Deliverable 1.1

Partners: TU/e, JKU

Task 1.1. (TU/e, JKU) "Synthesis of Hex-Si_xGe_{1-x} NW shells and branches". NW branches and shells will be grown for $0 \leq x \leq 1$ by MOVPE and will be characterized by electron microscopy (TEM) and Atom Probe Tomography (APT) with the aim to achieving defect free and pure Hex-Si_xGe_{1-x}. The details of the growth mechanism of the branches will be investigated. Obtaining high-quality Hex-SiGe is milestone 1 (M12).

D1.1 Synthesis of Hex-Si_xGe_{1-x} including structural and chemical analyses. [M12]

MS#	Milestone name	WP(s)	Est. date	Means of verification
1	Synthesis of high quality Hex-SiGe NWs	WP1	M12	Stacking fault density <1 μm^{-1}, and impurity levels < 1ppm. Large enough volume for optical measurements. At least a 50 nm thick SiGe shells, or 2 µm long SiGe branches

D1.1 Synthesis of Hex-Si_xGe_{1-x} including structural and chemical analyses. [M12]

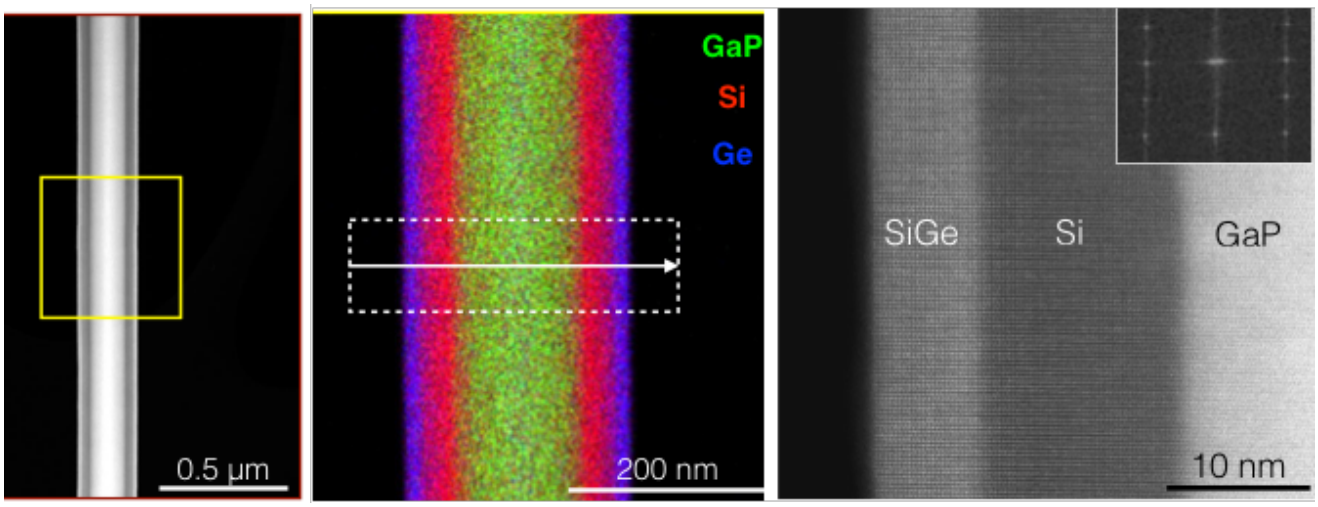

Figure 1. Overview TEM image of a hexagonal GaP/Si/SiGe core/shell/shell wire show the uniformity and defect-free nature of the wire. Elemental map of the wire showing the composition of the structure. HRTEM image of the wire demonstrating the hexagonal crystal structure. We note that a thin wire with a thin shell has been used for imaging, since it is very difficult (impossible) to obtain high resolution images from thicker samples.

Wurtzite GaP core wires with a diameter of 200 nm have been grown using a Au-catalyst as an epitaxial template for the growth of hexagonal SiGe shells. We have shown that we can grow single crystalline uniform layers of hexagonal SiGe layers up to 80% Ge at a temperature of 600 ^{0}C with a thickness of > 50 nm. The stacking fault density in the GaP and therefore also in the SiGe shell is less than <1 μm^{-1}. These wires have been studied with XRD by JKU. There are however some remaining challenges, which have to be addressed:

A) Impurities from the substrate (Ga and P) and from the Au catalyst may affect the optical properties of the Hex-SiGe. Atom Probe Tomography has been used to study the presence of these impurities.

B) The Ge-rich shells are heavily strained due to the ~4% lattice mismatch with the GaP core. Strain and strain-induced defects will detoriate the optical properties of the SiGe shells. We therefore investigate the possibility to use WZ GaAs as a lattice-matched core to for Ge.

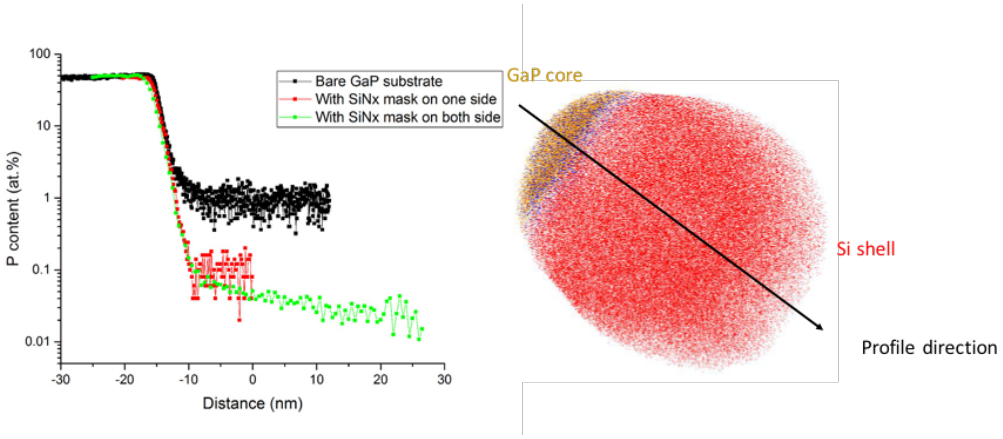

Figure 2. Atom Probe Tomography (APT) line scan of a hexagonal GaP/Si core/shell nanowire. Au and Ga are below the detection limit (1 ppm) of the APT. The P concentration in the Si shell is the highest (1%) when an uncapped GaP substrate is used and the is concentration decrease with the level of capping the GaP substrate.

These issues have been addressed during the first year and will be discussed below.

A) Possible sources of P and Ga are 1) diffusion from the GaP cores at the high temperatures (900 ^{0}C) used during growth of the Si shells, 2) evaporation from the GaP substrate, 3) background pressure in the MOVPE chamber. Atom Probe Tomography (APT) has been used to chemically analyse the samples. In Figure 2 an APT linescan is shown from this analysis we find a concentration of 1% P in the Si shell, and Ga is below the detection limit of the APT. In order to reduce this concentration, we have capped the GaP substrate with a SiNx capping layer. This reduces the P concentration by a factor of 10 when the SiN is only on the top side and by a factor of 100 when both sides of the substrate are covered. This shows that P evaporates from the substrate during the growth of the SiGe shell. In order to further reduce the P concentration in the Si shells, we have investigated alternative precursors which enable growth at lower temperatures. We have obtained tetrasilane (Si_4H_{10}) from Air Liquide, a precursor which can be cracked at lower temperatures than disilane (Si_2H_6), the precursor which we have used till now. In Figure 3 the growth rate versus temperature have been shown for the two different precursors. From HRTEM imaging, the growth rate has been obtained and the hexagonal crystal structure has been confirmed. It is clear that the cracking efficiency is about an order of magnitude higher for tetrasilane compared to disilane in the temperature range between 500 and 700 ^{0}C. An APT analysis of the shells grown with tetrasilane at 600 ^{0}C is currently running and will be included in the first-year report.

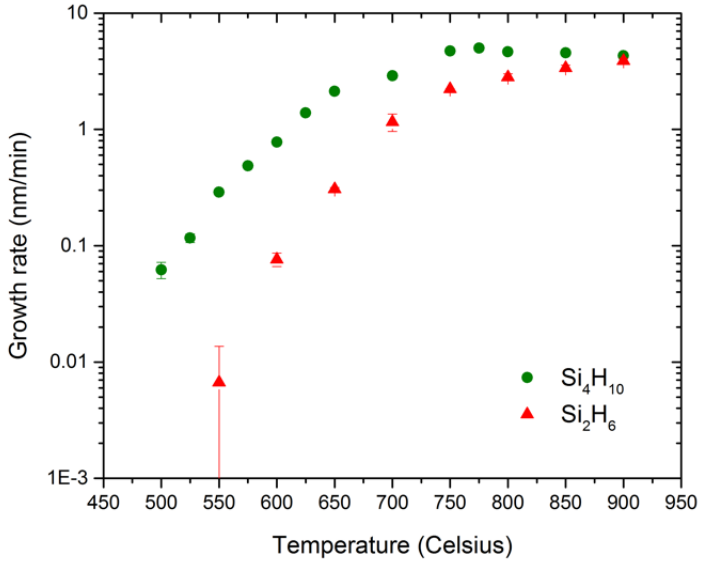

Figure 3. Growth of the hexagonal Si shell on WZ GaP core wires for two different precursors. Below 700 ^{0}C the growth rate with tetrasilane is 3-10 higher than with disilane due to the lower cracking temperature. We note that the real substrate temperature is 80-100 ^{0}C lower than the thermocouple set point temperature (T on x-axis) due to the thermal contact.

Au atoms can diffuse from the Au catalyst through the Si shell. This has been observed before for pure Si wires [1] and for Ge/Si core/shell nanowires [2]. From SEM and TEM images, we know that there are Au-clusters present on the surface of the Si-shells. Since Au will form deep traps in Si, killing the optical properties, we have developed a route to remove the Au particle after the GaP growth and before the Si shell growth. We use an aqueous solution containing I_3^-, which etches Au. It is very important to rinse the sample with deionized water afterwards to remove any Au residuals. After this etch, a GaP inner shell is first grown around the GaP core resulting in a well-defined flat facet. TEM studies have shown defect-free growth of the GaP shell with a smooth surface. Directly after this, the Si shell has been grown. APT studies do not reveal any Au atoms above the detection limit. These wires have been studied optically by different partners (WP2).

We have grown pure Ge branches from WZ GaP cores. The GaP substrate and GaP have not been capped with a protective layer. In Figure 4 an APT line scan of the full branch is shown. Ga, and Au are below the detection limit, but the P concentration is about 0.01%. These branches have been grown at low temperatures (300 ^{0}C), but the substrate was not capped with a protective layer and probably there was still a background P pressure in the reactor chamber. We have seen for cubic Ge/Si core/shell wires grown in the same reactor that the incorporated P in the wires can be significantly reduced by flushing the reactor for longer periods (up to 3 days). In this way, we reduced the incorporated P concentrations down to the 1-2 ppm level. We believe we can reach these levels also for the hexagonal core/shell and branch wires by combining all the steps presented above (substrate capping, low growth temperature, and reactor flushing).

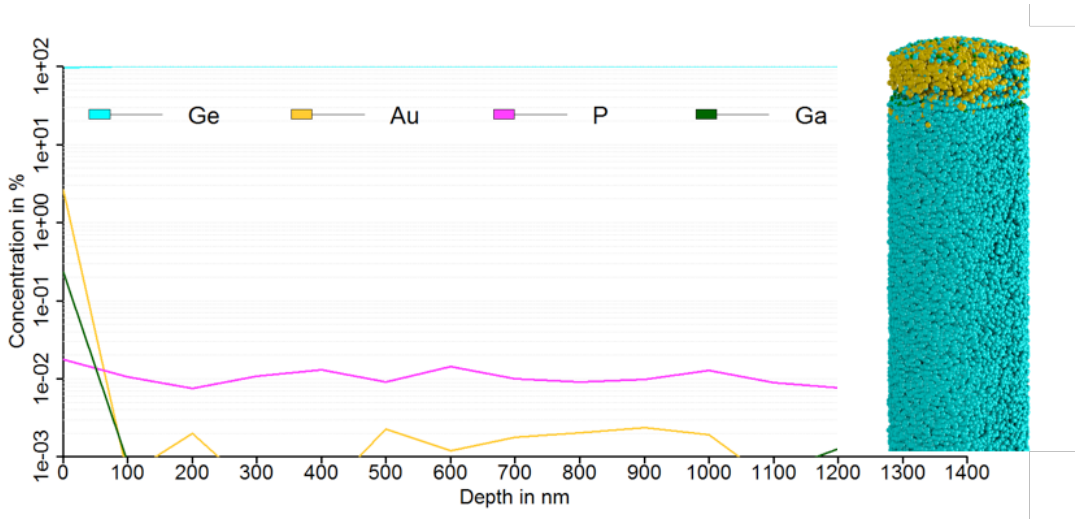

Figure 4. APT line scan of a hexagonal Ge branch grown from a WZ GaP stem wire. The reconstructed image shows Au atoms at the top of the wire (catalyst particle), and Ge atoms in the wire.

B) Ge-rich alloys are most interesting for these studies, since these are expected to show a direct band gap. Since Ge has a lattice mismatch of about 4% with GaP, we have decided to explore another core material. GaAs has a very small mismatch with Ge and has also been reported in the wurtzite crystal structure. We have developed the growth of WZ GaAs wires using a SiN mask to cap the substrate and avoid outgassing of As. The SEM image in Figure 5 shows an array of GaAs wires with a length of a few micrometer and a diameter of 150 nm. We can tune the GaAs wire diameter by the size of the hole opening in the SiN mask and the deposited Au thickness. Smallest diameters are around 30 nm. A small diameter will be relevant for minimizing the strain in the shell. A TEM analysis, as shown in Figure 5, shows the WZ crystal structure. From overview images, we find a stacking fault density ranging from 2 to 80 μm^{-1}, depending on the growth conditions. We have found that the parameter window in which pure WZ GaAs wires can be grown is much smaller than that of WZ GaP. Ge shells have been grown around the WZ GaAs wires using GeH_4 as a precursor and high-quality epitaxial growth has been observed at 400 ^{0}C. In Figure 5 a HRSTEM image is shown illustrating the perfect epitaxy of Ge on GaAs. The advantage of using Ge-rich shells is, besides the expectation of a direct band gap, that the growth temperature is significantly lower than for the Si-rich shells reducing the outgassing of group V elements from the substrate and reactor walls. We expect that by using all the steps as given above that we can reach acceptable impurity levels. We should note that As has a much lower vapour pressure than P, which will already lead to lower group V levels in the SiGe structures.

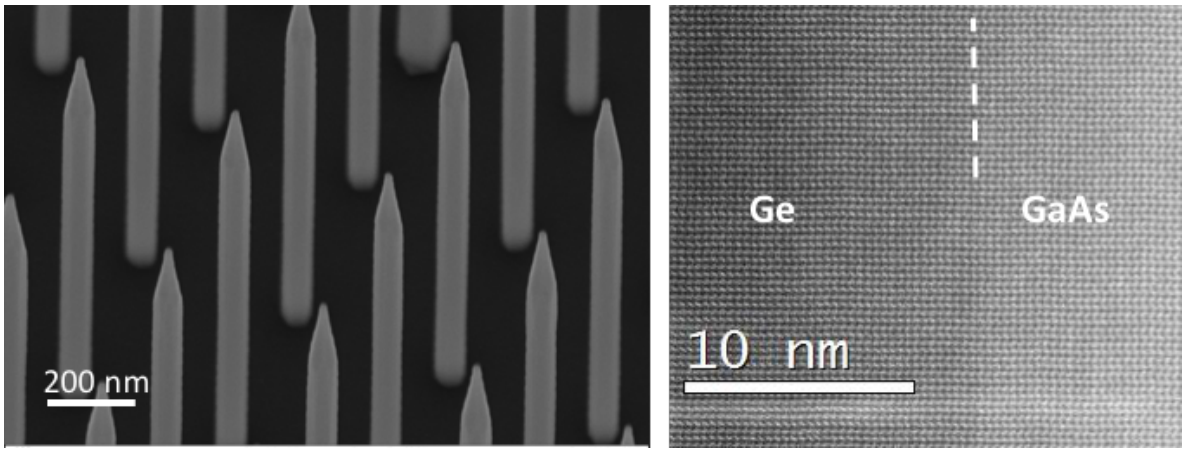

Figure 5. SEM image of WZ GaAs wires. E-beam lithography has been used to define the position of the Au catalysts in a SiN capping layer on a GaAs(111)B substrate. HR STEM image of the interface between the WZ GaAs core and the hexagonal Ge shell. From this image the epitaxial relation is clearly visible.

Outlook

- We will employ all steps in order to reach low impurity levels in the SiGe (substrate capping, low growth temperature, and reactor flushing)
- We aim to grow WZ GaAsP, which can be lattice matched to SiGe shells. Since the growth conditions of WZ GaP and WZ GaAs wires are comparable, we expect that we can grow high quality cores. Aim is to grow strain free SiGe shells with Ge concentrations >60%. The strain level will be determined together with JKU.
- A master student, Wouter Kaman, has started in October 2017 and will enhance the work on the growth of hex SiGe branches from GaP and/or GaAs core wires. This geometry has the advantage that it is a simpler system for optical studies.

References

1 J.B. Hannon *et al*. *Nature* 440 (2006), 69
2 S. Conesa-Boj *et al*. *Nano Letters* 17 (2017), 2259