Deliverable 2.1: Verification of the direct bandgap.

Milestone 2: Direct bandgap Hex-SiGe.

Verification: Observation of efficient PL emission with an Internal Quantum Efficiency (IQE)>1%, short Pl lifetime (<10 ns) at low temperature

1. Calculations of the bandstructure:

It has been established by the Jena group that hexagonal germanium (Hex-Ge) has a direct bandgap, as shown in **Fig. 1**. The gap is 0.29 eV using MBJLDA and 0.30 eV with HSE06 at zero strain, but it should be emphasized that the bandgap is strongly dependent on strain. The second conduction band lies at 0.63 eV (MBJLDA) and 0.61 eV (HSE06) at zero strain. Theoretical calculations on hexagonal silicon-germanium (Hex-SiGe) are in progress and will be presented in D1.3 in December 2018.
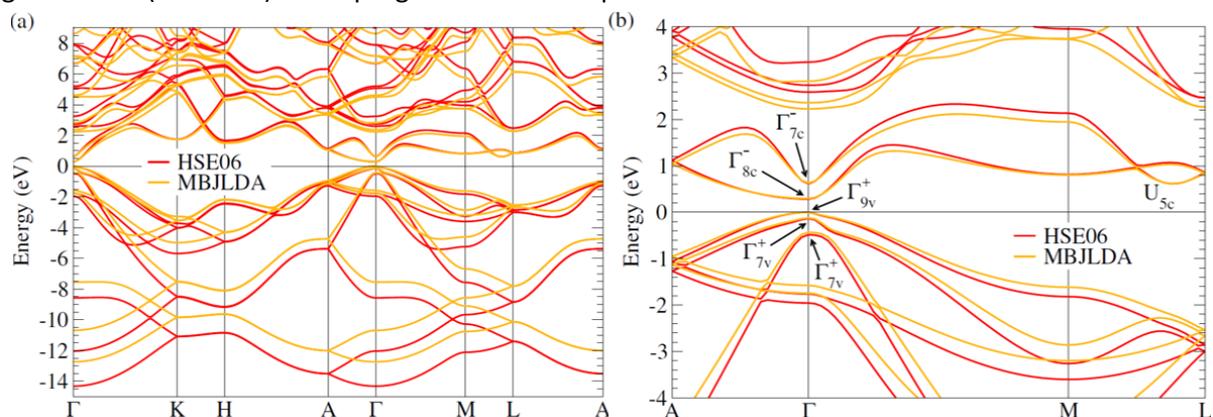
Fig. 1. *Band structures computed by the Jena group for Hex-Ge within the MBJLDA and HSE06 approaches. The double-group notation of the wurtzite structure is used to characterize the symmetry of the states at Γ.*

2. Tunability of the bandgap for Hex-SiGe

Measurements were performed on Hex-SiGe nanowire shells using a WZ-GaP nanowire core. We studied samples with varying atomic input germanium concentrations during growth in the reactor. The PL spectra of 5 samples are plotted in Fig. 2. The samples were excited with a 976nm laser with an excitation density of about 1.0 kW/cm^2 at a temperature of 4K. The PL of all the samples was measured using the same MCT detector, therefore intensities are comparable.

Typical spectra using a GaP core show a broad emission peak that do not allow for accurate deconvolution. This broad emission is probably due to a combination of alloy broadening, germanium content fluctuations and defects induced by the lattice mismatch between GaP and a germanium rich silicon-germanium alloy. However, these results show the trend that for increasing germanium content the emission shifts to the red and that the total intensity increases. This indicates that the emission wavelength can be tuned by controlling the germanium content in the material. It is important to note that we were not able to measure any PL from the 60% Ge sample (input concentration), indicating, but certainly not proving, that the samples with >80% Ge are probably direct bandgap, while the 70% sample probably has both direct and indirect bandgap regions.
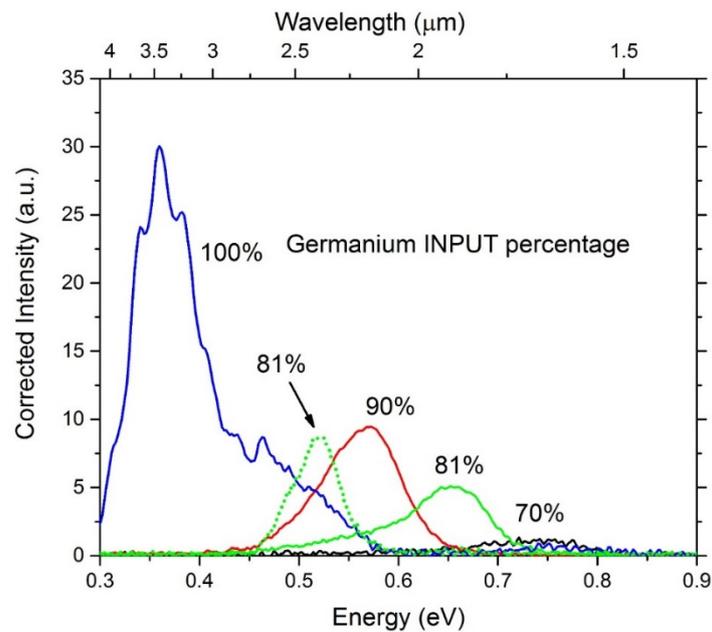
Fig. 2: *Photoluminescence spectra of core-shell GaP-Si$_{1-x}$Ge$_x$ nanowires taken at a temperature of 4K and excited of about 1.0 kW/cm^2 with different compositions. We show the input percentage of germanium atoms into the reactor for growing the wires.*

The bandgap related PL emission at 4 K of three samples with homogeneous shells are plotted in **Fig. 3** as a function of composition. A tunability of the emission from about 0.3 eV up to at least 0.7 eV is demonstrated. Moreover, our experimental results are nicely in accordance with the theoretical results of De and Pryor[1].
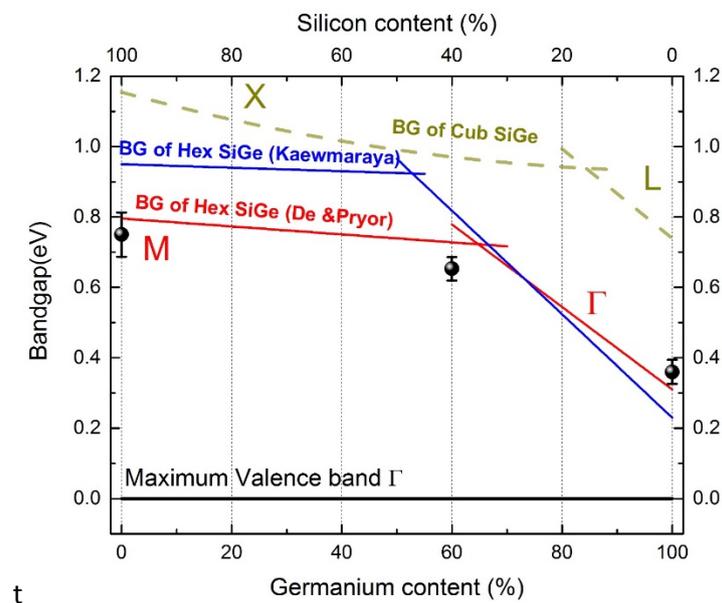
Fig. 3: *Peak energy of the measured PL spectra as a function of the germanium content of the shell of the nanowires. The error bars reflect the FWHM of the measured peaks.*

3. Comparison of Hex-Ge shells using different nanowire cores

We started the project by using GaP nanowire cores which have a small lattice mismatch with Si but which have a lattice mismatch of about 4% with Ge. Since we expect direct bandgap emission for 70-100% Ge, 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 expect a significantly higher internal quantum efficiency (IQE) for approximately lattice-matched shells, since the defect density and thus the density of nonradiative recombination centers will be significantly reduced in lattice-matched shells. In order to explore the optical quality of the Ge-shell for different nanowires cores, we plotted the volume corrected photoluminescence spectra in **Fig. 4**. It is obvious from this figure that the GaAs cores provide the highest integrated PL-intensity and thus the highest IQE, provided that these shells are capped with a thin layer of Si to protect and to passivate the surface. It is expected that surface passivation becomes more critical for higher quality samples where carrier are not localized anymore due to defects.
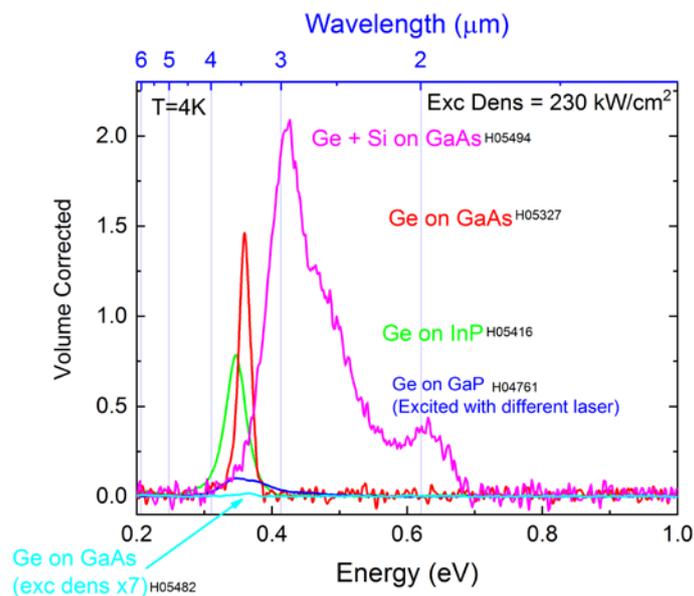
Fig. 4: Comparison of the volume corrected photoluminescence for Ge-shells grown around different WZ nanowire cores. The pink curve is a very thin Ge-shell around a GaAs core, which is almost defect free. The peak at 0.62 eV is due to cubic material.

4. Internal Quantum efficiency (IQE)

A first way to measure the IQE is to compare the ratio of the integrated PL intensity at 4K and at 300K. Since it is usually assumed that the IQE is 100% at 4K, this ratio provides the IQE at room temperature. In the case of Hex-Ge, we observe a ratio of the integrated PL at 4K and at 400K of more than 10% as shown in **Fig. 5a**. Unexpectedly, this ratio shows a minimum of 5% around 300K. Although these values are suggesting that we met our milestone 2, these data should be interpreted very carefully. The point is that the $\Gamma_{9v} \rightarrow \Gamma_{8c}$ transition is forbidden at zone center, while it is allowed outside k=0 as shown in **Fig. 5b**. The matrix elements are approximately increasing linearly with the k-vector, and become fully allowed at high enough k-values. As a consequence, the ratio of the integrated photoluminescence at 4K and at 300K is not a good metric anymore for the IQE, since the amount of integrated PL at low temperature is theoretically very small, unless e.g. p-excitons or other symmetry-breaking elements are incorporated.
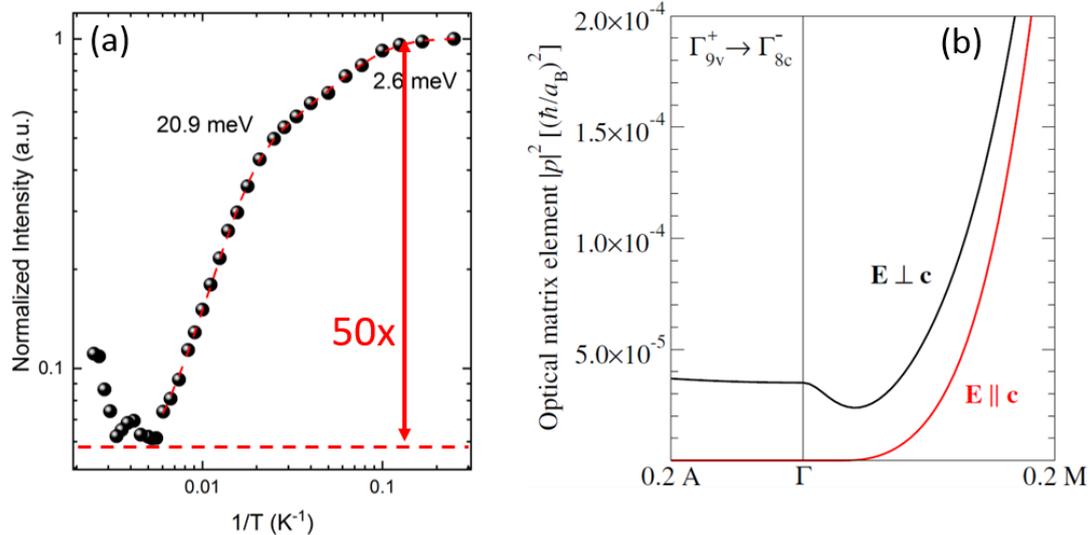
Fig. 5: (a) Ratio of the integrated PL between 300K and 4K, showing a minimum at 5% near 300K, while it increases to above 10% at 400K. In many cases, this ratio is interpreted as being the IQE. (b) Calculated matrix elements for Hex-Ge as a function of the k-vector by the Jena group. The calculations predict a strong increase of the matrix elements in the Γ→M direction

Fortunately, we obtained other evidence for the potential of Hex-Ge for reaching a high IQE. The matrix elements for the $\Gamma_{9v}\rightarrow\Gamma_{8c}$ transition in Hex-Ge , is shown in **Fig. 5b**. For Hex-Ge the matrix element is strongly increasing with the k-vector, until a high enough matrix element is obtained for reaching the threshold for stimulated emission.
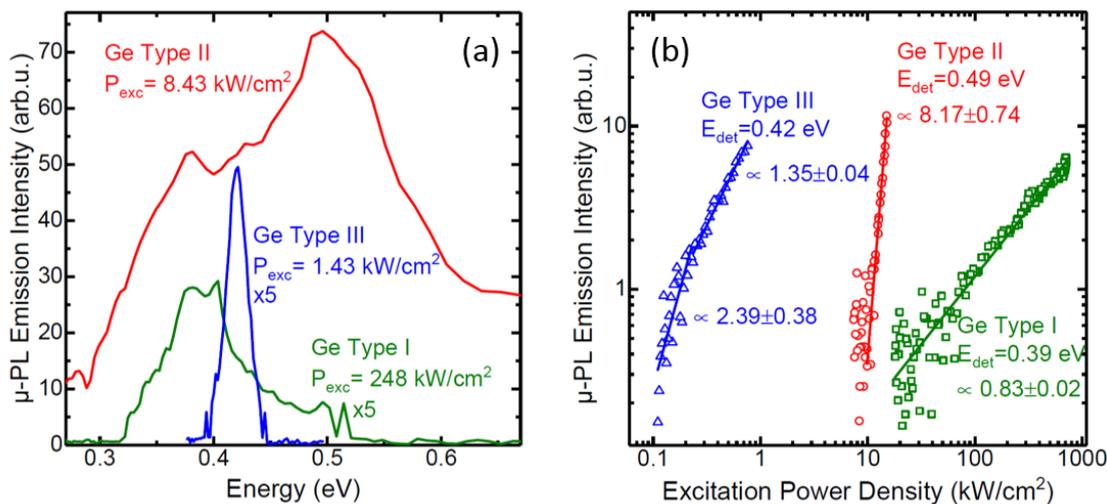
Fig. 6: (a) Observed photoluminescence for single nanowires at high excitation, showing stimulated emission for the blue curve. (b) PL emission intensity versus excitation density, showing a slope of 8.17±0.74 for type II NWs and a slope of 1.35±0.04 for Type III NWs

The TUM group measured the photoluminescence emission intensity as a function of the excitation density. Usually on observes a slope of unity for radiative recombination and a slope of two for nonradiative recombination. For the red curve we however observe a slope as high as 8.17 (see **Figure 6b**) which can only be explained by amplified spontaneous emission. The fact that the slope is much larger than unity implies that the probability for amplified spontaneous emission is larger than the probability for nonradiative decay. This is a strong indication that we reached IQE values above 1%.

The blue curve in **Fig. 6a** shows that at a high enough k-vector in the Γ_{8c}-band (or possibly at the onset of the $\Gamma_{9v}\rightarrow\Gamma_{8c}$ transition), the Hex-Ge material is capable to provide stimulated emission resulting in a narrowing of the emission spectrum, which is the first step towards lasing. We claim that the observation of both amplified spontaneous emission in type 1 nanowires (in red) and stimulated emission in type 2 nanowires (in blue) proves that the IQE is larger than 1%.

5. **Measurement of the photoluminescence lifetime**.

The conductivity lifetime in different Hex-SiGe nanowires has been measured by optical pump-terahertz probe spectroscopy at room temperature, yielding conductivity lifetimes of the order of 1 ns as shown in **Fig. 7**.
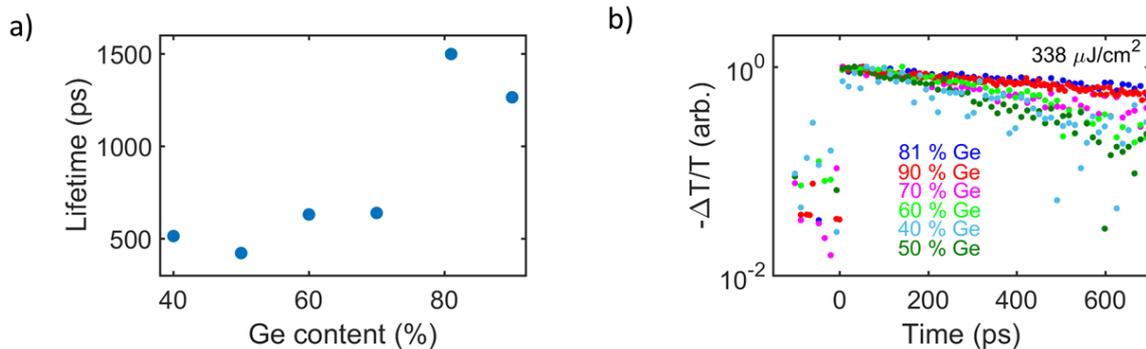
Fig. 7: a) Conductivity lifetime as function of Ge content and b) Photoinduced conductivity decays in nanowires with Ge content varying from 90% to 40% at 338 µJ cm².

The dependence of the conductivity lifetime on the Ge-composition suggests that the recombination mechanism is monomolecular due to nonradiative recombination since the bandgap becomes direct above 70% Ge, which should result in smaller radiative lifetimes. As a consequence, we cannot conclude from this measurement that we obtained clear evidence for a direct bandgap material.
TUM however performed pump-probe measurements on type III nanowires showing stimulated emission (blue curve in **Fig 6a,b**). The preliminary results are presented in **Fig.8** measured at 7K.
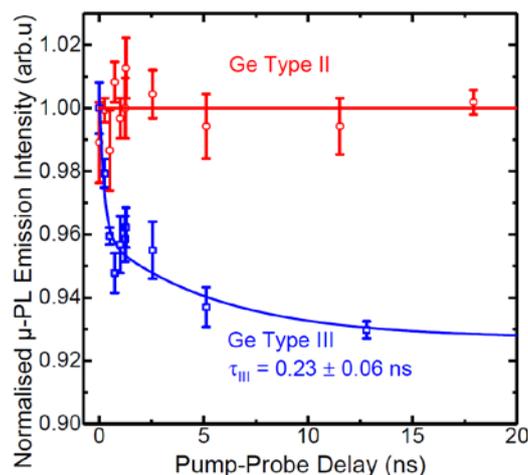
Fig. 8: Preliminary results of the Pump-Probe measurements on type II (red) nanowire as well as type III (blue) nanowires. Type III nanowires show a decay time of 0.23±0.06 ns while type 2 nanowires show a long lifetime due to a thermal population of the Γ_{7c} conduction band.

The observation of fast carrier dynamics (<1ns) is indicative of radiative processes which occur at strong excitation levels in selected nanowires. These fast dynamics were found to occur in parallel to much slower processes that take place over >>1µs timescales which are possibly photo-thermal in origin.

6. Interpretation of the photoluminescence of Hex-Ge with GaAs nanowire cores.

For the interpretation of the results, it is important to study the power dependent photoluminescence at 4K. These data are presented in **Fig. 9**.
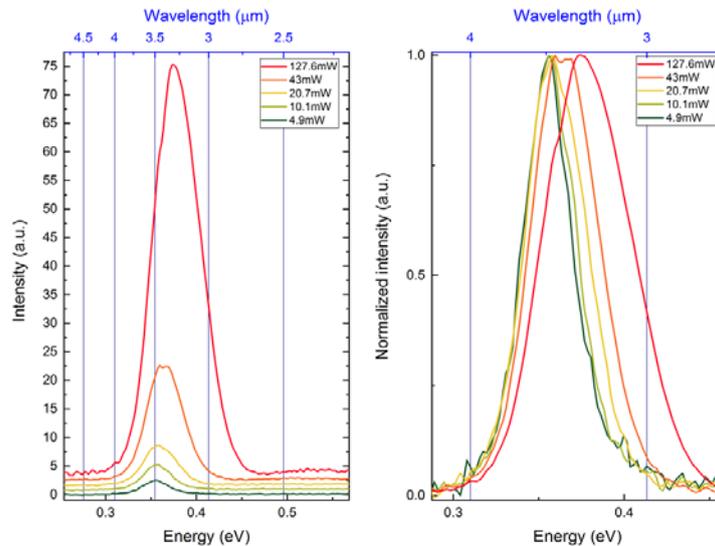
Fig. 9: Excitation dependence of the photoluminescence at 4K of hexagonal Ge shells grown around a WZ GaAs nanowire core showing the bandfilling behavior.

It is shown in Fig. 9 that we observe a strong bandfilling effect. It is a remarkable detail that once the peak starts to broaden at the high energy side due to bandfilling, the magnitude of the peak keeps on increasing with increasing excitation density. We can understand the increasing magnitude at higher excitation by an increase of the quasi Fermi level in the conduction band states. By populating these higher energy states in the Γ_{8c} conduction band, states with a higher k-vector become populated, resulting in the population of states with a larger matrix element. This results in the simultaneous observation of a higher PL in combination with a blue shift due to bandfilling.

7. Conclusions

In conclusion, we attribute the observed photoluminescence in Hex-Ge due to a direct band transition in which the matrix element is increasing from zero at the band edge towards a value that is sufficiently large for reaching amplified spontaneous emission and even stimulated emission in the first generation Hex-Ge nanowire shells. It is important to say that these results were obtained with Hex-Ge nanowire shells which were grown around a WZ GaP core, which were suffering large defect densities. We expect that we can grow better quality Hex-Ge nanowire shells be growing them around a lattice matched nanowire core. With better quality samples, we expect optical gain at smaller amounts of bandfilling. The other option is to engineer the strain to decrease the separation between the Γ_{7c} and the Γ_{8c} conduction band.

8. References:
    1. Amrit De and Greg Pryor, J. Phys.: Condens. Matter **26** (2014) 045801