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In situ TEM Study to Unravel Dynamic Processes and Phase Transition During the Synthesis of Ultrathin Crystalline ALD Nanotubes

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The creation of densely arranged hollowed nanostructures via template based Atomic Layer Deposition (ALD) is a well-established process [1] [2]. While amorphous nanotubes can be successfully made of various metal oxides [3] [4] the creation of high quality crystalline nanotubes for example made of sapphire [5] is still a challenging process. To control the crystal structure of ALD based systems, it is indispensable to use *in situ* techniques to understand the dynamic processes going on during phase transition. A controlled transition of the amorphous to a crystalline microstructure [6] would allow to achieve nanotubes with extraordinary behavior regarding the hardness [7], temperature stability [8] or optical properties [9]. In the framework of this idea, creating hollowed metal oxides with a defined ordered structures on small scale opens up the opportunity to design miniaturized building unit, which are interesting for applications in field of optoelectronics [10] or photocatalytics [11].

We present a universal approach to create ultrathin crystalline defect-free ALD nanotubes by using a comprehensive annealing process of specific core-shell nanowires (Nws). Diffusion phenomena and provoked phase transitions during temperature treatment are revealed by *ex situ* and *in situ* Transmission Electron Microscopy (TEM) studies, which provide novel insights into the dynamics occurring on atomic scale.

Core-shell nanowires consisting of a metal core and a thin metal oxide shell represent the starting material. The freestanding metal nanowires are produced via Physical Vapour Deposition (PVD) under elevated temperatures (60% of the melting temperature) with optimized parameters for sputtering instruments. The single-crystalline nanowire have thickness is in the range of 20-100 nm with lengths between 10 to 40 µm. The dimensions as well as the quality such as the surface properties, the microstructure and defects of the metal nanowire crucially determine the resulting quality of the crystalline ALD nanotube. To create core-shell nanowire, The PVD nanowire growth process is followed by an ALD step. The original nanowire represents now the metal core, which is totally covered by an amorphous 4 nm thick ALD shell.

The successful creation of nanotubes is only achievable with the purposely chosen PVD and ALD material system. As metal core, copper (Cu) with a melting temperature T_m of 1085°C is suitable. Already at relatively low temperatures sufficient material diffusion is thermally activated, which is also observed during solid-state dewetting of thin metallic films [12]. The ALD coating depends on the desired nanotube material as well as on the phase transition temperature. ALD grown Al_2O_3 for example crystallizes at temperatures > 1000°C into stable $\alpha-Al_2O_3$ [13].

Heating core-shell nanowires (e.g. Cu/ALD-Al_2O_3) at temperatures below 1000°C lead finally to the creation of a hollowed amorphous ALD nanotubes. Similar to the capillary effect, which describes the rising of a fluid in a narrow tube, we observe an inverse phenomena (here called inverse capillary effect). While the ALD shell is stable at elevated temperatures, the diffusion of the metallic core material is activated (see figure 1a). The conformal ALD shell acts as barrier for the material diffusion and forces the core to continuous retraction towards the cracked end of the nanowire, which was caused by the mechanical transfer onto the heating chip. Figure 1b shows an exemplary Scanning Transmission Electron Microscopy (STEM) image sequence with Energy Dispersive X-ray spectroscopy (EDX).

As a first phenomenon we observe the creation of voids, which is caused by vacancy agglomeration. Vacancies are induced during the PVD process at elevated temperatures and the amount of vacancies scales directly with the temperature [14]. However, heating for longer time, the voids and therefore the vacancies get compensated. The thermal activation for the material diffusion can be observed during high resolution imaging, displayed in figure 1c. To release an atom from the bonded state of the core lattice a specific amount of bond energy is required [15]. This energy barrier can be overcome by heat treatment and the released atoms diffuse within the inner cavity of the ALD tube. The time for releasing atoms scales directly with the temperature, which is illustrated in figure d.

By holding the temperature for longer time, no core material is left within the ALD framework and an amorphous nanotube is created. Increasing the temperature up to 1000°C induces a phase transition and a crystalline microstructure is achieved, which is exemplarily displayed in figure 2. The diffraction pattern of an initial core-shell nanowire only shows the <001> zone axis of the Cu core-nanowire and the ALD layer does not contribute to the crystalline pattern. During heating > 1000 °C, Moiré pattern (figure 2b) are observed, which indicates the crystallization of the ALD shell. By holding the temperature below the phase transition temperature, no moiré pattern have been observed. Figure 2c shows a typical diffraction pattern of a desired crystalline α- Al_2O_3 nanotube after processing. Based on the precise characterization of the microstructure in TEM, these type of ultrathin crystalline nanotubes show promising optical and mechanical properties and are the ideal candidate for further functionalization processes.

As conclusion, this work presents a complete workflow to create high-quality crystalline nanotubes based on specific core-shell nanowires as well as a comprehensive electron microscopy study. The analysis of the dynamic processes based on heat induced material diffusion give novel insights regarding the observed inverse capillary effect as well as on fundamental physical concepts. In future, we plan to go even one step further to optimize the nanotube functionality. For example a metallic third-party particle (e.g. Au, Mo) can be trapped within the inner cavity of the nanotube resulting an enhanced catalytic behavior.

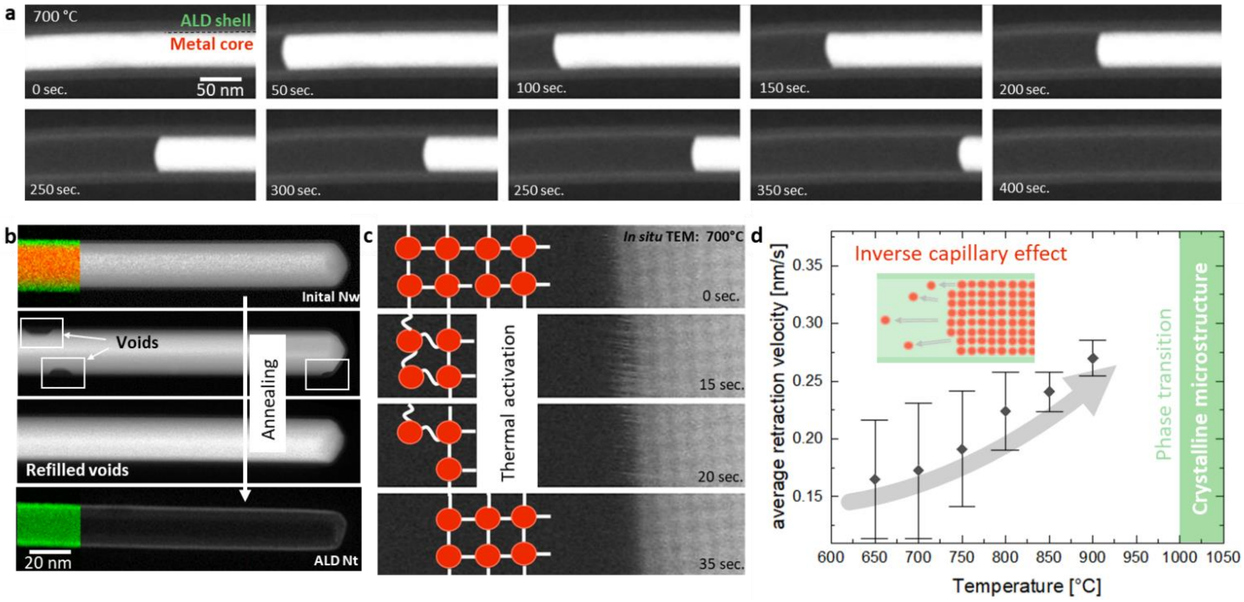

Figure 1. *In situ* TEM study: Heat treatment of core-shell nanowires (e.g. Cu/ALD-Al_2O_3). a) STEM image sequence showing the steady retraction of the nanowire core (inverse capillary effect). b) STEM images: Creation of voids, refill process and the final ALD nanotube. EDX mapping: Red: Cu, Green: Al. c) High-resolution image sequence of thermally activated lattice vibrations. d) Temperature dependency of the average retraction velocity of the core material.

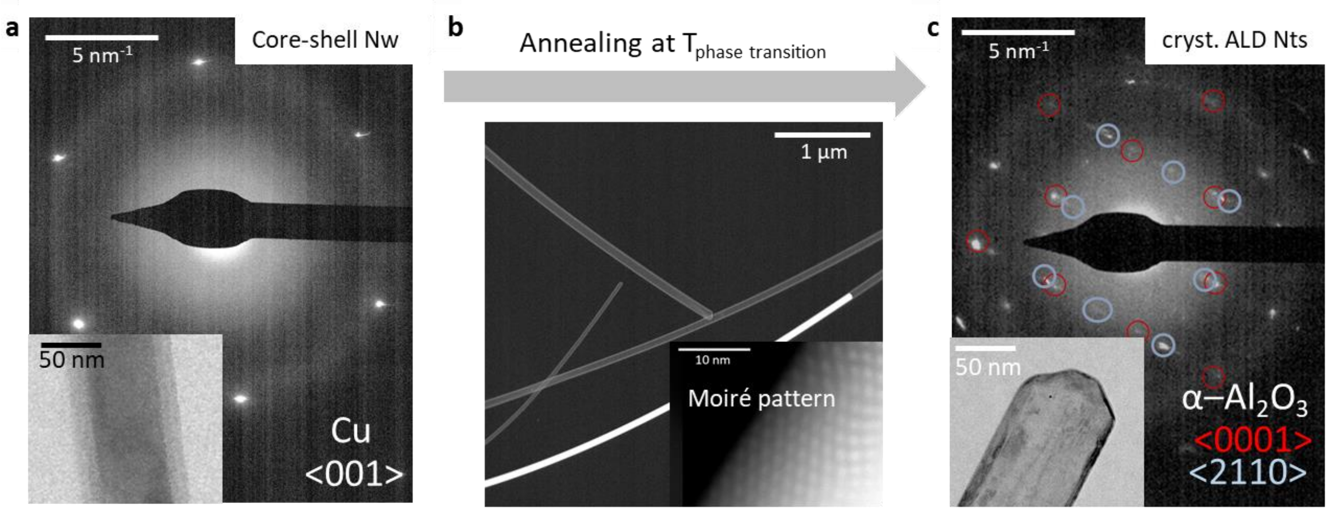

Figure 2. Exemplary TEM analysis. Phase transition of ALD- Al_2O_3 to crystalline α- Al_2O_3 at 1000°C. a) Diffraction pattern of an initial core-shell Cu/ALD-Al_2O_3 nanowire. Diffraction pattern corresponds to the Cu core. Inset: corresponding bright field TEM image. b) Annealing at phase transition temperature. Moiré pattern are observed. c) Diffraction pattern of a crystalline α- Al_2O_3 nanotube (Nt). Inset: corresponding bright field TEM image.

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