Supplementary Information

ESI1: Overview of the produced copper nanowires by sputtering. a) SEM image of nanowires emerging from a bulksubstrate (W-wire piece). b) STEM image of a nanowire tip and indicated growth direction of [110]. c) Diffraction pattern of a nanowire in [110] zone axis. D) High-resolution STEM image of copper nanowires with native oxide layer.

ESI1: Copper nanowires produced by advanced PVD.



ESI2: Effect of oxygen present during annealing. Oxygen present during heating leads to the creation of a diffusive couple at the metal-ALD interface. The Kirkendall effect describes the mutual diffusion of two metals through an interface [1] and is associated with vacancy diffusion and void formation [2]. At the nanoscale, this diffusional phenomenon based on an unequal material flow at the interface of two different solids has been used to create hollow nanoparticles [3] or nano-tubes [4] [5]. Typically, a metal nanostructure is exposed to oxygen under elevated temperatures, where a hollow nanostructure based on a binary metal-oxide composition is achieved [6]. The outward diffusion of the metal is much faster than the inward diffusion of oxygen and therefore the created vacancies at the interface coalesce into a void which results in a hollow nanostructure [7]. We observe a similar Kirkendall effect by heating the core-shell nanowires ex situ without constant argon flow. Instead of a pure ALD nanotube consisting of amorphous Al₂O₃, the resulting nanotube has a fuzzy copper oxide shell.



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ESI3: SEM images of freestanding nanotubes emerging from a substrate.



ESI4: Copper particles near nanotubes.



ESI5: *In situ* STEM video. Figure 3a in the main manuscript shows an exemplary image sequence of the experiment. **ESI6**: *In situ* HRSTEM video: line-by-line desorption of copper atoms from the surface.

ESI7: In situ HRSTEM video of the dynamic process.

ESI8: Delamination at the metal-metal oxide interface observed at nanowires which have been directly transferred to the ALD chamber without breaking the vacuum.



ESI9: Creation of complex multi-layered nanostructures. a) Working procedure. Cu NWs are coated with alternating layers of $ALD-Al_2O_3$ and ALD-ZnO. The resulting core-shell nanostructures are heated (following the heat treatment presented in the main manuscript) resulting in hollow nanolaminates. b) Exemplary STEM image of Cu NW coated with ALD-multilayers. c)EDX map (green: Al signal, violet: Zn signal) and corresponding STEM image of the hollow nanostructure.

