

Group IV nanowires as model systems to explore phase behaviour, nucleation and interface dynamics in nanoscale systems

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Abstract

Using in-situ electron microscopy we can reveal striking new crystal growth behaviour driven partly by large supersaturations in nanoscale systems that open many new kinetic pathways. We report on a new approach to form complex nanowire-heterostructures, on how nucleation barriers for crystal layers can be altered via wetting angle of the catalyst, and on catalyst mediated epitaxy of semiconductors on 2D materials.

1. Introduction

With a focus on diverse applications in the electronics and display industry, we aim at developing integrated process technology for nanomaterials, like semiconducting nanowires, 2D materials and their heterostructures. In order to go beyond empirical process calibrations, we systematically use in-situ metrology to reveal the mechanisms that govern the growth, interfaces and device behaviour of these nanomaterials in realistic process environments. This paper will focus on recent results on group IV and III-V nanowire growth, revealing some of the fundamental growth mechanisms and highlighting the use of these structures as model systems to explore generic aspects of phase behaviour, nucleation and interface dynamics in nanoscale systems.

2. The VLS growth concept and its extension

Nanowires can be grown with excellent control over length, diameter, crystal structure and composition by making use of the vapor-liquid-solid (VLS) growth mechanism. At the heart of the VLS growth mechanism lies the use of a catalyst which is effective in mediating NW nucleation and subsequent growth via vapor phase precursors. Due to its free-standing nature and nano-scale dimensions this system is ideally suited for environmental transmission electron microscopy (ETEM). Thus it can also serve as model system to directly observe nucleation and interface dynamics at the atomic scale. Very large supersaturations can occur in nanoscale systems, opening kinetic pathways generally unavailable in the bulk. We previously showed that this leads to metastable phase formation,[1] including a pathway to metastable AuGe phases under strictly isothermal conditions, the opposite limit from thermal quenching used for conventional

metallic glasses.[2] We can also use this model system to directly observe twin mediated crystal growth. [3] We propose that the nucleation barrier at the twin plane re-entrant groove is reduced by the presence of a line energy. Our results are of general validity and provide an important insight into the TPRES growth process of bulk materials.[3]

We found that this catalytic growth concept can be further expanded to tailor complex nano-heterostructures, in particular allowing the near perfect endotaxial incorporation of nanoscale crystals, or quantum dots, of controlled structure, dimensions and location into single nanowires.[4] Liquid droplets that catalyse nanowire growth in fact can act as a ‘mixing bowl’, in which growth materials are sequentially supplied to nucleate new phases. Growing within the liquid, these phases adopt the shape of faceted nanocrystals that are then incorporated into the nanowires by further growth. We demonstrate this concept by epitaxially incorporating metal silicide nanocrystals into Si nanowires with defect-free interfaces (Fig. 1)[4].

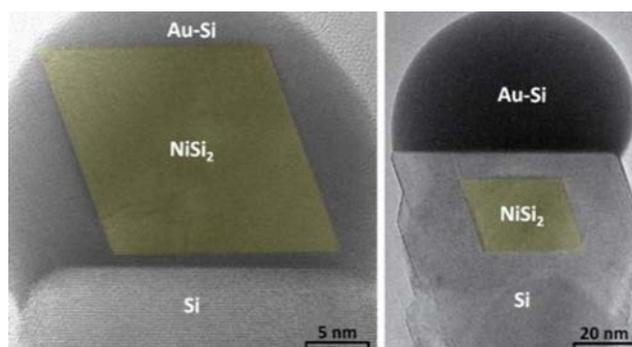


Fig. 1 In-situ TEM images showing the formation and incorporation of a nickel silicide (NiSi_2) nanoparticle (colored yellow) into a silicon nanowire during catalytic growth [4].

The entire sequential catalyst reaction process, from the deposition of Ni to the growth of the nanowire, can be repeated and multiple silicides can be embedded to form a complex silicide/silicon heterostructures. The distance between nanocrystals inside the wire is controlled through the growth time between Ni deposition steps, and the size of

each nanocrystal is controlled by the amount of deposited. Solid silicide nanocrystals have freedom to move and rotate in the liquid catalyst until a low-energy interface with the nanowire is found. After contact is made, certain types of nanocrystals remain attached to the nanowire while others break away without forming a permanent contact. Only the nanocrystals that remain attached to the nanowire can then be incorporated. We find that the mobile nature of the Si interface accommodates the initially misaligned new nanocrystal via step-flow, leading to a self-optimisation to epitaxial perfection. We have investigated several other materials systems to address the generality of the process. We have for instance nucleated single, well-faceted nanocrystals by supplying Co and Mn to liquid AuSi catalysts. Our method allows for instance nanocrystal inclusions to be controllably located at NW p-n junctions or compositional changes, and we envisage such new types of heterostructures to be highly interesting for integrated (opto-)electronics.

3. Catalyst mediated epitaxy on 2D materials

We introduce the concept of solid catalysts for epitaxial growth of a semiconductor onto a 2D substrate, using the example of Ge growth on graphene (Gr) or hexagonal boron nitride (h-BN) with an Au catalyst.[5] Free-standing Gr and h-BN membranes allow us to study such epitaxy directly by ETEM. Au when evaporated in ultra-high vacuum forms epitaxial triangular structures. We expose those Au structures to digermane at 150-200°C, and can the directly follow the selective Ge crystal nucleation at the Au/Gr and Au/h-BN interface with a relatively high degree of epitaxy. Aberration corrected images and diffraction provides details of the Gr and h-BN structure and semiconductor epitaxy while dark-field techniques yield crystal orientation relationships and defects. We can account for the epitaxial relationship of Au and Ge with Gr or hBN with simple considerations of the symmetry and nearest neighbour distances of each material. Symmetry suggests that $[111] \text{ Au} \parallel [0001] \text{ Gr}$ and that $\text{Au}\langle 110 \rangle$ should be parallel to $\text{Gr}\langle 01 \rangle$ or $\text{Gr}\langle 11 \rangle$.

Such directly visible growth provides intriguing opportunities for evaluating catalytic performance of individual particles as a function of shape or defects. The growth kinetics of individual Ge nanocrystals can be measured in situ. Nucleation is typically at the corner of the Au triangle or along the edge or in re-entrant sites. ETEM movies also show that the growing Ge remains fixed on the substrate and the Au is displaced. Strain fields associated with the deformation of the Au islands are visible. We highlight that uncatalyzed growth (i.e. direct CVD), and catalytic growth where the catalyst is liquid, require both higher temperature and produce Ge crystals that are typically not epitaxial.

Using alloy catalysts, we can expand this concept to produce epitaxial Si on free-standing Gr and h-BN, and in principle also other semiconductor materials. Another straightforward extension of the approach is to grow alloy semiconductors or heterostructures such as Si/Ge using sequential flow of the source gases. Patterning the catalyst could expand the possibilities further, making it interesting for integrated

(opto-)electronics and plasmonics.

4. Conclusions

We explore catalytic Si and Ge nanowire growth by ETEM. The excellent spatial and temporal resolution available in ETEM is useful in revealing the dynamic phenomena that underpin crystal growth, catalytic processes and nanoscale phase changes. We present findings that are interesting for scaled heterogeneous device integration and offer new insights and prospects for engineering at the nanoscale for applications in (opto-)electronics, plasmonics, sensors and energy generation/storage [6-10].

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