precursors diluted in ethanol, followed by hydration in water vapour and heating to 60 °C. High resolution transmission electron microscopy analysis of sample cross-sections shows that the surfaces are both smooth and continuous, and films of approximately 2 and 15 nm thickness were prepared by varying the precursor dilution factor. Electron diffraction analysis shows that the 15 nm film is an amorphous arrangement of Silicalite-1 precursors. Atomic force microscopy measurements confirm that the surface is smooth over a range of several microns.
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1. Introduction

Microporous (pore diameter <2 nm) and mesoporous (2–50 nm) silica and aluminosilica thin films have potential applications as supports for both catalysts and chemical sensors, and also as insulating and dielectric layers in the semi-conductor and microelectronics industry. While numerous microporous zeolite films of varying magnitude and pore structure have been prepared [1], truly ultra-thin films i.e. those with thickness in the region limited only by the zeolite unit cell dimension have not been reported. The synthesis of a smooth (roughness <1 nm) film/membrane of this size is highly desirable, as the corresponding throughput for a given reaction should be significantly enhanced relative to existing films. Metal nanoparticles encapsulated in mesoporous silicates have recently been synthesised as model porous catalysts with a view to studying and improving reaction selectivity [2]. An ultra-thin zeolite film of thickness <5 nm would be an ideal model zeolite structure for a wide range of novel surface science studies, as charging problems associated with analysis would be eliminated.

A number of methods have been employed to synthesise zeolite thin films. *LTA* (*Linde Type A*)

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is a three-dimensional small pore molecular sieve with eight membered ring openings (diameter ~0.41 nm) and possesses cubic symmetry. Films were prepared by chemical anchoring of LTA crystals on (3-mercaptopropyl)trimethoxysilane coupling layers bound to the surface of a quartz crystal microbalance. Additional hydrothermal treatment was performed and films with thickness 65–980 nm were produced [3]. These materials were subsequently used as humidity sensors. Silicalite-1 contains intersecting systems of 10 membered ring pores, one straight (about 0.53 nm) and one sinusoidal (about 0.51 nm). The three-dimensional pores have orthorhombic structure and are classified as *MFI* (Zeolite *S*ocony *M*obil *Fi*ve ZSM-5) type materials. Silicalite-1 films have been prepared by in situ crystallisation on stainless steel and aluminium alloy substrates. The *b*-axis of the zeolite was aligned perpendicular to the substrate surface and the film thickness was approximately 300 nm [4,5].

The method of spin-coating a solution of zeolite particles onto a smooth substrate surface offers the possibility of forming a smooth layer. It should also allow effective control of the film thickness by varying the concentration of solution and the spin-on rotation rate. This method requires a short synthesis time and, relative to in situ crystallisation, is suited to semi-conductor manufacture; films produced in this manner may therefore be applicable as microelectronic devices. This would also be a simple method of preparing ultra-thin silica films for use as model supports, relative to metal evaporation and oxidation in UHV conditions [6]. Microporous/mesoporous composite films, thickness 100–400 nm, were synthesised by spin-on of solutions containing Silicalite-1 nanoparticles and hexagonally ordered mesophase silica-surfactant assemblies [7]. Films containing Silicalite-1 only were also produced with similar dimensions by the same method. Analysis of these materials showed that smooth continuous films were not formed. Other samples prepared by spin-on of Silicalite-1 zeolite particles showed similar film thickness and unfavourable surface features [8,9]. The surface roughness is not surprising, since the structure is determined by the particle size, typically 15–60 nm, of the zeolite crystals. A smooth film should therefore be achieved by using the smallest possible zeolite particles. Martens and co-workers have identified the intermediates formed during the early stages of Silicalite-1 formation. The findings are described in detail elsewhere [10–12]. Briefly, the condensation of tetraethyl orthosilicate (TEOS) was studied in an aqueous solution of tetrapropylammonium hydroxide (TPAOH). Among the numerous zeolite nanoparticle structures detected in the resulting 'clear solution', 'precursor' species, containing a single TPAOH molecule surrounded by 33 Si
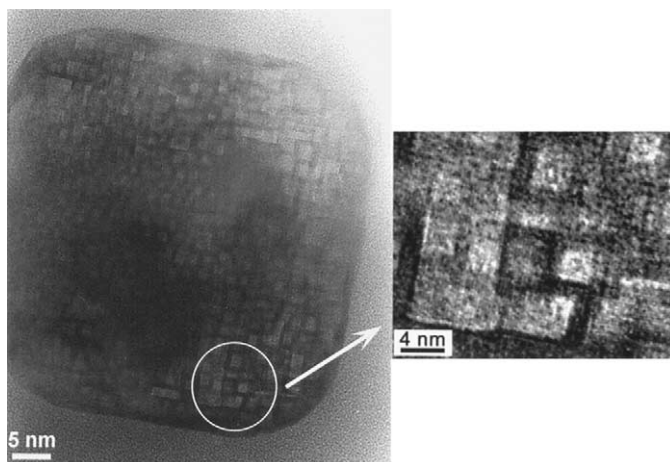

Fig. 1. TEM images of MFI zeolite nanoslabs spread on a grid [10].

atoms, were predominantly observed. These then combine to form $1 \times 4 \times 4$ nm^3 'nanoslabs', which agglomerate further to give bulk Silicalite-1. Fig. 1 shows an image of these nanoslabs, which have been spread on a grid for TEM analysis [10]. Some of the nanoslab particles have agglomerated but the 4×4 nm^2 surface is nonetheless clearly visible. Wang et al. have prepared a 300 nm thick film by spin-coating a clear solution of this type with a range of nanoparticle sizes onto a silicon wafer [13]. However, no meaningful topographical data is provided to confirm surface smoothness.

Here, we report the synthesis of a 2 nm thick zeolite film supported on Si(100). The film is smooth and was prepared by spin-coating a solution of Silicalite-1 'precursors' diluted in ethanol. A 15 nm thick film was prepared in a similar manner by using a more concentrated solution.

2. Experimental

2.1. Solutions

'Clear solution' was prepared by adding 37.32 g TEOS (Acros, 98%) to 32.13 g aqueous TPAOH (Fluka, 40%) with stirring. After 10–15 min, a solution of MFI type zeolite '*precursors*' was formed. Solutions were then prepared by ×1000 (solution A) and ×100 (solution B) dilution with absolute ethanol.

2.2. Spin-coating procedure

2×2 cm^2 Si(100) wafers were cleaned by heating in piranha solution of 70 vol.% concentrated H$_2$SO$_4$ and 30 vol.% H$_2$O$_2$ (35 vol.%) at 90 °C for 30 min. After removal, each substrate was washed with de-ionised water and then stored in de-ionised water. For zeolite film preparation, the substrate was placed in an Erichsen spin-coating apparatus, and an angular rotation rate of 1500 rpm was employed for 30 s to remove excess water. Films were prepared by adding a sufficient quantity of precursor solution to completely cover the stationary substrate surface, typically 4–6 drops, and the sample rotation was conducted immediately at 1500 rpm for 30 s, using a spin-up

rate of 300 rpm s^{-1}. Solutions A and B were used to prepare films A and B respectively. The samples were then placed in a vacuum oven overnight, after which they were exposed to water vapour in a 'hydrator' (sealed vessel containing saturated aqueous ammonium chloride) at 18 ± 1 °C for 24 h. Finally, all samples were cured at 60 °C for 24 h.

2.3. High resolution transmission electron microscopy and atomic force microscopy

Transmission electron micrographs and electron diffraction patterns were recorded on a Philips CM200 FEG microscope, operated at an accelerating voltage of 200 kV. Plan-view samples, i.e. 3 mm diameter disks with electron transparent regions were prepared from the 0.5 mm thick Si(100) wafer covered with the film by cutting and thinning. A 3 mm diameter disc was cut from the catalyst using an ultrasonic disk cutter (Gatan). The sample was then thinned mechanically using a polisher to 200 μm thickness and then to near transparency by ion beam edging. This resulted in a concave hole on the backside of the sample, making the center of the sample the thinnest part. Finally, the sample was thinned by bombardment with Ar$^+$ at 5 kV and a 5° angle, creating an electron transparent region in the center of the sample. Cross-sections were prepared by cutting the sample along a low-index direction, glueing the two film sides together, making another cut and further thinning as described above.

Atomic force microscopy (AFM) measurements were conducted on the as-prepared samples using a Topometryx DMX2010 instrument in contact mode.

3. Results and discussion

3.1. AFM

The samples were not calcined prior to analysis, therefore the TPAOH template remains in the zeolite films reported here. Fig. 2a shows an AFM image of the surface of film A, and a detailed analysis of the surface topography is provided in Fig. 2b and Table 1. Overall, the surface is
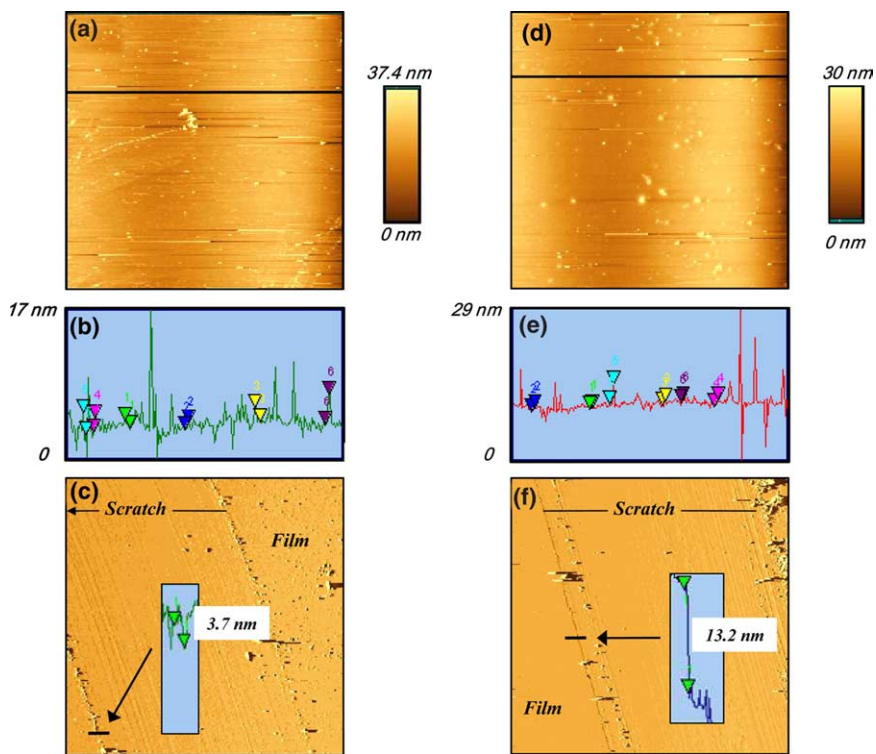
Fig. 2. AFM images of zeolite films, analysis area 70×70 μm: (a)–(c) film A, (d)–(f) film B, (a) and (d) are topography images. Scratched films (c) and (f) are presented in CDM and include film thickness measurements.

Table 1
AFM topographical data for films A and B

Sampling number	Film A (nm)	Film B (nm)
1	0.84	0.35
2	0.62	0.68
3	1.52	0.68
4	1.59	1.13
5	2.57	3.72
6	3.31	0.45

extremely smooth and there are large areas where the roughness of the surface varies by less than 1 nm. This feature typically extends uninterrupted over a range of 10 μm. There are also a number of locations on the film, seen as 'bright spots', corresponding to dust particles, where deviations from the baseline readings are observed. The film thickness was estimated by scratching the zeolite with a needle, and the corresponding images are presented in cantilever deflection mode (CDM) for

clarity. The difference in height between the smooth zeolite surface and the bottom of the scratch was then taken as a measure of the film thickness. These values were calculated from topographical recordings and are included in Fig. 2. A number of scratches were made and the results for film A, Fig. 2c, suggest that a film is present with a thickness in the range 2–4 nm. The film residue, which forms as a result of the scratch, is visible in the vicinity of the scratch/zeolite interface. Analysis of film B, Fig. 2d and e, also confirms the presence of a smooth zeolite layer. The data confirm that the surface roughness varies by less than 1 nm over a distance of 20 μm. AFM studies on the scratched film, Fig. 2f, showed that a film is present with a thickness 13 ± 2 nm.

It is well known that silicon wafers are covered with a thin layer of amorphous silica. Given the dimensions of this native oxide layer, it is difficult to image by TEM. However, using ellipsometry,

the oxide layer on a silicon wafer treated with piranha solution was determined to be approximately 1 nm [14]. Therefore, in order to determine if the native oxide layer contributes to the zeolite film thickness values, an attempt was made to scratch a clean silicon wafer with a needle. AFM results did not show the presence of a scratch. This implies that the native oxide layer and the underlying silicon substrate are not altered during scratching and subsequent AFM analysis. Therefore, the AFM height analysis (difference between zeolite surface and scratch base) is an accurate representation of the zeolite film thickness.

3.2. HR-TEM

High resolution TEM images of sample cross-sections are shown in Fig. 3. Film A, Fig. 3a, is determined to be ~3 nm thick. The film produces a weaker contrast than the Si substrate and the glue, and can be observed over several microns along the interface. The native oxide layer is indistinguishable from the zeolite film, and therefore the 3 nm film image contains a contribution from the native oxide. Assuming the thickness of the native oxide layer is 1 nm [14], the actual dimension of the zeolite film is 2 nm. To our knowledge, this is the thinnest zeolite film which has ever been reported. The higher magnification inset shows an atomically resolved image of the interface area. Although the Si lattice can be resolved, the presence of the zeolite film is less obvious at high magnification. TEM analysis of nanoslabs showed that despite using a defocused electron beam at low magnifications these particles survived for only a few seconds during analysis [10]. Therefore, we cannot exclude that the film decomposes under the high intensity electron illumination used for atomic resolution imaging. The image for sample B, Fig. 3b, clearly shows that a film of uniform thickness 15 nm was formed with the inset again showing the Si lattice in high magnification. The glue has apparently detached from the zeolite film during preparation (the zeolite film and glue can be easily distinguished since the carbon-based glue does not show a Si signal in energy-dispersive X-ray microanalysis (EDX)). The film is continu-
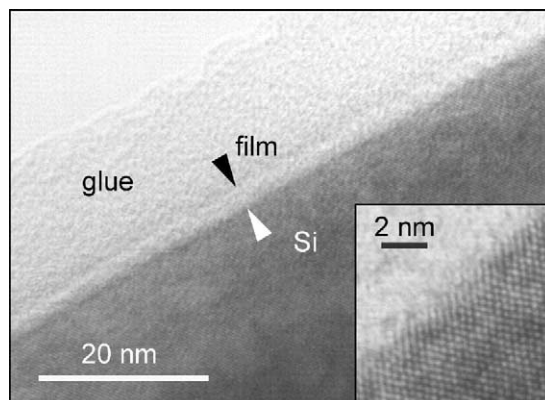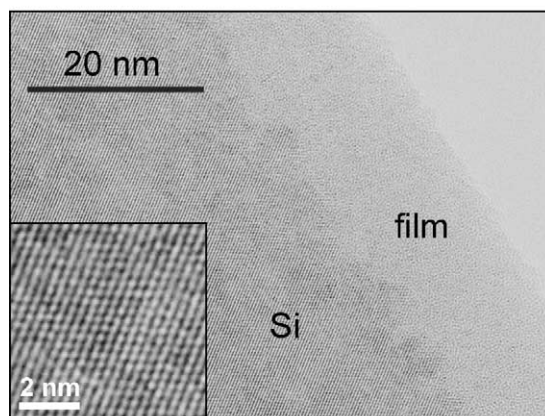
Fig. 3. TEM cross-section images (a) 2 nm film A and (b) 15 nm film B. The interface area of film A and the atomically resolved substrate of B are shown as insets.

ous and uniform, and breaks or inconsistencies were not observed. Overall, these results are in excellent agreement with AFM.

For the 15 nm film B, plan-view TEM samples were also prepared by thinning and ion-milling. Fig. 4 shows plan-view TEM images and corresponding electron diffraction patterns recorded at various distances from the central hole. The image in Fig. 4a was recorded at the thinnest region, i.e. the edge of the sample, where the influence of the underlying Si substrate should be smallest. However, the electron diffraction pattern, Fig. 4b, exhibits diffuse rings characteristic of an amorphous Si structure. ($\approx$0.3 and 0.17 nm interplanar spacings). The structure of the film is therefore believed
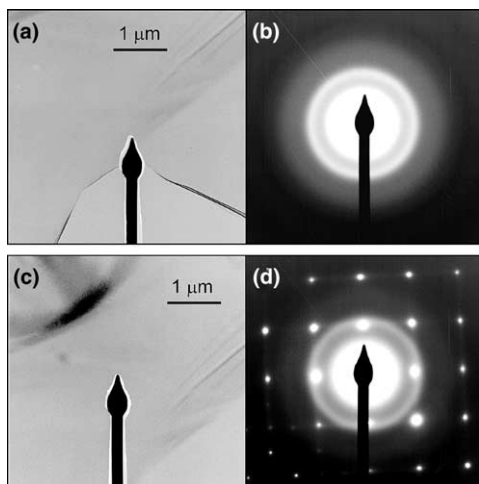
Fig. 4. TEM plan view images and electron diffraction patterns of 15 nm film B. (a) and (b) correspond to the zeolite film only, (c) and (d) correspond to the zeolite film and silicon wafer.

to be an amorphous arrangement of zeolite precursor particles. It is likely that the 2 nm film has a similar structure. Fig. 4c was taken at a location where both the film and silicon wafer are present, and diffraction spots characteristic for silicon(1 0 0) wafer are observed.

The total surface area of a crystalline Silicalite-1 film of 2–15 nm thickness was calculated to be under 1×10^{-4} m^2, which is below the detection limit (0.1–1 m^2) required for an accurate measurement by gas adsorption. Since the calcined amorphous films would have even lower total surface areas than that of the proposed Silicalite-1 film, a surface area measurement was not conducted.

4. Conclusion

2 and 15 nm ultra-thin zeolite films have been successfully prepared by spin-coating solutions of MFI type zeolite precursors on a silicon wafer. The thickness was controlled effectively by adjusting the dilution factor of the zeolite solution. The films are smooth and continuous, and do not contain any visible breaks or inconsistencies. The dimensions of the 2 nm zeolite film are such that it is suitable as a model catalyst for surface science studies.

Acknowledgements

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