Synchrotron studies of nanocrystal thin film self-assembly

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Motivation

Investigate fundamental aspects of nanocrystal selfassembly on solid substrates with particular attention to:

1. Intermediate thermodynamic equilibrium states rather than final products of irreversible non-equilibrium processes.
2. Effect of thin wetting solvent films on the assembly microstructure.
3. Nanocrystals with complex size distributions and stabilizing layers.
4. Influence of nanocrystal size and solvent quality.
5. In situ determination of nanocrystal-substrate separation and in-place nearest-neighbor distance.

Conventional investigative approach

(a) Deposit a droplet of nanocrystal solution on substrate.
(b) Let solvent evaporate.
(c) Study local microstructure by imaging techniques.

Our alternative approach

(1) Prepare dry nanocrystal layers on substrates.
(2) Generate stable nano-liquid wetting films.
(3) Measure equilibrium microstructure in-situ by surface X-ray scattering.

Typical particle size range: ~10-100 Å
Typical wetting film thickness range: ~1-100 Å

Methods

(1) Prepare nanocrystal monolayers on water: Langmuir isotherms
(a) Different types of isotherms: 1 = continuous, 2 = discontinuous, 3 = stacking monolayers.
(b) Isotherm of a single-layer nanocrystal film and homogeneous distribution of nanocrystals over particles
(c) Complete linearity of a relaxation isotherm (m=0).
(d) Monolayer swelling behavior of monolayers (m=0).

(2) Transfer monolayers to silicon substrates: Schaefer stamping
(a) Force of film removal and Schaefer plane (film-particle) oriented normal to water surface.
(b) Schematic view and Schaefer stamping procedures (horizontal film film).
(c) Typical dimension of 2D/50 Å substrate with monocrystal nanolayer transferred.
(d) Force of the water surface after stamping, showing sintering rings of the transferred monolayer.

(3) Form stable liquid wetting films: controlled nano-wetting
The thickness of the liquid film adsorbed on the substrate from vapor is controlled through the positive temperature offset ΔT:

\[ ΔT = T_1 - T_2 ≥ 0, \quad t = (ΔT)^{1/3} \]

(4) Measure average microstructure by surface X-ray scattering
X-ray reflectivity (XRR)
Measure microstructure normal to substrate
Grazing incidence diffraction (GID)
Measure microstructure in-plane microstructure

(B) Dry nanocrystal monolayers on silicon: X-ray results

(B1) Grazing Incidence Diffraction

(B2) X-ray reflectivity

(C) Controlled nano-wetting with a good solvent (toluene)

(C1) Grazing incidence diffraction (good solvent)

(D) Controlled nano-wetting with a poor solvent (ethanol)

(D1) XRR data with box model fit
(D2) Density profiles from XRR model
(D3) Depth of particles in lower layer
(D4) Height of the particle in upper layer
(D5) Substrate coverage
(D6) Large particles that are first promoted to upper layer

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Figure captions:

- (A1) Sample preparation and characterization.
- (B1) Grazing incidence diffraction.
- (B2) X-ray reflectivity (good solvent).
- (C1) Grazing incidence diffraction (good solvent).
- (D1) XRR data with box model fit.
- (D2) Density profiles from XRR model.
- (E1) Rod scans.
- (E2) 2D intensity maps (GISAXS).

Main results:

- Monolayer expansion up to 100% coverage.
- Further evolution resembles a layer transition.
- In-plane nearest particle distance.
- Large particles that are first promoted to upper layer.

This film regime similar to good solvent case.

Pictorial Summary

Ferroelectric/strictly polar ferroelectric
Proton/metallic (ferroelectric)
Nickel/metallic
BiFeO3/PbTiO3
Thin film regime similar to good solvent case.
Thick film regime very different: monolayer “destruction” and signature of 3D nanocrystal aggregates.

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