

## YY6.02/W6.02

The Catalyst Phase during Carbon Nanostructure Growth

*Bernhard C. Bayer<sup>1</sup>, Christoph T. Wirth<sup>1</sup>, Martin Fouquet<sup>1</sup>, Andrew D. Gamalski<sup>1</sup>, Santiago Esconjauregui<sup>1</sup>, Robert S. Weatherup<sup>1</sup>, Piran R. Kidambi<sup>1</sup>, Caterina Ducati<sup>1</sup>, Carsten Baehtz<sup>2</sup>, Raoul Blume<sup>3</sup>, Robert Schloegi<sup>3</sup>, John Robertson<sup>1</sup>, Stephan Hofmann<sup>1</sup>*

1. University of Cambridge, Cambridge, United Kingdom, 2. Helmholtz-Zentrum Dresden Rossendorf, Dresden, Germany, 3. Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

We study the catalyst state during chemical vapor deposition (CVD) of carbon nanostructures by complementary in-situ grazing-incidence X-ray diffraction, in-situ X-ray reflectivity, in-situ X-ray photoelectron spectroscopy and environmental transmission electron microscopy. For near-atmospheric pressure carbon nanotube forest CVD, we find that typical oxide supported Fe catalyst films form mixtures of bcc and fcc phased Fe nanoparticles upon reduction and that depending on this phase composition different growth modes occur. For fcc-rich Fe nanoparticle distributions, we find metallic Fe is the active catalyst phase, implying that carbide formation is not a prerequisite for nanotube growth. For bcc-rich catalyst mixtures, Fe<sub>3</sub>C formation more readily occurs and constitutes part of the CNT growth process. Our data indicates that metastable catalyst phases dominate the CNT growth. We propose that this behavior can be rationalized in terms of kinetically accessible pathways, which we discuss in the context of the bulk iron-carbon phase diagram with the inclusion of phase equilibrium lines for metastable Fe<sub>3</sub>C. In contrast, for low pressure CVD of single-wall nanotubes from Co catalysts we find that the catalyst state is purely metallic but that catalyst-support interactions (silicide formation) account for a remarkably narrow chiral distribution of the resulting tubes. Finally, we use the complementary in-situ metrology to compare the structural and chemical evolution of such nanoparticulate metals (1-d templates) to flat metal films (2-d templates) to elucidate similarities and differences between nanotube and graphene nucleation in CVD.