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D1.1 Preparation of Hex-SiGe: Towards device quality

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Authors	Marco Vettori, Erik Bakkers
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DESCRIPTION OF DELIVERABLE

MBE growth of an Au-free nanowire template on Si(111) or Ge(111).

INTRODUCTION AND MOTIVATIONS

Current electronics is largely dominated by cubic Si, the cheapest and most available semiconductor. Although its indirect band gap makes it unsuitable for optoelectronic applications, most of electronic devices on the market are based on this material. Consequently, to help make mass production of light-emitting hex-SiGe-based devices economically viable and technically feasible, it is necessary to achieve the integration of hex-SiGe nanostructures on Si substrates.

So far, our light-emitting hex-SiGe nanostructures have been achieved by depositing SiGe shells on wurtzite (WZ) GaAs cores previously grown on GaAs(111) substrates by Metal Organic Vapour Phase Epitaxy (MOVPE) with Au nanoparticles as catalysts,[1] therefore the easiest way to achieve this goal would be to employ Si(111) substrates for the growth of nanowires (NWs). However, it is not possible to adopt on Si the same growth approach used so far, due to the fact Au is highly diffusive in Si and extremely detrimental for the electronic properties of this material.[2,3]

This problem can be circumvented by growing the NWs in a gold-free process. Among all the many possible alternative catalysts,[4] Ga is by far the most suitable because the self-assisted Vapour-Liquid-Solid (VLS) growth with Ga nanodroplets prevents the risk of NWs contaminations, Ga being one of the components of GaAs. Moreover, Ga deposits selectively on Si when this substrate is patterned with SiO_2 mask, providing ordered arrays of nanostructures and limiting the parasitic growth among the NWs.[5] The self-assisted growth of GaAs NWs on Si substrates appears therefore as a convenient way to achieve the direct integration of light-emitting GaAs/hex-SiGe nanostructures necessary for the mass production.

EXPERIMENTAL PROCEDURE AND RESULTS

To attain direct integration on Si via self-assisted mechanism we proceeded through the growth by Molecular Beam Epitaxy (MBE). The substrates for the growth were realized from 2”-Si(111) wafers with 20-nm thick SiO_2 mask. The substrates were patterned and processed to have hexagonal arrays (2 µm pitch) of holes for NW nucleation (Fig. 1a). After dicing the wafers into squares (1.1 cm x 1.1 cm), these were treated with HF solution to remove SiO_2 from the bottom of the holes and to allow selective Ga deposition (Fig. 1b). The substrates were then introduced into the MBE system for growth.

Experiments were performed with the stationary growth approach, i.e. starting the growth of NWs in conditions that provide zinc blende (ZB) structure and growing sufficiently long until the NW length exceeds the surface diffusion length of Ga adatoms on the NW facets. At this point, the growth does not depend on the contribution of the Ga substrate diffusion anymore, and the contribution from facet diffusion is constant: this permits to achieve a state were the droplet contact angle tends asymptotically to stable values which depend only on the As/Ga ratio employed.[6]

Once in this regime, the precursors ratio can be adjusted to achieve contact angle between 90° and 125°, the range in which the growth of WZ is expected.[7] In this way it is possible to obtain Au-free GaAs NWs consisting of a short ZB “stem” followed by a very long segment of WZ,[8] which can act therefore as templates for the deposition of hex-SiGe shells (Fig. 1f).

In our case the growth of ZB stems lead to NWs with length comprised between 2 and 4 µm (Fig. 1c).

The main difficulty encountered so far with this approach consists in reproducing high vertical yields of NWs on these specimens. The vertical rate in fact varies a lot, lying within a range from ≈ 10 % (Fig. 1d) to ≈ 50 % (Fig. 1e) depending on the single specimen.

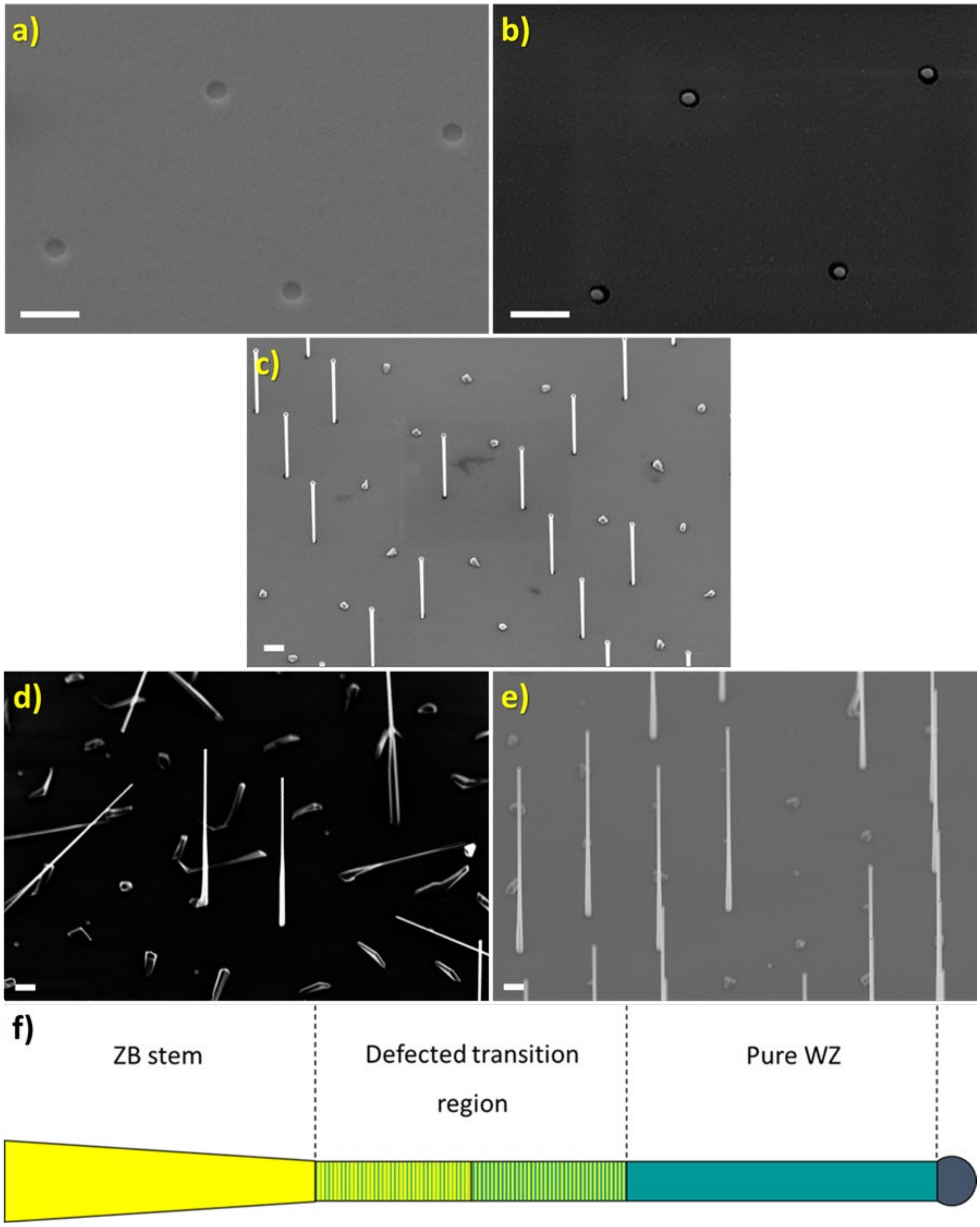

Figure 1: *SEM images of **a)** Nanoholes patterned in SiO_2 mask. **b)** Ga nano-droplets deposited selectively in the nanoholes after HF etch of bottom oxide. **c)** NWs consisting of ZB stems only. **d)** and **e)** NWs grown in stationary regime increasing the As/Ga ratio after ZB stem, with low (≈ 10 %) and high (≈ 50 %) vertical yield respectively. In all SEM images the white scale bar corresponds to 500 nm. Images a) and b) were acquired from top view, while c), d) and e) were acquired with tilt angle of 30°. **f)** Schematics of the expected final structure of a NW with terminal WZ segment synthesized via stationary growth.*

Such a lack of reproducibility not only is inconvenient for optimizing the sample fabrication process, but also affects the very crystal structure of our NWs. We observed in fact that the stationary growth of WZ is strongly influenced by verticality: in particular, the higher the yield, the lower the hexagonality of the system. This was highlighted by preliminary studies carried out by Transmission Electron Microscopy (TEM) on samples grown with the same procedure and growth parameters but resulting in different vertical yields. We saw indeed that samples with low yield grown with this method (cf. Fig. 1d) provided NWs of about 7 µm and with significantly long WZ top segments of about 2.5 µm (Fig. 2a) - and that could have been even longer if we had not stopped the growth. These WZ segments resulted also very pure in terms of crystal structure (Fig. 2b), meaning that the growth of this phase in the stationary regime is stable - a result that confirms the potential of this approach. However, samples grown in the same way but with higher vertical rate (cf. Fig. 1d) on the contrary result to consist of faulted ZB or in a ZB matrix with only short WZ segments at best (Fig. 2c,d).

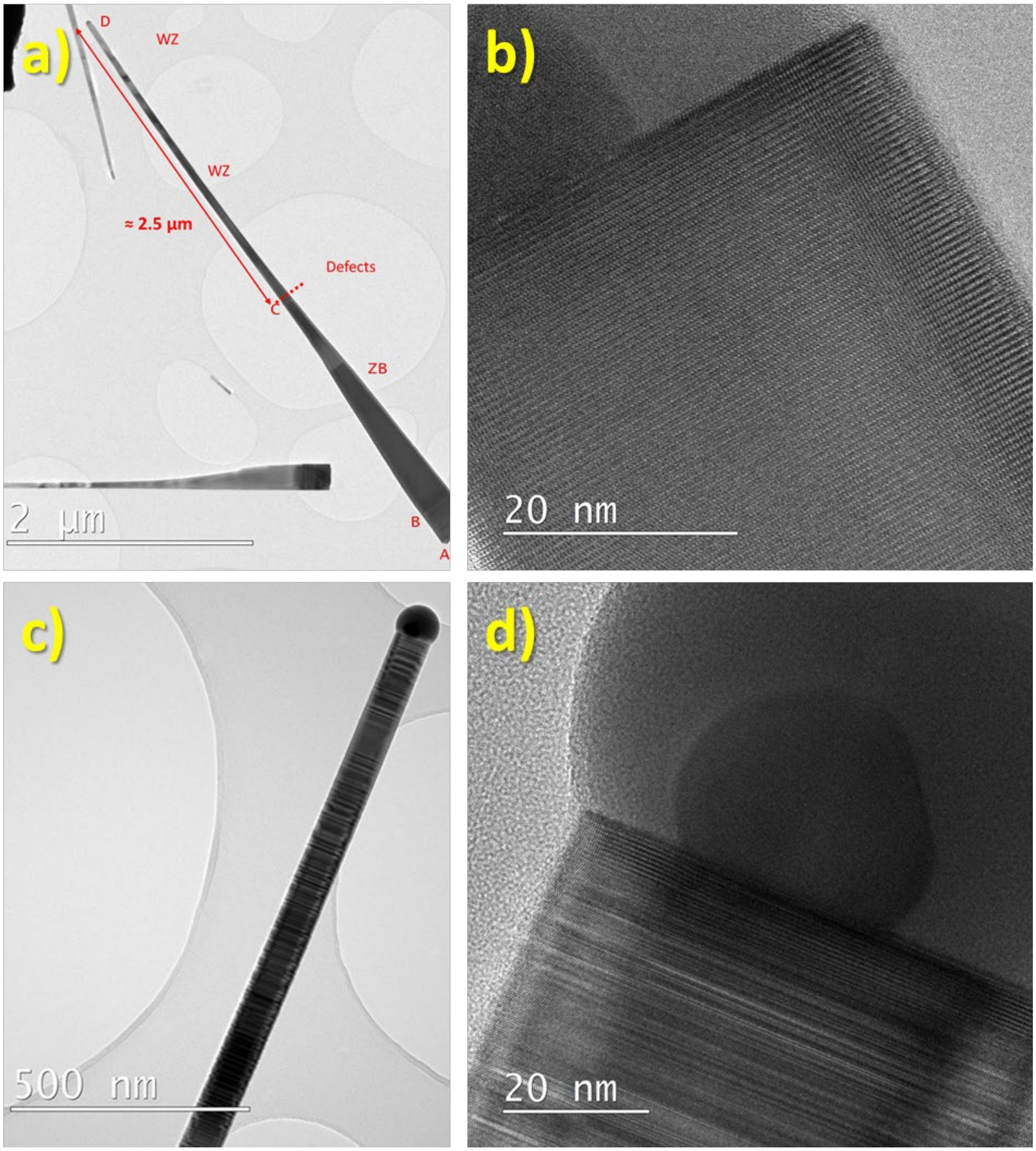

Figure 2: a) *TEM image and schematics representative of low-yield NWs (≈ 10 %): the final WZ segment is extremely pure and 2.5 µm long.* ***b)*** *High magnification image from the same NW showing the characteristic features of pure WZ. Such features are not observed along the whole hexagonal segment, confirming the elevated crystal purity of this part of the NWs and demonstrating the successfulness of the stationary-growth method.* ***c)*** *TEM image representative of high-yield NWs; the structure appears clearly defected with a mix of ZB and WZ phase.* ***d)*** *High magnification image from the same NW.*

Despite the reproducibility problem and the need for higher vertical rates for practical applications, the NWs grown with low yield are an important preliminary result since they confirm our assumption about the possibility to exploit the stationary-growth method to achieve self-assisted WZ GaAs. However, also samples with higher yield and lower degrees of hexagonality show significant behaviour for our purposes. In this regard we carried out a preliminary study depositing Ge by MOVPE on a high-yield sample (≈ 50 %) with the aim to obtain shells including hexagonal light-emitting material and investigating its optoelectronic properties: we were thus able to obtain the first hybrid core/shell nanostructures from self-assisted cores (cf. Fig. 3a). This specimen underwent Photoluminescence (PL) spectroscopic characterization to verify the presence of hex-Ge (cf. Fig. 3b – black curve), and the collected spectrum shows indeed the presence of the phase in question, with a characteristic peak around 0.4 eV. Such a peak is particularly intense, so that we can conclude that despite the limited hexagonality of the system related to the high vertical yield, the emission from hexagonal Ge is still very strong. The other peaks reported in the spectrum can be ascribed to a type-II WZ/ZB interface in GaAs (≈ 0.45 eV) and to cubic Ge grown on the ZB parts of the NWs (≈ 0.60 eV).

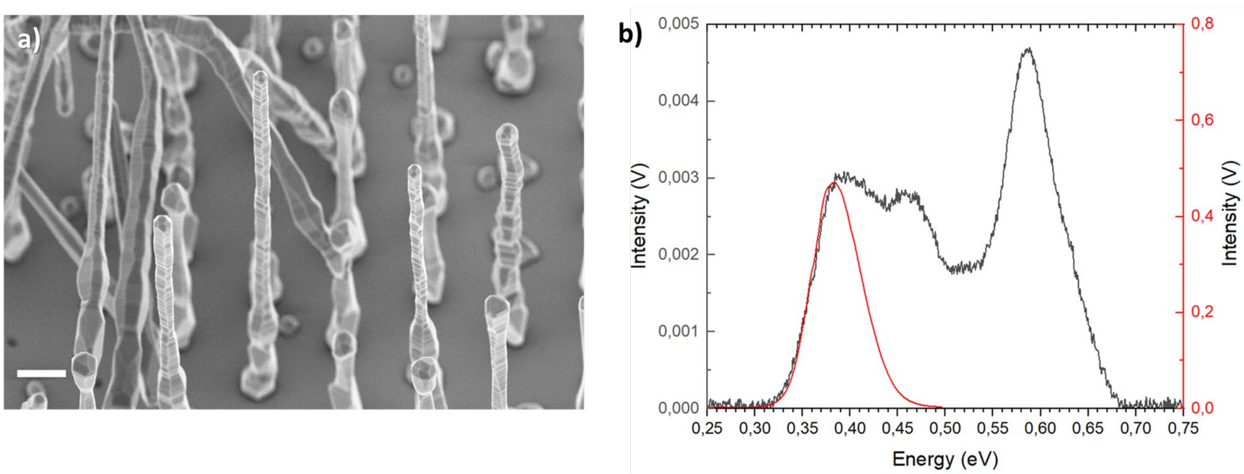

Figure 3: a) *Core/shell NWs obtained depositing 300 nm of Ge via MOVPE on GaAs self-assisted cores grown by MBE on Si substrate; the vertical yield on this sample is around 50 %, and the NWs appear rough and defected, consistently with the higher yield and suggesting the presence of limited WZ insertions rather than long WZ final segments. The tilt angle of the image is 30° and the white scale bar corresponds to 1 µm.* ***b)*** *PL spectra of a reference emission peak of pure hex-Ge grown on Au-catalyzed GaAs self-assisted cores by MOVPE as those published in ref. 1 (red curve), and of the self-assisted MBE-grown sample of Fig. 2a (black curve). Despite the lower hexagonality of the system, the emission from hex-Ge is significantly intense.*

We find these data particularly encouraging as a preliminary result because, despite the presence of cubic Ge, they show already a strong signal from the hex-Ge, thus suggesting that the characteristic features can improve a lot once the sample optimization is achieved.

CURRENT ISSUES AND PROPOSED SOLUTIONS

As above mentioned, the open issue of our experiments consists in the low reproducibility of the samples in terms of vertical yield which also affects the crystal structure of the NWs. We think that this is caused by the competition for re-emitted As among NWs, a contribution that is very important in the MBE VLS growth process.[9] As a result, when the NW yield is higher less As is available per NW, with lower chance for its contact angle to reduce and be within the range of 90°-125° necessary for growing WZ. This problem can be solved in principle by increasing the As/Ga ratio of the precursors, however optimization studies in this direction cannot be carried out unless a protocol to increase and stably reproduce the vertical yield is defined.

For this purpose, we plan to temporarily switch to the growth on patterned GaAs(111), because this substrate is likely to provide a much higher vertical yield which would allow us to optimize the conditions for the WZ growth on dense arrays of NWs. These optimized conditions will then be applied to the growth of WZ on Si once the problem of the vertical yield on such substrate is solved.

OUTLOOKS

The stationary growth approach here employed can lead to the growth of long WZ segments in self-assisted GaAs NWs that still present ZB stems on their very bottoms. Although these stems can be relatively short (2-4 μm), their presence can be detrimental to the optical properties of the core/shell structures by introducing cubic Ge after shell deposition. Because of this, it is good to define a protocol allowing to grow pure WZ GaAs from the very nucleation stage. Such a result has already been achieved by other groups (although with low vertical yields and for short NWs only).[10] For this purpose, it is necessary to constantly adapt the V/III ratio throughout the whole growth so as to keep a proper contact angle and remain in the WZ growth range. Defining the optimal V/III to obtain a certain contact angle is a difficult task but can be done through modelling and simulations. Therefore, once we increase enough the vertical yield, we could model the growth in our system and eventually carry out simulations to identify the optimal V/III ratio. For this purpose, we can adapt and employ the model already developed by Vettori *et al*.[6]

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