

Precipitation of $\text{In}(\text{OH})_3$ and InOOH Nanocrystals for the use in nanoelectronics: Phase Transition Behavior and Oriented Aggregation

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ABSTRACT

With respect to diverse applications in the wide field of nanoelectronics we characterize a specific phase transition behaviour and oriented aggregation (OA) during wet chemical synthesis of $\text{In}(\text{OH})_3$ nanocrystals as a wide band gap- and precursor material for In_2O_3 . Contiguous to the cubic $\text{In}(\text{OH})_3$ phase, also orthorhombic InOOH is formed in a precipitation route with indium acetate as the In^{3+} source. Nano- and microcuboids are observed that consist exclusively of $\text{In}(\text{OH})_3$. The InOOH phase stays semicrystalline even for long reaction times. On the basis of DFT calculations we find that for small crystallites the InOOH phase is more stable than the $\text{In}(\text{OH})_3$ phase, leading to a size-dependent transition from the InOOH phase to $\text{In}(\text{OH})_3$ above a critical crystallite size.

Keywords: precipitation, nanocrystals, oriented aggregation indium hydroxide, indium oxohydroxide

1 INTRODUCTION

Since In_2O_3 reveals interesting optical and electronic features because of its wide band gap of 2.93 ± 0.15 and 3.02 ± 0.15 eV for the cubic bixbyite and rhombohedral bulk polymorphs, respectively [5] in the past few years several attempts were made to synthesize indium hydroxide $\text{In}(\text{OH})_3$ nanocrystals with tailored size and shape as precursor material[3,4]. In our work we shed light on the specific growth characteristics of $\text{In}(\text{OH})_3$ nano and microcuboids in water[1]. We report a model which consists of three extraordinary steps. These steps are dominated by oriented attachment. We also give an explanation for the unusual phase transition behavior during colloidal synthesis of $\text{In}(\text{OH})_3$ nanocrystals in water. The InOOH phase remains semicrystalline even for long refluxing times. Our investigations were done by HRTEM, SEM, X-ray diffraction, and density functional theory (DFT) calculations.

2 EXPERIMENTAL SECTION

$\text{In}(\text{OH})_3$ samples were prepared by precipitation from $\text{In}(\text{Ac})_3$ in 99% purity with KOH ($\geq 85\%$ purity) in water (milli pore Qwater). All chemicals were purchased from Sigma Aldrich and used as received without further purification. For a typical synthesis the initial concentration of $\text{In}(\text{Ac})_3$ was 0.13 mol/L and KOH was 2.3 mol/L. Ten milliliters of the KOH solution was dropped into 40 mL of the indium acetate solution via a dropping funnel within less than 1 min followed by up to 24 h of refluxing.

3 RESULTS AND DISCUSSION

The irregular growth of the InOOH phase is explained by proton transfers from hydroxyl groups to oxygen ions within the InOOH lattice that lead to OH disorder and lattice strain. DFT calculations of the surface energies of ideal and water-saturated low-index InOOH and $\text{In}(\text{OH})_3$ surfaces predict that the $\text{In}(\text{OH})_3$ phase becomes energetically more favourable than InOOH above a critical crystallite size. This explains why InOOH is formed before the $\text{In}(\text{OH})_3$ phase, which is an unusual pathway for a hydrothermal process. Once InOOH has transformed to $\text{In}(\text{OH})_3$ by incorporation of water, the crystallites can grow without restriction due to the disappearance of OH-disorder-induced strain. These findings are discussed in more detail in our latest paper [1]. Exchanging the counter ion of the In^{3+} source directly determines the shape of the product particles. Therefore see figure 1.

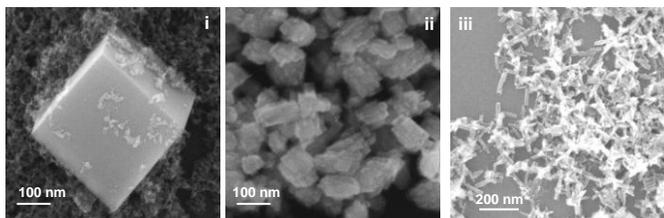


Figure 1: SEM image. 24h refluxing. i) acetate; ii) chloride; iii) acetyl-acetonate: different counter-ions lead to different shapes.

Figure 2 depicts a SEM image from a $\text{In}(\text{OH})_3$ microcuboid after 180 minutes of reaction time. The particles surface exhibits several linear defects and vacancy clusters. Also some single rods are attached to the surface which are oriented in parallel to the edges.

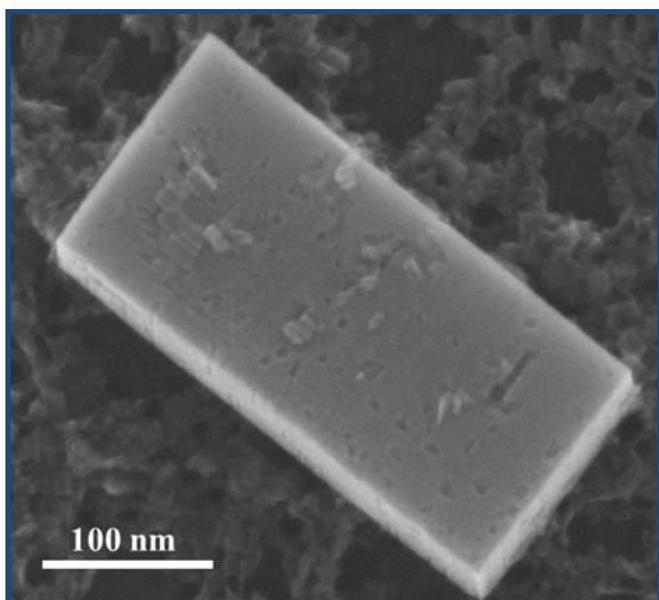


Figure 2: SEM image of an $\text{In}(\text{OH})_3$ microcuboid that is formed by oriented aggregation[1].

To explain the particle formation in a more descriptive way we present a scheme in Figure 3. The nano- and microcuboids form by three-step oriented aggregation (OA) from nanocubes: (i) one dimensional (1D) OA of nanocubes under formation of nanorods with an aspect ratio of two,(ii) 3D OA to parallel bundles of nanorods, (iii) merging of the rod bundles into cuboids similar to a former model reported by Jean et al.[1, 2].

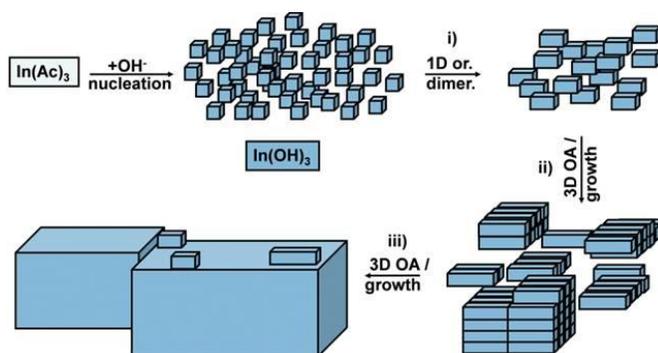


Figure 3: The cuboids form by three-step OA from nanocubes: (i) 1D OA of nanocubes under formation of nanorods with an aspect ratio of two,(ii) 3D OA to parallel bundles of nanorods, (iii) merging of the rod bundles into cuboids. [1].

Step (ii) is also shown in figure 4. A TEM image after 4.5 minutes nicely indicates the bundling of single $\text{In}(\text{OH})_3$ into cuboids.

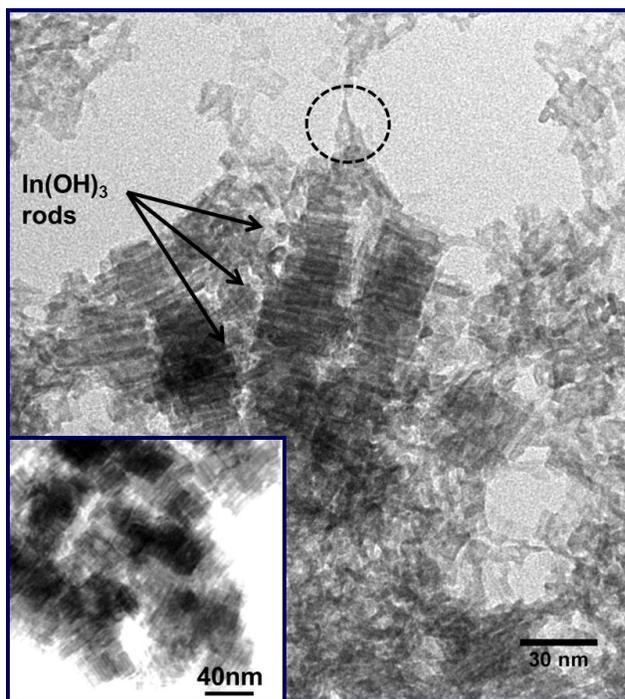


Figure 4: TEM image of an $\text{In}(\text{OH})_3$ / InOOH synthesis after 4.5 min. Beside a semicrystalline fraction of InOOH (e.g. dotted circle) $\text{In}(\text{OH})_3$ nanorods pack to bundles in a high orientational order: vectorial alignment along preferred indices.

For all the refluxing times the orthorhombic InOOH phase and the cubic $\text{In}(\text{OH})_3$ phase are identified by XRD, consistent with the TEM results. For the reflections associated to $\text{In}(\text{OH})_3$ the intensity increases and the FWHM decreases with refluxing time. This shows that the

crystallinity of the $\text{In}(\text{OH})_3$ phase increases with refluxing time. In contrast, the reflections related to the InOOH phase remain broad and weak even at $t = 180$ min. The XRD coherence lengths for the lattice planes of InOOH remain below 5 nm for all refluxing times[1].

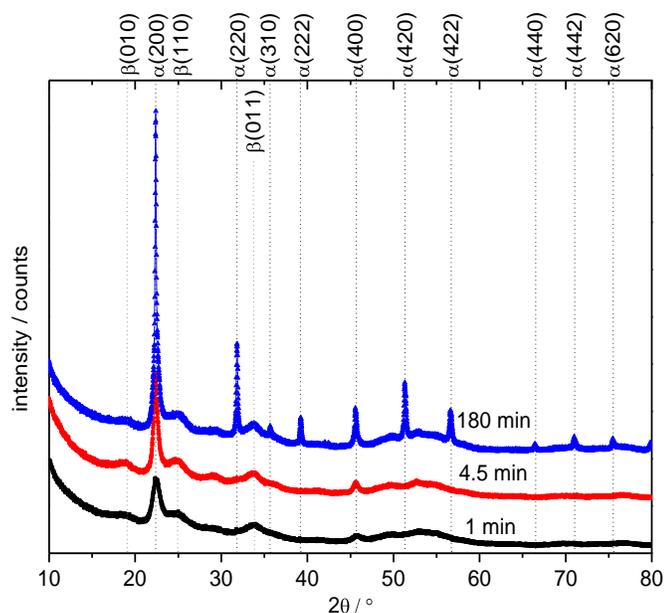


Figure 5: XRD patterns for samples taken after refluxing times of (a) 1 min, (b) 4.5 min, and (c) 180 min. The reflections can be assigned to cubic $\text{In}(\text{OH})_3$ (α) and orthorhombic InOOH (β).

4 CONCLUSIONS

Precipitation of In^{3+} with OH^- under the presence of acetate ions in water results in the formation of two different material fractions. One fraction is $\text{In}(\text{OH})_3$ that is formed by an OA process and leads to nano- and microcuboids. On the other hand we detect InOOH nanoparticles which remains semicrystalline.

REFERENCES

- [1] M. Klaumünzer, M. Mackovic, P. Ferstl, M. Voigt, E. Spiecker, B. Meyer, and W. Peukert; *J. Phys. Chem. C* **2012**, 116, 24529