

Inorganic crystal nucleation on self-assembled monolayers

C.-J. Yu, M.-H. Yun, G. Evmenenko, S. Kewalramani, P. Dutta, T. Marks
Northwestern University, Evanston, IL, U.S.A.

Introduction

Growth of inorganic materials controlled by organic surfaces is the pathway to biomineralization in nature. Results of numerous attempts to understand or mimic the natural process have been published [1-10]. The attempts have involved bottom-up micropatterned single-crystalline calcite growth (in contrast to current top-down technology) [10], control of single-crystalline calcite growth on self-assembled monolayers [6,7], growth of nanostructured semiconductors templated by lyotropic liquid crystals [4], and *in situ* studies of calcite growth rate under Langmuir monolayers [8]. However, few structural studies at the organic-inorganic interface.

It is generally believed that there are two ways to initiate such nucleation of inorganic materials: through interfacial registry to directly select the orientation of inorganic crystals with respect to the organic substrate [1, 2, 11, 12] and through a multistep process from an amorphous to a crystalline state [5, 10]. We recently reported the first direct evidence of molecular registry between floating Langmuir monolayers of heneicosanoic acid and an inorganic salt (barium fluoride) grown from an aqueous solution subphase containing barium chloride and ammonium fluoride at an appropriate stoichiometry [13]. The study showed (100) epitaxial growth of barium fluoride under the monolayer; both the organic and inorganic lattices were strained in order to achieve registry.

Understanding the nucleation behavior at various organic-inorganic interfaces will help us control growth of various inorganic materials. We thus present here our results for barium fluoride growth on self-assembled monolayers supported on silicon substrates (which are more robust and more easily used in practical applications than floating monolayers). To make good comparisons with the previous report, we tried to use similar conditions, except we used a solid (Si) rather than a liquid (water) support. We therefore used a carboxyl-terminated self-assembled monolayer and grew barium fluoride on this surface from supersaturated solutions.

Methods and Materials

The procedure for preparing self-assembled monolayers is as follows: 0.1-in.-thick (100) silicon substrates (Silicon Processing Company) were cleaned in strong oxidizer (sulfuric acid and 30% hydrogen peroxide in a volume ratio of 7:3) at a temperature between 80° and 90°C for 30 minutes. Then they were treated with an RCA-type solution (NH_4OH , 30% H_2O_2 , H_2O = 1:1:5) at

room temperature for 40 minutes while being sonicated. They were then washed with Millipore water, blown with nitrogen, and placed in the oven under air at 110°C. The cleaned silicon pieces were put in 1-10 mM of 8-(trichlorosilyl)-1-octene ($\text{H}_2\text{C} = \text{CH}-(\text{CH}_2)_6-\text{SiCl}_3$, used as purchased from Gelest) and dissolved in anhydrous toluene at 0°C under a nitrogen atmosphere for 5 hours, followed by cleaning with anhydrous toluene, chloroform, and acetone. The silanization reaction temperature of 0°C was chosen from the extrapolation of threshold temperature data for optimum grafting with respect to the number of carbon atoms of the n-alkyltrichlorosilane [14]. The oxidation process with the solution of KMnO_4 (5 nM): NaIO_4 (195 mM): K_2CO_3 (18 mM): H_2O = 1:1:1:7 for 24 hours at room temperature was used to change the vinyl group to carboxylic acid as described elsewhere [15]. We then washed the samples with NaHSO_3 (0.3 M), H_2O , HCl (0.1 N), pure water, and ethanol.

X-ray measurements were made *ex situ* and *in situ* at the MR-CAT sector 10 beamline at the APS and at beamline X18A (MATRIX) at Brookhaven National Laboratory. The x-ray energy was 27 or 10.5 keV and the incident beam size was 0.2 mm vertically and 2 mm horizontally.

For *ex situ* experiments, 25 × 25-mm silicon substrates, with or without the self-assembled monolayer, were placed on Teflon® supports. Both the substrates and the supports were immersed in a solution of BaCl_2 and NH_4F for 30 minutes. The samples were then rinsed in pure water and placed in a sample chamber under a helium flow to reduce radiation damage. X-ray reflectivity was used to check the quality of the self-assembled monolayers and an x-ray θ -2 θ scan was used to observe the oriented growth of BaF_2 .

For *in situ* experiments, 5 × 25-mm silicon substrates were used, and the 5-mm side was placed in the direction of x-ray incidence to reduce background scattering from the bulk solution. The surface of the substrate on which BaF_2 would be grown faced downward. The silicon substrate was located between two Kapton® films that were attached to two hollow, rectangular aluminum frames. After initial beam alignment, the Kapton film was punctured with a syringe needle through which the barium fluoride solution was injected into the *in situ* chamber until the silicon piece was immersed.

Results

We present the results of the *ex situ* experiment first in Fig. 1. The barium fluoride concentration was 16 mM at a

pH of 8. Figure 1(a) shows powder diffraction from barium fluoride grown on bare silicon. However, Fig. 1(b), with the self-assembled monolayer, shows (100)-oriented barium fluoride growth, similar to that reported in the previous report, under Langmuir monolayers. It is obvious that the presence of the self-assembled monolayer has a drastic effect on the growth of barium fluoride.

The growth rate of the oriented barium fluoride was studied *in situ* by scanning the (200) peak over time. A typical scan is shown in the inset of Fig. 2. We characterized the peak by fitting with a Gaussian after subtracting a linear background. We first fitted the last (strongest) peak; the parameter values obtained from this were used as initial values in searching for a fit to the preceding scan data, and so on. The resulting peak intensities and the peak widths are shown in Fig. 2. Except for the first point, the peak intensity grew over time to the power of 1.92 ± 0.01 , implying a linear increase in the size of the crystallites, until the intensity started to saturate at ~ 22 minutes. The peak width was rapidly reduced by half within 3 minutes and did not change much during the rest of scan.

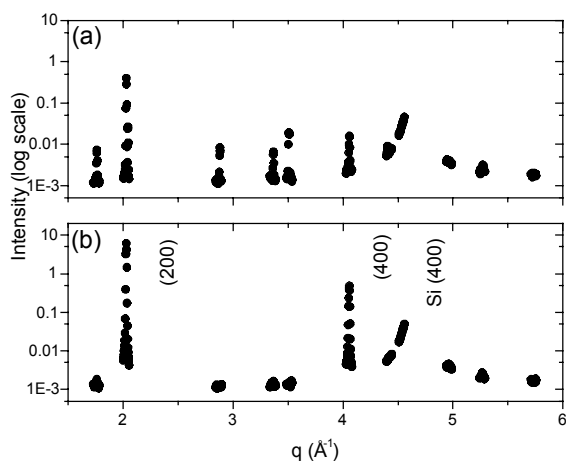


FIG. 1. X-ray θ - 2θ scan data (intensity in log scale for clarity) from barium fluoride grown on a (100) silicon substrate (a) with native oxide only, showing powderlike peaks, and (b) with a self-assembled monolayer showing (100)-oriented growth of BaF_2 .

Discussion

Some of our studies showed other trends in the growth of barium fluoride near the self-assembled monolayer: a longer induction time of nucleation, or a much slower growth rate than that indicated by the data shown in Fig. 2, or no growth at all (not even powderlike growth). This inconsistency could have resulted from the packing density or uniformity of the organic layers, so the organic layers on which *ex situ* samples had been grown were

characterized with x-ray reflectivity. The reflectivity is determined by the interface roughness, thickness of the organic layers, and relative electron density of the layer with respect to that of the substrate [16]. The resulting data, however, did not reveal noticeable structural differences between self-assembled films showing different rates of BaF_2 growth. Moreover, the inconsistency in barium fluoride growth was observed in samples prepared in the same batch or even on one sample surface (i.e., when only a portion of surface area was covered with oriented barium fluoride). So in this experiment, the packing density or uniformity of the self-assembled monolayer is not likely to explain the variability of barium fluoride growth. It may be simply a natural consequence of the rigid organic template anchored to the solid substrate. Further studies are underway.

In summary, we presented (100)-oriented growth of barium fluoride normal to the self-assembled monolayer in a solution of barium chloride and ammonium hydroxide. Although this result is expected from our previous study of the (100)-oriented growth of barium fluoride under a heneisanoic acid Langmuir monolayer in the same solution, the less lattice-flexible organic matrix presented in this study reduced the chance of barium fluoride growth drastically. This result may indicate the important role of flexible organic molecules in biomineralization.

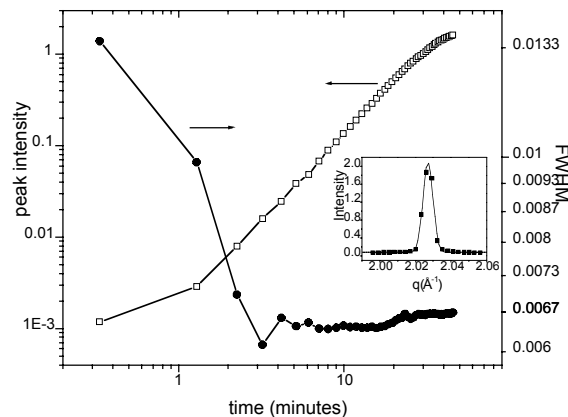


FIG. 2. Behaviors of the x-ray peak intensity and the full width at half-maximum (FWHM) of the (200) barium fluoride peak over time after a silicon substrate with the self-assembled monolayer is immersed in a solution of barium chloride and ammonium fluoride. The solid lines in the main pane are guides to the eye. The data are obtained by scanning the (200) peak region repeatedly over time *in situ*; an example is shown in the inset. These data are fitted (solid line in inset) with a Gaussian peak and linear background.

Acknowledgments

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