Nanoscale area selective ZnO growth between a monolayer of nanocrystals

Kilian Devloo-Casier¹, Jolien Dendooven¹, Karl F. Ludwig², Pieter Geiregat³, Zeger Hens³ and Christophe Detavernier¹

¹Dept. of Solid State Sciences, COCOON, Ghent University, Ghent, Belgium
²Dept. of Physics, Boston University, Boston, USA
³Dept. of Inorganic and Physical Chemistry, PCN, Ghent University, Ghent, Belgium

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/ZnO 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

Setup description

UV-Vis 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.

Structure analysis through in situ GISAXS

GISAXS pattern before and after ZnO growth

GISAXS data shows no shift in the peaks, hence the order is preserved. No coalescence or melt of the particles and no influence of the ALD on the order.

Growth analysis through in situ XRF

Zn Kα intensity as monitored during ALD growth of ZnO

GISAXS Peak Intensity ↓

Gradually increasing growth rate until the growth rate on a planar reference is reached.

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 ↑

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.