CATALYST DYNAMICS DURING Si NANOWIRE AND CARBON NANOTUBE CVD

S. Hofmann
Department of Engineering, University of Cambridge Cambridge CB3 0FA, UK
Email: sh315@cam.ac.uk

The self-formation and assembly of semiconducting nanowires and carbon nanotubes offer the prospect of device engineering at atomistic scale in compatibility with Si integrated circuit technology. The most controlled pathway for nanowire/tube formation at present is the exposure of transition metal catalyst particles to gaseous precursors at elevated temperatures, commonly referred to as catalytic chemical vapour deposition (CVD). The understanding of the role of the catalyst and the contributing atomic processes is, however, very incomplete and controversial, even for the most widely cited vapour-liquid-solid growth mechanism. This currently limits progress on more complex nanowire/tube device structures on route to their widespread application.

We present atomic-scale environmental transmission electron microscopy (ETEM) and in-situ X-ray photoelectron spectroscopy (XPS) of catalyst assisted growth of silicon nanowires (SiNWs) [1], single-walled carbon nanotubes (SWNTs) [2,3], and carbon nanofibres (CNFs) [2], combined with a large-throughput ex-situ catalyst screening by plasma assisted and thermal CVD [4,5,6]. We sample Ni, Fe, Au and Pd model catalyst films on SiO2 and Al2O3 supports upon disilane or acetylene exposure. We focus on catalyst island formation and support interactions upon temperature elevation and subsequent interactions with silicon or carbon precursors.

Video-rate ETEM shows that a Si crystal nucleus forms by phase separation for both liquid and solid catalyst systems [1]. We present a detailed comparison of nucleation dynamics and growth limiting processes for VLS and VSS mechanisms. For Pd silicide catalyst crystals (see Fig.) 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. Our results establish an atomistic framework for nanowire assembly from solid catalysts, relevant also to their contact formation.

We observe catalyst nano-particles to be highly deformable during SWNT/CNF growth, despite their core exhibiting a crystalline structure throughout the process [2]. For Fe and Ni, the active state of the catalyst is a crystalline metallic nano-particle, not the oxide. Graphitic networks do not form on oxidized Fe. Pd forms a silicide on SiO2 under reducing conditions. Pd (silicides) and Au are catalytically less efficient in terms of precursor dissociation, while the low adhesion of C on Au surfaces impedes nanotube nucleation. We observe Fe 2+ and 3+ interface states for metallic Fe on Al2O3 in the absence of measurable Al reduction [3]. This support interaction is much stronger than on SiO2 and it restricts Fe surface mobility. The resulting much narrower Fe catalyst particle size distribution on Al2O3 leads to a higher carbon nanotube nucleation density and a vertical nanotube alignment due to proximity effects, often referred to as “supergrowth”.

References:
[1] S. Hofmann et al., Nature Materials 7, 372 (2008)
[2] S. Hofmann et al., Nano Lett. 7, 602 (2007)
[3] Mattevi et al., J. Phys. Chem. C, in press
[4] M. Cantoro et al., Nano Lett. 6, 1107 (2006)
[5] S. Hofmann et al., Phys. Rev. Lett. 95, 036101 (2005)
[6] S. Hofmann et al., J. Appl. Phys. 94, 6005 (2003)

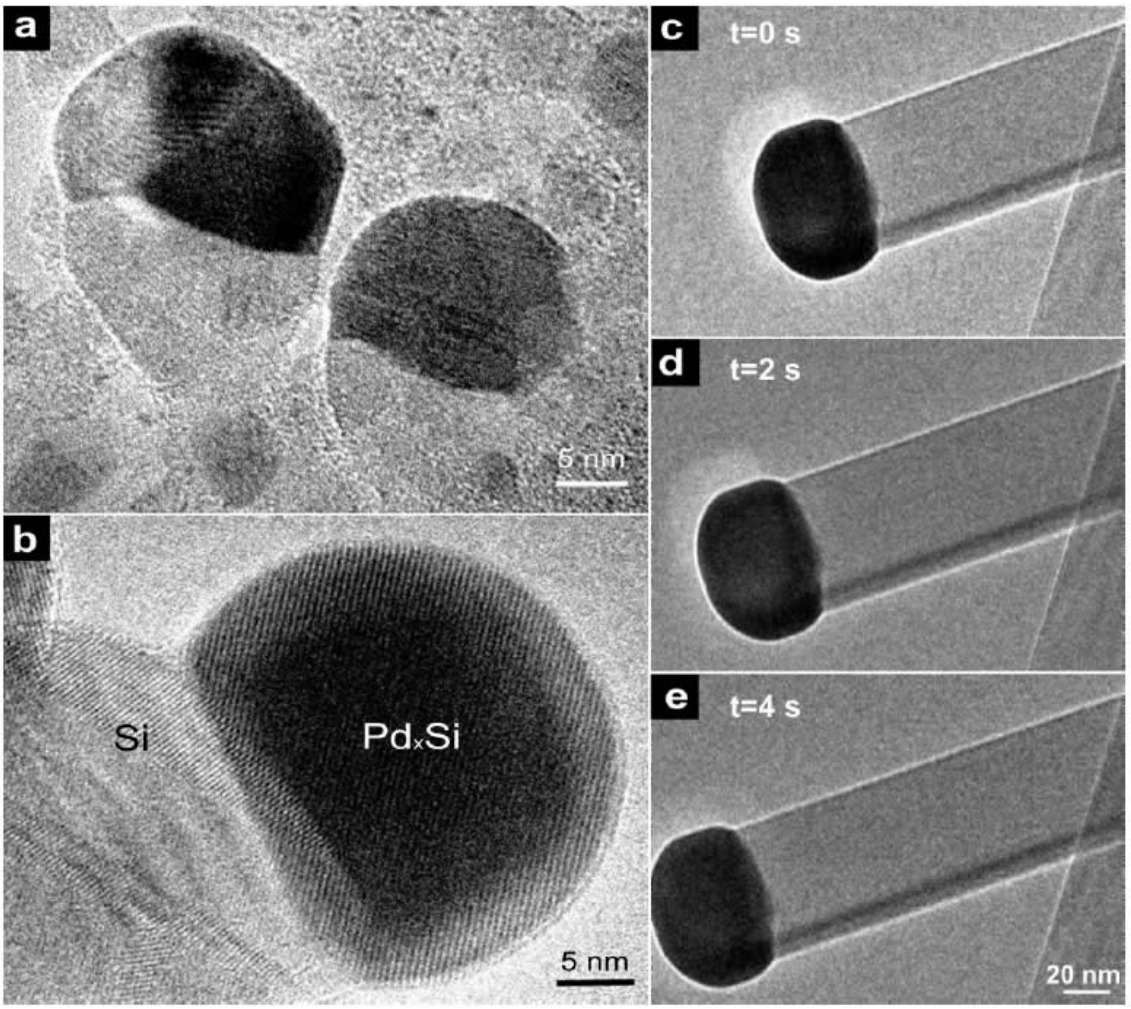

Figure ETEM images of 0.5-1 nm Pd film on SiOx membrane after exposure to ~1.2-1.6×10-2 mbar Si2H6. Image a shows the SiNW nucleation phase with Pd silicide particles at ~760°C. Image b and the sequence c-e show the tip region of growing SiNWs at ~710°C and ~625°C, respectively. t indicates elapsed time with respect to image c.