Micropatterned Oriented Zeolite Monolayer Films by Direct In Situ Crystallization

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Unique properties of zeolites make them attractive materials in designing thin films and coatings that could be utilized for a variety of applications such as separation membranes,[1−7] membrane reactors,[1] chemical sensors,[1] microreactors,[1] low-dielectric constant films for computer chips,[1,8,9] corrosion-resistant coatings for aerospace alloys,[1,10,11] and hydrophilic zeolite coatings for space stations.[1,12] Several of these applications could greatly benefit from a preferred crystal orientation. For example, oriented nanometer channel structures could affect the permeation and molecular sieving behavior of the film that are crucial for their application as chemical sensors, separation membranes, microreactors, and membrane reactors.[1] Preferred orientation can also impact other film properties including optical and electronic properties. Because of the attractive features of oriented thin films, there has been intense effort to prepare zeolite films with controlled orientation, and several approaches have been developed. Templated in situ growth[13,14] and assembly of preformed zeolite crystals[15−17] could produce oriented zeolite crystals, but the obtained layer was not continuous. Seeded growth[4−6] could generate continuous oriented zeolite LTA, *c*-oriented MFI, and ETS films. However, an extra step of substrate pretreatment before crystallization was required and micropatterning was not demonstrated. A very simple direct in situ crystallization method was developed recently for synthesis of *b*-oriented continuous MFI monolayer film on stainless steel and silicon wafer.[8,18,19] The *b*-oriented monolayer MFI film shows distinguished structural features: a set of straight nanometer channels (5.5 Å) of MFI crystals are perpendicular to the substrate and through the whole film thickness from the top to the bottom. Moreover, the film is very thin (about 400 nm) and the monocrystal layer nature of the film minimizes the effect of crystal boundaries. All these structural features are favorable for molecular diffusion and ensure higher flux compared to other currently available MFI membranes.[20]

The ability to micropattern a zeolite film or to selectively grow a zeolite film in a desired area is a critical issue to realize many of its potential applications such as low-*k* dielectric films, sensors, and microreactors.[21,22] We have recently succeeded in micropatterning zeolite films by employing “soft lithography” and by using zeolite nanocrystals as building blocks.[23] The film has well-defined micropatterns and bimodal pore size distribution. But it does not have preferred orientation. More recently, large micrometer-sized zeolite crystals have been patterned by photochemical modification of organic linkers.[15] The resulting film had preferred orientation but it was not continuous and the adhesion between crystals and substrate was weak. The goal of the present work is to develop a convenient way to *selectively* grow *continuous* and *oriented* zeolite film with excellent adhesion following designed patterns by direct in situ crystallization. Previous studies of zeolite synthesis on various metal substrates indicate that the interaction between the colloidal zeolite crystals and gold surface is weak.[18,19,24] In this communication, we took advantage of this weak interaction and used a “filling-in” strategy to produce patterned zeolite films. We constructed a patterned silicon wafer with square gold islands as substrate. Weaker attraction forces between gold surface and zeolite colloidal crystals resulted in the preferential growth of oriented crystals on silicon wafer between gold islands (Figure 1). This is the first demonstration of continuous oriented zeolite monolayer film with designed patterns.

Detailed preparation procedures are as follows. (100) silicon wafer was thoroughly washed in deionized water

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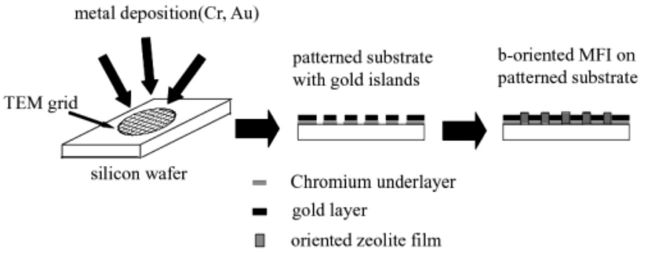

Figure 1. Preparation procedure of micropatterned oriented MFI film.

under ultrasonication. Then a 200-mesh copper TEM grid was glued to this silicon wafer. The substrate was then coated with 10 nm of chromium (99.99%, Alfa Asear), an underlayer for gold, using a CHA E-beam vacuum deposition system (CHA Industries, Menlo Park, CA) operating under 2×10^{-6} Torr at a deposition rate of 0.5 Å/s. Prior to gold deposition, final chromium thickness on silicon substrates was measured using a quartz crystal sensor positioned inside the deposition chamber. Following chromium deposition, gold (99.99%, Canadian Maple Leaf) was deposited to a final thickness of 300 nm with a deposition rate of 1.5 Å/s. After peeling off the TEM grid, the gold patterned silicon wafer was ready to use.

The synthesis mixture was prepared by slowly adding tetraethyl orthosilicate to a solution of tetrapropylammonium hydroxide and water under stirring, and the solution was aged for 4 h under stirring at room temperature. The final molar composition of the synthesis solution was 0.32:1:165 TPAOH:TEOS:H_2O. Then 20 g of the synthesis solution was loaded into a 45-mL Teflon-lined Parr autoclave where the gold patterned silicon wafer was vertically placed at the bottom. Crystallization was carried out at 165 °C for 2 h. The samples were recovered and thoroughly washed with deionized water and blow-dried in N_2 stream.

Figure 2 shows SEM micrographs (Philips XL-30 operated at 20 keV), EDAX elemental analysis results, and schematic drawing of the pore structure of the *b*-oriented MFI film on the substrate. An SEM image (Figure 2a) shows that a well-defined gold pattern on a silicon wafer was produced by E-beam deposition. After in situ crystallization, continuous zeolite film was formed (Figure 2b,c). From SEM images it is clear that zeolite crystals in the patterned film are *b*-oriented (Figure 2c). About 1 μm of space between the gold island edge and zeolite film was observed (Figure 2d). To understand the reason for the formation of this gap, elemental analysis in the corresponding area around the interface (spots labeled in Figure 2d) was performed with EDAX. As shown in Figure 2e, the peak at 1.75 keV is related to Si and the peaks at 2.15, 9.70, and 11.54 keV are associated to Au. At point 1, both Si and Au peaks are observed, which are related to the deposited gold and the underlying silicon substrate. A decrease of intensity of Au peak is observed from point 2, to 3, and to 4 and it finally disappears at point 4. This is consistent with the fact that zeolite film starts to grow on Si at point 4. EDAX results indicate that the gap between the gold island edge and zeolite film was caused by diffusion of gold underneath the TEM grid during E-beam evaporation.

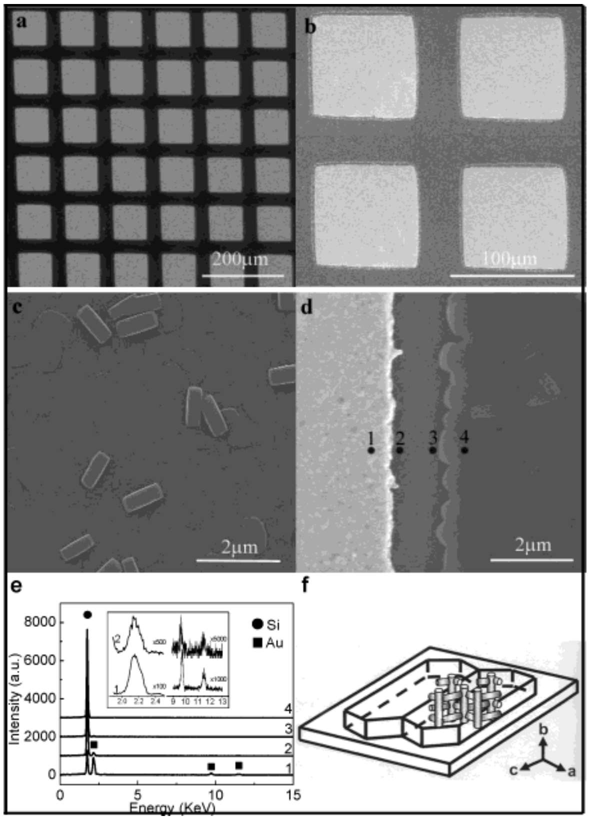

Figure 2. SEM images of (a) silicon wafer with gold islands, (b) after deposition of *b*-oriented MFI film, (c) MFI film between gold islands, (d) boundary area between gold islands and MFI film, (e) EDAX results of spots in (d), inset in (e) for gold peaks at high resolution, and (f) schematic drawing of the pore structure of *b*-oriented MFI.

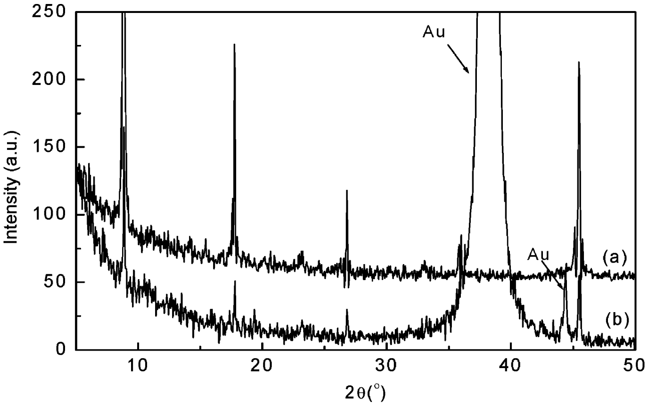

Figure 3. XRD patterns of (a) pure *b*-oriented MFI film and (b) gold patterned *b*-oriented MFI film.

Figure 3 shows XRD patterns of silicalite films on a silicon wafer with or without a gold pattern (Siemens D-500 diffractometer using Cu Kα radiation). In both cases, only (0 *k* 0) lines of the silicalite appear, which confirms that in both cases *b*-oriented films are formed. The (0 8 0) line at 36.15° in Figure 3b overlapped with the strong Au peak at 38.15°. For the film with gold patterns, the two lines at 38.15° and 44.45° are associated to Au (111) and (200) diffraction peaks. The lower intensity of (0 *k* 0) lines of patterned film compared to that of pure silicalite film is due to its smaller area of zeolite film (i.e., the size of a TEM grid).

In our previous work, we demonstrated that this oriented silicalite zeolite thin film has low dielectric constant and excellent mechanical strength and adhesion.[8] The patterning work presented here is a preliminary attempt related to the potential semiconductor device applications of this pure silica film. Although a very simple square pattern and MFI were used in this study, it is clear that the strategy demonstrated here can be readily extended to other much more sophisticated patterns and other zeolites. The substrates could be low-resistivity, high-resistivity, oxide-covered, or nitride-covered silicon wafer. A non-silicon substrate such as steel can also be used. In addition, other interesting features can also be introduced to this patterned film. For example, the gold islands can be modified with self-assembled monolayers (SAMs). Since pure-silica MFI are intrinsically hydrophobic, by using SAMs with hydrophilic terminal groups, the hydrophobic and hydrophilic property of the film can be varied on a micrometer-scale corresponding to a designed pattern. This could be useful in the design of optical devices by using patterned condensation figures.[25] In addition, thiols with particular functional groups that show high affinity for the desired biofunctional molecules, such as proteins and peptides, can be used. It can thus generate a biomolecule pattern and have potential application for biosensor fabrication. This patterned *b*-oriented MFI film can also be used as molecular sieving sensor arrays and template for nanowires arrays. Work in these areas is currently underway in our laboratory.

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