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D3.1 Measurement of the absorption spectrum of hex-SiGe

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DESCRIPTION OF DELIVERABLE

We have measured the absorption spectrum of hex-SiGe nanowires embedded into a PDMS flexible polymer to eliminate spurious absorption from the GaAs substrate and from parasitic growth of cubic SiGe in between the nanowires. We use Fourier Transform Infrared Spectroscopy combined with an integrating sphere to measure both the transmission, the reflection and the absorption in three different configurations. Unfortunately, we do not observe a clear absorption edge at the bandgap, but we observe a slowly rising absorption spectrum which is completely different as expected for a direct bandgap semiconductor with a large oscillator strength. Our measurement are in reasonable agreement with the theoretical results for the absorption spectrum from the Jena group [2], but it should be emphasized that the theoretical absorption spectra are broadened with a broadening function that smears out the expected absorption edge.

1. INTRODUCTION

For achieving opto-electronic functionality in hex-SiGe, and in particular to achieve lasing, it is important that the absorption spectrum of hex-SiGe reflects the spectrum of a direct bandgap semiconductor with an allowed optical transition. In other words, we like to verify whether the absorption spectrum is “well-behaved” with a clear absorption edge at the bandgap and an absorption strength similar to GaAs. It is important to realize that theory predicts a very small optical matrix element for a perfect crystal of hex-Ge, while the matrix element is predicted to increase for hex-SiGe due to breaking of the translational symmetry as a result of alloy disorder [1]. The experimental results on the photoluminescence of hex-SiGe seem to differ from theory in a very positive way. Hexagonal Ge is found to be an efficient light emitter [1] and initial measurements on the strain dependence on hex-Ge indicate stronger emission from the almost forbidden $\Gamma_{9v}^+ \rightarrow \Gamma_{8c}^-$ transition as compared to the allowed $\Gamma_{9v}^+ \rightarrow \Gamma_{7c}^-$ transition at 1.6% tensile strain, which is slightly beyond the conduction band inversion point. Another important observation is that we observe the first indications for lasing in hex-SiGe, which strongly indicates that the absorption spectrum is “well-behaved”.

For our present hex-SiGe nanowires, the challenge is to measure the absorption spectrum of hex-SiGe while eliminating possible absorption of the GaAs (111) substrate as well as from the cubic SiGe which grows parasitically in between the nanowires. In this report, we investigate the absorption spectrum of hex-SiGe by using integrated sphere absorption measurements using Fourier Transform Infrared Spectroscopy (FTIR) on hex-SiGe nanowires transferred into PDMS polymer and removed from their parent substrate.

2. EXPERIMENTAL

Hex-(Si)Ge nanowires on a GaAs substrate are coated with spin on glass (SOG) to encapsulate the wires and make them ready for transfer from the substrate. Polydimethylsiloxane (PDMS) is used that is made from Dow Corning Sylgard 184 base and cure solutions. PDMS has been shown to have been an effective medium for suspending InP nanowire arrays. Based on previous studies of suspending nanowire arrays, the optimized recipe used in [3]. A 2-layer spin on approach is used where each layer contains different cure-base-dilution ratios to achieve an optimal nanowire transfer percentage. The first layer that is directly spun on the MOVPE grown nanowires consists out of an 5-2 base-cure ratio and is diluted with 65% hexane. The hexane is added in order to decrease the viscosity of the PDMS solution. This improves the diffusion of the solution in between the nanowires before curing. The PDMS solution is prepared and put inside a vacuum desiccator with a beaker of hexane to prevent evaporation from the PDMS solution for a period of 25 minutes. This step is performed to remove air bubbles from the solution. The solution is then deposited onto the sample after which the sample with solution is put again inside the desiccator for a period of 25 minutes. The sample is then spun at a speed of 1000 RPM for a period of 60 seconds. The sample with now the first layer spun on is put in a vacuum desiccator again, leaving it to cure for 48 hours at room temperature. After the first layer is cured a second layer based on a 10-1 base-cure ratio is spun on. This layer serves as enhancement layer for the mechanical strength of the whole stack, This layer is therefore not diluted with hexane as this lowers the tensile strength of the cured solution and no decreased viscosity is required for this layer. The second layer-solution is first prepared and put inside a desiccator for 25

minutes after which it is deposited on top of the already cured first layer of PDMS. The sample is then spun for 1000 RPM for a period of 60 seconds. After spinning, the stack of materials is cured in an oven at 150 °C for 10-15 minutes until the PDMS at the top of the stack is fully cured.

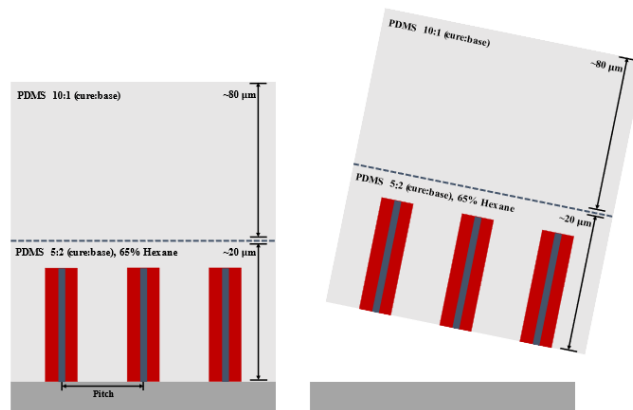


Fig. 1. Transfer of the hex-SiGe nanowires into PDMS and removing from the GaAs substrate.

A cured stack consisting of a substrate with wires and two cured layers of PDMS is now ready for mechanical extraction. The removal involves vertically cutting into the PDMS layers until the substrate is reached. The blade is then put a slight angle with respect to the surface normal during the extraction. The angle is then slightly increased as the wires are gradually removed in a single piece of PDMS.

Absorption spectroscopy measurements with an integrating sphere

A FTIR interferometer and movable MCT detector are used to perform transmission, reflection and absorption measurements with a reflective gold coated integrating sphere. The detector is now placed outside the FTIR, next to the exit of the integrating sphere. Light from two sources, including a high power 1550 nm supercontinuum (SC) laser, a white light source are first passed through the FTIR interferometer before reaching the sample and detector. Placing the sample in front of the entrance of an integrating sphere as depicted in figure 2a provides a method to determine the transmission percentage through the sample. If the sample is placed at the furthest entrance of the sphere as shown in figure 2b a reflection measurement can be performed. The absorption is measured with the integration sphere setup with the sample mounted in the center of the integrating sphere under an angle, which allows for a direct measurement the light absorption as depicted in figure 2c.

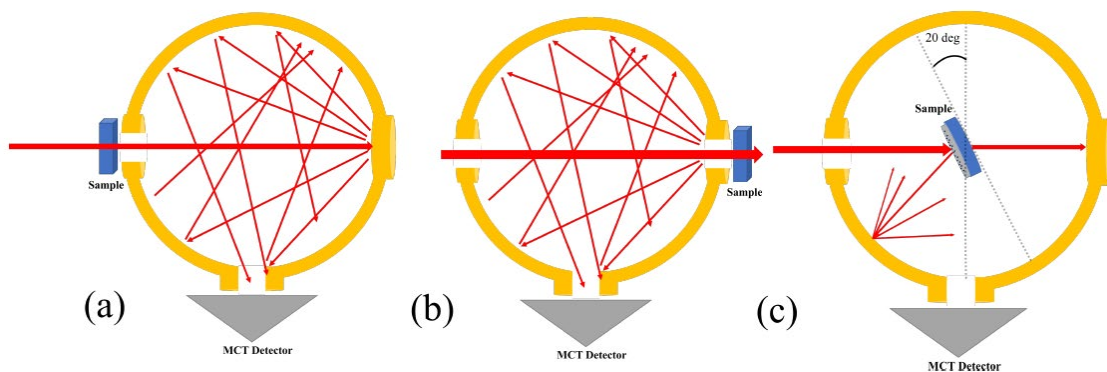


Figure 2: Three measurement configurations with the integrating sphere. (a): Transmission measurement with a sample in front of the front entrance (b): Reflection measurement with a sample at the back of the integrating sphere. (c): Absorption measurement with the sample in the integrating sphere.

3. RESULTS

PDMS is used to remove hex-(Si)Ge nanowire arrays from their substrate, leaving them encapsulated in PDMS. The optical properties of PDMS will thus be important when optically characterizing hex-(Si)Ge nanowires in PDMS.

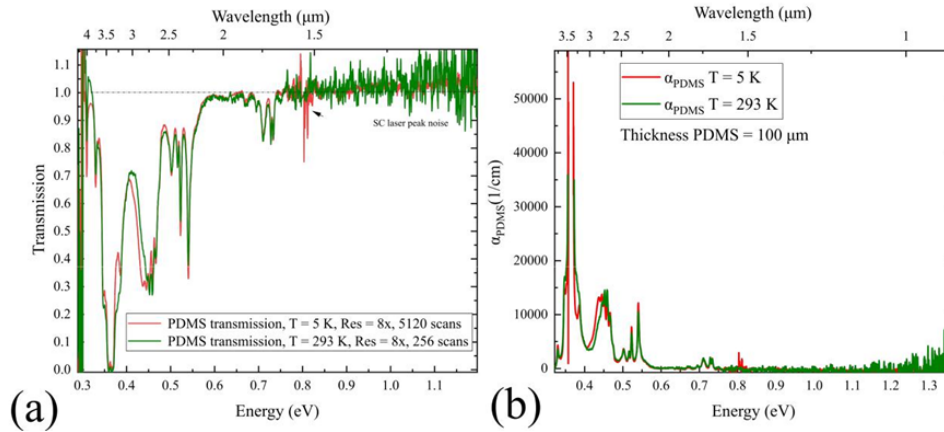


Figure 3: (a) Transmission spectrum of PDMS measured at 5 and 293 K, note the SC-laser peak at 1550 nm. (b): Calculated absorption coefficient from the data of (a).

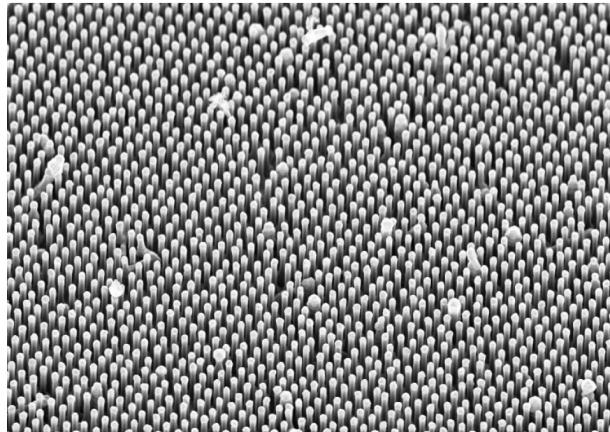


Fig. 4: Scanning electron microscopy image of sample A

Sample A consists of an array of 500 nm diameter hex-Si_{0.22}Ge_{0.78} nanowires with 2 μm pitch and is shown in Fig. 4. After embedding the nanowires into PDMS, the sample is put on a transparent sapphire wafer. What can be seen is that periodicity is only locally achieved within a length scale of 10's of microns. This length scale is smaller than the achievable beam size of the light sources during measurements. The probed arrays will thus not be fully periodic within the probed region. The transfer of nanowires into PDMS is also not perfect, further reducing the periodicity of the original nanowire array and the amount of absorbing material. The segment length of the suspended nanowires varies from wire to wire and some regions have a larger transfer yield than others.

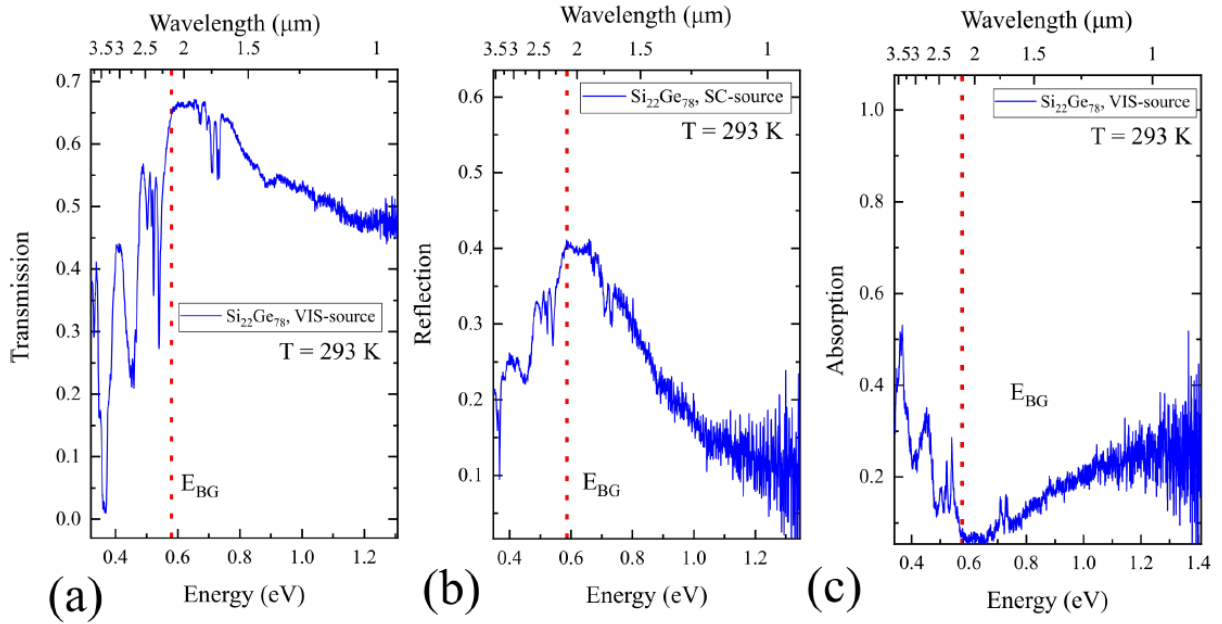


Figure 5: (a): Transmission spectrum of hex-SiGe in PDMS on a sapphire wafer measured in configuration shown in Fig. 2a. (b): Reflection spectrum of the same sample, now measured with a supercontinuum (SC) light source, measured in configuration shown in Fig. 2b. (c): Absorption spectrum of the same sample, measured in configuration shown in Fig. 2c. For all three figures the approximate band gap determined from the peak position the photoluminescence spectrum (not shown) is indicated with a dashed red line.

The results of the 3 types of measurements: transmission, reflection and absorption are shown in Fig. 5 for sample A. The absorption spectrum is clearly not “well behaved” as expected for a direct bandgap semiconductor since we do not observe clear absorption edge directly above the bandgap. One possible reason might be that the transfer into PDMS has strongly reduced the PL emission, e.g. due to oxidation of hex-SiGe during the transfer into PDMS and/or the subsequent annealing. Another explanation might be light scattering. The transmission and reflection measurements in figure 5a and 5b both show a decreasing signal towards high energy. The decrease of both the transmission and the reflection could indicate that light is increasingly scattered away at short wavelengths.

The independent absorption measurement on the same sample as shown in Fig. 5c, shows a slowly increasing amount absorption as a function of energy. This absorption measurement is less sensitive to scattering of light away from the detector since the sample is positioned in the center of the integrating sphere, thus reducing light scattering out through the entrance of the integrating sphere. The combined 3 experiments thus show that significant light absorption only becomes measurable above the band gap of the hex-SiGe alloy. Below the band gap, the spectra are dominated by the absorption of PDMS.

The measured absorption is now compared to the expected absorption according to predictions by DFT calculations [2] from the Jena group. The absorption coefficient α as used in Lambert-Beer’s equation can be calculated from the imaginary part of the dielectric functions of the hex-(Si)Ge alloys. The absorption coefficient α is plotted in Fig. 6 as a function of photon energy (eV). It should be noted that the dielectric function predicted by DFT uses a broadening function for the dielectric properties. This approximation broadens the sharp absorption edge of a direct semiconductor such as hex-SiGe.

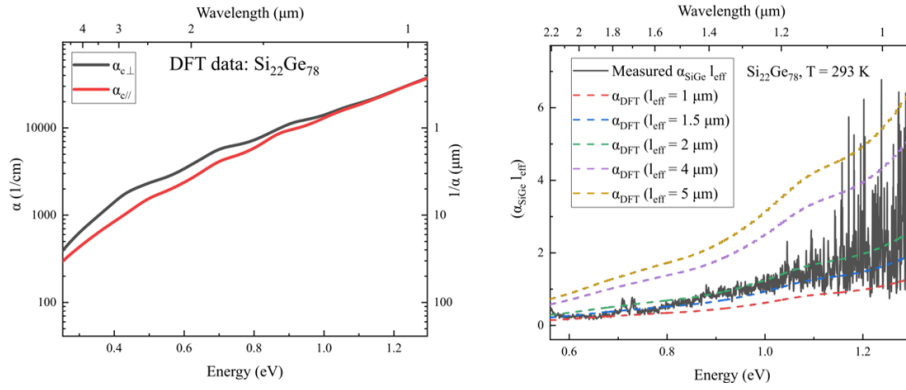


Figure 6: (a) Calculated absorption coefficients [2] for light polarized parallel and perpendicular to the c -axis. (b) Product of absorption coefficient of hex-SiGe, averaged over all polarization, α_{SiGe} , and the effective path length of light inside hex-SiGe, l_{eff} , as calculated from the absorption data in Fig. 5c. Also displayed is the DFT data from the Jena group [2] for values of l_{eff} within the bounded estimate.

The amount of hex-SiGe material in PDMS at the measured spot on the sample needs to be known to make a comparison with theory. The comparison of the integrated PL intensity from the substrate before (all NWs on the substrate) and after removal (most NWs removed, but NW stems remaining on the substrate still emit PL) provides an indication for the upper bound of the average length of hex-SiGe in PDMS, $l_{\text{eff-max}}$. A lower bound is estimated from the SEM image of the measured spot. The average length of transferred wires into PDMS l_{eff} is estimated to be $l_{\text{eff}} = (3 \pm 2) \mu\text{m}$. The large uncertainty is a direct consequence of the irreproducible transfer yield.

The absorption measurement in Fig. 5c is used as a starting point for the extraction of the absorption coefficient. The calculated product of α_{SiGe} and l_{eff} is compared in Fig. 6b to the product of the absorption coefficient from the DFT data with a range of effective path lengths. A constant value of $l_{\text{eff}} = (1.5 \pm 0.5) \mu\text{m}$ corresponds well to the measured absorption data. The theoretically predicted value of α_{SiGe} is thus of similar magnitude as the measured value α_{SiGe} within the error bounds set by the unknown path length. Only a qualitative comparison has been achieved as a consequence of the large uncertainty in the amount of transferred hex-SiGe.

The model is subsequently applied to the transmission and reflection measurements in Fig. 5a and 5b respectively, without using the absorption measurement in Fig. 5c. The calculated absorption coefficient of hex-SiGe is shown in Fig. 7a and 7b for the transmission and reflection data respectively.

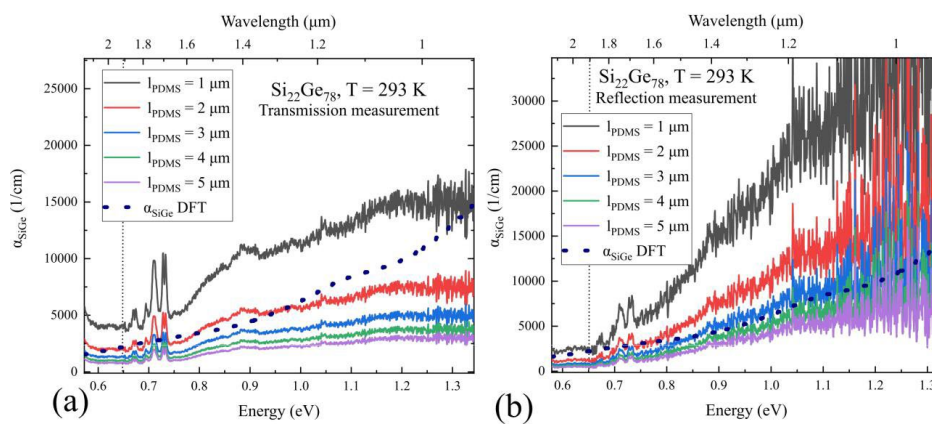


Figure 7: (a): Measured absorption coefficient of hex-SiGe, determined from transmission measurements. The extraction of α_{SiGe} is done under the assumption of an effective path length. The measured values of α_{SiGe} are plotted for these path lengths. Also plotted is α_{SiGe} as predicted by DFT calculations. (b): Measured absorption coefficient of hex-SiGe determined from reflection measurement. The dotted vertical line indicates the bandgap.

Between 0.65 and 0.75 eV several peaks can be seen, which have been identified as absorption peaks due to PDMS. The measured absorption onset is found to be situated at a minimal energy of approximately 0.65 eV. The appearance of PDMS absorption features in the spectra limit a more precise determination of the onset. It is possible that the expected absorption edge is shifted due to a Burstein-Moss shift due to bandfilling due to the high n-doping.

The absorption coefficient α_{SiGe} determined from the transmission and reflection measurement respectively are found to be of the same order of magnitude. The measured values also are of similar magnitude as the DFT predicted absorption coefficient. The magnitude of α_{SiGe} is now compared to the absorption coefficient of other direct band gap semiconductors, e.g. GaAs. For comparison is taken the magnitude of the absorption coefficient at an energy of 0.2 eV above the onset of absorption. α_{SiGe} is measured to have a value of $((5 \pm 4) \times 10^3) \text{ cm}^{-1}$ at 0.8 eV and the predicted value by DFT is 3446 cm^{-1} at 0.8 eV. GaAs is measured to have an absorption coefficient of $(1.5 \times 10^4) \text{ cm}^{-1}$ at 297 K after the absorption onset of the direct band gap. The measured and predicted absorption coefficient of hex-SiGe are therefore lower than that of GaAs which have been found to have a comparable radiative B-coefficient [1]. A comparable B-coefficient indicates that the transition probability for states near the band gap are comparable for these semiconductors. The absorption probability would therefore also be expected to be similar.

4. CONCLUSIONS

Unfortunately, the results from these absorption measurements are still inconclusive. The theoretically calculated absorption coefficients are still broadened with a broadening function which is smearing out the absorption edge. Surprisingly, our measurements are in reasonable agreement with the “smeared-out” theoretical results. The results obtained by suspending hex-SiGe nanowires into PDMS and measuring them has provided an absorption spectrum of hex-SiGe. However, the spectrum is not “well-behaved” and is lacking a clear absorption edge that would be expected, given the high B-coefficient deduced from photoluminescence lifetime measurements. Several possible reasons can be identified, with the first and foremost one being the unreliability of the current transfer method. The unknown length, facet quality and local transfer yield make it difficult to apply theoretical models of the effective interacting path length. Another uncertainty is the possible oxidation of hex-SiGe during transfer into PDMS and the subsequent anneal. Finally, the effect of light scattering might have a strong influence on the results.

To circumvent the transfer into PDMS, we are constructing a photoluminescence excitation (PLE) spectroscopy setup using a supercontinuum laser (0.9-4.2 μm tuning range) which is dispersed through a substrative double monochromator to establish a tunable wavelength source in the infrared.

5. REFERENCES

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