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$AlPO_4$-18 Seed Layers and Films by Secondary Growth

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$AlPO_4$-18 layers were prepared on Si wafers via spin-coating or the Langmuir−Blodgett (LB) method using nanosized crystals. Multilayers were deposited by spin-coating, whereas the seeds assembled by the LB technique were monolayers. The seeded layers were not stable upon secondary growth under microwave radiation, and no films were formed on the supports. Dense $AlPO_4$-18 films could be obtained by secondary growth after stabilization of the seed layers by adding prehydrolyzed tetraethylorthosilicate (TEOS) to the colloidal $AlPO_4$-18 suspension prior to support seeding. The stabilized seed layers and the grown $AlPO_4$-18 films were stable. The structure and the morphology of the films grown using the two types of seeded supports were similar, independent of the method used for seeding. The $AlPO_4$-18 nanocrystals used for seeding showed very high water capacity with low temperatures of water removal when heated. The layers and films prepared are of potential interest for sensing, heat pump, and cooling machines applications.

Introduction

Aluminophosphate ($AlPO_4$-*n*) molecular sieves are microporous materials built by interconnected alumina and phosphate tetrahedra.[1] In addition to their adsorption and molecular sieve properties, AlPOs and transition metal-substituted AlPOs are interesting heterogeneous catalysts.[2−4] In the case of zeolites, it is advantageous for a number of applications to have the zeolite as a thin supported layer. Whereas the preparation of zeolite films and membranes has received considerable attention in recent years,[5−16] the research into the synthesis of $AlPO_4$-*n* materials in the form of supported films is somewhat limited. The majority of reports on $AlPO_4$-*n* films are dedicated to the fabrication of $AlPO_4$-5.[17−21] $AlPO_4$-5 is a one-dimensional molecular sieve, and thus special efforts have been directed toward the preparation of oriented $AlPO_4$-5 films with channels perpendicular to the support. Xu et al. have grown $AlPO_4$-5 films on stainless steel mesh by in situ crystallization.[17] The crystal morphology and film orientation were controlled by the composition of the synthesis mixture used. The fabrication of dense *c*-oriented $AlPO_4$-5 films by a multistep synthesis procedure has been reported by Karanikolos et al.[18] $AlPO_4$-5 seeds were first assembled onto the support by the covalent linking method, highly oriented columnar $AlPO_4$-5 was secondary grown, and finally the intercolumnar gaps were filled by yet another growth reaction. $AlPO_4$-5 seed crystals have been aligned parallel to glass substrates under an electric field, and *c*-oriented layers were formed on the seeded supports by secondary growth under microwave radiation.[19] Microwave radiation has also been applied to prepare $AlPO_4$-5 films by secondary growth of preadsorbed nanosized crystals on gold-coated quartz crystal microbalances (QCMs).[20] Laser ablation has been used to prepare thin films of FeAPO-5, which were employed as capacitive-

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type humidity sensors.[21] Recently, the microwave synthesis of $AlPO_4$-11 and $SAPO_4$-11 films and their performance as corrosion-resistant coatings have been reported.[22]

$AlPO_4$-18 is another important member of the $AlPO_4$-*n* family with a three-dimensional small-pore system (3.8 × 3.8 $Å^2$).[23] The high water capacity and the low temperature of water desorption from $AlPO_4$-18 compared to zeolites makes $AlPO_4$-18 interesting for heat pumps, cooling machines, or thermochemical storage media applications.[24] $AlPO_4$-18 colloidal crystals have been prepared by hydrothermal treatment and spin-coated onto supports, which were then secondary grown into dense films.[25] The synthesis time used to prepare nanosized $AlPO_4$-18 was reduced to 30 min using microwave radiation.[26] $AlPO_4$-18 coatings on QCM supports have been prepared from micrometer-sized and nanosized $AlPO_4$-18 crystals by dip- or spin-coating and tested for gas-sensing applications.[27] However, attempts to secondary grow these layers by hydrothermal synthesis failed. The aim of the present work was to study in detail two different approaches for assembling nanosized $AlPO_4$-18 crystals onto flat supports, namely, the Langmuir−Blodgett (LB) method and spin-coating, and the use of the seeded supports for fabrication of $AlPO_4$-18 films by secondary growth under microwave radiation.

Experimental Section

Nanosized $AlPO_4$-18 crystals were synthesized according to the previously described procedure.[25,26] A clear precursor solution with the molar composition of $1Al_2O_3/3.16P_2O_5/3.16(TEA)_2O/186H_2O$ was prepared from aluminum-*sec*-butoxide (Aldrich), tetraethylammonium hydroxide (35 wt % in water, Aldrich), phosphoric acid (85 wt %, Aldrich), and distilled water. The precursor solution was transferred to a 100 mL PTFE microwave autoclave and heated at 150 °C for 10 min using a temperature-programmed mode microwave oven (Anton Paar) at 800 W and a ramping of 2.5 min. The obtained $AlPO_4$-18 nanocrystal suspension was purified by three times centrifugation and redispersion in distilled water in an ultrasonic bath. A part of the sample was freeze-dried and optionally calcined in air at 550 °C for 6 h at a heating rate of 15 °C min^{-1}.

The silicon wafer supports were cleaned by consecutive ultrasonic treatment for 15 min with acetone and 2-propanol and rinsed with distilled water prior to seeding. The $AlPO_4$-18 nanocrystals were redispersed in ethanol to obtain a concentration of the solid product of about 3 wt % and used for fabrication of seed layers via spin-coating. Spin-coated films were prepared with an SCS P6700 spin coater at an acceleration rate of 1000 rpm s^{-1}, spinning rate of 3500 rpm, and a spinning time of 30 s. Seed layers were also prepared after the addition of tetraethylorthosilicate (TEOS, >98%, Merck) to the $AlPO_4$-18 ethanol suspension at a weight ratio of 1:10. The TEOS was prehydrolyzed in a mixture of ethanol, water, and HCl (molar ratio of $1TEOS/0.06HCl/27H_2O/60EtOH$) on an orbital shaker overnight. For the preparation of LB films, the $AlPO_4$-18 crystals (1 wt %) were redispersed in 2-propanol containing 0.7 mM cetyltrimethylammonium bromide (CTAB, $C_{16}H_{33}N(CH_3)_3Br$, Aldrich) by ultrasonic treatment for 1 h.[28] Similarly to spin-coating, experiments were also performed using prehydrolyzed TEOS-containing suspension. An amount of 750 μL of this $AlPO_4$-18 of $AlPO_4$-18−TEOS suspension was spread at the air−water interface in an LB trough (NIMA 1232D1D2, Nima Technology, U.K.). Floating films were obtained upon compression at a barrier speed of 50 cm^2 min^{-1}. These films were transferred to silicon wafers by the vertical lifting method at a target surface pressure of 15 mN m^{-1} using a dip speed of 1 mm min^{-1}. The seeded supports obtained by the two methods were mounted vertically in a specially designed reactor and subjected to secondary growth in the precursor $AlPO_4$-18 solution. The crystal growth was carried out in a microwave oven at 150 °C for 10 min.

The freeze-dried $AlPO_4$-18 powder was analyzed by X-ray diffraction (XRD) with a STOE STADI-P X-ray diffractometer using Ge-monochromated Cu $K\alpha_1$ radiation. Nitrogen adsorption isotherms were measured with a Micromeritics ASAP 2010 surface area analyzer after degassing a calcined $AlPO_4$-18 sample at 300 °C for 12 h. The as-made and calcined $AlPO_4$-18 samples were subjected to thermogravimetric analysis (TGA). The powders were heated in corundum crucibles from 30 to 900 °C (10 °C min^{-1}) in a flow of synthetic air (25 mL min^{-1}) using a Netzsch STA 449 C Jupiter thermobalance. The particle size distributions in the coating suspensions containing pure $AlPO_4$-18 nanocrystals and stabilized with prehydrolyzed TEOS crystals used for LB layers deposition were measured by dynamic light scattering (DLS) using backscattering mode (ALV-NIBS/HPPS). The $AlPO_4$-18 seed layers and dense films were studied by scanning electron microscopy (SEM) using a Philips XL30 microscope. The seeded and grown $AlPO_4$-18 films were further investigated by grazing incidence X-ray diffraction (GID, $\lambda = 0.154$ nm) at the European Synchrotron Radiation Facility, ESRF, Grenoble, beamline ID01. The XRD patterns were collected at three different incident angles (α_i), 0.1°, 0.18°, and 0.3°, corresponding to X-ray penetration depth of 8, 15, and 280 nm, respectively.[29]

Results and Discussion

The purified and freeze-dried $AlPO_4$-18 was analyzed by XRD. The XRD pattern indicated the presence of a highly crystalline $AlPO_4$-18 material as a single phase (Figure 1A). The microporous nature of the sample was further confirmed by the high BET surface area of the calcined sample (515 m^2 g^{-1}) and the type I isotherm recorded (Figure 1B).

From an application point of view, the hydrophilic properties of $AlPO_4$-18 are of particular importance for vapor sensing and heat pumps. Figure 2 shows TG/DTG curves of the as-made and calcined $AlPO_4$-18 samples in comparison with $AlPO_4$-18−TEOS. The weight loss up to 110 °C attributed to loss of water was about 5 wt % for the as-synthesized sample and increased to about 45 wt % for the calcined sample. The water content in $AlPO_4$-18−TEOS sample is increased up to 49 wt %, which is due to presence of hydrophilic prehydrolyzed TEOS containing silanol

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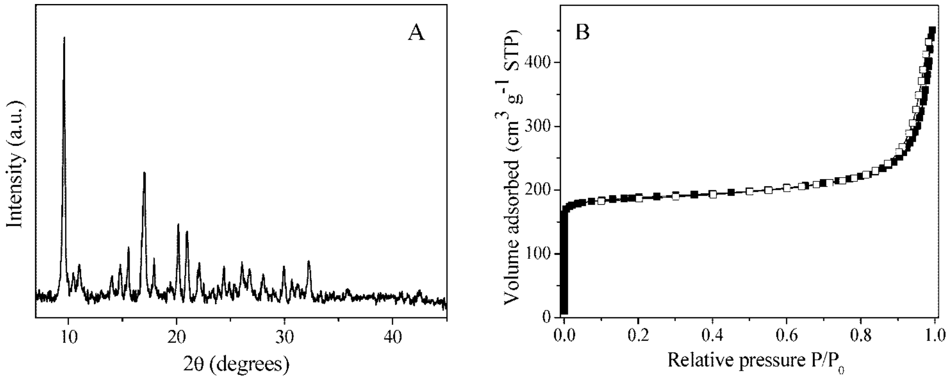

Figure 1. (A) XRD pattern and (B) nitrogen adsorption isotherms, closed symbols—adsorption, open symbols—desorption, of the AlPO$_4$-18 nanocrystals used for deposition of seed layers by LB and spin-coating approaches.

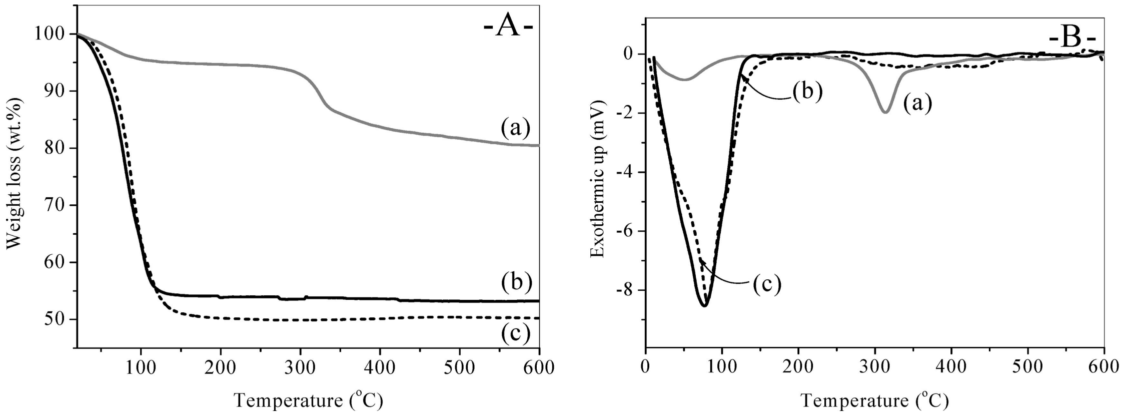

Figure 2. (A) TG and (B) DTG curves of the AlPO$_4$-18: (a) uncalcined and (b) calcined for deposition of seed layers by LB and spin-coating approaches and (c) AlPO$_4$-18−TEOS nanocrystals removed from the films by scratching.

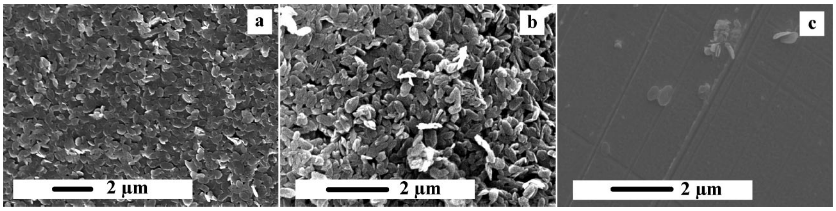

Figure 3. SEM images of seeded supports prepared by (a) the LB method, (b) spin-coating, and (c) representative SEM images of the support seeded by the two methods after secondary growth.

groups. The change of the water content in the AlPO$_4$-18−TEOS sample in comparison with the pure calcined AlPO$_4$-18 is negligible; however, the temperature of water desorption from the first sample increased with about 6 °C (see Figure 2B, curve c). The second weight loss in the 250−450 °C range for the uncalcined sample is related to the removal of the template molecules. The water weight loss measured for the calcined AlPO$_4$-18 sample was comparable or higher than the value for some highly hydrophilic zeolites.[25,30]

Seeded Si wafer supports were prepared by the LB method and spin-coating using the AlPO$_4$-18 nanocrystals from 2-propanol and ethanol suspensions, respectively, and corresponding SEM images are shown in Figure 3, parts a and b. 2-Propanol has been found before to produce LB zeolite layers of superior quality compared to ethanol, and for this reason 2-propanol was used as a solvent in the present work to prepare the LB AlPO$_4$-18 seed layers.[31]

The LB films were monolayers with a high degree of ordering of the AlPO$_4$-18 crystals (Figure 3a). The majority of the AlPO$_4$-18 nanocrystals seemed to be rested on their basal plane, and the crystals were closely packed. The seed layers prepared by spin-coating were disordered multilayers (Figure 3b). The seed layers prepared by both techniques were stable enough to withstand various laboratory manipulations. Similar spin-coated AlPO$_4$-18 layers have been used before to prepare films by secondary growth using conventional hydrothermal treatment.[25] Silicalite-1 seed layers arranged by the LB method were reported to be stable enough

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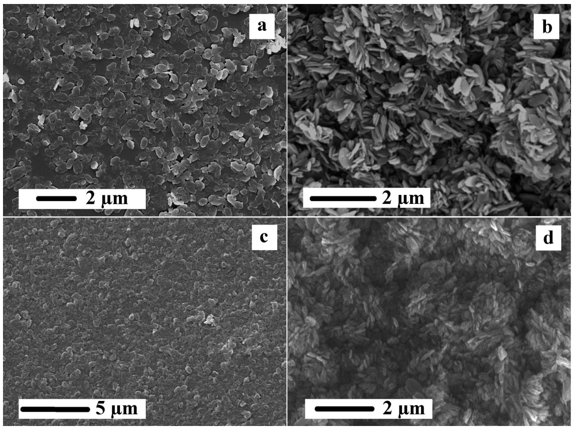

Figure 4. SEM images of seeded supports prepared by (a) the LB method and (c) spin-coating and (b and d) SEM images of the corresponding $AlPO_4$-18 films after secondary growth under microwave radiation.

to be used for fabrication of films by secondary growth.[32] The hydrothermal treatment conditions under microwave radiation are more severe compared to conventional heating, especially when it comes to film synthesis. For instance, the $AlPO_4$-18 seeded supports in previous work[25] were conventionally heated for 50 h at 100 °C during secondary growth, whereas in the present work the secondary growth under microwave heating was performed at 150 °C for only 10 min. In the latter case, the seed layers prepared could not survive the severe secondary growth conditions and no films were formed on the supports, independent of the method used for seed deposition (Figure 3c). Considering the substantial reduction in the synthesis time, further experiments directed at the optimization of the method to allow fabrication of $AlPO_4$-18 films by secondary growth under microwave radiation were performed. Best results were achieved by the addition of prehydrolyzed TEOS to the coating suspensions prior to seeding. Amorphous silica is commonly used as a binding material to increase the binding strength of the zeolite seed layers to the support.[33] The stabilized seed layers prepared via the LB method and spin-coating are shown in Figure 4. The LB $AlPO_4$-18−TEOS monolayers (Figure 4a) were similar to the LB $AlPO_4$-18 films (Figure 3a) except that the crystal density was lower and the presence of uncoated gaps was detected in the SEM images. The spin-coated films prepared from the TEOS-containing suspension were densely packed and smooth (Figure 4c). The TEOS-stabilized seed layers were more stable than pure $AlPO_4$-18 layers and films were formed upon secondary growth of the seeded supports using microwave heating. The secondary grown films prepared from the two types of seeded supports were similar (Figure 4, parts b and d). The films were rough with a thickness of about 1.5 μm. The TEOS-containing seed layers prepared can be used, e.g., for sensing applications without further modifications.[27] However, the adhesion strength of the films is substantially increased after secondary growth, and similar data have been reported before.[34] The mechanical properties of the $AlPO_4$-18−TEOS films were investigated by tape tests according to ASTM D3359 standard. The mechanical stability of the films stabilized with TEOS-containing seed layers was very high, and the films were not removed from the silicon wafer or even not partially destroyed. The efficiency of the binder (prehydrolyzed TEOS) depends on the size of the individual particles, which are in the range of 1−3 nm; thus, they have a high external surface and form Al−O−Si links between the $AlPO_4$-18 nanocrystals and the SiO_2 from the silicon wafer resulting in the formation of mechanically stable films. No deterioration in the crystallinity of the calcined films (550 °C for 2 h) or changes in the morphology or stability were found. Thus, despite their roughness, the increased thickness and improved adhesion of the $AlPO_4$-18 films prepared after secondary growth may be beneficial for certain applications.

The influence of the TEOS on the properties of the $AlPO_4$-18 suspension was studied by DLS. The DLS analysis of the $AlPO_4$-18 and TEOS−$AlPO_4$-18 suspensions in 2-propanol used for LB seed deposition (Figure 5A) indicated that the addition of TEOS had little influence on the particle size distribution. However, the surface pressure−area isotherms recorded upon compression of the suspensions at the air−water interface showed that the surface selectivity of the $AlPO_4$-18 crystals was altered as a result of the TEOS addition (Figure 5B). The substantial difference between the two isotherms can explain the differences in the morphology of the $AlPO_4$-18 and TEOS−$AlPO_4$-18 seed layers prepared by the LB method and spin-coating. The different hydrophilic/hydrophobic properties of the $AlPO_4$-18 and $AlPO_4$-18−TEOS suspensions used for spin-coating influence the spreading ability of the suspensions as well as the packing of the particles during the spin-coating process.

The seeded $AlPO_4$-18−TEOS films by spin-coating and the LB approach were subjected to additional hydrothermal treatment. The key features of the aluminophosphate films were obtained from the GID measurements recorded for the seeded layers and grown films at a constant incident angle of the X-ray beam (Figure 6). The results obtained for seed layers prepared by spin-coating and the LB method were similar. Also, the $AlPO_4$-18 and TEOS−$AlPO_4$-18 seed layers were similar except that a peak at ca. 5.75° 2θ was present in the XRD pattern of the latter. This probably indicates mesoporosity caused by the addition of TEOS. The fact that this peak was not detected in the LB seed layers showed that the CTAB added to modify the AlPO4-18 crystals did not contribute to the layer mesoporosity. The XRD patterns of the seed layers obtained by the two methods (spin-on and LB) reveal that some of the peaks are not present. For example, the Bragg reflections (111/−111), (112/−112), (−202/202), (022), (−113/113), (023), (−222/222), (−114/114), (−223/223), and (−132/132) in the $8° < 2\theta < 25°$ region are not detected in both seed layers. In the grown films, the disorientation of the crystals is confirmed by the presence of almost all the Bragg reflections characteristic of powder $AlPO_4$-18 material (see Figure 1). It is apparent that the crystals are more randomly oriented in the grown $AlPO_4$-18 films. Thus, the seeds have little influence on the structure

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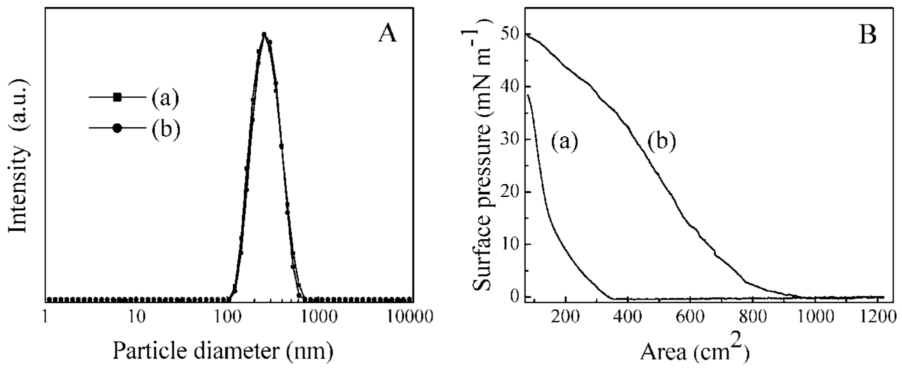

Figure 5. (A) DLS curves and (B) surface pressure−area isotherms of (a) AlPO$_4$-18 and (b) TEOS−AlPO$_4$-18 suspensions in 2-propanol.

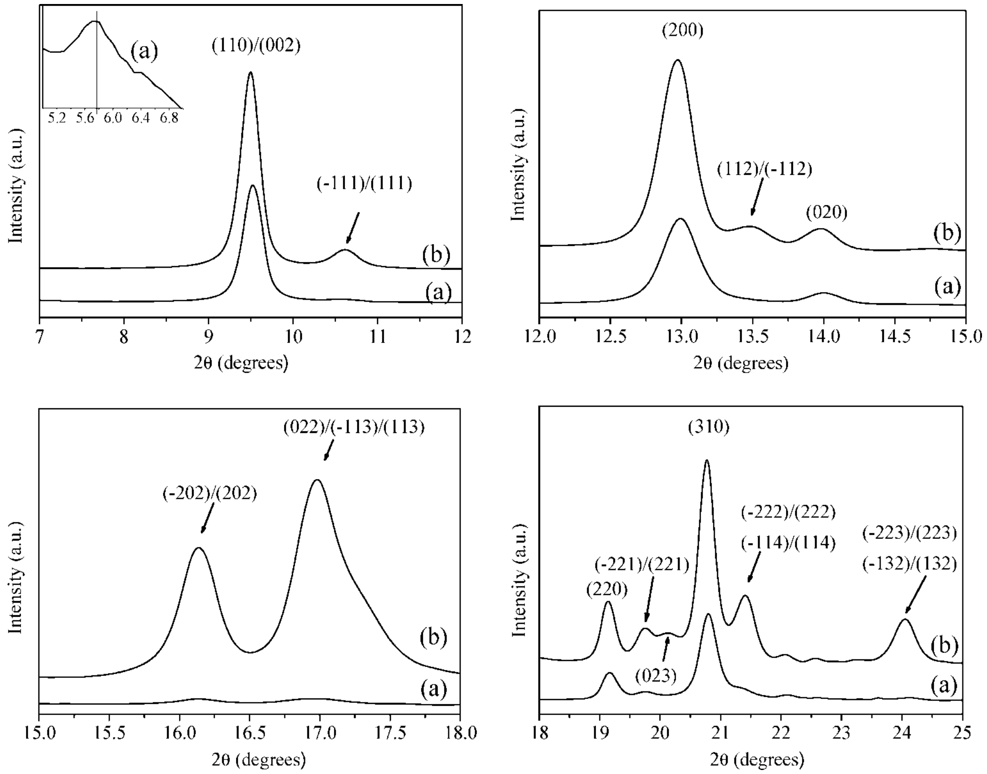

Figure 6. X-ray GID data of (a) spin-coated AlPO$_4$-18−TEOS seeded and (b) grown films at $\alpha_i = 0.3°$ in different 2θ regions. Inset: X-ray pattern of AlPO$_4$-18−TEOS seeded film in the range of 5−7° 2θ.

of the grown films but their presence is essential for the films to be grown on the supports. On the other hand, the increased intensity of the peaks in the grown films is due to the increased density and better packing of the nanocrystalline AlPO$_4$-18. The Bragg reflections in the films prepared by secondary growth of the two types of seed layers collected at different penetration depths were similar with only the intensity of the peaks increased with increasing penetration depth (Figure 7). This proves that the crystals along the film thickness do not change their orientation and the crystalline structure of the films is depth-independent.

In the case of AlPO$_4$-18, the crystals have a three-dimensional channel system based on eight-membered rings with size of 3.8 Å, which are running along the three (100), (110), and (001) axes.[23] Therefore, the orientation of the crystals in the films is not expected to have a significant importance on their performance; however, the high degree of disordering of the nanocrystals would develop the water sorption capability. It is anticipated that the high water content in the nanosized AlPO$_4$-18 particles is due to the water incorporated in the channels, but also the amount of surface water is increased significantly.

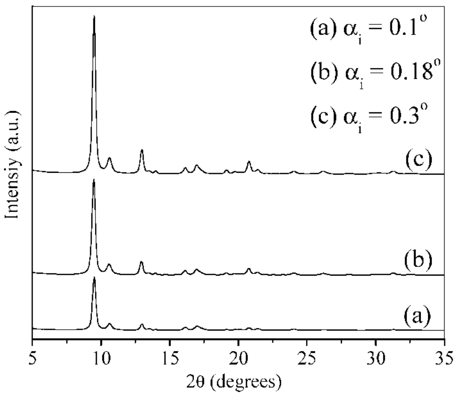

Figure 7. X-ray GID data of AlPO$_4$-18 grown films on seeded layers deposited by the LB method at different incident angles.

Conclusions

Highly crystalline $AlPO_4$-18 nanocrystals with high water capacity were assembled on Si wafers by two methods, spin-coating and the LB technique. However, the corresponding seed layers were not stable enough to withstand hydrothermal treatment under microwave radiation. Stabilized $AlPO_4$-18 layers were prepared by the addition of prehydrolyzed TEOS to the coating suspensions. The spin-coated seed layers were dense and consisted of closely packed crystals, whereas the LB layers were monolayers with a high crystal density. Thick $AlPO_4$-18 films were prepared by secondary growth using microwave heating for 10 min. The grown films had similar morphology and structure, independent of the method used for seeding, indicating that the seeds were essential for the films to be formed but had little influence on the properties of the films. The secondary grown films were rough and highly disoriented. The film roughness and disorientation would be beneficial for increasing the water capacity of the films. Both seeding techniques can be applied to large flat substrates with the maximum substrate size limited by the LB trough dipping area and the spin-coating machine chamber. The stabilized $AlPO_4$-18 layers and $AlPO_4$-18 films prepared by secondary grown films are of interest for applications as humidity sensors, heating pumps, and cooling machines.

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