Gold-seeded growth of Ge nanostructures inside channelled substrates by supercritical fluid-liquid-solid (SFLS) method

Nikolay Petkov, Richard Phelan, Guillame Audoit, Michael A. Morris and Justin D. Holmes
Department of Chemistry, University College Cork, Cork, Ireland
n.petkov@ucc.ie

The ability to pack high densities of memory storage and processing circuitry into specific nanoscale arrays, and utilise the unique transport properties associated with these architectures, is expected to lead to future generations of computer processors with device sizes many times smaller and faster than current silicon based processors. However, both physical constraints and economics are expected to limit continued miniaturisation of electronic and optical devices using current 'top-down' lithography based methods [1]. The necessity to develop alternative non-lithographic methodologies for fabricating mesoscopic features of integrated circuitry will soon be needed [2]. One possible approach is to use well ordered and aligned channelled architectures as hard templates to host and guide the growth of 1 D nanostructures, thereby enhancing their electrical or optical properties.

In our group we have pioneered the development of supercritical fluid (SCF) inclusion-phase techniques for forming ordered arrays of semiconductor, metal and metal oxide nanowires within the pores of mesoporous materials and columnar channels of anodic alumina membranes (AAMs) [3]. The process involves decomposition of suitable precursors at high temperatures and pressures that results in filling the porous supports but also forms undesirable blocking, surface converge and poor crystallinity of the products. On the other hand, gold-seeded SFLS has been developed and well studied for the batch production of single crystalline semiconductor nanowires [4]. In this report we present a new approach for growing Ge nanostructures "in-place" by first positioning gold-seeds inside the channelled substrates, followed by SFLS growth at temperatures slightly higher than the Au/Ge eutectic point.

Two different types of channelled supports were used in the study: (i) AAMs with nominal channel sizes of 200 and 60nm and (ii) grooved Si-wafers with thermally grown SiO_2 layer (150 nm) with a SiN (150 nm) capping layer provided by CRANN/Intel (Ireland). The alumina and silica surfaces were modified with organo-silane resulting in covalently anchored thiol or primary amine groups. In a second step colloidal gold (5-6 nm particles) were assembled on the thiol modified surfaces or 30 mM $H[AuCl_4]$ solutions were used to impregnate the amino-modified substrates. In the course of these reactions, gold seeds were introduced along the channelled substrates that were further used for SFLS growth in SC hexane at 375 ^oC and 1000 psi with diphenyl germane as a Ge precursor.

The deposition of the gold seeds, and the subsequent growth of the Ge nanostructures was followed by cross-sectional SEM, plan-view TEM, selected area electron diffraction (SEAD) and EDX measurements. For example, Figure 1 shows cross-sectional SEM images of the Ge nanostructures inside the 200 and 60 nm columnar channels of AAMs. 1D nanostructures are seen to protrude out of the channels, aligned along the direction of the channels. The structures appear grainy, composed of crystalline domains. The nanowires are embedded and at the same time isolated from each other inside the porous alumina matrix yielding high density, semi-ordered array of 1D nanostructures. TEM images of the isolated nanowires obtained after dissolving the alumina template in phosphoric acid showed well shaped nanowires extending for more than several microns and with diameters corresponding to the diameters of the channelled substrates. Figure 1c shows typical TEM image of one such structure where the dark spots can be attributed to the gold-seeds that are encapsulate in the

Ge matrix. Thus polycrystalline, grainy 1D nanostructures were formed that can be envisioned as chain of gold-nanoparticles connected through semiconductor Ge crystallites.

Similar approach was used when Ge nanostructres were grown "in place" along grooved Si wafers. Figure 2a shows gold seeds preferentially assembled on the SiO_2 surface that was modified with thiol functionalities. The SiN capping layer served as a coating that passivated the SiO2 surface and hindered its subsequent modification with organo-silane molecules. Thus the gold seeds were assembled only inside the trenches and gave growth to the Ge nanostructures "in place". The structures appear again grainy, composed of small crystallites filling completely the channels.

In summary, a new synthetic approach for the growth of semiconductor nanostructures is presented that relies on selective modification of channelled alumina or silica surfaces with gold seeds that guide the growth of 1D nanostructures by SFLS mechanism .

References:

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Figures:

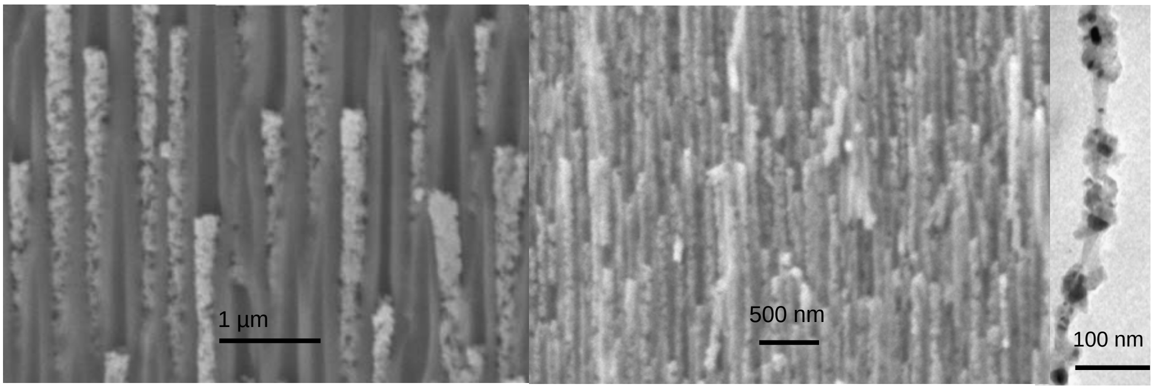

Figure 1 Cross-sectional SEM images of the gold-seeded Ge nanostructures grown inside the a) 200 and b) 60 nm channels of the AAMs, and c) TEM image of an isolated nanowire.

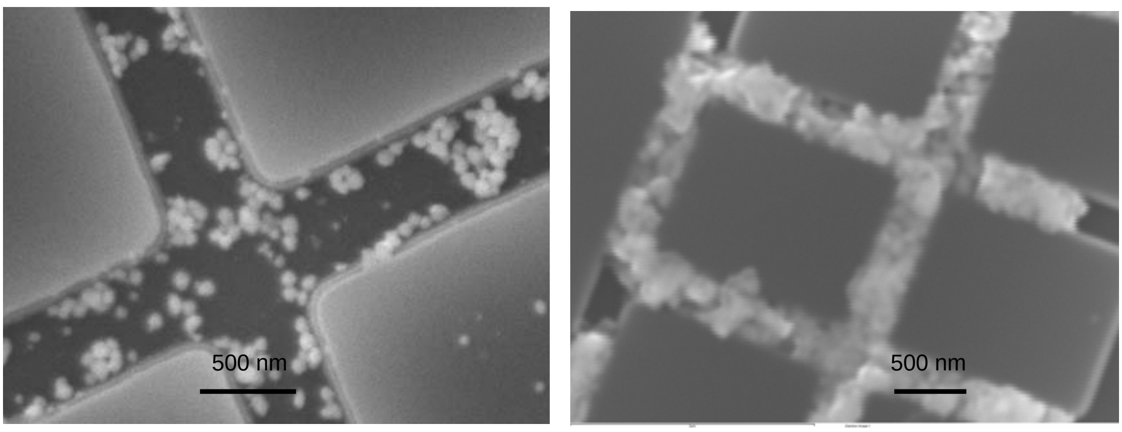

Figure 2 Plan-view SEM image of grooved substrates that were a) modified with gold-seeds and b) after SFLS growth of Ge nanostructures.