

Oriented assembly of inorganic crystals at soft-hard interfaces.

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Introduction

In many biological processes, organic substrates direct the growth of precisely controlled assemblies of inorganic crystals. We show that two different pathways can lead to oriented crystalline growth at soft surfaces: an epitaxial match between the organic and inorganic lattices, and spontaneous inorganic self-aggregation at the template surface.

Methods and Materials

Langmuir monolayers of simple fatty acids, floating at the surface of supersaturated aqueous subphases, are used as simple models for studying crystal nucleation and growth at organized organic templates. Structures and structural rearrangements of the organic and inorganic lattices are simultaneously monitored by performing in-situ grazing incidence X-ray diffraction scans during the nucleation process.

Results

At the onset of crystal growth, both the organic and the nucleating inorganic structures undergo rearrangements to form a commensurate match. An epitaxial match makes the crystal growth energetically favorable along a particular crystallographic direction and is the mechanism for inorganic crystal face selection at the organic substrate surface. The perfect orientation of the nucleate, observed at low concentrations, is distorted at higher concentrations. However, the misorientation may not increase monotonically. Rather, the crystals can realign at the substrate surface via spontaneous self-aggregation.

Discussion

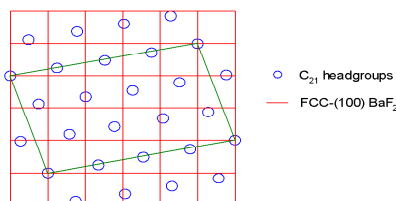


Fig. 1. Real space lattices of $\{1\ 0\ 0\}$ BaF₂ and organic headgroups. The ratio of the unit cell areas is 1.5. The large tilted rectangle is the common supercell.

Barium fluoride grown under fatty acid Langmuir monolayers [1] is oriented with its $\{1\ 0\ 0\}$ crystal face parallel to the water surface. Grazing incidence diffraction (GID) shows that in the early stages of nucleation the inorganic film is very thin (~ 15 Å) and is contracted from its bulk spacing by as much as 4%. The organic lattice also distorts to achieve a commensurate match with the inorganic lattice (Fig. 1). Very similar results are obtained for strontium fluoride.

Epitaxial growth of a different type is observed during the crystal growth of hydrocerussite, $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ [2]. Hydrocerussite nucleates oriented with $(0\ 0\ 1)$ direction vertical. In addition to the monolayer and the bulk peaks, fractional order diffraction peaks corresponding to a $\sqrt{7} \times \sqrt{7}$ supercell of the bulk surface lattice are observed (Fig. 2). The organic lattice forms a commensurate match with the supercell lattice. Thus, the superlattice helps match the unconstrained bulk structure to the organic lattice.

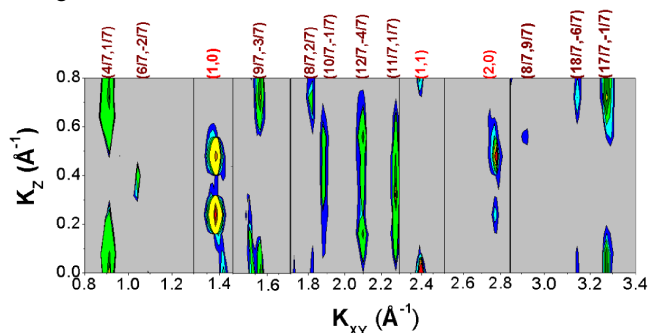


Fig. 2. Intensity contours, reconstructed from diffraction data, during hydrocerussite growth. Integer order diffraction peaks correspond to bulk mineral lattice. The fractional order peaks are from the interfacial supercell (~ 40 Å thick).

Crystal orientation in BaF₂ and SrF₂ deteriorates with increased supersaturation. A contrasting phenomena is observed for CdCO₃ and MnCO₃ [3]. At “low” supersaturations the nucleate are nearly 3-D powder like. However, at higher supersaturations, crystals are preferentially oriented with $\{0\ 1\ 2\}$ direction vertical (Fig. 3). Scanning electron microscope images of corresponding samples show that at low concentrations the growth consists of discrete crystals and at higher concentrations the crystallites self-aggregate to form linear chains and sheets.

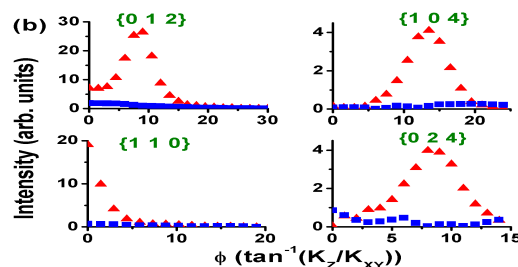


Fig. 3. “Debye” ring scans for inorganic peaks, during CdCO₃ crystal growth (■, 0.2 mM and ▲, 0.4 mM).

[1] J. Kmetko *et. al. Phys. Rev. Lett.* 89, 186102 (2002).

[2] S. Kewalramani *et. al. Surface Science* 591, 286 (2005).

[3] S. Kewalramani *et. al.* in preparation.