Continuous *c*-Oriented $AlPO_4$-5 Films by Tertiary Growth

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c-Oriented $AlPO_4$-5 films were synthesized by seeded growth on silicon substrates. Secondary hydrothermal treatment of the seeded substrates under conditions that favor *c*-out-of-plane growth yielded non-intergrown, highly oriented columnar crystals with a length of 7 μm. Modifying the conditions so that in-plane growth is favored and executing yet another ("tertiary") growth, the crystals obtained by secondary treatment were grown in-plane, along the *a*-, *b*-directions, filling the gaps between the columnar grains and yielding well-intergrown, highly oriented, continuous $AlPO_4$-5 films. The oriented films obtained by the technique presented here can be potentially useful for separations and catalysis as well as electronic and electrochemical applications.

Introduction

Aluminophosphate $AlPO_4$-5, with an AFI structure, is composed of alternating AlO_4 and PO_4 tetrahedra, forming a framework with one-dimensional, electrically neutral cylindrical pores of uniform cross section (7.3 Å) that are extended parallel to the long (*c*) axis of the crystal.[1] Controlling the orientation of the subnanometer-sized channels of $AlPO_4$-5 and related molecular sieves is of particular interest for size-selective chemical sensors, separation membranes, and optical systems[2] and has been the subject of many investigations.

Caro et al.[3] aligned large $AlPO_4$-5 crystals with an average length of more than 200 μm by means of electric field, with emphasis on three potential applications: materials for optical second harmonic generation, molecular sieve membranes, and host frameworks to orient guest molecules for spectroscopy. Sano et al.[4] synthesized polycrystalline SAPO-5 in Teflon by in situ hydrothermal treatment, whereas Feng et al.[2] prepared $AlPO_4$-5 crystals that were assembled vertically on a gold substrate, which was premodified with organophosphonate layers. Noack et al.[5] developed an "$AlPO_4$-5-in-nickel membrane" by electrochemically embedding $AlPO_4$-5 crystals into a perforated nickel matrix. Orientation of the crystals in the holes of the grid was achieved by means of electric field, and the voids between the crystals were sealed by subsequent metal deposition. The idea of crystal growth in geometrically confined environments was adopted by Wu et al.,[6] who synthesized $AlPO_4$-5 crystals in parallel channels of anodic porous alumina by hydrothermal growth. The same group also applied a two-step microwave heating, using floating anodized alumina substrate at the vapor-solution interface, in order to align $AlPO_4$-5 crystals vertically to substrate.[7] The technique was later expanded to include synthesis of SAPO-5.[8] Munoz and Balkus[9] deposited metal-substituted $AlPO_4$-5 films on TiN-coated silicon wafers using pulsed laser ablation, followed by a vapor-phase treatment. FeAPO-5 films in particular were employed as the dielectric phase in a capacitive type chemical sensor. Laser ablation of MAPO-39, a small pore (4 Å) magnesium aluminophosphate molecular sieve, onto porous stainless steel substrates resulted in crystalline MAPO-39 films with the pores oriented primarily normal to the porous metal substrate.[10] Mintova et al.[1] demonstrated the microwave synthesis of nanosized $AlPO_4$-5 crystals and their use in preparation of thin films on gold substrates by seeded growth. The same technique was employed for synthesis of $AlPO_4$-18 films, where colloidal $AlPO_4$-18 crystals were deposited on Si wafers by spin-coating, and $AlPO_4$-18 films were subsequently grown by hydrothermal treatment using the initial precursor solution.[11,12] Zhang and Wang[13,14] prepared in situ a variety of aluminophosphate molecular sieve films ($AlPO_4$-14, CoAPO-

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44, ZnAPO-34) on porous or dense alumina substrates using different mixture compositions and hydrothermal growth conditions. Following a novel seeding approach, Yates and co-workers synthesized fibrous $AlPO_4$-5 using microemulsions,[15] which then deposited on glass substrates by sequential deposition, under an applied electric field that provided control over film thickness and orientation. The fibers were aligned parallel to the glass substrate.[16] By secondary growth of these deposits, oriented layers with the pores perpendicular or parallel to the support were made depending on the seed layer density.[17] Xu at al. reported a simple, one-step in situ synthesis method for continuously coating a stainless steel mesh with $AlPO_4$-5 crystals.[18] The same group also reported a technique for the epitaxial growth of $AlPO_4$-5 deposits on millimeter-sized $AlPO_4$-5 single-crystal substrates.[19]

Our group has demonstrated the secondary growth of MFI-supported films with columnar microstructure[20] and the growth mechanism was simulated using a front tracking technique in two spatial dimensions.[21] Needlelike titanosilicate film (ETS-4) was also grown by secondary growth and the space between crystals was filled by another molecular sieve with a similar structure (ETS-10) using heteroepitaxial growth.[22] Here, we present a novel seeded growth technique for synthesis of oriented $AlPO_4$-5 molecular sieve films. The technique is based on sequential growth treatments of substrates that have been covered by a uniform monolayer of $AlPO_4$-5 seeds. Executing secondary and subsequently tertiary hydrothermal growth under conditions that favor c-out-of-plane and in-plane growth respectively, we were able to produce non-intergrown or highly intergrown $AlPO_4$-5 films that exhibit very good orientation along the film thickness with the AFI channels perpendicular to substrate.

Experimental Section

Silicon wafers were cleaned[23] by immersion in a 1:1:7 hydrogen peroxide (H_2O_2, 30%, Fisher):ammonium hydroxide (NH_4OH, 29%, Fisher):deionized (DI) water solution for 20 min. They were then washed with DI water and immersed in a second solution with a composition of 1:1:7 H_2O_2 (30%):hydrochloric acid (HCl, 37%, Mallinckrodt):DI water for an additional 20 min and washed with DI water. Silicon substrates were functionalized according to the method developed by Ha et al.[24] A silane coupling agent, 3-chloropropyltrimethoxysilane (3CP-TMS, 97%, Aldrich), was used to covalently link seeds to the substrate surface. All reactions were carried out in a humidity-free environment using thoroughly dried equipment, under dry argon and dry toluene atmospheres. First, a silicon substrate was placed vertically inside a specially designed reactor with the aid of a Teflon holder. Next, 40 mL of dry toluene (anhydrous, Aldrich) was poured into the reactor under a flow of argon, and 3 mL of 3CP-TMS was added into the solution. The reactor was immediately closed and the mixture was heated to reflux (approximately 110 °C) for 3 h under a flow of argon. Pretreated $AlPO_4$-5 particles were used as seeds. They were prepared by stirring $AlPO_4$-5 powder in DI water for 2 h and subsequently breaking the powder by sonication using a Branson 1210, 50/60 Hz ultrasonic bath, for another 2 h. The final dispersion was centrifuged and the seeds were dried at 85 °C overnight. Forty-five milligrams of the pretreated seeds was placed in a dry reactor, followed by the addition of 40 mL of dry toluene. The reactor was immediately sealed and placed into the ultrasonicator for 1 h to finely disperse all seeds in toluene. Next, the functionalized silicon substrate was placed in between two glass slides and put vertically into the seed solution. The mixture was sonicated for 5 min. The glass/silicon/glass assembly was then put horizontally into the seed solution and sonicated for an additional 2 min. Finally, the silicon substrate was washed with fresh toluene and stored in an oven at ~110 °C for secondary growth.

For the secondary growth procedure, aluminum isopropoxide (98%, Aldrich) was hydrolyzed in DI water for approximately 4.5 h under stirring. Phosphoric acid (85%, Aldrich) was then added dropwise under stirring, and the solution was allowed to homogenize for 1 h. Next, the structure-directing agent (SDA, triethylamine, Aldrich) was added dropwise, and the precursor solution was allowed to age for 12 h under stirring. Thirty milliliters of the final precursor solution was subsequently transferred to a Teflon-lined stainless steel autoclave. The seeded silicon substrate was placed vertically inside the solution with the aid of a Teflon holder, and the autoclave was sealed and placed into an oven that was preheated to the desired temperature. When the growth was complete, the autoclave was removed and quenched with tap water, and the sample was taken out and washed with DI water. The procedure was repeated with fresh precursor solution during tertiary growth treatment. A 2 h precrystallization before introducing the substrate for tertiary growth was found to yield a more controllable and uniform growth due to nucleation/growth rate suppression.

Top-view and cross-sectional morphology of samples was examined by scanning electron microscopy (SEM) using a JEOL 6500 microscope. X-ray diffraction (XRD) characterization was performed on a Bruker-AXS (Siemens) D5005 using a 2.2 kW sealed Cu Source. The system was operated on a $\theta/2\theta$ geometry.

Results and Discussion

A schematic representation of the technique is shown in Figure 1. A silane coupling agent, 3-chloropropyltrimethoxysilane, which has chloro and methoxyl functional groups, was used to covalently link seeds to the substrate surface. Sonication in the seeds-in-toluene solution with substrate stacking in between two glass slides has been demonstrated to be very effective in preparing monolayers of zeolite microcrystals with a high degree of coverage, close packing, and good binding strength.[25] The seeded substrates were exposed to secondary hydrothermal treatment under conditions that favor *c*-out-of-plane growth and yielded columnar,

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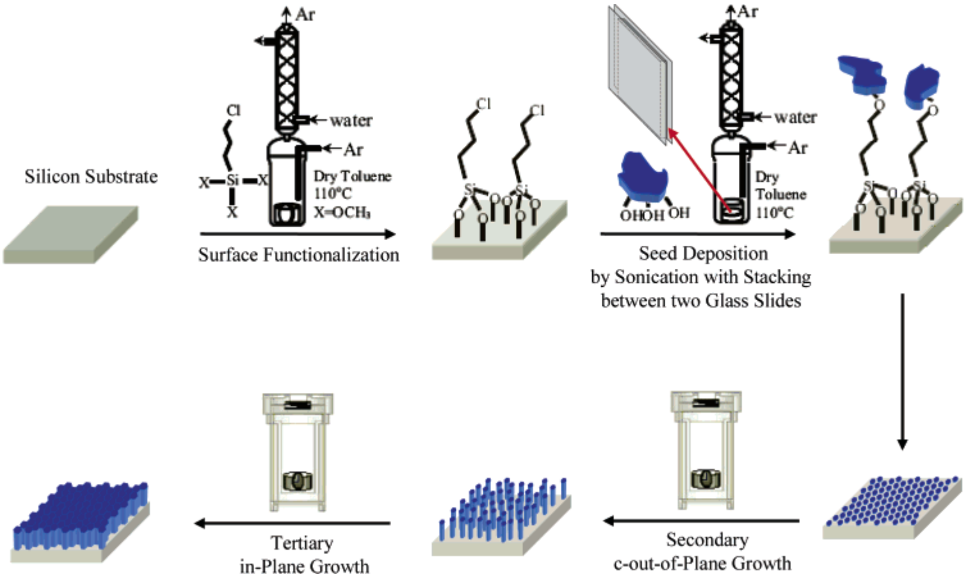

Figure 1. Schematic of the tertiary growth procedure for synthesis of $AlPO_4$-5 oriented films.

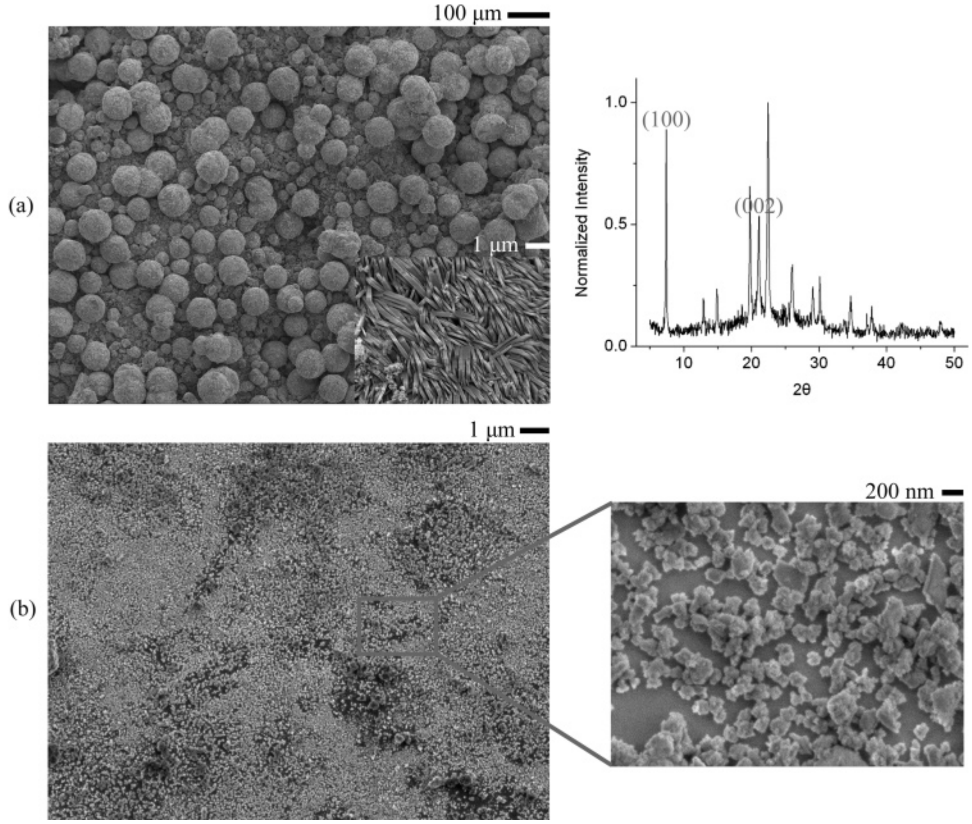

Figure 2. (a) SEM and corresponding XRD image of $AlPO_4$-5 powder used to prepare seeds for seeded growth. The inset is a higher-resolution SEM image of the powder. (b) SEM images of the deposited $AlPO_4$-5 seeds on functionalized silicon substrate.

poorly intergrown but highly oriented $AlPO_4$-5 crystals. Subsequently, the film that was obtained by secondary growth was used as a scaffold in another (tertiary) growth under conditions that, by favoring in-plane growth, resulted in complete filling of the gaps between the columnar grains and yielded well-intergrown, highly oriented $AlPO_4$-5 films.

Seeds for secondary growth were prepared by breaking $AlPO_4$-5 powder by sonication, as described in the Experimental Section. The powder was synthesized using a precursor solution with a 1:1.3:1.2:100 Al_2O_3:P_2O_5:TEA:H_2O molar composition heated at a temperature of 150 °C for 10 h. According to SEM imaging (Figure 2a), the powder consists of big spherical particles with an average diameter of 50 μm. Higher-resolution SEM imaging (inset in Figure 2a) reveals that the powder particles consist of platelike, highly intergrown crystals having an average thickness of 200 nm. The XRD pattern exhibits the characteristic peaks of the AFI framework structure, confirming that the powder consists of crystalline $AlPO_4$-5. The morphology of the deposited seeds on functionalized silicon substrates is shown in Figure 2b. According to the SEM images, seeds generated

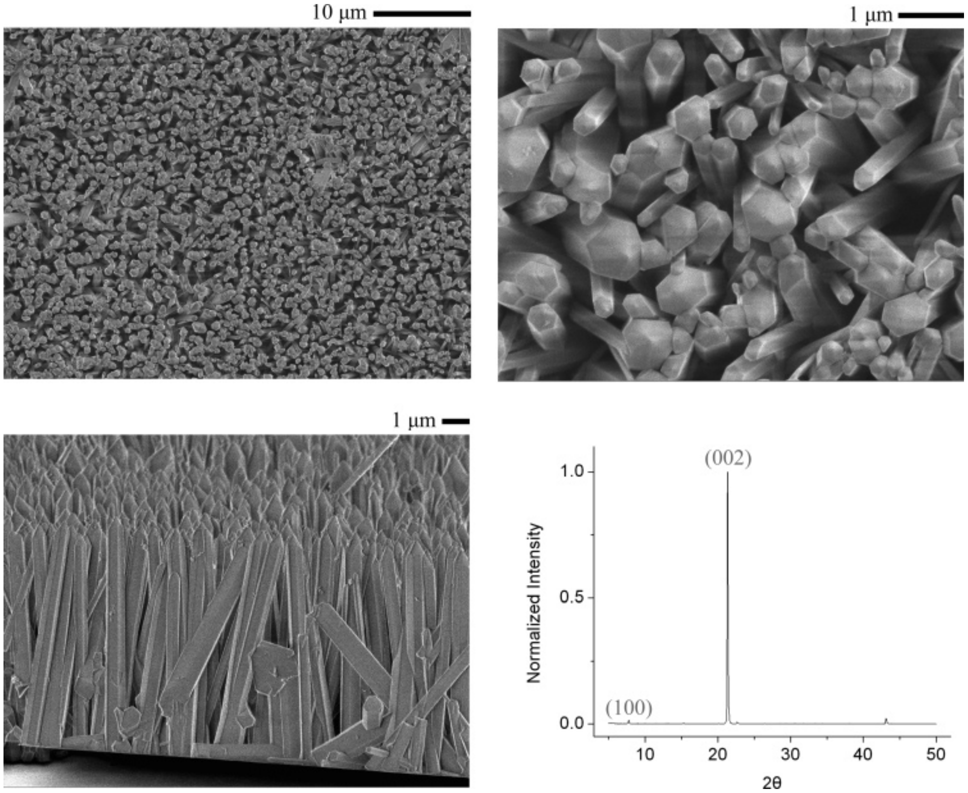

Figure 3. SEM and XRD images of $AlPO_4$-5 crystals oriented with the *c*-axis perpendicular to the substrate after secondary growth under conditions that favor *c*-out-of-plane growth.

by powder breakage have an average size of 200 nm, are irregular in shape, and form a monolayer with uniform coverage on the substrate.

Experiments performed by varying the molar composition of the synthesis precursor mixture revealed that the water content plays an important role in the morphology of the crystals. A low water:Al_2O_3 molar ratio favors preferential growth along the *a*- and *b*-axes of the crystal. For example, spherical particles consisting of platelike, well-intergrown crystals that were used to prepare seeds for secondary growth (Figure 2a) were synthesized using a water:Al_2O_3 molar ratio of 100. Increasing the water content in the synthesis mixture suppresses the reaction/nucleation rate and favors one-dimensional growth along the *c*-axis of the AFI framework. A water:Al_2O_3 molar ratio of 400 was shown to give columnar $AlPO_4$-5 crystals in powder form and used for secondary growth on the seeded silicon substrates. The synthesis mixture composition for secondary growth was 1:1.3:1.2:400 Al_2O_3:P_2O_5:TEA:H_2O heated at 150 °C for 10 h.

After secondary growth, a poorly intergrown but highly oriented columnar film was obtained (Figure 3). According to the SEM images, the $AlPO_4$-5 crystals have an average thickness of 500 nm and are oriented perpendicular to substrate, forming a film with a thickness of $\sim$7 μm. The SEM top view reveals that this film appears to be similar to one reported by Lin and Yates.[17] However, a difference that might be important for certain applications is that the current film is not grown on a seed layer that has its channels parallel to the support. Also, the current film is thinner and well-oriented all the way down to the substrate, in contrast to the film grown by Lin and Yates, which has a thickness of $\sim$30 μm and exhibits random orientation for the first 10 μm close to substrate.

XRD characterization confirms the orientation of the film synthesized by secondary growth. As the XRD pattern in Figure 3 reveals, the peak at 2θ of 20.97°, which corresponds to the (002) reflection of the $AlPO_4$-5 framework, is strongly enhanced, indicating that the channels are oriented perpendicular to substrate. To investigate the effect of the seed layer, we performed control experiments using nonfuctionalized/unseeded and functionalized/unseeded silicon substrates. In both cases, no uniform deposition was achieved, and only a few crystals with random morphology and orientation were found on the substrates (data not shown).

The film synthesized by secondary growth (Figure 3), although it exhibits uniform orientation with the channels perpendicular to substrate throughout its thickness, would not be efficient for separation applications because of poor crystal intergrowth. For such applications, a continuous, highly intergrown, oriented membrane would be preferable. To achieve this, we exposed the film that was obtained by secondary growth to a tertiary hydrothermal treatment under conditions that favor in-plane growth, in order to completely fill the gaps between the columnar grains and yield continuous and oriented $AlPO_4$-5 films.

A series of tertiary growth experiments were performed in order to find the optimal conditions (synthesis mixture composition, hydrothermal conditions) that would result in in-plane growth and yield a continuous film with the desired characteristics. In-plane growth of the original columnar crystals was achieved by using a low water:Al_2O_3 molar ratio. The synthesis mixture composition was 1:1.3:1.2:100 Al_2O_3:P_2O_5:TEA:H_2O, and the tertiary growth temperature was

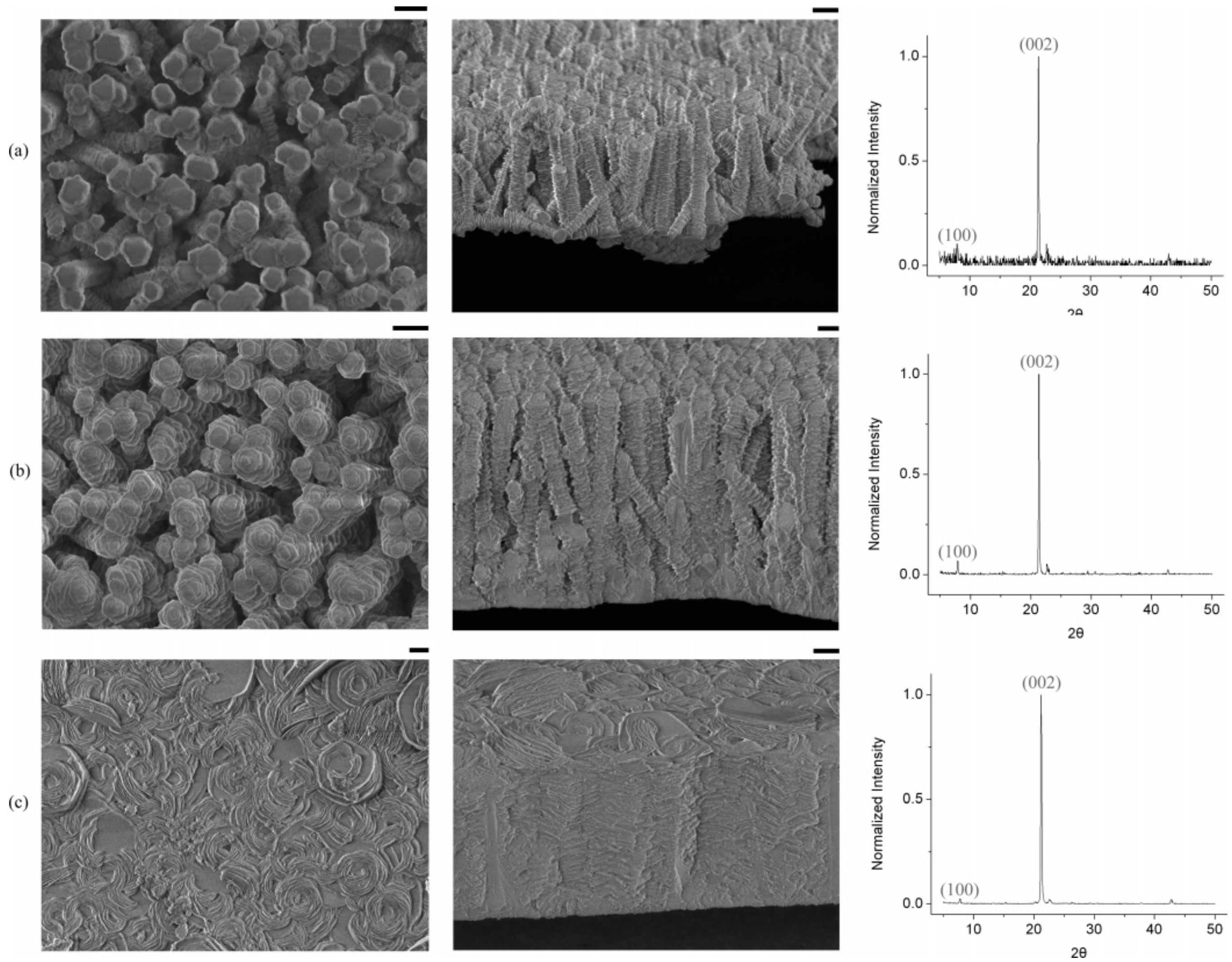

Figure 4. Top-view (left) and cross-sectional (middle) SEM images and corresponding XRD patterns (right) of $AlPO_4$-5 films oriented with the *c*-axis perpendicular to the substrate after tertiary growth for (a) 1 h, (b) 1 h 15 min, and (c) 2 h under conditions that favor in-plane growth. The scale bars correspond to 1 μm.

150 °C. A precrystallization treatment of the precursor mixture at 150 °C for 2 h before introducing the substrate was found to be necessary in order to reduce the nucleation/growth rate and achieve a more controllable and uniform growth.

Figure 4 shows SEM and corresponding XRD images of the films obtained for different tertiary growth times. Figure 4a corresponds to a tertiary growth time of 1 h. According to the SEM images, nucleation takes places at different spots on the sides of the initial columnar crystals, which then grow along the *a*- and *b*-axes. After 1 h and 15 min, the platelike crystals that have been nucleated on the original columnar ones continue to grow in-plane and start intergrowing with each other (Figure 4b). After a 2 h tertiary treatment, the crystals have merged completely to form a uniform and continuous oriented film, as shown in the SEM images in Figure 4c. The uniform nucleation/growth along the original columnar crystals all the way down to substrate, as realized by the cross-sectional SEM images, can be justified by the short diffusion time of the precursor molecules in water. Making an approximate calculation using the Stokes–Einstein equation and assuming a precursor size of 5 Å and a diffusion path length equal to the length of the original columnar crystals (i.e., ~7 μm) yields a diffusion time that is much smaller than 1 s. Therefore, considering the long experimentally observed growth times (on the order of 1 h), diffusion limitations do not prohibit complete filling. Moreover, as the cross-sectional SEM images in Figures 3 and 4 reveal, the thickness of the film remains almost unchanged after tertiary growth with an average value of 7 μm, which indicates that using a low water content in the tertiary growth synthesis mixture prevents the original crystals from further growing along the *c*-direction, and only in-plane growth takes place, filling the gaps between the existing columnar crystals.

According to XRD patterns (Figure 4), the peak that corresponds to reflection from the (002) plane (i.e., channels perpendicular to substrate) is the dominant one for all the different hydrothermal times, with the rest of the characteristic AFI peaks (shown in Figure 2a) being drastically suppressed (for example, the reflection from the (100) plane that corresponds to channels parallel to substrate). This confirms that during the tertiary treatment, in-plane nucleation and growth follow the orientation of the original columnar crystals and that growth of new misoriented crystals is minimal or nonexistent.

It has been suggested that transport in unidimensional $AlPO_4$-5 channels will be much faster than through similarly sized multidimensional zeolite channels. For example, on the basis of previous studies,[5,26] it is expected that $AlPO_4$-5 films may exhibit a 1000-fold flux increase compared to MFI films. This will be the subject of future investigations. Along the same direction, targeting high flux membranes, we are currently working on growing carbon nanotubes in the $AlPO_4$-5 films[27] in order to investigate high flux transport through these materials.[28−31]

Conclusions

A tertiary growth technique for synthesis of oriented $AlPO_4$-5 films is reported for the first time. By manipulating the synthesis mixture composition and the hydrothermal conditions, we successfully controlled the direction of the crystal growth. A secondary growth on seeded silicon substrates using a high water:Al_2O_3 molar ratio favored *c* out-of-plane growth, yielding non-intergrown, highly oriented columnar crystals. Exposing the crystals obtained by secondary growth to another (tertiary) growth, using a low water:Al_2O_3 molar ratio and precrystallization, resulted in in-plane growth of the original columnar crystals and yielded well-intergrown, highly oriented, continuous $AlPO_4$-5 films.

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