Deliverable 3.1: Terahertz conductivity

Description of work
Task 2.2. (UOXF, TU/e, TUM) "Optimisation of the optical quality by elimination of defects and nonradiative recombination centres". Optical Pump Terahertz Probe Spectroscopy is the ideal technique for extracting recombination rates and charge carrier densities in this new material.

Task 3.1. (UOXF, TU/e, Jena) "Non-contact electrical terahertz measurements" will reveal the extrinsic carrier concentrations and mobilities as well as the surface recombination velocity in passivated NWs. This work includes theoretical support.

In February 2018, the Oxford group received new batches of nanowire samples from the TU/e Group with two different growth series (which are the Hex-Si nanowires with GaP core and the Hex-Ge nanowires with GaAs core), and performed optical-pump THz-probe (OPTP) spectroscopy measurements on them.

The first series contains seven Hex-Si shell nanowire samples with a 135-nm-diameter GaP core. The Hex-Si shell thickness varied from 23 nm to 260 nm. Firstly, the photoconductivity lifetime measurements were performed on these nanowire samples using OPTP spectroscopy at room temperature. The nanowires were optically excited with a near-infrared regenerative amplifier laser with 35-fs pulses of 1.55 eV photons at a repetition rate of 5kHz. The extracted lifetime valued under different excitation fluences (from 3.2 to 320 $\frac{\mu J}{cm^2}$) are listed in table 1.

Sample ID	Thickness of the Si (nm)	Lifetime for 100% fluence (ps)	Lifetime for 75% fluence (ps)	Lifetime for 50% fluence (ps)	Lifetime from global fit (ps)
H05221	23	1344	1465	1275	1354
H05357	50	1240	987	720	1016
H05350	70	2694	2951	2746	2761
H05351	100	1367	1378	1334	1343
H05022	130	954	947	774	909
H05369	130	1258	1468	1185	1274
H05360	260	2205	2015	1658	2006

Table 1: Overview of photoconductivity lifetime of the GaP core, Hex-Si shell nanowires with varying Si shell thickness. The shell thickness and the lifetimes were taken while illuminated with 100%, 75% and 50% laser excitation power. The last column gives the lifetime extracted by globally fitting the scans from the same sample under different levels of photoexcitation excitation.

It was expected that the photoconductivity lifetimes of the Hex-Si shell nanowires would become longer for thicker diameters *d*, because the effect of surface recombination becomes less dominant as the surface area-to-volume ratio increases if the nanowires is reduced. By comparing the photoconductivity lifetimes in the seven samples of differing Hex-Si shell thickness, the surface recombination velocity S of the nanowires was expected to be extracted out, determined by

$$\frac{1}{\tau} = \frac{1}{\tau_{volume}} + \frac{4S}{d}$$

where d is the nanowire diameter, S is the surface recombination velocity, τ stands for the charge carrier lifetime of the sample and τ_{volume} for the lifetime of the bulk. However, the lifetimes we measured for the Hex-Si nanowires with different shell thickness show no trend and were inconsistent as can be seen in figure 1. Therefore, it was not possible to extract the surface recombination velocity for Hex-Si nanowires using these samples. Examination of the samples via scanning electron microscopy (SEM) showed that significant and non-sequential morphological differences occurred between nanowires with differing Hex-Si shell thickness.

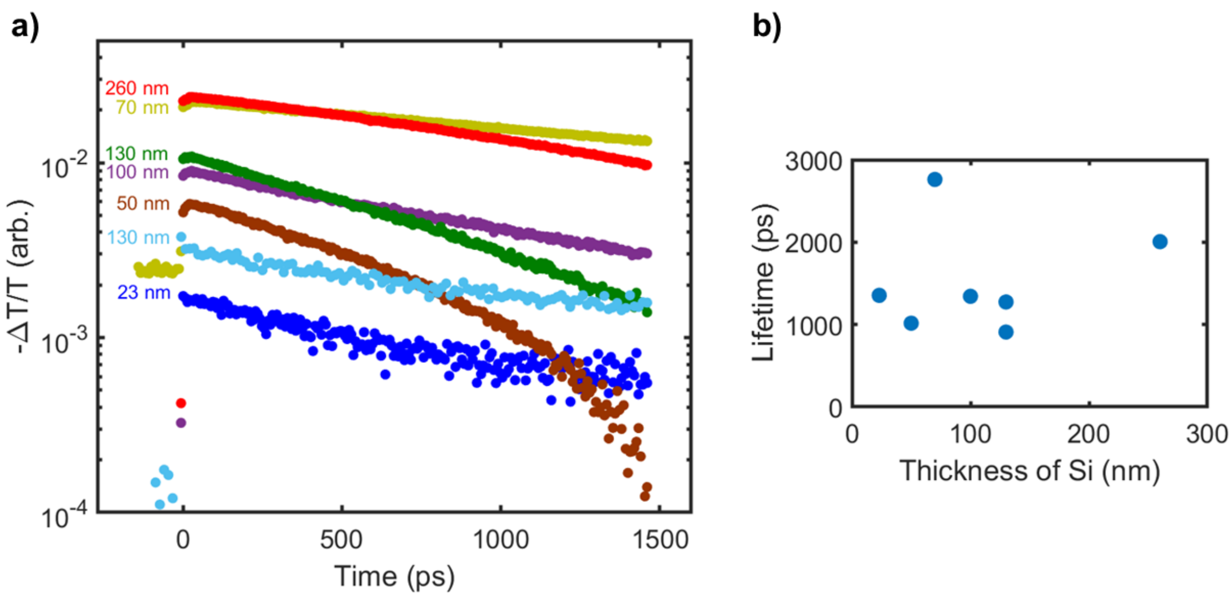

Figure 1:
a) Photoinduced change of THz transmission for different Hex-Si shell nanowires at 50% fluence.
b) graphic overview of the lifetimes from different samples. Each one of them was excited at three different fluences. Theses scans were globally fitted, and a global lifetime was extracted from it.

Figure 1a) shows the change in THz transmission (directly relating to the material photoconductivity and carrier density) for different samples is independent on the Hex-Si shell thickness. The global lifetime is plotted against the thickness of the Si as shown in figure 1b), which indicates that the global lifetime for different samples is also independent on the Si shell thickness. This parameter (global lifetime) was extracted by globally fitting three pump scans of the same sample at different fluences with the rate equation

$$\frac{dn}{dt} = -k_1 n - k_2 n^2 - k_3 n^3$$

where n stands for the time dependent carrier density. k_1 describes the monomolecular recombination processes, k_2 the bimolecular radiative recombination and k_3 Auger processes. The decay in these samples is mainly determined by monomolecular recombination processes, suggesting that **Shockley-Read-Hall (SRH) recombination is the dominate charge recombination mechanism in Hex-Si Nanowires**. Thus there exists a high density of defects in the Hex-Si nanowires. Significantly the sample with **70nm Hex-Si shell width has a long photoconductivity lifetime (1/ k_1 ~2.7 ns) indicating a significantly lower density of SRH recombination centres, and hence good samples quality**. This agreed with a subsequent SEM and TEM study which showed the 70nm shell sample contained straight nanowires with low defect density, in contrast with the other nanowires in the series. Further TEM studies on the series of samples are currently being conducted at TU/e to quantify the defect density in each samples and correlate with the photoconductivity lifetime data.

The second series contains four Hex-Ge shell nanowire samples with a 20-nm-diameter GaAs core. The Ge shell thickness is very thin varying from 10 nm to 50 nm. Similarly photoconductivity lifetime measurements were performed using OPTP spectroscopy to extract charge carrier lifetimes at room temperature. Unfortunately, no change in THz transmission as a result of photoexcitation were measured for any of the Hex-Ge nanowire samples, and thus no photoconductivity lifetimes could be extracted from the OPTP measurements. This could be attributed to the low quality of the Hex-Ge nanowires from Feb 2018 with very thin and un-passivated Ge shell which still contained many defects. The TU/e Group is currently developing and optimising the growth recipes for the Hex-Ge shell nanowires with GaAs cores. A new series of the Hex-Ge shell nanowire samples will be sent to Oxford for OPTP measurements in July 2018.

Full AC photoconductivity spectra of Hex-Si nanowires at room temperature were obtained over a broad frequency range (50GHz – 4THz) using the OPTP technique. This allowed the charge carrier mobility of the Hex-Si nanowires to be obtained. Figure 2 shows the photoconductivity spectrum for sample H05350 (nanowires with a 70 nm thick Si shell) under different excitation fluences. The blue data points represent the real part and red the imaginary part of the photoconductivity. The values of the scans are shown as dots and the error bars represent the standard deviation of 12 repeat scans. The solid lines represent the globally fitted plasmon model:

$$\sigma(\omega) = \frac{ne^2}{m^*}\frac{i\,\omega}{\omega^2 - \omega_0^2 + i\omega}$$

where e stands for the electronic charge, m^* for the effective mass, ω for the frequency and ω_0 for the plasmon frequency. This model enables us to extract mobility, carrier density, scattering rate and doping density of the measured nanowires. Comparing the spectra in figure 2, it can be seen, that the error for the measurement increases for higher frequencies. **The extracted charge-carrier density and mobility are 1.0 $\times 10^{14}$ cm^{-3} and 121.5 $cm^2V^{-1}s^{-1}$ for sample H05350 (70nm Hex-Si shell) at fluence of 160 μJ cm^{-2}**, which are both lower than expected. This could be attributed to two reasons: 1) the fitting model needs to be further adjusted owing to the coaxial geometry of the nanowires and 2) the not yet fully optimized growth of the nanowires. For these core-shell Hex-Si nanowires, the OPTP measurements are conducted under a photoexcitation wavelength of 800 nm, at which only the Si shell, but not the GaP core is optically excited. The plasmon model works well when studying the core-only nanowires or the core material of the core-shell nanowires in the past. To study the shell of the nanowires in this project, the model for data fitting is required to be further developed. Also, it has been observed by SEM, in some Hex-Si nanowire samples, there are clusters of material on the nanowires and even branched nanowires growing out of the original nanowires. Because of the non-uniformity in the nanowire morphology, the model modification for data fitting became more difficult as the shape of the spectra for different samples looks different (which is not only caused by the change of Si shell thickness). For some cases, the plasmon frequency of the nanowire sample is too high frequency, which cannot be measured completely by the current THz system, and thus it is not reliable to perform the data fitting on them. For example, the spectra of the sample H05022 with 130 nm silicon shell could not be fitted as shown in figure 3.

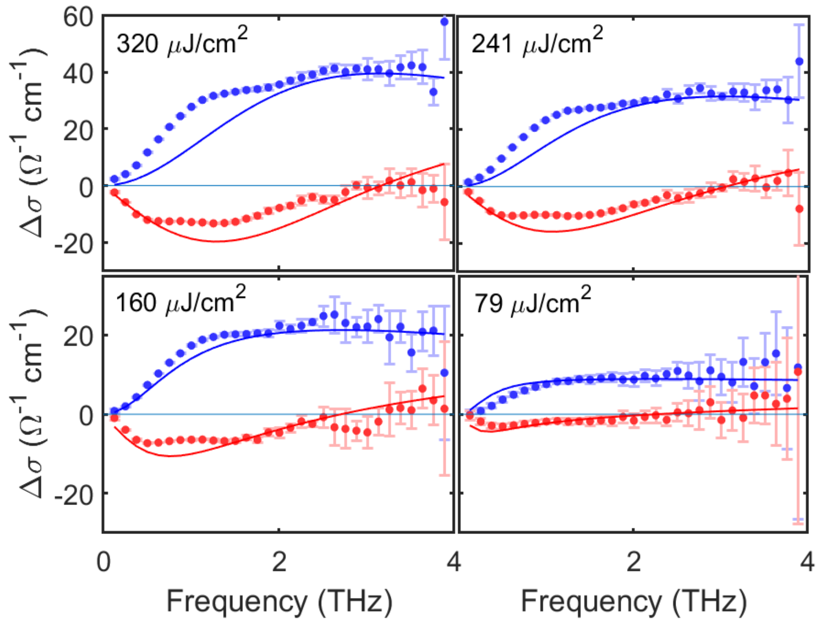

Figure 2:
Frequency dependent changes in photoconductivity for sample H05350 (70nm Si shell thickness) excited with varying excitation power. The blue dots depict the real part of the photoconductivity and the red dots the imaginary one. The bars show the standard deviation for 12 scans. The blue and red lines present the globally fitted plasmon responses. b) Plasmon resonant frequencies in dependence on the photoexcited carrier density.

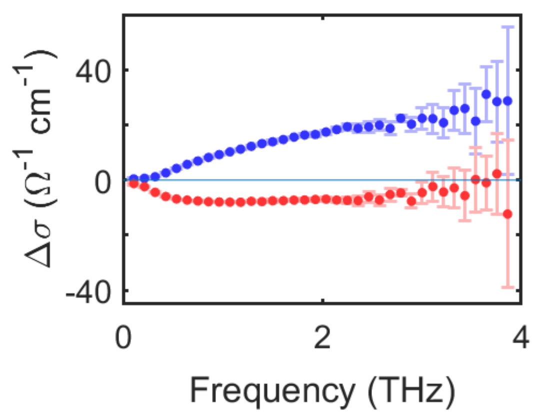

Figure 3: Photoconductivity spectrum for sample H05022 (130 nm Si shell thickness).

The next step is to regrow and remeasure this series with optimised nanowire quality. TU/e recently succeeded to significantly reduce the defect density in the Ge-shells, which will be made available for Oxford in the near future. For a better understanding of the GaP core and its effect on the THz measurements, the defect density, the surface recombination velocity and the composition of core-only GaP nanowires will be investigated.

Furthermore, for the Hex-Ge shell nanowires with a GaAs core, the data analysis and model modification are expected to be harder as both GaAs core and Ge shell will be photoexcited during the OPTP measurements. To distinguish the core and shell contributions in the photoconductivity properties of the nanowires, the Oxford group has developed a selective (wet) etching method for removal of the GaAs core from the GaAs-Ge core-shell nanowires (see figure 4). So far, the etching rate has been calibrated as a function of time and temperature with a result of a smooth surface. Comparisons between the etched and non-etched GaAs-Ge nanowires using the OPTP measurements will be conducted in July 2018.

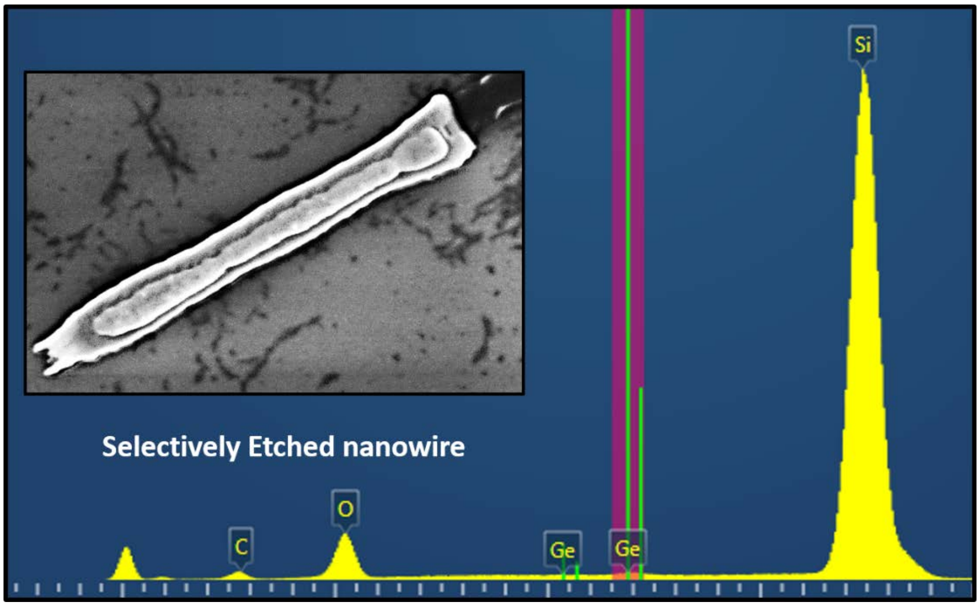

Figure 4: EDS analysis for a single nanowire from sample H05444, whose GaAs core has been selectively removed via wet etching. There is no presence of Ga or As in the etched nanowires.