Nanoscale area selective ZnO growth between a monolayer of nanocrystals

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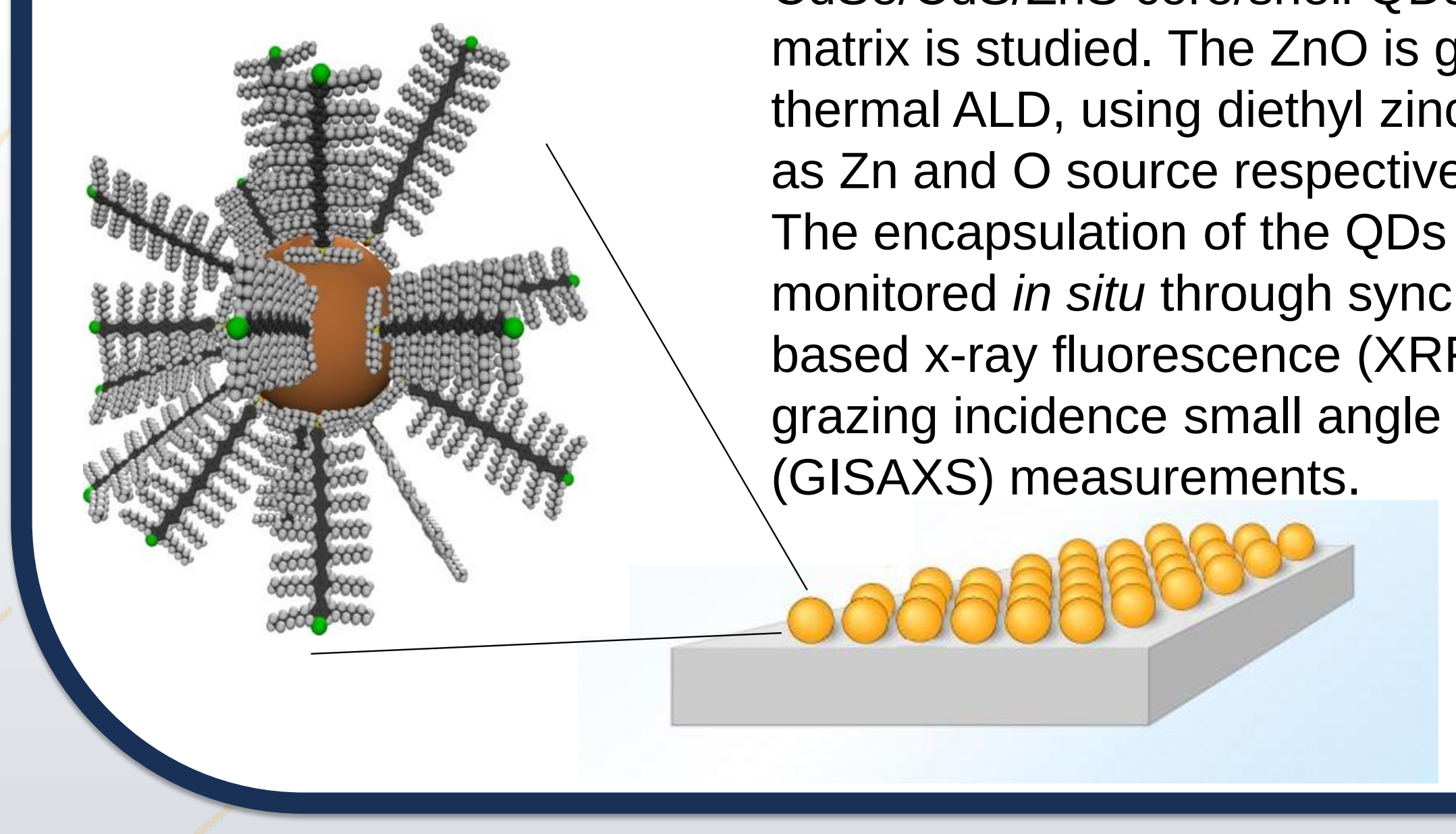
Introduction

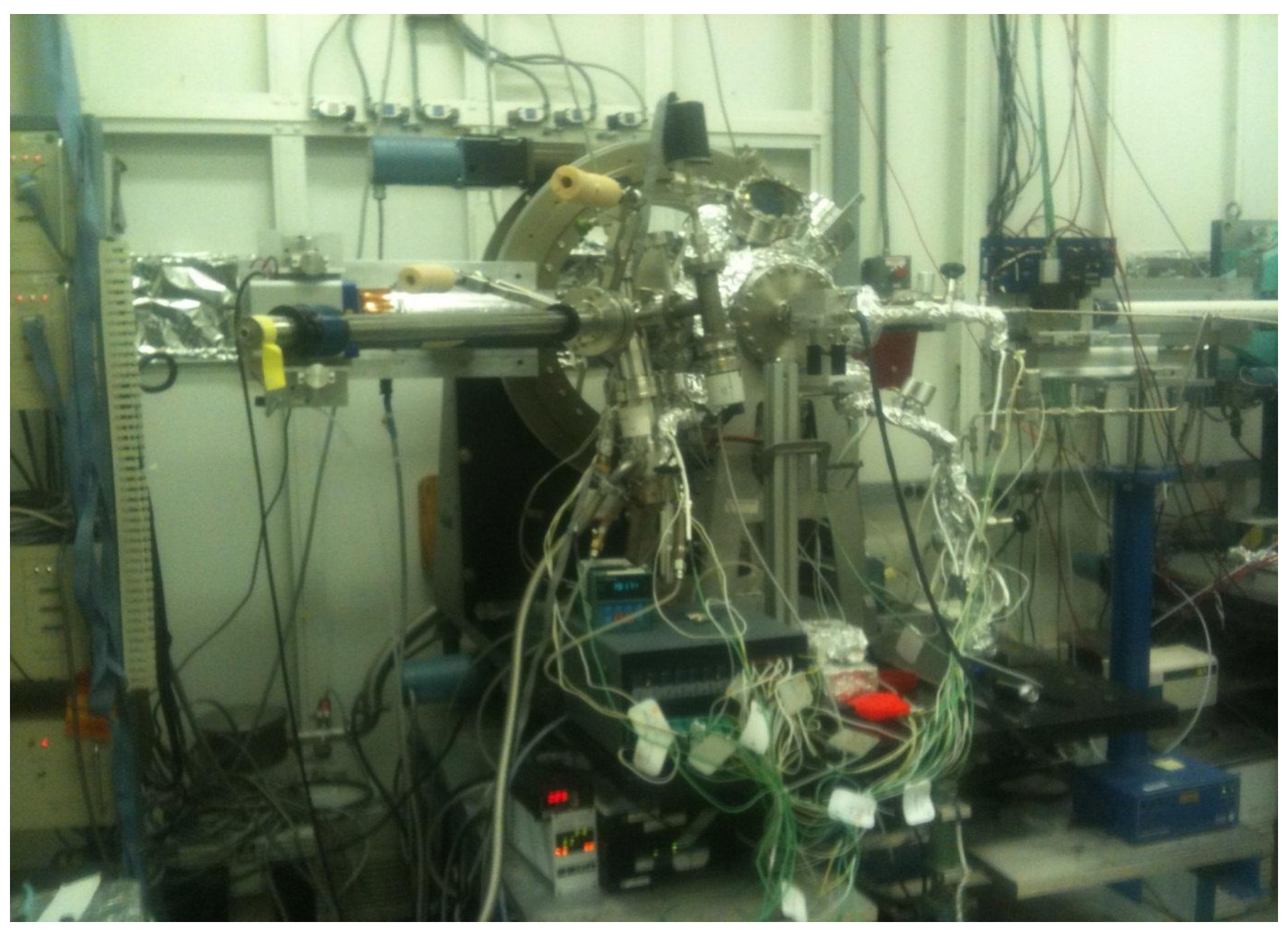
Colloidal semiconductor nanocrystals or quantum dots (QDs) combine a broad absorption spectrum with a narrow, highly efficient and tunable emission. Therefore they are actively investigated for applications in opto-electronic devices such as light emitting diodes, amplifiers or lasers and photovoltaic cells.
For many applications, QDs need to be embedded in a solid matrix, either to reduce degradation due to exposure to moisture and oxygen or to allow efficient injection or extraction of electron-hole pairs.

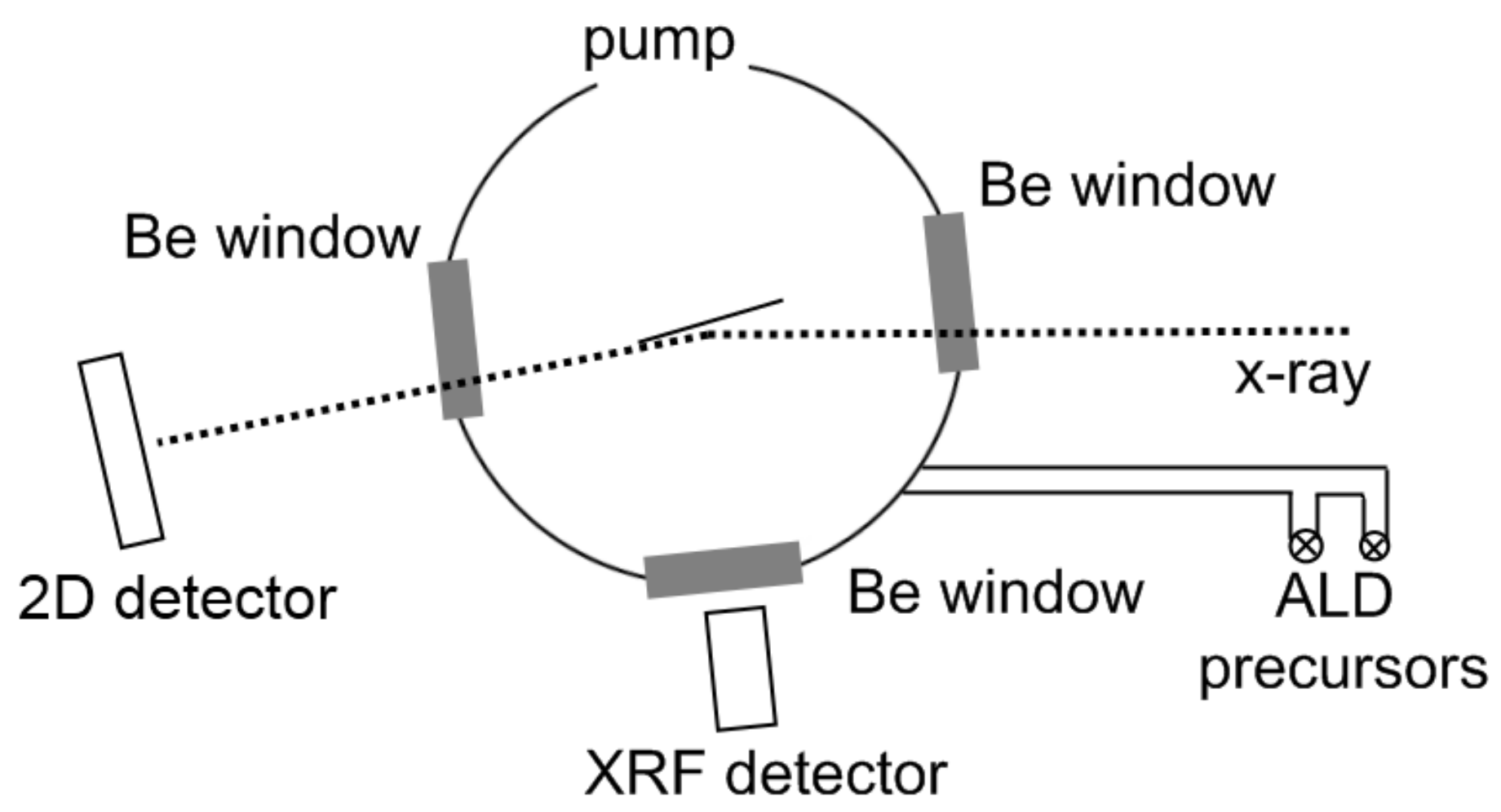
Here, the encapsulation of a monolayer of CdSe/CdS/ZnS core/shell QDs in a ZnO matrix is studied. The ZnO is grown by thermal ALD, using diethyl zinc and water as Zn and O source respectively.
The encapsulation of the QDs was monitored *in situ* through synchrotron based x-ray fluorescence (XRF) and grazing incidence small angle scattering (GISAXS) measurements.



Experimental setup


http://www.nsls.bnl.gov/



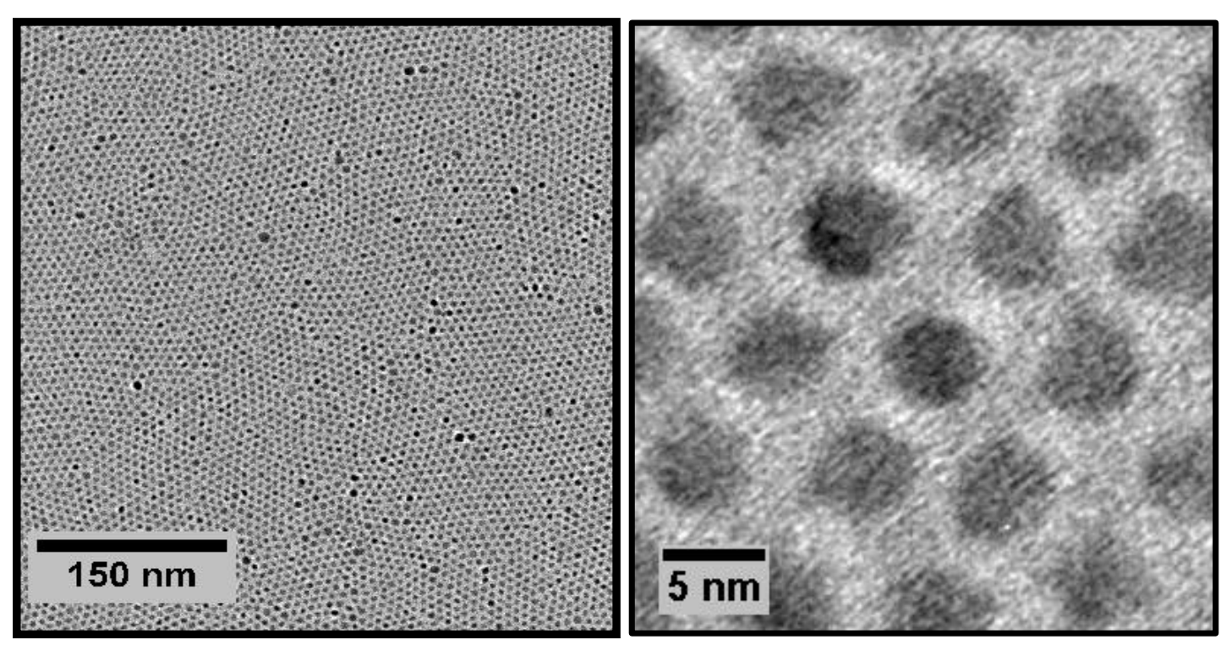


Setup description
UHV film growth facility, adapted for ALD, installed at beamline X21 of the National Synchrotron Light Source at Brookhaven National Laboratory.

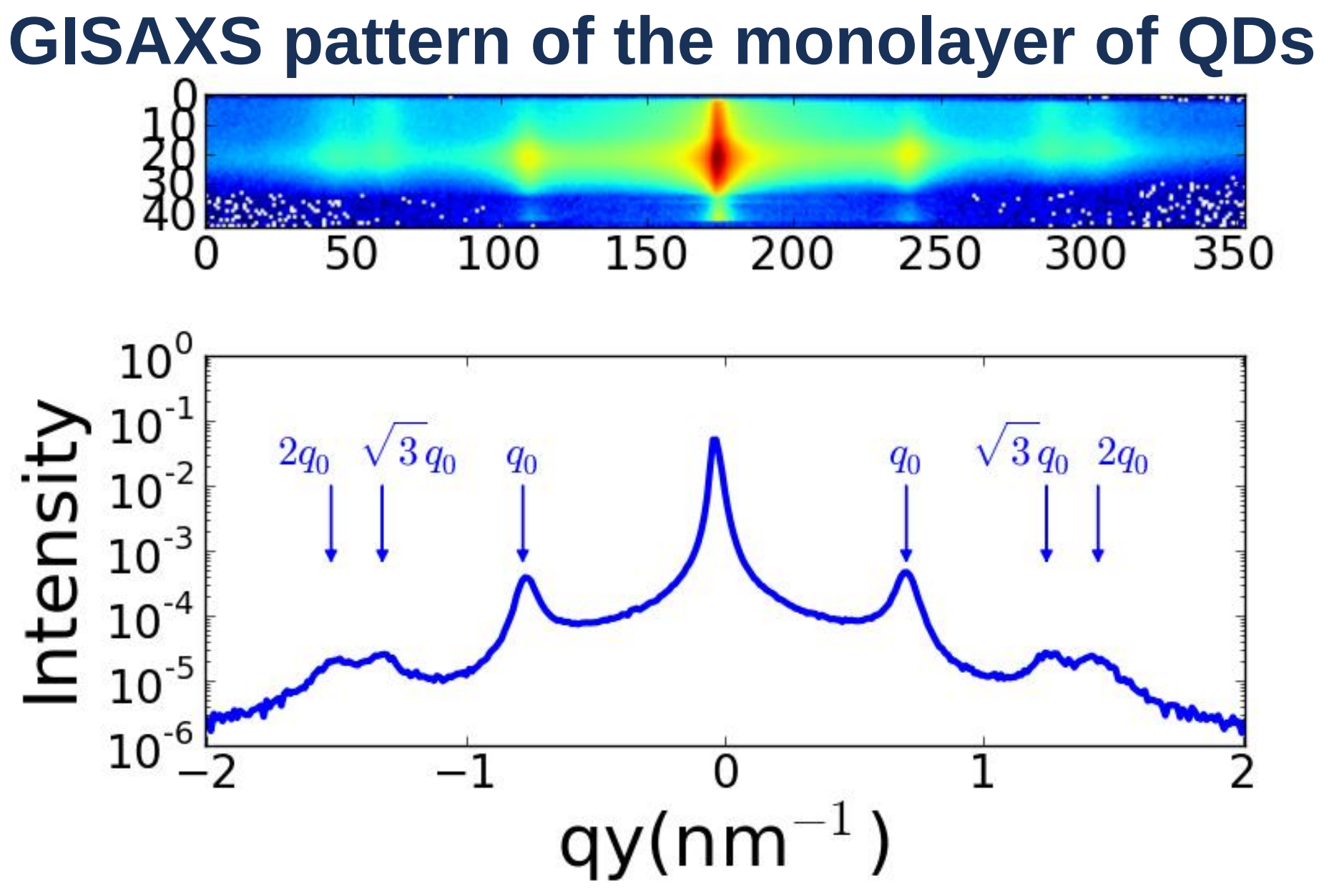
Sample description

A monolayer of core/shell QDs with an overall diameter of 10 nm that are capped with oleate ligands was formed on a silicon substrate by Langmuir-Blodgett deposition. This ensures the deposition of a single monolayer of QDs, ordered in a hexagonal pattern.

TEM image of ordered QDs

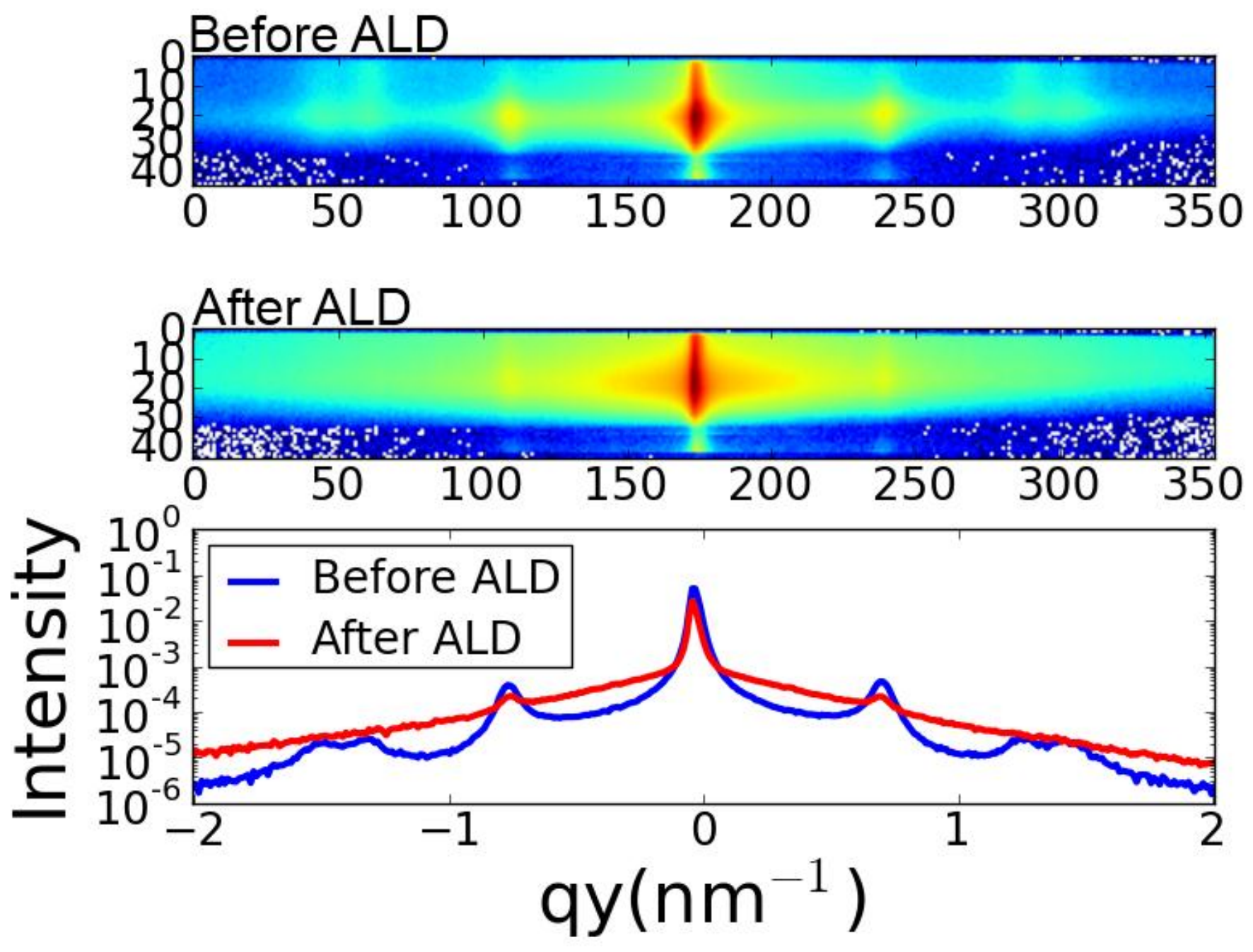


GISAXS pattern of the monolayer of QDs



Structure analysis through *in situ* GISAXS

GISAXS pattern before and after ZnO growth



Analyses of order:

The GISAXS data shows no shift in the peaks

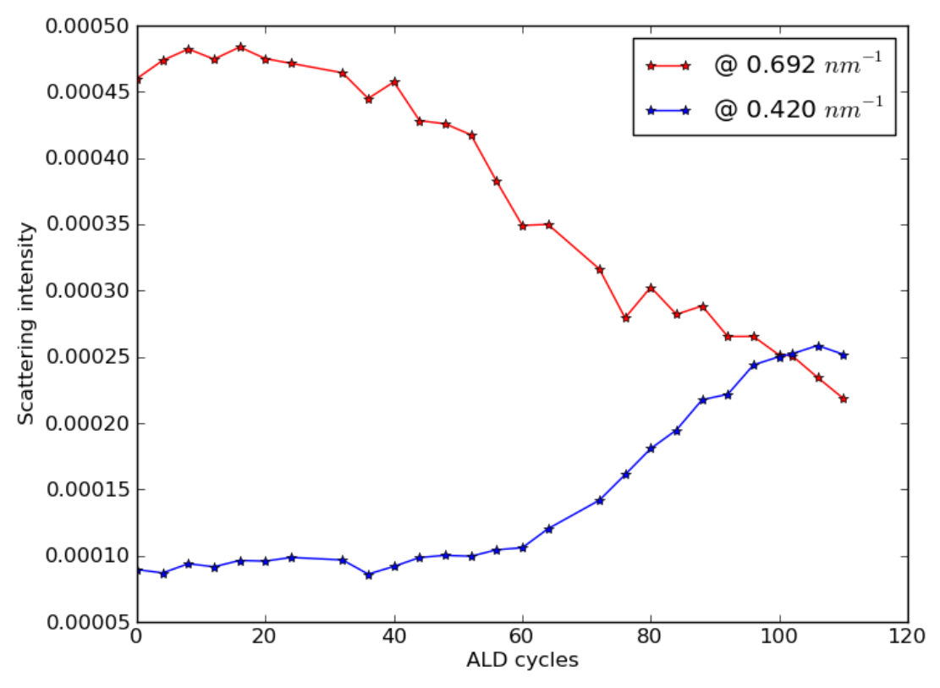
Order is preserved

- No coalescence or melt of the particles
- No influence of the ALD on the order

Influence of the ZnO layer

- ZnO overgrows the QDs
  ⇨ Lower density contrast between QDs and matrix
    ⇨ GISAXS Peak Intensity ↓
- Creation of ZnO interface
  ⇨ Random scattering ↑

Evolution of the scatter intensity



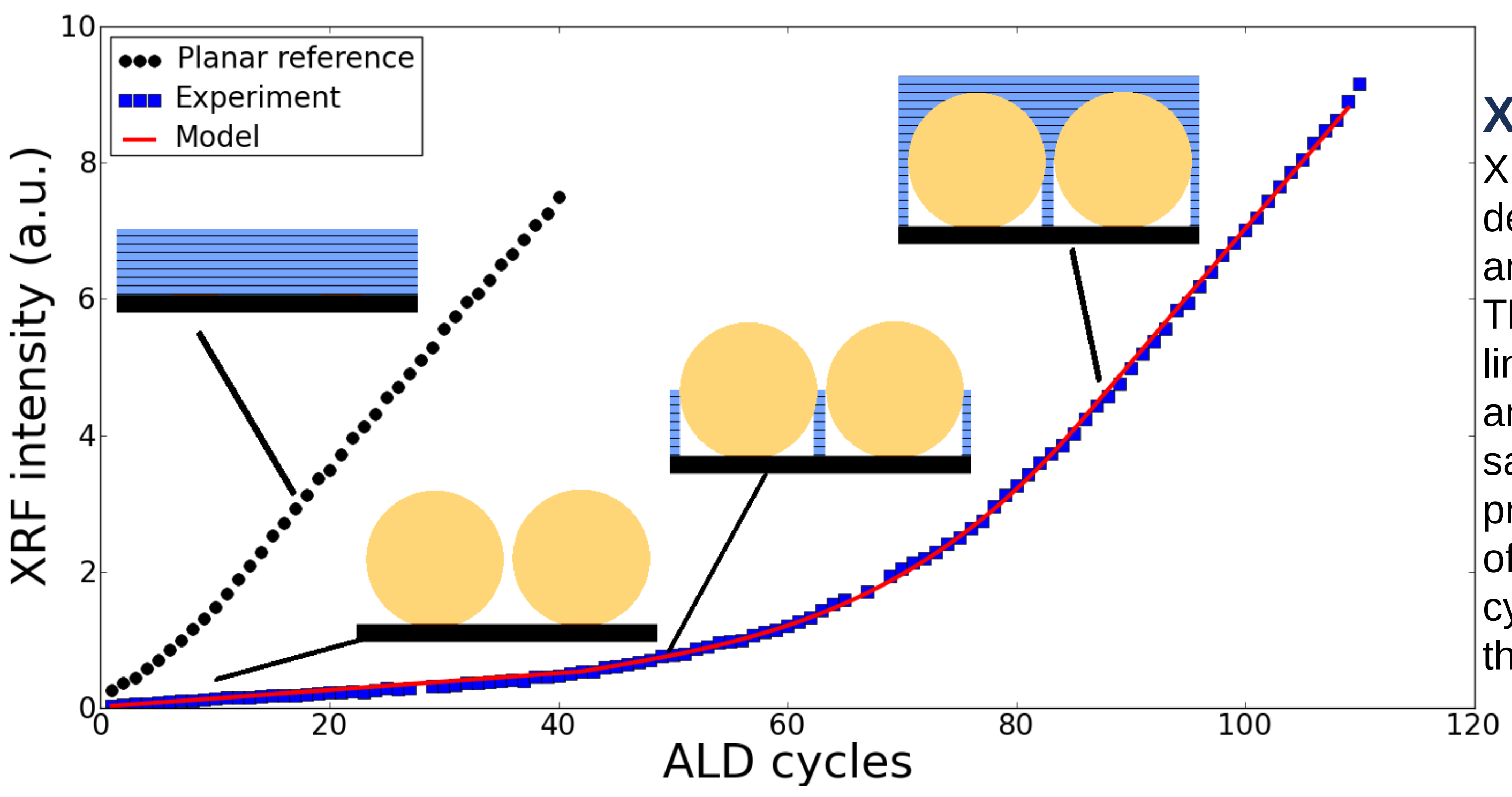
0 - 40 ALD cycles:
- Little change

40 - 60 ALD cycles:
- Peak Intensity ↓
- Random scattering ↑

60 - 80 ALD cycles:
- Peak Intensity ↓
- Random scattering ↑↑↑

Growth analysis through *in situ* XRF

Zn Kα intensity as monitored during ALD growth of ZnO



XRF principle

XRF allows for *in situ* determination of the amount of ZnO deposited. The intensity of the Zn Kα-line is proportional to the amount of Zn in the sample. This in turn is proportional to the amount of ZnO. This allows a cycle by cycle analysis of the ALD process.

0 - 80 ALD cycles:
- Growth rate on QDs < growth rate on planar reference
  ⇨ Less surface area available for ALD
- Growth rate gradually increases

80 - … ALD cycles:
- Growth rate on QDs similar to planar reference
  ⇨ Overgrown QDs resemble planar reference

Proposed growth mechanism

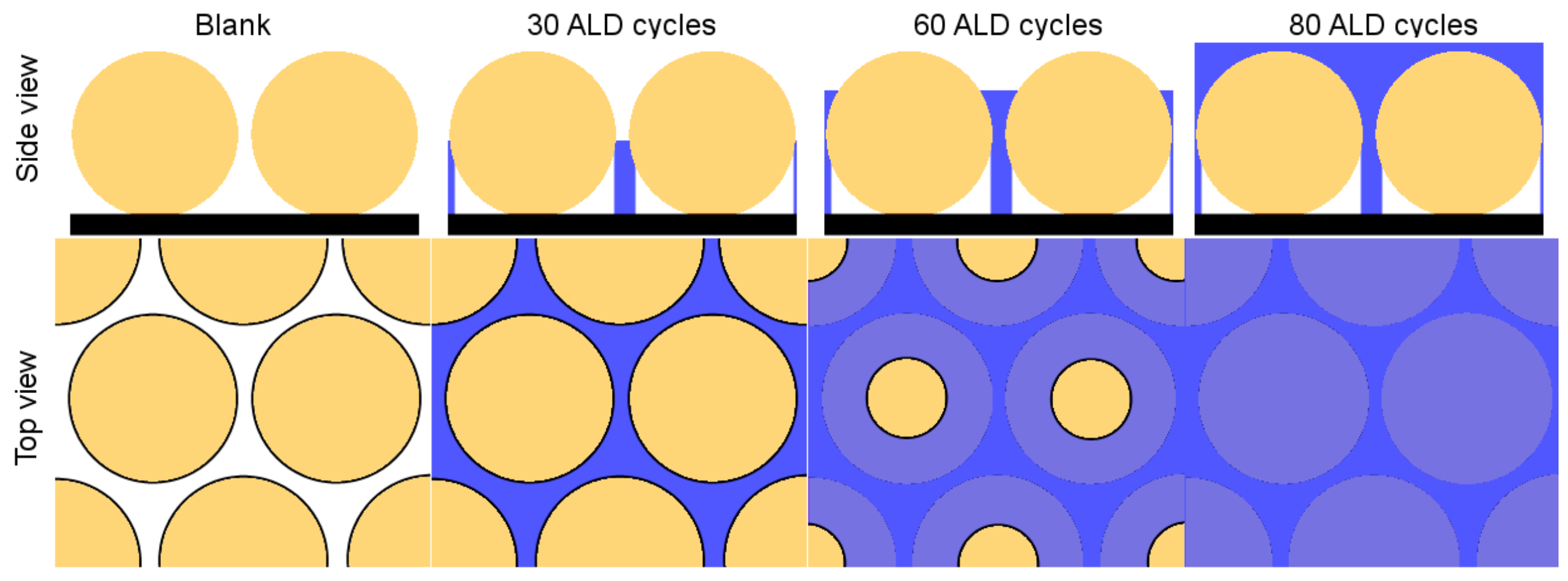
What do we learn from the data?

GISAXS analysis learns:
- Peak intensities drop from ALD cycle 40 (layer thickness ≈ radius QD)
- Random scattering increases from ALD cycle 40

XRF analysis learns:
- Low growth rate during the first 80 ALD cycles, (layer thickness ≈ diameter QD)
  This suggests less available surface area during the first cycles
- Gradually increasing growth rate until the growth rate on a planar reference is reached

Possible growth mechanism

The ALD precursor can't chemically react with the oleate ligands covering the QDs. Thus the precursors only react with the bare Si surface in between of the QDs., resulting in a low growth rate. As the layer reaches half the diameter of the QDs, the layer starts overgrowing the QDs, effectively increasing the available area. Once the QDs are fully overgrown, the growth proceeds as it would on a planar substrate.



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