

Preparation of Zeolite UTD-1 Films by Pulsed Laser Ablation: Evidence for Oriented Crystal Growth

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Thin films composed of crystalline zeolite molecular sieves have attracted interest because of their potential applications in areas such as separations, catalysis, and sensors.¹ Microporous zeolite molecular sieves offer several advantages over dense inorganic or polymeric thin-film materials which include high selectivity due to uniform pore size, thermal stability, and facile diffusion. Of particular interest are crystalline films that are oriented in such a way that specific pores define the exposed surface. A variety of strategies have been developed for the fabrication of continuous zeolite films.² The deposition and growth of crystals from solution onto a substrate is the most common approach, but this generally results in isolated crystals that must be grown sufficiently large so as to merge and form a continuous film. This aspect can make the preparation of thin films a challenge especially in the nanometer range. Recent efforts in controlling reaction conditions and the use of nanometer-sized seed crystals have improved the quality of synthesized zeolite films and in some cases led to growth of oriented films. For the most part these advancements have been limited to small and medium pore size zeolites such as those with the MFI^{2,3} and LTA topologies.^{4,5} The large-pore one-dimensional channel type zeolite L (LTL) has been crystallized as a continuous membrane, but the crystals are randomly oriented.⁶ We have employed pulsed laser ablation to prepare molecular sieve films. In this process a high-intensity excimer laser beam (KrF*, 248 nm) strikes a pressed pellet of zeolite which generates a plume of ejected particles that deposit on a temperature-controlled substrate. The substrate may be a variety of compositions ranging from polymers to metals depending on the application for the film. This method has several advantages including preparation of continuous films and control of film thickness over a range of several hundred nanometers to a few microns depending on experimental parameters.

In this paper we report the preparation of partially oriented films of the large-pore zeolite UTD-1 via the

laser ablation method. UTD-1 is a high-silica molecular sieve having a one-dimensional (1-D) channel system where the pores are defined by 14 tetrahedral (T) atoms with dimensions of $10 \times 7.5 \text{ \AA}$.^{7–11} Because UTD-1 is the largest pore zeolite known, it is an attractive material for use in thin film applications. Since the structure of UTD-1 involves 1-D channels that run parallel to each other, it would be desirable to fabricate a film where the channels are perpendicular to the substrate. We have found that subjecting laser-deposited UTD-1 films to a hydrothermal treatment results in crystal growth that appears to be partially oriented. The laser deposited and hydrothermally treated UTD-1 films in this study were characterized by X-ray diffraction and scanning electron microscopy.

The all-silica version of UTD-1 was synthesized using the structure-directing agent bis(pentamethylcyclopentadienyl)cobalt(III) hydroxide according the published procedure.^{9,10} Thin films of UTD-1 were prepared via pulsed laser ablation of the as-synthesized zeolite using an excimer laser as previously described.¹² Briefly, the as-synthesized UTD-1 (containing template) crystals were pressed into a solid pellet ~2.5 cm in diameter and placed into a controlled-atmosphere chamber positioned 2.5 cm above a polished silicon wafer substrate. During the deposition the silicon substrate was heated to ~160 °C and a background pressure of O₂ was maintained at 150 mTorr. The UTD-1 pellet was then ablated using the excimer laser (KrF*, 248 nm) with an energy output of 90–100 mJ/pulse and a repetition rate of 10 Hz. Figure 1A shows an SEM of a uniform, continuous as-deposited film derived from UTD-1 that is approximately 650 nm. The as-deposited films appeared to be largely amorphous by powder X-ray diffraction (XRD). This was not unexpected; however, we have found that the laser-deposited surfaces can act as seed layers or nucleation sites for the recrystallization of the film. For example, in the case of the laser-ablated AlPO₄ and MeAPO molecular sieves a posthydrothermal treatment was found to enhance the crystallinity of the deposited films.^{12–17} In most cases the films could be reorganized with little or no increase in film thickness and without growing crystals in solution. Therefore, we decided to hydrothermally treat the laser-deposited UTD-1 films

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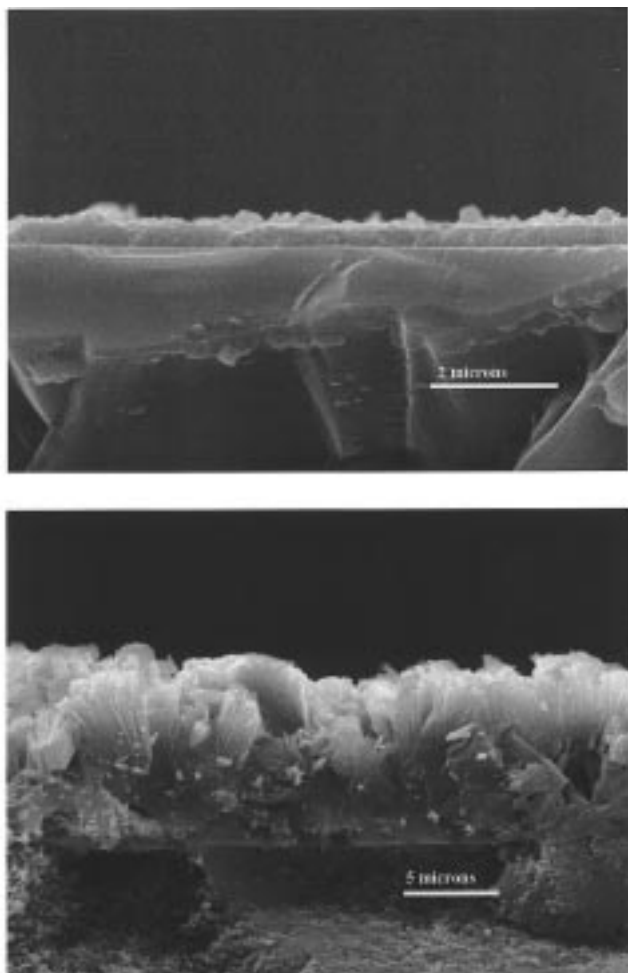


Figure 1. SEM cross-section view of UTD-1 film (A) as-deposited and (B) after posthydrothermal treatment in UTD-1 synthesis gel at 175 °C for 3 days.

in order to improve the crystallinity. The silicon wafers coated with the laser-deposited UTD-1 films were placed in a Teflon-lined Parr reactor containing a UTD-1 synthesis gel at 175 °C for 3 days under static conditions. The silicon substrate was positioned in the Teflon liner tilted at an angle of approximately 60° with the laser-deposited film facing down so as to avoid having material deposit directly from the gel onto the wafer as opposed to reorganizing the as-deposited film surface. After 3 days of hydrothermal treatment, the coated substrate was removed from the reaction vessel and washed with deionized water. A continuous film approximately 11 μm thick had grown from the laser-deposited film as shown in Figure 1B. A nonuniform deposit of UTD-1 also formed on the opposite side of the silicon wafer (not shown). The morphology of the continuous film is similar to that typically observed for bulk UTD-1 crystals which are generally composed of bundles of needles or planklike crystals. It would appear that the aggregates of these plank-shaped crystals radiate up from the laser-deposited surface where the 1-D channels are oriented along the length of the planks (*b*-axis). In contrast, the loosely bound crystals deposited on the reverse side are randomly oriented with the channels largely positioned parallel to the substrate surface. The original laser-deposited film is continuous, but as the crystals were allowed to grow to more than 10 times

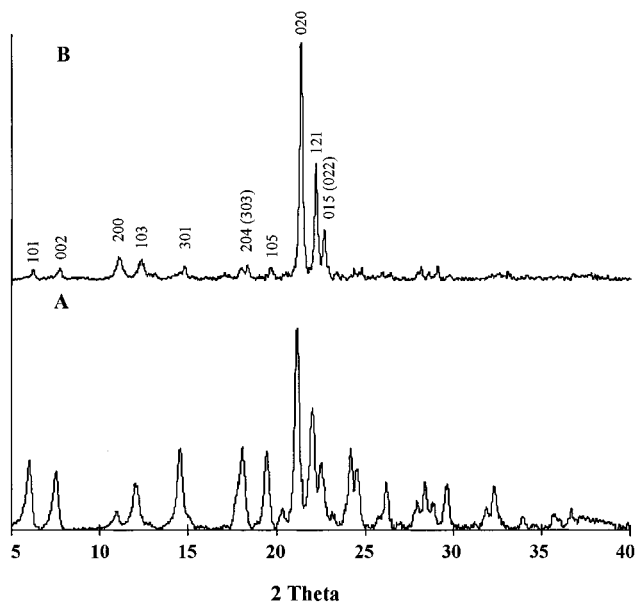


Figure 2. X-ray diffraction patterns of UTD-1 films (A) deposited on the unpolished side of the silicon wafer and (B) grown from the laser-deposited film.

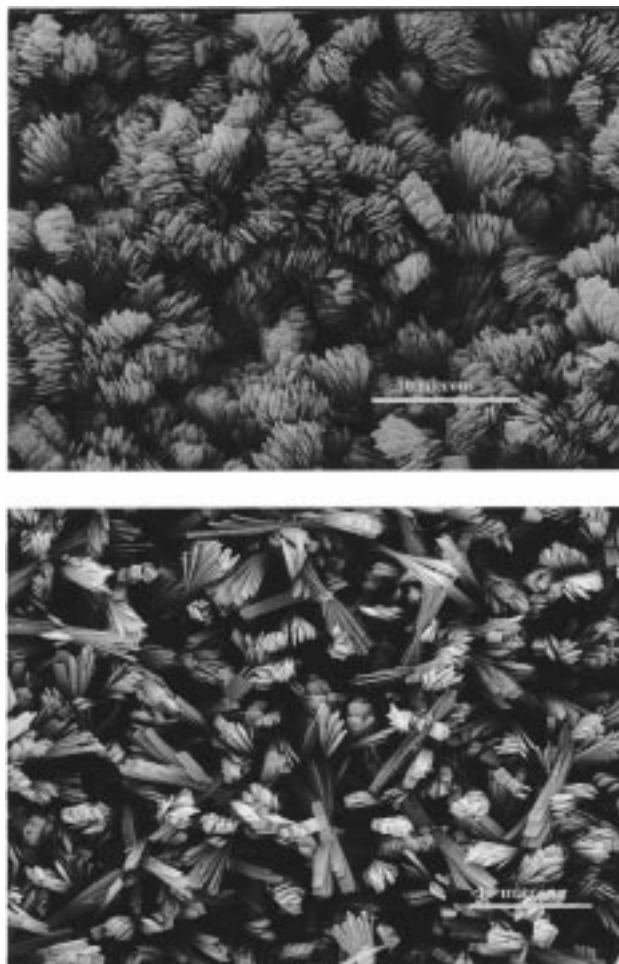


Figure 3. SEM image of UTD-1 polycrystalline films (A) grown from a laser deposited UTD-1 film and (B) grown on a polished silicon wafer.

the thickness, the crystals at the surface separate but maintain the preferred orientation.

The apparent orientation of the zeolite UTD-1 film was surprising but verified by the XRD patterns for each

side of the silicon wafer shown in Figure 2. The thick, nonuniform material coated on the unpolished silicon wafer backside produced an XRD pattern (Figure 2A) comparable to a randomly ordered powder of as-synthesized UTD-1 crystals. In contrast, the diffraction pattern of the UTD-1 film grown from the laser-deposited surface (Figure 2B) shows a dramatic change in the relative peak intensities. In particular, the (020) reflection has increased in intensity while most of the (*h*0*l*) reflections are depressed. This result is consistent with a preferred orientation of the crystals emanating from the laser-deposited surface where the direction of the channels (*b*-axis) is mostly perpendicular to the substrate.

Close inspection of Figure 1B reveals that the edges of the silicon substrate is etched during the hydrothermal treatment at high pH (~pH 11). It is unclear how this may affect the reorganization of the laser-deposited film. However, the silicon wafer has polished and unpolished sides, which might influence the deposition of crystals from solution. Therefore, we conducted a blank experiment where the silicon wafer without a laser-deposited film was placed in a UTD-1 synthesis gel at 175 °C for 3 days. Figure 3A shows the top view of the laser deposited and reorganized film whose cross section is shown in Figure 1B, while Figure 3B shows the film of UTD-1 crystals coating the polished side of a blank silicon wafer. Clearly, in Figure 3B the crystals

are randomly oriented and the film easily flakes off the substrate. In contrast, the UTD-1 film grown from the laser-deposited surface is oriented and well adhered to the silicon surface. It appears that the laser-deposited UTD-1 surface is necessary to grow well adhered and partially oriented films. It should also be noted that the organometallic template must be present in both the target and ablated films in order to grow the oriented UTD-1 film. We might view the laser-deposited film as a reasonable model for nucleation where the zeolite fragments are too small to exhibit long-range order but can reorganize under hydrothermal conditions to form a continuous crystalline film. The mechanism of the oriented crystal growth is the subject of a continuing investigation but is probably dependent on the nature of the laser-ablated film. Now that we have prepared the first films of extra-large-pore zeolites, we can begin to explore the laser ablation/hydrothermal treatment variables as well as a range of support materials. It is anticipated that many applications for these films in separations, catalysis and chemical sensors will be forthcoming.

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