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Zeolite microtunnels and microchunnels

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Using a new fabrication strategy, novel, self-enclosed microporous silicalite-1 zeolite microtunnel and microchunnel architectures were successfully prepared.

Microporous, crystalline zeolite and molecular sieve materials find applications as catalysts, adsorbents, ion-exchangers and membranes.[1] Molecules and clusters can reside within the zeolite cages at well-defined spatial locations imparting the material with many unique electronic and opto-electronic properties.[2] Zeolites and molecular sieves also host the synthesis of many advanced materials, such as nanostructured semiconductor clusters, single-wall carbon nanotubes and quantum wires.[2–4] The incorporation of these materials in microsystem architectures has been the focus of recent researches. Zeolite coatings and films have been successfully grown onto flat and micropatterned silicon substrates using various synthesis methods.[5,6] The directed growth of structurally-engineered zeolites within the confined space of microfabricated channels has been successfully demonstrated for different MFI-type zeolites (*i.e.*, Sil-1, ZSM-5 and TS-1) for applications in catalytic microreactors for chemical production and zeolite micromembranes for gas permeation.[7–10] This paper reports on the fabrication of novel, self-enclosed zeolite-based microtunnel and microchunnel structures. Enclosed channel structures fabricated using patterned sacrificial layers (*e.g.*, photoresists) as temporary molds on surfaces of flat substrates (*e.g.*, silicon) are often referred to as microtunnels, whereas the enclosed channels *etched* onto substrates through the microporous zeolite layer will be referred to as a microchunnels.

Zeolite microtunnels were fabricated onto silicon wafers using the following procedure. A 6-μm thick layer of polymer resist (AZ4620) was spin-coated onto the silicon wafer, and micropatterned using standard photolithography techniques.[11] The pattern consists of one hundred parallel lines with a linewidth of 100 μm and line spacing of 100 μm. The length of the lines is 20 mm. The pattern was coated with poly(diallylmethylammonium chloride) (PDMAC) polymer electrolyte onto which was adsorbed a layer of nanometer sized zeolite seeds (*i.e.*, 120 nm TPA-Sil-1).[12] A layer of silicalite-1 film was grown onto the seeded pattern following hydrothermal synthesis in a mixture containing tetraethylorthosilicate, tetrapropylammonium hydroxide and water (40:10:20 000) at 398 K for 48 h. A Teflon-lined stainless steel autoclave with a reactor volume of 150 cm^3 was used in the zeolite crystallization and growth. The tetrapropylammonium ions residing within pores of the as-synthesized zeolites were removed using oxygen plasma (RF = 400 W, 473 K). Once the zeolite pore channels were free of the occluding organic template molecules, the polymer resist can then be etched and removed by the oxygen plasma. The treatment condition is important since the escape of the gaseous products from the polymer etching is through the microporous zeolite walls of the microtunnels. The etching rate must be kept slow to avoid gas build up from damaging the microtunnels. The procedure for preparing zeolite microchunnels is different. A layer of Sil-1 zeolite film was first grown onto the surface of the silicon substrate. The zeolite was then coated with metal protective layer (*i.e.*, TiW-Au layers) and micropatterned using a standard procedure.[11] After selectively etching away the metal from the developed pattern, the exposed zeolites were treated under oxygen plasma to remove the organic template molecules. The sample was then immersed in a wet etchant (*i.e.*, 25 wt.% tetramethyammonium hydroxide–water solution) to etch away the silicon underneath the exposed zeolite pattern, and thus create a microchunnel architecture. The experiment indicates that the etching rate of silicon through a microporous zeolite barrier of 1 μm is about 20 times slower, and this is mainly due to the mass transfer resistance through the zeolite layer.

Fig. 1(a) and (b) display the architecture of zeolite microtunnels fabricated onto the silicon wafer. The 100-μm wide microtunnels are evenly spaced, faithfully reproducing the line pattern used as a template for the tunnel architecture (Fig. 1(a)). The individual microtunnels are arch-shaped with an average tunnel height and width of 25 and 80 μm, respectively. The shape of the tunnel is caused by swelling of the polymer resist during the hydrothermal synthesis of the zeolite due to both the temperature and the presence of ethanol formed by the decomposition of the organosilicon precursor. The SEM picture in Fig. 1(b) shows that the free-standing zeolite film forming the wall of the microtunnels is thicker (*i.e.*, 20 μm) than the zeolite deposited on the substrate (*i.e.*, 10 μm). However, both zeolite layers are well intergrown and have similar (101) film orientation. Although larger tunnel cross-sections could be obtained by using thicker resist layer, a different tunnel

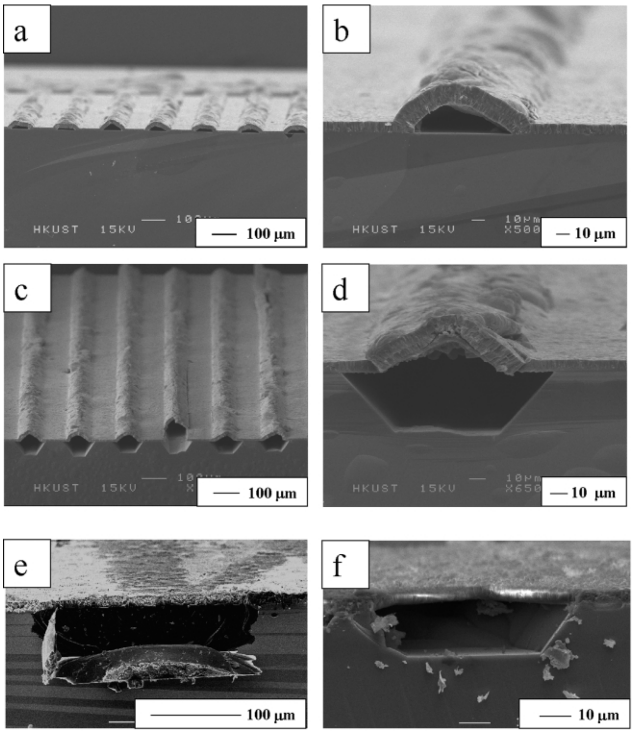

Fig. 1 (a), (b) Zeolite microtunnels with porous silicalite-1 wall supported on silicon; (c), (d) enlarged zeolite microtunnel, (e) 200-μm and (f) 40-μm wide zeolite microchunnels.

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enlargement method based on a variation of the microchunnel fabrication procedure was employed in Fig. 1(c) and (d). The wafer containing the enclosed, zeolite microtunnels was placed in a silicon etching solution. The etchant diffuses through the porous zeolite layer and etches the exposed silicon support beneath the microtunnel. Using this method, an eight-fold increase in the cross-sectional area of the microtunnels was obtained as shown in the figures. The familiar trapezoidal channel produced by the anisotropic etching of (100) silicon wafer is evident in the micrograph (Fig. 1(d)). The etched channel is wider than the microtunnel, since the etchant could also penetrate the zeolite layer deposited onto the silicon. It is important to note that prior to the sectioning of the sample for analysis with a scanning electron microscope (JEOL JSM6300), the zeolite film uniformly covers the entire substrate forming self-enclosed microtunnel structures.

Fig. 1(e) and 1(f), respectively, display large and small zeolite microchunnels fabricated onto the silicon substrate. In both samples, a 4-μm thick, (101)-oriented Sil-1 film was first grown onto the silicon (Fig. 2). The 250 μm (Fig. 1(e)) and 50 μm (Fig. 1(f)) line patterns were transferred onto the zeolite–silicon composite using the fabrication method discussed in the experimental section. The removal of the organic templates from the exposed zeolite line pattern produces a porous zeolite layer through which the etchant can penetrate and dissolve the silicon to form the subsurface channels (*i.e.*, chunnels) of 200 and 40 μm widths. Areas of the zeolite film from which the organic templates have not been removed remain impermeable to the etchant. This enables the subsurface patterning and micromachining of the silicon substrate. The etching rate is slow due to the slow diffusion rates of the etchant and dissolved silicon through the microporous zeolite membrane layer. Although smaller chunnels (< 100 μm) have trapezoidal cross-section, a more irregularly shaped etch cross-section were obtained for chunnels that are wider than 100 μm (*cf.* Fig. 1(e) and 1(f)). This may be due to inefficient removal of etched silicon from the larger microchunnels, which have smaller zeolite membrane area-to-cavity volume ratio.

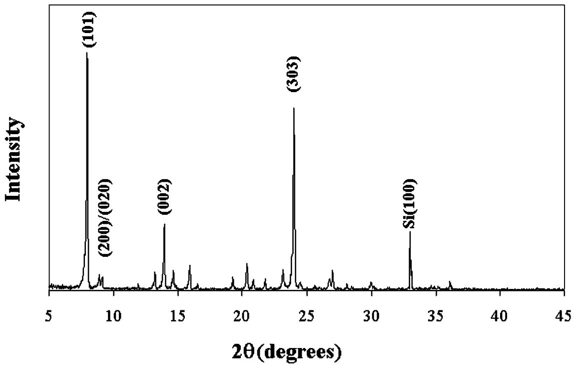

Fig. 2 XRD pattern corresponding to the zeolite microchunnels shown in Fig. 1(e) and (f).

The self-enclosed architecture of zeolite microtunnels and microchunnels is suitable for microreactors and membrane microseparators. The zeolite wall of the microtunnels and microchunnels could function as structural, catalytic or membrane materials, and can actively participate in chemical processes (*e.g.*, reaction and separation) occurring within the microsystem. These architectures could also be useful for microsensors where the zeolite could act as a selective membrane and protective barrier for the sensing device (*e.g.*, electrode). The three-dimensional structure of a zeolite microtunnel is advantageous for microdevices where mass and heat transfers with the surroundings are required (*e.g.*, sensors and miniature heat exchangers). However, the same architecture also made their sealing and integration of other MEMS and computing devices more difficult. Microchunnels with flat surfaces are easier to adapt to most MEMS application, but at the cost of smaller membrane area. Using the microchunnel fabrication strategy, both impermeable and selectively-permeable enclosed cavities could be created for applications in smart micromechanical and bio-chemical sensors. These cavities could also serve as chemical and biological storage and delivery systems for microdevices.

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