

Towards an understanding of crystal growth on the nano-scale: in-situ probes for graphene, nanotube and -wire CVD

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The understanding of the role of transition metal templates in the chemical vapour deposition (CVD) of nano-materials, such as graphene, carbon nanotubes and Si/Ge nanowires, remains incomplete, which limits a widespread utilisation of these materials. We investigate nanometrology that allows a monitoring of the catalytic CVD process and the contributing atomistic processes under high temperatures and reactive gas atmospheres, i.e. under typical reactor conditions. Our results aim to establish a framework for detailed growth modelling and an understanding of the materials and chemistry on the nano-scale.

We use high-pressure X-ray photoelectron spectroscopy (XPS) supported by environmental transmission electron microscopy (ETEM) and in-situ X-ray diffraction (XRD) to compare the behaviour of thick, poly-crystalline and nano-particulate catalysts during hydrocarbon exposure at temperatures ranging from 300-900°C, and during cooling to room temperature. For carbon nanotube (CNT) CVD, we find that oxide supported Fe and Ni are active as crystalline metallic nanoparticles [1,2]. For these systems, control over CNT growth is closely linked to catalyst-support interactions [3] and to pre-treatment conditions that prevent excessive coarsening and result in a suitable catalyst phase and topography [4]. On the other hand, we find that nano-particulate zirconia neither reduces to a metal nor forms a carbide while nucleating CNTs [5]. Such oxide-based catalysts or “metal-free” systems indicate a surface-based nanotube formation mechanism and/or significant deviations from bulk equilibrium phase diagrams. In order to study size- and solubility-dependent mechanisms, we compare catalyst nanoparticles with different diameters and use thick (>300 nm), poly-crystalline catalyst films, which we optimised for graphene growth. We focus on graphene nucleation and graphene domain size in relation to the catalyst grain size distribution and the C chemical potential. Time-resolved XPS allows a detailed comparison of transient states prior to graphene formation and C/metal core level signatures for CVD and bulk precipitation experiments, based on which we model the growth process.

Although it is generally agreed that the phase diagrams of nanoscale systems can be substantially different than compared to the bulk, there is very little direct experimental evidence demonstrating such size effects under growth conditions. We use Ge/Au as a model system and our ETTEM data shows the formation of a liquid Au-Ge layer on sub-30 nm Au catalyst crystals, and the transition of this two-phase Au-Ge/Au coexistence to a completely liquid Au-Ge droplet during isothermal digermane exposure at temperatures far below the bulk Au-Ge eutectic temperature [6]. Upon Ge crystal nucleation and subsequent Ge nanowire growth, the catalyst either re-crystallizes or remains liquid, apparently stabilised by the Ge supersaturation. Kinetic and thermodynamic modeling gives insight into the importance of surface energies and catalyst-interface dynamics [7] to nanowire growth and geometry. We believe that such metastable nanoparticle phases are relevant to other materials systems and of key importance to controlled bottom-up crystal growth and materials design for nanotechnology.

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