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Catalyst Dynamics during Carbon Nanotube and Si Nanowire CVD

S. Hofmann,[*] R. Sharma,[**] R. Blume,[***] C. T. Wirth, [*] C. Ducati,[****] T. Kasama, [****]
R. E. Dunin-Borkowski,[*****] D. Teschner, [***] J. Drucker,[******] P. Bennett,[******] A. Knop-Gericke, [***]
R. Schloegl, [***] J. Robertson[*]

[*]Department of Engineering, University of Cambridge, Cambridge CB3 0FA, UK
[**]LeRoy Eyring Center for Solid State Science, Arizona State University, Tempe AZ85287-1704, USA
[***] Fritz Haber Institute of the Max Planck Society, Faradayweg 4-6, 14195 Berlin, Germany
[****]Department of Materials Science and Metallurgy, University of Cambridge, Cambridge CB2 3QZ, UK
[*****]Center for Electron Nanoscopy, Technical University of Denmark, DK-2800 Kongens Lyngby, Denmark
[******]Department of Physics, Arizona State University, Tempe AZ85287-1704, USA

Self-assembled nanowires and nanotubes offer the prospect of accurate and scalable device engineering at an atomistic scale. However, deterministic nanotube growth and the control of nanowire dopant profiles and heterostructures are limited by an incomplete understanding of the role of commonly used catalysts and specifically their interface dynamics.

We present atomic-scale environmental transmission electron microscopy (ETEM) and in-situ X-ray photoelectron spectroscopy (XPS) of catalyst assisted growth of single-walled carbon nanotubes (SWNTs) [1], carbon nanofibres (CNFs) [1] and silicon nanowires (SiNWs) [2], combined with a large-throughput ex-situ catalyst screening by plasma assisted and thermal CVD [3,4,5]. We sample Ni, Fe, Au and Pd model catalyst films on SiO_x and Al_2O_3 supports upon acetylene or disilane exposure. We focus on catalyst island formation and support interactions upon temperature elevation and subsequent interactions with carbon or silicon precursors.

We observe Ni catalyst nano-particles to be highly deformable during SWNT/CNF growth, despite their core exhibiting a crystalline structure throughout the process. Time-resolved XPS results show that Fe, Ni are metallic when catalysing a rapid transition from initial chemisorbed carbon to a sp^2 graphitic carbon network. For a CNF, the graphene layer stacking is determined by the successive elongation and contraction of the catalyst nano-particle at its tip. A SWNT nucleates by lift-off of a carbon cap. Cap stabilization and nanotube growth involve the dynamic reshaping of the catalyst nano-crystal itself.

XPS shows a strong interaction between Fe and Al_2O_3 layers, which prevents excessive Fe island sintering and homogenises their size distribution. We observe with an optical camera how this triggers the growth of vertically aligned, mm-long SWNT/CNF forests. Combining ETEM and substrate micro-structuring, we show that, apart from their catalyst anchorage, SWNTs are often not in direct contact with the substrate. This allows us to grow gas-flow aligned, mm-long lateral nanotube arrays.

We show ETEM videos of the nucleation and growth of Si nanowires for liquid and solid catalyst systems [2]. In both cases, Si nuclei form by phase separation before expanding and pushing the catalyst onto the tip of the forming wires. For Pd silicide catalyst crystals we directly resolve how the dominant, coherent Si nanowire growth interface advances by the lateral propagation of ledges. We propose that interfacial ledge propagation plays a central role in nanowire self-assembly.

References:

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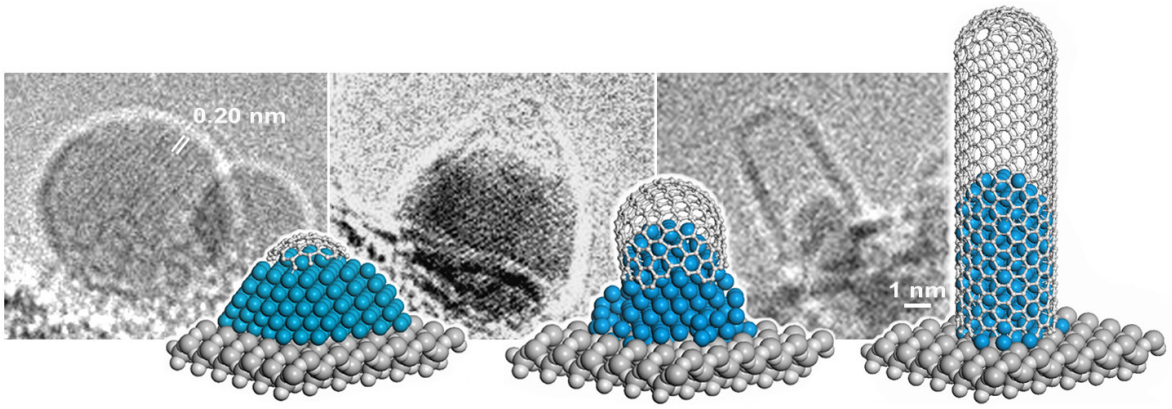

Fig. 1 ETEM images of Ni catalyst nanoparticles on SiO_x membrane at 615°C before (in vacuum, 10^{-6} mbar), during and after (post-growth TEM) exposure to 8×10^{-3} mbar C_2H_2. The ball-and-stick models schematically highlight the different nucleation stages of carbon nanotube growth.

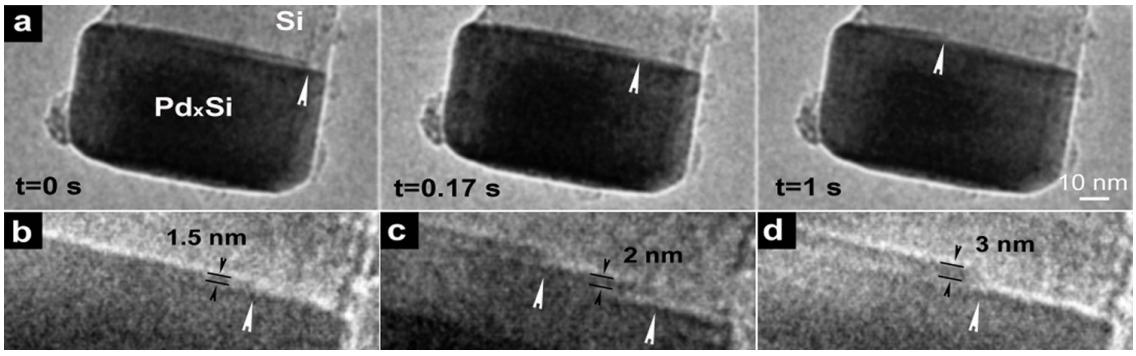

Fig. 2 a ETEM image sequence of step-edge dynamics for Pd-silicide catalysed SiNW at ~560°C in ~1.2×10^{-2} mbar Si_2H_6. t indicates elapsed time with respect to the first image. ETEM images b-d show various step-edge configurations at the Pd silicide/SiNW interface.