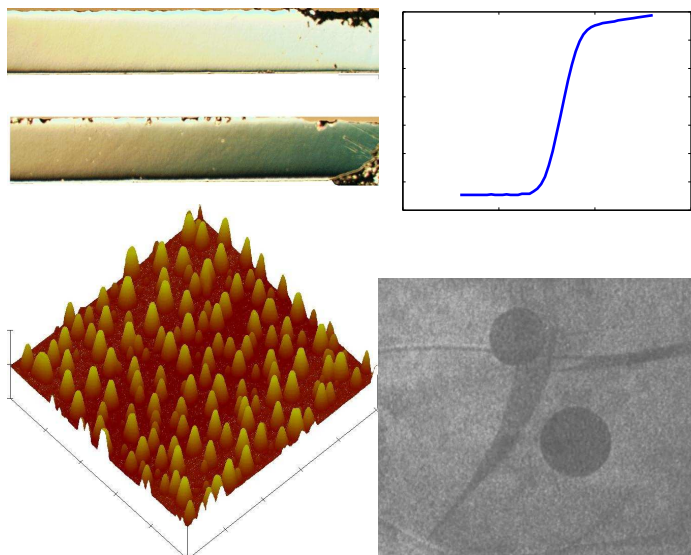


Günther Palfinger

Low Dimensional Si / SiGe Structures Deposited by UHV-CVD for Thermophotovoltaics



Dissertation

zur Erlangung des akademischen Grades
des Doktors der Naturwissenschaften (Dr. rer. nat.)
an der Universität Konstanz Fakultät für Physik
angefertigt am Paul Scherrer Institut, Schweiz
vorgelegt von Günther Palfinger

Tag der mündlichen Prüfung: 24. Februar 2006

Referenten: Priv. Doz. Dr. Gerhard Willeke
und Priv. Doz. Dr. Detlev Grützmacher

Palfinger, Günther:

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Cover picture:

As failing experiments are also part of experimental science and often even as important as successful ones, I placed these pictures on the title page to represent those experiments that are usually not mentioned: *Top left*: A differential interference visible light micrograph of two facets of absorption samples. It was taken to investigate the reason for not being able to obtain absorption measurements on an absolute scale. *Bottom left*: An AFM picture of SiGe quantum dots. The stacking of these dots resulted in amorphous structures and the size of the dots was not reproducible. *Top right*: IV curve of a photocell with embedded SiGe structures with a poor minority carrier lifetime of the epitaxial layer. *Bottom right*: A darkfield visible light micrograph of a sample after the UHV-CVD process, expected to be smooth, i. e. uniformly black. The cause for the deviation was never found.

Abstract

Photocells low band gap, i. e. smaller than that of Si, can be applied in multi-junction solar cells and in thermophotovoltaics (TPV). Such band gaps can be achieved by embedding layers of SiGe nanostructures between Si spacers. Such a stack placed into the space charge region of a Si *pin* diode enhances the infrared sensitivity of the photocell. Compatibility to the mainstream Si technology is assured by using crystalline Si wafers as a substrate and UHV-CVD (Ultra High Vacuum-Chemical Vapour Deposition) epitaxy for material growth, promising more cost efficient mass fabrication in comparison with other low band gap materials as e. g. GaSb. Due to the lattice mismatch between Si and Ge of about 4%, the SiGe structures will be strained, limiting the amount of SiGe that can be epitaxially deposited. As absorption of light is a necessary condition for photovoltaic conversion and the total thickness of SiGe is small in comparison to the thickness of a Si photocell, the absorption coefficient of the SiGe nanostructures should be much higher than that of Si to achieve comparable quantum efficiency. The spacial confinement of charge carriers in the SiGe nanostructures causes a spreading of the wave function in momentum space, leading to a higher probability of a direct transitions of charge carriers from the valence to the conduction band. Thus, it was expected that these transition without the need for a phonon increase optical absorption significantly. This work investigates for the first time the optical absorption of SiGe nanostructures on an absolute scale and compares it with a photocurrent measurement. Additionally, it estimates the cost of electricity produced by TPV, a potential application of low band gap photocells.

Optical absorption of SiGe structures was measured by internal reflection spectroscopy, where the light passes more than 400 times through the stack of SiGe layers. The total reflection of the light results in a standing electromagnetic wave. The absorption coefficient was obtained from the measurement data, taking the geometry and the electric field distribution into account. The experimental results are compared with a theoretical model, considering the band structure of strained SiGe and confinement effects. The comparison of the photocurrent- with the absorption measurement indicates that some of the absorbed photons with energies below 1 eV are not converted into photocurrent. Without light trapping, more than 1000 layers of SiGe structures are needed to absorb 1 % of the light with a photon energy of 1 eV. Light trapping and further improvements in growth technology are necessary to obtain SiGe structures that are applicable for photocell production.

A detailed cost estimate is performed for a Si photocell based TPV system, a projected GaSb photocell based system and a future, highly efficient system with inexpensive photocells, expected to be achievable with low band gap photocells based on Si compatible technology. For the calculation of the price of electricity, a lifetime of 20 years, an interest rate of 4.25 % per year and maintenance costs of 1 % of the investment is presumed. To

determine the production cost of TPV systems with a power of 12-20kW, the costs of the TPV components and 100 EUR/kW_{el,peak} for assembly and miscellaneous were estimated. Alternatively, the system cost for the GaSb system was derived from cost of the photocells and from the assumption that they account for 35 % of the total system cost. The calculation was done for four different TPV-scenarios which include a Si based prototype system with existing technology (system efficiency $\eta_{sys} = 1.0\%$), leading to 3 000 EUR/kW_{el,peak}, an optimised Si based system using conventional, available technology ($\eta_{sys} = 1.5\%$), leading to 900 EUR/kW_{el,peak}, a further improved system with future technology ($\eta_{sys} = 5\%$), leading to 340 EUR/kW_{el,peak} and a GaSb based system ($\eta_{sys} = 12.3\%$ with recuperator), leading to 1 900 EUR/kW_{el,peak}. Thus, prices of the electricity from 6 to 25 EURcents/kWh_{el} (including gas of about 3.5 EURcents/kWh) were calculated and compared with that of fuel cells (31 EURcents/kWh) and gas engines (23 EURcents/kWh).

Kurzfassung

Photozellen mit niedriger Bandlücke, d.h. kleiner als jene von Si, können in Tandem-Solarzellen oder in der Thermophotovoltaik (TPV) angewandt werden. Niedrige Bandlücken können durch das Einbetten von Lagen mit SiGe-Nanostrukturen in Si erzielt werden. Befindet sich solch ein Stapel in der Raumladungszone einer *pin* Diode, erhöht sich dadurch die Infrarot-Sensibilität der Photozelle. Die Kompatibilität zur Si-Technologie wird durch die Verwendung von kristallinen Si-Scheiben als Substrat und durch Ultrahochvakuum-Epitaxie aus der Gasphase (UHV-CVD – Ultra High Vacuum-Chemical Vapour Deposition) gewährleistet, das eine kosteneffizientere Massenfertigung im Vergleich zu anderen Materialien mit niedriger Bandlücke, wie z. B. GaSb, verspricht. Die Gitterfehlpassung zwischen Si und Ge von ca. 4% führt zur Stauchung der SiGe Strukturen, welche die maximale Dicke, die epitaktisch abgeschieden werden kann, limitiert. Da Absorption des Lichtes eine Voraussetzung für die photovoltaische Umwandlung in Elektrizität ist, und die abscheidbare SiGe-Dicke klein im Vergleich zur Dicke einer Si Photozelle ist, wird für eine vergleichbare Quantenausbeute ein entsprechend höherer Absorptionskoeffizient der SiGe Nanostrukturen benötigt. Die örtliche Begrenztheit der Ladungsträger (Confinement) in den SiGe Nanostrukturen bewirken eine Verbreiterung ihrer Wellenfunktion im Impulsraum, die zu einer höheren Wahrscheinlichkeit eines direkten Übergangs der Ladungsträger vom Valenz- zum Leitungsband führt. Deshalb kann erwartet werden, dass diese Übergänge, die kein Phonon benötigen, die optische Absorption signifikant erhöhen. In dieser Arbeit wird die optische Absorption von SiGe Nanostrukturen zum ersten Mal in absoluten Einheiten untersucht und die Ergebnisse mit einer Photostrommessung verglichen. Darüberhinaus werden die Gestehungskosten von Elektrizität, die durch TPV erzeugt wird, abgeschätzt.

Die optische Absorption der SiGe Strukturen wurde mittels interner Vielfachreflexions-Spektroskopie gemessen, bei der das Licht den Stapel von SiGe Lagen mehr als 400 mal durchläuft. Die Totalreflexion des Lichtes bewirkt eine stehende elektromagnetische Welle. Der Absorptionskoeffizient wurde aus den experimentellen Daten unter Berücksichtigung der Geometrie und der Verteilung des elektrischen Feldes gewonnen. Das Messergebnis wurde mit einem theoretischen Modell verglichen, das die Bandstruktur des gestauchten SiGe, sowie Confinement-Effekte berücksichtigt. Der Vergleich von der Photostrom- mit der Absorptionsmessung weist darauf hin, dass einige Photonen mit einer Energie $< 1\text{ eV}$ nicht in Photostrom umgewandelt werden. Ohne Lichteinfang wären 1000 Lagen mit SiGe Strukturen notwendig, um 1% des Lichtes mit einer Photonenenergie von 1 eV zu absorbieren. Lichteinfang und eine Verbesserung der Abscheide-Technologie ist erforderlich, um SiGe Nanostrukturen zu erhalten, die für den Einsatz in der Photozellen-Produktion geeignet sind.

Es wurde eine detaillierte Kostenabschätzung für TPV-Systeme angefertigt, die auf drei verschiedenen Photozell-Technologien basieren: Si Photozellen, GaSb Photozellen und Photozellen mit niedriger Bandlücke, zu einem Preis, wie er mit Si-kompatibler Technologie zu erwarten ist. Für die Berechnung der Kosten der Elektrizität wurde eine Lebensdauer von 20 Jahren, ein jährlicher Zinssatz von 4.25% und ein jährlicher Wartungsaufwand von 1% der Investitionskosten angesetzt. Für die Bestimmung der Produktionskosten eines TPV-Systems mit einer thermischen Leistung von 12-20kW wurden die Kosten der TPV-Einzelkomponenten zuzüglich 100 EUR/kW_{el,peak} für die Fertigung und Klein-
teile angenommen. Die Kosten des GaSb basierten Systems wurde von den Kosten der Photozellen und der Annahme, dass diese 35% der Gesamtkosten betragen, berechnet. Die Berechnung wurde für vier verschiedene TPV-Szenarien durchgeführt: Ein Prototyp-System, das auf existierender Si Solarzellen Technologie basiert (Systemwirkungsgrad $\eta_{\text{sys}} = 1.0\%$), ergibt Investitionskosten von 3 000 EUR/kW_{el,peak}, ein optimiertes Si Photozellen basiertes, mit verfügbarer Technologie fertigbares System ($\eta_{\text{sys}} = 1.5\%$) ergibt Investitionskosten von 900 EUR/kW_{el,peak}, ein weiter optimiertes System, das auf zukünftiger, kostengünstiger Technologie basiert ($\eta_{\text{sys}} = 5\%$) ergibt Investitionskosten von 340 EUR/kW_{el,peak} und ein auf GaSb Photozellen basiertes System ($\eta_{\text{sys}} = 12.3\%$ mit Wärmetauscher) ergibt Investitionskosten von 1 900 EUR/kW_{el,peak}. Die daraus resultierenden Elektrizitätskosten betragen zwischen 6 und 25 EURcents/kWh_{el} (inklusive 3.5 EURcents/kWh für das Gas) und wurden mit jenen einer Brennstoffzelle (31 EURcents/kWh) und eines Gasmotors (23 EURcents/kWh) verglichen.

Contents

Abstract	III
Kurzfassung	V
1 Introduction	1
2 SiGe Growth with UHV-CVD	5
2.1 Introduction	5
2.2 Experimental Setup	6
2.3 CVD Growth regimes	9
2.4 Gas Phase Reactions	9
2.5 Reactant Transport	10
2.6 Surface Processes during Transport	11
2.6.1 Pure Si (1 0 0) Surface	11
2.6.2 Hydrogen Passivated Surface	12
2.6.3 Surface Reactions of Si H ₄ and Ge H ₄ and Kinetic Models of Growth	12
2.6.4 Summary	14
2.7 Surface Preparation	14
2.8 Structural Analysis	15
2.8.1 Transmission Electron Microscopy (TEM)	15
2.8.2 X-Ray Diffractometry	21
2.9 Impact of Growth Parameters on the Deposition of SiGe	27
3 Optical Absorption of SiGe Quantum Wells	31
3.1 Band Structure of Si, SiGe and SiGe Quantum Wells	31
3.2 Transition Energy due to Strain and Confinement	34
3.2.1 Influence of Strain	35
3.2.2 Influence of Confinement	36
3.2.3 Minimum Transition Energy of Unstrained Bulk SiGe and Strained SiGe Quantum Wells	37
3.2.4 Macfarlane-Roberts Expression	39
3.3 Absorption of a Standing Electromagnetic Wave and Effective Thickness .	39
3.3.1 Electromagnetic Waves in Conducting Media	40
3.3.2 Electric Field in Multiple Layers	42
3.3.3 Superposition of Incident and Reflected Electric Field Components	46

3.3.4	Si/SiGe Multilayer	49
3.4	Measurement Setup	49
3.5	Measurement Accuracy, Reproducibility and Artefacts	50
3.6	Experimental Results	52
3.6.1	Impact of Free Carrier Absorption	53
3.6.2	Benefit of the Fourier Transform Spectrometer	53
3.6.3	Measurements with Grating Spectrometer	56
3.6.4	Measurements with Fourier Transform Spectrometer	60
3.7	Summary	65
4	Comparison of Photocurrent with Absorption	67
4.1	Sample Preparation and Measurement Set-Up	67
4.1.1	MBE	67
4.1.2	Fabrication of the Diodes for the Photocurrent Measurement	68
4.2	Absorption Measurement	68
4.3	Photocurrent Measurement	70
4.4	Comparison of Photocurrent and Absorption Measurement	71
4.5	Summary	72
5	TPV Cost Estimate	73
5.1	Introduction	73
5.2	TPV Technologies	74
5.2.1	Comparison of Systems with Porous and Gas-tight Emitters	74
5.2.2	Si Based Porous Emitter System	76
5.2.3	GaSb Based Gas-tight Emitter Systems	78
5.3	Cost Estimates	78
5.3.1	Scenarios	79
5.3.2	The Investment Cost	80
5.3.3	Cost of Electricity	84
5.3.4	AC/DC and Inverters	85
5.4	Conclusion	85
6	Conclusions	87
	Acknowledgement	89
A	Computer Programme wavem for Absorption Measurement Analysis	91
B	List of Samples	97
	List of Figures	99
	List of Tables	104
	Bibliography	107

Chapter 1

Introduction

One of the factors supporting economic growth in the last decades was the semiconductor industry, allowing an ever-greater degree of automation in virtually every field of daily life. The dynamics of the semiconductor industry can be characterised by the empirical Moore's Law: Doubling the number of transistors per unit area every three years. Quantum mechanical limitations will set an end to the validity of Moore's law in about 2 decades. Nanostructures, i. e. structures smaller than 100 nm, are under active investigation to maintain Moore's law valid for, as long as possible and to find new concepts as e. g. in quantum computing.

Considering materials used in device production, the by far largest share in the semiconductor industry is held by Si. Thus, it is often economically and scientifically rewarding to develop materials with new properties on the basis of this well established, mainstream technology. One of the most important properties characterising a semiconductor is the difference in energy between the top of the valence band and the bottom of the conduction band, i. e. its band gap. For both, Si and Ge, the conduction band minimum and the valence band maximum are at different positions in momentum space, i. e. they are indirect semiconductors. Thus, the transitions between valence band maximum and conduction band minimum or vice versa, being photon absorption or emission, respectively, need phonons for momentum conservation. By alloying Si with Ge, the band gap can be adjusted by the concentration ratio to any value between 0.67 and 1.12 eV – i. e. the band gap of Ge and Si, respectively – allowing to influence band gap dependent properties, like the absorption edge, accordingly. Using Si as a substrate for epitaxial growth has many economical and technical advantages.

The lattice mismatch between Si and Ge of about 4% causes compressive strain in a Si Ge alloy when deposited on a Si substrate. This strain decreases the band gap even further. However, the strain restricts the epitaxial growth of SiGe structures on Si substrate to a thickness in the nanometer scale for Ge concentrations $> 10\%$. By stacking several SiGe layers between Si spacers, the total amount of SiGe that can be deposited epitaxially can be increased in comparison to a single SiGe layer of the same composition. The embedding of SiGe nanostructures in Si causes charge carrier confinement, which is expected to lead to useful effects: Due to the confinement in spatial coordinates, the wave function of the charge carriers spreads in momentum space. Thus, the probability of a transition without the aid of a phonon is expected to increase. This increase can be observed in emission. The

no-phonon photoluminescence increases in nanostructured SiGe in comparison to bulk Si. Hence, the absorption coefficient is expected to increase due to the increased probability of a transition without the aid of a phonon¹.

Epitaxially deposited SiGe is compatible with mainstream Si technology, has a lower band gap than Si and an increase in absorption can be expected. Consequently, these properties might be utilised for a photocell which can convert photons with an energy below that of the Si band gap energy. Possible applications are a bottom cell in a tandem configuration of a solar cell and photocells for thermophotovoltaics (TPV).

The first step in photovoltaic energy conversion is absorption. Light that is not absorbed cannot be converted into electricity. For Si, there are good absorption data available. For Ge, however, the absorption coefficients from different sources vary by one order of magnitude. Bulk SiGe has been investigated for some alloy concentrations. The absorption of nanostructured SiGe, however, was not available in the literature prior to this work. Hence, the purpose of this thesis is to fabricate SiGe structures and determine some of their properties, e. g. absorption, morphology, Ge concentration, strain, band gap and minimum transition energy of charge carriers between the allowed states in the valence and conduction band. The knowledge of these properties allows to draw comparisons between SiGe nanostructures and bulk Si and SiGe and to investigate the potential for their usage in low band gap photocells.

The investigated structures are grown with ultra-high vacuum chemical vapour deposition (UHV-CVD). X-ray diffractometry, transmission electron microscopy (TEM) and infrared / Fourier transform infrared (IR/FTIR) spectrometry are the most important methods for their in-depth analysis.

One of the motivations for research in low band gap photocells is thermophotovoltaics (TPV). TPV is the conversion of heat into electricity. Figure 1.1 shows the principle set-up of a TPV system, where photons originate from the heated emitter, transverse the optional filter and are converted by the photocell into electricity. The system efficiency (electrical output power divided by heat input power) depends on the overlap of incident spectrum and quantum efficiency of the photocells. A large overlap can be achieved by using a selectively emitting material as emitter and further improvements are possible by attaching a filter that transmits convertible photons and reflects non-convertible photons back to the emitter. It is obvious that a filter should have little absorption. The use of TPV in combination with heat production reduces the generation of entropy and has the advantage over e. g. a gas engine that no moving parts are needed. The TPV systems presented to date suffer from a relatively low system efficiency, especially in comparison with fuel cells. This disadvantage can be considered irrelevant in applications where heat is the prime product. A possibly huge market is its use in domestic heating systems that generate the electricity for their control

¹ To estimate the size of structures needed to increase absorption significantly, the charge carriers are considered Gaussian distributed wave packets confined in the structure of width w . The Heisenberg uncertainty principle for a Gaussian distributed wave packet with spatial half width Δx and the half width of the wave vector Δk can be written as: $\Delta x \cdot \Delta k \approx 1$. This yields $\Delta x \approx 0.25 \text{ nm}$ for $\Delta k = 4 \text{ nm}^{-1}$, i. e. the difference between valence band maximum and conduction band minimum of Si in k -space. The absorption coefficient of a direct semiconductor is several orders of magnitude higher in comparison to an indirect semiconductor. Consequently, it can be assumed that the probability for a direct transition is several orders of magnitude higher in comparison to an indirect transition. Thus, the maximum size w for a structure in which the confinement effects increase the absorption significantly, is in the order of several Δx , i. e. in the order of $1 - 2 \text{ nm}$.

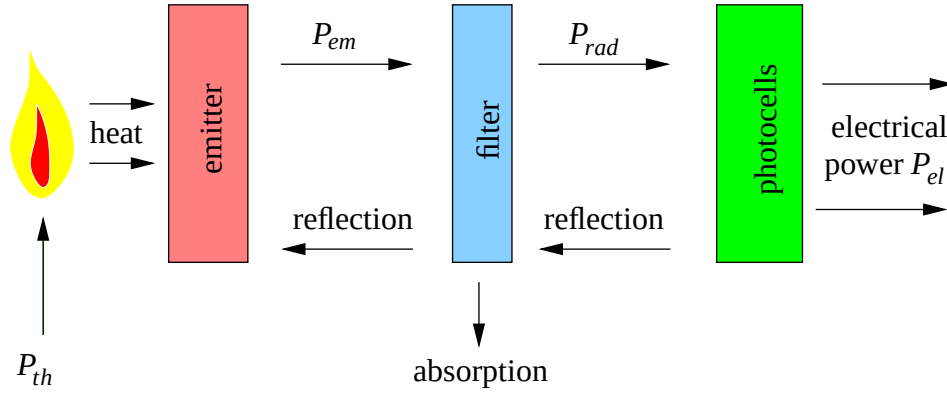


Figure 1.1: Principle of operation of a TPV system. An emitter is heated by thermal power P_{th} and emits electromagnetic radiation power P_{em} that is filtered (P_{rad}) and converted into electrical power P_{el} by the photocells. The purpose of an optional filter is to transmit the convertible photons and to reflect the rest back to the emitter.

units and circulation pumps by a TPV generator. This TPV-generated electricity has less losses for generation and transfer than centralised power generation if the heat generated by the photocells of the TPV system is utilised. Furthermore, such a heating system can run independently from the grid, giving a higher security of heat supply for countries with frequent power failures or in case of natural disasters leading to interruptions of power lines, e. g. avalanches or windstorms. However, the market for domestic heating systems is under a very high cost pressure. Thus, the extension of a heating system with a TPV system must not significantly increase its price in comparison to a conventional heating system. In the following, it will be shown that photocells with a lower band gap than that of Si can lower the cost of TPV-electricity, when the cost of the cells does not depend on the band gap. It is assumed that the latter condition can be at least approximately maintained, when employing Si compatible technology, as SiGe nanostructures deposited on Si substrates.

Due to Planck's law, a blackbody at higher temperature has a higher radiation density per unit area and unit photon energy interval for *every* photon energy. This statement can be generalised to every body, when its emissivity can be considered independent of its temperature. Thus, the radiation power density of the emitter increases with increasing emitter temperature, e. g. by the power of 4 for a blackbody (Stefan-Boltzmann-Law). The emitter temperature of fuel driven TPV systems is limited to about 1800 K by NO_x emission regulations. The band gap of the photocell determines the portion of the emitted spectrum that is converted into electricity. The electrical output power density depends on the emitter temperature and the band gap of the photocells. As the emitter temperature has its optimum at its upper limit, i. e. 1800 K, a simplified calculation estimating the influence of the band gap of the photocell on cost of electricity is presented in Figure 1.2, showing the electrical output power density versus the band gap of the photocell of an idealised TPV system². The electrical output power density has a maximum at around 0.64 eV and decreases sharply

² The photocells have an open circuit voltage of 0.4 V below the band gap energy. Their quantum efficiency is 1 for photons with an energy above the band gap and 0 for photons with an energy below the band gap. They have a fill factor of 0.7. Quantum efficiency and fill factor are not dependent on the band gap of the cells. The incident radiation is a tenth of a blackbody at 1800 K.

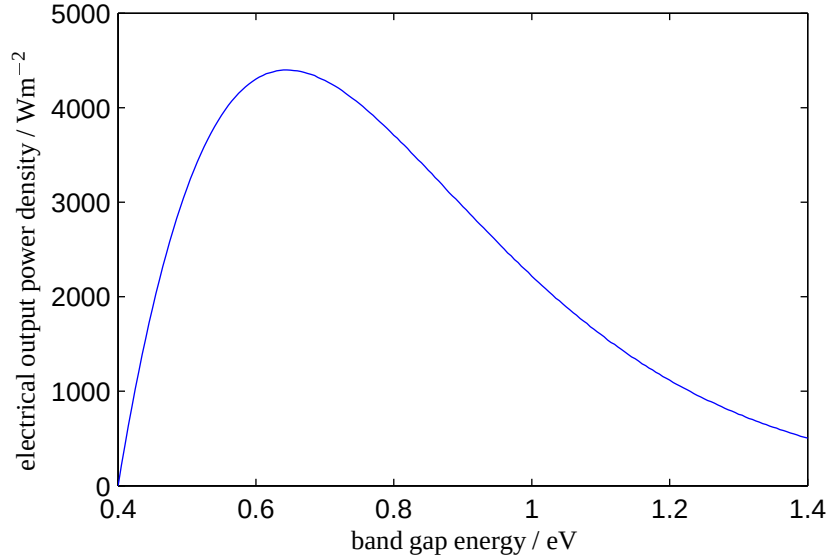


Figure 1.2: Electrical output power density of an idealised TPV system as a function of band gap energy of the photocell used. The emitter is a blackbody at 1800K.

towards higher band gap energies. It is about 2.5 times as high at 0.8 eV than at the Si band gap of 1.12 eV. Under the estimate that the price per unit area of the photocell does not depend on the light concentration and on its band gap, the cost of electricity is inversely proportional to the electrical output power density. Consequently, the cost of electricity from a photocell with a band gap of 0.8 eV is one third of the cost of a Si photocell. Note that at the maximum in Figure 1.2, the TPV cells deliver $4400 \text{ W}_{\text{el}}/\text{m}^2$. This is more than 20 times the power density of a solar cell with an efficiency of 20%³ under AM1.5 irradiation. Thus, the cost of photocells per unit electrical output power density is less than $1/20^{\text{th}}$ for the TPV in comparison to the solar application. A detailed study on cost of TPV is presented in chapter 5.

³ That is the maximum efficiency obtained from an idealised cell as described in the previous footnote under a 5700 K (temperature of the surface of the sun) blackbody spectrum.

Chapter 2

SiGe Growth with UHV-CVD

2.1 Introduction

The SiGe material system has become part of Si integrated circuit technology because of its wide range of applications in electronic devices, e. g. the heterojunction bipolar transistor or the quantum well infrared photodetectors. [1]

While molecular beam epitaxy (MBE) was and still is a viable tool for performing basic studies, chemical vapour deposition (CVD) has considerable advantages for device manufacturing. The single wafer design and its system complexity renders the MBE technique less favourable for mass production in comparison with suitable CVD techniques. Furthermore, CVD grown structures have frequently exhibited lower defect levels than MBE grown structures. Almost all of the structures which have been demonstrated by MBE can successfully be grown by at least one of the CVD growth techniques.

The ultra-high vacuum CVD (UHV-CVD) growth technique was first described by Meyerson in 1986 [2]. The UHV-CVD reactor is a quartz tube which is inserted into a furnace. A batch of closely spaced wafers mounted in a quartz boat can be processed at a time. Figure 2.1 shows the principle geometry of the system. The gases flow through mass flow controllers (MFC) from the left into the reactor. The pressure during growth is in the order of 0.5 Pa and needs to be kept below 0.1 – 1 mPa (10^{-9} – 10^{-8} mbar) when no gases are let in. SiH₄ and GeH₄ are used to grow SiGe and B₂H₆ (diluted in He) for *p*-type doping. The reactor and the samples are heated to around 500° C. The reactants decompose at the

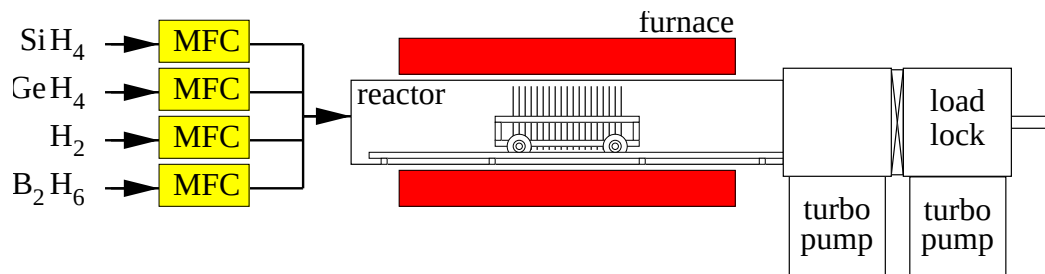


Figure 2.1: Side view of a UHV-CVD reactor. Mass flow controllers (MFC) determine the ratio of the gas mix entering the heated reactor chamber, where they decompose into the elements and Si, Ge and B gets deposited.

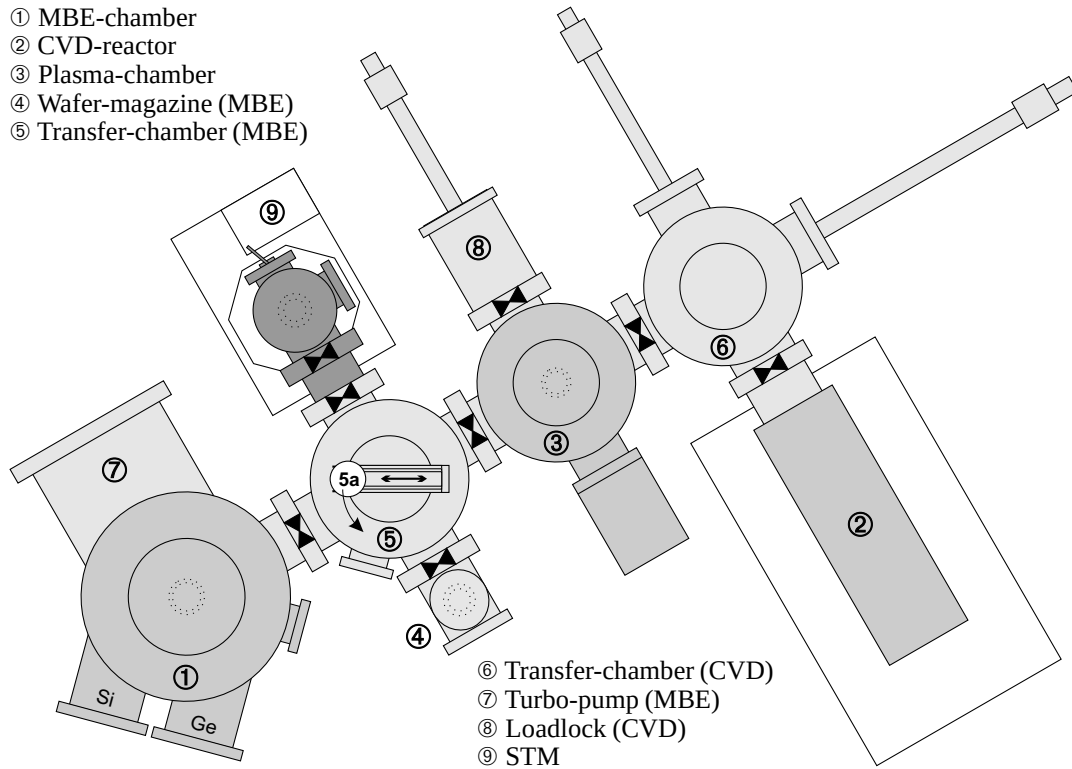


Figure 2.2: Setup of SiGe epitaxy tools: The UHV-CVD is connected via a transfer chamber and the plasma chamber to the loadlock. Samples can be in situ interchanged with an attached MBE system and analysed with a scanning tunnelling microscope (STM).

hot surfaces – especially at the samples – and Si, Ge and B is deposited. The ratio of the deposited materials depends on the gas mix let into the reactor at a given temperature and pressure. However, the growth rate of each component not only depends on the amount of its precursor, as for example Si grows about ten times faster when doped with B than undoped. Thus, calibration of this tool causes considerable effort. One of the main disadvantages of UHV-CVD growth technique is the memory effect for *n*-type dopants, i. e. the dopant persists in the reactor, so that it gets built into the deposited material, even when its precursor gas was not let into the reactor for months.

For epitaxial growth with a low level of defects, the hydrogen passivation (saturation of the dangling bonds at the surface of the sample) is an important prerequisite. It is obtained by a dip into hydrofluoric acid (HF) immediately before pushing the wafers into the load lock. The surface coverage of hydrogen decreases sharply at temperatures above 550° C. As the growth rate increases exponentially with the temperature, the window of operation is restricted to relatively small values when the low level of defects needs to be maintained.

2.2 Experimental Setup

The epitaxy tools available at the Paul Scherrer Institut are a MBE and UHV-CVD, which are connected to each other via a plasma-chamber (see Figure 2.2). Each epitaxy tool has its own loadlock and they can be operated completely independent of each other.

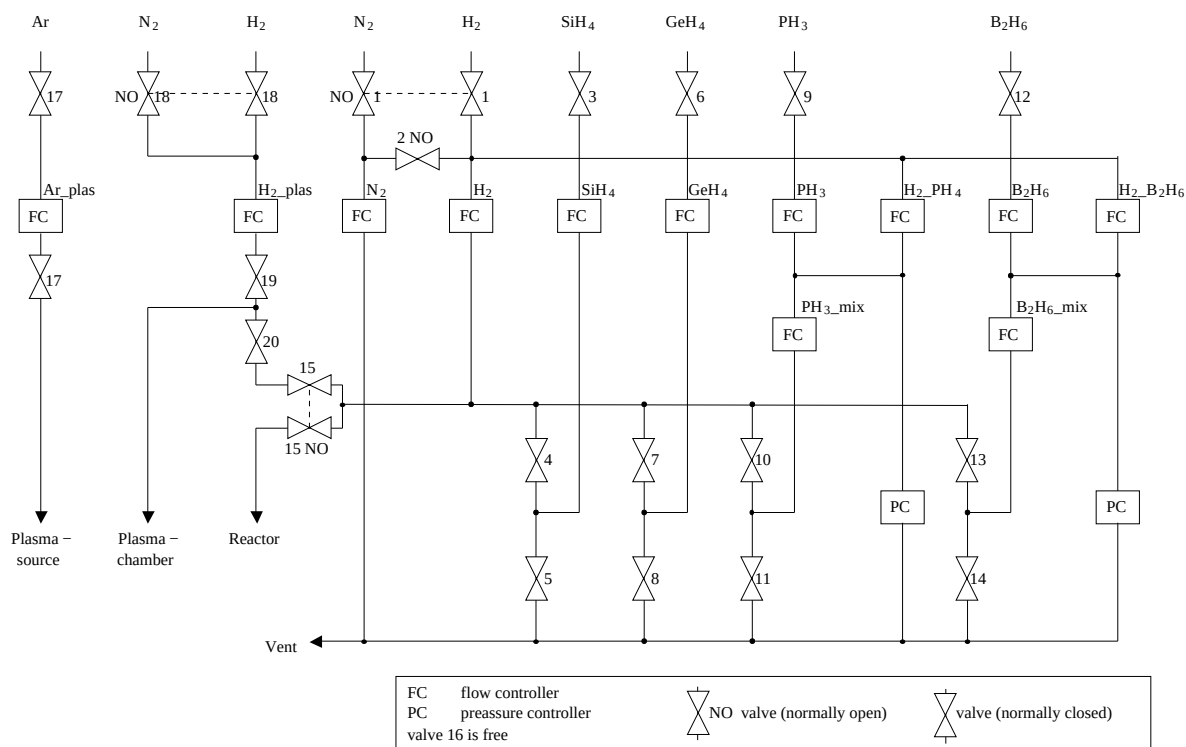


Figure 2.3: Gas system of the UHV-CVD. The different gases bypass a line valve and a mass flow controller (FC). Most of them can be switched between the vent, a tube leading to the roots pump, and the reactor, allowing abrupt interfaces between layers. Furthermore, a non-fluctuating gas flow is thereby ensured. By mixing the doping gases with hydrogen, a wide range of dilutions are achievable. The gas mixture can also be directed to the plasma-chamber. The valves and mass flow controllers are controlled by a computer programme. Its graphical user interface is shown in Figure 2.4.

The wafers are cleaned (see section 2.7), put in a quartz boat and pushed into the loadlock. As soon as the turbo pump goes to normal operation at about 3×10^{-5} Pa (3×10^{-7} mbar), the quartz boat, which resembles a wagon on rails, is brought into the reactor, bypassing the plasma- and transfer-chamber. As it takes several minutes until the wafers reach the growth temperature, a Si buffer layer is deposited for the first hour of the process, ensuring constant temperature and growth rates thereafter.

Figure 2.3 shows the gas system schematically. SiH₄, GeH₄ and B₂H₆ serve as process gases for SiGe growth and boron doping, respectively. There are two lines with B₂H₆. Both use helium as carrier gas, but B₂H₆ is differently diluted to 1000ppm and 50ppm, allowing a wide range of boron doping concentration, which is further enhanced by mixing the doping gas with hydrogen. Any doping between 10^{15} cm^{-3} and $5 \times 10^{21} \text{ cm}^{-3}$ can be achieved. Within this thesis, a computer programme in Visual Basic® was written to control the valves and flow controllers and to log their states and mass flows. A screenshot of the graphical user interface of the programme is shown in Figure 2.4.

In the following three sections, the chemical reactions, the reactant transport and the processes on the surface are discussed, leading to a kinetic model of growth.[1]

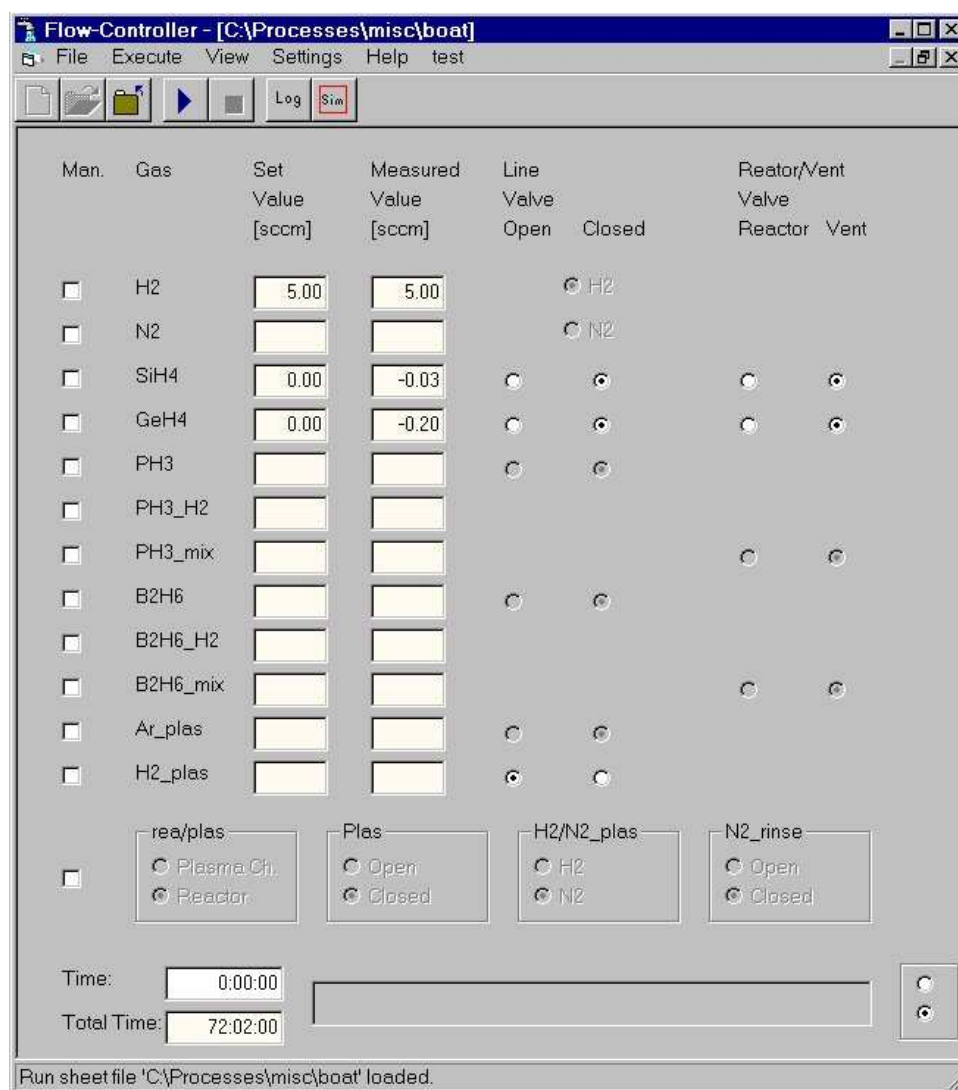


Figure 2.4: Graphical user interface of the programme controlling valves and mass flow controllers shown in Figure 2.3 and logging the data.

2.3 CVD Growth regimes

In the following, the growth regimes of CVD techniques in general is discussed. The chemical vapour deposition process can be divided into four steps:

1. gas phase reaction, e. g. $\text{SiH}_4 \rightleftharpoons \text{SiH}_2 + \text{H}_2$
2. reactant transport to the surface
3. chemical reactions on the surface and surface diffusion
4. incorporation and desorption of the reaction products from the surface

For epitaxial growth in conventional Si integrated circuit technology, dichlorosilane (SiH_2Cl_2) diluted in hydrogen is used at or near atmospheric pressure under a temperature of typically 1100°C . The gas phase reactions (step 1) always result in a large number of different species, especially SiCl_2 , which is thought to be responsible for growth. For growth temperatures around 1100°C , the transport of SiCl_2 to the surface (step 2) is limited by diffusion, which is also the limiting factor for the growth process. Due to heavy intermixing at such high temperatures, SiGe layers with an appreciable high Ge concentration cannot be obtained.

Thus, systems with much lower temperatures ($\approx 600^\circ\text{C}$) must be employed. This also limits relaxation of metastable strained SiGe epitaxial layers. At such low temperatures and even more so at a lower pressure, gas phase reactions do practically not occur. Under these conditions, the growth is limited by surface reactions (step 3) and desorption processes (step 4), which have large thermal activation energies.

2.4 Gas Phase Reactions

Growth of Si is usually dominated by a highly reactive species. When using SiH_4 , the reaction $\text{SiH}_4 \rightleftharpoons \text{SiH}_2 + \text{H}_2$ produces silene (SiH_2) at a rate constant k_{uni} , which is thermally activated and proportional to the pressure. However, at 600°C and 0.1 Pa , the conversion from silane to silene is negligible [2]. This suppression of silene is important for UHV-CVD batch reactors because the highly reactive gas has a sticking coefficient of almost unity, leading to a depletion of SiH_2 and a higher growth rate at the edge in comparison to the centre of the wafers that are separated by only a few mm.

At higher temperatures and pressures, additional gas phase reactions may also occur. Higher silanes are formed by reactions of silane with silene, e. g. $\text{SiH}_4 + \text{SiH}_2 \rightleftharpoons \text{SiH}_6$. Figure 2.5 shows a mass spectrum of the gas composition in the reactor at 520°C with a SiH_4 flow of 10 sccm . The mass spectrometer ionises the molecules by electron bombardement. As ionized molecules are much less stable than non-ionised ones, they form numerous Si-H compounds, like atomic Si and Si with 1-6 hydrogen atoms, as well as Si_2H_x compounds. Double-ionised molecules, labelled with SiH_x^{++} in Figure 2.5, show up at half their mass. The water in the reactor causes an ion current, which is 4 orders of magnitude lower than the SiH_x peaks.

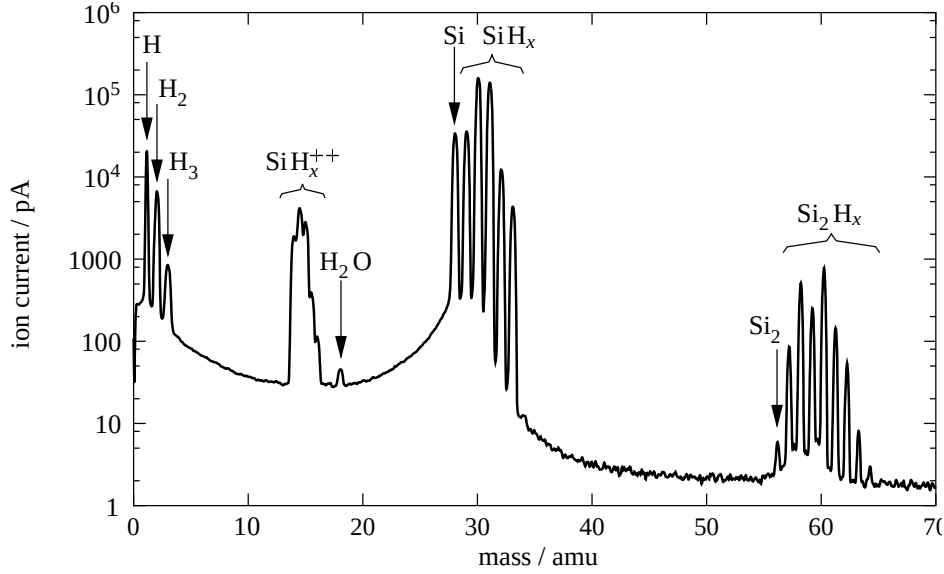


Figure 2.5: Mass spectrometer measurement of reactor chamber with Si H₄ flow.

2.5 Reactant Transport

There are three different regimes of flow: The viscous laminar flow at high pressures, molecular flow at low pressures and the Knudsen flow at intermediate pressures. The actual value of the pressure depends on the characteristic length of the system L , i. e. approximately the diameter of the reactor, and the molecular mean free path λ . λ is inversely proportional to the pressure and the square of the diameter of the molecule, the gas consists of.

The gas flow is considered to be viscous laminar when $\lambda < L/100$, or in terms of pressure p ,

$$p > \frac{0.6 \text{ Pa} \cdot \text{m}}{L} = \frac{0.6 \text{ mbar} \cdot \text{cm}}{L} \quad (2.1)$$

Viscous laminar flow is characterised by the presence of a uniform flow direction of the molecules. A stagnant boundary layer is formed at objects that are obstacles such as the boat or wafers. The reactant must diffuse through this layer to reach the surface of the sample.

The flow is considered molecular, when scattering of the molecules takes place rather at walls of the reactor than among molecules themselves, i. e. $\lambda > L/2$ and in terms of pressure:

$$p < \frac{0.013 \text{ Pa} \cdot \text{m}}{L} = \frac{0.013 \text{ mbar} \cdot \text{cm}}{L} \quad (2.2)$$

It is characterised by no presence of a uniform flow direction of the molecules. In the molecular flow regime, the flux density of reactant ϕ [molecules $\text{m}^{-2} \text{s}^{-1}$] is

$$\phi = 2.67 \cdot 10^{24} \cdot \frac{p [\text{Pa}]}{\sqrt{MT}}, \quad (2.3)$$

where M is the molar mass and T is the absolute temperature.

The intermediate Knudsen flow regime is the one prevalent in the UHV-CVD setup shown in Figure 2.2. Following (2.1) and (2.2), it is defined in terms of free mean path $L/100 < \lambda < L/2$ and in terms of pressure:

$$\frac{0.013 \text{ Pa}\cdot\text{m}}{L} < p < \frac{0.6 \text{ Pa}\cdot\text{m}}{L}. \quad (2.4)$$

The flux density of reactant to the sample given in (2.3) can be considered the upper limit in the Knudsen flow regime.

2.6 Surface Processes during Transport

In this section, the pure and hydrogen terminated Si (1 0 0) surface as well as the surface processes are discussed and the basic parameters determining the growth rate is presented. The hydrogen terminated surface facilitates CVD growth at moderate temperatures and low pressures with reasonable technical means and is achieved by dipping the Si wafers into diluted hydrofluoric acid. For UHV-CVD growth, the surface chemical processes are rate-limiting. Thus, the decomposition of SiH_4 and the desorption of the reaction products is reviewed.

2.6.1 Pure Si (1 0 0) Surface

Unreconstructed surfaces can be thought of atoms that retain the bonds towards bulk as if they were bulk atoms and replace the bonds pointing away from the bulk by dangling bonds, but keeping the bonding direction. In the case of a Si or Ge (1 0 0) surface, each atom of an unreconstructed surface is bonded to two atoms beneath the surface layer and two dangling bonds pointing upwards. This structure is energetically less favourable than some reconstruction of the surface. Si and Ge have extensively been studied with low energy electron diffraction (LEED), reflection high energy electron diffraction (RHEED) and scanning tunnelling microscopy (STM). In the lowest energy state, two adjacent (1 0 0) surface atoms are bond to each other, forming a dimer and leaving only one dangling bond per surface atom. The dimers arrange in rows along the $\langle 1\ 1\ 0 \rangle$ direction. Surface structures are labelled by expressing the periodicity of the surface in terms of periodicity of the atoms forming the surface. Thus, a (1 0 0) surface in the lowest energy state is known as a 2×1 (1 0 0) surface structure.

Due to the inevitability of some misalignment of the wafer cut, the real (1 0 0) surface must exhibit steps and terraces. Si wafers with misalignments below 2.5° that are prepared by thermal cleaning at temperatures of approximately 1000°C have surfaces with single-layer steps [3]. There are two different types of steps which are distinguished by the two different ways the dimers can be aligned relative to the step edge resulting in two different energies per unit length of the step edge for each type, respectively. These steps do, however, have no great influence on the number of dangling bonds available for chemical reactions in comparison with terrace atoms.

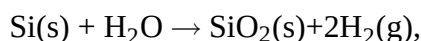
2.6.2 Hydrogen Passivated Surface

A clean Si surface reacts instantly with oxygen when exposed to air at atmospheric pressure, forming a native oxide of a thickness in the order of 1 nm. Such large concentrations of interfacial oxygen prevents the growth of epitaxial layers while smaller concentrations can generate defects associated with micro-twin aggregates [4]. A hydrogen passivated surface can be exposed to room ambient for many minutes without significant oxidation. There are three common technologies to achieve hydrogen passivation: Thermal cleaning in UHV at around 800°C, plasma cleaning and wet chemical treatment with hydrofluoric acid (HF). Only the latter was used and will be discussed in the following.

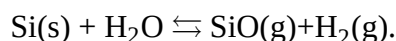
The passivation is obtained by termination of the dangling bonds with hydrogen. The HF-treated (1 0 0) surface is similar to a surfaces exposed to atomic hydrogen, which adsorbs 1.9 monolayers of hydrogen when saturated at 210 K [5]. Hydrogen passivated (1 0 0) surfaces have a 1×1 structure. While surfaces exposed to atomic hydrogen contain only monohydride and dihydride, HF-treated surfaces contain additionally a trihydride species [6].

The purity of the reactants is usually the determining factor for residual contaminations of the hydrogen terminated surface. An HF concentration of about 5% in water has been found to be optimal [7, 8]. Higher concentrations have higher fluorine concentrations and surfaces with higher fluorine concentrations are more readily oxidised in water. Furthermore, under usual wet chemical cleanroom laboratory conditions, the purity of de-ionised water is usually much higher than the purity of HF. Both, carbon and oxygen concentration increase with HF-concentrations lower or higher than 5%. Carefully prepared surfaces have oxygen and carbon coverages of a few percent of a monolayer, i. e. a concentration in the low 10^{13} cm^{-2} range [7, 8, 9].

The influence of water on the oxidation depends on the partial pressure and the temperature. At a growth temperature used for the samples preparation in this work of 520°C, water is oxidising for a partial pressure of water $> 2 \times 10^{-7} \text{ Pa}$ ($2 \times 10^{-9} \text{ mbar}$), following the reaction



while water is etching for a partial pressure of water $< 2 \times 10^{-7} \text{ Pa}$ ($2 \times 10^{-9} \text{ mbar}$), following the reaction



The value of the partial pressure of water is taken from an extrapolation [10, 11] depicted in Figure 2.6, showing the border line between Si oxidation and Si etching in a graph where the partial pressure of water is plotted against the inverse temperature.

2.6.3 Surface Reactions of SiH₄ and GeH₄ and Kinetic Models of Growth

In this section we discuss the surface reactions that determine the growth rate for conditions prevalent in UHV-CVD, i. e. a substrate temperature between 400 and 600°C and a pressure below 10 Pa. The reactions of SiH₄ on a Si (1 0 0)- 2×1 reconstructed hydrogen passivated surface can be modelled by series of interactions between unpassivated dangling bonds,

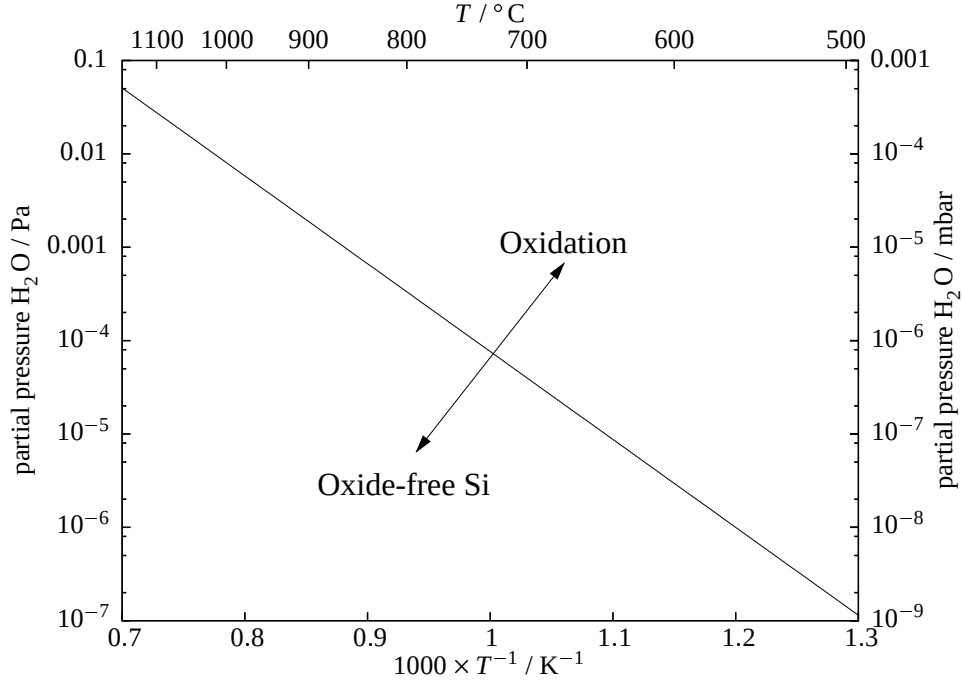
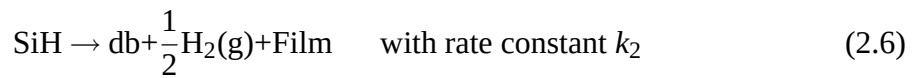


Figure 2.6: Extrapolation of formation of SiO_2 versus Si etching by SiO evaporation in equilibrium. The for an oxide-free Si surface necessary partial pressure of water depends linearly on the inverse temperature $1/T$. [10, 11]

SiH_4 and its decomposition products. Although these processes also generate unoccupied dangling bonds, the net effect is that two unoccupied dangling bonds are utilised while only one is generated, which must be compensated by hydrogen desorption.

A microscopic model [12, 13, 14, 15, 16, 17] of epitaxial growth with SiH_4 describes the deposition in several steps: Adsorption of SiH_4 , decomposition into SiH_3 , SiH_2 and SiH and desorption of hydrogen. For UHV-CVD growth, the decomposition is so fast that a simplified model consisting only of two steps can be applied:



Both reactions have rate constants of the Arrhenius form, i. e. $k_i = A_i \cdot \exp(-E_i/k_B T)$, where A_i is a proportional factor and E_i is the activation energy.

The coverage of unoccupied dangling bonds Θ_{db} approaches 0 for temperatures below 400°C and 1 ML above 700°C . Under steady state conditions, the Si growth rate is proportional to the adsorption rate of SiH_4 k_1 , the SiH_4 flux F_{SiH_4} and the square of the number of unoccupied dangling bonds Θ_{db} [17]:

$$R_{\text{Si}} = k_1 F_{\text{SiH}_4} \Theta_{\text{db}}^2 \quad (2.7)$$

Because of the chemical similarity of GeH_4 and SiH_4 , the reactions of GeH_4 with a Si Ge surface are qualitatively the same as for SiH_4 on a Si surface. The relevant differences are the adsorption rate and the strength of the hydrogen bonds.

For temperatures around 500° C, the Si to Ge fraction in the gas phase is about 3 orders of magnitude higher than in the film. This leads to the conclusion, that the adsorption rate of Ge H₄ is three times the adsorption rate of Si H₄. As the Ge-H bond is weaker than the Si-H bond, the hydrogen desorption rate increases with an increasing Ge content in the surface, increasing the number of dangling bonds and leading to an increase in growth rate (see (2.7)).

2.6.4 Summary

A clean Si surface in its lowest energy state is characterised by one dangling bond per surface atom and the formation of dimers, i. e. a bond between two neighbouring surface atoms. To prevent the surface from oxidation, the dangling bonds are passivated with hydrogen by dipping the Si wafers into 5% hydrofluoric acid prior to the process, permitting to expose the wafer to atmospheric conditions for several minutes. Under growth conditions at temperatures around 520° C, the hydrogen passivation is still preserved. Thus, the partial pressure of water can be considerably higher than for surfaces without hydrogen passivation.

The growth rate of Si from Si H₄ is limited by surface chemical processes. Two dangling bonds are necessary to adsorb a Si H₄ molecule. Once adsorbed, it can desorb two hydrogen molecules and incorporate the Si atom into the crystal. Thus, the growth rate depends on the dangling bond coverage, which depends on the temperature. The second growth rate determining factor is the Si H₄ decomposition, which depends exponentially on the temperature. The third factor is the Si H₄ flux. A SiGe alloy can be deposited by mixing Si H₄ with Ge H₄. Due to the weaker bond with hydrogen for Ge in comparison to Si, the dangling bond coverage increases, leading to an increasing growth rate.

2.7 Surface Preparation

In the previous section, the importance of obtaining a hydrogen passivated surface was emphasised. In this section, the actual procedure is described. The details, temperature of the etches and time of exposure, are parameters obtained by experience within the laboratory at the Paul Scherrer Institut.

Prior to the dip in HF, a cleaning step in Caros-, also known as Pirhania-, etch is performed. Caros etch is a 2:1 mixture of sulfuric acid (H₂SO₄) and hydrogen peroxide (H₂O₂). It removes organic substances from the Si wafers and forms an oxid of about 10nm thickness at the Si surface. A subsequent dip in HF removes the oxid and passivates the surface with hydrogen. The HF bath was prepared by a 1:10 mixture of 50% HF with water. While the HF bath was always mixed immediately before the cleaning of the wafers, the Caros etch was reused several times and changed about once a week.

The following cleaning procedure was used for all Si wafes processed with UHV-CVD:

1. 8 minutes Caros etch at 90° C
2. Put into quickdump rinser
3. 1 minute HF dip at ambient temperature

4. Put into quickdump rinser
5. 8 minutes Caros etch at 90° C
6. Put into quickdump rinser
7. 1 minute HF dip at ambient temperature
8. Push into reactor as soon as possible

The crucial step is the HF dip. The wafers must be pulled out of the bath with constant speed and they have to be completely dry.

2.8 Structural Analysis

2.8.1 Transmission Electron Microscopy (TEM)

TEM images are a viable tool to obtain information about local sample characteristics as morphology and to some extent crystallinity and composition. For high resolution imaging elastic scattering of an electron beam of typically 200-300 keV is assumed. The specimen has to be very thin (for light elements up to a maximum of about 100 - 150 monolayers) so that elastic scattering dominates the image formation. The resulting interference pattern reflects the periodicity of the crystal lattice. If the distance between the individual crystal planes is large enough, i.e. larger than the point-to-point resolution of the microscope, this interference pattern can be interpreted as rows of atoms or molecules for certain imaging conditions. In order to decide whether bright or dark dots of a TEM image correspond to atomic positions, simulations for the respective imaging conditions are usually necessary.

Additional to the contrast caused by interference of elastically scattered electrons, which shows the periodicity of the lattice, these images contain chemical information. The heavier an atom is, the larger is the angle under which an electron of the incident beam is scattered. Regions containing heavier atoms, therefore, contribute more to higher-order Bragg reflections than lighter atoms. An aperture, which is usually positioned at the diffraction plane of the TEM in order to minimise the effects of lens aberrations, further enhances the image contrast: As such an aperture cuts out higher order reflections in reciprocal space, the intensity from areas containing heavier atoms is selectively reduced. Consequently these areas appear darker. In the case of the SiGe system, areas which contain more Si appear brighter than those containing more Ge.

The thicknesses of the wells were determined in 2 ways: With X-ray diffractometry (see section 2.8.2) and by measuring the dark regions of the TEM images with a ruler. Alternatively, the layer thickness can be derived from a high resolution TEM picture by counting the number of atomic layers in the SiGe structure and the well known lattice constant. However, the main error enters with the decision where the interface between Si and SiGe lies. As the measurement with a ruler is much faster than a layer count, it results in a better statistics and a smaller error bar. For thin wells, the layer thicknesses derived from the TEM picture are significantly greater than those derived from X-ray diffractometry. This might be caused by the gradient of the Ge concentration across the interface. Already a very

Table 2.1: Comparison of the width of the Si spacers w_{Si} and SiGe wells w_{SiGe} obtained with TEM and X-ray diffractometry (XRD). The latter delivers also the Ge concentration x . n is the number of SiGe layers in the sample. See text for discussion of the error bars.

sample	n	$w_{Si,TEM}$ nm	$w_{Si,XRD}$ nm	$w_{SiGe,TEM}$ nm	$w_{SiGe,XRD}$ nm	x
17	30	18.7 ± 0.2	19.6	3.3 ± 0.2	2.3 ± 0.2	0.30 ± 0.02
46	10	14.1 ± 0.4	14.3	3.0 ± 0.4	$1.7 -0.7+1.3$	0.40 ± 0.08
47	10	13.7 ± 0.5	14.8	1.9 ± 0.5	$1.2 -0.5+0.9$	0.45 ± 0.08
25	40	2.0 ± 0.3	3.0	2.5 ± 0.3	1.5	0.45 ± 0.02
24	20	4.1 ± 0.6	4.8	3.4 ± 0.6	2.7	0.45 ± 0.08
22	10	10.6 ± 0.9	6.5	5.3 ± 0.9	4.0	0.45 ± 0.10

small Ge concentration might be sufficient to mark the interface between Si and SiGe layer on a TEM picture, leading to an increase in SiGe layer thickness. The determination of the thickness by both methods, TEM and X-ray diffractometry, are summarised in Table 2.1.

All but one samples presented here are manufactured with UHV-CVD at a growth temperature of 520°C and total pressure of 0.5 Pa ($5 \times 10^{-3}\text{ mbar}$). The growth is initiated with an about 5 nm thick Si buffer layer deposited for one hour, making sure that the wafers reach their final temperature, leading to predictable growth rates. The MBE grown sample is produced with Sb surfactant at 700°C (see section 4.1.1 for more details on the deposition technology employed).

In the following, the TEM pictures of the samples that are used in this thesis are discussed. They are ordered by proximity to the critical layer thickness¹:

Figure Figure 2.7 shows the TEM picture of a stack of $3.3 \pm 0.2\text{ nm}$ thick $\text{Si}_{0.7}\text{Ge}_{0.3}$ layers between $18.7 \pm 0.2\text{ nm}$ thick Si spacers. The interfaces between Si and SiGe layers are very smooth, except for the first one towards the substrate, which might be influenced by impurities at the surface prior to the growth. These impurities are clearly visible about 5 nm below the first SiGe layer. The X-ray diffractometer measurement of the same sample is shown in Figure 2.15.

The sample shown in Figure 2.8 has a higher Ge concentration, but much thinner wells. It has 10 periods with SiGe and Si layers that measure $3.0 \pm 0.4\text{ nm}$ and $14.1 \pm 0.4\text{ nm}$ on the TEM picture, respectively. The X-ray diffractometer measurement is shown in Figure 2.19 yields a Ge concentration of 40% in the wells. The X-ray diffractometer measurement of this sample is shown in Figure 2.19.

Sample 47 is made up of wells with a slightly higher Ge concentration, but very thin wells. Its TEM picture is shown in Figure 2.9 and the wells and spacers are $1.9 \pm 0.5\text{ nm}$ and $13.7 \pm 0.5\text{ nm}$ wide, respectively. The interfaces between Si and SiGe layers are still perfectly flat, as in the samples discussed above. The interface between substrate and Si buffer layer is more expressed then in Figure 2.8, but does not disturb consecutively deposited layers. The X-ray diffractometer measurement of the same sample is shown in Figure 2.20.

¹ The critical layer thickness is the thickness of SiGe that can maximally be epitaxially deposited on Si. It strongly depends on the Ge concentration, but also on the deposition method.

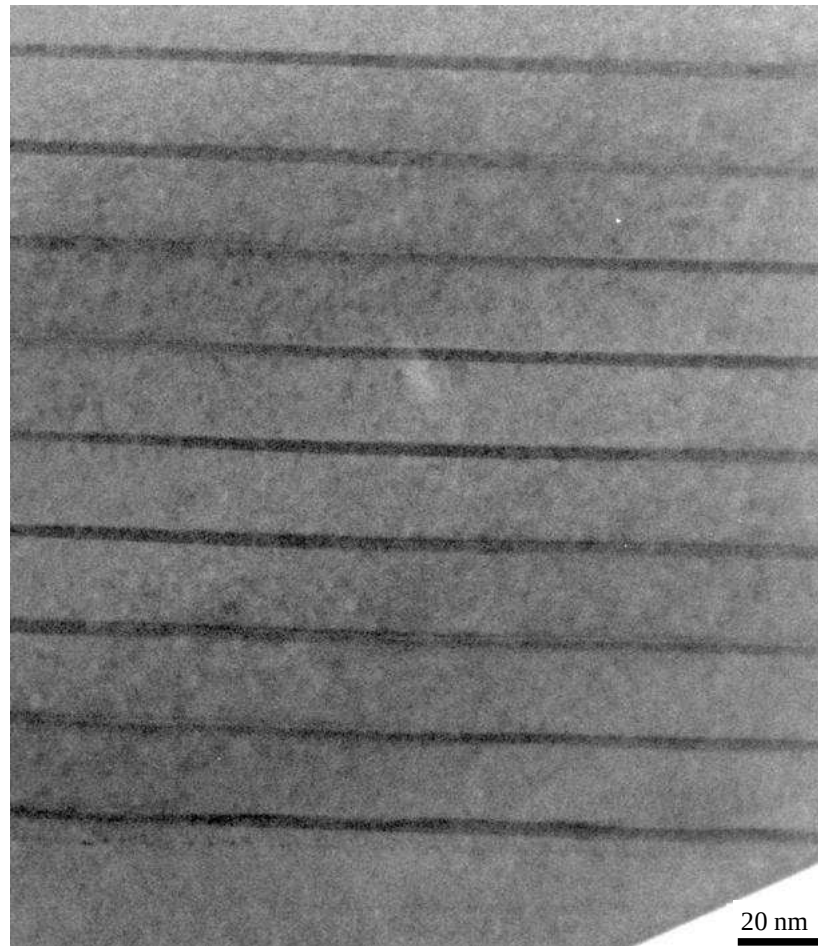


Figure 2.7: TEM micrograph of sample 17, with SiGe layers of 3.3 ± 0.2 nm thickness embedded between 18.7 ± 0.2 nm wide Si layers. From the X-ray diffractometer measurement shown in Figure 2.16 a Ge concentration x of 30% is obtained.

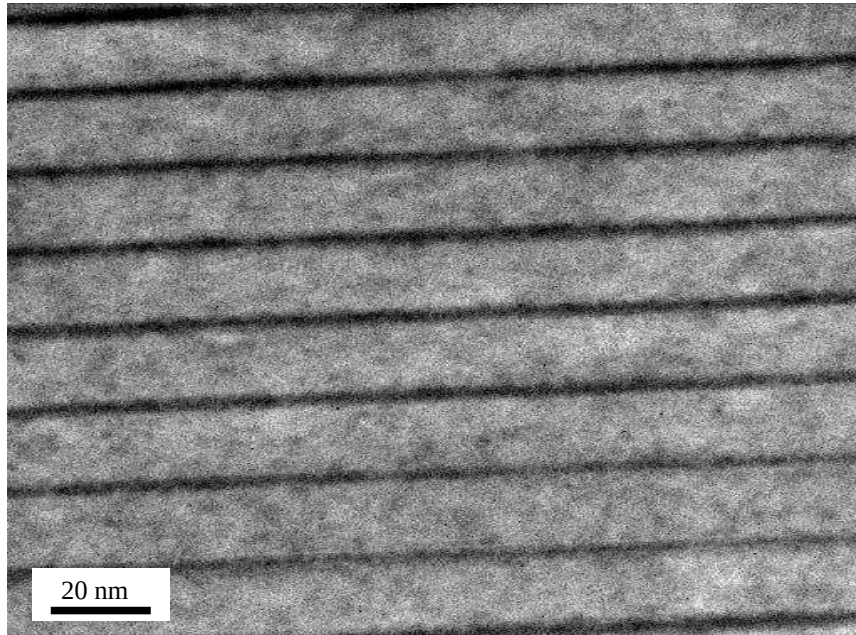


Figure 2.8: TEM micrograph of sample 46, with SiGe layers of 3.0 ± 0.4 nm thickness embedded between 14.1 ± 0.4 nm wide Si layers. From the X-ray diffractometer measurement shown in Figure 2.16 a Ge concentration x of 40% is obtained.

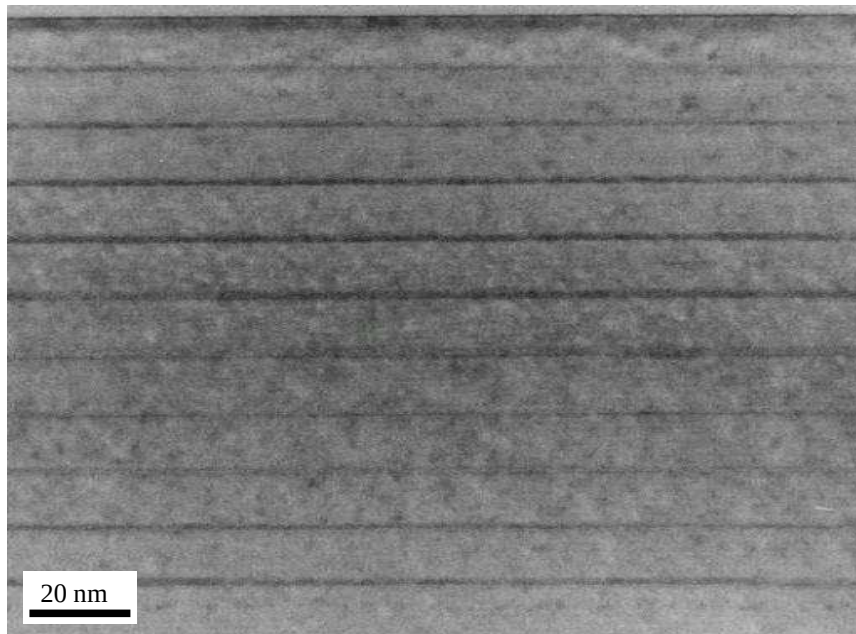


Figure 2.9: TEM micrograph of sample 47, with SiGe layers of 1.9 ± 0.5 nm thickness embedded between 13.7 ± 0.5 nm wide Si layers. From the X-ray diffractometer measurement shown in Figure 2.20 a Ge concentration x of 45% is obtained.

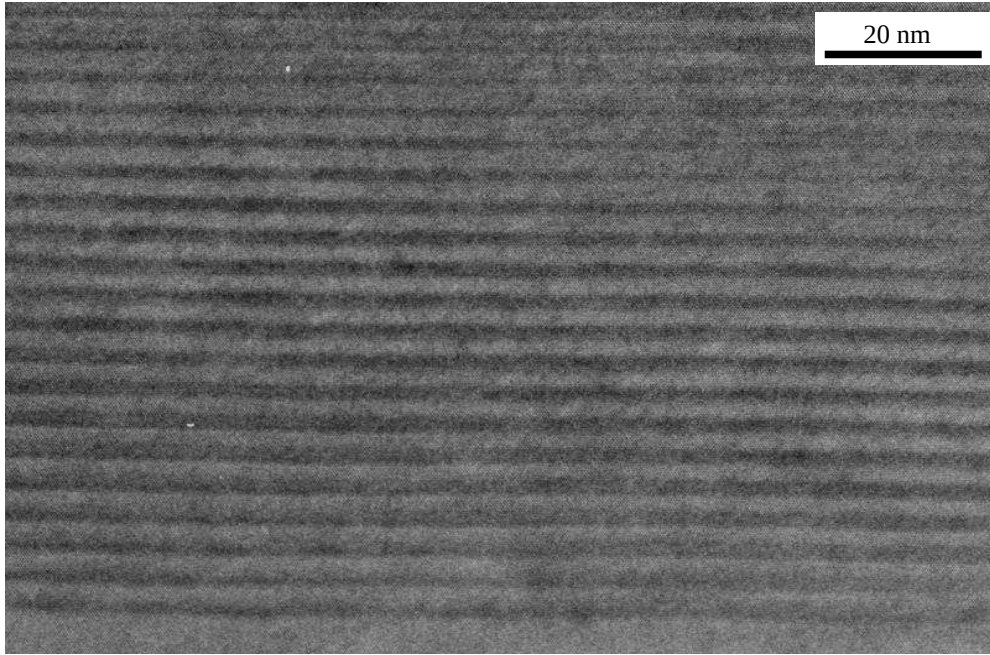


Figure 2.10: TEM micrograph of sample 25, with SiGe layers of 2.5 ± 0.3 nm thickness embedded between 2.0 ± 0.3 nm wide Si layers. From the X-ray diffractometer measurement shown in Figure 2.18 a Ge concentration x of 45 % is obtained.

With increasing thickness of the SiGe layers, the interface roughness also increases, which is clearly visible in Figure 2.10, showing sample 25. With a SiGe layer thickness of 2.5 ± 0.3 nm and a Si layer thickness of 2.0 ± 0.3 nm, the strain is not sufficient for the formation of islands. From the X-ray diffractometer measurement shown in Figure 2.18, the same Ge concentration of 45 % as the previous sample is determined.

When increasing the Ge layer thickness further, as in sample 24, SiGe islands form, reducing the average strain in the layer [18]. Figure 2.11 shows a TEM picture of this sample, where the thickness of the SiGe layers varies laterally, resulting in self organised thicker regions between thinner regions, forming SiGe island structures. While the Ge concentration of this sample of 45 % is still the same as that of the previous one, the SiGe and Si thicknesses increased to 3.4 ± 0.6 nm and 4.1 ± 0.6 nm, respectively. The corresponding X-ray diffractometer measurement is shown in Figure 2.17.

The island formation is more pronounced in sample 22, shown in Figure 2.12. The strain propagates through the Si spacers and induces the formation of an island in the consecutively grown SiGe layer, so that the islands in the higher layers grow approximately above the islands of the first layer [19]. The SiGe layer thickness is with 5.3 ± 0.9 nm is significantly greater than in the previous sample and the Ge concentration is 45 %, the same as in the last two samples. Note that the measurement accuracy for the Ge concentration obtained by X-ray diffractometry given in Table 2.1 for some samples is rather poor, which is discussed in the next section. The X-ray diffractometer measurement of sample 22 is shown in Figure 2.16.

The TEM picture of the MBE grown sample is shown in Figure 2.13. Due to the growth conditions (see section 4.1.1), the area density of the islands is significantly higher than

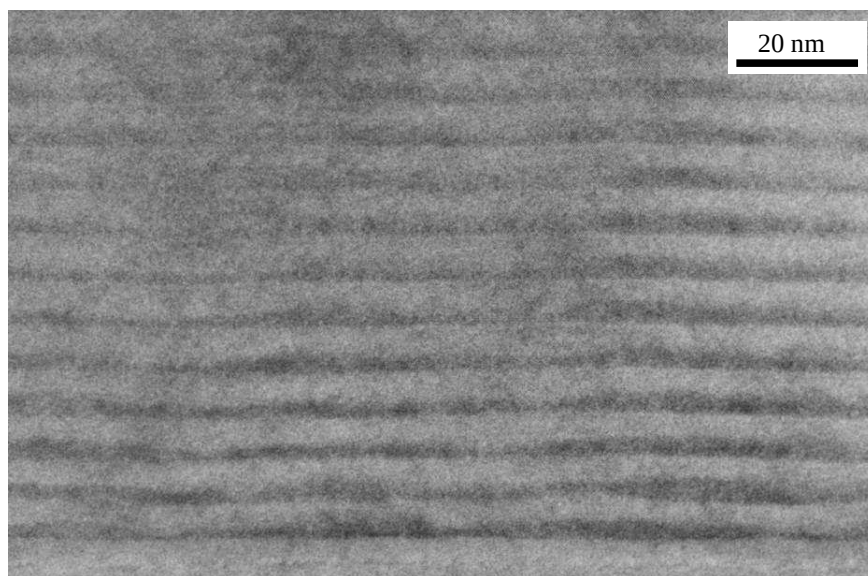


Figure 2.11: TEM micrograph of sample 24, with SiGe layers of 3.4 ± 0.6 nm thickness embedded between 4.1 ± 0.6 nm wide Si layers. From the X-ray diffractometer measurement shown in Figure 2.17 a Ge concentration x of 45% is obtained.

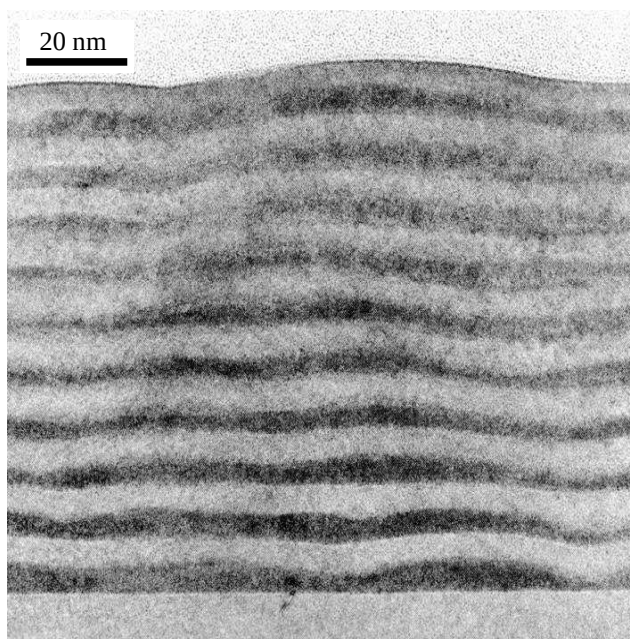


Figure 2.12: TEM micrograph of sample 22, with SiGe layers of 5.3 ± 0.9 nm thickness embedded between 10.6 ± 0.9 nm wide Si layers. From the X-ray diffractometer measurement shown in Figure 2.16 a Ge concentration x of 45% is obtained.

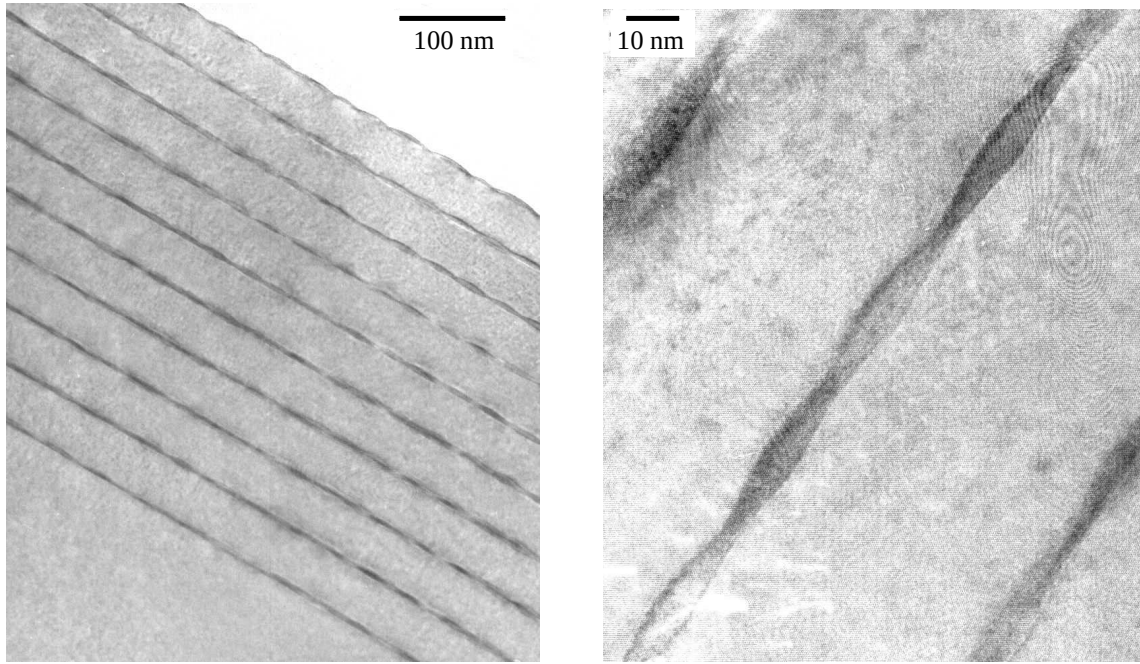


Figure 2.13: 2 magnifications of a TEM micrograph of 10 periods with Ge islands embedded in 40 nm Si spacers grown with Sb surfactant by MBE at 700° C. [20, 21]

in the last two samples. Due to the high Ge concentration (pure Ge was deposited, which intermixes with the surrounding Si during growth), the high interface roughness and the small thickness of the SiGe layers, a useful interpretation of the X-ray diffractometer measurement was not possible with the simple model used for this thesis.

2.8.2 X-Ray Diffractometry

X-rays are diffracted by a crystal in directions where the reciprocal lattice touches the Ewald Sphere. The investigated structures are superlattices of alternating layers of SiGe and Si as depicted in Figure 2.14. The X-ray source is Cu K_α radiation with a wavelength of 0.15406 nm (i. e. a photon energy of 8.0479 keV), which is monochromated with 4 Ge crystals. The X-rays hit the samples under an incident angle ω and is detected at an angle 2θ by a scintillator counter. As for some cases the number of counts per measurement point n is in the order of a few counts and the statistical deviation of a count rate $\Delta n = \sqrt{n}$ is very high in these cases, neighbouring measurement points with less than about 100 counts are averaged over, leading to a statistical standard deviation of around 10% and a much higher signal to noise ratio. A Seifert XRD 3003 PTS-HR X-ray diffractometer was used for the measurement. It allows to rotate of the sample around all three axes and move it in all three spacial directions. The accompanying software permits to do measurements automatically and provides a means to fit parameters of a model to the data. The sample has to be set up into the position (three angles and three spacial coordinates), where the (004) substrate peak is reflected with maximum intensity, theoretically at $\omega=34.56428^\circ$. Relative to this position, $2\theta:\omega$ can be changed in the ratio 2:1 to obtain a rocking curve. In this section the rocking curves of the samples presented in this thesis are discussed, resulting in the

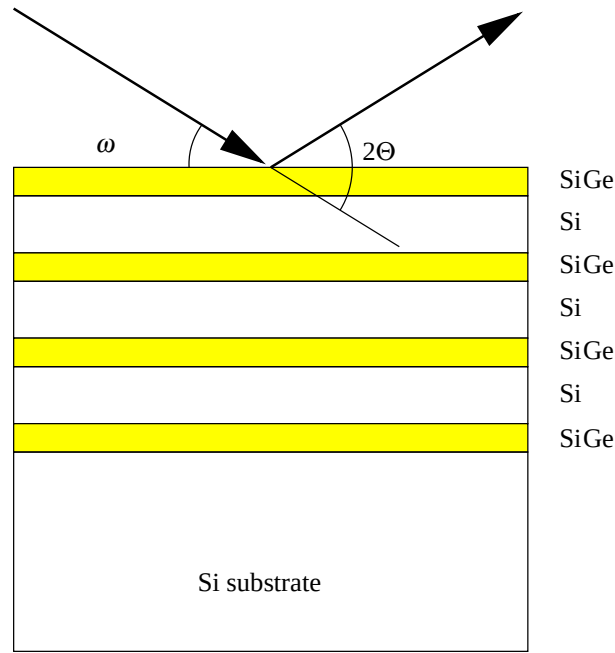


Figure 2.14: X-rays impinging under a glancing angle ω on the sample with a stack of Si and SiGe layers on Si substrate. The diffraction occurs under the angle 2θ .

thickness and Ge concentration of the layers. For some samples, two fits are presented in order to give an estimate of the error bar.

Figure 2.15 shows the rocking curve of sample 17 with a stack of 30 periods of 3.3 nm thick $\text{Si}_{0.7}\text{Ge}_{0.3}$ and 19 nm thick Si. The dots are the measurement points and the solid lines are fits. The rocking curve shows the following features:

- A substrate peak from the Si substrate at $\omega=0^\circ$
- A peak at $\omega=-0.1^\circ$ caused by the addition of Bragg reflections from the Si and SiGe components of the stack. This is the zero-order or average mismatch peak, which is determined by the average composition of the stack.
- A set of subsidiary satellite peaks symmetrically surrounding the zero-order peak, with spacing determined by the periodicity of the layers.

The fit software minimises the root mean squares of the deviations between measured and calculated values χ^2 . The substrate peak has the main impact on χ^2 . Its height and width is determined by the intensity of the X-ray source and the curvature of the sample, respectively, which have to be adjusted manually. The region between the peaks can be adjusted by diffuse scattering parameters. The average mismatch peak and its satellites carry the structural information and is determined by:

1. The spatial period of the structure
2. The thickness of the SiGe layers

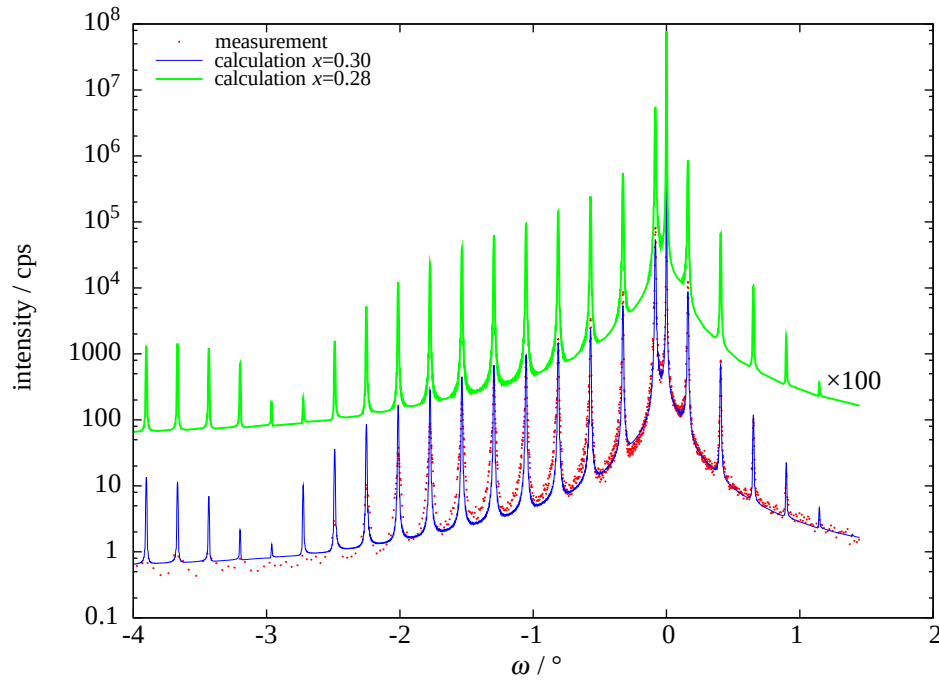


Figure 2.15: X-ray diffraction results of sample 17. The ordinate shows the glancing angle ω relative to the Si substrate peak. The symbols are the measurements and the solid lines are the simulations with a Ge concentration x of 28% ($\times 100$, thick line) and 30% (thin line). With increasing Ge concentration, the satellite peak with minimum intensity, here at $\omega = -3^\circ$, occurs further away from the substrate peak. The thick line fits the minimum Ge concentration, because at a lower concentration the satellite peak at $\omega = -2.5^\circ$ would become too weak to fit the measurement. The sample has 30 periods and its TEM picture is shown in Figure 2.7.

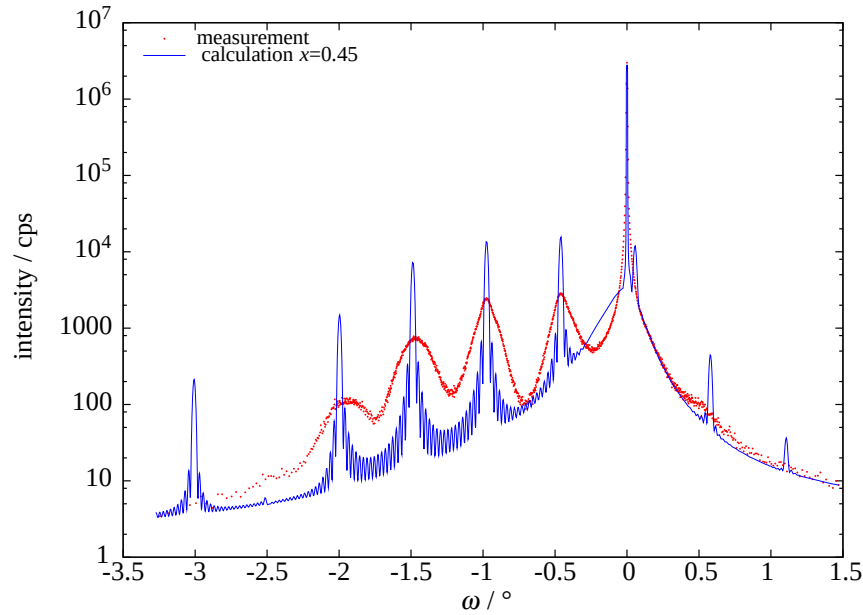


Figure 2.16: X-ray diffraction results of sample 22. The ordinate shows the glancing angle ω relative to the Si substate peak. The symbols are the measurements and the solid lines is the simulation with a Ge concentration x of 45%. As the measurement does not reveal the satellite peak with minimum intensity, x cannot be determined very accurately. The very broad satellite peaks indicate a rough surface, which is confirmed by the TEM picture shown in Figure 2.12. The sample has 10 periods.

3. The Ge concentration of the SiGe layers
4. The dispersion in the repeating period
5. The interface roughness
6. The interface grading

The spatial period of the structure depends on the position of the satellite peaks and can easily and with high accuracy be obtained from a fit. The interface roughness and grading and the dispersion in the repeating period influences the width of the satellite peaks and their decay towards higher orders. Sample 22 shown in Figure 2.16 has very broad peaks, indicating a rough interface or a high dispersion of the repeating period.

The fit also yields the average Ge concentration of the stack, but minimising χ^2 often gives wrong results for the width and composition of the SiGe layers. A correct result can be achieved, when a higher order satellite peak has a smaller intensity than lower order satellite peak, as can be seen in Figure 2.15 at $\omega = -3^\circ$, where 2 different fits can be compared with the measurement. The thick line models 28% Ge concentration and the thin line 30%. Both have very weak satellite peaks at $\omega = -3^\circ$ and changing the Ge concentration in the model moves these minima to another position. Thus, the accuracy of the Ge concentration can be estimated to $\pm 2\%$.

It is much less accurate to determine the Ge concentration of the SiGe layers from X-ray diffractometry measurements which do not exhibit a lower order satellite peak that

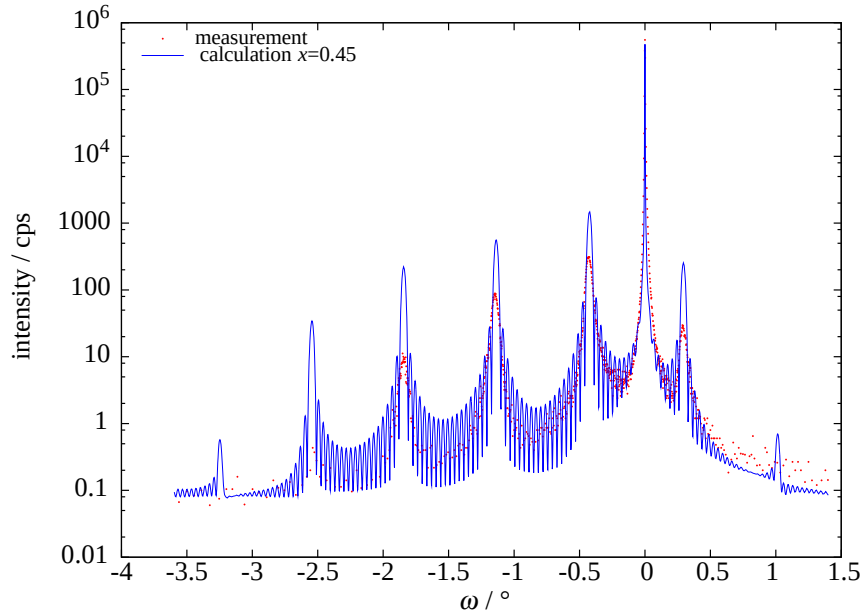


Figure 2.17: X-ray diffraction results of sample 24. The ordinate shows the glancing angle ω relative to the Si substate peak. The symbols are the measurements and the solid lines is the simulation with a Ge concentration x of 45%. As the measurement does not reveal the satellite peak with minimum intensity, x cannot be determined very accurately. The sample has 20 periods and its TEM picture is shown in Figure 2.11.

is less intense than the higher order satellite peak. Examples for this situation are shown in Figure 2.16, 2.17, 2.19 and 2.20. All these samples have thin SiGe layers with a high Ge concentration, which causes the satellite peak with minimum intensity to occur further away from the substrate peak, where the higher order peaks vanish below noise level. Additionally, the high Ge concentration causes a high strain and limits the layer thickness to low values, decreasing the intensity of the satellite peaks even further. This can be compensated with a higher number of periods, as in sample 25, which has 40 periods. Its X-ray diffractometry measurement is shown in 2.18. The fourth order peak at $\omega = -5^\circ$ has a significantly lower intensity than the fifth order peak at $\omega = -6.2^\circ$, which is well reproduced by the fit. The narrow peaks and the fact that a peak more than 6° away from the substrate peak is still visible, indicates a narrow dispersion of the period and a crystallinity of high quality. The X-ray measurement time of 24 hours for this sample shows in a lower noise level in comparison to the other samples.

In cases where the X-ray diffractometer measurement alone cannot deliver reliable results for both, well thickness and Ge concentration, a consistent result can often be obtained by using the well thickness obtained from the TEM as a fixed property and get the Ge concentration from X-ray measurement (see Figure 2.16). For the two samples shown in Figure 2.19 and Figure 2.20, however, this strategy leads to Ge concentrations that are too low to give a reasonable fit of the X-ray measurements. Figure 2.20 shows a measurement with two fits. The fit for a Ge concentration $x = 0.45$ (thin line) is in good agreement with the measurement. The fit for a Ge concentration $x = 0.35$ (thick line) can be considered the lower bound for the Ge concentration, because the peak at $\omega = -4^\circ$ is so weak that it would

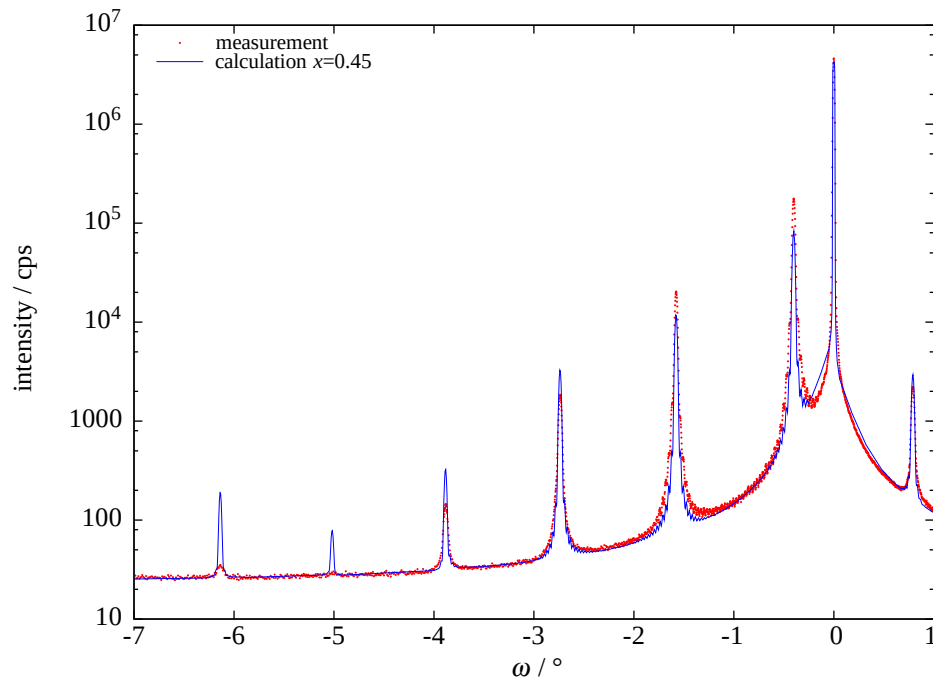


Figure 2.18: X-ray diffraction results of sample 25. The ordinate shows the glancing angle ω relative to the Si substrate peak. The symbols are the measurements and the solid line is the simulation with a Ge concentration x of 45%. Due to the high number of 40 periods, the satellite peak with minimum intensity at $\omega = -6.2^\circ$ can be seen in the measurement and allows an accurate determination of the Ge concentration. The TEM picture of the sample is shown in Figure 2.10.

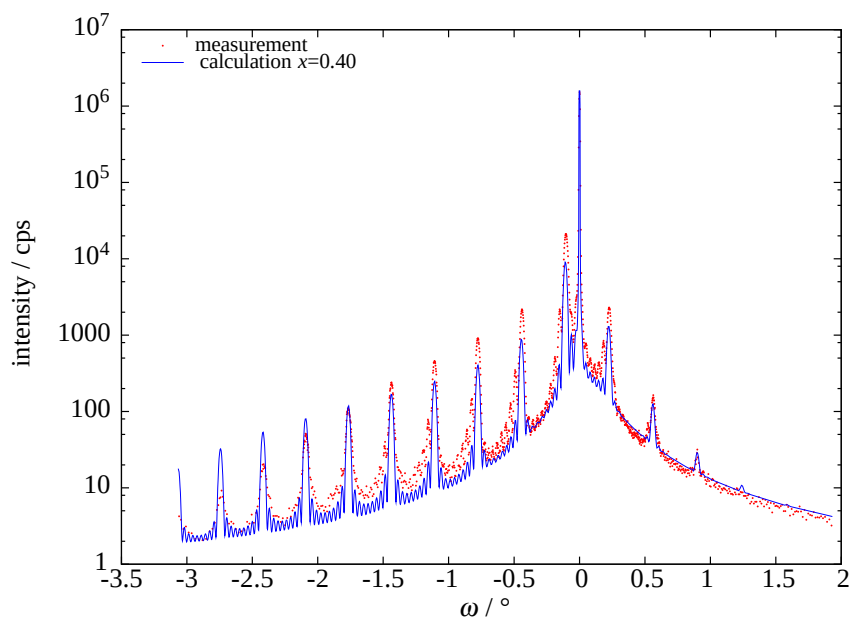


Figure 2.19: X-ray diffraction results of sample 46. The ordinate shows the glancing angle ω relative to the Si substrate peak. The symbols are the measurements and the solid lines are the simulations with a Ge concentration x of 40%. The sample has 10 periods and its TEM picture is shown in Figure 2.8.

disappear in the measurement. Note, that in all fits shown here, the measured satellite peaks decay more with higher orders than the calculated peaks. The differences can be reduced by modelling several steps (a gradient is not possible with the software available), as done for the $x=0.45$ fit in Figure 2.20, but the differences remain significant. From the two fits in Figure 2.20, an accuracy of the Ge concentration of ± 0.08 and the well width of -40% was estimated. The upper limit of the accuracy for the well width is estimated 75% and is obtained by taking the measurement from the TEM picture into account.

2.9 Impact of Growth Parameters on the Deposition of SiGe

The most important growth parameters are the growth temperature, the gas composition and pressure in the reactor chamber and the reactor geometry. The pressure in the reactor is determined by the gas inlet and the displacement capacity of the connected vacuum pumps. To minimise the number of changing growth parameters, the growth pressure was held constant to 0.5 Pa (5×10^{-3} mbar) by a regulating valve and the growth temperature was kept at 520°C.

The deposition of SiGe is characterised by its composition and growth rate. As discussed in section 2.6, the Ge fraction in the deposited material depends non-linearly on the GeH₄ fraction of the gas in the reactor chamber. Thus, the equipment has to be carefully calibrated, utilising tools for structural analysis as discussed in section 2.8. Lists of samples grown within this thesis are shown in appendix B.

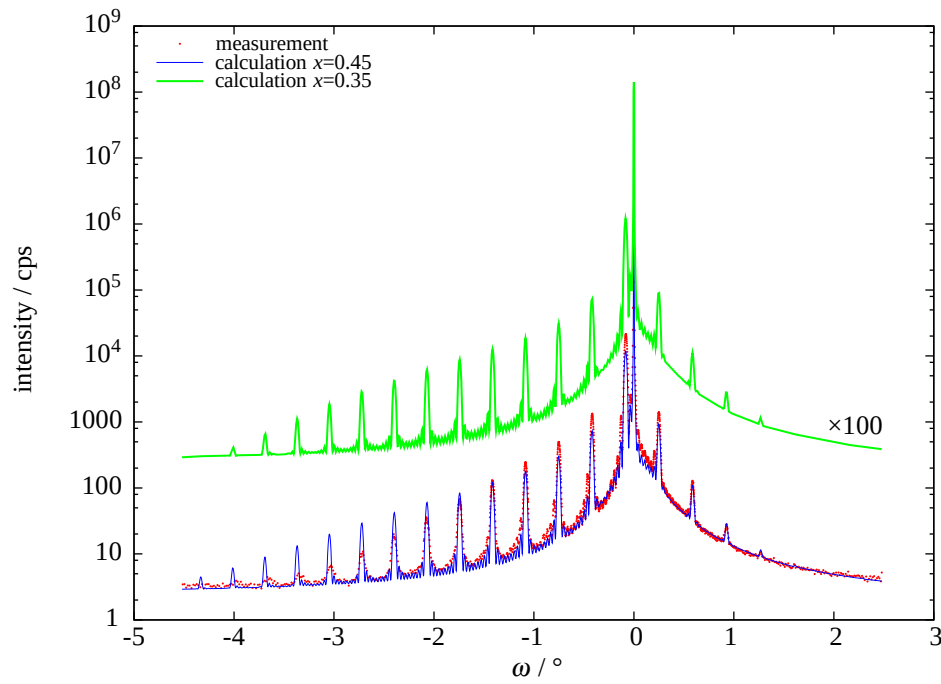


Figure 2.20: X-ray diffraction results of sample 47. The ordinate shows the glancing angle ω relative to the Si substrate peak. The symbols are the measurements and the solid lines are the simulations with a Ge concentration x of 45% (thin line) and 35% ($\times 100$, thick line). The fit for $x=35\%$ (thick line) represents the one for the minimum Ge concentration, because at a lower concentration the satellite peak at $\omega=-4^\circ$ would become too weak to fit the measurement. The sample has 10 periods and its TEM picture is shown in Figure 2.9.

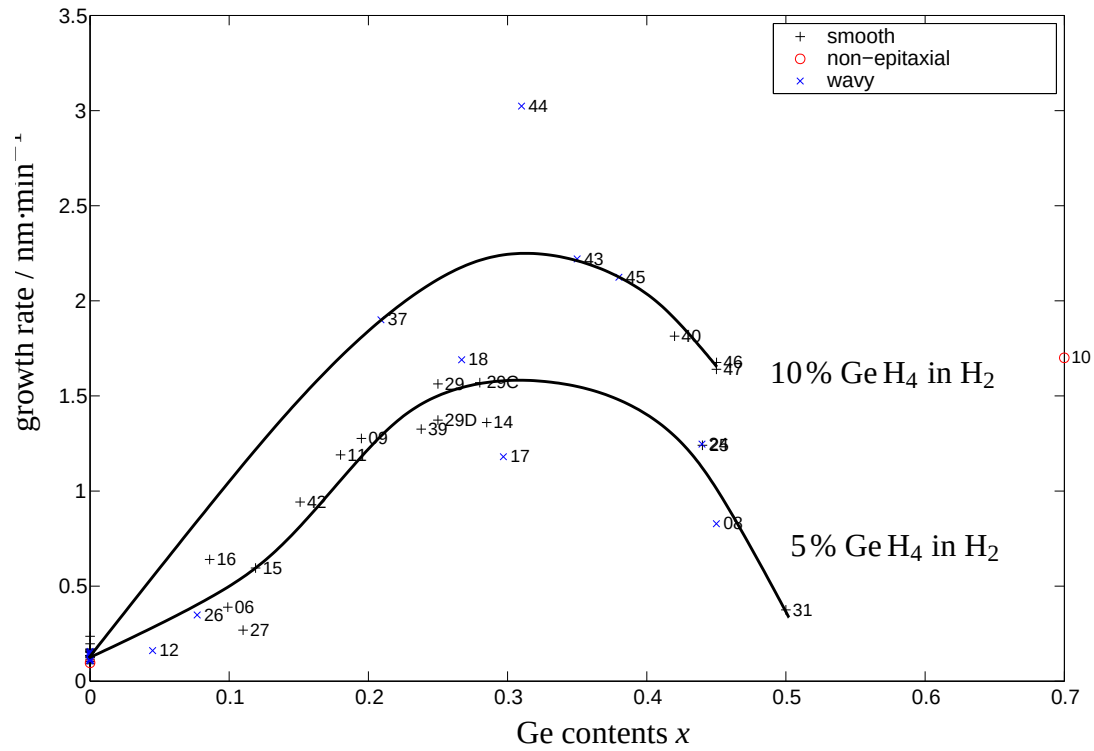


Figure 2.21: SiGe growth rate as a function of the deposited Ge contents. The symbols indicate the morphology of the SiGe structures: Smooth (+) and wavy (x) interfaces between Si and SiGe layers and non-epitaxial deposition (o). The sample numbers are positioned to the right of the symbols. The lines are approximate interpolations for the two different GeH_4 dilutions of 5% and 10% in hydrogen used for the deposition.

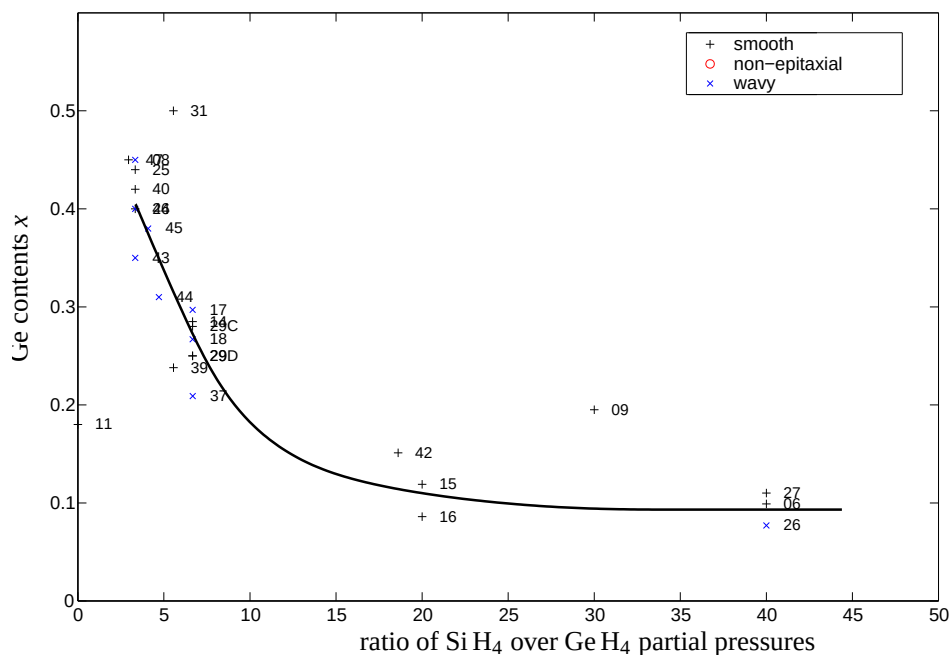


Figure 2.22: Ge content x in the deposited SiGe alloy as a function of the ratio of the Si H₄ over the Ge H₄ partial pressures. The symbols indicate the morphology of the SiGe structures: Smooth (+) and wavy (x) interfaces between Si and SiGe layers and non-epitaxial deposition (o). The sample numbers are positioned to the right of the symbols. The line is an approximate interpolation.

The growth rate as a function of the Ge content x in the deposited SiGe alloy is shown in Figure 2.21. The growth rate increases with increasing Ge content from 0.15 nm/min at no Ge content to a maximum of about 2 nm/min at Ge content of around 0.35 and decreases with higher Ge contents. The increase is due to the weaker Ge-H bond, resulting in an increased number of dangling bonds (see section 2.6.3). The decrease can be explained by the 5% (10% beginning with sample 37) dilution of Ge H₄ in hydrogen: With increasing inlet of the Ge H₄/hydrogen mixture into the reactor chamber, the partial pressure of Si H₄ decreases, leading to a decrease in growth rate.

Figure 2.22 shows the Ge content x in the deposited SiGe alloy as a function of the ratio of the Si H₄ over the Ge H₄ partial pressures, which was calculated under the assumption that both gases are equally well pumped. This ratio rather than the Ge H₄ mass flow was chosen to be able to compare the results obtained with the two different Ge H₄ dilutions and, indeed, no significant difference between the sample numbers < 37 (5% Ge H₄ in H₂) and ≥ 37 (10% Ge H₄ in H₂) can be observed. The reproducibility is rather poor, as the Ge contents varies by around 20% about their mean value for all multiply measured Si H₄ to Ge H₄ ratios. This variation can only partly be explained by changes in the set-up, e. g. a new reactor chamber or mass flow controller. It has been found that the growth rate increases with increasing growth time or layer thickness. This might be caused by increasing surface roughness during deposition, which is visible by comparing the surface roughness of sample with different thicknesses of deposition. A possible reason for the increasing surface roughness might be the relatively high base pressure of the reactor chamber of around 3 μ Pa (3×10^{-8} mbar), leading to an incorporation of oxygen into the deposited material.

Chapter 3

Optical Absorption of SiGe Quantum Wells

The goal of the absorption measurement is to optimise SiGe structures for their use in photocells with a reduced band gap. Some basic properties – crystal structure, reciprocal lattice and band structure – for Si and Ge as well as for SiGe is given in the introductory first section. A discussion on theoretical grounds of indirect band gap absorption in quantum wells yields a qualitative description of an idealised semiconductor. A measurement setup was developed that allows for more than 200 internal reflections, providing the means to investigate very thin SiGe layers. In order to allow a comparison of SiGe quantum well samples with different Ge contents and well width, but with the same absorption edge, the determining property, i. e. the minimum transition energy in strained SiGe quantum wells is discussed. For the calculation of the absorption coefficient from the absorption measurement, an in-depth investigation of the interference phenomena occurring in our samples and their consequences for the absorption is presented. For several samples, the absorption coefficient was determined and compared to with each other and with literature data of bulk SiGe.

3.1 Band Structure of Si, SiGe and SiGe Quantum Wells

Some optical properties of a semiconductor depend on the edges of the valence and conduction band in reciprocal space. In this section, the crystal structure of Si and Ge, its transformation into the reciprocal k -space and the band structure as a function of the wave vector $\vec{k}$ is presented. [22]

Each point of the Si or Ge crystal lattice is defined in terms of the basis, consisting of the 2 identical atoms at position (0 0 0) and ($\frac{1}{4}$ $\frac{1}{4}$ $\frac{1}{4}$), and the primitive cell. The more commonly used unit cell is face-centred cubic (fcc) for both, Si and Ge as well as for any SiGe alloy. The unit cell is depicted in Figure 3.1. Each atom is covalently bound to its 4 nearest neighbours. At a temperature of 22.5° C, the lattice constant for Si is 0.357 nm [23] and for Ge it amounts to 0.357 nm [24], i. e. 4.18% larger. A reasonable approximation of the lattice constant a of $\text{Si}_{1-x}\text{Ge}_x$ is the linear interpolation, also known as Vegard's law.

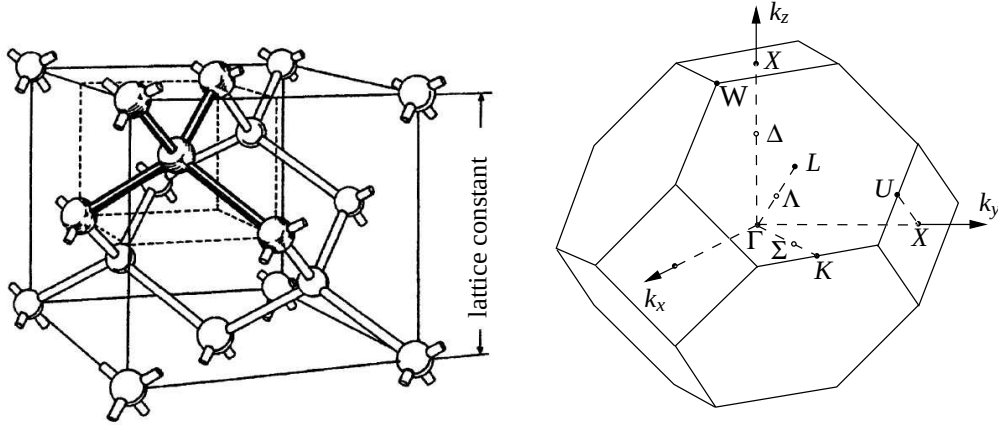


Figure 3.1: The crystal structure of Si and Ge is face-centred cubic (fcc) on the left and its first Brioullin zone on the right. The symmetry axes and and some important points in the first Brioullin zone are labelled with commonly used letters.

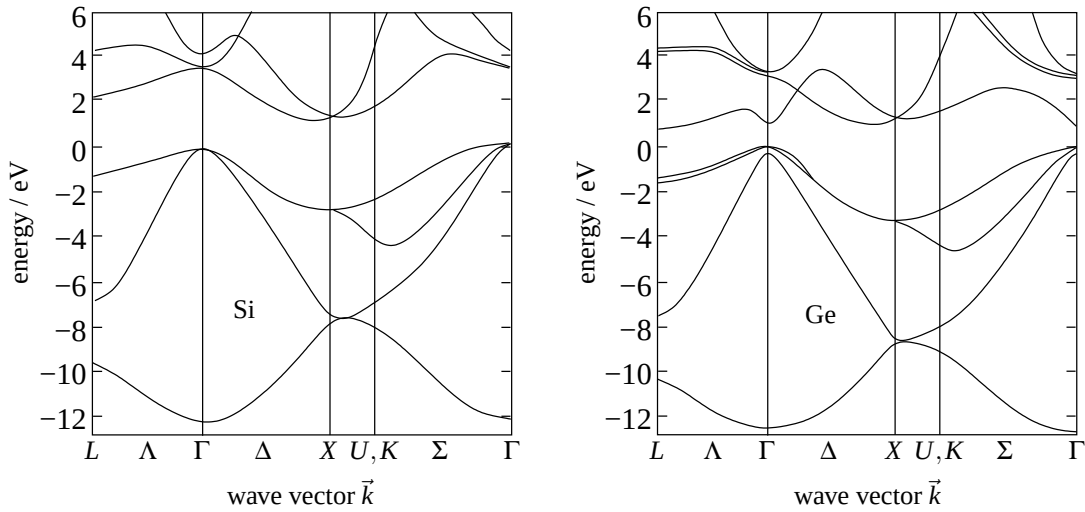


Figure 3.2: Band structure of Si and Ge. The letters at the abscissae are points and symmetry axes in k -space as depicted in Figure 3.1. Note that the band gap of Si is between the X point in the conduction band and the Γ point in the valence band, while it is between the L point in the conduction band and the Γ point in the valence band in Ge.

A better fit to experimental data [25] is given by the cubic equation

$$a(\text{Si}_{1-x}\text{Ge}_x) = 0.5431 - 0.00125x + 0.01957x^2 + 0.00436x^3. \quad (3.1)$$

The maximum deviation of the two methods is 1.2% at a Ge concentration of 52%.

The reciprocal lattice of a fcc lattice is a body-centred cubic (bcc). The first Brillouin zone of the reciprocal lattice, i.e. the Wigner-Seitz cell, is shown in Figure 3.1 (right). Important symmetry axes and points are marked with letters, which can also be found in Figure 3.2, the band structure of Si and Ge. The energy is plotted against the wave vector $\vec{k}$ along 4 lines of the Wigner-Seitz cell, i.e. from left to right on the abscissae from the centre of a hexagonal face (L) to the centre of the cell (Γ), continuing to the centre of a square face

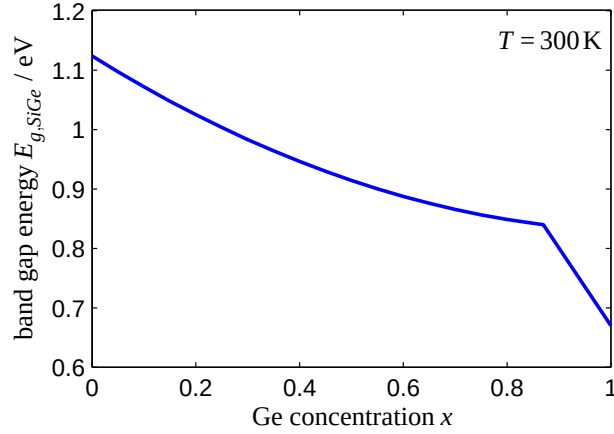


Figure 3.3: Band gap of $\text{Si}_{1-x}\text{Ge}_x$ versus Ge concentration x as calculated with (3.2) and (3.3). The band gap is Si like for $x \leq 0.87$ and Ge like for $x > 0.87$, causing the kink at $x=0.87$.

(X) and further to the centre of an edge (U and K) and back to the centre of the cell (Γ). For the onset of optical absorption, the band gap, i. e. the difference between the maximum of the valence band and the minimum of the conduction band, is most important.

The valence band maximum is positioned in the centre of the Brillouin zone (Γ point at $k = 0$) and is fourfold degenerated. They differ in spin and effective mass, thus being labelled heavy and light hole states. There are two further states with an energy of 40 meV and 300 meV [26] for Si and Ge, respectively, below due to spin-orbit coupling. This band is labelled split-off band.

The conduction band minimum of Si is at the Δ symmetry axis between the Γ and X point, i. e. the $[100]$ direction in reciprocal space. It is often called Δ valley. As there are 6 X points, i. e. 6 square faces in the Wigner-Seitz cell in Figure 3.1, there are also 6 Δ points and 6 equivalent states in the conduction band minimum, leading to a sixfold degeneracy of the conduction band minimum. In Ge, the conduction band minimum is at the L point at the edge of the first Brillouin zone at the centre of each of the 8 hexagons in the Wigner-Seitz cell. Hence, the conduction band minimum is eightfold degenerated.

In both materials, Si and Ge, the valence band maximum and the conduction band minimum is at a different position in k space, i. e. their gap is indirect. In $\text{Si}_{1-x}\text{Ge}_x$, the band gap is at the Δ position in the conduction band for $x < 0.87$ [27] and at the L position for $x > 0.87$. The bandgap of bulk SiGe $E_{g,\text{SiGe}}$ at 300 K is approximated by [28]:

$$E_{g,\text{SiGe}}^{\Delta} = (1-x) \cdot E_{g,\text{Si}}^{\Delta} + x \cdot E_{g,\text{Ge}}^{\Delta} - \beta \cdot x \cdot (1-x) \quad \text{for } x \leq 0.87 \quad (3.2)$$

$$E_{g,\text{SiGe}}^L = (1.98 - 1.31x) \text{ eV} \quad \text{for } x > 0.87, \quad (3.3)$$

where $E_{g,\text{Si}}^{\Delta} = 1.124 \text{ eV}$ and $E_{g,\text{Ge}}^{\Delta} = 0.83 \text{ eV}$ are the bandgaps of Si and Ge at the Δ point, respectively, x is the Ge concentration and $\beta = 0.25$ is the bending factor. The band gap of SiGe as a function of the Ge concentration described in (3.2) and (3.3) is depicted in Figure 3.3. The kink at 0.87 eV is clearly visible. It originates from the change of the band gap from the Si like Δ to the Ge like L conduction band minimum.

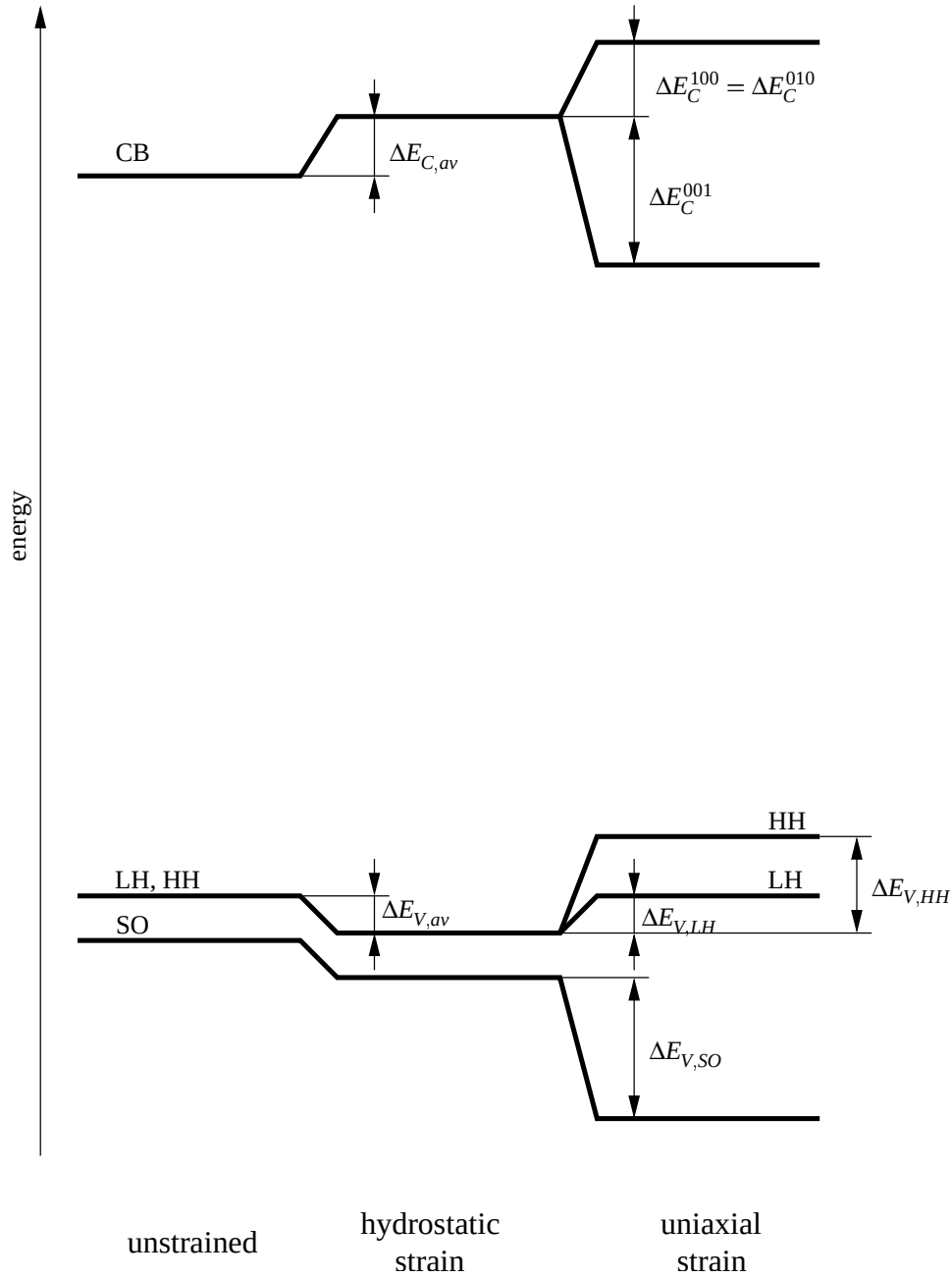


Figure 3.4: Band edges of unstrained SiGe and their deformation due to hydrostatic and additional uniaxial strain. The latter represents SiGe deposited pseudomorphically on Si. Hydrostatic strain increases the band gap. The additional uniaxial strain removes the degeneracy of the light hole (LH) and heavy hole (HH) bands and splits the conduction band (CB) into two, resulting in a reduction of the fundamental band gap in comparison to unstrained SiGe.

3.2 Transition Energy due to Strain and Confinement

In this section the influence of strain and confinement of a SiGe layer embedded in Si on the band edges is discussed, resulting in a derivation of the minimum transition energy, i. e. the energy between the lowest allowed conduction band edge and the highest allowed valence

band edge. The epitaxially grown SiGe has to conform to the in plane lattice constant of the Si substrate leading to compressive strain in the plane of the interface. Thus, the lattice constant of the plane perpendicular to the interface gets tensilely strained. In literature, this is usually modelled by a hydrostatic strain that is superimposed by a uniaxial tensile strain perpendicular to the interface. The strain leads to a distortion of the band structure, which is schematically drawn in Figure 3.4. The hydrostatic strain increases the bandgap, while the additional uniaxial strain results in a band splitting, which overcompensates the increase and leads to a smaller band gap in comparison to unstrained SiGe. For the calculation of the strain and its influence on the valence and conduction band the model-solid theory was used which is well described by Van de Walle [29], who also gives all necessary properties of Si and Ge, which are linearly interpolated for SiGe. The dimensions of the SiGe structures are small enough for quantum effects to play a significant role. They are covered by a basic quantum mechanical description of quantum wells.

3.2.1 Influence of Strain

The structures were grown on (1 0 0) wafers. The direction of growth is [0 0 1]. The diagonal elements of the strain tensor ϵ_{ii} are defined by [29]:

$$\epsilon_{11} = \epsilon_{22} = \frac{a_{Si}}{a_{SiGe}} - 1 \text{ and } \epsilon_{33} = -D_{SiGe} \cdot \epsilon_{11}, \quad (3.4)$$

where a_{Si} and a_{SiGe} is the lattice constant in equilibrium for Si and SiGe, respectively, D_{SiGe} is the Poisson's ratio given from the elastic constants by $D = 2 \cdot c_{12}/c_{11}$ for (0 0 1) interfaces. All off-diagonal elements of the strain tensor are zero.

The model-solid theory takes the effect of the fractional volume change on the band structure into account. In general, the valence band consists of three bands: The split-off band and the under unstrained conditions degenerate light and heavy hole bands. As the model-solid theory does not consider band splitting, the shift of the average valence and conduction band is computed and the band splitting is added in a subsequent step. The fractional volume change $\Delta\Omega/\Omega$ of the unit cell is the trace of the strain tensor:

$$\frac{\Delta\Omega}{\Omega} = \epsilon_{11} + \epsilon_{22} + \epsilon_{33} \quad (3.5)$$

The relative shift of the average valence and conduction band $\Delta E_{V,av}$ and $\Delta E_{C,av}$ in terms of the fractional volume change $\Delta\Omega/\Omega$ is defined by:

$$\Delta E_{V,av} = a_V \cdot \frac{\Delta\Omega}{\Omega} \text{ and} \quad (3.6)$$

$$\Delta E_{C,av} = a_C \cdot \frac{\Delta\Omega}{\Omega}, \quad (3.7)$$

where a_V and a_C is the hydrostatic deformation potential for the valence and conduction band, respectively.

For strain along [0 0 1] the shift of the highest valence bands is calculated with respect to their average $E_{V,av}$:

$$\Delta E_{V,HH} = -\frac{1}{6}\Delta_0 + \frac{1}{4}\delta E_{001} + \frac{1}{2} \cdot \sqrt{\Delta_0^2 + \Delta_0 \cdot \delta E_{001} + \frac{9}{4}(\delta E_{001})^2}, \quad (3.8)$$

where Δ_0 is the spin orbit splitting and δE_{001} is given by

$$\delta E_{001} = 2b(\epsilon_{33} - \epsilon_{11}), \quad (3.9)$$

where b is the share deformation potential for strain of tetragonal symmetry.

$E_{V,HH}$ and $E_{V,LH}$ represent the light and heavy hole band and $E_{V,SO}$ the split off band at the Γ point. The heavy hole is a pure $|3/2, \pm 3/2\rangle$ state, while the split off and light hole band is a mixture of $|3/2, \pm 1/2\rangle$ and $|1/2, \pm 1/2\rangle$ states.

For pseudomorphic layers grown in $[001]$ direction, the band along $[100]$ and $[010]$ split off from the one along $[001]$. The splitting of the bands with respect to their average $\Delta E_{C,av}$ is given by

$$\Delta E_C^{001} = \frac{2}{3}\Theta_u \cdot (\epsilon_{33} - \epsilon_{11}) \text{ and } \Delta E_C^{100} = \Delta E_C^{010} = \frac{1}{3}\Theta_u \cdot (\epsilon_{33} - \epsilon_{11}), \quad (3.10)$$

where Θ_u is the deformation potential of the conduction band minimum along the Δ valley.

3.2.2 Influence of Confinement

A Si/SiGe/Si structure forms a quantum well in the valence band and a considerably smaller barrier in the conduction band so that the latter can be neglected for the influence of confinement on the bandgap. The depth of the quantum well in the valence band V_0 is given by

$$V_0 = E_{g,Si,bulk} - E_{g,SiGe,bulk} + \Delta E_{V,av} + \Delta E_{V,HH},$$

where $E_{g,Si,bulk}$ and $E_{g,SiGe,bulk}$ is the bandgap of bulk Si and SiGe, respectively. From basic quantum mechanics [30] the energy eigenvalues for bound states are given by the solution of the transcendental equations

$$\left| \cos \frac{k \cdot w}{2} \right| = \frac{k}{k_0}, \quad \left| \sin \frac{k \cdot w}{2} \right| = \frac{k}{k_0} \text{ and } \tan \frac{k \cdot w}{2} > 0,$$

where k and k_0 is given by

$$k^2 = \frac{2m(E + V_0)}{\hbar^2} \text{ and } k_0^2 = \frac{2mV_0}{\hbar^2}, \quad (3.11)$$

where m is the effective hole mass and w is the well width. As the heavy hole band is the highest in energy and therefore assumed to dominate the bandgap near absorption, it is the only one considered. The value of the effective heavy hole mass ranges from 0.18 to 0.44 times the free electron mass, depending on the Ge concentration, carrier density, sample structure and measurement method¹. [31] We used $m = 0.29$ times the free electron mass published for Si/SiGe structures by [32]. The light hole mass was linearly interpolated. The shift due to confinement ΔE_{conf} results from reordering (3.11):

$$\Delta E_{conf} = V_0 + E = \frac{\hbar^2 k^2}{2m}. \quad (3.12)$$

Taking the uncertainty of the effective hole mass into account, results in an error bar on the energy of confined states of 20-40 meV

¹ Due to the non-parabolicity of the band, the hole mass depends on charge carrier density. As the measurements with the different methods are carried out with different charge carrier densities, the resulting hole masses differ accordingly.

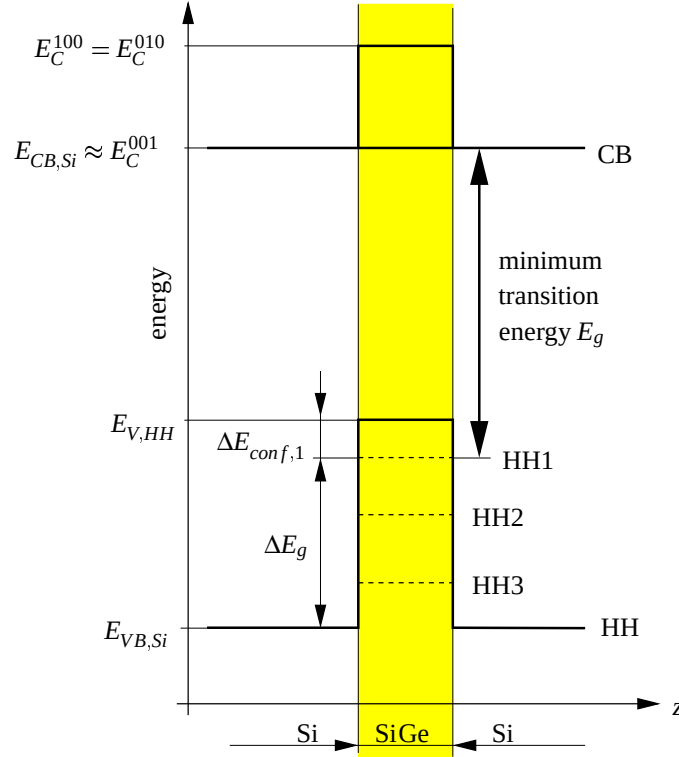


Figure 3.5: A SiGe layer embedded in Si forms a quantum well for holes in the valence band. The deepest well is obtained in the heavy hole (HH) band, which is depicted at the bottom. The band edges are drawn as solid lines and the allowed energies in the quantum well as dashed lines, labelled HH1, HH2 and HH3. The conduction band (CB) splits in two, where the band in [001] direction is the lowset in energy and forms a negligibly small barrier and the bands in [100] and [010] directions are much higher in energy and form a barrier. The minimum transition energy is given by the difference between the CB E_C^{001} and ground state in the HH band $E_{V,HH} - \Delta E_{conf,1}$.

3.2.3 Minimum Transition Energy of Unstrained Bulk SiGe and Strained SiGe Quantum Wells

The minimum transition energy is the difference between the ground state of the quantum well in the valence band (i.e. a heavy hole state) and the lowest conduction band edge (see Figure 3.5). For the calculation of the band gap energy of unstrained bulk SiGe $E_{g,SiGe}^\Delta$, (3.2) [28] was used. Finally, the minimum transition energy of the strained SiGe quantum wells E_g is calculated by adding the energy shifts given in (3.6), (3.7), (3.8), (3.10) and (3.12) to the bandgap of the unstrained bulk SiGe (3.2). Note that the valence band energy shifts get a positive and conduction band energy shifts a negative sign:

$$E_g = E_{g,SiGe}^\Delta + \Delta E_{V,av} - \Delta E_{C,av} + \Delta E_{V,HH} - \Delta E_C^{001} + \Delta E_{conf}. \quad (3.13)$$

Figure 3.6 illustrates the resulting band edges and their confined states (relative to the bulk Si valence band edge) of a 3.4nm $Si_{0.55}Ge_{0.45}$ layer between Si bulk for the conduction (CB), heavy hole (HH), light hole (LH) and split off (SO) band and depicts schematically the density of states (DOS).

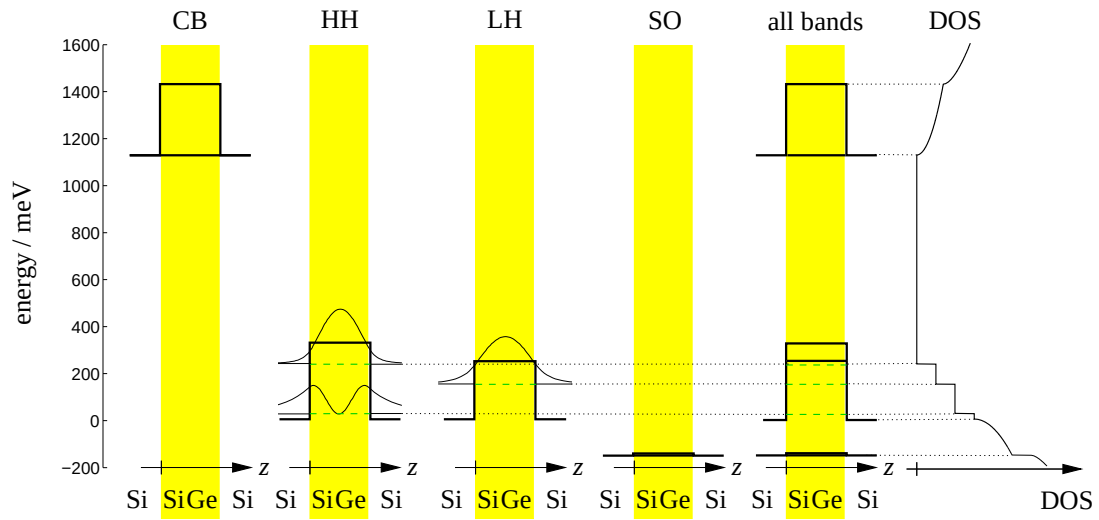


Figure 3.6: Band edges (thick solid lines) and their confined states (dashed lines) relative to the bulk Si valence band edge of a 3.4 nm $\text{Si}_{0.55}\text{Ge}_{0.45}$ layer between Si bulk. A Si/SiGe/Si structure forms a QW in the valence band and constitutes a considerably smaller, here neglected, barrier in the conduction band (CB). The strain removes the degeneracy of the heavy hole (HH) and the light hole (LH) band, while the changes of the split-off (SO) band is small. For pseudomorphic layers grown in $[001]$ direction, the CB along $[100]$ and $[010]$ split off from the one along $[001]$. The barrier in the lowest CB is smaller than the accuracy of the calculation so that it is neglected. The energy eigenvalues for bound states in a QW are obtained from solving the 1D-Schrödinger equation for parabolic bands. The probability density $|\phi|^2$ of the confined holes is drawn above their states. The density of states (DOS) is schematically drawn.

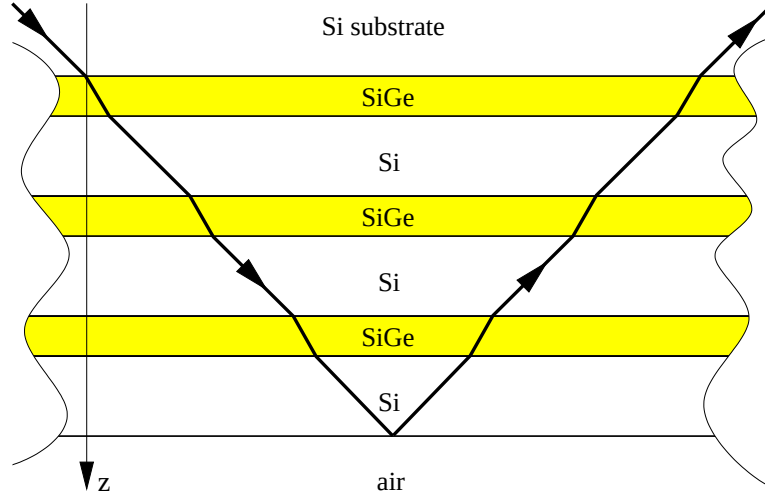


Figure 3.7: Typical arrangement of three SiGe layers embedded in Si spacers. The ray of light is coming from the Si substrate, traverses the weakly absorbing SiGe thin films and is totally reflected at the Si-air interface at the bottom. The reflected and the incident wave superimpose and form a standing wave.

3.2.4 Macfarlane-Roberts Expression

$\text{Si}_{1-x}\text{Ge}_x$ is an indirect semiconductor, hence absorption can only take place if it is assisted by a phonon being either emitted or absorbed to conserve momentum. According to [33], the absorption coefficient α can be represented by:

$$\alpha = A \left[\frac{(h\nu - E_g - k\Theta)^2}{1 - \exp(-\frac{\Theta}{T})} + \frac{(h\nu - E_g + k\Theta)^2}{\exp(\frac{\Theta}{T}) - 1} \right], \quad (3.14)$$

where $h\nu$ is the photon energy, T is the temperature, Θ is the phonon equivalent temperature, k is the Boltzmann constant and A is an inherently temperature-independent factor. If $E_g - k\Theta < h\nu < E_g + k\Theta$, only the first term in square brackets of (3.14) is to be considered which refers to phonon absorption. The second term refers to phonon emission. The absorption coefficient α is zero for $h\nu < E_g - k\Theta$.

3.3 Absorption of a Standing Electromagnetic Wave and Effective Thickness

The absorption of SiGe structures is measured by internal reflection spectroscopy. The total internal reflection occurs at the Si-air interface, which is close to the SiGe structures to be measured. The for this measurement typical arrangement is drawn in Figure 3.7. The SiGe structures are modelled as plain layers and the ray of light is modelled as a plain electromagnetic wave. Due to total reflection of the light at the Si-air interface, a standing wave is formed by the superposition of the incident and the reflected wave. Hence, the electric field amplitude is a function of the distance to the totally reflecting surface z . In an absorbing – i. e. conducting – medium, the absorption of an electromagnetic wave is

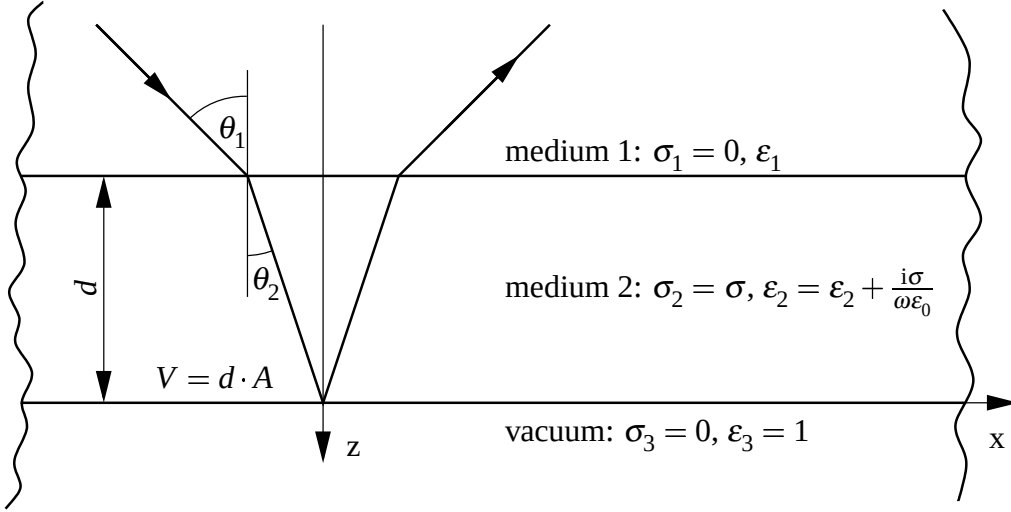


Figure 3.8: Ray of light from non-absorbing medium 1 (e.g. Si), through weakly absorbing medium 2 (e.g. SiGe) being totally reflected at interface between medium 2 and vacuum (or in good approximation air). σ_j and ϵ_j are the conductivity and the permittivity of medium j , respectively.

proportional to the square of the electric field. As the field amplitude depends on z , the absorption of each of the SiGe layers in Figure 3.7 is different and needs to be calculated. This section discusses how the electric field amplitude is computed, how it influences the absorption and how the effective thickness of the SiGe layers is obtained.

3.3.1 Electromagnetic Waves in Conducting Media

In the following we consider the absorption of plain electromagnetic waves in linear and homogeneous media. For simplicity, only a single absorbing layer, which is thin compared to the wavelength, is accounted for, so that the amplitude of the electric field is constant across the layer. In the end, the result is generalised to an arbitrary number of layers of arbitrary thickness and coordinate dependent electric field amplitudes. The arrangement is depicted in Figure 3.8: The incident wave in medium 1, e.g. Si, has an electric field amplitude of E_0 and is non-absorbing in the range of photon energies under consideration. The electric field E in the absorbing medium 2, e.g. SiGe, will be calculated later. Medium 3 is vacuum or in good approximation air, leading to total reflection if the angle Θ_2 is greater than the critical angle.

From basic electrodynamics, the radiation power P averaged over time dissipated in a volume V is [34]:

$$P = \frac{1}{2} \vec{E} \cdot \vec{j}^* V = \frac{1}{2} \sigma \vec{E} \cdot \vec{E}^* V = \frac{1}{2} \sigma |\vec{E}|^2 V = \frac{1}{2} \sigma E^2 V, \quad (3.15)$$

where $\vec{E}$ is the electric field vector in medium 2, $\vec{j}$ is the current density vector and σ is the conductivity. The factor $1/2$ and the complex conjugate, denoted by the $*$, evolves from averaging over time and the fact that E represents the amplitude rather than the root mean square value of the electric field.

The power density S of an electromagnetic wave per unit area in medium 1 (Pointing vector) can be written as:

$$S = \frac{1}{2} \sqrt{\frac{\epsilon_1 \epsilon_0}{\mu_0}} |\vec{E}_0|^2,$$

where ϵ_1 is the permittivity of the medium 1 and ϵ_0 the permittivity of vacuum, μ_0 is the permeability of vacuum and $|\vec{E}_0|$ is the amplitude of the electric field in medium 1. Hence, the incident power P_0 of an electromagnetic wave impinging on an area A with an incident angle Θ_1 is given by:

$$P_0 = SA \cos \Theta_1 = \frac{1}{2} \sqrt{\frac{\epsilon_1 \epsilon_0}{\mu_0}} |\vec{E}_0|^2 A \cos \Theta_1. \quad (3.16)$$

The absorptivity a is defined as P/P_0 , which results with (3.15) and (3.16) in:

$$a = \frac{P}{P_0} = \frac{\sigma V}{\sqrt{\frac{\epsilon_1 \epsilon_0}{\mu_0}} A \cos \Theta_1} \left| \frac{\vec{E}}{\vec{E}_0} \right|^2. \quad (3.17)$$

Equivalently,

$$a = 1 - e^{-\alpha d_{eff}} \approx 1 - (1 - \alpha d_{eff}) = \alpha d_{eff}, \quad (3.18)$$

where α is the absorption coefficient and d_{eff} is the effective thickness the electromagnetic wave traverses. The approximation of the exponential function yields an error $< 0.01\%$ for $a < 0.01$. The connection of the two definitions of a can be derived from the definition of the amplitude of the wave vector k in medium 2 [35];

$$k^2 = \left(\beta + i \frac{\alpha}{2} \right)^2 = \mu \frac{\omega^2}{c^2} \eta_2 = \mu \frac{\omega^2}{c^2} \left(\epsilon_2 + i \frac{\sigma}{\omega \epsilon_0} \right), \quad (3.19)$$

where η_2 is the (complex valued) permittivity of medium 2 and ϵ_2 its real part, $c = 1/\sqrt{\mu_0 \epsilon_0}$ is the speed of light in vacuum, β is the real part of the amplitude of wave vector and μ the permeability of medium 2 which is set to 1 in the following. With these definitions, an attenuated plane wave is described as expected:

$$\vec{E} = E e^{i\vec{k}\vec{r}} = |\vec{E}| e^{-\alpha \vec{e}_k \vec{r}} e^{i\beta \vec{e}_k \vec{r}} \quad (3.20)$$

where $\vec{e}_k = \vec{k}/|\vec{k}|$ is the unit vector of the wave vector $\vec{k}$.

With (3.19) and the assumption that $\alpha \ll \beta$, the relationship between the conductivity σ and the absorption coefficient α can be expressed as:

$$\sigma = \alpha \sqrt{\frac{\epsilon_2 \epsilon_0}{\mu_0}} \quad (3.21)$$

By replacing σ in (3.17) by (3.21) we obtain:

$$a = \frac{\alpha / \sqrt{\frac{\mu_0}{\epsilon_2 \epsilon_0}} d}{\sqrt{\frac{\epsilon_1 \epsilon_0}{\mu_0}} \cos \theta_1} \left| \frac{E}{E_0} \right|^2 = \frac{\alpha d}{\cos \theta_1} \sqrt{\frac{\epsilon_2}{\epsilon_1}} \left| \frac{E}{E_0} \right|^2 = \frac{\alpha d}{\cos \theta_1} \cdot \frac{n_2}{n_1} \left| \frac{E}{E_0} \right|^2. \quad (3.22)$$

In the last step, the permittivities in medium 1 and 2 were expressed in terms of their refractive indices according to $n = \sqrt{\epsilon}$.

To generalise this equation for coordinate depending electric field amplitudes and absorbing layers of arbitrary thickness², the product of the electric field amplitude and the thickness $E \cdot d$ has to be replaced by $\int_0^d E(z) \cdot dz$ and (3.22) becomes:

$$a = \frac{\alpha}{\cos \theta_1} \cdot \frac{n_2}{n_1} \int_0^d \left| \frac{E(z)}{E_0} \right|^2 dz \quad (3.23)$$

When applying the definition of the absorptivity (3.18) approximated by $a = \alpha d_{eff}$ to the problem of a thin layer in which constructive or destructive interference occurs, i. e. the electric field amplitude depends on wavelength and coordinate, the effective thickness d_{eff} becomes dependent on wavelength. It is obtained from combining (3.18) with (3.23), in agreement with [36]:

$$d_{eff} = \frac{1}{\cos \theta_1} \cdot \frac{n_2}{n_1} \int_{z=0}^d \left| \frac{E(z)}{E_0} \right|^2 dz \quad (3.24)$$

The effective thickness converges to $d_{eff} = \frac{n_2}{n_1} \frac{2d}{\cos \theta_1}$ for $d \gg \lambda$, the wavelength (see (3.24) and the following discussion). At first glance, it is astonishing that the effective thickness depends on θ_1 while the geometric thickness $d_{geom} = 2d / \cos \theta_2$ depends on θ_2 (footnote³).

3.3.2 Electric Field in Multiple Layers

In the stack of SiGe layers embedded in Si, the interfaces separate regions with different indices of refraction. At every interface, the incoming light is split in a transmitted and reflected part. These parts are calculated by the Fresnel's equations yielding different amplitudes and phase shifts for waves with different polarisations. In a p-polarised wave, the electric field vector oscillates parallel and in an s-polarised wave, the electric field vector oscillates perpendicular to the plane of incidence. The latter is defined by the wave vector of the incoming light and the normal vector of the interface (see Figure 3.9).

The coordinate system is defined so that the interfaces are parallel to the x-y plane and the air-Si interface is defined by the x-y plane at $z = 0$. The incoming wave propagates downwards. A matrix formalism taken from [38] is implemented in a computer programme. By using this matrix formalism, the problem can be solved for an arbitrary number of layers⁴.

² The thickness is limited by the coherence length of the light, which is infinity in the case of a plain wave.

³ With Snells Law, $n_1 \sin \Theta_1 = n_2 \sin \Theta_2$, Θ_1 can be expressed in terms of Θ_2 , n_1 and n_2 , however, the geometric and the effective thickness are always different, when $\Theta_1 \neq \Theta_2$. This is because the effective thickness takes the non-attenuated reflection between medium 1 and medium 2 into account, while the geometric thickness does not.

⁴ A first computational approach was to calculate all reflected and transmitted parts until the amplitude gets negligible and to add up all these parts for each layer. This gave good approximations, but had the disadvantage that computation time increases exponentially with the number of layers, rendering this algorithm uncalculable, i. e. for 10 layers, the computation time is in the order of hours and for 20 layers, it might well be in the order of centuries or more.

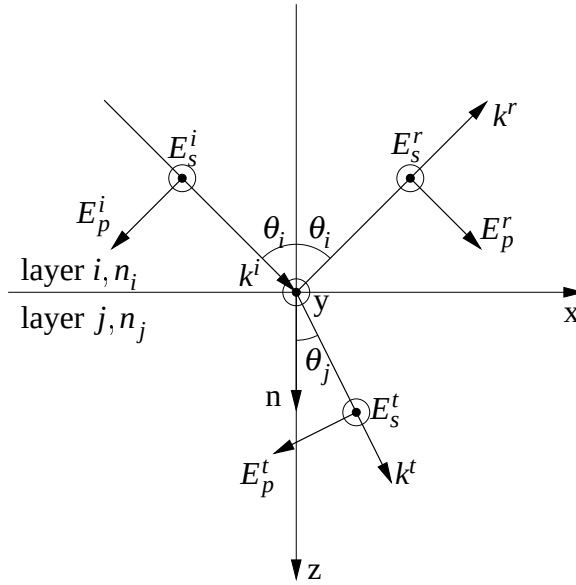


Figure 3.9: Reflection and refraction with polarisation parallel (p) and perpendicular (s) to the plane of incidence. The incident, transmitted and reflected vectors are labelled with an i , t and r superscript, respectively. The interface between layer i and $j = i + 1$ is the $x - y$ plane with its unit normal direction n [37].

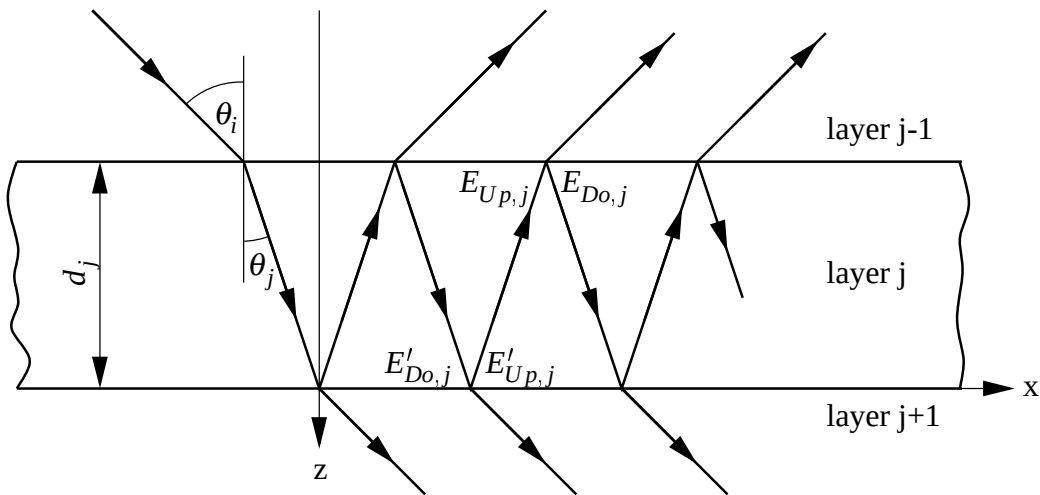


Figure 3.10: Ray of light being multiple reflected within a layer.

Figure 3.10 shows a stack of 3 layers in which a ray is multiple times reflected. The electric field of the downwards running wave at the top of layer j is labelled $E_{Do,j}$, while it is labelled with an extra dash at the bottom, i. e. $E'_{Do,j}$. For upwards running waves, the subscript Do is replaced by Up . The electric field at the lower side of an interface between layer i and j can be calculated by:

$$E_{Do,j} = E'_{Do,i}\tau_{ij} + E_{Up,j}\rho_{ji}, \quad (3.25)$$

where τ_{ij} and ρ_{ji} are the transmission and reflection coefficients. The first index indicates the layer the wave is coming from and the second index the layer the transmitted wave is going into. Similarly to (3.25), the electric field of the upper side of the interface between layer i and j :

$$E'_{Up,i} = E_{Up,j}\tau_{ji} + E_{Do,i}\rho_{ij}. \quad (3.26)$$

The transmission and reflection coefficients τ_{ij} and ρ_{ij} can be obtained from the Fresnel's equations [37], which fulfil the following properties:

- Angle of reflection equals angle of incidence.
- Snell's law: $n_i \sin \theta_i = n_j \sin \theta_j$
- The intensity of the incident light equals the sum of the intensities of reflected and transmitted light.
- The normal components of the displacement is continuous across the interface.
- The tangential components of the electric field is continuous across the interface.

Snell's law results in an imaginary angle θ_j for total reflection, e.g. at the Si-air interface in our samples. The interpretation of the imaginary angle is that no energy is transported into the layer of the rarer medium and the component of the wave vector pointing into z direction, $k_z = k \cdot \cos \theta_j$ is purely imaginary, leading to an exponentially decaying evanescent wave as the exponent in wave equation $E = E_0 \cdot \exp(-ik_z z)$ becomes real. The transmission and reflection coefficients τ_{ij} and ρ_{ij} depend on the polarisation of the wave which is indicated by the s and p subscript:

$$\tau_{s,ij} = \frac{E_s^t}{E_s^i} = \frac{2n_i n_j \cos \theta_i}{n_j \cos \theta_i + n_i \sqrt{n_j^2 - n_i^2 \sin^2 \theta_i}}, \quad (3.27)$$

$$\rho_{s,ij} = \frac{E_s^r}{E_s^i} = \frac{n_j \cos \theta_i - n_i \sqrt{n_j^2 - n_i^2 \sin^2 \theta_i}}{n_j \cos \theta_i + n_i \sqrt{n_j^2 - n_i^2 \sin^2 \theta_i}}, \quad (3.28)$$

$$\tau_{p,ij} = \frac{E_p^t}{E_p^i} = \frac{2n_i \cos \theta_i}{n_i \cos \theta_i + \sqrt{n_j^2 - n_i^2 \sin^2 \theta_i}} \quad (3.29)$$

and

$$\rho_{p,ij} = \frac{E_p^r}{E_p^i} = \frac{n_i \cos \theta_i \sqrt{n_j^2 - n_i^2 \sin^2 \theta_i}}{n_i \cos \theta_i + \sqrt{n_j^2 - n_i^2 \sin^2 \theta_i}}, \quad (3.30)$$

where the indices i and j refer the layer number. The calculation of the electric field for s and p polarisation differs only in the transmission and reflection coefficients and whenever τ_{ij} or ρ_{ij} appears, it can be replaced by its appropriate counterpart for s and p polarised waves. Keep in mind that both polarisations must be calculated for unpolarised light.

Together with the symmetry relations of the Fresnel's equations $\rho_{ij} = -\rho_{ji}$ and $\tau_{ji}\tau_{ij} + \rho_{ij}^2 = 1$, (3.25) and (3.26) can be rewritten:

$$E'_{Up,i} = \left(\frac{1}{\tau_{ij}} \right) E_{Up,j} + \left(\frac{\rho_{ij}}{\tau_{ij}} \right) E_{Do,j}. \quad (3.31)$$

This

$$E'_{Do,i} = \left(\frac{\rho_{ij}}{\tau_{ij}} \right) E_{Up,j} + \left(\frac{1}{\tau_{ij}} \right) E_{Do,j} \quad (3.32)$$

can be written with a matrix formalism as:

$$\mathbf{E}'_i = \mathbf{H}_{ij} \mathbf{E}_j, \quad (3.33)$$

where the following definitions where used:

$$\mathbf{E}_j = \begin{pmatrix} E_{Up,j} \\ E_{Do,j} \end{pmatrix}, \mathbf{E}'_j = \begin{pmatrix} E'_{Up,j} \\ E'_{Do,j} \end{pmatrix} \text{ and } \mathbf{H}_{ij} = \frac{1}{\tau_{ij}} \begin{pmatrix} 1 & \rho_{ij} \\ \rho_{ij} & 1 \end{pmatrix}. \quad (3.34)$$

When the wave traverses a layer j from top to bottom, a phase factor of $e^{i\beta_j}$ has to be added, where

$$\beta_j = \frac{2\pi}{\lambda_0} n_j d_j \cos \theta_j,$$

where λ_0 is the wave length in vacuum, n_j is the refractive index of layer j , d_j is the thickness of layer j and θ_j is angle between the wave vector and the interface normal vector. Equivalently, a phase factor of $e^{-i\beta_j}$ has to be added, when the wave traverses layer j from bottom to top. In matrix formalism, this is written as:

$$\mathbf{E}_j = \mathbf{L}_j \mathbf{E}'_j, \quad (3.35)$$

where $\mathbf{L}_j$ is defined as:

$$\mathbf{L}_j = \begin{pmatrix} e^{i\beta_j} & 0 \\ 0 & e^{-i\beta_j} \end{pmatrix}. \quad (3.36)$$

For the last layer N , no light is coming upwards, i. e. $E_{Up,N} = 0$, and we can write as a boundary condition:

$$\mathbf{E}_N = \begin{pmatrix} 0 \\ E_{Do,N} \end{pmatrix}. \quad (3.37)$$

Combining (3.33) and (3.35) gives:

$$\mathbf{E}'_1 = \mathbf{H}_{12}\mathbf{L}_2\mathbf{H}_{23}\mathbf{L}_3 \cdots \mathbf{L}_{N-1}\mathbf{H}_{N-1,N}\mathbf{E}_N = \mathbf{S}_{1N}\mathbf{E}_N, \quad (3.38)$$

where $\mathbf{S}_{1N}$ is the system matrix which represents the combination of all effects of all layers, including the multiple reflections. With the boundary condition $E_{Up,N} = 0$ (3.37), a given incident field, e. g. $E'_{Do,1} = 1/\sqrt{2}$ to obtain an incoming intensity ($|E_s|^2 + |E_p|^2$) of 1, and the known system matrix $\mathbf{S}$, (3.38) yield the transmission and reflection coefficient⁵ ρ and τ for the whole stack:

$$\rho = \frac{E'_{Up,1}}{E'_{Do,1}} = \frac{S_{12}}{S_{22}} \text{ and } \tau = \frac{E'_{Do,N}}{E'_{Do,1}} = \frac{1}{S_{22}}.$$

Thus, the electric field at the top of each layer for both, the down- and upwards running wave, can be obtained by recursively applying:

$$\mathbf{E}_{j-1} = \mathbf{L}_{j-1}\mathbf{H}_{j-1,j}\mathbf{E}_j. \quad (3.39)$$

3.3.3 Superposition of Incident and Reflected Electric Field Components

The electric fields are added up by decomposing them into their x , y and z components, taking the phase and the polarisation into account. In case of total reflection and negligible absorption, a standing wave is formed.

Assuming unpolarised light, the intensity is equally divided into an s - and p -polarised wave. Its decomposition of the electric field vectors is easily derived from Figure 3.9:

$$\begin{aligned} E_y^r &= E_{Up,s} \\ E_y^i &= E_{Do,s} \\ E_x^r &= E_{Up,p} \cdot \cos \theta^i \\ E_x^i &= -E_{Do,p} \cdot \cos \theta^i \\ E_z^r &= E_{Up,p} \cdot \sin \theta^i \\ E_z^i &= E_{Do,p} \cdot \sin \theta^i \end{aligned}$$

The coordinate system was chosen so that the s polarised wave points only in y direction, while the p polarised wave has an x and z component.

The wave vectors of the incident and reflected wave decomposed in a similar manner from Figure 3.9:

$$\begin{aligned} k_x^r &= k_x^i = k^i \sin \theta^i \\ k_y^r &= k_y^i = 0 \\ k_z^r &= -k_z^i = -k^i \cos \theta^i, \end{aligned}$$

⁵ The transmissivity T and reflectivity R are: $T = \frac{n_N \cos \theta_N}{n_1 \cos \theta_1} |\tau|^2$ and $R = |\rho|^2$.

To reduce the number of indices, the following definitions are employed:

$$\begin{aligned} k_x &= k_x^i \\ k_z &= k_z^i. \end{aligned}$$

In the absorption measurement setup, total reflection occurs at the Si-air interfaces at the front and the back of the samples. In the following, total reflection and negligible absorption for a single transition of the light through the stack is assumed. Thus, the amplitude of the field of the incident and reflected wave are equal within every layer⁶ and can be defined as $E_0 = |E^r| = |E^i|$. The wave equation for the incident and reflected wave can be written as:

$$\begin{aligned} E^i &= E_0 e^{i(k_x x + k_z z - \omega t + \varphi^i)} \\ E^r &= E_0 e^{i(k_x x - k_z z - \omega t + \varphi^r)}, \end{aligned}$$

where φ^i and φ^r is the phase of the incident and reflected wave, respectively.

We build the sum, yielding the superposition of the electric field of the incident and reflected wave $E = E^i + E^r$ and separate the amplitude from the phase by using $\varphi^i = (\varphi^i + \varphi^r)/2 + (\varphi^i - \varphi^r)/2$ and $\varphi^r = (\varphi^i + \varphi^r)/2 - (\varphi^i - \varphi^r)/2$:

$$E = 2E_0 \left[e^{i(k_z z + (\varphi^i - \varphi^r)/2)} + e^{-i(k_z z + (\varphi^i - \varphi^r)/2)} \right] e^{i(k_x x - \omega t + (\varphi^i + \varphi^r)/2)}. \quad (3.40)$$

The expression in brackets equals $\cos(k_z z + (\varphi^i - \varphi^r)/2)$ and is real valued, i. e. its imaginary part equals zero. The amplitude of the two superimposed electric fields is the absolute value of $E^i + E^r$. As $|e^{ix}| = 1$ for all real valued x , we can omit the latter exponential function in (3.40). With these two simplifications we obtained:

$$|E| = 2E_0 \cos \left(k_z z + \frac{\varphi^i - \varphi^r}{2} \right)$$

As the integral of the square of E/E_0 determines the effective thickness d_{eff} in (3.24), (3.40) is brought into the required form, using the relation $2 \cos^2 x = 1 + \cos 2x$:

$$\left| \frac{E}{E_0} \right|^2 = 2 [1 + \cos(2k_z z + \varphi^i - \varphi^r)]. \quad (3.41)$$

Note that E_0 was defined as the absolute value of the electric field of the incident wave and is, therefore, a real positive quantity, i. e. $E_0 = |E_0|$.

By combining (3.24) and (3.41), the effective thickness d_{eff} can be written as:

$$d_{eff} = \frac{1}{\cos \theta_1} \cdot \frac{n_2}{n_1} \int_{SiGe} 2[1 + \cos(2k_z z + \varphi^i - \varphi^r)] dz, \quad (3.42)$$

where the integral has to be taken over the absorbing SiGe layers.

The square of the amplitude of the superposition of all reflected and refracted rays is obtained in (3.41) and describes a standing wave in layer j with the wavelength $\lambda_{SW} = 2\pi/(k_z) = \lambda_j / \cos \theta_j$ as illustrated in Figure 3.11.

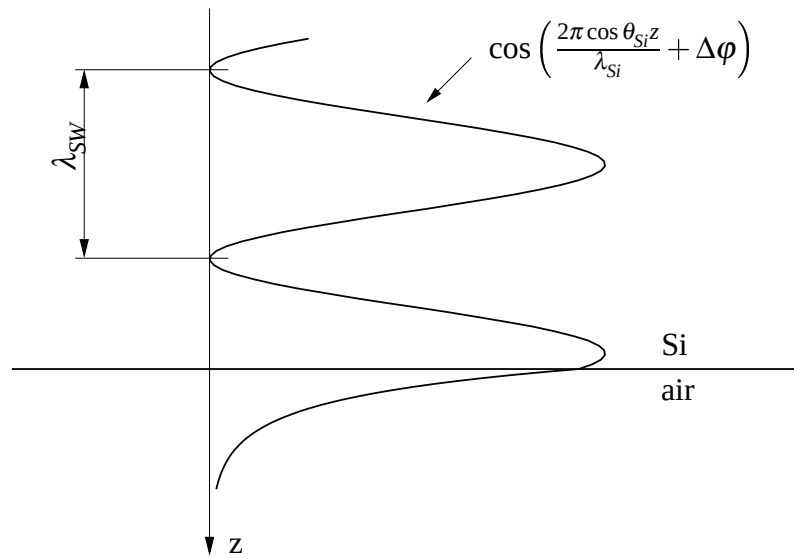


Figure 3.11: Square of the amplitude of the electric field at a totally reflecting Si-air interface. In Si a standing wave is formed, while in air an evanescent wave is obtained.

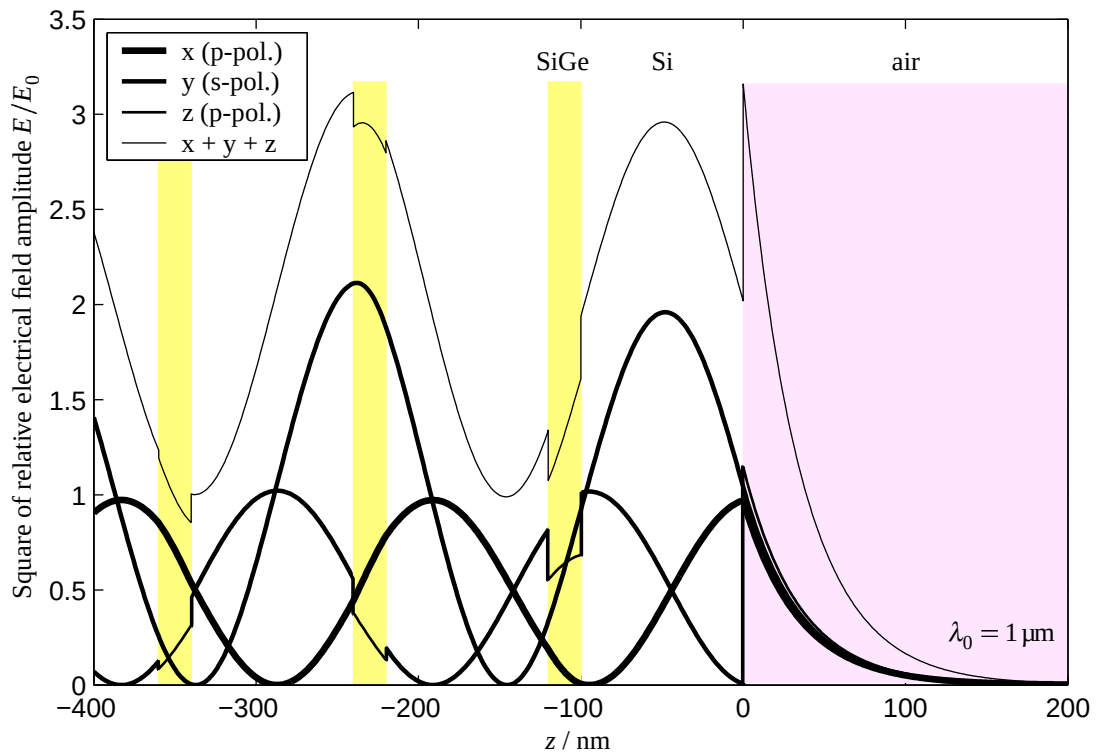


Figure 3.12: Square of the amplitude of the electric field relative to the amplitude of the electric field of the incoming wave. The angle of incidence $\theta_{Si} = 46^\circ$. The shaded areas represent air (for $z > 0$) and SiGe. In Si and SiGe a standing wave is formed, while in air an evanescent wave is obtained.

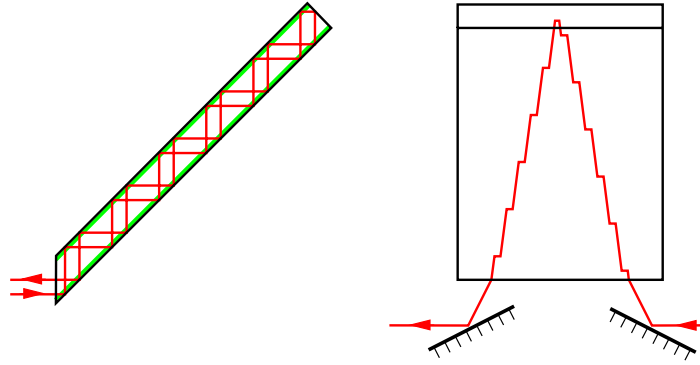


Figure 3.13: Side view (left) and top view (right) of the ray of light passing through the sample. The thickness of the sample is tenfold exaggerated, thus the number of reflections is 10 times higher, i. e. 234 and 200 for a sample thickness of $325\text{ }\mu\text{m}$ and $380\text{ }\mu\text{m}$, respectively. The SiGe structures are at the top and bottom of the sample, close to where the light is totally reflected.

3.3.4 Si/SiGe Multilayer

The computation has to be executed for x , y and z direction, in every layer and for every photon energy under consideration. In Figure 3.12, the relative amplitude of the electric field E/E_0 for the 3 directions and its sum is plotted. The abscissa represents the coordinate perpendicular to the interface (z) and at $z = 0$ the Si-air interface is positioned. The shaded patches indicate air (for $z > 0$) and SiGe (for $z < 0$). While x and y directions are continuous, the field in z direction exhibits non-continuities at each interface due to a difference in permittivity of the materials.

3.4 Measurement Setup

To increase the sensitivity of the absorption measurements, internal reflection spectroscopy was employed. The measurement setup is depicted in Figure 3.13. The ray of light coming from a halogen lamp is deflected by the first mirror towards the sample. It is coupled into the sample at its right hand side, suffering multiple total reflections within the sample and leaves it at its left hand side. A second mirror deflects the light into the detector.

The samples are made from $325\text{ }\mu\text{m}$ and $380\text{ }\mu\text{m}$ thick Si wafers that are polished on both sides and on which Si/SiGe structures are epitaxially deposited. They are cut into rectangles of the size $20 \times 38\text{ mm}^2$. The edges are polished at the short sides to 45° and 90° facets, respectively. The number of internal reflections amounts to approximately 200, leading to strong amplification of the light absorption in the SiGe structures. The transmission of the sample with SiGe wells were measured and compared to a bulk Si reference using a Perkin-Elmer Lambda 19 grating spectrometer and a Bruker Equinox 55 Fourier transform spectrometer. All measurements were performed at 295 K. To determine the absorption of the SiGe layers from the transmission measurement, a Matlab[®] programme was written for a 3D-calculation of the path of the light through the sample determining the internal reflec-

⁶ This holds also true when decomposed into the 3 directions, i. e. $|E_x^r| = |E_x^i|$, etc. Thus the x , y and z subscripts are omitted for simplicity.

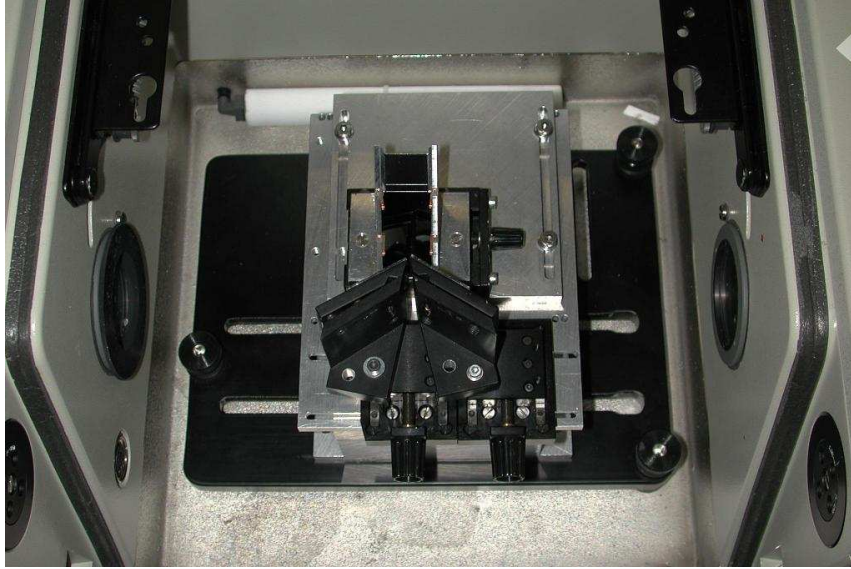


Figure 3.14: Absorption measurement setup in the Fourier transform spectrometer. The sample is the dark rectangle in the centre of the picture. Its lower end with the 45° facet is behind two mirrors. The light enters the sample chamber from the right, is deflected by the first mirror into the direction of the sample. The focus of the light is close to the right hand side of the 45° facet. The path of the light through the sample is depicted in Figure 3.13. The light, after leaving the sample at the left hand side of the 45° facet, gets deflected by the second mirror into the detector.

tion angle at the front and back surface Θ_{Si} and the number of reflections N . With the help of this programme, it could be proved that the change in refractive index of Si n_{Si} with the wavelength of the light and the divergence of the ray influences the number of reflections and the reflection angle Θ_{Si} only insignificantly.

A photograph of the sample setup and the two adjustable mirrors is shown in Figure 3.14. A sample made of quartz was fabricated, which allowed to see by eye the light after passing through the sample and served to adjust the mirrors and the sample. As the refractive index of quartz is much smaller than that of Si, the sample had to be significantly shorter, when the path of the light outside the samples should be the same for both, the Si samples and the quartz sample. The appropriate length of the quartz sample could be determined with the help of the above mentioned computer programme. After the first adjustment of the setup, no further changes were made at the first mirror in order to optimise the reproducibility of the measurements. However, for each measurement, the second mirror was adjusted for maximum light intensity on the detector.

3.5 Measurement Accuracy, Reproducibility and Artefacts

Figure 3.15a shows the raw transmission data versus photon energy of a SiGe sample and a Si reference sample. Photons with a higher energy than the band gap energy are absorbed and photons with a lower energy are mostly transmitted, resulting in the sharp drop in the

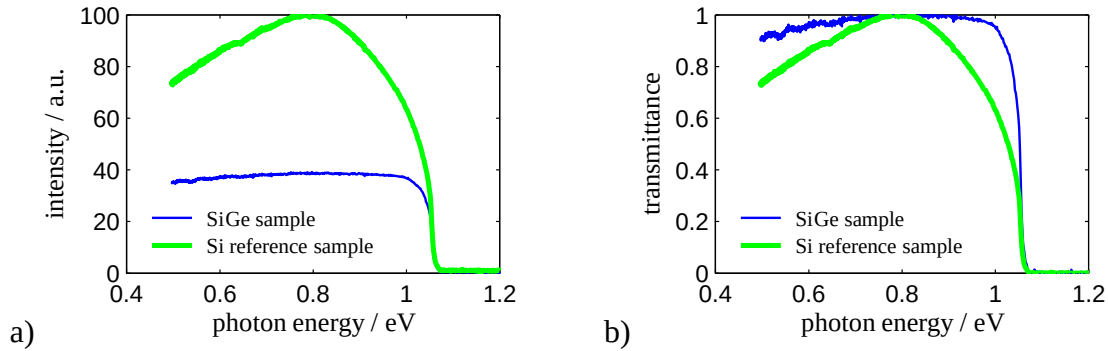


Figure 3.15: a) Raw transmission data of a SiGe sample and a Si reference sample as a function of the photon energy measured with a Perkin Elmer grating spectrometer. b) Same data as in a) but scaled to obtain the transmittance under the estimate that the absorption is negligible for some photon energy, i. e. scale the maximum to 1.

curve. The SiGe sample shows additional absorption below the Si band gap due to the absorption of the SiGe structures. Both of the samples are made from a 1-10 Ωcm substrate and measured with a Perkin Elmer Lambda 19 spectrometer. It uses a sensor that is strongly non-linear and, thus, the intensity is measured by adjusting the size of a slit positioned in front of the sensor so that the sensor delivers a constant signal. The measured intensity is derived from the size of the slit.

In the following, principle measurement problems derived from Figure 3.15a and their reasons are summarised:

- A dent around 0.63 eV, which is more expressed in the SiGe sample, but could be found in all samples measured. This could be traced back to a side effect of the Perkin Elmer grid spectrometer (in particular to the variable slit with) as it also showed when replacing the sample with a slit of the size of the 45° facet of a sample.
- In the low photon energy region, where both samples are expected to be completely transparent, their transmission differ by a factor of more than 2. This is on the one hand due to the way the measurement was conducted – an absolute measurement was not intended in favour of an increased signal-to-noise ratio – and on the other hand, tiny geometrical differences seem to have a significant effect.
- The drop of the intensity towards lower photon energies: This could at least partly be attributed to free carrier absorption. The relatively wide specification of the conductivity of the substrate (1-10 Ωcm) allows for significant differences between samples, which could explain the differences between the samples. A significant influence of free carriers in the epitaxial layers could be ruled out by conductivity measurements.

The last two items are discussed in the following.

The effective transmission is obtained by dividing the transmission of the SiGe sample by the transmission of the Si reference sample. However, this implies that the transmissions are measured on an absolute scale. This can be achieved by assuming total absorption for photon energies < 1.1 eV and total transmission for photon energies 200 meV below the

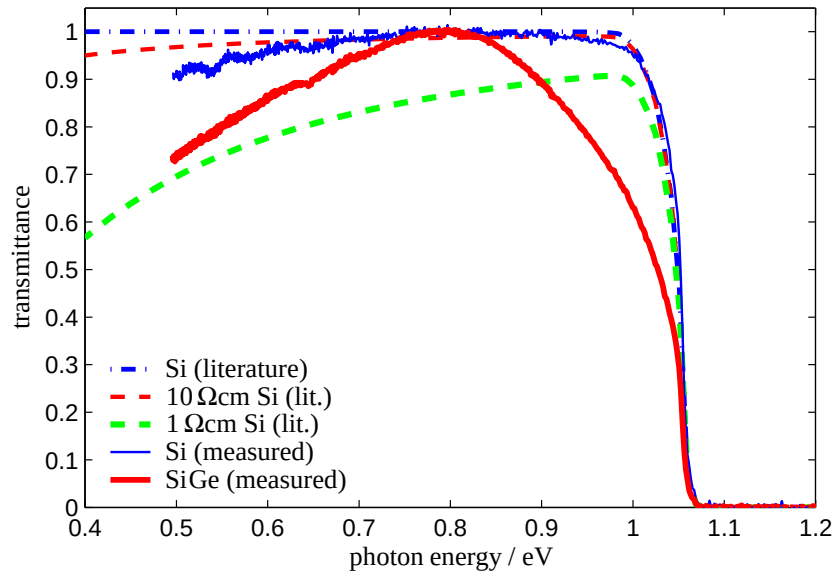


Figure 3.16: Transmission of SiGe sample and Si reference sample (thick and thin solid line) in comparison with transmission calculated from literature data [39], taking free carrier absorption of undoped and 1 and 10 Ωcm n doped Si into account (dashed lines). The doping concentration of the substrate the samples are made of is specifies as 1-10 Ωcm n type.

band gap of the material under investigation. The error bar for this operation calculated for Si with literature absorption coefficients [39] is $< 10^{-6}$. Due to the problems described above, the scaling was performed so that the average value for photon energies between 1.1 and 1.2 eV is 0 and the maximum of the curve averaged over 25 consecutive points becomes 1, by adding an offset and multiplying with a photon energy independent factor. The result is the transmittance⁷, shown in Figure 3.15b. The decrease in intensity towards low photon energies is much more marked for the SiGe sample than for the Si reference sample, leading to the investigation of the free carrier absorption.

3.6 Experimental Results

The absorption coefficient is obtained by measuring the transmission of a sample with SiGe structures and an equally shaped Si reference sample. By dividing the transmission of the SiGe sample by the transmission of the reference sample, the influence of the Si substrate is cancelled out and the effective transmission of the SiGe structures is obtained, leading together with the effective thickness (see section 3.3) and the number of reflections to the absorption coefficient of the SiGe structures.

3.6.1 Impact of Free Carrier Absorption

The free carrier absorption is calculated with the Drude model. It predicts that the absorption coefficient is proportional to the square of the wavelength. An empirical model was first presented by Schroder [41]. The absorption coefficient due to the absorption of free carriers α_{FC} is [42]:

$$\alpha_{FC} = 1 \cdot 10^{-24} n \lambda^2 + 2.7 \cdot 10^{-24} p \lambda^2, \quad (3.43)$$

where α_{FC} is measured in cm^{-1} , the electron and hole density n and p is measured in cm^{-3} and the wavelength λ is measured in nm.

Figure 3.16 shows the transmittance of the Si and SiGe sample shown in Figure 3.15b (solid lines) in comparison with data calculated from literature (dashed lines), using $T = \exp(-(\alpha_{Si} + \alpha_{FC}) \cdot l_{Si})$, where α_{Si} is the absorption coefficient of Si taken from [39]⁸, α_{FC} as given by (3.43) and l_{Si} is the length of the path the light takes through the sample, i. e. 11.8 cm. The curves taken from literature data are calculated for undoped and n doping concentration of $4.5 \cdot 10^{14}$ and $5.0 \cdot 10^{15} \text{ cm}^{-3}$, representing the upper and lower bound of the specification of the resistivity of the substrate used ($1\text{-}10 \Omega\text{cm}$). The theoretical curve for the highest doping concentration has a maximum transmittance of 0.9, revealing a considerable high systematic error being introduced when scaling to 1. This systematic error strongly depends on the doping level. As its error bar is nearly as big as its average value, it was not corrected for. Note that small differences of Si transmissivities between the literature and the measurement can be explained by photon energy dependent reflectivity of the two mirrors and two Si/air interfaces involved in the measurement set-up.

The solution to the free carrier absorption problem was to use higher ohmic substrates. In order to exclude effects originating from the spectrometer, e. g. the dent around 0.63 eV, the set-up was adapted for a different spectrometer.

3.6.2 Benefit of the Fourier Transform Spectrometer

Figure 3.17a shows the raw transmission measurement data of a SiGe and a Si reference sample measured with a Bruker Equinox 55 Fourier transform spectrometer. In comparison with the measurements from the Perkin Elmer grating spectrometer shown in Figure 3.15, the data measured with the Bruker spectrometer are clearly advantageous in the following respects:

- Noise: The signal-to-noise ratio of the Bruker spectrometer is vastly improved. This, however, comes with an increase in solid angle of the incoming light.
- The spectral range towards lower photon energies is limited to 0.5 eV when using the Perkin Elmer, while it is practically limited to about 0.2 eV by the lack of intensity of the light reaching the sample when using the Bruker spectrometer.

⁷ Transmittance is the fraction of incident light at a specified photon energy that passes through a sample. Note that the term transmission refers to the physical process of light passing through a sample, whereas transmittance refers to the mathematical quantity. [40]

⁸ In addition to the literature data, the absorbance of pure Si was assumed to be negligible for photon energies $< 0.85 \text{ eV}$.

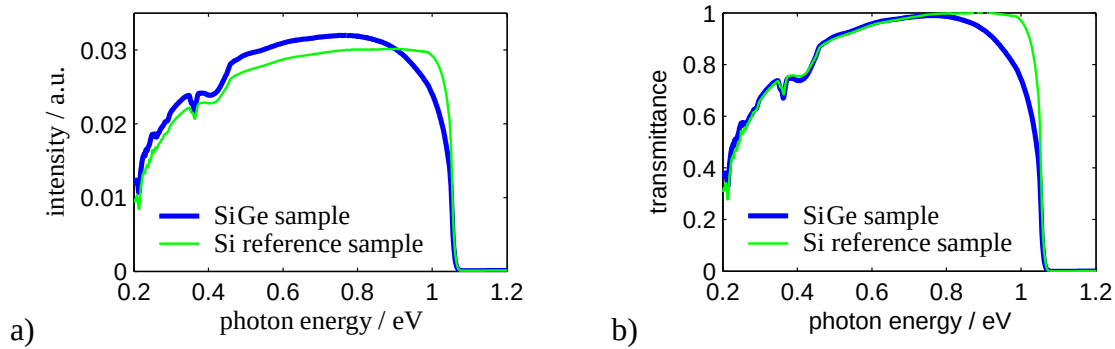


Figure 3.17: a) Raw transmission data of a SiGe sample and a Si reference sample as a function of the photon energy measured with a Bruker Fourier transform spectrometer. b) Same data as in a) but scaled to overlap at around 0.7 eV. The excellent overlap for photon energies < 0.8 eV indicates that the systematic error introduced by the scaling is small.

- Most importantly, the spectral shape in the low photon energy region between 0.5 and 0.8 eV is well preserved, allowing to scale the two curves in a much cleaner way, avoiding the systematic error due to scaling mentioned above.

Rather than scaling the maximum to 1, the two curves are scaled to overlap around 0.7 eV. The result is shown in Figure 3.17b. The two curves overlap excellently below 0.7 eV. The decrease in transmittance towards lower photon energies is still present and cannot be explained by free-carrier absorption as it is insignificant for the doping concentration of the substrate of the samples. Thus, another absorption mechanism, e. g. transition via deep levels, causes absorption at the low photon energy end. In fact, its existence is irrelevant in so far as a resulting absorption coefficient can only be given in the photon energy range from about 0.8 to 1.05 eV, especially as the absorption in both, the SiGe and the Si reference sample, are the same below 0.8 eV, giving a high degree of confidence that this method of scaling does not give rise to a significant systematical error.

An absolute measurement of the transmission would be desirable. In principle, this would be much easier to achieve with the Bruker spectrometer in comparison with the Perkin Elmer spectrometer. But different measurements of the same sample yield different intensities, while the spectral shape remains reasonably well preserved. This is illustrated in Figure 3.18 showing different measurements of the transmission of a Si reference sample, where the transmission is relative to the transmission of a blank measurement T_0 , i. e. the measurement of the empty, N_2 purged sample chamber. The differences can only be explained by the differences in the set-up, i. e. small adjustments of the second mirror to maximise the detector signal and positioning of the sample as nothing else has been changed. This is the case albeit great care was taken to always position the sample at the same place, to control the temperature to the same value within an accuracy of 0.5°C and to switch on the light source (a halogen lamp) the day before to ensure that its intensity changes as little as possible between the blank measurement and the measurements of the samples.

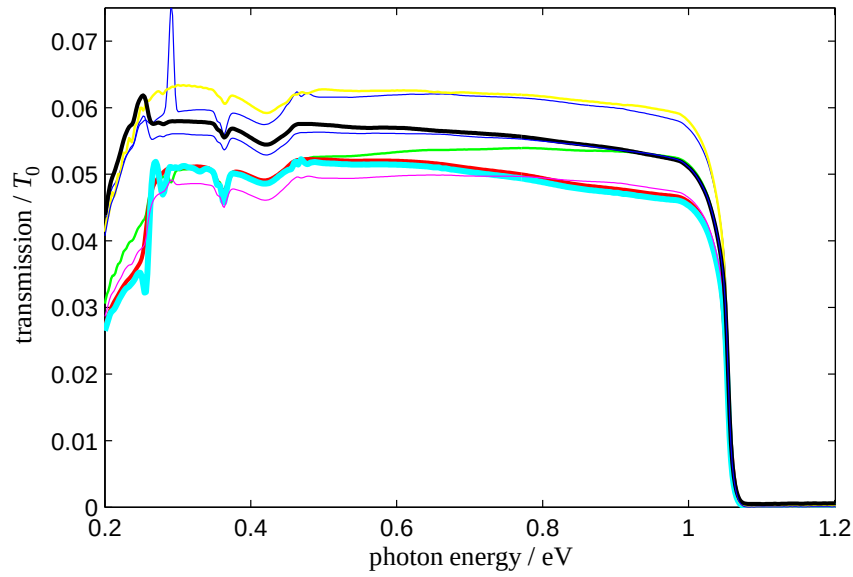


Figure 3.18: Transmission of different measurements of the Si reference sample as a function of the photon energy. T_0 is the transmission of the empty, N_2 purged sample chamber. The spectral shape is reasonably well preserved, but a transmission measurement on an absolute scale is not reproducible.

Table 3.1: Number of wells n , QW thickness d_{SiGe} and Ge concentration x , of the measured samples with the calculated minimum transition energy from the lowest conduction band to the heavy and light hole band E_g calculated with (3.13).

n	d_{SiGe} nm	x	E_g meV
30	3.3	0.3	860
10	5.4	0.45	690
20	3.4	0.45	720
40	2.5	0.45	750

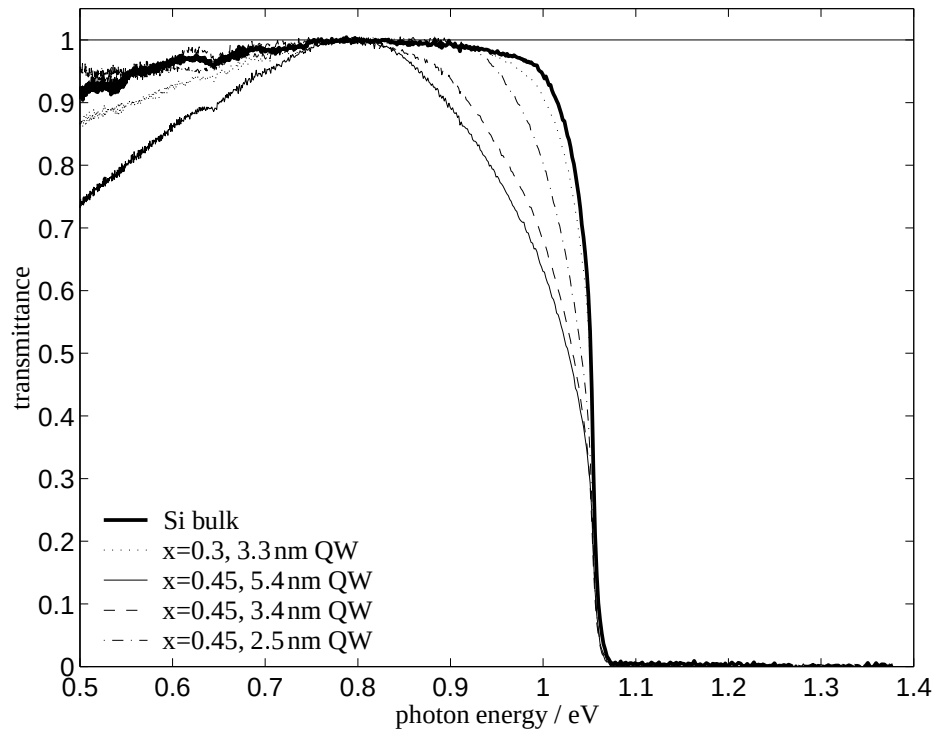


Figure 3.19: Measured transmittance of four $\text{Si}_{1-x}\text{Ge}_x$ samples with different well thickness compared to a Si bulk reference.

3.6.3 Measurements with Grating Spectrometer

The first approach with respect to instrumentation was the Perkin-Elmer Lambda 19 grating spectrometer. It has the advantages over the Bruker fourier transform spectrometer that it offers a well adjusted halogen lamp as light source, is less temperature dependent and delivers the light in a smaller solid angle to the sample.

Four samples with different quantum well (QW) thicknesses were investigated of which three have a Ge concentration of 0.45 and one of 0.3 (see Table 3.1). Si wafers with a thickness of $380\text{ }\mu\text{m}$ and a resistivity of $1\text{--}10\text{ }\Omega\text{cm}$ were used as substrates. Figure 2.12 shows as an example a TEM micrograph of the structure with $5.4\text{ nm Si}_{0.55}\text{Ge}_{0.45}$ wells. Due to strain a wavelike structure is formed, which is much less marked in all other samples. The ratio of Si to SiGe layer thickness was determined by measuring them on the TEM micrographs. The statistics of these multiple measurements resulted in a standard deviation of 10–20%, depending on the waviness of the structure of the sample. X-ray diffractometry (see Figure 2.16) yields the period (with negligible inaccuracy) and the Ge concentration with an estimated error bar of 10 to 20%. Investigations with X-ray diffractometry of variations across the wafer resulted in another 10 to 20% for both, the Ge concentration and the thickness of the SiGe layer.

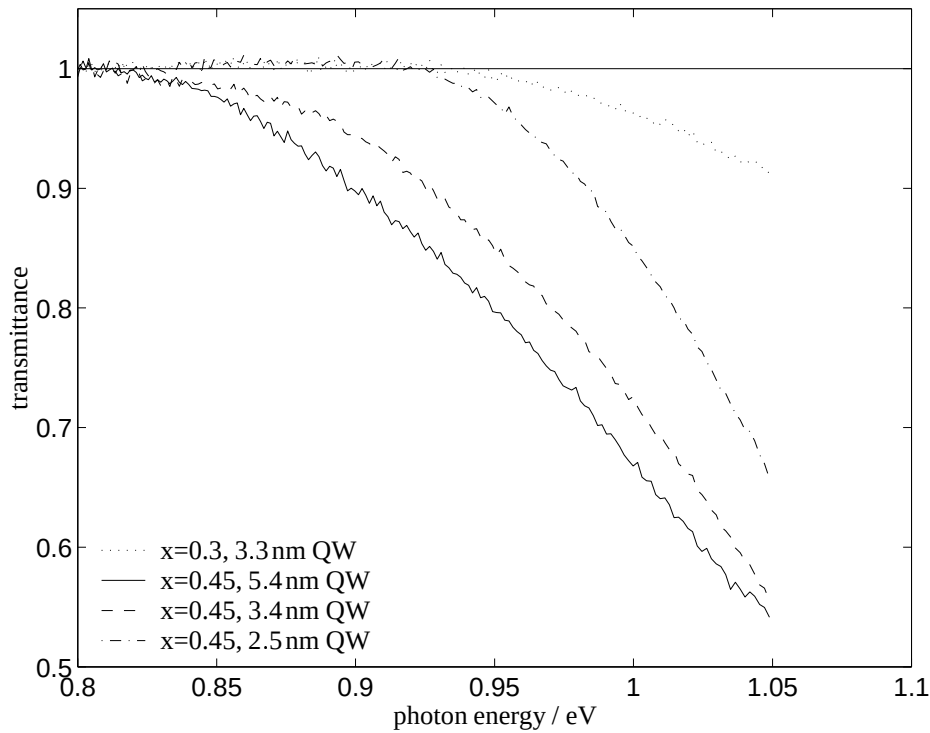


Figure 3.20: Effective transmittance ($T_{\text{SiGe}}/T_{\text{Si}}$) of the SiGe structures in $\text{Si}_{1-x}\text{Ge}_x$ samples with different well thickness and Ge concentrations x .

Transmission Measurements on Samples with SiGe Structures on Si Substrates

Under the presumption that the sample is completely transparent for low energy photons and completely absorbing for high energy photons, the raw data of the transmission measurement were scaled so that the minimum and the maximum of the smoothed⁹ curve becomes 0 and 1, as described above. The transmittance obtained is shown in Figure 3.19 for one reference sample of pure Si and the four samples with SiGe QWs on the Si substrate.

The SiGe samples show an increased absorption below the Si bandgap. For all samples a significant decrease of the transmittance at photon energies below 0.8 eV was detected. This effect is not completely understood up to now. Although measurements indicate that it is independent of temperature in the range of 20°C to 100°C, this effect can at least partly be attributed to free carrier absorption (see (3.43)).

Effective Transmission of SiGe Structures

To obtain the effective transmittance of the SiGe layers without the contribution of Si substrate, the transmittance of the SiGe sample was divided by the transmittance of the Si reference sample. The result is shown in Figure 3.20. The transmittance decreases for the samples with high Ge content. For the samples with the high Ge content, the transmittance

⁹ The smoothing was done by averaging 25 consecutive data points.

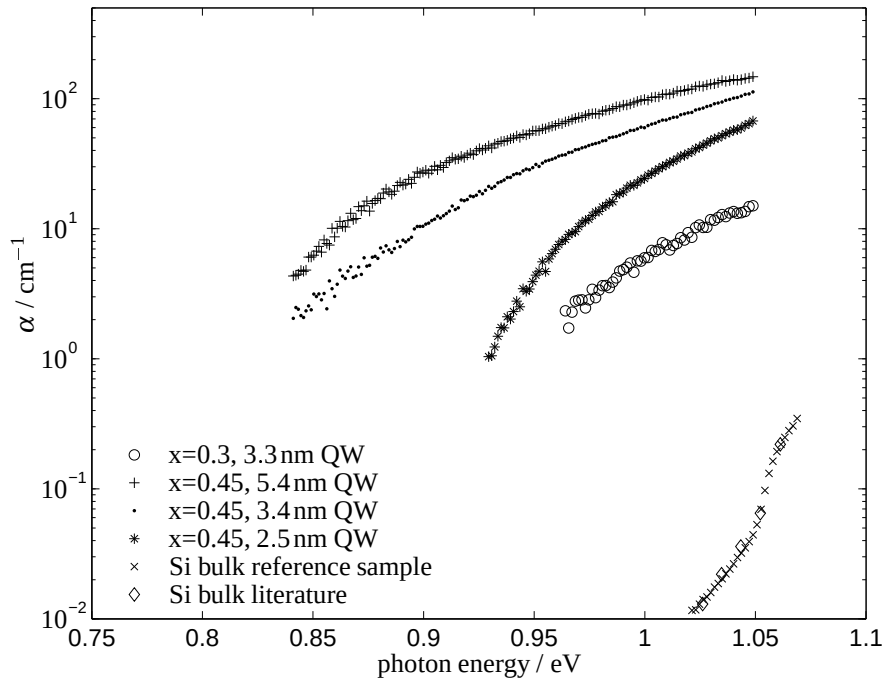


Figure 3.21: Absorption coefficient α of $\text{Si}_{1-x}\text{Ge}_x$ samples with different well thickness and for the reference Si bulk sample in comparison with Si bulk literature data [39].

decreases with increasing well width. For a comparison of the samples between each other and with bulk SiGe, the absorption coefficient, as defined in (3.18), which is independent of well width and number of wells has to be used.

Absorption Coefficient of SiGe Structures

From the effective transmittance and the effective thickness calculated by (3.24) the absorption coefficient was obtained. The absorption coefficient of the samples in comparison with bulk Si literature data [39] is shown in Figure 3.21 from which the following results are inferred:

- The measured absorption coefficient from the Si reference sample is in excellent agreement with literature values [39].
- The comparison of three QW samples with $x = 0.45$ shows that the absorption coefficient is smaller for the samples with thinner wells. In QWs the transition energies are increased due to the confinement shift with decreasing well thickness.

The accuracy on the absorption coefficient is determined by the uncertainty of the SiGe layer thickness, which is 30%. From the measured Ge concentrations and well thickness, the minimum transition energy for electrons from the confined states in the heavy and light hole band to the lowest conduction band were calculated and are shown in Table 3.1. The accuracy of the calculated transition energies is determined by that of the effective mass

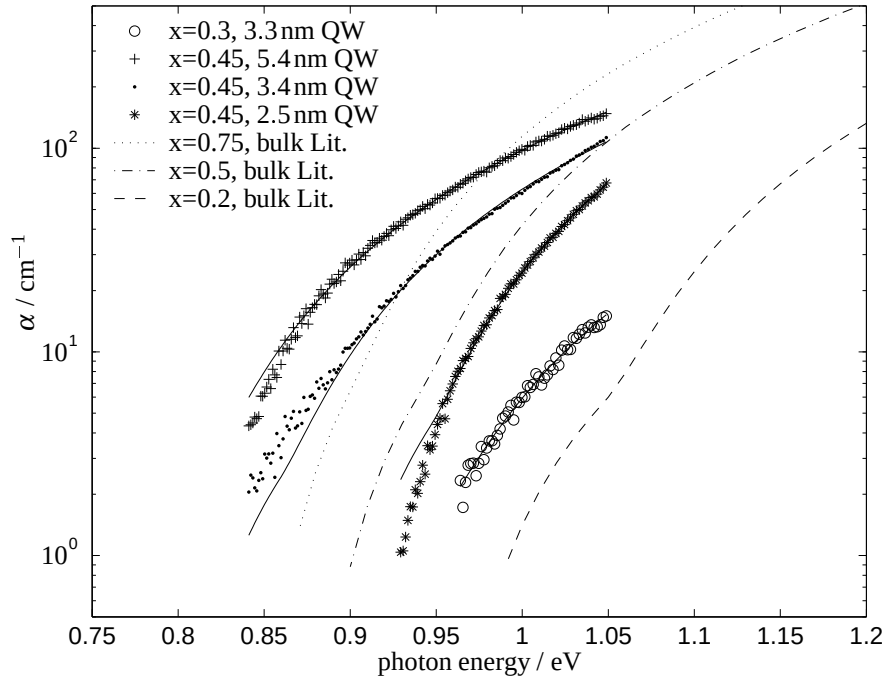


Figure 3.22: $\text{Si}_{1-x}\text{Ge}_x$ absorption coefficient α of the measured samples in comparison with bulk literature data. The solid lines are least square fits of parameters in (3.14) to the measured data.

(data from [31] were used), the well width and the calculation of the influence of strain (30 – 50 meV). In total, the error bar on the transition energies is estimated to 100 meV.

Discussion

The absorption coefficient for the SiGe QW samples in comparison with bulk SiGe literature data [43] is shown in Figure 3.22 from which the following can be seen:

- The 5.4 nm $\text{Si}_{0.55}\text{Ge}_{0.45}$ sample has a significant higher absorption coefficient for photon energies below 1.05 eV than the bulk $\text{Si}_{0.5}\text{Ge}_{0.5}$ material. This is well explained by the reduction of the bandgap due to strain. The strain has a stronger influence than the 5% difference in Ge concentration.
- To compare the absorption in bulk and in QWs, the absorption in bulk material with comparable minimum transition energy (i.e. bandgap for bulk) is considered¹⁰: For bulk $\text{Si}_{0.25}\text{Ge}_{0.75}$ a bandgap of 870 meV was obtained¹¹ being comparable with the minimum transition energy of 860 meV of the sample with 3.3 nm $\text{Si}_{0.7}\text{Ge}_{0.3}$ QWs. Figure 3.22 clearly shows that the absorption coefficient of the 3.3 nm QW sample is about one order of magnitude lower than that of bulk $\text{Si}_{0.25}\text{Ge}_{0.75}$ material.

¹⁰ The bandgap is an important parameter for electronic properties of a semiconductor, e.g. it mainly determines the open circuit voltage of a photocell.

¹¹ The bandgap E_g and the proportionality factor A were obtained by fitting literature data [43] to (3.14) with the equivalent phonon temperature taken from [27].

- α is below 1/cm for all samples at the photon energy corresponding to the minimum transition energy (see Table 3.1). In a similar way, the onset of the light induced current from SiGe photocells appears at higher photon energies than expected from the theoretical minimum transition energy as described in the literature [44].
- The solid lines through the measurement data points are the least square fits of (3.14). Although this equation contains only absorption mechanisms of bulk semiconductors, the Macfarlane-Roberts expression fits the data astonishingly well, confirming findings in [45, 46]. Quantum effects, like kinks in the absorption coefficient, which can be expected from the DOS given in Figure 3.6, are not visible.

Conclusions

Our strained SiGe layers show a strong increased absorption coefficient compared to bulk material with an identical Ge content. But the onset of the absorption appears at higher photon energies than expected from a theoretical calculation of the minimum transition energy. Quantum effects, which are expected to cause bucklings in the absorption coefficient, were not observed. Furthermore, our measurements show no evidence that the absorption in QWs is enhanced due to spatial confinement. To achieve absorption of at least 10% in a strained SiGe structure with 100nm total thickness and a light trapping factor of 10, α should be at least 10^3 cm^{-1} . For photon energies below 1.05 eV the absorption coefficient in our SiGe samples is at least one order of magnitude too low to reach 10% absorption under the afore mentioned conditions. Whether SiGe QWs can be used to sufficiently increase the infrared sensitivity of photocells, therefore, remains uncertain. Possibly, structures providing a higher degree of confinement – quantum wires or quantum dots – may lead to an absorption enhancement at low photon energies.

3.6.4 Measurements with Fourier Transform Spectrometer

In order to circumvent some of the problems discussed in section 3.5, the absorption measurement set-up was adapted for the Bruker Equinox 55 Fourier transform spectrometer and a substrate material with a resistivity of 88-102 Ωcm was chosen to prevent free carrier absorption from influencing the measurement.

A series of samples with a stack of multiple SiGe wells between Si spacers was targeted to have different well widths (different degree of confinement), but the same minimum transition energy. The minimum transition energy $E_g = E_{g,\text{Si}} - \Delta E_g$, where E_g is the Si band gap and ΔE_g is the energy difference between the ground state of the quantum well and the Si valence band edge $E_{VB,\text{Si}}$ depicted in Figure 3.5. Two quantum wells with different thickness can have the same ΔE_g , if the thinner is made deeper. In the SiGe material system, this can be achieved by increasing the Ge concentration in the thinner well, as illustrated in Figure 3.23. By measuring the absorption coefficient and comparing the result to a bulk SiGe with the same minimum transition energy (band gap), it is investigated whether confinement has a significant influence on the absorption coefficient.

Two QW samples came out close enough to the expectations to fit into the series. TEM micrographs of them are shown in Figure 2.8 and Figure 2.9 and X-ray diffraction

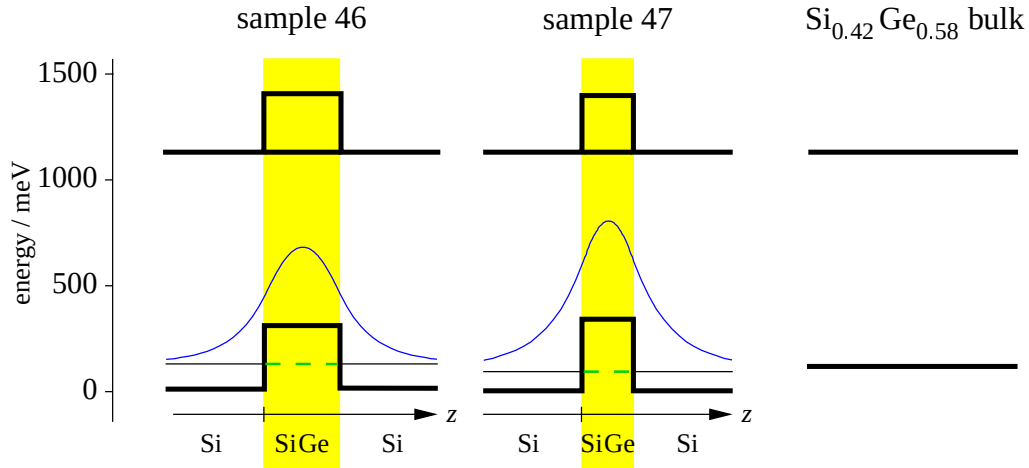


Figure 3.23: Highest valence band edges, i. e. that of the heavy holes, and lowest conduction band edges of two samples with a SiGe QW between Si spacers in comparison with a bulk $\text{Si}_{0.42}\text{Ge}_{0.58}$ (thick lines). The dashed lines indicate the allowed energy states in the quantum wells with the thin lines above are the probability densities of the holes. Note that all three have approximately the same minimum transition energy (being the band gap for a bulk semiconductor). The energy scale is relative to the highest Si valence band edge.

Table 3.2: Minimum transition energy of SiGe QW samples shown in Figure 2.8 and Figure 2.9 in comparison with band gaps of bulk SiGe with three different Ge concentration. The values in parentheses are estimated accuracies. The two QW samples and $\text{Si}_{0.42}\text{Ge}_{0.58}$ bulk have similar minimum transition energies, while $\text{Si}_{0.7}\text{Ge}_{0.3}$ has a minimum transition energy equal to the upper accuracy limit of the two QW samples and $\text{Si}_{0.25}\text{Ge}_{0.75}$ has a minimum transition energy equal to one third of the lower accuracy limit of the two QW samples. The latter two were used to for the error bar of the absorption coefficient in Figure 3.26. The effective width is the width in which the probability to find a hole is 68%.

sample	Ge concentration %	well width nm	min. trans. energy meV	eff. well width nm
46	40 (± 8)	1.7 (-40% +75%)	882 (-130 +100)	1.9 (-0.0 +0.9)
47	45 (± 8)	1.1 (-40% +75%)	900 (-130 +80)	2.1 (-0.4 +1.3)
bulk	58	-	893	-
bulk	30	-	983 = 893+90 ¹²	-
bulk	75	-	857 = 893-34 ¹³	-

measurements in Figure 2.19 and Figure 2.20. See section 2.8 for the discussion of how the thickness and Ge concentration of the SiGe layers and their error bars were determined.

The quantum wells in sample 46 are considerably wider than those in sample 47, i. e. 1.7 nm as opposed to 1.1 nm. However, the probability to find a hole inside the well is much smaller for the thinner well. It can be derived from the probability densities of the holes depicted in Figure 3.23 and is 62% and 44% for sample 46 and 47, respectively. In

¹²Mean of the minimum transition energy *plus* mean error bar

¹³Mean of the minimum transition energy *minus* one third of mean of error bar

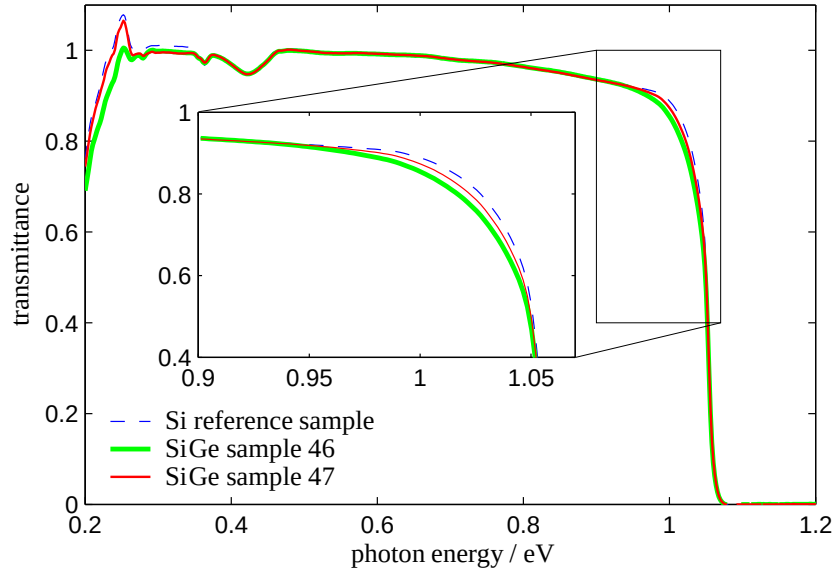


Figure 3.24: Transmittance of a Si reference sample (dashed line) and the 2 SiGe samples 46 and 47 shown in Figure 2.8 and Figure 2.9 (thick and thin solid line) as a function of the photon energy measured with a Bruker Fourier transform spectrometer. The overlap of the three samples is excellent for photon energies between 0.35 and 0.95 eV. Due to the small amount of SiGe deposited, the additional absorption of the SiGe is only visible in the small range of photon energies depicted in the inset.

order to be able to compare the localisation of holes in different samples with each other, the effective well width is defined – in similarity to Gaussian wave packets – as the width in which the probability of finding the hole is 68%. The probability density as drawn in Figure 3.23 is a sine within the well and an exponential decay outside. Due to the stronger decay of the wider well, the effective width of the wider well is smaller than that of the thinner well, i. e. 1.9 nm and 2.1 nm for sample 46 and 47, respectively (see also Table 3.2).

Transmittance

The transmittance of two SiGe samples (solid lines) in comparison with a Si reference sample (dashed lines) as obtained by the overlapping method described in section 3.5 is plotted in Figure 3.24. The excellent overlap of the three curves for photon energies between 0.35 and 0.9 eV proves the validity of the overlapping method. The absorbance of SiGe sample and Si reference sample differ only in the photon energy interval between 0.95 and 1.05 eV significantly. Thus, results only in this interval can be derived.

The effective transmittance of the SiGe structures is obtained by dividing the transmittance of the SiGe sample by the transmittance of the Si reference sample. It is plotted against the photon energy in this interval in Figure 3.25. The thicker wells with the lower Ge concentration has a stronger absorption than the thinner SiGe wells with higher Ge concentration.

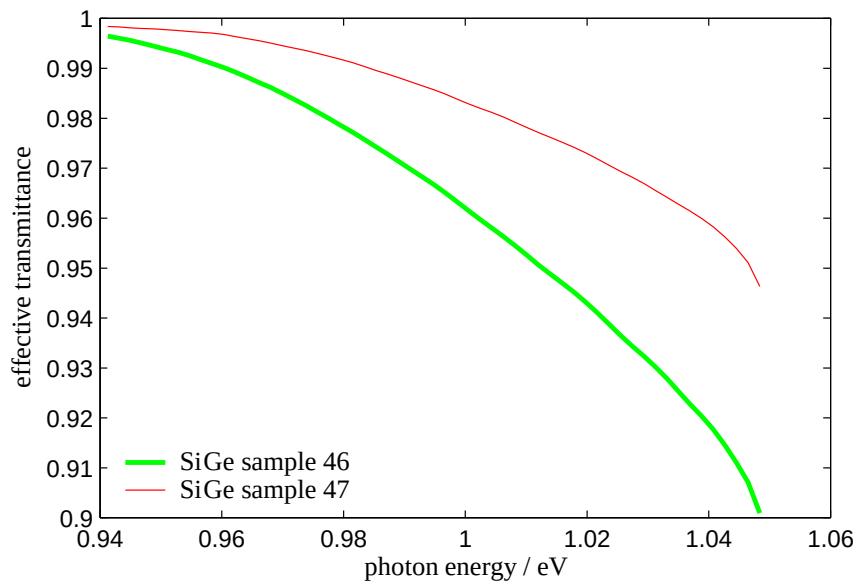


Figure 3.25: Effective transmittance of SiGe sample 46 and 47 shown in Figure 2.8 and Figure 2.9 as a function of the photon energy. The curves are derived from the data shown in Figure 3.24.

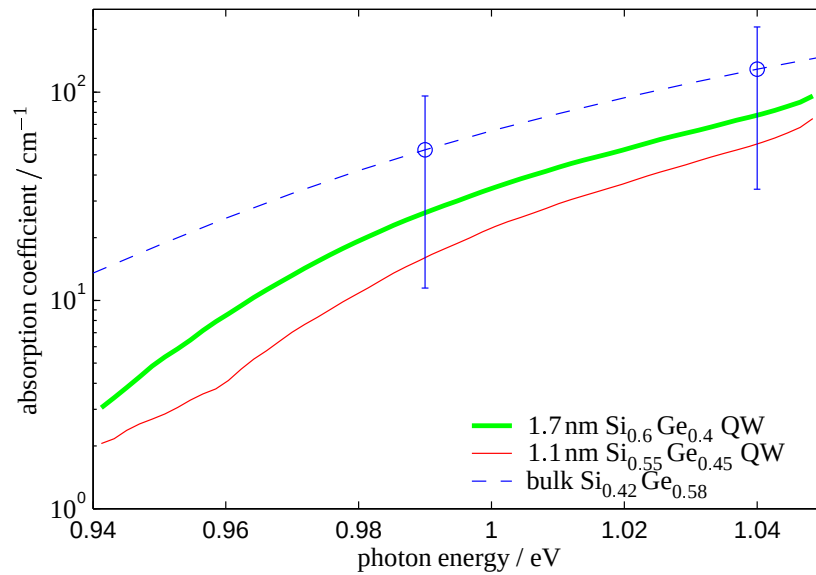


Figure 3.26: Absorption coefficient of SiGe quantum well (QW) samples with well thicknesses of 1.7 nm (sample 46) and 1.1 nm (sample 47) shown in Figure 2.8 and Figure 2.9 in comparison with interpolated literature data [43] of unstrained bulk $\text{Si}_{0.42}\text{Ge}_{0.58}$ as a function of the photon energy. The QW curves are derived from the data shown in Figure 3.25. For all samples a minimum transition energy between 880 meV and 900 meV was calculated. The error bars refer to the bulk absorption coefficient and include estimated accuracies of the minimum transition energy. The upper ends of the error bars refer to one third of the calculated error (see text and Table 3.2).

Absorption Coefficient

Being thickness independent, the absorption coefficient is the quantity best suited to compare materials with each other with respect to their light absorbing properties. It is calculated by taking the effective thickness (3.24) into account. It is depicted for the two quantum well (QW) samples as well as for bulk SiGe in Figure 3.26. The Ge concentration of bulk SiGe was chosen so that its band gap is of a similar value as the minimum transition energy of the SiGe QW samples. The absorption coefficient of bulk SiGe are linear interpolations from [43] of Ge concentrations of 50 % and 75 %.

In order to determine the significance of the data, an error bar was estimated for Si Ge bulk, which can be considered representative for the error bars of all samples. From the estimated error bar of the Ge concentration and the well width of the QW samples, an upper and lower limit for the minimum transition energy was calculated. Bulk $\text{Si}_{0.7}\text{Ge}_{0.3}$ and $\text{Si}_{0.25}\text{Ge}_{0.75}$ have band gaps equaling these minimum transition energy limits. For these Si Ge alloys, the upper and lower limits of the absorption coefficient are obtained for literature data[43]. Table 3.2 gives an overview of the sample properties and their accuracies. The details of the error bar estimates are presented in the following paragraph.

All errors that influence the three curves in Figure 3.26 alike, e. g. in the calculation of the band gap, are neglected. Furthermore, the error in the calculation of the reduction of the bandgap by strain is neglected as well, because it can be considered small compared to the errors accounted for. The error bar for the minimum transition energy is calculated from an estimated accuracy of ± 0.08 in the Ge concentration and -40% and $+75\%$ for the well width. From the minimum transition energy, a bulk Ge concentration with an equivalent band gap is searched. However, the minimum band gap of SiGe is at the Δ direction in reciprocal space for Ge concentrations $< 87\%$ and at the L point for Ge concentrations $> 87\%$ (see also section 3.1 and [28]). Thus a search for a Ge concentration with a band gap of about 763 meV (893 – 130 meV), the lower limit of the estimated error of the band gap) leads to Ge concentration $> 87\%$ and to a comparison of transitions in which two different conduction band valleys are involved. This is circumvented by choosing a Ge concentration of 75 % to ensure that the Δ conduction band valley has the main influence and the absorption mechanism is comparable. Thus, the error bars in Figure 3.26 have different meanings for their upper ends than for their lower ends, being the estimated accuracy for its upper end and one third of the estimated accuracy for the lower end.

Discussion and Conclusion

The absorption coefficient plotted in Figure 3.26 is about a factor of 3 to 8 higher for bulk Si Ge than for the QW sample with the thinnest wells. Although the error bar is slightly larger than the difference between the curves, a tendency that the absorption coefficient decreases with decreasing well width can be observed. This confirms the results of section 3.6.3 and [47] where a comparable experiment yielded a factor > 10 , but contrasts the expectation that confinement increases absorption, as discussed in chapter 1.

A possible explanation for this is that the strain induced shift of the band edges is a split of two – in the case of unstrained material degenerated – bands in nature and reduces the band gap for one band edge, while increasing it for the other Figure 3.6. As a consequence, the density of states (DOS) in the band edges forming the band gap is effectively reduced,

leading to a decreased transition probability and absorption. A potential increase in absorption due to confinement effects could not compensate for its strain induced decrease. The logical step forwards to increase confinement effects, i. e. reduce the size of the structures, is presented in the next chapter.

3.7 Summary

For several quantum well samples, the absorption coefficient was determined. Quantum wells have a higher absorption coefficient than bulk SiGe with the same Ge concentration (see Figure 3.22), due to strain that reduces the band gap. It could be shown that the confinement shift compensates this effect only by a fraction, even for very small structures. Comparing two quantum well samples and bulk SiGe with the same minimum transition energy indicates a decreasing absorption coefficient with decreasing well width as depicted in Figure 3.26. A possible explanation is that the splitting of the valence and conduction bands leads to an effective reduction of the density of states at the edges of the bands. As a consequence, the probability for a transition decreases and so does the absorption coefficient. An indication of an increased absorption due to confinement effects could not be observed. The for photovoltaic applications necessary absorption coefficient is at least one order of magnitude too low for photon energies below 1.05 eV. Thus, it remains uncertain, whether SiGe quantum wells can be used to sufficiently increase the infrared sensitivity of photocells. This might possibly be obtained with structures with a higher degree of confinement, i. e. quantum wires or quantum dots.

Chapter 4

Comparison of Photocurrent with Absorption

The highest degree of confinement is a quantum dot, which is confined to zero dimensions. A good approximation of such dots are SiGe islands embedded in Si as shown in a TEM micrograph in Figure 2.12. Even smaller islands and a higher area density of SiGe islands, can be achieved by an antimony (Sb) surfactant. However, Sb has a memory effect in the growth chamber, i. e. Sb from previous cycles remains in the reactor and is partly built into consecutively deposited material. Intrinsic layers can only be obtained by co-doping. To prevent Sb contamination of the tool available at the Paul Scherrer Institut, a cooperation was sought. Samples deposited with MBE and Sb surfactant that were optimised for a high area density of Ge islands were provided by Johannes Konle and Hartmut Presting from DaimlerChrysler Research Center, 89081 Ulm, Germany.

4.1 Sample Preparation and Measurement Set-Up

Two samples were prepared with similar Ge islands on Si substrate for an absorption and a photocurrent measurement, respectively. After a standard RCA cleaning procedure, the Ge islands were epitaxially deposited with MBE [48] on 4 inch Si(100) wafers. For the absorption sample, a double-sided polished substrate was used. All measurements were carried out at room temperature.

4.1.1 MBE

The growth temperature of the MBE was around 700° C and the base pressure in the chamber was typically 1 nPa and could be held at 100 nPa during growth. An e-gun was used to evaporate the Si, while Ge, B and Sb were incorporated by conventional effusion cells.

Sb is an established surfactant in SiGe MBE leading to a high area density ($\approx 5 \times 10^{10} \text{ cm}^{-2}$) of islands [48], as well as to a reduced interdiffusion at the Si/SiGe interfaces. 1 ML of Sb was deposited prior to the growth of the Ge islands. Intrinsic material was deposited by continuously co-doping with Boron to compensate for the incorporation of the Sb into the epi-layers. 8 ML of pure Ge between considerably thicker Si spacers were

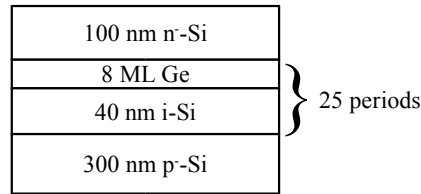


Figure 4.1: Thinned *pin*-diode for photocurrent measurement with 25 layers of Ge islands in the space charge region

deposited in the Stransky-Krastanov growth mode to form the islands. Due to intermixing with the Si, the Ge concentration is expected to vary across the island and reach an estimated maximum of $> 70\%$ at its centre.

Figure 2.13 shows a TEM micrograph of a similar sample, fabricated using the same growth parameters as for the other Ge islands samples. The TEM analysis indicates perfect crystallinity of the sample and the absence of extended defects such as dislocations.

4.1.2 Fabrication of the Diodes for the Photocurrent Measurement

For the photocurrent measurement, a small *pin*-diode with a diameter of about 1 mm was fabricated with the emphasis on minimising the photocurrent generated in the Si and maximising it in the Ge islands. This was achieved by removing most of the substrate after growth. The final structure is shown in Figure 4.1. Between the *n* and *p* layers, 25 periods with 8 ML Ge and 40 nm intrinsic Si were deposited. The bottom of the active diode is an unpolished surface, which was contacted to a metal with a silver epoxy glue. A Si reference sample without Ge, but otherwise equally built was fabricated for comparison.

4.2 Absorption Measurement

The raw transmission data of the Ge quantum dot sample and the Si reference sample are plotted as function of the photon energy in Figure 4.2. As the SiGe islands are not expected to absorb at photon energies below 0.7 eV, the Ge quantum dot sample was scaled to overlap with the Si reference sample in the photon energy range of 0.45 to 0.7 eV, where no water absorption lines are visible. Although the samples were purged in nitrogen during measurement, a water film is expected to remain at the surface of the samples. The deviations of the two curves below 0.45 eV can be attributed to absorption of a differently thick water film. The good overlap at photon energies between 0.45 and 0.7 eV allow a reliable method of scaling. The absorption of the Ge islands can clearly be seen in the photon energy range between 0.8 and 1.05 eV. The excellent match of the spectral shape in the photon energy range between 0.45 and 0.7 eV and the high signal to noise ratio of this measurement is a significant improvement in comparison to earlier work (see also section 3.5 and [47]). By dividing the transmission of the Ge quantum dot sample by the transmission of the Si reference sample, the effective transmission T_{eff} of the SiGe islands is obtained. The division also cancels out:

- Effects attributed to the substrate, such as free carrier absorption.

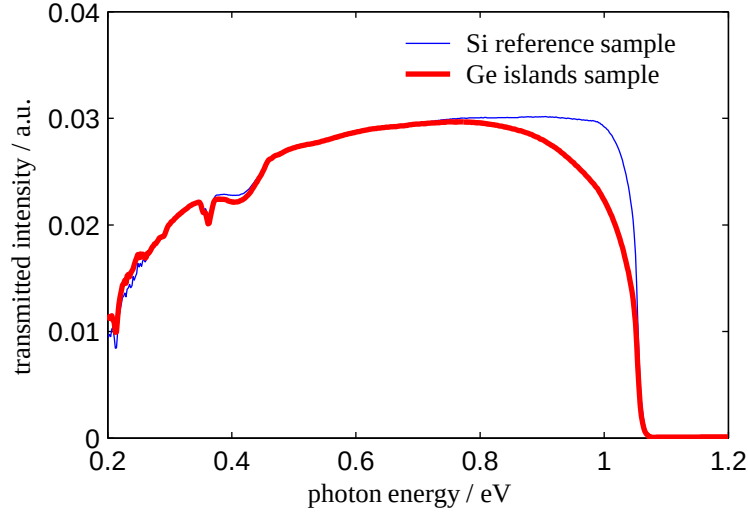


Figure 4.2: Comparison of transmission through Si reference sample (thin line) and Ge islands sample (bold line). The absorption of Ge islands is clearly visible in the photon energy range of 0.8 to 1.05 eV. The Ge quantum dot sample is scaled to overlap with the Si reference sample in the photon energy range from 0.45 to 0.7 eV.

- Effects originating from the measurement set-up, e.g. absorption at optical components.

The absorption coefficient α is defined as:

$$\alpha = \frac{T_{eff}}{d} \quad (4.1)$$

However, at every totally reflecting Si-air interface a standing wave is formed by the superposition of the incoming and reflected wave. Its influence on the absorption is taken into account by replacing in (4.1) the thickness of the absorbing structure d by an effective thickness d_{eff} , which also depends on the electric field of the standing wave across the Ge islands. The calculation of the effective thickness d_{eff} and the absorption coefficient are described in more detail in section 3.3.

Figure 4.3 depicts the absorption coefficient of the Ge islands in comparison with literature values of bulk SiGe [43] and bulk Si [39]. The absorption coefficient of the Ge islands is more than 4 orders of magnitude higher than that of Si at 1 eV. The absorption coefficient in the Ge islands is higher than in bulk SiGe with high Ge concentration for photon energies < 0.9 eV. Due to the high Ge concentration, it was not possible to determine the Ge concentration from an X-ray diffractometer measurement. Thus, strain and confinement effects that strongly influence the minimum transition energy of charge carriers from the valence to the conduction band could not be calculated. These, however, are the basis for a detailed comparison between bulk and nanostructured SiGe. Although the absorption coefficient is more than 4 orders of magnitude higher in the Ge islands than in bulk Si at 1 eV photon energy, without the use of light trapping more than 1000 layers of islands are necessary to absorb 1% of the incoming 1 eV photons. However, using appropriate light trapping structures, the number of island layers is significantly reduced.

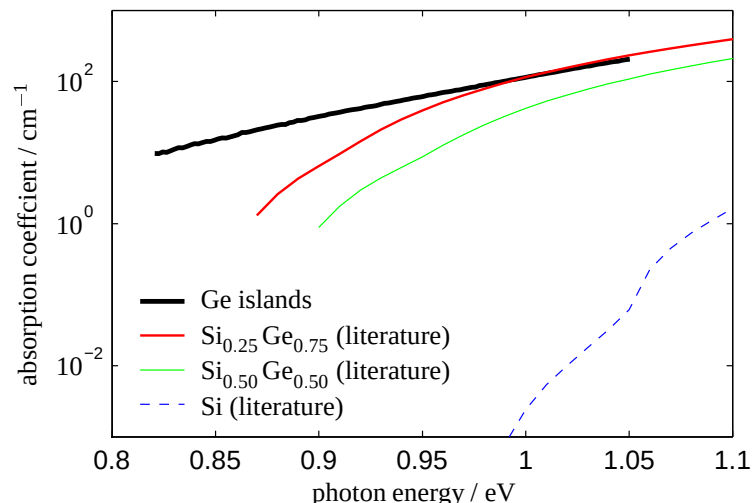


Figure 4.3: Absorption coefficient as a function of the photon energy of the Ge islands in comparison with literature values of bulk SiGe [43] and bulk Si [39].

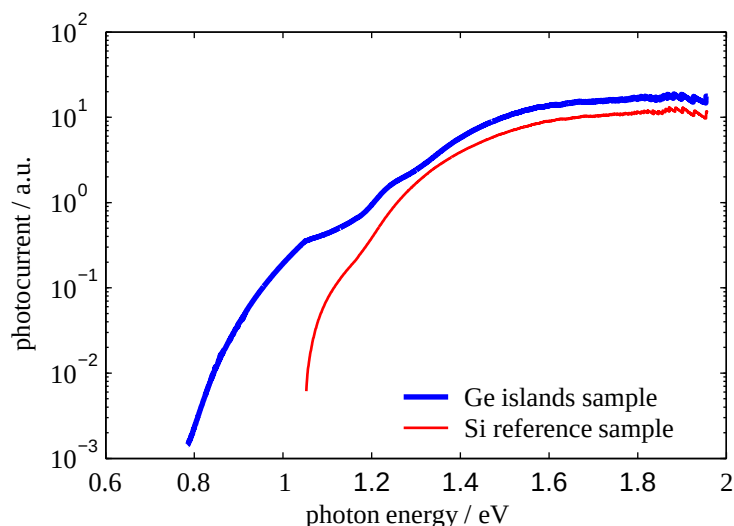


Figure 4.4: Photocurrent as a function of the photon energy of the Ge islands sample in comparison with a reference sample without Ge.

4.3 Photocurrent Measurement

The photocurrent was measured with a Fourier transform spectrometer by using the photodiode itself as detector of the spectrometer. Figure 4.4 shows the measured photocurrent as a function of the photon energy of the Ge islands sample in comparison with the pure Si reference sample. The current was corrected for the variation of the intensity of the light source with the photon energy.

The photocurrent of the sample with the Ge islands is about 1.5 times as high as in the reference sample for photon energies above 1.3 eV. This indicates that the Ge islands deliver 1/3 of the photocurrent in 1/30 of the volume even at photon energies above 1.3 eV. While the reference sample delivers a measurable photocurrent only for photon energies

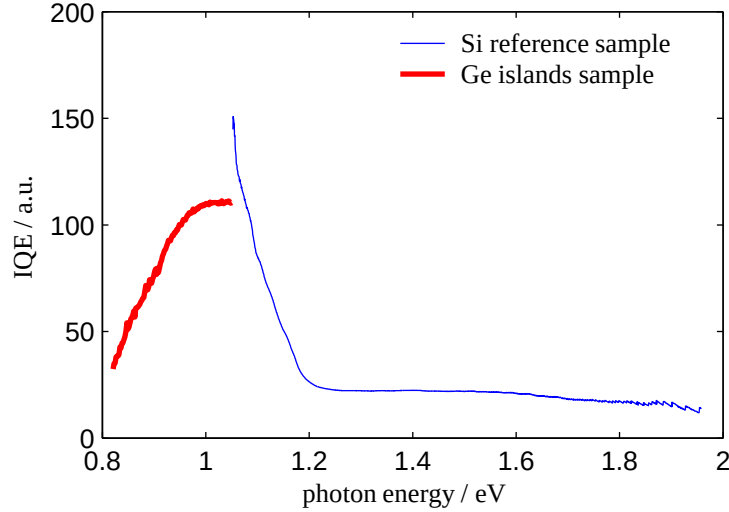


Figure 4.5: Internal quantum efficiency IQE (charge carriers collected at contacts divided by the number absorbed photons) as a function of the photon energy for the Ge islands sample and the Si reference sample.

above 1.05 eV, the Ge islands sample delivers the same photocurrent already at 0.85 eV.

4.4 Comparison of Photocurrent and Absorption Measurement

For a comparison of the photocurrent with the absorption measurement, we computed the internal quantum efficiency (IQE), defined as the number of electron-hole pairs collected at the contacts per absorbed photon. As the photocurrent is measured in arbitrary units, the IQE is also given in arbitrary units. The length of path the light takes within the sample is significantly increased in comparison to a perpendicular single pass because of diffuse reflection at the back. The light trapping factor f_{LT} is defined as the average length of the path a ray of light takes through the sample divided by the thickness of the sample (the measurement was done with perpendicular incidence of the light). A light trapping factor of $f_{LT}=3.8$ has been calculated by treating the front of the diode as a smooth Si-air interface and the back as a 50 % diffusely reflecting mirror. The penetration depth d_p is greater than the thickness of the diode D for all investigated photon energies. At photon energies $< 1.3\text{ eV}$, $d_p \gg D \cdot f_{LT}$, so that the light trapping factor f_{LT} enters as a constant factor into the IQE that is irrelevant on a scale in arbitrary units. Figure 4.5 shows the IQE obtained from the absorption coefficient (Figure 4.3) and the photocurrent (Figure 4.4) for the Ge islands and the Si reference sample. The IQE of the Ge islands sample varies by a factor of 3 within the range of photon energies that could be covered by the absorption measurement, i.e. 0.82 eV to 1.05 eV. It is flat around 1 eV and drops towards lower photon energies. One possible explanation of the variation is that there are other absorption mechanisms than inter-band absorption. Another possible explanation is that the charge carriers get absorbed

in the quantum dot, but they recombine within the quantum dot before they are able to escape into the continuum.

The IQE of the Si reference sample shows that the photocurrent measurement are in good agreement with the literature absorption data [39] for photon energies above 1.2 eV. The slight decrease at photon energies above 1.6 eV can be attributed to measurement inaccuracies, where the intensity of the source is decreasing and the noise is increasing. However, the sharp increase of the IQE of the Si reference sample for photon energies below 1.2 eV could not be explained, even when considering that the photocurrent was at its lower measurement limit, where the measurement error is increased.

4.5 Summary

Samples containing a high sheet density of dislocation-free Ge islands have been successfully grown on Si substrates using Sb mediated growth by MBE. The absorption of the Ge islands could be determined in the photon energy range from 0.82 to 1.05 eV with increased accuracy compared to previous work. The absorption data reveal that without light trapping, more than 1000 layers of islands are needed to absorb 1 % of the light with a photon energy of 1 eV. A thin *pin* diode with Ge islands in the space charge region has been fabricated, allowing the measurement of the photocurrent that is predominantly generated in the Ge islands. The sample with Ge islands yielded a 10 to 100 times higher photocurrent than the Si reference sample without Ge in the photon energy range between 0.85 to 1.05 eV. The comparison between absorption- and photocurrent measurement of the Ge islands sample shows no dependency on the photon energy around 1 eV, but indicates that the probability for an absorbed photon to contribute to the photocurrent decreases with decreasing photon energy. The comparison of the photocurrent of the Si reference diode with absorption coefficients from literature show a good agreement for photon energies above 1.2 eV. Light trapping and further improvements in growth technology to increase the Ge island volume density as well as carrier lifetimes seem necessary to obtain Ge island structures that are applicable for photocell production.

Chapter 5

TPV Cost Estimate

A crucial parameter for the market penetration of TPV is its electricity production cost. In this work a detailed cost estimate is performed for a Si photocell based TPV system, which was developed for electrically self-powered operation of a domestic heating system. The results are compared to a rough estimate of cost of electricity for a projected GaSb based system.

5.1 Introduction

TPV has a large variety of possible applications starting with solar TPV systems [49] to industrial usage like converting excess heat in a glass factory to electricity [50] and standalone battery chargers [51]. Yet, no application has become a product, which had to stand the competition with other electricity (co-) generating techniques. For many applications the cost of the electricity produced is the deciding factor for a successful market penetration. One of the key characteristics of a system that converts fuel to electricity is its system or fuel-to-electricity efficiency which is defined as electrical energy out divided by chemical energy in. As TPV fuel-to-electricity efficiencies are low compared to, e.g. gas/diesel engines or fuel cells, the cost of non-co-generating TPV-electricity can hardly be competitive in respect to cost of electricity¹. As a consequence, cost competitiveness can more easily be achieved for co-generated electricity when the heat is the primary demand. Clearly, when comparing a TPV co-generating system and a conventional heating system that produce the same amount of heat and suffers the same amount of losses, the TPV equipped system will need some excess fuel to generate electricity. For heat driven applications the excess-fuel-to-electricity efficiency, being defined by the electrical energy out divided by the chemical energy of the excess fuel in, is another key characteristics of a co-generating system. In fact, when a TPV system for heating purposes uses the waste heat inherent to TPV electricity production, the excess-fuel-to-electricity efficiency is close to 100% [52]. As a consequence, the use of TPV in residential gas heating systems are targeted as one of its first applications [53].

TPV is a technology in a state of research and only very few estimates on cost were performed, of which the most detailed are for a TPV system based on Si photocells [52, 54]

¹ This is not necessarily true for niche markets, e.g. in the low power range.

and, less detailed, for a system based on GaSb photocells [55]. This chapter focuses on cost estimates on combined heat and power (CHP), i. e. co-generating systems with a total power of 12 to 20kW. In order to compare the cost of Si based and GaSb based systems the same write off conditions and similar cost bases in respect to estimating end user prices were assumed.

As pointed out earlier, TPV systems have to compete with other techniques such as gas engines and fuel cells. Here we compare these techniques with respect to their cost structure to TPV systems under the condition that all systems are employed for co-generation of heat and power. TPV systems consist of several compounds, which have to be added to a conventional heating furnace. The main parts, the selective emitter, the filter and the photocells, including some arrangement to cool the cells are typically produced on laboratory scale up to now and their prices can be only approximated from todays production costs or from the costs of similar products. In all estimates a certain production volume is presumed and further developments are taken into account by drawing scenarios. It is especially difficult to estimate the production and retail costs of low band gap cells, since up to now they are fabricated only in research and development centres being far away from production scale technologies. Even their substrate, monocrystalline GaSb wafers, is only produced in laboratory scale. To overcome this problem and to estimate the cost of low band gap cells, the 'scaling law' for Si solar cells is used which claims that the price per unit volume decreases by 50% when its production volume 10-folds.

The cost of co-generated electricity in CHP systems depends on the total investment and the amount of electrical energy the system is capable to deliver, i. e. investment cost per unit output power. If the total investment cost is direct proportional to the photocell area, the cost of co-generated electricity is inverse proportional to the output power per unit photocell area. The electrical output power density of a TPV system rises with the temperature of the emitter, because the radiation density at the emitter surface rises with the temperature of the emitter (according to Boltzmann's law for a blackbody). For the range of bandgaps and emitter temperature under discussion in this paper, the electrical output power of an idealised photocell/emitter combination increases with decreasing band gap of the cell². Before the results of the cost analysis are discussed, a brief description of the TPV systems, which have been studied is introduced.

5.2 TPV Technologies

5.2.1 Comparison of Systems with Porous and Gas-tight Emitters

One of the crucial parameters determining the efficiency of TPV systems is the emitter temperature. It is limited by regulations on NOx emission (of for example 80 mg / m³ in Switzerland [56]) and material properties. The NOx emission increases with the combustion temperature. From experience with heating systems, the maximum permissible com-

² It is presumed that the temperature of the emitter is less than 1800K. The photocell is idealised with respect to fill factor, external quantum efficiency and $q \cdot V_{OC} = E_G - 0.4$ eV being constant for all E_G (where q is the electron charge, V_{OC} is the open circuit voltage of the cell and E_G is the band gap of the cell). It is easy to show that under these conditions the optimum band gap for a blackbody emitter at 1800K is 0.65 eV. For lower temperatures of the emitter, the optimum band gap is lower. See also Figure 1.2.

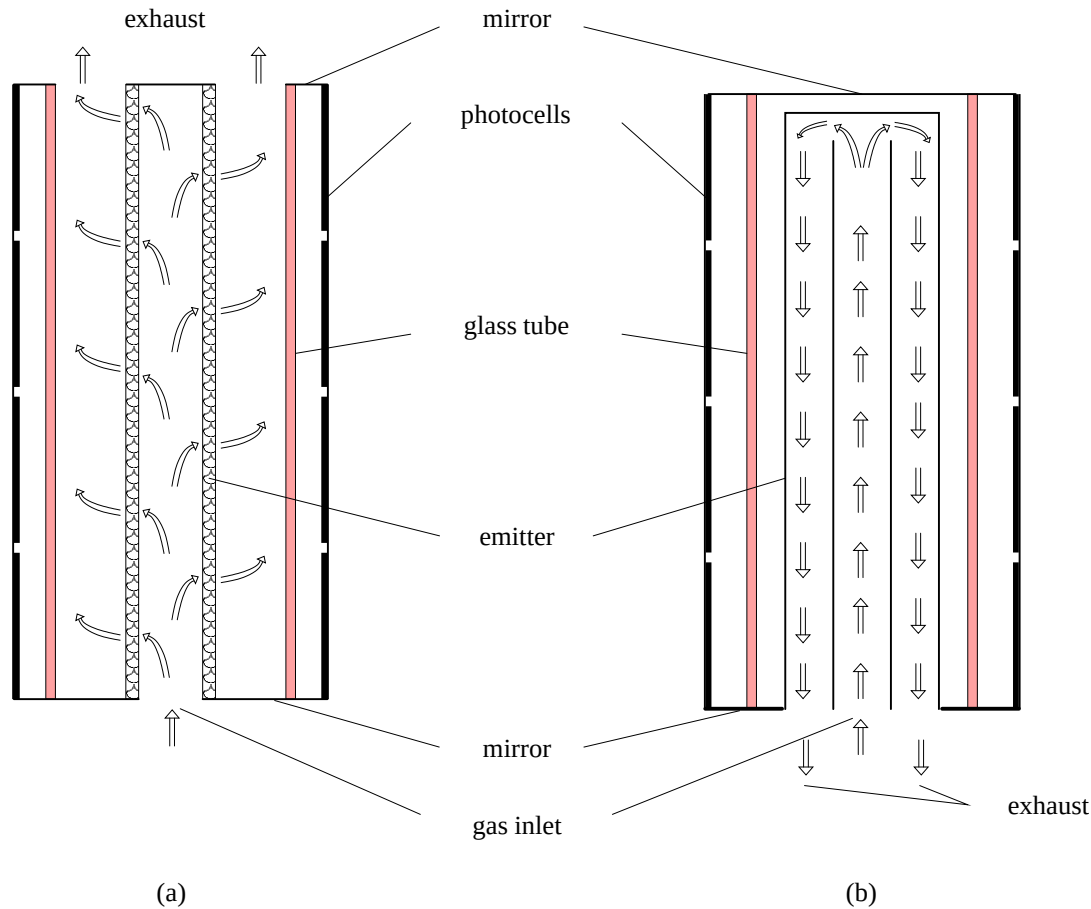


Figure 5.1: Schematic drawing of a porous (a) and a gas-tight (b) emitter system with cylindrical symmetry.

bustion temperature is 1 800 K. Thus, an optimal TPV system would work with an emitter operating at 1 800 K and a photovoltaic cell with a low band gap cell. The systems discussed in this paper are still far from optimum, either using Si photocells with a band gap of 1.1 eV or with a lower temperature of the emitter.

There are two different designs of emitters of fuel driven TPV systems: Porous and gas-tight emitters, i. e. the fuel and the exhaust gas can penetrate through the emitter or not. In Figure 5.1 schematic drawings of possible setups for systems with a porous (Figure 5.1a) and gas tight (Figure 5.1b) emitters are given. Although, in principle, emitter type and cell type are independent, we discuss the combinations Si photocell and porous emitter [52] as well as GaSb photocell with gas-tight emitter[55]. The system furnished with a gas tight emitter uses GaSb photovoltaic cells, having a band gap of 0.7 eV. The maximum temperature of the emitter surface pointing to the photocells was found to be 1 530 K [55]. The gas-tight emitter configuration has the advantage that the photocells are completely separated from the flame and the fume gases. More importantly, the space between emitter and photovoltaic (PV) cells can be optically perfectly closed by mirrors as indicated in Figure 5.1b. Moreover, the distance between PV cells and emitter can be minimised in order to maximise the radiation density on the cells and minimising their area.

In the porous emitter the fuel and exhaust fumes can penetrate through the emitter, consequently, some space is needed for fume gases to escape and an optically closed cavity is difficult to achieve. In addition the fume gases absorb some of the IR light decreasing the radiation, which illuminates the photovoltaic cells. The PV cells have to be protected; in the studied system [52], this has been achieved by inserting a glass tube. Further constraints arise from the space necessary, thus the larger distance between PV cells and emitter limits the radiation density and increases the area to be covered with PV cells. However, the porous emitter configuration has the advantage that the thin emitter structure is in close contact to the flame. The temperature of the emitter was found to be 1736 K in a smaller demonstration system [57].

To elaborate on the space needed between a porous emitter and the glass tube in front of the PV cells, it is assumed that the fuel burns only inside the pores of the emitter and that the average temperature is 400 K in the volume enclosed by the emitter and 1200 K³ in the volume between emitter and glass tube, volume V1 and V2 in Figure 5.1a, respectively. If the average speed of the gas in V1 and in V2 is kept constant, $V2 = 1200/400 \times V1 = 3 \times V1$. For a cylindrical geometry, this leads to a glass tube diameter of $\sqrt{3+1} = 2$ times the emitter diameter (the volume inside the glass tube has to cover inside and outside of the emitter) and, consequently, the radiation density at the glass tube is roughly half as high as at the emitter surface. Therefore, the electrical output power per unit cell area is lower in porous emitter systems by about a factor of 2. But the higher emitter temperature of porous emitters also results in a spectrum that is shifted towards higher photon energies. This allows to use low-cost photocells made of e.g. silicon, whereas in gas-tight emitter systems, generally, low band gap photocells are used that are, so far, only produced in laboratory scale.

5.2.2 Si Based Porous Emitter System

The estimates for this type of systems are based on the prototype system shown in Figure 5.2, which has been previously described [54, 58]. It is a heating system with a maximum thermal power of 20 kW and its fuel-to-electricity efficiency is 1% at 12 kW and 0.8% at 20 kW thermal input power. The TPV generator produces sufficient electricity to run the system independently of the grid in the full power range of 12-20 kW_{th}. It consists of an Yb₂O₃ mantle emitter, a quartz glass tube and monocrystalline silicon solar cells mounted on water cooled heat sinks. Its cylindrical shape minimises the geometrical losses of radiation since it allows for a high view factor of the cells, even when there is no reflector at the top of the system.

The cylindrical emitter resembles an incandescent mantle of a gas lamp. It is fabricated by coating of textile material with a solvent containing Yb. After the textile raw mantle has been pyrolysed, a fragile Yb₂O₃ structure remains [53].

The surface of the cylindrical emitter radiates with about 100 kW/m² (100 times solar

³ The average temperatures are chosen to give a rough estimate on the space necessary between a porous emitter and the glass tube. The temperature distribution is non-linear in both, axial and radial direction. For a temperature of the gas at the inlet of about 300 K and an emitter temperature of 1800 K, we assume a preheating of the incoming gas of about 100 K in average and a cooling of the exhaust gas in the spacing between emitter and glass tube to about 600 K in average.

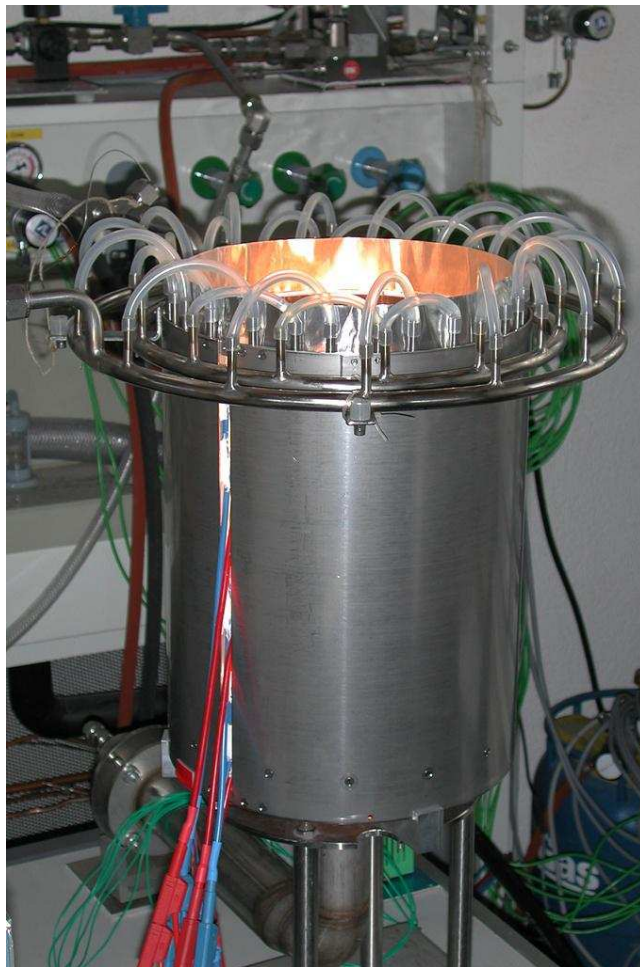


Figure 5.2: Experimental setup of a 20kW Si based porous emitter system.

irradiation AM1.5) at 1 800K. 24% of the radiation has a wavelength below 1.1 μm so that it can be converted by silicon photocells. A filter is not used and a quartz tube suffices to protect the photocells from the hot fume gases.

As cells optimised for non-concentrated solar irradiation are used, the fill factor decreases to 0.5 as opposed to 0.72 at AM1.5 irradiation which can be attributed to a series resistance problem. In scenario TPV2, the decreasing fill factor and the series resistance problem is avoided by using photocells that are built for higher light concentrations. They also allow to reduce the diameter of the glass tube and the photocell area to half of their size without sacrificing any system efficiency. With these measures, the system efficiency can be expected to be increased to 1.5%⁴.

5.2.3 GaSb Based Gas-tight Emitter Systems

JX Crystals Inc. has designed a number of systems with remarkable performance figures. It also has already performed field tests with a few dozens of systems of the first generation called Midnight Sun® [59]. The system[55] described in this section was designed by JX Crystals Inc. and has the advantage of using an industrially available burner.

The GaSb based TPV system has a maximum electrical output power of 1.5 kW when driven with 12.2 kW fuel. It is built around a low NO_x industrial radiant burner tube built by WS Inc. The burner tube is made of SiC and measures 100 mm in diameter and 950 mm in length and can operate at a temperature of up to 1 525K. It consists of two further SiC tubes inside the outer radiant tube which form a recuperator. The burner was modified by wrapping it into an anti-reflection coated refractory metal foil and using a higher quality SiC for the inner burner tube made of bonded SiC, which is limited to 1 625K. The foil forms an optimised emitter which has - together with a filter - the effect that 75% of the radiant energy is put into the cell convertible band. To make best use of the precious cells, the gap between emitter and cells is reduced to an extent that it is negligible in comparison to the diameter of the emitter. Hence, the radiation density at the cells is practically only reduced by the filter. The gap is filled with krypton to prevent corrosion of the emitter and minimise heat conduction.

Unfortunately, the system has not been built up and the performance figures are projections based on data from WS Inc, the experience of JX Crystal Inc and Monte Carlo simulations using TracePro software. With a presumed burner/recuperator efficiency of 80%, the system electric efficiency is predicted to be 12.3%.

5.3 Cost Estimates

The cost estimate is restricted to cost of electricity production and does not include whatever is necessary for a conventional heating system as cost of boiler and installation. The investment cost presented here are derived from retail prices as far as possible, so that they include manufacturing, the sales route and all profit margins. The sum of the investment

⁴ A system efficiency of 1.5% has been demonstrated on a similar system [57] using the same photocells as in scenario TPV1.

cost for the components and cost for miscellaneous (assembly, etc.) is the end user investment cost. The cost of electricity is obtained by that amount of money per unit electrical energy that amortises this end user investment plus interest, cost of maintenance, running expenses and fuel. If there is no sales route with wholesalers and retailers, as e. g. for GaSb cells, wholesale- and retail price are approximately equal within the overall accuracy of the estimate.

For porous emitter systems, the production cost of the TPV system was determined by the estimated costs of the individual components of the system - emitter, glass tube, photocells or photocell module and cell cooling elements (if applicable) - and 100 EUR/kW_{el,peak} were added to account for assembly and miscellaneous parts. The cost of electricity was calculated so that it amortises the investment over the lifetime of the system.

The cost of the gas-tight emitter system was estimated under the assumption that the photocells make up 35% of the total system cost. This percentage is taken from [60] and conforms with the estimates of the porous emitter systems presented here. The gas tight TPV system being equipped with GaSb photocells serves as an example for a highly efficient TPV system. In order to achieve a high system efficiency, it has to use high quality components as well as a recuperator and a filter. It also serves another market as systems with lower efficiencies.

5.3.1 Scenarios

Up to now, no TPV-CHP system has been produced as an industrial product. Even some components, as emitters or low band gap photocells fall into this category. In order to estimate the cost of an industrially produced TPV-CHP-system, scenarios of possible future developments in respect to both, technology and availability of key components at a price of comparable products, are made. The latter strongly depends on the production volume so that a price of a product can be converted to a cumulative production volume by the 'scaling law'.

Four TPV scenarios are presented, of which TPV1 and TPV2 cover porous emitter systems, TPV4 a gas-tight emitter system and TPV3 a future system, that leaves the configuration open. For comparison, a gas engine and a fuel cell scenario is given as well.

Scenario TPV1

This scenario represents the current state of the technology that can easiest be transferred to a production process, because monocrystalline Si solar cells are installed. A prototype of the system already exists [54, 58]. It consists of a porous emitter made of an Yb₂O₃ mantle, a heat resistant glass tube and the photocell module. In order to be able to utilise solar cells, the radiation density has to be relatively low with 20 kW / m² (20 suns), i. e. 1/5 of that of the surface of the emitter.

As there were no life time tests yet being performed, the stability of the emitter is still questionable. The fuel-to-electricity efficiency was measured to be 1%. The fill factor of the cells decrease from 0.72 under AM1.5 solar irradiation to 0.64 under Yb₂O₃ irradiation

at 60 % thermal power and to 0.5 under Yb_2O_3 irradiation at full thermal power, indicating that some efficiency was sacrificed because of a too high concentration level.

In order to convert the fuel into heat with a high efficiency, a boiler that condenses the water vapour in the combustion gases is used. This has also the advantage for TPV that the temperature of the water circulating through the boiler system is low enough that it can be used to cool the photocells. The loss in efficiency of the photocells due to the elevated temperature is neglected.

Scenario TPV2

This scenario describes the following improvements over scenario TPV1: The solar cells are replaced by photocells built for higher concentrations with a reduced series resistance that allows for a higher radiation density to reduce the size of the system and increase the system efficiency to 1.5 %. The state-of-the-art measured system efficiency of such a Si based system without recuperators is 2.4 % [53]. The radiation density at the photocells is increased by a factor of 2 with respect to scenario TPV1, i. e. 1/3 of the radiation density at the emitter. To reduce cost compared to scenario TPV1, the quartz glass tube is replaced by a DURAN® glass tube and the cell cooling is thought to be achieved by gluing laminated cells into the boiler housing. The heat generated by the photocells is transferred to the boiler water.

Scenario TPV3

This future scenario allows for further advances in technology. An increase in system efficiency to 5 % is presumed, but keeping the costs as in scenario TPV2. This increase in efficiency can be achieved if either low bandgap cells become available at a low price or by increasing the emitter temperature. The latter requires either an NOx filter or the fuel has to be burnt with pure oxygen instead of air to keep the NOx emissions within legal limits. NOx filters are too expensive to date, but might get low cost if they are frequently used in diesel engines of cars due to new EU and US exhaust gas regulations. Whereas oxygen might be a byproduct obtained from the electrolysis of water for hydrogen production.

Scenario TPV4

As there are only little detailed cost considerations found in literature for low band gap systems, the system cost is estimated from the cost of the cells. For low band gap cells, the price for the GaSb wafer is used as this material system is the most advanced in this field and new technologies often use GaSb as a substrate. The cell processing and the module fabrication is neglected. A projected system efficiency of 12.3 % [55] was presumed.

5.3.2 The Investment Cost

The investment cost for scenario TPV1-TPV3 is the sum of the costs of the main components plus the 100 EUR/kW_{el,peak} for miscellaneous purposes. For scenario TPV4, the investment cost is deduced from the estimated cost of the photocells. To be able to compare cost of systems with different power, the investment cost per unit peak electrical output

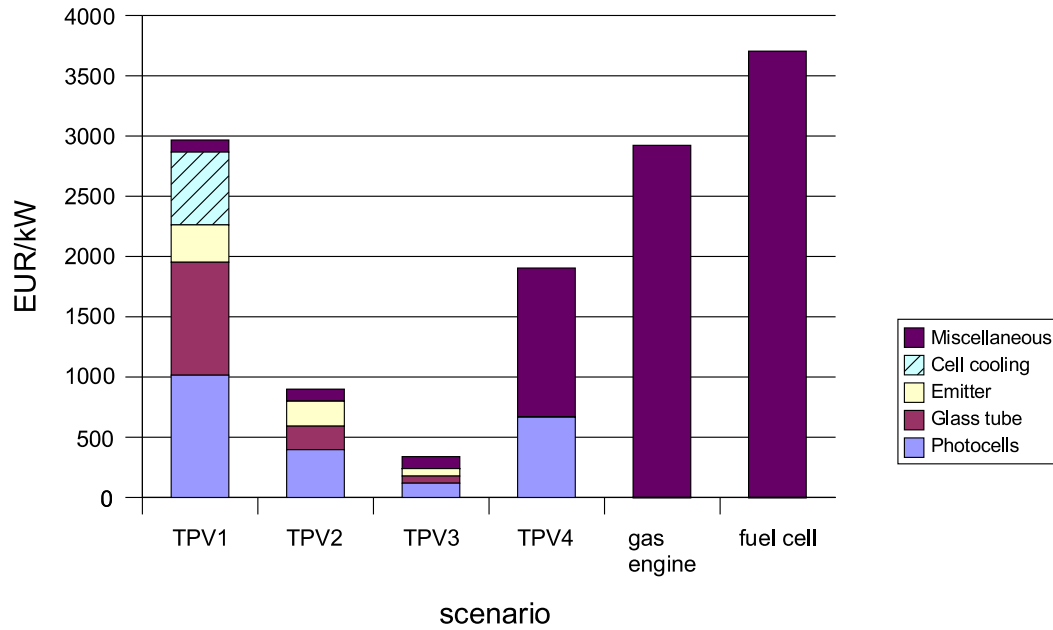


Figure 5.3: Investment cost per unit peak electrical output power for 4 different TPV scenarios, a gas engine and a fuel cell.

power is shown in Figure 5.3 for the 4 different TPV-scenarios as well as for the gas engine and the fuel cell. See Table 5.1 for details of the calculations.

Estimates for Scenarios TPV1 and TPV2

The emitter cost is deduced from the retail price per unit weight of a standard Yttrium oxide (Y_2O_3) incandescent mantle emitter for lighting purposes, weighing 1.5 g. The result is about 20 times the price of the textile mantle and the 10 g Yb_2O_3 , the final emitter consists of. Because of the similar production process, the Y_2O_3 incandescent mantle was used to estimate the end user price of an Yb_2O_3 mantle emitter.

For the cost of the glass tube the retail price of a quartz tube in scenario TPV1 and a DURAN® glass tube in scenario TPV2 was used. The prototype system contains ASE SH2 solar cells bought for 1 000 EUR / m², which is about 3 times the price of standard solar cells. This high price allows for improved cells also in scenario TPV2. The cell cooling blocks were handmade for the prototype. Its production is not representative even for a very small series so that its production and assembly is not fully covered. The cost for the cooling elements is accounted for by taking the material price of 1 cm thick copper blocks. The cooling blocks are not needed in scenario TPV2, instead, the cost of encapsulation into a laminate is considered with material cost of 23 EUR / m² plus 150 EUR / m² for assembly, cell cutting and -tabbing [61].

Note, that in scenario TPV2 Si cells built for higher concentrations are needed. While they also have an application in concentrator solar cell modules, it has not yet reached the

⁵interest, maintenance, running expenses

⁶Mean of the minimum transition energy *minus* one third of mean of error bar

Table 5.1: Cost estimate for 4 TPV scenarios and a gas engine and a fuel cell for comparison. The *emphasised* cost figures are end user prices of available components. The **bold** numbers are based on experimentally achieved values.

scenario	TPV1	TPV2	TPV3	TPV4	gas engine	fuel cell
photocell material	Si	Si	any	GaSb		
area of the photocells (m ²)	0.20	0.10	0.10	0.1		
system efficiency (%)	1	1.5	5	12.3	25	40
peak thermal input power (kW)	20	20	20	12.2	18.8	10
peak electrical output power (kW)	0.20	0.30	1.0	10.7	4.7	4.0
average thermal input power (kW)	13	13	13	7.9	12	6.5
average electrical output power (kW)	0.13	0.2	0.65	1	3.1	2.6
photo cells (EUR)	200	120	120			
quartz/DURAN-glass tube (EUR)	190	59	59			
emitter (EUR)	62	62	62			
cell-cooling (EUR)	120	0	0			
100 EUR / kW _{peak,el} for miscellaneous	20	30	100			
total investment cost (EUR)	590	270	340	2 900	14 000	15 000
total investment per kW _{peak,el} (EUR)	3 000	900	340	1 900	2 900	3 700
yearly electricity production (kWh)	230	350	1 200	1 800	5 500	470
yearly electricity production (kWh / m ²)	1 200	3 500	12 000	18 000		
EURcents / kWh excluding capital costs ⁵	13	3.8	1.5	8	12	16
EURcents / kWh including capital costs	22	6.6	2.5	14	21	27
-"- incl. gas ⁶	25	10	6.0	17	25	31

low price level presumed in scenario TPV2. However, it is not necessary to build new factories exclusively for concentrator cells, because an existing line can be modified to run both, normal and concentrating Si photocells by modifying only few steps as the width of the fingers and probably some doping levels. Hence, it can be expected that the presumed price level for Si concentrator cells is in reach in the near future.

Estimates for Scenario TPV3

If realised as a porous emitter system, the cost of the components are presumed to be the same as in scenario TPV2. It can also be realised as a gas-tight emitter system which is considered at the end of the next section.

Estimates for scenario TPV4

According to [55] today's cost of GaSb cells is about 10 000 EUR/kW_{el}, i.e. 100 000 EUR/m² at 10 kW_{el}/m², at a cumulative production volume of 5 m², i.e. 2500 wafers of 2 inch in diameter. This price is in good agreement with quotations we received from 4 different companies offering GaSb wafers for 85 000 - 250 000 EUR/m² for a quantity of 20 wafers of 2 inch in diameter, when neglecting cost of cell production.

Parallelling the evolution of Si cell prices, the 'scaling law' can be formulated as:

$$c = c_0 \times 2^{-\log_{10} \frac{V}{V_0}} = 100\,000 \text{ EUR/m}^2 \times 2^{-\log_{10} \frac{V}{5\text{m}^2}} \quad (5.1)$$

where c_0 is today's cost of GaSb cells per unit area, V_0 is today's cumulative production volume and c is the GaSb cost per unit area when the cumulative production volume becomes V . Note, that the crystalline Si photocells are still produced from Si waste of the semiconductor industry that also is responsible for most of the knowledge about the technology. A similarly evolving industry to aid GaSb is not in sight.

In order to judge how far this 'scaling law' can be pushed, world production volume and stock market prices⁷ for Ga and Sb are presented: Sb is mined in the order of 100 000 tons per year at a price of 400 EUR/m² of a sheet with a thickness of a cell of 0.5 mm and the yearly Ga world primary production is estimated to be about 100 tons with estimated reserves of several million tons [62]. The price of 99.99999% Ga was 1 900 EUR/m² at the spot market and 15 000 EUR/m² of a sheet with a thickness of a cell of 0.5 mm at a laboratory retailer when bought at a quantity of 10 g. Averaging the price for Ga and Sb gives that the cost of the raw material will not play a limiting role as long as the cost of the cells predicted by the 'scaling law' stay above roughly 1 000 EUR/m².

Considering (5.1) and assuming a cumulative production volume of 100 000 systems with 1.5 kW_{el}, i.e. 10 000 m² of cells, the cell price reduces to about 10 000 EUR/m², when advanced cells with 15 kW/m² (1.5 W/cm²) of electrical output power are used. This volume represents nearly 2% of the boilers sold per year in the EU. Note, while the 100 000th system can be made with cells costs of 10 000 EUR/m², the 1st system has to be made with cell costs of 100 000 EUR/m². This gives average cost of the cells of the

⁷ To ease comparison, the prices are converted from EUR/unitweight to EUR/m². No cost for sheet casting, etc. is included.

100 000 systems of 14 000 EUR/m². The problem here is, as with every new product, to find customers for the first 1 000 and 10 000 systems being prepared to pay the according price, as e. g. satellite manufacturers did for silicon photocells. Hence, a system based on standard Si solar cells as the one presented in scenario TPV1 does not need such a high production volume to be producible at the assessed cost.

Presuming cell cost of 10 000 EUR/m², the investment cost of the system is estimated by assuming that the cells cover 35% of the total TPV system cost, hence 2 900 EUR.

If scenario TPV3 is realised as a gas-tight emitter system, the same cost can be achieved, when the cells deliver 30 kW_{el}/m², i. e. twice the electrical power density in scenario TPV4, and the cells cost 3 500 EUR/m², which is achievable according to (5.1), with a cumulative production volume of 300 000 m² or about 3 million systems.

Estimates for the Gas Engine and the Fuel Cell

The price of a fuel cell CHP system and CHP gas engine was obtained from Vaillant GmbH [63] and Ecopower Energy Solutions AG [64], respectively. The fuel cell CHP system and the gas engine also fulfil the function of the boiler. To determine the cost of electricity production the cost of conventional heat production, i. e. the cost of a boiler, has to be excluded. It is presumed that the cost of a boiler scales linearly with the thermal output power within the overall accuracy of this cost estimate. As a 20 kW boiler costs about 2 200 EUR, the cost of heat production is about 110 EUR/kW_{peak,heat}. The gas engine and the fuel cell CHP systems produce 13.8 kW and 6 kW peak heat output power, respectively, which is therefore equivalent to a credit of about 1500 EUR and 700 EUR, respectively, when substituting a conventional boiler of corresponding size.

The figure for the total investment cost of the gas engine in Table 5.1 was obtained by deducting 1 500 EUR for a boiler from the retail price of the gas engine [52].

For the price of a CHP fuel cell, Vaillant GmbH, Switzerland provided an estimated price with an accuracy of 30% when introduced into the market. The fuel cell CHP system is equipped with an inverter to convert DC into AC electricity. In this cost estimate only cost of electricity natively produced by each systems is determined. Hence, the cost of the inverters of 700 EUR/kW_{el,peak} are excluded for the fuel cell system. The figure for the total investment cost of the fuel cell in Table 5.1 was obtained by deducting the cost of a boiler (700 EUR) and inverter cost from the retail price of the Vaillant CHP fuel cell system. Note that this price does not necessarily reflect real cost.

5.3.3 Cost of Electricity

The cost of electricity is the amount of money per unit electrical energy that is necessary to write off the investment cost under the following conditions: That the lifetime of the systems is 20 years and the interest rate is 4.25% per year. Yearly maintenance cost of 1% of the investment was taken into consideration. The amount of produced electricity was deduced from the assumption that the systems run for 1800 hours per year at 65% of their maximum power.

If a system is optimised in respect that it heats the emitter to the maximum permissible temperature and the system cost is represented as a multiple of the cell cost then filters and

recuperators cannot increase the electrical output power per unit area. As a consequence, the use of filters and recuperators does neither reduce the investment cost, nor the price of electricity [52].

A comparison with solar photovoltaics shows that the scenarios TPV1/2/3/4 yields 8/23/80/120 times as much electricity per year and unit cell area as a solar cell under operating conditions as in Zürich, Switzerland [52].

5.3.4 AC/DC and Inverters

The cost of electricity natively produced by each system, i. e. AC for the gas engine and DC for the others, is compared in Table 5.1. Although there are some applications in which DC is favoured, like self powering boilers and island applications storing in batteries, the mass market is feeding into the grid, making inverters necessary. The use of inverters causes investment costs that exceeds that of scenario TPV3 and can be converted to an increase in cost of electricity of 5EURcents/kWh, considering the same conditions detailed in the previous subsection.

5.4 Conclusion

This study shows that TPV can become a cost efficient technology for the decentralised co-generation of heat and electricity in the very near future. Although the accuracy of this cost estimate does not allow to give clear predictions, some trends can be stated: The comparison with a fully developed gas engine yields that even a non-cost-optimised Si TPV system tends to be competitive. With some medium term available improvements, as outlined in scenario TPV2, the obtained cost of electricity is less than 1/3 of that from a gas engine. The comparison with fuel cells, which have drawn a lot of attention from funding agencies recently, shows that fuel cell electricity might be produced at a cost 25% higher than that of TPV, even when compared with the more experimental TPV system as outlined in scenario TPV1. This difference in cost is, however, within the cost uncertainty of the fuel cell of 30%. For the GaSb based system, which has a higher efficiency than Si based systems, the obtained cost of electricity is 32% less than that from a gas engine and 45% less than that from a fuel cell.

Moreover, TPV shows a huge potential, for both, to increase the efficiency and to cut cost. However, the mix of heat and electricity differs significantly for TPV on the one hand and gas engine and fuel cells on the other hand so that they cover different market segments. Only the GaSb based system lies in terms of efficiency somewhere in between. While for the presented Si based system the stability of the emitter needs further investigation, the GaSb technology needs to create a mass market to become competitive. A first TPV-application might be a self powering boiler with high heat supply security. This extra comes for free as it pays off with the electricity savings.

Chapter 6

Conclusions

Several samples containing SiGe nanostructures have been grown in good quality on Si substrates using UHV-CVD. For the first time, the absorption of the SiGe structures was measured on an absolute scale. Due to the strain in the SiGe layers, they show a strongly increased absorption coefficient compared to bulk material with the same Ge content. The absorption coefficient of SiGe nanostructures is about five times smaller in comparison with bulk SiGe with the same band gap as the minimum transition energy of the SiGe nanostructures. Although the error bar is slightly larger than the differences between the samples, a tendency that the absorption coefficient decreases with decreasing well width can be observed.

The photocurrent measurement of a thin *pin* diode with SiGe structures in the space charge region was compared with the absorption data of same SiGe structures. The photocurrent shows no dependency on the photon energy around 1 eV, but indicates that the probability for an absorbed photon to contribute to the photocurrent decreases with decreasing photon energy.

The absorption data reveal that without light trapping, more than 1000 layers of SiGe structures are needed to absorb 1% of the light with a photon energy of 1 eV. The measurements show no evidence that the absorption in the SiGe structures is enhanced due to spatial confinement. Whether SiGe structures can be used to sufficiently increase the infrared sensitivity of photocells, therefore, remains uncertain. Light trapping and further improvements in growth technology to increase the volume density of SiGe structures as well as carrier lifetimes seem necessary to obtain SiGe structures that are applicable for photocell production.

The study on cost estimates shows that TPV can become a cost efficient technology for the decentralised co-generation of heat and electricity in the very near future. The cost of electricity of a TPV system with some medium term available improvements is estimated 60% and nearly 70% below that of a gas engine or a fuel cell, respectively. The GaSb photocells based system, which has a higher efficiency than Si photocell based systems, the obtained cost of electricity is 32% less than that from a gas engine and 45% less than that from a fuel cell. Moreover, TPV shows a huge potential, for both, to increase the efficiency and to cut cost. While for the presented Si based system the stability of the emitter needs further investigation, the GaSb technology needs to create a mass market to become competitive. A first TPV-application might be a self powering boiler with high heat

supply security. This extra comes for free as it pays off with the electricity savings.

This work proves that SiGe structures embedded in Si cannot be applied for low band gap cells with present technology due to the insufficient absorption. CuInSe₂ photocells have a lower band gap than that of Si and can be produced at competitive cost in comparison with Si photocells. Thus, CuInSe₂ photocell based TPV has the potential to increase system efficiency and decrease cost of TPV generated electricity. As it has received little attention to date, more research in this field is needed to tap its full potential.

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Appendix A

Computer Programme wavem for Absorption Measurement Analysis

The programme is written for Matlab[®] or its free alternative GNU Octave [65]. Most of the variable names stick to the nomenclature of section 3.3. In the following the listing:

```
%WAVEM is a calculation of the absorption by calculating E field with matrices
% [dEff, dGeom] = wavem(EPh,t,d,n,absorb)
%   EPh ..... photon energies in eV. Must be a vector
%   t ..... t(j) – incident angle in layer 1 and photon energy EPh(j)
%           (if the same for all photon energy, it can be a scalar)
%   d ..... thicknesses of each layer in m. Must be a vector
%   n ..... n(i,j) – refractive index of layer i and photon energy EPh(j)
%           (if the same for all photon energy, it can be a vector)
%   absorb ... absorbing layers (vector)
% Results:
%   dEff .... effective thickness in m
%   dGeom...geometric thickness in m
%
% t (theta) is the angle with respect to the perpendicular line of the surface.
% There are a number of global variables, e.g.: EsUp EsDo EpUp EpDo k_z, where
% E, s, p, Up, Do stand for el. Field, perpendicular (senkrecht) and parallel
% to plane of incidence and up and down, respectively. k_z is the z component
% of the wave vector.
%
% Literature : [1] M. Klein, T. Furtak, "Optik", Springer Lehrbuch, 1986 John
%              Wiley & Sons, Inc., pp. 230 –– 234
%              [2] J. Jackson, "Classical Electrodynamics", 2nd ed, 1962 John
%              Wiley & Sons, Inc., sect. 7.4, pp.278––282
%
% Example: [de dg] = wavem(1, 45*pi/180, [0 100E-9 0], [3 4 1]', 2)
%           % gives [2.1203e-07 2.3591e-07]
%           [de dg] = wavem(1, 0.78539, [0 100E-9 0]', [3.51314 4.32498 1]', 2)
%           [de dg] = wavem([1 1.2], [45*pi/180 45*pi/180], [0 100E-9 0], ...
```

```

%                                     [3 4 1;3 4 1]', 2)
%
% See also: testwavem, wavemqw

% $Revision: 1.00 $ $Date: 2004-03-03 00:00:00 GP $
% Changlog:
%     1.00 2004-02-26:
%         - Improved wave.m algorithm by using matrix formalism

% -----
% 1 (e.g. Si)
% -----
% 2 (e.g. SiGe)
% -----
% ...
% -----
% nLay - 1
% -----
% nLay (e.g. air)
% -----> x
% (y is pointing out of the plane)
% (z is pointing downwards)
%
% Def. of Up/Down: A ray goes from layer 1 to layer 2 goes _down_
% Es{j} = [EsUp(j); EsDo(j)] % s-pol. wave running up/down in layer j
% Es{j} is the field at the upper side of layer j
% Es_{j} is the field at the lower side of layer j
% H{j} is the 2x2 matrix describing the properties of the interface between
%     layer j and layer j+1, so that E_{j}=H{j}*E{j+1}
% L{j} is the 2x2 matrix describing the property of layer j so that
%     E{j}=L{j}*E_{j}
% For p-polarised waves, the nomenclature is Ep{j}, Hp{j} and L{j}=Lp{j}=Ls{j}

function [dEff, dGeom] = wavem(EPh, t, d, n, absorb)
    global WAVEM;
    nLay = length(d); % No of rows = No of layers
    nLam = length(EPh); % Number of columns = No of EPh values

    if (nargin ~= 5), error('Number of arguments must be 5'); end;
    if (~isnumeric(EPh)), error('Parameter 1 is not numeric'); end;
    if (min(size(EPh)) > 1), error('Parameter 1 must be a vector'); end;
    if (size(EPh, 1) > 1), EPh = EPh'; end; % Must be row vector
    if (~isnumeric(t)), error('Parameter 2 is not numeric'); end;
    if (min(size(t)) > 1), error('Parameter 2 (t) must be a vector'); end;
    if (size(t, 1) > 1), t = t'; end; % Must be row vector
    if (length(t) == 1), t = t * ones(1, nLam); end;
    if (length(t) ~= nLam),
        error('Parameter 2 (t) must have the same length as Parameter 1 (EPh)');

```

```

end;
if (~isnumeric(d)), error('Parameter 3 is not numeric'); end;
if (min(size(d)) > 1), error('Parameter 3 must be a vector'); end;
if (size(d, 2) > 1), d = d'; end; % Must be column vector
if (~isnumeric(n)), error('Parameter 4 must be numeric'); end;
if (min(size(n)) == 1), n = n(:) * ones(1, nLam); end;
if (any(size(n) ~= [nLay nLam])),
    error(['Parameter 4 (n) must be a matrix length(d) x length(EPh) ' ...
        'or a vector of same length as d' ]);
end;
if (~isnumeric(absorb)), error('Parameter 5 must be numeric'); end;

% Convert lam and d to matrix for convinience
lam = ones(nLay, 1) * ev2m(EPh); % lambda
dM = d * ones(1, nLam); % thickness of layer in m

for iLay = 2 : nLay, % angle of light in layer iLay
    t(iLay, :) = asin(real(n(iLay - 1, :)) ./ real(n(iLay, :)) ...
        .* sin(t(iLay - 1, : )));
end;
k_z = 2 * pi * n ./ lam .* cos(t); % z component of wave vector k
kr = k_z .* dM; % inner product of the wave vector k with space vector .
% Note that x and y are zero and within a layer j, we go
% d(j) in z direction so that only k_z.*dM remains.

H = cell (nLay-1, 1);
L = cell (nLay, 1);
Es = cell (nLay, nLam); Ep = Es;
EDo.x = zeros(nLay, nLam); EDo.y = EDo.x; EDo.z = EDo.x;
EUp.x = EDo.x; EUp.y = EDo.x; EUp.z = EDo.x;
for iLam = 1:nLam, % for each wavelength
    % Define property of interface H{iLay} between layer iLay and iLay+1
    for iLay = 1:nLay-1, % for each interface
        % Fraction of reflected and transmitted E at interface between
        % layers j and j+1:
        [Ers Erp Ets Etp] = fresnel (n(iLay, iLam), n(iLay+1, iLam), ...
            t(iLay, iLam));
        Hs{iLay} = [1 Ers; Ers 1] ./ Ets;
        Hp{iLay} = [1 Erp; Erp 1] ./ Etp;
    end;
    % Define property of layer iLay: L{iLay}
    for iLay = 1:nLay, % for p and s pol. the same
        L{iLay} = [exp(i * kr(iLay, iLam)) 0; 0 exp(-i * kr(iLay, iLam))];
    end;
    Es(:, iLam) = E_layers(Hs,L);
    Ep(:, iLam) = E_layers(Hp,L);

    % Decompose E vectors in x, y and z direction :

```

```
for iLay = 1:nLay,  
    % s components point in y direction  
    EUp.y(iLay, iLam) = Es{iLay,iLam}(1);  
    EDo.y(iLay, iLam) = Es{iLay,iLam}(2);  
    % p components point in x (opposite) and z (same) direction  
    EUp.x(iLay, iLam) = Ep{iLay,iLam}(1) .* cos(t(iLay,iLam));  
    EDo.x(iLay, iLam) = -Ep{iLay,iLam}(2) .* cos(t(iLay,iLam));  
    EUp.z(iLay, iLam) = Ep{iLay,iLam}(1) .* sin(t(iLay,iLam));  
    EDo.z(iLay, iLam) = Ep{iLay,iLam}(2) .* sin(t(iLay,iLam));  
end;  
end;  
  
% integrate over the square of the E fields in absorbing layers and get  
% effective thicknesses :  
dxEff = zeros(1, nLam);   dyEff = dxEff;   dzEff = dxEff;  
for iLay = absorb,  
    z = -sum(d(iLay:nLay));  
    fac = n(iLay, :) ./ n(1, :) ./ cos(t(1, :)); % factor  
    dxEff = dxEff + fac .* IntE2(EDo.x(iLay, :), EUp.x(iLay, :), ...  
                                k_z(iLay, :), d(iLay));  
    dyEff = dyEff + fac .* IntE2(EDo.y(iLay, :), EUp.y(iLay, :), ...  
                                k_z(iLay, :), d(iLay));  
    dzEff = dzEff + fac .* IntE2(EDo.z(iLay, :), EUp.z(iLay, :), ...  
                                k_z(iLay, :), d(iLay));  
end;  
dEff = (dxEff + dyEff + dzEff); % These are the squares => can be summed up  
dGeom = 2 * sum(dM(absorb, :) ./ cos(t(absorb, :)), 1); % geom. thickness  
  
% calculate reflectivity and transmissivity  
WAVEM.R = abs(EUp.x(1,:)).^2 + abs(EUp.y(1,:)).^2 + abs(EUp.z(1,:)).^2;  
WAVEM.T = abs(EDo.x(nLay,:)).^2 + abs(EDo.y(nLay,:)).^2 ...  
        + abs(EDo.z(nLay,:)).^2;  
  
% save some values globally  
WAVEM.EPh = EPh;  
WAVEM.t    = t;  
WAVEM.d    = d;  
WAVEM.n    = n;  
WAVEM.absorb = absorb;  
WAVEM.dEff = dEff;  
WAVEM.dGeom = dGeom;  
WAVEM.k_z = k_z;  
WAVEM.EDo = EDo;  
WAVEM.EUp = EUp;  
return  
%%%%%%%%%% end of function %%%%%%%%%%
```

```

% H... nLay x 1 cell matrix of 2x2 matrices
% L... nLay x 1 cell matrix of 2x2 matrices
% E... nLay x 1 cell matrix of 2x1 matrices
function E = E_layers(H, L)
    nLay = length(L);
    E = cell(nLay,1);

    % Represent properties of all layers in S
    S = H{1};
    for iLay=2:nLay-1, S = S * L{iLay} * H{iLay}; end;

    E{nLay} = [0; 1];
    % Calculate incoming wave for EUp = 0 and EDo = 1 in layer nLay
    E{1} = S * E{nLay};

    % Correct E{nLay}: E{1} becomes [Er 1/sqrt(2)] for each polarisation so
    % that incoming Es^2 + Ep^2 = 1
    E{nLay} = E{nLay} / E{1}(2) / sqrt(2);

    % calculate E in all layers starting from the bottom
    for iLay=nLay-1:-1:1, E{iLay} = L{iLay} * H{iLay} * E{iLay+1}; end;

    % Some consistency checks
    if (abs(E{1}(2) - 1/sqrt(2)) > 1E-10),
        error('Incoming wave amplitude wrong. '); end;
    if (abs(E{nLay}(1)) > 1E-10),
        error('Up wave amplitude wrong in last layer. ');
    end;
return

% t in rad
% the reflecting interface is a xy plane
% Ei ... Electric field of the incoming wave in media with refractive index n1
% Returns the electric field of a refl. (Er) and transmitted refracted (Et)
% Both have components perpendicular (senkrecht) (Es) and parallel (Ep)
% to the incident plane
% Er = [Ers Erp] and Et = [Ets Etp]
%
% Equations see Jackson 2nd ed. 1962, 1975, p.281 - 282 eq. 7.39 and 7.41
% Note the direction of the E fields in Fig 7.6 and 7.7
function [Ers, Erp, Ets, Etp] = fresnel(n1, n2, t)
    ct = cos(t);
    n21 = n2 ./ n1;
    n212 = n21 .^ 2;
    nct = n212 .* ct;
    ct2 = (n212 - (sin(t) .^ 2)) .^ 0.5; % cos angle of refracted wave / n21
    % (purely imag. for total refl)

```

```

Ers = ( ct - ct2) ./ ( ct + ct2);
Erp = (nct - ct2) ./ (nct + ct2);
Ets = 2 .*      ct ./ ( ct + ct2);
Etp = 2 .* n21 .* ct ./ (nct + ct2);
return

%IntE2 Integrate over the square of a standing wave
% I = IntE2(Do, Up, k_z, z1, z2);
% Integrate over the square of a standing wave given by a Do and Up wave
% between 0 and d. k_z is the wave vector in z (down) direction
function I = IntE2(Do, Up, k_z, d);
    if (max(abs(abs(Up)-abs(Do)))>1E-10), error('No total reflection '); end;
    phi = angle(Do) - angle(Up); % Phase shift at top of layer between up
                                % and down wave
    I1 = 2 * abs(Up) .^ 2 .* (0 + 0.5 ./ k_z .* sin(      0 + phi ));
    I2 = 2 * abs(Up) .^ 2 .* (d + 0.5 ./ k_z .* sin(2 * k_z .* d + phi ));
    I = I2 - I1;
    %fprintf(' %e ', k_z, d);
return

```

Appendix B

List of Samples

The list is divided into two tables: Quantum dot samples Table B.1, which were extensively investigated with AFM and multi-quantum-well samples Table B.2, used for the absorption measurement.

Table B.1: UHV-CVD grown samples, with maximum possible Ge content, i. e. no Si H₄ was used to deposit the SiGe structures. After the Si buffer, the Ge rich structures were deposited for time t_{GeH_4} , capped with Si, deposited for time t_{SiH_4} (the Si growth rate is about 1.2 nm min⁻¹). The Si H₄ and Ge H₄ (5% Ge H₄ in H₂) flow was 20 sccm. The Table gives statistical values of height, area, volume and diameter of the islands, derived from atomic force microscopy (AFM) measurements.

sample	t_{GeH_4} min	t_{SiH_4} min	density 10^8 cm^{-2}	height nm	area 10^{-14} m^2	volume 10^{-22} m^3	diameter nm
L010621_04	8	100	4.32	74.6 ± 21	8.86 ± 6.9	48.1 ± 37.6	$336 \pm 39\%$
L010621_05	8	500	13.9	42.1 ± 17.3	2.62 ± 4.58	10.5 ± 24.8	$183 \pm 87\%$
L020304_03	20	0	6.04	59.5 ± 17.5	6.6 ± 3.62	21.2 ± 14.3	$290 \pm 27\%$
L020304_04	10	0	6.54	46.8 ± 12.3	3.54 ± 1.58	7.85 ± 5.14	$212 \pm 22\%$
L020304_05	6	0	5.96	38.1 ± 8.07	2.93 ± 0.98	5.02 ± 2.52	$193 \pm 17\%$
L020304_06	8	0	7.64	41.7 ± 13	3.09 ± 1.44	6.74 ± 4.26	$198 \pm 23\%$
L020304_07	10	20	6.82	45.3 ± 14.5	5.71 ± 2.9	12.9 ± 8.16	$270 \pm 25\%$
L020304_08	20	20	6.32	54.5 ± 15.5	6.38 ± 3.17	17.6 ± 10.8	$285 \pm 25\%$
L020304_09	8	20	6.66	40.9 ± 12.7	5.01 ± 2.37	10.6 ± 6.22	$253 \pm 24\%$
L020304_10	8	200	6.2	40.1 ± 10.2	3.71 ± 1.7	6.68 ± 3.56	$217 \pm 23\%$
L020304_11	8	500	5.9	42 ± 11.4	4.93 ± 2.79	9.3 ± 5.76	$251 \pm 28\%$
L020304_12	8	100	5.32	39 ± 7.75	4.71 ± 1.94	7.27 ± 3.39	$245 \pm 21\%$
L020304_13	5	0	6.36	33.2 ± 10.4	2.94 ± 1.41	5.23 ± 3.73	$193 \pm 24\%$
L020304_14	5.5	0	3.86	36.7 ± 8.82	2.7 ± 1.05	4.49 ± 2.62	$185 \pm 20\%$
L020304_15	4.5	0	6.26	29 ± 9.96	3.1 ± 1.49	5.53 ± 3.81	$199 \pm 24\%$
L020304_16	4	0	1.36	32.3 ± 4.98	2.25 ± 0.42	3 ± 0.967	$169 \pm 9\%$

Table B.2: List of UHV-CVD grown multi quantum well samples, where x is the Ge concentration in the SiGe alloy, h_{SiGe} and h_{Si} is the height of the SiGe and Si layer, respectively, q_{SiH_4} , q_{GeH_4} , t_{SiH_4} and t_{GeH_4} are gas flow parameters for Si H₄ and Ge H₄, respectively and n is the number of wells.

sample	x %	h_{SiGe} nm	h_{Si} nm	$\frac{q_{\text{SiH}_4}}{q_{\text{GeH}_4}}$	q_{SiH_4} sccm	q_{GeH_4} sccm	t_{SiH_4} min	t_{GeH_4} min	n
L010108_06	9.9	9.72	7.48	40.0	20.0	10.0	60	25.0	10
L010108_07	-	-	-	13.3	20.0	30.0	60	10.0	10
L010108_08	45.0	4.14	6.43	3.3	5.0	30.0	60	5.0	10
L010108_09	19.5	6.38	7.76	30.0	15.0	10.0	60	5.0	10
L010108_10	70.0	4.25	11.58	3.3	5.0	30.0	120	2.5	40
L010108_11	18.0	1.19	9.49	0.0	0.0	10.0	90	1.0	10
L010108_12	4.5	9.65	-	200.0	20.0	2.0	-	60.0	10
L010108_14	28.5	2.72	10.43	6.7	5.0	15.0	90	2.0	10
L010108_15	11.9	1.19	8.23	20.0	10.0	10.0	90	2.0	10
L010108_16	8.6	1.28	9.21	20.0	5.0	5.0	90	2.0	10
L010108_17	29.7	2.36	19.66	6.7	5.0	15.0	180	2.0	30
L010108_18	26.7	3.38	20.75	6.7	5.0	15.0	180	2.0	15
L010108_19	-	-	-	6.7	5.0	15.0	90	2.0	10
L010108_20	-	-	-	6.7	5.0	15.0	90	2.0	15
L010108_24	40.0	3.08	4.38	3.3	5.0	30.0	30	2.5	20
L010108_25	44.0	1.55	2.95	3.3	5.0	30.0	15	1.2	40
L010108_26	7.7	1.74	1.42	40.0	20.0	10.0	12	5.0	50
L010108_27	11.0	0.67	1.01	40.0	20.0	10.0	6	2.5	100
L010108_28	-	-	-	40.0	20.0	10.0	12	5.0	200
L010108_29	25.0	3.13	12.13	6.7	5.0	15.0	90	2.0	10
L010108_29B	-	-	-	6.7	5.0	15.0	90	2.0	10
L010108_29C	28.0	3.14	12.08	6.7	5.0	15.0	90	2.0	10
L010108_29D	25.0	2.75	12.21	6.7	5.0	15.0	90	2.0	10
L010108_30	-	-	-	3.3	5.0	30.0	60	1.2	40
L010108_31	50.0	0.75	14.15	5.6	5.0	18.0	60	2.0	40
L010108_32	-	-	-	20.0	10.0	10.0	60	3.0	10
L010108_33	-	-	-	3.3	5.0	30.0	60	5.0	10
L010108_34	-	-	-	-	0.0	-	13800	-	1
L010108_35	-	-	1030.00	-	0.0	-	7130	-	1
L010108_36	-	-	-	-	0.0	-	60	-	10
L010108_37	20.9	3.80	11.76	6.7	8.0	12.0	90	2.0	10
L010108_38	-	-	-	-	0.0	-	2160	-	1
L010108_39	23.8	2.65	13.62	5.6	7.1	12.9	90	2.0	10
L010108_40	42.0	3.63	14.33	3.3	5.0	15.0	90	2.0	10
L010108_41	-	-	-	-	0.0	-	2160	-	1
L010108_42	15.1	4.71	9.40	18.6	13.0	7.0	60	5.0	20
L010108_43	35.0	5.55	8.36	3.3	5.0	15.0	60	2.5	20
L010108_44	31.0	9.07	13.40	4.7	6.4	13.6	90	3.0	10
L010108_45	38.0	3.61	14.10	4.1	5.8	14.2	90	1.7	10
L010108_46	40.0	1.67	14.30	3.3	5.0	15.0	90	1.0	10
L010108_47	45.0	1.23	14.90	2.9	5.0	17.0	90	0.8	10
L010108_48	-	-	-	-	0.0	-	900	-	1

List of Figures

1.1	Principle of operation of a TPV system. An emitter is heated by thermal power P_{th} and emits electromagnetic radiation power P_{em} that is filtered (P_{rad}) and converted into electrical power P_{el} by the photocells. The purpose of an optional filter is to transmit the convertible photons and to reflect the rest back to the emitter.	3
1.2	Electrical output power density of an idealised TPV system as a function of band gap energy of the photocell used. The emitter is a blackbody at 1800K.	4
2.1	Side view of a UHV-CVD reactor. Mass flow controllers (MFC) determine the ratio of the gas mix entering the heated reactor chamber, where they decompose into the elements and Si, Ge and B gets deposited.	5
2.2	Setup of SiGe epitaxy tools: The UHV-CVD is connected via a transfer chamber and the plasma chamber to the loadlock. Samples can be in situ interchanged with an attached MBE system and analysed with a scanning tunnelling microscope (STM).	6
2.3	Gas system of the UHV-CVD. The different gases bypass a line valve and a mass flow controller (FC). Most of them can be switched between the vent, a tube leading to the roots pump, and the reactor, allowing abrupt interfaces between layers. Furthermore, a non-fluctuating gas flow is thereby ensured. By mixing the doping gases with hydrogen, a wide range of dilutions are achievable. The gas mixture can also be directed to the plasma-chamber. The valves and mass flow controllers are controlled by a computer programme. Its graphical user interface is shown in Figure 2.4.	7
2.4	Graphical user interface of the programme controlling valves and mass flow controllers shown in Figure 2.3 and logging the data.	8
2.5	Mass spectrometer measurement of reactor chamber with Si H ₄ flow.	10
2.6	Extrapolation of formation of Si O ₂ versus Si etching by SiO evaporation in equilibrium. The for an oxide-free Si surface necessary partial pressure of water depends linearly on the inverse temperate $1/T$. [10, 11]	13
2.7	TEM micrograph of sample 17, with SiGe layers of 3.30.2 nm thickness embedded between 18.70.2 nm wide Si layers. From the X-ray diffractometer measurement shown in Figure 2.16 a Ge concentration x of 30% is obtained.	17
2.8	TEM micrograph of sample 46, with SiGe layers of 3.00.4 nm thickness embedded between 14.10.4 nm wide Si layers. From the X-ray diffractometer measurement shown in Figure 2.16 a Ge concentration x of 40% is obtained.	18
2.9	TEM micrograph of sample 47, with SiGe layers of 1.90.5 nm thickness embedded between 13.70.5 nm wide Si layers. From the X-ray diffractometer measurement shown in Figure 2.20 a Ge concentration x of 45% is obtained.	18
2.10	TEM micrograph of sample 25, with SiGe layers of 2.50.3 nm thickness embedded between 2.00.3 nm wide Si layers. From the X-ray diffractometer measurement shown in Figure 2.18 a Ge concentration x of 45% is obtained.	19
2.11	TEM micrograph of sample 24, with SiGe layers of 3.40.6 nm thickness embedded between 4.10.6 nm wide Si layers. From the X-ray diffractometer measurement shown in Figure 2.17 a Ge concentration x of 45% is obtained.	20

2.12	TEM micrograph of sample 22, with SiGe layers of 5.30.9nm thickness embedded between 10.60.9nm wide Si layers. From the X-ray diffractometer measurement shown in Figure 2.16 a Ge concentration x of 45% is obtained.	20
2.13	2 magnifications of a TEM micrograph of 10 periods with Ge islands embedded in 40nm Si spacers grown with Sb surfactant by MBE at 700C. [20, 21]	21
2.14	X-rays impinging under a glancing angle ω on the sample with a stack of Si and SiGe layers on Si substrate. The diffraction occurs under the angle 2Θ	22
2.15	X-ray diffraction results of sample 17. The ordinate shows the glancing angle ω relative to the Si substate peak. The symbols are the measurements and the solid lines are the simulations with a Ge concentration x of 28% ($\times 100$, thick line) and 30% (thin line). With increasing Ge concentration, the satellite peak with minimum intensity, here at $\omega = -3^\circ$, occurs further away from the substrate peak. The thick line fits the minimum Ge concentration, because at a lower concentration the satellite peak at $\omega = -2.5^\circ$ would become too weak to fit the measurement. The sample has 30 periods and its TEM picture is shown in Figure 2.7.	23
2.16	X-ray diffraction results of sample 22. The ordinate shows the glancing angle ω relative to the Si substate peak. The symbols are the measurements and the solid lines is the simulation with a Ge concentration x of 45%. As the measurement does not reveal the satellite peak with minimum intensity, x cannot be determined very accurately. The very broad satellite peaks indicate a rough surface, which is confirmed by the TEM picture shown in Figure 2.12. The sample has 10 periods.	24
2.17	X-ray diffraction results of sample 24. The ordinate shows the glancing angle ω relative to the Si substate peak. The symbols are the measurements and the solid lines is the simulation with a Ge concentration x of 45%. As the measurement does not reveal the satellite peak with minimum intensity, x cannot be determined very accurately. The sample has 20 periods and its TEM picture is shown in Figure 2.11.	25
2.18	X-ray diffraction results of sample 25. The ordinate shows the glancing angle ω relative to the Si substate peak. The symbols are the measurements and the solid line is the simulation with a Ge concentration x of 45%. Due to the high number of 40 periods, the satellite peak with minimum intensity at $\omega = -6.2^\circ$ can be seen in the measurement and allows an accurate determination of the Ge concentration. The TEM picture of the sample is shown in Figure 2.10.	26
2.19	X-ray diffraction results of sample 46. The ordinate shows the glancing angle ω relative to the Si substate peak. The symbols are the measurements and the solid lines are the simulations with a Ge concentration x of 40%. The sample has 10 periods and its TEM picture is shown in Figure 2.8.	27
2.20	X-ray diffraction results of sample 47. The ordinate shows the glancing angle ω relative to the Si substate peak. The symbols are the measurements and the solid lines are the simulations with a Ge concentration x of 45% (thin line) and 35% ($\times 100$, thick line). The fit for $x = 35\%$ (thick line) represents the one for the minimum Ge concentration, because at a lower concentration the satellite peak at $\omega = -4^\circ$ would become too weak to fit the measurement. The sample has 10 periods and its TEM picture is shown in Figure 2.9.	28
2.21	SiGe growth rate as a function of the deposited Ge contents. The symbols indicate the morphology of the SiGe structures: Smooth (+) and wavy (x) interfaces between Si and SiGe layers and non-epitaxial deposition (o). The sample numbers are positioned to the right of the symbols. The lines are approximate interpolations for the two different Ge H_4 dilutions of 5% and 10% in hydrogen used for the deposition.	29
2.22	Ge content x in the deposited SiGe alloy as a function of the ratio of the Si H_4 over the Ge H_4 partial pressures. The symbols indicate the morphology of the SiGe structures: Smooth (+) and wavy (x) interfaces between Si and SiGe layers and non-epitaxial deposition (o). The sample numbers are positioned to the right of the symbols. The line is an approximate interpolation.	30

3.1	The crystal structure of Si and Ge is face-centred cubic (fcc) on the left and its first Brioullin zone on the right. The symmetry axes and some important points in the first Brioullin zone are labelled with commonly used letters.	32
3.2	Band structure of Si and Ge. The letters at the abscissae are points and symmetry axes in k -space as depicted in Figure 3.1. Note that the band gap of Si is between the X point in the conduction band and the Γ point in the valence band, while it is between the L point in the conduction band and the Γ point in the valence band in Ge.	32
3.3	Band gap of $\text{Si}_{1-x}\text{Ge}_x$ versus Ge concentration x as calculated with (3.2) and (3.3). The band gap is Si like for $x \leq 0.87$ and Ge like for $x > 0.87$, causing the kink at $x=0.87$	33
3.4	Band edges of unstrained SiGe and their deformation due to hydrostatic and additional uniaxial strain. The latter represents SiGe deposited pseudomorphically on Si. Hydrostatic strain increases the band gap. The additional uniaxial strain removes the degeneracy of the light hole (LH) and heavy hole (HH) bands and splits the conduction band (CB) into two, resulting in a reduction of the fundamental band gap in comparison to unstrained SiGe.	34
3.5	A SiGe layer embedded in Si forms a quantum well for holes in the valence band. The deepest well is obtained in the heavy hole (HH) band, which is depicted at the bottom. The band edges are drawn as solid lines and the allowed energies in the quantum well as dashed lines, labelled HH1, HH2 and HH3. The conduction band (CB) splits in two, where the band in $[001]$ direction is the lowset in energy and forms a negligibly small barrier and the bands in $[100]$ and $[010]$ directions are much higher in energy and form a barrier. The minimum transition energy is given by the difference between the CB E_C^{001} and ground state in the HH band $E_{V,HH} - \Delta E_{conf,1}$	37
3.6	Band edges (thick solid lines) and their confined states (dashed lines) relative to the bulk Si valence band edge of a 3.4 nm $\text{Si}_{0.55}\text{Ge}_{0.45}$ layer between Si bulk. A Si/SiGe/Si structure forms a QW in the valence band and constitutes a considerably smaller, here neglected, barrier in the conduction band (CB). The strain removes the degeneracy of the heavy hole (HH) and the light hole (LH) band, while the changes of the split-off (SO) band is small. For pseudomorphic layers grown in $[001]$ direction, the CB along $[100]$ and $[010]$ split off from the one along $[001]$. The barrier in the lowest CB is smaller than the accuracy of the calculation so that it is neglected. The energy eigenvalues for bound states in a QW are obtained from solving the 1D-Schrödinger equation for parabolic bands. The probability density $ \varphi ^2$ of the confined holes is drawn above their states. The density of states (DOS) is schematically drawn.	38
3.7	Typical arrangement of three SiGe layers embedded in Si spacers. The ray of light is coming from the Si substrate, traverses the weakly absorbing SiGe thin films and is totally reflected at the Si-air interface at the bottom. The reflected and the incident wave superimpose and form a standing wave.	39
3.8	Ray of light from non-absorbing medium 1 (e.g. Si), through weakly absorbing medium 2 (e.g. SiGe) being totally reflected at interface between medium 2 and vacuum (or in good approximation air). σ_j and ϵ_j are the conductivity and the permittivity of medium j , respectively.	40
3.9	Reflection and refraction with polarisation parallel (p) and perpendicular (s) to the plane of incidence. The incident, transmitted and reflected vectors are labelled with an i , t and r superscript, respectively. The interface between layer i and $j = i + 1$ is the $x - y$ plane with its unit normal direction n [37].	43
3.10	Ray of light being multiple reflected within a layer.	43
3.11	Square of the amplitude of the electric field at a totally reflecting Si-air interface. In Si a standing wave is formed, while in air an evanescent wave is obtained.	48
3.12	Square of the amplitude of the electric field relative to the amplitude of the electric field of the incoming wave. The angle of incidence $\theta_{Si} = 46^\circ$. The shaded areas represent air (for $z > 0$) and SiGe. In Si and SiGe a standing wave is formed, while in air an evanescent wave is obtained.	48

3.13	Side view (left) and top view (right) of the ray of light passing through the sample. The thickness of the sample is tenfold exaggerated, thus the number of reflections is 10 times higher, i. e. 234 and 200 for a sample thickness of 325m and 380m, respectively. The SiGe structures are at the top and bottom of the sample, close to where the light is totally reflected.	49
3.14	Absorption measurement setup in the Fourier transform spectrometer. The sample is the dark rectangle in the centre of the picture. Its lower end with the 45°facet is behind two mirrors. The light enters the sample chamber from the right, is deflected by the first mirror into the direction of the sample. The focus of the light is close to the right hand side of the 45°facet. The path of the light through the sample is depicted in Figure 3.13. The light, after leaving the sample at the left hand side of the 45°facet, gets deflected by the second mirror into the detector.	50
3.15	a) Raw transmission data of a SiGe sample and a Si reference sample as a function of the photon energy measured with a Perkin Elmer grating spectrometer. b) Same data as in a) but scaled to obtain the transmittance under the estimate that the absorption is negligible for some photon energy, i. e. scale the maximum to 1.	51
3.16	Transmission of SiGe sample and Si reference sample (thick and thin solid line) in comparison with transmission calculated from literature data [39], taking free carrier absorption of undoped and 1 and 10 Ωcm n doped Si into account (dashed lines). The doping concentration of the substrate the samples are made of is specifies as 1-10 Ωcm n type.	52
3.17	a) Raw transmission data of a SiGe sample and a Si reference sample as a function of the photon energy measured with a Bruker Fourier transform spectrometer. b) Same data as in a) but scaled to overlap at around 0.7eV. The excellent overlap for photon energies < 0.8eV indicates that the systematic error introduced by the scaling is small.	54
3.18	Transmission of different measurements of the Si reference sample as a function of the photon energy. T_0 is the transmission of the empty, N_2 purged sample chamber. The spectral shape is reasonably well preserved, but a transmission measurement on an absolute scale is not reproducible.	55
3.19	Measured transmittance of four $\text{Si}_{1-x}\text{Ge}_x$ samples with different well thickness compared to a Si bulk reference.	56
3.20	Effective transmittance ($T_{\text{SiGe}}/T_{\text{Si}}$) of the SiGe structures in $\text{Si}_{1-x}\text{Ge}_x$ samples with different well thickness and Ge concentrations x	57
3.21	Absorption coefficient α of $\text{Si}_{1-x}\text{Ge}_x$ samples with different well thickness and for the reference Si bulk sample in comparison with Si bulk literature data [39].	58
3.22	$\text{Si}_{1-x}\text{Ge}_x$ absorption coefficient α of the measured samples in comparison with bulk literature data. The solid lines are least square fits of parameters in (3.14) to the measured data.	59
3.23	Highest valence band edges, i. e. that of the heavy holes, and lowest conduction band edges of two samples with a SiGe QW between Si spacers in comparison with a bulk $\text{Si}_{0.42}\text{Ge}_{0.58}$ (thick lines). The dashed lines indicate the allowed energy states in the quantum wells with the thin lines above are the probability densities of the holes. Note that all three have approximately the same minimum transition energy (being the band gap for a bulk semiconductor). The energy scale is relative to the highest Si valence band edge.	61
3.24	Transmittance of a Si reference sample (dashed line) and the 2 SiGe samples 46 and 47 shown in Figure 2.8 and Figure 2.9 (thick and thin solid line) as a function of the photon energy measured with a Bruker Fourier transform spectrometer. The overlap of the three samples is excellent for photon energies between 0.35 and 0.95eV. Due to the small amount of SiGe deposited, the additional absorption of the SiGe is only visible in the small range of photon energies depicted in the inset.	62
3.25	Effective transmittance of SiGe sample 46 and 47 shown in Figure 2.8 and Figure 2.9 as a function of the photon energy. The curves are derived from the data shown in Figure 3.24.	63

3.26	Absorption coefficient of SiGe quantum well (QW) samples with well thicknesses of 1.7 nm (sample 46) and 1.1 nm (sample 47) shown in Figure 2.8 and Figure 2.9 in comparison with interpolated literature data [43] of unstrained bulk $\text{Si}_{0.42}\text{Ge}_{0.58}$ as a function of the photon energy. The QW curves are derived from the data shown in Figure 3.25. For all samples a minimum transition energy between 880 meV and 900 meV was calculated. The error bars refer to the bulk absorption coefficient and include estimated accuracies of the minimum transition energy. The upper ends of the error bars refer to one third of the calculated error (see text and Table 3.2).	63
4.1	Thinned <i>pin</i> -diode for photocurrent measurement with 25 layers of Ge islands in the space charge region	68
4.2	Comparison of transmission through Si reference sample (thin line) and Ge islands sample (bold line). The absorption of Ge islands is clearly visible in the photon energy range of 0.8 to 1.05 eV. The Ge quantum dot sample is scaled to overlap with the Si reference sample in the photon energy range from 0.45 to 0.7 eV.	69
4.3	Absorption coefficient as a function of the photon energy of the Ge islands in comparison with literature values of bulk SiGe [43] and bulk Si [39].	70
4.4	Photocurrent as a function of the photon energy of the Ge islands sample in comparison with a reference sample without Ge.	70
4.5	Internal quantum efficiency IQE (charge carriers collected at contacts divided by the number absorbed photons) as a function of the photon energy for the Ge islands sample and the Si reference sample.	71
5.1	Schematic drawing of a porous (a) and a gas-tight (b) emitter system with cylindrical symmetry.	75
5.2	Experimental setup of a 20 kW Si based porous emitter system.	77
5.3	Investment cost per unit peak electrical output power for 4 different TPV scenarios, a gas engine and a fuel cell.	81

List of Tables

2.1	Comparison of the width of the Si spacers w_{Si} and SiGe wells w_{SiGe} obtained with TEM and X-ray diffractometry (XRD). The latter delivers also the Ge concentration x . n is the number of SiGe layers in the sample. See text for discussion of the error bars.	16
3.1	Number of wells n , QW thickness d_{SiGe} and Ge concentration x , of the measured samples with the calculated minimum transition energy from the lowest conduction band to the heavy and light hole band E_g calculated with (3.13).	55
3.2	Minimum transition energy of SiGe QW samples shown in Figure 2.8 and Figure 2.9 in comparison with band gaps of bulk SiGe with three different Ge concentration. The values in parentheses are estimated accuracies. The two QW samples and $Si_{0.42}Ge_{0.58}$ bulk have similar minimum transition energies, while $Si_{0.7}Ge_{0.3}$ has a minimum transition energy equal to the upper accuracy limit of the two QW samples and $Si_{0.25}Ge_{0.75}$ has a minimum transition energy equal to one third of the lower accuracy limit of the two QW samples. The latter two were used to for the error bar of the absorption coefficient in Figure 3.26. The effective width is the width in which the probability to find a hole is 68%.	61
5.1	Cost estimate for 4 TPV scenarios and a gas engine and a fuel cell for comparison. The <i>emphasised</i> cost figures are end user prices of available components. The bold numbers are based on experimentally achieved values.	82
B.1	UHV-CVD grown samples, with maximum possible Ge content, i. e. no SiH_4 was used to deposit the SiGe structures. After the Si buffer, the Ge rich structures were deposited for time t_{GeH_4} , capped with Si, deposited for time t_{SiH_4} (the Si growth rate is about 1.2nmmin^{-1}). The SiH_4 and GeH_4 (5% GeH_4 in H_2) flow was 20sccm. The Table gives statistical values of height, area, volume and diameter of the islands, derived from atomic force microscopy (AFM) measurements.	97
B.2	List of UHV-CVD grown multi quantum well samples, where x is the Ge concentration in the SiGe alloy, h_{SiGe} and h_{Si} is the height of the SiGe and Si layer, respectively, q_{SiH_4} , q_{GeH_4} , t_{SiH_4} and t_{GeH_4} are gas flow parameters for SiH_4 and GeH_4 , respectively and n is the number of wells.	98

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