Doctoral Thesis

Electrical and optical properties of silicide-silicon heterostructures

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Publication Date:
1995

Permanent Link:
https://doi.org/10.3929/ethz-a-001426279

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Electrical and optical properties of silicide - silicon heterostructures.

A dissertation submitted to the
SWISS FEDERAL INSTITUTE OF TECHNOLOGY ZÜRICH

for the degree of
DOCTOR OF NATURAL SCIENCES

presented by

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1995
TO
YVONNE
AND
MY PARENTS
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Nach einer kurzen Übersicht über das Co - Si Phasendiagram und einigen wichtigen Kristallstrukturen im zweiten Kapitel, wird im Kapitel drei die erstmalige Stabilisierung von pseudomorphem CoSi mit CsCl Struktur beschrieben. In Volumenform weist CoSi unter Normalbedingungen die sogenannte FeSi Struktur auf. Zum ersten Mal gelang es mir diese metallische Monosilizid - Phase mit Molekularstrahl - Epitaxie auf Si(111) zu stabilisieren. In einem ersten Schritt wird das Wachstum sowie der strukturelle Nachweis der CsCl - Phase dargestellt. Diese Phase hat ganz andere Eigenschaften als die volumenstabile Phase, was sich insbesondere in der elektronischen Struktur durch UPS Messungen und in elektrischen Transportmessungen äußert. Während in der neuen pseudomorphen Phase der elektrische Transport lochartig ist, ist er in der volumenstabilen Phase elektronartig. Die Stabilität vom pseudomorphenen CoSi, die allerdings sehr beschränkt ist, sowie der Phasenübergang zur volumenstabilen ε-Phase werden anhand von Totalenergie - Rechnungen plausibel gemacht und mit denjenigen der isostrukturellen FeSi Phasen verglichen.

Im Kapitel vier werden einige strukturelle Eigenschaften, insbesondere neue Resultate von Spannungsmessungen an dünnen kohärenten CoSi₂ - Filmen auf Si(111) und Si(001) vorgestellt. Wegen dem Gitteranpassungsfehler von -1.2 % erfordert das kohärente Filmwachstum elastische Verspannung der Schichten. Die Relaxation von epitaktischen CoSi₂ Filmen auf Si(111) konnte quantitativ mit der Theorie von Matthews beschrieben werden. Einer der wichtigsten Parameter ist dabei die kritische Schichtdicke, bei der die Bildung von Versetzungen zur Verminderung der gespeicherten elastischen Energie beginnt. Für Si(111)
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beträgt sie ~45 Å und auf Si(100) ~ 75 Å. Detaillierte Spannungsmessungen mit RBS channeling an Siliziden und Silizid - Silizium Heterostrukturen werden vorgestellt.

Das Beherrschen des Wachstums verspannter zweidimensionaler Silizide war Voraussetzung für ein erfolgreiches Überwachsen mit Si, welches in Kapitel fünf dokumentiert ist. Um die Heterostrukturen für Anwendungen in der Mikro - und/oder Opotelektronik verwenden zu können, ist eine einwandfreie kristalline Qualität erforderlich. Das Wachstum sowie die strukturelle Charakterisierung solcher Silizid - Silizium Heterostrukturen wird ausführlich beschrieben. Es stellte sich heraus, dass das Hauptproblem des Silizium - Überwachstums die Relaxation der Silizide ist. Die kleine Fehlorientierung der Substrate führt zu unvermeidbaren Defekten an den CoSi₂/Si(111) Grenzflächenstufen, was absolut kohärentes Wachstum, auch dünnster, Silizide verhindert. Silizium muss deshalb zu Beginn verspannt aufwachsen. Im Gegensatz zu Si(001) Substraten konnten auf Si(111) die Wachstumsprobleme gelöst werden, unter anderem durch geeignete Substratwahl, d. h. mit kleiner Substrat - Fehlorientierung.

ABSTRACT

In the introductory chapter one, some aspects of epitaxial growth are summarized. The concept of pseudomorphism, which relates to epitaxial stabilization of bulk unstable phases, is introduced. Since in general epitaxial films have a small lattice mismatch relative to the substrate, they are strained. Obviously strain is a form of energy which has to be considered when dealing with epitaxial systems. Important information about the strain state of thin epitaxial films have been obtained from strain measurements using Rutherford backscattering spectrometry (RBS) ion channeling. The experiment is briefly described therein.

After a summary overview of the Co - Si System with some important crystal structures of Co - Si phases in chapter two, the epitaxial stabilization of pseudomorph CoSi with CsCl structure is presented in chapter three. In bulk form the monosilicide adopts the so called FeSi structure. For the first time I have succeeded to stabilize the metallic, pseudomorph CoSi with CsCl structure by MBE on Si(111) using a thin CoSi₂ template. In the first few paragraphs the growth and the structural identification are presented. The most important point is the striking behavior to the isostoichiometric bulk stable ε-CoSi which is particularly observable in UPS measurements and in electric transport measurements. Transport in the pseudomorph CoSi is predominantly hole - like whereas in the bulk phase it is electron - like. This pseudomorph phase, however, is only metastable. Explanation for the stabilization and the phase transition of CoSi and the isostructural FeSi phases is given by total energy calculations.

In the following chapter four, some structural aspects of coherent CoSi₂ films on Si(111) and Si(001) are discussed. Thin epitaxial CoSi₂ films were grown on Si(111) and Si(001) substrates. Since CoSi₂ has a lattice misfit of -1.2 % in respect to Si, coherent growth of thin films imposes strain on the films. The relaxation of epitaxial silicide films is quantitatively described with the model of Matthews. One of the main parameter therein is the critical thickness for strain relaxation through formation of misfit dislocations. This thickness is ~ 45 Å for silicides grown on Si(111) and ~ 75 Å on Si(001). Detailed strain measurements by RBS channeling have been carried out on silicides and on heterostructures.

Mastering the growth of thin, strained silicides is a prerequisite for a successful overgrowth with Si, which is documented in chapter five. To be useful in micro- and/or optoelectronic applications, the heterostructures have to have an impeccable crystalline
quality. Growth and structural characterization of such silicide - silicon heterostructures are discussed in detail. The main problem of silicide overgrowth with Si turns out to be the relaxation of the silicide. Since the wafers in practice are always slightly misoriented, defects at the CoSi$_2$/Si(111) interface prevent absolutely coherent silicide growth. Thus the Si has to grow with a compressive strain in the initial stages of overgrowth. However, the problems could be solved at least for Si(111), whereas on Si(001) no promising results were obtained.

A novel type of infrared detector, fabricated with PtSi/Si/CoSi$_2$ and CoSi$_2$/Si/CoSi$_2$ heterostructures on Si(111), is presented in the final chapter six. This sensor consists essentially of two back to back connected Schottky barriers. The silicon between the two metal layers is undoped and hence depleted, yielding a trapezoidal energy band diagram. Depending on the bias condition of the detector, impinging light leads to two or even to four different internal photoemission processes. Even though Schottky barrier detectors are widely used nowadays they have the drawback of a fixed sensing range. In contrast the device presented in this thesis has a variable detecting range. With the tuning behavior depending strongly on the choice of the metals, the cutoff energy in PtSi/Si/CoSi$_2$ sensors could be tuned by an externally applied bias between 0.8 and 0.4 eV. The way to truly wavelength resolved, i.e. colored, IR imaging with existing Si signal processing technology is open.
1. Thin epitaxial films

I spent a lot of time at the old van de Graaff accelerator at the University Zürich, measuring thin films of Ni, Fe and Co silicides, SiGe superlattices, Zn$_x$P$_y$, and several samples of other materials with Rutherford backscattering spectrometry (RBS). In particular I measured strain of thin films with RBS channeling. Since new results of strain measurements will be presented in the following chapters, I want to describe this method in some detail. In addition some terminology and concepts used in epitaxial systems are presented in a rather short way.

1.1. Epitaxy

Two ancient Greek words ἐπί (epi - placed or resting upon) and τάξις (taxis - arrangement) are the roots of the modern word epitaxy. Epitaxy refers to extended single-crystal film formation on top of a crystalline substrate and was first observed to occur in alkali halide crystals over a century ago. Two types of epitaxy are distinguished, namely homoepitaxy, which refers to the case where the film and the substrate are identical, i.e. epitaxial silicon on a Si substrate, and heteroepitaxy, where the film material is different from the substrate. In the case of homoepitaxy the lattice parameters match perfectly and no interfacial bond straining occurs. In the case of heteroepitaxy on the other hand, the lattice parameters of the film $a_f$ and the substrate $a_s$ differ by a small amount, which is indicated by the lattice mismatch $\eta$ according to

$$\eta = \frac{a_f - a_s}{a_s}.$$  \hspace{1cm} (1.1)

Epitaxial growth occurs in one of three distinct modes as is illustrated in Figure 1.1. Frank van der Merwe (FM) growth proceeds one monolayer at a time which corresponds to real two-dimensional growth. In the Volmer - Weber (VW) growth mode, three-dimensional islands form from the beginning of growth. With increasing film thickness the islands coalesce to form a continuous film. Stranski - Krastanov (SK) is a combination of the FM and VW growth modes. The first few monolayers grow in a layer by layer fashion followed by the formation of three-dimensional nuclei.
1. Thin epitaxial films

Figure 1.1: Three different growth modes for thin films. Frank - van der Merwe growth (FM) corresponds to layer by layer growth (i.e. two dimensional growth), Volmer - Weber (VW) mode to the growth of three-dimensional islands. In the Stranski - Krastanov (SK) mode the films first grow layer by layer (FM) before three-dimensional islands (VW) are formed.

It is obvious that one attempts to grow films in the FM mode. This however depends on the misfit $\eta$ and the interaction strength between the film and the substrate. For two-dimensional epitaxial film growth and on the assumption that the behavior of the system is governed by lowest energy principles, some predictions about the system can be made [1].

1) large mismatch at the interface is accommodated by misfit dislocations

2) when the misfit and the thickness of the overgrowth are small enough the overgrowth is coherent [2], i.e. the misfit is entirely accommodated by a homogeneous strain in the film

3) when the misfit and/or thickness is large enough both homogeneous strain and misfit dislocations are present

4) a film whose growth is initially coherent becomes unstable at a critical thickness $h_c$ and misfit dislocations are introduced

5) as the film increases in thickness beyond $h_c$ the homogeneous strain decreases

Another possibility, which recently has attracted much interest, is the growth of thin films that adopt a crystal structure that is well lattice matched to the substrate but which differs from the crystal structure that the film normally would adopt in bulk form. This phenomenon is called pseudomorphism [2]. Initially the pseudomorphic phase grows coherently on the substrate. Similar to bulk stable films, there exists a critical thickness $h_s$ for

---

1) The film atoms are in registry with the substrate atoms. (Also called commensurate)
pseudomorphic films, where misfit dislocations begin to nucleate in order to lower the stored elastic energy of the film. It is possible that the total energy of a pseudomorphic film is higher at a certain film thickness than that of the corresponding bulk stable phase. The film is then in a metastable state and there exists a new critical thickness $h_e$ for epitaxial stability. Films thicker than $h_e$ may undergo a phase transition to the energetically more favorable phase. The stabilization of pseudomorphic films can be qualitatively understood within the framework of continuum elasticity as was presented by Zunger and Wood [3,4]. If there are two competing phases as for FeSi and CoSi (stable bulk phase, called $\varepsilon$-phase and pseudomorphic CsCl phase) the total energy curves for both phases have to be calculated. This will be needed for the discussion of stability of the new CoSi phase (Chapter 3).

1.2. Strain of thin films

Linear elasticity theory, as presented in Appendix A, is used in all theories dealing with thin film systems, which is allowed only for small misfits $\eta$. When a thin film with equilibrium lattice parameter $a_f$ grows coherently on a substrate with lattice parameter $a_s$, it is usually elastically distorted parallel to the interface, resulting in a planar strain $\varepsilon_{||} = (a_{||} - a_f) / a_f$. Simultaneously a perpendicular strain $\varepsilon_{\perp} = (a_{\perp} - a_f) / a_f$ is introduced by the Poisson effect [5] (Figure 1.2; see also Figure 1.3 and B.1).

![Figure 1.2: Schematic drawing of a substrate lattice unit cell with lattice parameter $a_s$ and a film cell, which, grown coherently to the substrate, has a parallel lattice parameter $a_{||}$ and a perpendicular lattice parameter $a_{\perp}$. The broken line shows the film cell in equilibrium condition with lattice parameter $a_f$.](image)

Now $a_{||}$ and $a_{\perp}$ stand for the parallel and perpendicular lattice parameter of the strained film, respectively. For completely coherent growth the planar strain $|\varepsilon_{||}|$ is roughly equal to the
lattice misfit $\eta$ ($\eta$ is defined relative to the substrate lattice constant $a_s$ and $\varepsilon_{\parallel}$ relative to the lattice constant $a_f$ of the relaxed film). With XRD it is possible to determine $a_{\parallel}$ and $a_{\perp}$ separately by measuring symmetrical and asymmetrical Bragg reflexes, whereas with RBS only the trigonal/tetragonal\(^1\) strain $\varepsilon_t$ can be determined (see next paragraph and Appendix B).

\[
\varepsilon_t = \frac{a_{\parallel} - a_{\perp}}{a_f} = \frac{a_{\parallel} - a_f}{a_f} - \frac{a_{\perp} - a_f}{a_f} = \varepsilon_{\parallel} - \varepsilon_{\perp}
\]  

The value of $\varepsilon_t$ depends on the bulk elastic constants $C_{ij}$ according to

\[
\varepsilon_t = (1 + A) \varepsilon_{\parallel}
\]

with

\[
1 + A = \frac{C_{11} + 2C_{12}}{C_{11} + \frac{2}{3}C}
\]

For (111) and (100) surfaces $C = 2C_{44} - C_{11} + C_{12}$ and $C = 0$, respectively [6]. See also appendix A for the definition of elastic constants. Since the lattice parameters in general have different thermal expansion coefficients, strain and misfit are a function of temperature.

### 1.3. Strain determination with RBS channeling

RBS is probably one of the most frequently used characterization techniques for quantitative analysis of compositions. Stoichiometry, thickness, depth profiles, crystalline quality and strain of thin solid films near the surface region (10 - 10000 Å) can be determined in a straightforward way. RBS has its origin in particle physics and evolved in the last few years into a major materials characterization method. In most cases, He or H beams with energies in the range of 1 - 2 MeV are used. The method is often referred to as a "non-destructive" one. However, in the case of strain measurements one can observe that the bombardment alters the crystalline structure in an irreversible manner. When an ion beam bombards a solid surface, the majority of the ions penetrate the solid, slowing down due to ionization and excitation of the target atoms and momentum transfer to the target atoms. At the end of their range below the surface, the majority of the ions stop. The surface region is thus modified by the bombardment process, i.e. defect formation and implantation (first order

\(^1\) Tetragonal strain refers to distortions along (100) axes since the deformation is towards a tetragonal Bravais lattice, whereas on (111) surfaces the strain is trigonal since the deformation is rather towards a trigonal Bravais lattice.
process). During the ion - beam bombardment a minute amount of the ions will backscatter from the target nuclei at and beneath the surface, and only some of the scattered ions will escape again from the solid (scattering angle > 90°, second order process). Since the scattering process in this energy range follows the Rutherford scattering law, the quantitative analysis received the name *Rutherford backscattering spectrometry* (RBS). For more information see e.g. in [7] and [8] or for a recent review of new trends in ion - beam analysis in [9] and for low - energy ion scattering at surfaces in [10].

Epitaxial films grown on a substrate with a lattice misfit \( \eta \), have a slightly distorted lattice due to the strain imposed by the substrate. Off - normal crystallographic axes of the silicide are hence tilted by a small angle \( \Delta \theta \) from the corresponding axes of the substrate, as is schematically shown in Figure 1.3.

![Schematic diagram showing the relationship between the substrate, film, and the misfit angle \( \Delta \theta \).](image)

*Figure 1.3: Light circles indicate the substrate and black circles the film. Dotted circles show the atoms of the silicide in their bulk equilibrium positions. Due to the finite lattice misfit \( \eta \) between film and substrate, the film is strained when grown coherently onto the substrate (arrows to the right side). The Poisson - effect leads to a relaxation in the perpendicular direction. The crystal axes of the film are therefore tilted by a small angle \( \Delta \theta \), which is shown schematically for one direction.*

With channeling measurements it is possible to determine the exact position of off - normal axes of the film and substrate separately, whenever at least one constituent of film and substrate is different and the film thickness does not exceed a certain thickness. Therefore the tetragonal/trigonal distortion \( \varepsilon_t \) is connected with the angular distortion \( \Delta \theta \) in the following way (see Appendix B) [11,12].
1. Thin epitaxial films

\[ \Delta \vartheta = \frac{1}{2} \left( \frac{a_{\parallel}}{a_{\perp}} - 1 \right) \sin(2 \vartheta_s) \approx \frac{1}{2} e_r \sin(2 \vartheta_s) = \frac{1}{2} (1 + A) e_r \sin(2 \vartheta_s) \] (1.5)

As long as the incident beam is not too far away from the exact channeling direction of the film, it can be successfully steered into this direction, thereby falsifying the misalignment angle \( \Delta \vartheta \) [7]. See for example [5] for an analysis of the steering effect as a function of primary beam energy measured using a thick NiSi\(_2\) film. Steering depends on the channel width \( \psi_{\parallel} \), which itself depends on the crystal axis, and on the incident beam energy. To be sure that steering can be neglected, I therefore usually measured two symmetric \(<110>\) channels with respect to the surface normal of the substrate beneath the film, which within the experimental uncertainty, gave an angle difference equal to the no strain value of 70.53° and 90.00° for (111) and (100) surfaces, respectively. In the experiments beam steering came into play for films thicker than \( \sim 100 \text{ Å} \) which is the upper limit of film thickness for strain measurements with 2 MeV He\(^+\).

One has to be careful doing strain measurements, since the particle bombardment alters the microstructure of the strained film and hence the strain of the film. In a recent paper about strain measurements on TaSi\(_2\) and MoSi\(_2\), a strong relation between the implanted dose and the strain was reported by Hardtke et al.. They even observed a change of tensile strain into compressive strain [13]. Therefore the smallest possible dose was used, in order to minimize the beam influence. In order to assess the beam damage, the strain behavior of a CoSi\(_2\) film as a function of implanted dose was examined. The tilt angle decreased only 10% after a dose corresponding to ten times the dose used in typical strain measurements had been accumulated. Results were therefore not corrected for beam damage since the statistical errors due to the short integration times are much larger.

1.4. Strain relaxation

In a thin film, which has a lattice mismatch \( \eta \) relative to the substrate, elastic energy \( E \) is stored when it is grown coherently onto the substrate.

\[ E = \frac{1}{2} C_{11} \left( \varepsilon_{xx}^2 + \varepsilon_{yy}^2 + \varepsilon_{zz}^2 \right) + C_{12} \left( \varepsilon_{xx} \varepsilon_{yy} + \varepsilon_{yy} \varepsilon_{zz} + \varepsilon_{zz} \varepsilon_{xx} \right) + \frac{1}{2} C_{44} \left( \varepsilon_{xy}^2 + \varepsilon_{yz}^2 + \varepsilon_{zx}^2 \right) \] (1.6)

The interesting question is now, up to which thickness coherent or pseudomorphic film growth is possible. If the film thickness and the misfit between the two lattices were both sufficiently small, the coherent state is indeed the energetically most favorable. Theoretical
calculations [1, 14, 15, 16] based on thermodynamic equilibrium between a grid of misfit dislocations and the strained epitaxial film predict that coherent growth takes place until a critical thickness \( h_c \) is reached. Beyond this film thickness, films reduce their elastic energy by introducing so called \textit{misfit dislocations}, which relieve part of the misfit strain. The misfit dislocation density increases until the strain is totally eliminated and the film can grow with its equilibrium bulk lattice constant. The critical thickness \( h_c \) and the strain relaxation can be roughly estimated using the model proposed by Matthews [14] which is summarized in appendix C. In the case of pseudomorphic films the situation is more complicated, since the system is not always in the state of lowest energy [3, 4].
2. Co - Si system

In this work properties of epitaxial films of CoSi$_2$ and CoSi are presented. Although epitaxial films behave differently than the same material in bulk form, the binary bulk phase diagram of Co and Si is reproduced here [17].

![Binary bulk phase diagram of Co and Si](image)

Figure 2.1: Binary bulk phase diagram of Co and Si [17].

I first cite the metallic CoSi$_2$, since among all the refractory silicides, CoSi$_2$ seems to be the favorite because of its very low specific electrical resistivity ($\sim$ 15 $\mu$Ωcm at RT) and its ability to grow epitaxially on Si [18]. It crystallizes in the cubic CaF$_2$ lattice structure, shown in Figure 2.2 a). The unit cell is face - centered cubic with a lattice parameter of 5.364 Å [19]. This bulk - phase has a good temperature stability with a melting temperature of 1326 °C. Epitaxial growth of coherent CoSi$_2$ onto Si is possible because of the moderate lattice mismatch of -1.2 % relative to Si.

The other phase I want to mention is CoSi with the cubic B20 - structure (also referred to as FeSi structure), which is shown in Figure 2.2 b). A primitive cell contains four CoSi formula units and has a lattice parameter of 4.447 Å [19]. This structure can be derived from the rocksalt structure by considerable displacements along [111] directions [20]. Precipitates
of epitaxial CoSi(111)||Si(111) with CoSi[-110]||Si[11-2] and with a lattice mismatch of -5.6% relative to Si, have been reported by D'Anterroches [21]. The monosilicide bulk phase will in the following be referred to as ε-CoSi according to the phase nomenclature of the Fe-Si system [22].

Figure 2.2: The cubic cobalt silicide phases of a) CoSi₂; CaF₂ structure, b) bulk ε-CoSi; FeSi structure and c) pseudomorph CoSi; CsCl structure. In a) and c) the cell size was chosen equivalent to the Si unit cell size. However, for the FeSi structure a simplified representation of the simple-cubic primitive unit cell is shown. Bulk equilibrium lattice parameters are indicated.

The third phase shown in Figure 2.2 c), the CsCl phase of the monosilicide, is not existent in the bulk phase diagram. Since a unit cell of (CsCl)CoSi has a lattice parameter of 2.74 Å which is close to half the Si lattice constant, eight unit cells are shown in Figure 2.2 c). In this representation the strong similarities between the CsCl and the CaF₂ structure are visible. The lattice mismatch of the (CsCl)CoSi with Si is +0.9%. As will be outlined below,
this phase can only be stabilized by coherent growth of thin CoSi films onto silicon. In the literature this phenomenon is called pseudomorphism [2].
3. New epitaxial CoSi - phase on Si(111)

3.1. Introduction - motivation

Structural phase transformations induced by epitaxy have been of great interest both theoretically [2,3] and experimentally [23,24] in the past few years. The existence of pseudomorphic phases, i.e. of crystal structures which do not exist in bulk form, is particularly intriguing, since it offers new possibilities to synthesize materials with unusual properties. Externally applied pressure may change the crystal structure of a material. The same effect can be achieved by growing films epitaxially, since the material is strained in the same order of magnitude. Moreover, strain can be both, negative and positive, in contrast to the external pressure, which normally is positive. Being stabilized by favorable epitaxial interfaces, these phases are stable only in thin film form. Recently discovered examples are epitaxial growth of bcc-Co on GaAs(110) [24], which in bulk form adopts the hcp structure, or epitaxial Fe$_{1-x}$Si crystallizing with the CsCl structure or structures derived therefrom, when grown by MBE on Si(111) with the substrates kept at sufficiently low temperatures [25]. Electrical transport measurements [26] along with ab initio band structure calculations by Mäder [27] showed that stoichiometric FeSi with the CsCl structure is a nonmagnetic metal with a low density of states (DOS) at the Fermi level $E_F$ in contrast to the stable bulk phase, called $\varepsilon$-FeSi, for which there is evidence for a small gap at $E_F$ and magnetic behavior has been reported [28].

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<tr>
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<tr>
<td>Os</td>
<td>Ir</td>
<td>Pt</td>
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Figure 3.1: Detail of periodic table, showing the position of group VIII transition metals. Monosilicides with CsCl structure are known only for Ru, Rh, Os and for Fe in form of thin epitaxially stabilized films.
The existence of epitaxial FeSi with the CsCl structure is interesting, since the only monosilicides known to crystallize with this structure are those of Ru, Os and Rh, and they seem to do so only under very special conditions [29]. Note that Ru and Rh are situated right below Fe and Co, respectively, in the periodic table (see Figure 3.1). Further bulk stable ε-CoSi crystallizes in the same FeSi structure (Pearson symbol cP8) as ε-FeSi [17,30] (Figure 2.2). These facts led us to speculate that perhaps an epitaxial CoSi phase with the CsCl structure might exist as well. To the best of my knowledge, a CoSi phase with the CsCl structure has never been reported before. Epitaxial CoSi with FeSi structure on the other hand has already been observed as a precipitate during CoSi2 formation by solid phase epitaxy [21]. Results of the first observation of CoSi with CsCl structure [31] will be described in the following.

3.2. Growth

Si(111) substrates (n - doped, 800 - 1200 Ωcm) with an unintentional wafer misorientation of less than 0.3° were introduced into the molecular beam epitaxy (MBE) system as received from the manufacturer. After an annealing to outgas the wafer, the native oxide was desorbed at ~840 °C while exposing the wafer surface to a weak Si flux. Then a 1000 Å thick Si buffer was routinely grown. Details about buffer preparation as well as the MBE system can be looked up, e.g. in [32].

Thin CoSi films were grown by MBE on CoSi2 templates. The latter have either been grown by depositing 1 - 2 monolayer of pure Co at room temperature (RT) or by depositing Co and Si stoichiometrically at RT followed by an anneal to ~ 350 °C forming a 3 - 11 Å thick silicide. Monosilicides with film thicknesses between 25 and 200 Å were then grown by codepositing Co and Si stoichiometrically onto the template with the substrate kept close to RT. The results were essentially the same for both kinds of templates except an improved structural quality when growing onto thick templates or templates made by codeposition. Epitaxial growth of the silicide was monitored in situ by reflection high - energy electron diffraction (RHEED). With increasing film thickness the spots faded slowly as well as the Kikuchi pattern which was merely visible for films thinner than ~90 Å. A sudden disappearance of the RHEED pattern was observed when annealing (CsCl)CoSi films at temperatures between 100 - 200 °C or growing them thicker than ~175 Å. As will be shown below, the pseudomorphic CsCl phase was then transformed into the bulk stable ε-phase.
3.3. Structure

In typical RHEED observations, the intensity of the spots and the Kikuchi pattern were rather low from the beginning of growth of (CsCl)CoSi and a structure analysis with a RHEED panorama, therefore, did not yield the complete structure information. The observation of faint RHEED patterns is either due to the RT deposition which leads to incomplete reaction or to the bad stability of this phase. In Figure 3.2 characteristic RHEED patterns of a 44 Å thick (CsCl)CoSi film are shown. Together with TEM and x-ray analysis the phase was identified to have cubic symmetry and an epitaxial orientation of CoSi(111)||Si(111) and CoSi[11-2]||Si[-1-12]. This means that CoSi is oriented in the same way as the underlying CoSi₂ template, i.e. is rotated by 180 degrees around the substrate normal relative to the Si substrate.

Figure 3.2: Typical RHEED patterns of pseudomorph (CsCl)CoSi on Si(111). a) [01-1] and b) [11-2] azimuth. (W1232; after 44 Å (CsCl)CoSi with 7 Å CoSi₂ template)

Figure 3.3 a) shows a low resolution cross-sectional TEM image of a 70 Å thick CoSi film on top of a 10 Å thick CoSi₂ template. The corresponding diffraction pattern is displayed in Figure 3.3 b). It is indexed according to a cubic unit cell with the lattice parameter $a_{\text{Si}}$ of Si,
with the result that all odd-order reflections of CoSi are absent. This is consistent with the CsCl structure and a lattice parameter of the film close to \(a_s/2\). Figure 3.3 c) shows a high-resolution image and the corresponding computer simulation of the CoSi layer, taken along the [1-10] zone axis. An image of the interface region with the CoSi\(_2\) template is displayed in Figure 3.3 d). There the type B interface can be clearly seen.

![Image](image.png)

Figure 3.3: a) Low resolution cross-sectional TEM image of a 70 Å thick pseudomorphic CoSi film with CsCl structure, grown on top of a 10 Å thick CoSi\(_2\) template on Si(111). b) Selected area diffraction pattern of the silicide region. All spots in the leftmost column are indexed according to a cubic unit cell with the lattice parameter of Si. The diffraction pattern is consistent with B-type orientation of (CsCl)CoSi. c) High-resolution image and corresponding computer simulation of the CoSi layer, taken along the [1-10] zone axis. d) High-resolution image of the interface region between the CoSi\(_2\) template and the Si substrate, taken along the [1-10] zone axis.

With x-ray diffraction (XRD) (Cu K\(_\alpha\)) the same reflection pattern as previously observed for FeSi with the CsCl structure was found [25,33]. All reflections with odd order indices were found to be absent, when indexing according to a cubic unit cell with the Si
lattice parameter. This is consistent with assuming the CsCl structure and a lattice parameter of \( \sim a_{Si}/2 \). With XRD the lattice parameter and the Poisson number were further determined to be \( 2.74 \pm 0.02 \) Å and \( \nu = 0.32 \), respectively. Since \( 2a_{0} \) is larger then \( a_{Si} \), films below a critical thickness \( h_{c} \) are under a compressive biaxial strain \( \epsilon_{||} \). By XRD and RBS the trigonal strain \( \epsilon_{t} \) was measured to be at maximum \( 2.80 \pm 0.30 \% \). A strong correlation between strain and wafer misorientation prevails. Trigonal strain values significantly higher than 1.5 \% were only found in films with the unintentional wafer misorientation smaller than 0.1 °. In addition on wafers of comparable miscut, the strain is constant for films with thicknesses up to 100 Å, indicating the critical thickness for strain relaxation to be larger. The wafer misorientation leads to a stepped wafer surface and consequently misfit dislocations are formed at every monolayer step in the CoSi\(_2\) template [34]. Moreover RBS channeling dips were more pronounced (i.e. deeper) in strongly strained films, which indicates better crystal quality. Since CoSi\(_2\) has a misfit of -1.2 \%, i.e. a lattice parameter smaller than Si, relaxation of the CoSi\(_2\) template increases the mismatch between CoSi and the template. The best growth condition for pseudomorphic CoSi is hence a coherent template without strain relieving dislocations. Since strain relieving misfit dislocations are present at interfacial monolayer steps [34], small wafer miscut is therefore necessary for growth of pseudomorphic CoSi with good crystal quality.

A first order phase transition to the stable bulk \( \varepsilon \)-phase for film thicknesses exceeding 20Å occurred upon annealing the CsCl phase to 100 - 200 °C. The phase transition could also be triggered by growing the CsCl phase thicker than \( \sim 175 \) Å. This transition was observed by a rapidly vanishing RHEED pattern. Additional confirmation for the transition to \( \varepsilon \)-CoSi was obtained from the appropriate spacing of the Debye - Scherrer rings observed by transmission electron diffraction where a lattice parameter of 4.44 Å was derived. Film morphology as observed by STM exhibited a pronounced change as well, manifested in a vanishing topographic contrast due to buried Si surface step at the phase transition.

3.4. Electronic structure

The angle integrated ultraviolet photoelectron spectroscopy (UPS) spectrum \((h\nu = 21.2 \text{ eV})\) for (CsCl)CoSi, shown in Figure 3.4, exhibits a distinct Fermi - edge, indicating the phase to be metallic. The phase transition is accompanied by a striking change of the spectrum with a broad metal 3d - band emission peak at 1.1 eV for (CsCl)CoSi being replaced by peaks located at 0.3, 1.1 and 2.5 eV for \( \varepsilon \)-CoSi (see Figure 3.4). These three
peaks were present in all ε-CoSi films, and are therefore characteristic for this phase. Repeated measurements on ε-CoSi capped with Si evidenced that the pronounced peak at 0.3 eV is not a surface effect. Apart from this pronounced peak, the spectral features of the ε-phase are in agreement with reported UPS measurements of the stable bulk phase [35,36]. For comparison the UPS spectrum of the same film after transformation to CoSi₂ (annealing to 600 °C for about 5 minutes) is also included together with DOS calculations by Mattheiss and Hamann [37]. The correspondence between experiment and theory for CoSi₂ [37,38,39,40] is fair, as well as with other UPS spectra of CoSi₂ films [32]. Due to the relatively poor crystalline quality of the monosilicide phases, their peaks in the UPS spectra are more broadened than in the CoSi₂ spectrum. In order to quantitatively understand the experimentally observed features, density of states (DOS) calculations, using a parametrized tight-binding model, for both monosilicide phases have been carried out by Miglio [41] (Figure 3.4 b)).

Figure 3.4: a) UPS spectrum (hv = 21.2 eV) of a 44 Å thick CoSi film with the CsCl structure grown onto a 7 ÅCoSi template, after the phase transition to the bulk stable ε-CoSi phase (annealing at 250 °C for 2 minutes) and after transformation to CoSi₂ (for better temperature stability, the silicide was capped with 2 monolayers Si before annealing to 600 °C for 2 minutes). b) Calculated DOS of the monosilicide phases by Miglio [41] and CoSi₂ by Mattheiss and Hamann [37].
The relative positions of the main features of his calculations are present in the measurements, but a discrepancy of nearly 0.8 eV in the absolute position is existent for the monosilicides. This shift, already reported for the Fe silicides [25], is not understood theoretically up to date. This is even more embarrassing since for CoSi$_2$ always good agreement between theory and experiment was found. However, the calculations show as well that (CsCl)CoSi is a metal since the Fermi level is located in a region of rather high density of metal $d$ states.

CoSi$_2$ has a 'quasigap' in the density of states near $E_F$ separating bonding and antibonding states of Si $sp^3$ hybrids and metal $3d$ states. This quasigap was claimed by Tersoff and Hamann to be crucial in stabilizing the CaF$_2$ structure of CoSi$_2$ [37,39,40]. DOS calculations of RuSi and RhSi by Ivanovskii showed that in RuSi $E_F$ lies in a region of low density of states (DOS) just below a peak due to non-bonding 4$d$ states [24]. For RhSi on the other hand $E_F$ is located right in the middle of the DOS peak [42]. This shift of $E_F$ can also be understood assuming rigid-band conditions, where Rh having one electron more than Ru has states filled up to higher energies than Ru. In fact, comparing the DOS of (CsCl)CoSi (Figure 3.4 b) with the DOS of (CsCl)FeSi [27] shows that the position of $E_F$ is displaced to higher energies and falls in a strong peak representing nonbonding metallic 3$d$ states (see Figure 3.4). This can be related to enhanced destabilization of this phase [39,40,42] and it indicates that the material is likely to be magnetic [27]. This latter statement is somewhat delicate since in fact the band structure calculations with spin polarized bands should be performed. Compared to (CsCl)FeSi the pseudomorphic (CsCl)CoSi phase should be less stable which indeed is manifested in the low transition temperature (100 - 200 °) and the instability of thick films (FeSi was found to be stable at least up to 900 Å in contrast to CoSi with a maximum thickness of < 175 Å).

3.5. Stability

The stability of the CsCl phase of CoSi and FeSi as proposed by Miglio [41], is discussed in the following. The CoSi bulk phase could in principle grow coherently on Si(111) with a lattice mismatch of - 5.6 % when the epitaxial orientation is rotated by 30 ° around the [111] direction i.e. with CoSi(111)||Si(111) and CoSi[-110]||Si[11-2] [43]. During CoSi$_2$ formation precipitates with this orientation have been reported by D'Anterroches [21]. The lattice mismatch of pseudomorphic (CsCl)CoSi with silicon on the other hand amounts to
+ 0.9 % (relative to $a_{Si}/2$). Thus the epitaxial stabilization of the CsCl phase is mainly due to the fact that its lattice mismatch is much smaller than that of the bulk phase. But when having a look at the situation of FeSi one is surprised that (CsCl)FeSi is more stable than (CsCl)CoSi because the former has a lattice mismatch $\eta = +2\%$ and the corresponding bulk phase has $\eta = -4.7\%$. To elucidate this topic, Miglio et al. calculated the total energy of the CoSi and FeSi phases which are shown in Figure 3.5 as a function of relative difference from the Si lattice parameter [41]. For coherency, the energy of the $\varepsilon$-phase (black circles) is lower than the one of the CsCl structure (black squares) by about 0.75 eV per formula unit for CoSi and 0.54 eV for FeSi. The occurrence of the NaCl structure both in bulk and epitaxial form is prevented by its high internal energy. When only taking into account elastic energy contribution for a coherent interface, the $\varepsilon$-phase is the most stable phase in both systems. But in the case of FeSi a kinetic phase diagram could be established showing that pseudomorphic (CsCl)FeSi films with thicknesses below 15Å remain structurally stable up to 500 °C, apart from exhibiting a gradual change of the stoichiometry towards FeSi$_2$ with increasing temperature [44]. This in turn cannot be understood in terms of elastic energy contributions of the interface only, since the energy diagram of FeSi looks very similar to that of CoSi (Figure 3.5). Miglio then proposed to take into consideration energy contributions due to interface bonding. He argues that the energy of broken bonds at the interface from atoms of the silicide which do not perfectly match the silicon substrate atoms has to be included. Since for the CsCl phase registry of nearly all atoms is observed and for the coherent $\varepsilon$-phase only one of three atoms is in registry, the energy of the $\varepsilon$-phase is increased by twice the energy of a broken bond. He estimates this energy by assuming equal energy per bond for the NaCl and CsCl phase and hence divides the energy difference of these two phases (for silicon matching condition) by the difference in the coordination number of these two phases. This corrected energy curve for the $\varepsilon$-CoSi is shown in Figure 3.5 by open circles. For the FeSi this energy at the silicon lattice parameter is higher than the CsCl phase which then renders the CsCl phase stable. Thus the CsCl phase is stable up to the critical thickness $h_e$, which is equivalent to the experimentally observed 15 Å [44]. Above this thickness the CsCl phase is only metastable and can be transformed into the stable $\varepsilon$-phase. In the case of CoSi the CsCl phase is always higher in energy than the $\varepsilon$-phase. Thus even the thinnest (CsCl)CoSi films are in a metastable state. This interface bonding energy term decreases roughly with $h^{-1}$ for increasing film thickness $h$. 

Figure 3.5: a) Total energy curves for CoSi and FeSi with NaCl (filled triangles), the CsCl (filled squares), and the ε-phase (filled circles) as a function of the lattice parameter, expressed in terms of the relative deviation from $a_{Si}$ [41]. Open circles indicate the total energy increase in the monolayer limit of the ε-CoSi phase with respect to (CsCl)CoSi, when its unfavorable interface contribution is taken into account. b) Qualitative variation of the total energy per formula unit of ε and CsCl phases as a function of the layer thickness $h$. 
On the right side of Figure 3.5 the total energy of the CsCl- and ε-phase are schematically shown as a function of film thickness. Indicated is the critical thickness \( h_m \) where films transform to the ε-phase. The critical thickness of strain relaxation by misfit dislocation \( h_s \) is about 70 Å for FeSi [45] and is not accessible to experiment for CoSi. Due to kinetic barriers, pseudomorphic (CsCl)CoSi films, which are metastable at every film thickness, can be grown. However, the system can lower its total energy by undergoing a phase transformation to the ε-phase which may be induced by thermal treatment or by growing thick films. Transformations have been observed for temperatures between 100 and 200 °C while thinner films tended to be stable up to higher temperatures than thick films. Hence the kinetic barriers must be a complex interplay of elastic and thermodynamical energy terms. This reasoning gives evidence for the bad stability of pseudomorphic (CsCl)CoSi and the enormous difficulties I had to grow and characterize it.

Recently very thin (CsCl)CoSi films (< 10 Å) have been annealed immediately after growth. At a temperature of 180 - 200 °C a weak 2×1 surface reconstruction appeared which remained up to temperatures of ~ 270 °C. With UPS the phase could not be identified to be ε or CsCl, because of enhanced template and substrate contributions. Further experiments are needed to verify the structure of this phase. Since the ε-phase is the energetically most favorable phase, a phase transition from coherent (CsCl)CoSi to coherent ε-CoSi should be possible. The much larger lattice mismatch relative to Si of the latter phase may probably explain why (CsCl)CoSi with larger film thickness (≥ 20 Å) always transforms to polycrystalline ε-CoSi.

3.6. Electrical and magnetic properties

While the electrical resistivity of thick FeSi films showed a behavior typical for Kondo systems [26], CoSi with the CsCl structure is likely to order magnetically as explained above. Electrical resistivity, Hall effect and magnetoresistance were measured by the standard Van der Pauw technique [46] or by the four - terminal method on structures defined by photolithography and wet - chemical etching, in the temperature range between 1.4 and 300 K. The average residual resistivity at 4 K of (CsCl)CoSi films scattered around 150±30 \( \mu \)Ωcm. Until the temperature of ~ 60 K the resistivity increases roughly linearly with increasing temperature (see Figure 3.6). Above this temperature electric conduction of the low doped substrate (800 - 1200 \( \Omega \)cm) leads to a decrease of the measured resistivity. However,
the temperature dependence below 100 K is rather small for conventional electron-phonon contribution (linear increase) and no real saturation towards a residual resistivity at low temperatures is observed. Because of a mean free path of the order of one lattice constant\(^1\), electric transport is determined primarily by the structural disorder of the crystal rather than by phonon- or by surface scattering. Possibly scattering at magnetic moments is responsible for this effect. In contrast to FeSi no increase of resistivity at low temperatures (i.e. 1.4 K) [26], typical for Kondo systems [47] and electron-electron interactions [48], was observed in (CsCl)CoSi (see insert of Figure 3.6).

![Graph of typical temperature dependence of the electrical resistivity of coherent (CsCl)CoSi, measured at a 96 Å thick film (W1232). The drop above ~ 60 K is due to increasing substrate conduction (substrate resistivity: 800 - 1200 Ωcm).](image)

Evidence for magnetic ordering stems from the pronounced anomalous Hall effect observed at low temperatures. Within the accuracy of the measurement setup, no hysteresis could by detected. Figure 3.7 shows the Hall resistance measured on a 96 Å thick film at 4.2 K. For ferromagnetic materials the Hall resistivity \( \rho_H \) increases linearly at small fields and changes to a second linear rise with a smaller slope at higher fields. It may be written as the sum of the normal linear Hall effect with a behavior expected from a simple consideration of the Lorentz force, and a second term corresponding to the spontaneous magnetization of the material. This latter term has a strongly temperature dependent proportionality factor \( R_I \) [48].

\[
\rho_H = R_0 B + R_1 M. \quad (3.7)
\]

\(^1\) determined assuming the Drude model for one conduction band, i.e. \( \rho_0 = m v_f / n e^2 \lambda \).
Such an anomalous Hall effect is not restricted to ferromagnetic materials, but can also appear in any material where there are large, localized magnetic moments [48]. The curve in Figure 3.7 a) bears a close relationship to the anomalous Hall effect of magnetic materials, since there are two regions with a linear dependence of the Hall resistance with increasing magnetic field. Indeed I observed a strong temperature dependence of the Hall effect, which normally is attributed to $R_T$. As in FeSi the Hall constant is positive indicating predominant hole conduction as is the case in CoSi$_2$ [26,49,37]. The hole density$^1$ of the sample shown in Figure 3.7 is $5 \cdot 10^{22}$ cm$^{-3}$ (determined at $B > 2$ T) which is equivalent to one hole per formula unit, thus indicating (CsCl)CoSi to be metallic. Interestingly, the Hall effect changes sign after the phase transition to ε-CoSi, as can be seen in Figure 3.7 b). The Hall effect in ε-CoSi deviates a little from normal behavior which is probably due to magnetic impurities. In contrast to the pseudomorphic phase, electric transport in ε-CoSi is electron-like which was also reported to be the case in bulk (ε) material [50]. The latter bulk metal has also a virtually temperature-independent diamagnetic susceptibility in contrast to the isostructural bulk FeSi which is paramagnetic [28]. Since surface scattering induced by a magnetic surface oxide might give rise to similar anomalies in the Hall effect, the experiments were repeated on films capped with Si, yielding identical results, however. Further the oxide on bare surfaces was investigated by XPS after they have been exposed to air for several days. It is quite clear that the oxide consists mainly of nonmagnetic SiO$_2$ and not of Co$_x$O$_{y}$. Thus surface effects can be excluded for sure. In order to estimate the effect of magnetic impurities caused by incomplete reaction or stoichiometry variations in (CsCl)CoSi, CoSi$_2$ films were grown exactly in the same way (RT codeposition on thin template) with only the stoichiometry adjusted. The Hall effect was positive and completely normal (not the slightest deviation from a linear relation) with a constant carrier i.e. hole density of $1.8 \cdot 10^{22}$ cm$^{-3}$ in the temperature range between 4 and 50 K$^2$ and did not change after annealing the sample to 600 °C for 30 minutes. This is in full agreement with published data and theory [37,49,50,51] (i.e. in CoSi$_2$ the Fermi surface consists of three nested hole pockets centered at the Brillouin zone center [37]). Similar to FeSi one could argue that magnetic bcc-Co clusters may be formed by excess Co atoms sitting in the center of Co-cubes (see also Figure 2.2). This kind of structural inhomogeneities can naturally not be excluded and are probably responsible for the anomalous Hall effect. Although the better better crystalline quality of (CsCl)FeSi in contrast

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$^1$ The carrier density obtained assuming a one-band model, i.e. $R_H = 1/ne$.  
$^2$ Despite the high substrate resistivity, substrate conduction is the major effect at temperatures above ~ 50 K.
to the (CsCl)CoSi which was evidenced by quantitative XRD and RBS experiments, the Hall anomaly of (CsCl)CoSi films is much more pronounced at any temperature.

Figure 3.7: Hall resistance of a) pseudomorphic 96 Å thick (CsCl)CoSi film (W1202) and b) of a 70 Å thick ε-CoSi film (W1209), measured at 4 K. For (CsCl)CoSi a second Hall measurement with a different experimental setup was carried out with magnetic fields up to 10 T. The anomaly in the Hall effect is typical for magnetic materials. After phase transition to ε-CoSi the sign of the Hall constant changes, indicating electron like conduction.

In conclusion magnetic surface effects can be excluded to cause the Hall anomaly. Further the ε-phase behaves equivalently to bulk ε-CoSi. The Hall anomaly in (CsCl)FeSi is much smaller than in (CsCl)CoSi and is not observed on CoSi₂ films grown with equal growth conditions. However, the nature of the magnetic behavior is not yet clear. It might be that it is due to localized magnetic clusters or it is a bulk effect, thus relied with the band structure of the CsCl phase. Preliminary results of magnetic torque measurements by Madar with the magnetic field parallel to the surface showed indeed a ferromagnetic hysteresis at temperatures below 40 K with a Curie - Weiss temperature dependence. Thus I tend to favor the second hypothesis, i.e. that (CsCl)CoSi is a magnetic material. Unfortunately SQUID magnetometer measurements as well as Brillouin scattering measurements failed to give direct evidence of magnetic ordering in (CsCl)CoSi films.

Perpendicular magnetoresistance at 4 K of all three Co silicide phases was positive and for low magnetic fields proportional to $B^2$. Since the product $\omega_c^2 \tau_0^2$ is much smaller than unity, classical magnetoresistance, which occurs whenever at least two energy bands
contribute to the conduction [47], can be neglected. Electron - electron interaction on the other hand may probably explain the positive magnetoresistance.

3.7. Summary

The existence of monosilicides of Ru and Rh as well as the epitaxial stabilization of FeSi with the CsCl structure let me to search for the existence of this phase of CoSi. Thin films of CoSi were deposited by MBE on a template layer of CoSi₂. RHEED, XRD and TEM analysis proved the phase to have the CsCl structure. This phase is very unstable and transforms to the ε-phase (stable bulk phase) when annealing above 100 - 200 °C or growing films thicker than ~175 Å. The epitaxial stability of both phases (ε and CsCl) of CoSi and FeSi was discussed using total energy calculations which includes interface bond energy. The two CoSi phases have different electronic structures as could be shown by UPS measurements. DOS calculations of the stable bulk phase as well as of the pseudomorphic phase are in qualitative agreement with UPS experiments. Further the Hall effect of these two phases differ dramatically. Whereas for the pseudomorphic CsCl phase a strong anomalous Hall effect, with predominant hole - like conduction was observed, the stable bulk phase has a practically normal Hall effect with predominant electron - like conduction. Since surface effects could be excluded, the crystal structure and the band structure associated thereby must be responsible for this completely different behavior of these two phases. However, direct measurements of magnetism of (CsCl)CoSi are either not complete or failed up to now.
4. CoSi$_2$ on Si(111) and Si(001)

4.1. Introduction - motivation

As integrated circuits become increasingly complex and are required to operate at ever greater speeds, the individual components within the IC will have to be smaller and more closely packed. But the benefits of this drive towards very large scale integration (VLSI) will be lost if the material connecting the components imposes unacceptable delays on circuit operation. Therefore new, low resistivity materials which are thermally stable and compatible with current Si processing technologies become important. Silicide technology has been introduced to achieve low - resistance contacts to active device regions. Although TiSi$_2$ is the mainstream material in 0.5 μm technology, CoSi$_2$ as well is already used in the IC industry [52]. The thermal stability and low resistivity as well as the formation of excellent Schottky barriers, renders CoSi$_2$ useful for ohmic contacts, low resistivity gate metallization and interconnects in micro and optoelectronic device applications [18]. Metallic behavior has been observed over a large range of film thickness down to 10Å [53]. While MBE growth onto Si(111) is nowadays well mastered [32], the situation is more complicated in the case of (001) substrates where various epitaxial orientations are possible and have been observed [54]. Single oriented films have been realized by the use of the template technique [55] and codeposition of Co and Si at Co - rich ratios and substrate temperatures of 500 °C [56,57].

Much time was devoted to the problem of growing continuous and coherent CoSi$_2$ films because of the importance for the subsequent epitaxy of Si on top of it. In order not to repeat earlier publications and theses about CoSi$_2$ growth and characterization by our group (see e. g. [32,58,59,60]), only some important points are summarized. Newer results of strain measurements on the other hand are presented in detail.

4.2. Growth

All films have been grown in a Vacuum Generators V80 MBE system, having a base pressure better than $10^{-10}$ mbar. Cobalt and silicon were both electron beam evaporated at typical deposition rates of 1 Å/s. The deposition chamber is equipped with high - energy
electron diffraction (RHEED) which allows in situ surface characterization. In the same vacuum system we can probe the samples by x-ray as well as ultraviolet photoelectron spectroscopy (XPS and UPS) and by scanning tunneling microscopy (STM).

As substrates I used 3 inch n-doped Si(111) and Si(001) wafers which were oriented to within better than 0.3° and for later studies even better than 0.10°. The preparation of the substrates was carried out by one of the three following methods.

1) Wafers were introduced into the MBE system as received and the natural oxide was desorbed at 840 °C while exposing the surface to a very weak Si flux.

2) Wafers before being introduced into the MBE system were chemically precleaned using the so-called "Shiraki" etch [61]. The thin oxide was then removed in the same manner as in the first method.

3) Only recently we have now the opportunity to clean the wafers in a H-plasma in an UHV chamber attached next to the deposition chamber. Because of the surface roughness of 30 - 40 Å of the cleaned wafers, low temperature Si deposition at ~400 °C was needed to obtain again an atomically flat surface. For details see e.g. in Ref. [62]. This method allowed to reduce the defect density on Si(111) buffers by one order of magnitude.

STM topographies showed a well-oriented surface with parallel monolayer-steps related to the misorientation of the wafer, after a ~1000 Å thick Si-buffer grown at 700 °C and with a deposition rate of 1 Å/s was annealed to 840 °C for 2 minutes [32]. Silicide growth was performed by a template technique [32,55] consisting of the deposition of 1 - 2 Å of pure Co followed by stoichiometric codeposition of 7 Å CoSi₂ near RT. Annealing to ~350 °C resulted in a ~11 Å thick coherent CoSi₂ film. Silicides were then grown up to the final thickness by further RT codeposition and annealing. This template method is absolutely necessary to grow a) continuous films with one epitaxial relation and b) strained silicides on both, Si(001) and Si(111).
4.3. Structure

4.3.1. CoSi$_2$/Si(111)

Hamann and Hoek have shown that the eightfold coordinated B-type CoSi$_2$/Si interface is the energetically most favorable structure [63,64]. Indeed such B-type interfaces were always observed in MBE growth [53,34] (such a B-type interface can be seen on a TEM cross section of a silicide-silicon heterostructure in Figure 5.2). In order to obtain thermally stable films, they have to have a Si-rich surface. Strain, which will be discussed later, leads to the formation of a 2×1 surface reconstruction, which can be observed in situ with RHEED and STM [65]. This reconstruction is only present in films with $h < h_c$. Growing relaxed silicides either by omitting the template layer or by growing films thicker than the critical thickness $h_c$, leads to a network of interfacial dislocations, which can be directly detected by STM [66]. With this method the critical thickness was found to be 40 - 45 Å and 70 - 100 Å for CoSi$_2$ on Si(111) and Si(001), respectively. However, when growth was done in one step, the critical thickness is much lower.

4.3.2. CoSi$_2$/Si(001)

Growth of thin coherent CoSi$_2$ films on Si(001) substrates is by far more challenging than on Si(111) substrates, since various epitaxial orientations are possible in the former case [54]. This is because the surface energy for Si is lower than that for CoSi$_2$ in the same plane and the energies of the (111) planes are lower than those of the (001) planes for both Si and CoSi$_2$ [67]. This explains the stability and the surface morphologies of thin CoSi$_2$ films. Grown on Si(111) they form continuous films. From the viewpoint of surface energy, formation of pinholes in CoSi$_2$(111), exposing the Si substrate, lowers the energy of the system and is therefore a more stable situation. On the other hand the surface energy of CoSi$_2$(001) is higher than that of CoSi$_2$(111). Therefore it is natural for CoSi$_2$(001) films on Si(001) substrates to lower the energy by decreasing the area of CoSi$_2$(001) and increasing the area of CoSi$_2$(111).

At interfacial monolayer steps dislocations of type $a/2<110>$ are always present in the silicide, whereas in the case of double layer steps, the crystal periodicity parallel to the interface is preserved and there are no dislocations, i.e. the Burgers vector is zero [68]. In
recent studies on Si(001) surfaces, it was demonstrated, that with increasing angle of miscut, the surface undergoes a transition from the monolayer to the double-layer regime [69]. Alerhand et al. reported about STM experiments where for annealed surfaces the transition between single to double layer stepped surfaces occurred in the range of $1^\circ \leq \Theta_c \leq 3.5^\circ$ [70]. Calculations by Pehlke and Tersoff [71] evidenced that the transition involves a mixed phase consisting of a complex sequence of single and double steps in agreement with earlier calculations by Chadi [72]. First experiments on intentionally misoriented wafers ($3^\circ$ towards [110]) showed indeed predominantly double layer steps. Using this kind of substrates could be the key for defect-free silicide growth, but as will be explained later, the film resistivity is then no longer isotropic.

As for the (111) surface orientation, it was found that a Si-rich surface is thermally stable in contrast to the Co-rich surface, which transforms into the Si-rich surface accompanied by pinhole formation when annealing to about 500 °C [60]. Co-rich surfaces normally showed a ($\sqrt{2}\times\sqrt{2}$)R45 surface reconstruction in contrast to the (3$\sqrt{2}\times\sqrt{2}$)R45 surface reconstruction of the Si-terminated surface. From the experimental point of view, these different surface reconstructions are very practical, since the stability of the films during the film annealing can be easily controlled by RHEED.

4.3.3. Strain and critical thickness $h_c$ of CoSi$_2$ on Si(111)

With the lattice misfit of $\eta = -1.2\%$ with respect to Si at RT and using the elastic constants of CoSi$_2$ determined by Brillouin scattering$^1$ [73], a maximum trigonal strain $\varepsilon_t$ of 2.33% results. A slightly smaller value (2.0%) is obtained by using the elastic constants determined with ultrasonic velocity measurements on single cobalt disilicide crystals by Guénin and co-workers$^2$ [74]. I determined the trigonal strain with angular scan measurements about the [110] direction of the silicide (Figure 4.1). The minimum of the [110] channeling dip of the film is detected at a larger angle than that of the substrate, i.e. $\Delta \Theta = 0.42^\circ$ for the 30 Å thick CoSi$_2$ film in Figure 4.1 a), in accordance with tensile strain of the silicide. On the same substrate another 30 Å of CoSi$_2$ on half of the surface have been deposited, resulting in a total layer thickness of 60 Å. A strain of only 1.18% was measured on the thick side (Figure 4.1 b)), in contrast to 1.55% measured on the thin side. Figure 4.2 shows the trigonal strain of various films, grown under comparable conditions, with

$^1$ $C_{11} = 222\pm15 \text{ GPa}; C_{12} = 140\pm14 \text{ GPa}; C_{44} = 68\pm10 \text{ GPa}$

$^2$ $C_{11} = 228\pm4 \text{ GPa}; C_{12} = 140\pm4 \text{ GPa}; C_{44} = 83\pm1 \text{ GPa}$
thicknesses up to 500 Å. It has to be mentioned, that the data for the films thicker than 100 Å were obtained by XRD, since RBS gives faulty results because of beam steering.

![Image](image_url)

Figure 4.1: Angular scan measurements of Co silicide films on Si(111), where full dots correspond to Co, and open dots to Si. Because of the B-type growth of the silicide, the silicide <110> direction and the Si substrate <114> direction were measured, which is reflected in the different shapes of the dips of Si and Co. In a) the layer was 30 Å thick whereas in b) on the same substrate a 60 Å thick layer was grown with equivalent growth conditions. An angular misalignment of 0.42° results on the thin side a), corresponding to \( \varepsilon_t = 1.55\% \), whereas on the thicker side the misalignment was only 0.32°, corresponding to \( \varepsilon_t = 1.18\% \). The film is totally strained on the thin side (apart from the uniaxial relaxation) and partly relaxed on the thicker side, indicating that the critical thickness \( h_c \) lies between 30 and 60 Å.

It is also seen from Table 4.1 that the strain was almost constant with \( \varepsilon_t = 1.6 - 1.8\% \) for films thinner than \( \sim 45 \) Å and decreased for thicker films. When the elastic energy, which is proportional to the film thickness and the square of the parallel strain, is sufficiently high, it will be energetically favorable for the film to relieve part of its strain by introducing misfit dislocations [75]. The thickness at which the formation of such dislocations starts, is called the critical thickness \( h_c \), which for CoSi\(_2\) on Si(111) amounts to \( \sim 45 \) Å, in accordance with previous STM experiments [66] (see Figure 4.2). The strain relaxation for films thicker than \( h_c \) can be described by the model proposed by Matthews (see appendix C) [14, 76]. In addition to the elastic constants, the kind of dislocation has to be known, which for this system has been determined by Bulle - Lieuwma [34] to be mainly of \( a/6 <112> \) type. Plotted in Figure 4.2 is the calculated curve employing the theory of Matthews for which

\[
\varepsilon_t = \frac{G_s b (1 + A)}{4\pi (G_0 + G_s) (1 + v) h (\ln \frac{h}{b} + 1)},
\] (4.1)
where \( v \) is the Poisson ratio, \( b \) the absolute value of the Burgers vector and \( G_0 \) and \( G_s \) are the shear moduli of the film and the substrate, respectively. Since the films were annealed at 890 K, where they were in thermodynamical equilibrium, one has to add an additional, thickness independent term, which describes the thermal strain obtained by cooling down to RT. The difference of the linear thermal expansion coefficients of \( 6.5 \times 10^{-6} \, \text{K}^{-1} \) leads to the additional thermal distortion \( \varepsilon_{\text{t(thermal)}} = 0.74 \% \) at RT, assuming that during the cooling process no more additional dislocations are introduced in the films. It is seen that the thick films in Figure 4.2 were completely relaxed at the annealing temperature and the measured strain is thermal - induced.

As I mentioned above, films with \( h < h_c \) should be fully strained, however this has never been observed. Since the used substrates (commercially available Si wafers) are always slightly \((0.1 - 0.3 \, ^\circ)\) misoriented relative to the nominal crystal axis, the surface exhibits a step structure with step heights of one monolayer \( a/3[11\bar{1}] \). They were therefore spaced at a mean distance of \( L = 690 - 1500 \, \text{Å} \), as was also observed by STM. According to Bulle - Lieuwma, a partial dislocation with Burgers vector of \( a/6 <112> \) type is formed at every interface monolayer or bilayer step in the silicide [34].

<table>
<thead>
<tr>
<th>sample</th>
<th>thickness [Å]</th>
<th>( \Delta \Theta ) [°]</th>
<th>( \varepsilon_t ) [%]</th>
<th>miscut [°]</th>
<th>( \varepsilon_{t, \max} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1165</td>
<td>25</td>
<td>0.46±0.06</td>
<td>1.70±0.22</td>
<td>0.14±0.03</td>
<td>1.97±0.07</td>
</tr>
<tr>
<td>1169</td>
<td>30</td>
<td>0.42±0.05</td>
<td>1.55±0.18</td>
<td>0.22±0.03</td>
<td>1.77±0.08</td>
</tr>
<tr>
<td>1164</td>
<td>32</td>
<td>0.48±0.04</td>
<td>1.78±0.15</td>
<td>0.26±0.03</td>
<td>1.67±0.08</td>
</tr>
<tr>
<td>1161</td>
<td>42</td>
<td>0.48±0.04</td>
<td>1.78±0.15</td>
<td>0.15±0.03</td>
<td>2.03±0.08</td>
</tr>
<tr>
<td>1169</td>
<td>60</td>
<td>0.32±0.03</td>
<td>1.18±0.11</td>
<td>0.22±0.03</td>
<td>1.77±0.08</td>
</tr>
</tbody>
</table>

Table 4.1: CoSi\textsubscript{2} films grown on Si(111) substrates. Indicated is the nominal thickness of the silicide, the angular distortion determined by RBS angular scan measurements, the trigonal tensile strain derived therefrom by using the elastic constants, the wafer misorientation as determined by XRD and finally the maximum residual strain derived therefrom. For films with \( h < h_c \geq 45 \, \text{Å} \) the measured strain corresponds practically to the theoretical maximum strain \( \varepsilon_{t, \max} \) which means that the films are fully strained.

Assuming that the only dislocations present are those expected due to the wafer misorientation, the residual strain \( \varepsilon \) in the direction of the steps can be calculated according to
The wafer misorientation for a set of samples as determined by XRD, is listed in Table 4.1, together with the angular misalignment. In the last column of the table, the maximum trigonal strain obtained by this method is listed.

The maximum possible strain shown in Figure 4.2 was determined using an average misorientation for the various substrates (values between 0.15 and 0.24°). The theory of Matthews was therefore only applied when the strain was smaller than the maximum value, e.g. when misfit dislocations were present. From Figure 4.2 and Table 4.1 one can see, that the measured values reached nearly the calculated ones for silicides thinner than 45 Å, which means that the films are indeed fully strained, apart from the uniaxial relaxation (i.e. in the direction of the misorientation) due to the wafer misorientation.

Strain measurements were also carried out at the three equivalent <110> axes of the (111) surface to verify the angular dependence of the uniaxial strain relaxation. Within the measurement accuracy no angular dependence of the uniaxial strain relaxation was found,
which can be explained with the occurrence of dislocations in more than one direction. This interpretation of the results would imply further that the critical thickness depends on the misorientation of the substrate. Qualitatively this can be understood easily, since a wafer with a misorientation of about 1° would in fact completely relax the silicide uniaxially due to misfit dislocations at monolayer steps. Thus a larger critical thickness for biaxial relaxation would be expected for strongly misoriented substrates.

At steps of height $a/3[111]$ and $2a/3[111]$ partial dislocations in the silicide are always present, whereas in the case of step heights of $a[111]$ the steps preserve the crystal periodicity parallel to the interface, and there are no dislocations, i.e. the Burgers vector is zero [34]. Probably with intentionally misoriented wafers, a transition to a regime with steps of three monolayer height might be induced equivalently to the Si(001) surface. Defect-free silicides should then really have the full strain as given by elasticity theory. This would simplify further overgrowth with the drawback of enhanced film anisotropy, which is mainly manifested in the sheet resistivity.

4.3.4. Strain and critical thickness $h_c$ of CoSi$_2$ on Si(001)

With the elastic constants determined in [73], a tetragonal strain of $\varepsilon_{t,\text{max}} = 2.7\%$ is expected which is also obtained with the values of Guénin [74]. RBS angular scan measurements on films with various thicknesses always showed strains between $\varepsilon_t = 2.1 - 2.7\%$ where the highest strain values were measured on samples with an annealing temperature of 600 to 650 °C. A noticeable correlation was observed between the strain and the final annealing temperature that varied between 460 and 650 °C. Beside the increasing tetragonal strain, the channeling dips of the Co window get more pronounced with increasing final annealing temperature $T_A$. Thus the crystal quality is considerably improved by annealing at higher temperatures. Thermal stability required growth of Si-rich silicide surfaces [60]. Thus for films with thicknesses between 49 and 77 Å, annealing temperatures between 870 and 920 K and a Si-rich surface, the highest strain values of $\varepsilon_t = 2.5 - 2.7\%$ were measured. These values correspond to the maximum possible strain, which means that the films are coherent. For a layer of 105 Å the strain $\varepsilon_t$ was still about 2.3 %. STM images on this film showed clearly a network of dislocations, stemming from the relaxation process. Because relaxation starts only at about this layer thickness, the relaxation process as a function of film thickness cannot be observed as easily by RBS as for CoSi$_2$(111), due to the
steering effect. It has to be stressed that the critical thickness \( h_c \) depends on the substrate orientation, being \( \sim 45 \text{ Å} \) for CoSi\(_2\)(111) and ranging between 70 and 100 Å for the (001) surface [66].

![Graph of RBS strain measurements on CoSi\(_2\)(001) at different temperatures.](image)

**Figure 4.3:** RBS strain measurements on CoSi\(_2\)(001) at different temperatures. Open squares denote the tetragonal strain and the dark circles the FWHM of the Co channeling dips. The strain shows a temperature dependence due to the different thermal expansion coefficients of the film and substrate. The dotted line represents the theoretical value obtained with bulk thermal expansion coefficients and assuming completely coherent growth.

Temperature dependent channeling measurements of a CoSi\(_2\) layer reflect the different thermal expansion coefficients of Si and CoSi\(_2\). With the difference of the thermal expansion coefficients of \( 6.5 \cdot 10^{-5} \text{ K}^{-1} \) [77], the tetragonal strain decreases with increasing temperature by the theoretical factor of \( -1.5 \cdot 10^{-3} \% \text{K}^{-1} \). I measured the tetragonal strain of a 42 Å thick CoSi\(_2\) film at 123, 203, 297 and 393 K and determined thereby the temperature dependence of the tetragonal strain to \( -2.0 \pm 0.6 \cdot 10^{-3} \% \text{K}^{-1} \) (see Figure 4.3). Within the experimental uncertainty this result is in good agreement with the theoretical value. Thus by assuming bulk thermal expansion coefficients the measured strain is in good agreement with that of a coherent film. If the layer had been fully relaxed at RT, the slope in figure 5 would only be \( -0.65 \cdot 10^{-3} \% \text{K}^{-1} \) [78], which can be completely excluded for this film. Just as a marginal note, the FWHM of the Co channeling dips clearly changed with the temperature (Figure 4.3). So did the channeling yield, which is strongly related to the FWHM which is equivalent to the acceptance angle \( \psi_{\lambda} \) [7]. This effect can be understood qualitatively and was also calculated.
by Barret in 1971, using Monte Carlo simulations [7,79]. The axial channels at larger temperatures are narrowed by the increasing thermal vibration amplitudes of the atoms (phonons), thus yielding higher channeling yields and smaller channel widths. According to Barret's theory I calculated a decrease of the FWHM of 0.16° for the temperature increase between 123 and 393 K, which is very close to the observed increase shown in Figure 4.3. However, the experimental values are larger by about 0.24° which is due to the very small film thickness which leads to some additional divergence in the acceptance angle. Also simple geometric reasoning evidences that the acceptance angle gets wider with decreasing film thickness. Thus the temperature effect can also be understood quantitatively. Although this effect has been demonstrated for different bulk materials, it is to my knowledge the first observation of the acceptance angle temperature dependence of an epitaxial film with a thickness as small as 42 Å.

4.4. Electric transport properties

The resistivity parallel to the surface of CoSi$_2$ films was measured in the temperature range between 1.4 and 300 K, using a four terminal method on six legged bridges defined by photolithography and wet-chemical mesa-etching. Hall-effect and magnetoresistance were measured on the same structures at 4 K with a superconducting magnet supplying fields of maximum 5 T. Contacts were applied by ball point gold wire bonding.

It is well known and was always observed that Matthiessen's rule [47] can be applied for thin metallic CoSi$_2$ films [80]. Thus the resistivity is expressed in an additive fashion, as $\rho(T) = \rho_0 + \rho_{ph}(T)$. Here, $\rho_{ph}(T)$ is the contribution of electron-phonon scattering, which can be described with the Bloch-Grüneisen relation

$$\rho_{ph}(T) = \rho_\Theta \left( \frac{T}{\Theta_D} \right)^n \int_0^{\Theta_D/T} 4 z^n \frac{e^z}{(e^z - 1)^2} \, dz,$$  

where $\Theta_D$ is the Debye temperature. For $T > 0.2 \, \Theta_D$, $\rho \propto T$ and for $T \ll \Theta_D$, $\rho \propto T^n$. The exponent $n$ was is normally found to be smaller than the theoretical value $n = 5$. Exponents of $4 \leq n \leq 4.5$ [32] and $n = 3$ [81] have been reported to fit best the experimental data. At low temperature the resistivity tends toward the residual resistivity $\rho_0$ which is due to carrier scattering by structural defects, impurities, etc., and which can be written in terms of an elastic scattering length $\lambda$ (Drude model). ($v_F$ is the Fermi velocity and $n$ the carrier density)
4.4 Electric transport properties

\[ \rho_0 = \frac{mv_F}{n e^2 \lambda} \]  

(4.4)

However, a strong correlation between film thickness and residual resistivity prevails as was previously reported [82,83,84]. There the residual resistivity is treated as the sum of the residual resistivity of bulk and a part \( \rho_s \) which is only due to surface scattering.

On samples (films < 100 Å) where the direction and magnitude of the wafer misorientation has been determined by XRD and STM, the structures for the resistivity measurements were aligned at a well defined angle with respect to the surface steps. Comparing resistivity curves for a direction parallel \( \rho_\parallel \) and perpendicular \( \rho_\perp \) to the surface steps indicated, that the curve of the perpendicular direction is shifted to higher resistivities (Figure 4.4).

![Figure 4.4: Resistivity of a 35 Å thick CoSi\(_2\)(111) film measured parallel (\( \rho_\parallel \)) and perpendicular (\( \rho_\perp \)) to the wafer step structure. The steps are related with the unintentional wafer misorientation of 0.14°. Fits of the resistivity according to \( \rho(T) = \rho_0 + \rho_{\text{ph}}(T) \) are included. The Bloch - Grüneisen term was fitted with \( n = 5 \), resulting in an average Debye - temperature \( \Theta_D \) of 415 K.](image)

Measuring the resistivity at an angle of 45° to the surface steps, yielded exactly the average resistivity of \( \rho_\parallel \) and \( \rho_\perp \). This fact is a strong evidence that surface scattering at the step edges leads to an additional resistivity. Indeed when measuring at different angles between 0 and 90° relative to the steps, the resistivity varied as expected. Further evidence is given by comparing the relative change of \( \rho_\parallel \) and \( \rho_\perp \) with respect to \( \rho_\parallel \) as a function of wafer...
misorientation. In Table 4.2 the relative resistivity change of four films and the appropriate wafer misorientation, as determined with XRD, are listed.

<table>
<thead>
<tr>
<th>#</th>
<th>$T_A$ [°C]</th>
<th>$h$ [Å]</th>
<th>miscut [°]</th>
<th>$(\rho_\perp - \rho_\parallel) / \rho_\parallel$ [%]</th>
<th>$L$ [Å]</th>
<th>$\lambda$ [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1406</td>
<td>630</td>
<td>35</td>
<td>0.03</td>
<td>13.9</td>
<td>6000</td>
<td>530</td>
</tr>
<tr>
<td>1407</td>
<td>650</td>
<td>100</td>
<td>0.045</td>
<td>16.5</td>
<td>4000</td>
<td>350</td>
</tr>
<tr>
<td>1192</td>
<td>550</td>
<td>39</td>
<td>0.12</td>
<td>18.3</td>
<td>1500</td>
<td>400</td>
</tr>
<tr>
<td>1191</td>
<td>550</td>
<td>35</td>
<td>0.14</td>
<td>27.5</td>
<td>1290</td>
<td>280</td>
</tr>
</tbody>
</table>

Table 4.2: Relative resistivity change measured by four-terminal method. The wafer misorientation was determined using XRD. $T_A$ is the final annealing temperature and $L$ is the average terrace length, derived from the miscut. The elastic mean free path $\lambda$ was calculated using eq. (4.4) and $\rho_\parallel$. With increasing wafer miscut the surface scattering resistivity term increases.

Further the average terrace length $L$, assuming monolayer steps, is derived from the miscut. The mean free path $\lambda$ was calculated with the measured residual resistivities $\rho_\parallel$ and carrier concentrations, assuming the Drude model. It has to be mentioned that the carrier density as determined with Hall measurements did not at all show such an anisotropy. The unequivocal correlation between the wafer misorientation and the relative resistivity change is evident. Even the mean free path seems to correlate with the terrace length, indicating that scattering at surface and interface steps is not at all specular.

For the device reported in chapter 6, the Schottky barrier of the A-type CoSi$_2$/Si interface is of importance. Schottky barriers of silicide - silicon contacts will be discussed in the next chapter.

4.5. Summary

Thin strained films of CoSi$_2$ on Si(111) and Si(001) have been grown using a template technique. Continuous, pinhole-free silicides on both kind of substrates have been grown as was evidenced by STM. However, growth on Si(001) is more difficult because of unfavorable surface energy of CoSi$_2$ in respect to the (111) orientation.
Detailed RBS strain measurements revealed that in the case of CoSi$_2$(111) the theoretical maximum strain cannot be reached due to misfit dislocations at interface steps, which are associated with the wafer misorientation and lead to uniaxial strain relaxation. The critical thickness was determined to be of the order of $h_c = 45$ Å. Further the relaxation of the strained films could be well described by the model of Matthews in the case of (111) orientation. Epitaxial CoSi$_2$ films on Si(001) on the other hand have a larger critical thickness $h_c$, which must lie in the region of 70 - 100 Å.

Resistivity of CoSi$_2$ films can be described as the sum of a temperature dependent phonon contribution (Bloch - Grüneisen) and a residual resistivity, which itself shows a remarkable anisotropy on the wafer surface. This anisotropy could be related with the surface and interface step structure, which stems from the small wafer misorientation.
5. CoSi$_2$ - Si heterostructures on Si(111)

5.1. Introduction - motivation

Growth of epitaxial heterostructures consisting of Si/CoSi$_2$/Si has received much interest in the past due to their potential application as metal- and permeable-base transistors (MBT, PBT) [85,86,87,88]. Band structure calculations, however, indicated that parallel momentum conservation needed for the ballistic transport is only possible in (001) oriented Si/CoSi$_2$/Si structures [37]. Although first devices were produced on Si(111), successful fabrication of a metal base transistor using thin CoSi$_2$ layers buried in Si(001) remains an intriguing challenge. Buried CoSi$_2$ films formed by implantation are actually used as interconnects in integrated circuit technology as e.g. in the Alpha AXP - chip of Digital (DEC) [89]. Optical application of silicide - silicon - silicide heterostructures as tuneable infrared detector was recently reported [90,91,92] and will be the main topic of the next chapter.

Up to now high-quality Si/CoSi$_2$/Si(111) and Si/CoSi$_2$/Si(001) heterostructures have been grown by ion beam synthesis (IBS) [93], also called mesotaxy$^{1}$ by White et al. [94], and recently by molecular beam allotaxy$^{2}$ (MBA) [95,96]. In these processes, the silicide layers are formed in the final thermal treatment that induces the coalescence of CoSi$_2$ precipitates imbedded in the silicon matrix into a continuous layer. Although high quality silicide - silicon heterostructures have been fabricated by IBS, the drawback of this method is the relatively high density of dislocations and damage which is produced during implantation and the final high temperature anneal [93]. Fathauer et al. reported on a new deposition process, labeled endotaxy$^{3}$, where Co, deposited on Si at low rates and high temperatures, diffuses through a Si cap and grows on a buried CoSi$_2$ seed region [97]. Although noteworthy results have been obtained by all these methods, they are not well suited to form thin buried silicides with device quality. MBE growth of Si/CoSi$_2$/Si heterostructures has recently been reported by von Känel onto Si(111) [53] and by Via et al. onto Si (001) [98]. Both reported that in order to

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1) By analogy with epitaxy
2) In Greek the prefix 'allo' means 'different', indicating a possible difference in structure between the final compound layer and the substrate.
3) 'Endotaxy' refers to oriented growth within a substrate rather than upon it.
avoid three-dimensional nucleation of silicon on CoSi$_2$, it is necessary to reduce the substrate temperature, e.g. for a deposition rate of $\sim 1$ Ås$^{-1}$ the substrate has to be kept around 350 °C [53].

The goal of this work is to demonstrate the feasibility of MBE to grow heterostructures with device quality. They have to have continuous silicide films without any pinholes, a defect-free silicon and atomically abrupt interfaces which is of utmost importance for device operation (e.g. for the MBT). In this chapter I will, therefore, describe the more suited MBE growth and the structural characterization of silicide-silicon heterostructures. Transport properties and a possible optical device application of these heterostructures are then presented in the chapter 6.

5.2. Growth

Growth of Si on top of CoSi$_2$ is a challenging task because of the tendency of island formation of both type A and type B islands when growing at usually employed Si-MBE temperatures ($\sim 600$ °C) [53,98]. This is evident since STM studies indicated that the Si diffusion length on CoSi$_2$ at comparable temperature is larger than one micron [99]. Experiments evidenced that at temperatures of 350 °C and deposition rates of $\sim 1$ Ås$^{-1}$ the nucleation of 3D islands is strongly suppressed. Because of the lattice mismatch between CoSi$_2$ and Si, overgrowing silicide films with silicon would be simplest when the silicide is completely coherent, i.e. has exactly the same lateral lattice parameter as bulk silicon. I therefore always tried to overgrow silicides with thickness $h$ well below the critical thickness $h_c$. As was outlined before, even silicides with $h < h_c$ are somewhat relaxed and coherent overgrowth with silicon leads consequently to strained silicon films. For enhanced thermal stability the silicide surfaces were always grown with a Si-rich surface [100]. The preparation of epitaxial CoSi$_2$ films has already been described before.

After the final annealing step of the silicide, the wafer was cooled down to 350 °C. There a first deposit of $\sim 25$ Å Si at a rate of $\sim 1$ Ås$^{-1}$ followed. At the moment of opening the main shutter, the temperature was ramped up with 50 °C min$^{-1}$. The wafer was then annealed for 2 minutes typically at 500 °C before cooling down to 400 °C. The RHEED pattern until this point always showed a clear 1×1 reconstruction and Kikuchi bands, which just after the deposit were rather faint. Some very weak streaks stemming from the Si 7×7 reconstruction could already be observed at this stage. A second deposit of another 25 Å Si in the same way
as the first one followed. The temperature after this step was typically raised to 630 °C. Normally the RHEED pattern during deposition did not deteriorate much. With increasing temperature the Si 7×7 reconstruction became more and more intense. The growth procedure was continued with cycles of deposition at gradually increasing growth and annealing temperatures. When the Si thickness reached 150 Å, the temperature was raised to 700 °C. Growth until reaching the final thickness was then continued at this temperature or even at 750 °C. A final anneal to 840 °C similar as for the buffer growth was optionally performed. The RHEED pattern of such prepared silicon surfaces showed a perfect Si 7×7 reconstructed surface which could not be distinguished from that of a clean Si substrate. The most critical point of overgrowth is the deposit of the first few monolayers. Growing at too low temperatures leads to growth of amorphous Si which has to be recrystallized in an annealing step. But Si should rather grow epitaxially from the first layer on in order to obtain defect - free overgrowth. This can be achieved at an elevated wafer temperature. However, annealing the wafer too high leads to undesirable pinhole formation in the silicide and subsequent 3D - nucleation of silicon. Although these holes will be buried when thick Si films are grown, the surface will be wavy and lots of defects in the Si will render the heterostructure useless for device application. A quick method to check the flatness of the surface is to shine with a fiber light on the wafer. Perfect heterostructures reflect the light like mirrors whereas the others have a milky gleam. The Si/CoSi₂/Si heterostructures were then either removed from the growth chamber or a subsequent overgrowth of Si with CoSi₂ was carried out in the same way as for the first silicide layer.

Unfortunately growth of epitaxial Si on epitaxial CoSi₂(001) films lead always to three - dimensional nucleation. It was not possible to obtain films of equivalent morphology and crystalline quality as on Si(111). Recent results by Via et al. gave a channeling minimum at the surface Si as high as 37% [98].

5.3. Structure

After buffer growth parallel steps due to the unintentional wafer misorientation are present. Two - dimensional growth of the silicide has been optimized in order to leave this stepped surface unchanged. The goal of overgrowing the silicides with silicon consisted in preserving this structure and in avoiding to produce pinholes and defects in the silicon. STM topography of good heterostructures showed smooth surfaces with the same parallel
monolayer step-structure, where sometimes the edges are frayed out a little. This means that the Si overlayer grows essentially in the desired step flow regime. The surface after Si overgrowth appeared pinhole-free (i.e. on 4×4 μm² STM scans no pinholes were detected). Unfortunately they contained a high density of threading dislocations (>10⁸ cm⁻²) probably due to the uniaxial strain relaxation of the underlying silicide. In Figure 5.1 a 31 Å thick CoSi₂ film grown on a 500 Å Si/25 Å CoSi₂/Si(111) heterostructure is shown. Here as well, the silicide reflects closely the morphology of the original Si substrate with parallel steps of monolayer height. Closer inspection of Figure 5.1 shows that each surface step is decorated with a planar, bright stripe starting at the step edge and extending up to ~500 Å into the terrace. These regions are higher by 0.8-1 Å than the darker terrace regions to the left. Further I have to mention that the surface was grown Si-rich, thus the first three atomic layers at the surface are Si [58]. This contrast was claimed to be due to a stacking fault in the third layer with a translation vector of a/6<2-1-1>, which changes the Co coordination from eight- to sevenfold and reverses the orientation of the top bilayer from type A to type B [101]. A possible driving force for this surface phase transition could be the surface strain relaxation. Two orientations of buried silicides in Si(111) have been observed: type A silicides are only

Figure 5.1: STM of a CoSi₂/Si/CoSi₂/Si(111) heterostructure. (W1307; 31 Å CoSi₂ on 500 Å Si and 25 Å CoSi₂). Final annealing temperature 550 °C. Monolayer surface steps due to the wafer miscut of 0.24° are directed towards [-1-12].
observed for IBS - formed silicides, while type B silicides are always observed in UHV deposition techniques (e. g. MBE) [34,102]. The silicon - CoSi₂ interface on the other hand was always reported to be of type A [34,53]. Thus the silicon grown on CoSi₂ is always of type B.

Figure 5.2: High resolution TEM cross-section of CoSi₂/Si/CoSi₂ heterostructures on Si(111). a) Both silicides are of homogeneous thickness and Si is almost defect-free. b) Detail of an edge of a discontinuous buried silicide. The upper Si grows with type A orientation on the silicide leading to a Si-Si B-type interface. c) Detail of a). (a) and c) W1307; b) W1184)
TEM cross sections, as shown in Figure 5.2 a) and c), showed homogeneously thick continuous silicides with very abrupt interfaces. The representative TEM detail shows the almost defect-free intermediate Si. As can be well seen in part c), silicides grow twinned on Si (type B interface), whereas the Si grows in A-type orientation on CoSi2. Since for the final annealing the surface was kept Si-rich, Si islands formed occasionally as could be directly observed by STM and also by TEM cross-sections shown in Figure 5.2 a) and c).

Unfortunately, not all wafers had a continuous buried silicide. Our MBE-STM system allowed a surface investigation before Si overgrowth, without major influence on the following overgrowth. Some wafers examined by STM after silicide growth were found to be pinhole-free. But after overgrowth with silicon the same wafers had some kind of silicide islands as was evidenced by TEM cross sections (Figure 5.2 b)). In this picture the edge of such a grain is shown. The silicon-silicide substrate interface is B-type and the silicide-silicon interface is A-type as for a continuous film (e.g. a) and c)). Thus the overlying Si is rotated by 180° in respect to the substrate. In the regions where the intermediate silicon is in contact with the substrate, a perfect A-type interface is observed. Close inspection shows that the interfaces are not exactly at the same level as the silicide-substrate interface. The shift corresponds roughly to a[111] and according to Bulle-Lieuwma no dislocation is thereby associated at this edge [34]. However, silicon had to grow uniformly with a type A interface on the silicide in the early stage of growth. After it reached a certain thickness the silicide formed islands, leaving the Si in the same orientation. Otherwise the Si-Si interface would not be B-type. This silicide disintegration is astonishing since in mesotaxy and allotaxy the reverse mechanism, the coarsening of precipitates also called Ostwald ripening [103], is observed during high temperature annealing [93,94]. It seems that the silicide film thickness plays an important role, whether the film is thermally stable or not. Although buried CoSi2 layers have a better thermal stability than a surface CoSi2 layer of similar thickness, disintegration of the former has already been reported for annealing at high temperatures [104]. Mantl has given an estimate for the dissolution by diffusion of the buried silicide [93]. The resulting dissolution thickness for my annealing conditions is by far too small to explain the observed disintegration of my buried silicide films. On the other hand it is known that spheroidization of a buried thin film into two-dimensional arrays of spheroids occurs because of the surface energy reduction associated with this configuration [105]. Comparing the total energy of a buried thin film with a ball could eventually explain my observations. If

Overgrowth was then started with a deposit of 5 Å Si at RT and then annealing to 350 °C.
assuming equal specific interface energies and comparing the surface of a thin layer with that of a ball of equal volume yields the result that a layer with a thickness $d < 2/3 \ r$ has a larger interface energy than the corresponding spherical particle with radius $r$. Further Mantl showed that the elastic energy of a coherently strained particle is significantly larger than that of a coherently strained thin layer which sets a lower limit for the $d/r$ ratio. The most important result of his estimations is the recognition that a thin layer is a metastable configuration. The system is not at a minimum in total energy. In reality misfit dislocations might also come into play and may destabilize the buried layer further. Thus, to obtain perfect heterostructures, growth has to be carried out at high temperature in order to get Si with good crystal quality but on the other hand the temperature must not be too high in order to prevent disintegration of the buried silicide. Therefore a procedure which allows to grow heterostructures with reproducible high quality has been developed.

Some of my heterostructures have been characterized with grazing incidence x-ray diffraction by J. Stettner [106]. A comparison of the heterostructure layer thicknesses obtained by this method and by sophisticated analysis of my RBS measurements yielded great discrepancies mainly for the buried silicide. Thicknesses determined from RBS spectra were always in agreement with the nominal thickness. With RBS only the Co area - density is effectively measured and the film thickness is derived by assuming a continuous layer of perfect CoSi$_2$. The x-ray method on the other hand measures the effective electron density. This density was sometimes lower than the theoretical value and the derived film thickness therefore larger than the RBS value. But the calculated effective particle area density was in agreement with the RBS results. As was also inferred from TEM cross-sections, this is a consequence of silicide island formation. Thus comparing the RBS and x-ray results is a quick method to give a quantitative estimate of the ratio of islands to the hole area.

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<td>25</td>
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Table 5.1: Film thicknesses as measured by the quartz balances during growth, by RBS, by high-resolution TEM cross sections and by grazing incidence x-ray.
In Table 5.1 thickness of silicide and intermediate silicon layers measured with different techniques are listed. Since the values from RBS and x-ray measurements are almost identical and low resolution TEM cross-sections neither showed pinholes, this film is supposed to be continuous (see also Figure 5.2 a) and c)).

Since RBS channeling measurements are sensitive to defects [7,8], they were routinely carried out in the [111], [110] and [114] direction. Samples cut from different parts of a wafer, yielded results which within the measurement accuracy were equal, indicating very homogeneous growth of the heterostructures over the whole wafer surface. Because of the B-type growth of CoSi₂ on Si and the A-type interface between the CoSi₂ and the overgrown Si, the latter (intermediate Si) is rotated by 180° with respect to the silicon substrate. Thus a <110> direction of the substrate is equivalent to a <114> of the intermediate silicon and vice versa. Channeling in low indexed directions gives a lower backscattering yield than in high indexed ones [7]. The larger channeling yield \( \chi_{\text{min}} \) of the <114> direction can be seen in Figure 5.3 for a CoSi₂/Si/CoSi₂/Si(111) heterostructure. The sample was adjusted in order to have the lowest channeling minimum yield in the Si, which was as low as 8% in the [111] direction. In the Co peaks of the two silicides a small channeling can be seen although the signals reflect essentially the energy resolution of the detector. In the front silicide (higher energy) the channeling yield is larger, which is mainly due to the surface peak enhancement.

Obviously heterostructures without a top silicide layer had lower channeling minimum yields. Values ranging between 4.7 and 7.5 % have been measured in the [111] direction of a set of heterostructures grown on similar substrates and equal growth conditions, apart from the final Si thickness. A clear correlation between the buried silicide film thickness and \( \chi_{\text{min}} \) exists, where for the thicker silicides the \( \chi_{\text{min}} \) in [111] is higher regardless of the Si thickness. Because the thickest silicides had almost reached the critical thickness \( h_c \), some strain relaxation of the silicide film is evident. This in turn leads to slightly unfavorable Si growth condition. Thus additional defects are formed which lead to a larger dechanneling compared to the [111] direction. This can be seen more clearly when comparing the \( \chi_{\text{min}} \) of the off-normal directions (e.g. [110]). Theoretically for the diamond structure the [110] direction has the smallest \( \chi_{\text{min}} \) [7], which was only rarely observed. However, the best heterostructure I had grown (W1439) and which was later used for the fabrication of asymmetrical infrared detectors, had a \( \chi_{\text{min}} \) of 4.7% in Si[111] and of only 3.5% in Si[110]. These values are not far away from the theoretical limits, reached only by perfect single crystals.
Heterostructures with a top silicide had slightly higher $\chi_{\text{min}}$ in the Si, because of dechanneling in the top silicide. The heterostructure shown in Figure 5.3 with its good $\chi_{\text{min}}$ of 8% in Si[111], is among the best and was chosen to demonstrate the separated Co peaks, representing the two silicide layers.

![Channeling Spectra](image)

**Figure 5.3:** RBS channeling spectra of a CoSi$_2$(39 Å)/Si(1400 Å)/CoSi$_2$(39 Å)/Si(111) heterostructure. Random and channeling spectrum of the [111] direction are shown in the left figure and the two channeling spectra in the Si[110] and Si[114] direction are shown on the right side. $\chi_{\text{min}}$ in [111] direction is 8.0 %. The insert shows two clearly resolved Co peaks stemming from the two silicides. Due to the B-type growth of CoSi$_2$, the intermediate Si is also rotated by 180° which is reflected in the different channeling yields of Si substrate and Si film in the <110> and <114> direction. (Substrate was cleaned in H-plasma)

5.3.1. Strain and critical thickness $h_c$ of Si

It is impossible to determine the strain of the buried silicide layer overgrown with more than ~200 Å by means of RBS because of beam steering effects. On the other hand, the top Si film is expected to be distorted, since the underlying silicide is never in practice truly coherent, due to the finite substrate misorientation, as discussed before. It is, however, possible to determine the lattice distortion of the top Si layer. For RBS channeling measurements energy windows were chosen such that only the extreme surface layer of the Si (100 - 200Å) contributed to the backscattering signal. I measured the angle between two axial
channels ([210] channel, 78.463° in case of zero strain), which are symmetrical about the surface normal and which lie in the same crystal plane\(^1\). The difference between the geometric zero-strain angle and the measured spherical angle corresponds to the trigonal strain of the top Si. In Figure 5.4 the in-plane strain \(\varepsilon_p\), which was determined by using the elastic constants of Si [107], versus the Si thickness is plotted. All heterostructures have been grown consecutively on substrates with an identical unintentional misorientation of \(\sim 0.24°\) as was determined by XRD and STM. A decrease of the strain similar to that of CoSi\(_2\) was observed. As stated before, thin epitaxial Si has to grow strained on the silicide whose average lattice constant is smaller than that of Si. It is obvious that relaxation will occur as the Si becomes thicker than its critical thickness \(h_c\) (see Figure 5.4).

![Figure 5.4](image)

**Figure 5.4:** The in-plane strain \(\varepsilon_p\), determined by RBS channeling, of silicon grown on thin CoSi\(_2\)(111) layers (7 - 38 Å) is plotted versus the Si thickness. All silicide layers were thinner than the critical thickness \(h_c\). The films were grown on similar substrates, having the same wafer misorientation of 0.24°. With increasing silicon thicknesses the strain relaxes. Theoretical and fit curve employing the theory of Matthews for strain relaxation are indicated, yielding a critical thickness \(h_c\) of \(\sim 350\) Å for Si.

With the known misorientation of the substrate the theoretical maximum strain of CoSi\(_2\) amounts to \(\varepsilon_{\text{max}} = 0.90\%\), as explained previously. For sufficiently thin Si overlayers, i.e. for overlayers coherent with the underlying silicide, the strain of the silicide (\(\varepsilon_\parallel = 0.90\%\)) and that of the Si must add up to the total lattice mismatch \(|\eta| = 1.2\%\) of CoSi\(_2\) with Si. The

\(^1\) The [210] channel is narrower than e.g. the [110] channel and is therefore better suited for accurate strain measurements.
maximum strain in the Si is hence found to be $|\varepsilon| = 0.30\%$. In Figure 5.4 the strain
dependence according to the Matthews theory and a fit to the data with eq. (4.1) is plotted.
The dislocations to be included for the relaxation process have been reported by Bulle-
Lieuwma to be of type $a/2 <110>$ [34]. No additional thermal strain term as for the thin CoSi$_2$
films was used. The theoretical curve reaches $\varepsilon = -0.30\%$ at 220 Å and the fit curve at 350 Å
which corresponds to the critical thickness $h_c$ for strain relaxation of silicon. Looking at
Figure 5.4 one expects that the trigonal surface strain tends to zero for thick Si films according
to the theory. I conclude that for a misorientation of $0.24^\circ$ the critical thickness of strained Si
on CoSi$_2$(111) is of the order of 350 Å. A decrease of strain is associated with an undesired
increase of threading dislocations. To obtain low defect densities in the silicon layers, the
substrates, therefore, have to have the lowest possible misorientation. On these substrates the
CoSi$_2$ films are practically completely strained for $h < h_c$ and the silicon can therefore grow
nearly unstrained. For growth of my heterostructures I used specially manufactured wafers
with misorientations smaller than $0.10^\circ$. These considerations provide an explanation for the
fact that the synthesis of Si/CoSi$_2$/Si heterostructures with low defect densities has proven to
be so difficult in the past.

5.4. Summary

Dewetting, the existence of type A and type B interfaces, the large diffusion length of Si
on CoSi$_2$ are reasons for the enormous difficulties encountered in overgrowth of CoSi$_2$ films
with coherent Si. The most serious problem stems from the fact that silicide films, even for
$h < h_c$, are never truly coherent because of the misfit dislocations associated at the interface
steps. Thus in the initial stages epitaxial Si films grow necessarily in a state of compressive
strain. On Si(111) substrates nearly perfect heterostructure growth was achieved by using a
procedure with cycles of depositing and annealing Si films with gradually increasing
temperature. RBS channeling measurements were used to monitor the crystal quality,
reflected in channeling minimum yields $\chi_{\text{min}}$ as low as 4.7% in Si[111] and 3.5% in Si[110]
for a 1600 Å Si/35 Å CoSi$_2$/Si(111) heterostructure. STM topographies and TEM cross
sections proved the silicides to be continuous. Although pinhole - free heterostructures have
been synthesized, they still contain a relatively high density of dislocations, associated mainly
with the strain relaxation. Strain in Si grown on top of epitaxial CoSi$_2$(111) was measured
using RBS channeling techniques. The critical thickness $h_c$ of Si grown on partially strained
CoSi$_2$/Si(111) was then deduced to be of the order of 350 Å. The strain relaxation with increasing Si film thickness could be identified as one of the main sources for the defects found in Si/CoSi$_2$/Si heterostructures. In order to minimize the number of such defects, the wafer misorientation was kept as small as possible, i.e. below 0.10°. Thermal limited stability of thin buried silicide films complicated the growth procedure even more. Even though excellent results on Si(111) were obtained, heterostructure growth on the industry standard Si(001) was not very successful.
6. Application of silicide - silicon heterostructures to tunable infrared detector

6.1. Introduction - motivation

Si technology lacks the possibility of optical integration because of the indirect nature of the Si band gap (1.12 eV at 300 K). One approach towards solving this problem could be to integrate semiconducting silicides. Among the known semiconducting silicides (ReSi$_2$, CrSi$_2$, Mn$_{12}$Si$_{26}$, Ir$_4$Si$_7$, OsSi$_2$, ß-FeSi$_2$) only ReSi$_2$ (E$_G$ = 0.12 eV), CrSi$_2$ (E$_G$ = 0.3eV) and ß-FeSi$_2$ (E$_G$ = 0.87eV) have been grown epitaxially on Si so far [108,109,110]. Since the former two have an indirect bandgap [111], the latter is the most promising candidate for integrated optoelectronic applications since evidence for a direct energy band gap of 0.87 - 0.89 eV (~1.41 μm), which suits well the transmission window of most used optical fibers (λ = 1.3 - 1.55 μm), was claimed by Bost and Mahan [112,113]. However, the nature of the gap is still a controversial topic since band - structure calculations by Christensen [39] and absorption measurements by Giannini [114] gave evidence for an indirect gap just a few tens of meV lower than the direct one. A convincing proof of suitable photoelectric properties of ß-FeSi$_2$ is still lacking [110].

On the other hand metallic silicides are widely used as Schottky barrier infrared (IR) detectors [115]. Silicide/silicon Schottky barrier detectors (SBD) are based on the photoexcitation of metal electrons or holes across the metal/silicon (Schottky barrier) interface. PtSi/p-Si SBD have a barrier height of Φ = 220 meV, the second lowest barrier height of all silicides known to date [116] and are, therefore, well suited for infrared detection in the 3-5 μm wavelength range [117]. They represent the most established SBD technology [115]. Alternative silicides of interest are Pd$_2$Si and IrSi with cut - off wavelengths of λ = 3.7 μm and λ = 7.3 - 12.4 μm, respectively [115,118,119,120]. It has been reported before on the use of cobalt and nickel silicides as SBD [121]. For a review of Schottky barrier imaging technology, see e.g. in Ref. [115]. The cutoff wavelength of these SBD is entirely determined by the Schottky barrier height and silicon doping and can only slightly be varied
by the Schottky effect which rarely exceeds a few tens of meV. The resulting tuning range and responsivity change are rather small.

Larger modulation effects can be expected in metal - semiconductor - metal heterostructures. The effective barrier height and consequently the photoresponse and cutoff wavelength can be tuned with an applied bias, because the potential barriers, which are formed by the Si valence and conduction band edge and the externally applied bias, are greatly modified. The first such asymmetrical (two different metals) Tunable Internal Photoemission Sensor (TIPS) with Pt/Si/ErSi₂ was reported in 1992 by Pahun and Badoz having a cutoff wavelength shifting range between 1.4 and 5.0 μm [90,122]. Our group then reported in 1993 the first symmetrical (both metal layers of same material) TIPS made with epitaxial CoSi₂/Si/CoSi₂ heterostructures exhibiting a barrier variation of 0.1 eV [91]. Asymmetrical TIPS with Ir/Si/ErSi₂ were next reported by the same French group, where the cutoff wavelength was shifted up to 6 μm [92,123]. In this work symmetrical TIPS with CoSi₂/Si/CoSi₂ heterostructures and asymmetrical TIPS with PtSi/Si/CoSi₂ heterostructures are presented. These devices behave differently compared to the Ir/Si/ErSi₂ TIPS because of a different Schottky barrier configuration. Although the fact that uniform focal plane arrays of conventional SBD can be processed [115], their drawback is the lack of responsivity and cutoff wavelength control. Integration of TIPS focal plane arrays with existing Si technology could open the way to wavelength resolved IR imaging, covering the whole spectrum of existing Schottky detectors, i.e. from 1 μm to above 12 μm. Further the pixel to pixel response uniformity which imposes problems in conventional SBD could be electronically adjusted in TIPS. However, TIPS as well as conventional SBD can only reasonably be operated at liquid nitrogen temperature.

6.2. Schottky - contacts

Braun in 1874 made the first observation of rectifying contacts [124]. Rectifying metal - semiconductor contacts frequently called Schottky - contacts play the central part of SBD and TIPS. Despite the many theoretical and experimental studies published in the past, a universal model describing the physical mechanism of Schottky - barrier formation does not exist [125]. The first model was proposed by Walter Schottky in 1939 where the "Schottky" barrier height Φ is entirely determined by the metal work function χ [126]. In nature the slope S = dΦ/dχ for a certain semiconductor turned out to be smaller than unity in disagreement with the Schottky
6. Application of silicide - silicon heterostructures to tunable infrared detector

- Mott rule (e.g. [88]). Bardeen in 1947 then proposed the presence of interface states so that depending on their density, the slope parameter $S$ varies between $S = 0$ and the Schottky - Mott value $S = 1$ [127]. Moreover, empirical rules to describe the Schottky - barrier height $\Phi$ of transition metal silicides with the metal work function [128], the heat of formation [129] or the core level shifts [130] have been reported. More recent theories are based on the metal induced gap state model [131,132] or the defect state model which was proposed by Spicer [133]. Theories of Schottky - contacts can be looked up in textbooks like Refs. [88,125,134,135] and are not reproduced here.

According to Tung the Schottky barrier $\Phi$ of epitaxial NiSi$_2$ on n - type Si(111) amounts to 0.65 and 0.79 eV for type A and type B interfaces, respectively [136]. From the theoretical point of view, this difference of 0.14 eV cannot be explained by theories based on the knowledge of the bulk band structure only. Only self - consistent band - structure calculations, which take into account the microscopic structure of the interface can explain this effect [137]. Recent Schottky barrier calculations of NiSi$_2$ and CoSi$_2$ by Magaud - Martinage, using a self - consistent tight - binding approach, are in good agreement with measurements [138] (i.e. a barrier height of 0.7 eV for CoSi$_2$ on n - type Si was reported).

Barrier heights in Schottky diodes can be determined from current - voltage ($I-V$), capacitance - voltage ($C-V$) and photoresponse - wavelength ($I-\lambda$) characteristics and ballistic electron emission microscopy (BEEM). Measuring the $I-V$ characteristics, which obeys the thermionic emission theory [88,125], is the most straightforward method to determine the Schottky barrier height $\Phi$. From the forward characteristics not only the barrier height, but also the ideality factor $n$ and the series resistance $R_s$ can be obtained. See in Appendices D and E for a detailed description of the Cheung method (D) and the Werner method (E). The method of photoresponse measurement was mainly used throughout this work and is described in details in the next paragraphs.

Whenever an electric field $E$ persists at a metal - semiconductor interface, the Schottky barrier $\Phi$ is lowered by $\Delta \Phi$ due to the image - force according to eq. (6.1). This image - force - induced lowering of the Schottky barrier is called Schottky effect.

$$\Delta \Phi = \sqrt{\frac{e E}{4 \pi \varepsilon \varepsilon_0}}$$  (6.1)
6.3. Internal Photoemission

The first quantitative description of the emission of electrons across a metal surface barrier was performed by Fowler in 1931 [139]. Further developments of the Fowler model were carried out by Dalal [140] and Vickers [141], who both proposed independently the concept of an increased sensitivity by using ultrathin silicide films (< 100 Å).

Photoemission of charge carriers from a metal film into silicon may be divided into three elementary processes, which are schematically shown in Figure 6.1.

1) photon absorption in the metal film by free charge carriers
2) transport of the photoexcited carriers towards the interface
3) emission of the photoexcited carriers across the interfacial barrier

![Schematic electron energy band diagram of a silicide/n-type silicon Schottky barrier. The three elementary processes involved in the photoemission across the barrier Φ are indicated by arrows. EF denotes the Fermi energy.](image)

6.3.1. Photoexcitation

Photons absorbed in the metal excite electrons in the silicide to states above the Fermi level $E_F$ creating holes below $E_F$. Electrons are then found at energies larger than the Fermi level and holes at energies smaller than $E_F$, called hot electrons and hot holes, respectively, whenever $E - E_F \gg kT$. However, it should be pointed out that the metal cannot be considered...
to contain a hot - electron or hot - hole gas because the short relaxation time limits the number of carriers excited at a particular moment (Photon flux of the lamp is relatively low). Because of the complex absorption process, which can only be described by quantum mechanics using the band structure of the silicide, only experimental information about the photoexcitation can be given. The absorption of light in a thin film is uniform and is characterized by the absorption length. For PtSi it was reported to be 20 nm, independent of wavelength in the spectral range between 0.3 and 1 eV [142]. For CoSi$_2$ the absorption length $L$ is about 8 nm in the spectral range between 0.7 and 1 eV [143]. The number of absorbed photons depends on the film thickness and the incident IR light wavelength, since in thin metal films light multireflections at air/silicide and silicide/silicon interfaces can lead to an enhanced absorption in the metal films. In PtSi films the wavelength dependent absorption has a maximum of 30 - 60% at a silicide film thickness of 100 - 250 Å [119,144]. Illumination through the silicon (back illumination) leads to a higher absorption than for front illumination since silicon acts as an optical index matching medium [144]. Antireflection coatings and optical cavities can further increase the absorption [117,119].

For my analysis I used the fact that the change of the Poynting vector is proportional to the number of absorbed photons $N_{\text{ph}}$ in the region $x$ and $x+dx$ [143].

$$N_{\text{ph}}(x) \, dx = \frac{1}{h\nu} \frac{\partial P}{\partial x} \, dx \quad (6.2)$$

The number of photoexcited holes $N_{\text{ex}}$ is assumed to be proportional to the number $N_{\text{in}}$ of photons incident on the detector, when any other absorption processes are ignored. The optical yield $Y_{\text{opt}}$ is then defined as

$$Y_{\text{opt}} = \frac{N_{\text{ex}}}{N_{\text{in}}} \quad (6.3)$$

6.3.2. Transport

For thin films internal reflections of charge carriers from the metal/air and metal/semiconductor interfaces have to be considered. Several possible ballistic paths of photoexcited hot carriers are shown in Figure 6.2. Most of the carriers are lost for emission because they head into the wrong direction, they lose energy by inelastic scattering (with phonons, electrons, etc...) or they are scattered away from the barrier. Obviously, for metal films with thicknesses much larger than the elastic mean free path of hot carriers, the
redirection and reflection processes (4) and (5) do not contribute to the emission yield. Fowler in his theory considered only those charge carriers which are generated at the metal/semiconductor interface and have enough forward momentum for emission [139]. Dalal [140] and Vickers [141] studied, therefore, the thin film enhancement through the redistribution of momentum by phonon and wall scattering which in effect scatters hot carriers otherwise lost into the set of states within the escape cap, thus leading to an enhanced quantum yield (see below). Their theory was further developed by Mooney and Silverman [145]. Elabd and Kosonocky developed a different model for thin film enhancement in terms of multiple reflections of hot carriers at the silicide - air and the silicide - silicon interface [117]. Czernik et al. computed the internal photoemission process with a Monte Carlo simulation summing up the probabilities of all possible routes shown in Figure 6.2 [119]. They obtained an optimum PtSi film thickness close to the escape depth of 20 - 30 Å. The important feature is that the quantum yield exhibits a sharp maximum for a metal thickness of the order of the escape depth $L$. This sounds obvious, because for thinner films absorption decreases with film thickness and for larger films carriers excited far from the barrier are thermalized instead of being collected.

![Figure 6.2: Schematic representation of some possible ballistic paths of charge carriers in the silicide after photoexcitation. (1) most common path; charge carrier is lost for emission by misorientation and inelastic scattering (a); (2) direct emission; (3) emission after phonon scattering (b); (4) emission after diffuse wall scattering (c); (5) path gained for emission after a too shallow incidence on the barrier (d) by diffuse wall scattering (c); (6) path gained for emission by wall scattering (e).](image_url)

Turner et al. [146] reported an attenuation length of $L = 40$ Å for electrons with an energy of 1 eV above the Fermi level whereas Niedermann et al. [147] reported a mean free
path of electrons of $L = 76$ Å. Both results were obtained by RT ballistic - electron - emission microscopy (BEEM) studies of PtSi/Si(100). The energy dependent attenuation length $L$ of electrons in my CoSi$_2$ films was measured by BEEM and found to be $\sim 60$ Å at 1 eV above Fermi level [148].

Different mechanisms may contribute to the relaxation of the hot carriers, involving acoustic or optical phonons and cold carriers. Defect scattering is essentially elastic and does not contribute to the hot carrier relaxation [149]. Although high - energy acoustic phonons (energy up to 10 meV) can be emitted, the average energy transfer remains small compared to the hot carrier energy. Thus their contribution may be neglected. However, they may play an important role in thin films because of the momentum redistribution as was proposed by Dalal and Vickers [140,141,149]. On the other hand optical phonons may contribute significantly to the energy relaxation since their energy is equal to or even higher than $kT$. And finally the interaction with a cold carrier leads also to an important energy decrease and was attributed to be mainly responsible for the decrease of the escape depth with increasing electron excess energy in CoSi$_2$ [143].

6.3.3. Emission across the interface barrier

For simplicity, this paragraph is cast in the language of electrons but all arguments are equivalently applicable to holes. Electrons in the metal are approximated by a free electron gas with a spherical Fermi surface $k(E_F)$ as is schematically shown in Figure 6.3. For typical device operating temperatures of 77 K, electron states up to the Fermi energy $E_F$ are filled and states above $E_F$ are empty. Electrons accessible to photoexcitation are presumed to be within a spherical shell in $k$ - space with $k(E_F - \hbar\nu) < k < k(E_F)$ (dotted space in Figure 6.3). For electrons to be emitted across the Schottky barrier $\Phi$, the Energy - momentum relation (6.4) must be fulfilled (see also Figure 6.3).

$$\frac{1}{2m} \left( \frac{\hbar}{2\pi} \right)^2 \left( k_x^2 + k_y^2 + k_z^2 \right) + \hbar\nu \geq E_F + \Phi \quad (6.4)$$

Only those electrons with a momentum directed towards the metal/semiconductor interface may escape. This would for example imply that $k_z > 0$ if the interface is in the x - y plane and with the semiconductor in the positive $k_z$ region. The important assumption is conservation of momentum parallel to the interface $k_\parallel$. Then only electrons with sufficient momentum normal to the interface $k_\perp > k(E_F - \hbar\nu + \Phi)$ can escape. Hence, conservation of $k_\parallel$
restricts the escaping electrons to a cap of an escape cone, as is illustrated in Figure 6.3. Without taking into consideration the band structure of the metal and semiconductor and the assumption that the effective mass of the electrons does not change when they cross the interface, one can then find the minimum $k_z$ using eq. (6.4) with $k_x = k_y = 0$.

\[
\frac{1}{2m} \left( \frac{\hbar}{2\pi} \right)^2 k_z^2 + \hbar v = E_F + \Phi \quad \text{and} \quad k_z > 0. 
\] (6.5)

![Figure 6.3: Cross-sectional view of escape cone model for Schottky emission shown in momentum space for $T = 0$ K. The outer sphere represents the Fermi surface $k(E_F)$. The inner sphere indicates the spherical shell of photoexcitation with energy $E = E_F - \hbar v$. The dotted area indicates energy values accessible by photoexcitation. The hatched area defines the emission cap obtained with conservation of parallel momentum $k_x$.](image)

The internal quantum yield $Y_{\text{int}}$ is defined as the probability that a photoexcited carrier will escape and is determined by the ratio of the number of escaping carriers to the number of photoexcited carriers. Since the density of states is uniform in reciprocal space, the ratio of the volume of the spherical cap for escape to the volume of the spherical shell of excitation yields the internal quantum yield $Y_{\text{int}}$. This ratio is given in first order of $\hbar v/E_F$ and $\Phi/E_F$ by the modified Fowler equation (6.6). (In CoSi$_2$ and PtSi $E_F$ lies typically between 3 and 5 eV)

\[
Y_{\text{int}} = \frac{(h v - \Phi)^2}{8 E_F \hbar v} 
\] (6.6)
6.3.4. Responsivity - quantum efficiency

The spectral responsivity $R(h\nu)$, which can be determined by detector measurements is defined by the photocurrent $I_{\text{phot}}$ measured per incident light power $P_\phi(h\nu)$ according to

$$R(h\nu) = \frac{I_{\text{phot}}}{P_\phi(h\nu)} \propto \frac{e Y_{\text{opt}} Y_{\text{int}}}{h\nu} [A/W]. \quad (6.7)$$

The responsivity shows the well known Fowler-type dependence (eq. (6.6)) on photon energy,

$$R(h\nu) \propto (h\nu - \Phi)^2 \quad (6.8)$$

where the prefactor $C$ is now written as

$$C \propto A(h\nu) G(h\nu). \quad (6.9)$$

$A(h\nu)$ is the optical absorption in the silicide and $G(h\nu)$ is the internal efficiency gain of hot carriers due to multiple reflections. This relation is normally applied in the so-called Fowler Plot (i.e. $A(h\nu)$ and $G(h\nu)$ with negligible dispersion), to obtain a straight line which crosses the energy axis at the barrier height $\Phi$.

$$h\nu \sqrt{R(h\nu)} \propto h\nu - \Phi \quad (6.10)$$

The quantum efficiency $Y_{\text{QE}}$ is the ratio of the number of measured photoelectrons to the number of photoexcited photoelectrons and can be derived from the responsivity employing

$$Y_{\text{QE}} = \frac{R(h\nu) h\nu}{e}. \quad (6.11)$$

6.4. Principle of Tunable Internal Photoemission Sensor

The basic device consists of two back to back Schottky diodes, where the two metal films are separated by a thin undoped silicon layer. The separating Si spacer is therefore fully depleted so that in the energy diagrams the potential barrier, representing the Si bandgap, is trapezoidal with some small modifications for image force corrections. Light, with photon energy smaller than the Si bandgap, incident on such a heterostructure is absorbed in both

\[^1\) With silicon always the silicon between the two metal films is meant. For all properties discussed below, the silicon substrate does not come into play.
metal layers, creating photoexcited electrons and holes, on condition that the silicides are thin enough and that not the whole light intensity is absorbed in one layer. Photoemission of these carriers over their respective barrier into the Si occurs which leads to four different photoemission processes. The photoresponse is strongly dependent on the illumination and the bias condition. I distinguish between symmetrical TIPS and asymmetrical TIPS. In the former both metals are identical, thus the Schottky barrier heights on both sides of the silicon spacer are identical. In the latter (asymmetrical) the two metals are different, forming different Schottky barriers and therefore leading to an asymmetrical energy band diagram. For more clarity I discuss the symmetrical and asymmetrical TIPS energy band diagrams for different bias conditions separately.

6.4.1. Symmetrical TIPS

In Figure 6.4 the energy band diagram of a symmetrical TIPS as e.g. for CoSi$_2$/Si/CoSi$_2$ devices, at zero bias and at a general bias condition are sketched. Schottky barrier lowering, due to the electric field at the interface according to eq. (6.1) is not included in Figure 6.4. Numbers 1 through 4 indicate the four different possible photoemission processes, but will also be used to refer to the Schottky barrier of that particular process. As the device and hence its energy band diagram is symmetric, electric and photoelectric properties will by symmetrical in bias.

For zero bias the photocurrents 1 and 2 as well as 3 and 4 cancel each other on condition of equal currents. Thus the total photocurrent will be rather low. When a small bias is applied, photocreated carriers emitted above ('below' for holes, since increasing hole energy is directed towards the bottom) Schottky barriers 1 and 4, drift down the built - in electric field and are then collected in the other silicide film giving rise to a photocurrent (see Figure 6.4 b)). One can describe the effective barrier of processes 2 and 3 as the sum of the applied potential difference $V$ and the Schottky barrier (i.e. the cutoff wavelengths of these processes are shifted towards smaller wavelengths). Thus photocreated carriers emitted over the effective potential barrier have to cross the silicon against the electric field, before being collected in the other silicide. Since the Si thickness is much larger than the ballistic mean free paths of hot carriers in Si, the carriers are thermalized and processes 2 and 3 do not contribute to the overall photocurrent even at very small bias. (i.e. only hot carriers with an energy exceeding the potential barrier maximum by the energy which is lost during the path through Si, can be
collected. Thus the cutoff is shifted to smaller wavelengths). Electron photocurrent 1 and the hole photocurrent 4 will therefore dominate in the IR range. Since the holes head in the reverse direction compared to the electrons, both photocurrents have the same sign.

![Energy band diagrams of symmetrical TIPS (e.g. CoSi$_x$/Si/CoSi$_y$) for zero bias a) and bias V b), which because of the device symmetry represents the general bias condition. Since the intermediate Si is thin and undoped, it is assumed to be completely depleted and a trapezoidal potential barrier results. The four possible photoemission processes are labeled 1 - 4. Schottky effect is not included in b), which would lower the barriers of processes 1 and 4. Since for the electrical and photoelectric measurements the silicon substrate is of no importance, it is omitted in this figure.](image)

The respective magnitude of each photocurrent depends on the photon energy, the applied bias and of the spectral absorption in the silicides. The cutoff modulation is therefore mainly due to the ratio of the electron and hole currents as well as to the image - force barrier lowering. With increasing electric fields in the silicon a significant increase in the photocurrent can be expected. However, one has to bear in mind that a bias of 1 V across a TIPS with a 1000 Å thick silicon layer leads to electric fields of the order of $10^5$ V/cm which is very close to the electric breakdown field of $\sim 3 \cdot 10^5$ V/cm for Si [88]. If the silicide - silicon interfaces form ideal Schottky - contacts, the electric dark current in these symmetrical as well as in asymmetrical TIPS may be described by thermionic emission across the four different Schottky barriers. For this reason the current will be mainly governed by the lowest barrier at a given voltage, which in the case of my symmetrical TIPS is the CoSi$_x$/p-Si Schottky barrier.
6.4.2. Asymmetrical TIPS

For asymmetrical TIPS most remarks made in the paragraph above for symmetrical TIPS are equally valid and are not repeated here. The only change compared to the symmetrical device has to be made for the electron and hole Schottky barrier of PtSi. Thus the energy band diagram is no longer symmetrical at any bias. In Figure 6.5 the situations for negative and positive bias are sketched. Since the flat - band condition, i.e. where the energy bands in Si are horizontal, is no longer at zero bias as is the case for the symmetrical devices, this as well as the zero bias condition are also included in Figure 6.5. The Schottky effect is small and for more clarity is not indicated in the figure. The photoemission processes are discussed assuming comparable light absorption in both metal films.

In a) the effective potential barrier of process 2 and 3 is increased with the externally applied bias and hence the cutoff wavelength is shifted to shorter wavelengths. Process 1 and 4 will be the dominating processes in the IR. Their respective Schottky barriers are affected by the Schottky effect, leading to a small change of the cutoff energy and simultaneously to an increase of photoresponse. Because of the reverse direction of holes compared to electrons, the photocurrent is the sum of these two processes. The cutoff wavelength is given by the process across the smallest barrier which in this case is the CoSi$_2$ hole barrier.

At zero bias b), the energy bands in Si are not yet horizontal, as is the case for symmetrical TIPS. Otherwise the situation is close to a) but now all four processes contribute to the photocurrents in the IR, since the barriers for the emission processes 3 and 4 as well as 1 and 2 have the same height and the electric field in the Si is small. For both electron contributions the barrier height corresponds to the PtSi electron Schottky barrier. On the other hand, the holes have to cross the larger of the two hole barriers, namely the CoSi$_2$ barrier. But the situation for holes originating from CoSi$_2$ and PtSi is quite different. When the photoexcited holes in CoSi$_2$ have reached the silicide - silicon interface and have been emitted into the Si, they are accelerated by the electric field. On the other hand the photoexcited holes in PtSi have first to cross the Si against the electric field ballistically before they can cross the potential barrier. As already mentioned for the asymmetrical TIPS, the ballistic mean free path of hot holes in silicon is much smaller than the Si thickness which renders this process to be rather unlikely. Photocurrents of holes and electrons in both directions add with their respective sign.
Figure 6.5: Energy band diagrams for asymmetrical TIPS (e.g. PtSi/Si/CoSi₂) sketched for negative bias a), zero bias b), the flat-band condition c) and for positive bias in d) (the definition of negative and positive bias as sketched here, is used consistently in this work). Since the intermediate Si is thin and undoped, it is assumed to be completely depleted and a trapezoidal potential barrier results. The four different photoemission processes are labeled 1 - 4. Schottky effect in a), b) and d) is not included. The silicon substrate, having no importance for the devices, is omitted for simplicity.

At the forward flat-band bias $V_{FB}$ c), which is correlated with the Schottky barriers according to

$$e V_{FB} \approx \Phi_{e}^{PtSi} - \Phi_{e}^{CoSi_2} \approx \Phi_{h}^{CoSi_2} - \Phi_{h}^{PtSi},$$

(6.12)
the energy bands in Si are horizontal. With the experimentally determined Schottky barrier heights a flat - band voltage $V_{FB}$ of ~ 0.2 V results. No Schottky effect occurs in this situation. All four different processes contribute to the photocurrent, which because of a missing electric field in the silicon, is small. Further the mutual cancellation of the four different electron and hole emission processes lowers the overall photocurrent. The lowest barrier is now the PtSi hole barrier which defines the cutoff energy. Thus between zero bias and $V_{FB}$ the potential barrier maximum shifts linearly with bias from the CoSi$_2$ to the PtSi hole barrier. Since the direction of the PtSi holes is reverse to the CoSi$_2$ holes, the photocurrent will change sign in this bias range or at least at $V_{FB}$, depending on the relative amounts of the photocurrents.

For bias larger than the flat - band condition, the barrier for holes in the PtSi remains the smallest and determines the cutoff energy d). The barrier will even slightly decrease due to the Schottky effect. The effective potential barriers for processes 1 and 4 increase with bias and their contributions to the photocurrent in the IR range decreases.

If the absorption was mainly in the PtSi film, only photocurrents 1 and 3 would be important and a shift of cutoff energy between the PtSi hole and electron Schottky barrier could be achieved. The large modulation range can be controlled with bias varying about 0.5 V. The first TIPS reported by Pahun et al. with a modulation range between 0.25 and 0.87 eV for a bias change of 0.7 V, operated in this way [90]. The TIPS later reported by Sagnes et al. consisted of two metals where the electron Schottky barrier height of one silicide was nearly equal to the hole Schottky barrier height of the other silicide, also leading to a large modulation with bias between 0 and 1 V [92].

If thermionic emission is the dominant current transport process, the lowest barrier, i. e. the hole barriers, will therefore determine the $I$-$V$ characteristic. In contrast to the symmetrical devices the barrier will decrease from the CoSi$_2$/p-Si barrier height for bias smaller than zero, down to the PtSi/p-Si barrier height at the flat - band condition and remain nearly constant for a further increase bias, except for a slight decrease due to the image - force barrier lowering. The current will change its direction at zero bias but the effective barrier decreases until $V_{FB}$ is reached.
6. Application of silicide - silicon heterostructures to tunable infrared detector

6.5. Fabrication of TIPS

The fabrication process for both symmetrical and asymmetrical TIPS structures was identical beside the growth and patterning of the top silicide. For the symmetrical devices CoSi$_2$/Si/CoSi$_2$ heterostructures, were used. Growth and structural properties have already been described in chapter 5. I used PtSi as the top metal layer for the asymmetrical structures, because it is handy and has a high PtSi/n-Si Schottky barrier. Since the formation of good Schottky contacts is vital for the operation of TIPS sensors, I will first briefly summarize the most important points of the growth of PtSi and some properties of PtSi/Si Schottky barriers.

6.5.1. Growth and characterization of PtSi

Since I had no Pt source available in our MBE system, the wafers had to be moved to another evaporation system. The Pt was then evaporated through a lift-off mask with the samples held close to RT. Just before introducing the samples into that system, the surface was cleaned in a CF$_4$/O$_2$ plasma in order to remove hydrocarbons and the wafers were then dipped into a dilute HF solution in order to remove the oxide. PtSi was formed during a rapid thermal annealing (RTA) step with a halogen lamp, where the samples were heated to within five seconds up to 600 °C, staying at such a temperature for 20 to 60 seconds. Upon heating the Pt film firstly Pt$_2$Si is formed and only after the complete reaction of Pt towards Pt$_2$Si the Pt monosilicide is formed. This reaction scheme is observed for several transition and refractory metals [103,150,151,152]. During the reaction the silicide - silicon interface moves into the substrate (Si - buffer) [125,153]. Because this interface is formed at some distance below the original surface of the silicon it is free from contamination and should behave very close to an ideal Schottky contact. The stoichiometry of the silicide was determined by RBS. For 1000 Å thick Pt film the stoichiometry was almost equal to PtSi after a RTA step of 20 seconds at 600 °C. To get the Pt monosilicide at lower annealing temperatures one had to anneal for a longer time.

The resistivities of PtSi films were between 33 and 40 μΩcm which is in the range of published data (see e.g. [150,18]). Schottky barrier heights of PtSi/Si contacts were determined by analyzing $I$-$V$ curves according to the methods described in appendices D and E. It has to be mentioned that for the PtSi test diodes I used the same low - doped Si - substrate as for the growth of the heterostructures which were later used for TIPS fabrication. The relatively high substrate resistivity is thus responsible for the rather large ideality values.
n, which scattered in the range between 1.04 and 1.5. Although the ideality factor $n$ and the Schottky barrier $\Phi$ can be extracted from one $I$-$V$ characteristic (see appendices D and E) and should be in principle independent from each other [154,155]. Experimentally I found them to be linearly correlated, as is shown in Figure 6.6.

![Graph showing Schottky barrier height $\Phi$ and ideality factor $n$ for PtSi/Si diodes with various diameters.](image)

**Figure 6.6:** Schottky barrier height $\Phi$ and ideality factor $n$ of PtSi/Si diodes with various diameters, determined by the methods described in Appendices D and E, are linearly correlated. For an ideal diode (i.e. $n = 1$) the Schottky barrier can be extrapolated to $\sim 0.88$ eV.

With increasing ideality factor $n$ (the diodes become less ideal) the Schottky barrier decreases. This increase of the ideality factor and decrease for barrier height was mainly observed for small diode diameters. The soft behavior of the reverse current in addition cannot be accounted for by image-force lowering of the barrier height alone. Wittmer observed a similar effect at PtSi/Si(100) diodes and assumed that carrier recombination in the depletion layer due to enhanced electrical fields in reverse bias conditions has to be included in the conduction mechanism [116]. The barrier height of an ideal PtSi/Si contact, i.e. for $n = 1$, can be linearly extrapolated. It is $\sim 0.88$ eV at RT, which is in agreement with published data [18,128]. Sze reported 0.84 eV [88] for PtSi formed at 300 °C. For annealing temperatures above 350 °C barrier heights of 0.86 eV for RTA and 0.84 eV for furnace annealing were reported by Dimitriadis [156]. They did not see any significant variation of the barrier height and ideality factor with annealing time and with higher annealing temperatures. Wittmer measured a barrier height of 0.88 eV for PtSi/Si(100) diodes formed at 400 °C [116]. RT
ballistic - electron - emission microscopy (BEEM) studies of PtSi/Si(100) (n-type) by Turner et al. indicated a Schottky barrier of 0.87 eV [146] and by Niedermann et al. of 0.89 eV [147].

Despite of the ex - situ growth procedure of the PtSi films, the quality of the interface is quite good when the Schottky barriers are compared with previously reported values.

6.5.2. Photolithography process

Circular TIPS structures were fabricated by using standard photolithography and etching to define structures having active area diameters ranging between 10 and 1000 μm. In a first step a several thousand Angstrom deep mesa structure was etched with a HF - CrO3 - H2O etchant [157]. For the symmetrical TIPS the upper silicide was wet - chemical - etched with buffered HF. On the other hand Pt was lift - off evaporated on top of the mesa of Si/CoSi2/Si(111) heterostructures for asymmetrical devices. After every photolithography step, the samples were ultrasonically cleaned first in acetone and then in ethanol for about 5 minutes each, and finally rinsed in nanopure, deionized water.

The most delicate step was to selectively etch the intermediate Si in such a way that the underlying silicide could ultimately be contacted. I have chosen a CF4/O2 - plasma which etched the Si much faster than the silicide. Solid CoF2 and CoF3 are the only compounds being formed by cobalt and fluorine. Cobalt with oxygen forms CoO and Co3O4, which are also solids. From the values of the formation enthalpy a preferred formation of the fluorides is expected, which in an atmosphere containing oxygen easily react to the above mentioned oxides. This in turn suppresses the etching process additionally. Since there are no volatile Co compounds and a preferred formation of Co oxides is expected, perfect CoSi2 films should not be etched by a CF4/O2 - plasma [158]. Before the etching process, possible residual photoresist on the surface to be etched, was removed routinely in a pure O2 - plasma (100 mTorr O2, 200 W incident rf power, 2 minutes). Silicon was then etched in a CF4/O2 - plasma (~ 80 mTorr with 96 mass% of CF4 and 4 mass% of O2) at RT with an incident rf power of 200 W. The principal reaction of silicon is

$$\text{Si} + \text{CF}_4 + \text{O}_2 \rightarrow \text{SiF}_4 + \text{CO}_2.$$  

In figure 6.7 the etch depth as a function of time is plotted for two silicide films which have been overgrown with Si. Filled squares refer to W1185 (nominal 1000 Å Si/15 Å
CoSi$_2$/Si(111)) and open circles to W1184 (nominal 1200 Å Si/40 Å CoSi$_2$/Si(111)). The etch depth was determined by measuring Mireau interference fringes.

![Graph showing etch depth vs etch time](image)

**Figure 6.7:** Etch depth of CF$_4$/O$_2$ plasma etched Si/CoSi$_2$/Si(111) heterostructures as a function of etch time. (filled squares refer to #1185 1000 Å Si/15 Å CoSi$_2$/Si(111), open circles to #1184 1100 Å Si/40 Å CoSi$_2$/Si(111)). A clear etch stop when reaching the CoSi$_2$ layer is observed for 40 s < t < 90 s. The silicide is completely etched away and the underlying Si is etched for t > 90s.

For the film with the thicker silicide a very clear etch stop can be observed after about 40 seconds at a depth of ~1000 Å which lasts for about 45 seconds. The etch depth remains roughly constant during that time with a value close to the nominal Si film thickness. The etch rate of the silicide thus amounts to 0.74 Å/s which has to be compared with the etch rate of ~30 Å/s of the upper Si film. With a selectivity factor of ~40 it is therefore possible to lay open the silicide. After the silicide is etched through, the Si etch rate increases rapidly to about 100 Å/s. Surface roughening during silicide etching results in a larger net area which may explain the increase in the Si etch rate. Even for the film having only a 15 Å thick silicide, a short etch stop can be observed. Similar etch rates for Si etching as for #1184 can be determined. I further noticed that the etch rates were somewhat higher on my Si films than on virgin wafers. Thus the etch rate is very sensitive to the defect density and to surface roughness. Size and form of the samples also influences the electric fields in the plasma and hence the rate and uniformness of the etching process. In practice for each wafer the optimum etch time had to be determined in a series of etch tests. Photoresist with its organic components is etched away by O$_2$, forming mainly H$_2$O and CO$_2$. The etch rates of the
photoresist and the Si are of the same order of magnitude. I did not have to worry about the photoresist thinning because of the much thicker photoresist compared to the Si intermediate layer (at least factor 10 thicker).

![Diagram of process steps for fabrication of symmetrical TIPS](image)

**Figure 6.8**: Main process steps for the fabrication of symmetrical TIPS. a) Mesa structure is etched with a wet chemical etch, b) part of the upper silicide is removed selectively with a buffered HF etch, c) Si is selectively etched in a CF<sub>4</sub>/O<sub>2</sub> plasma, d) electrical insulation against the Si substrate is applied, e) lift-off sputtering of Cr/Au for electric contacts.

Electrical insulation of the metal pads and wires to the Si substrate was provided by applying a ~ 2 µm thick polymer coating before the metallization step. This was achieved by baking the developed photoresist at 200 °C for at least one hour. Before the final metallization step, the samples were cleaned in an O<sub>2</sub> plasma for 1 minute in order to remove residual photoresist. A short HF-dip was further applied to etch the oxide. A Cr/Au (100/2000 Å) metallization was then applied by lift-off sputtering. In Figure 6.8 the main process steps for the fabrication of symmetrical TIPS are sketched schematically and a successful operating TIPS is shown in Figure 6.9.

Symmetrical and asymmetrical TIPS structures were prepared from different wafers. Film quality (e.g. low defect density), was of utmost importance for successful Si etching and following CoSi<sub>2</sub> contacting. If the buried silicide is discontinuous, firstly the etch stop was very bad, and secondly the silicide cannot act as a contact, since the current cannot flow between islands. Substrate dopant diffusion, high defect densities, pinholes in the silicon, inhomogenous quality of the heterostructure are further reasons why not all processed
heterostructures yielded operating TIPS. All these defects lead to poorly rectifying behavior or even to an ohmic behavior. Only the wafers listed in Table 6.1 had the required heterostructure quality needed for successful operation of TIPS.

![Light microscope pictures of symmetrical TIPS](image)

Figure 6.9: Light microscope pictures of symmetrical TIPS. On the left side a complete device with a Si diameter of 175 µm and on the right side a detail of a 750 µm device are reproduced. The circular gold contacts shine bright. Light contrast due to the different etch depths can mainly be seen on the enlarged picture.

<table>
<thead>
<tr>
<th>wafer</th>
<th>TIPS</th>
<th>d(CoSi₂) [Å]</th>
<th>d(Si) [Å]</th>
<th>d(CoSi₂) [Å]</th>
<th>d(PtSi) [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1191</td>
<td>symmetrical</td>
<td>35</td>
<td>1300</td>
<td>46</td>
<td>-</td>
</tr>
<tr>
<td>1433</td>
<td>symmetrical</td>
<td>35</td>
<td>1500</td>
<td>45</td>
<td>-</td>
</tr>
<tr>
<td>1439</td>
<td>asymmetrical</td>
<td>35</td>
<td>1600¹</td>
<td>-</td>
<td>380</td>
</tr>
</tbody>
</table>

¹) The initial Si thickness was ~1850 Å (determined with RBS). Silicidation of Pt consumes 1.3 Å Si per Å Pt. Reacting 200 Å Pt to PtSi thus consumes ~260 Å of Si yielding a 380 Å thick silicide [150].

Table 6.1: List of all heterostructures/wafers which yielded operating TIPS. Film thicknesses are nominal values.
6.6. Electrical characterization of TIPS

The metal pads were either directly contacted with metal tips or gold wire bonded. One has to be careful with the contacted structure since a voltage of only a few volts across the Si leads to electric fields larger than the breakdown field and causes irreversible damage. All electric measurements were carried out in the dark. All I-V measurements are dc measurements, while the C-V measurements were carried out with lock-in technique.

6.6.1. I-V measurements

Assuming thermionic emission theory, the current across a symmetrical or asymmetrical TIPS should be the sum of the two currents of reverse biased Schottky barriers (i.e. currents 1 and 4 in Figure 6.4 b)). These saturation currents are proportional to $T^2 \exp(-e \Phi/k T)$. Further the Schottky effect (eq. (6.1)) is responsible for the decrease of the barriers and to the thereby associated increase in current. As an example in Figure 6.10 I-V curves of a 250 μm asymmetrical TIPS at different temperatures are reproduced.

![Figure 6.10: I-V characteristics of a 250 μm asymmetrical TIPS (W1439) for different temperatures are plotted. The temperature is given in K and is lower by 20 K for subsequent curves. In forward direction, i.e. where the PtSi/p-Si barrier is the lowest potential barrier, series resistance effects are present even for small bias.](image-url)
In forward direction, i.e. where the PtSi/p-Si barrier is the lowest potential barrier, the curves are strongly influenced by the series resistance even for small bias. In the reverse direction, the behavior is similar to a single Schottky contact in reverse bias condition, at least at high temperatures. Lowering the temperature, leads to an exponential decrease of the current density with some changes of the $I-V$ curves at low temperatures. Besides the thermionic current contribution, additional transport processes as e.g. hopping or Poole-Frenkel emission come probably into play, which can only be observed at low temperatures. However, it is difficult to distinguish Schottky barrier lowering effects, Poole-Frenkel and hopping effects only by Arrhenius plots [103]. For symmetrical TIPS the $I-V$ curves are almost symmetrical and look similar to the reverse current of the asymmetrical device shown in Figure 6.10.

![Figure 6.11: Potential barrier determined from the single reverse $I-V$ characteristics as a function of temperature. (W1439, 100 μm device)](image)

Saturation current densities, which were obtained by extrapolating the current to zero bias in a semilog - plot, have been compared with the theoretical values computed using thermionic emission theory (eq. D.4). For devices fabricated on heterostructures of W1191, the measured saturation currents were larger by a factor of 10 - 50. On the other hand, the devices fabricated with the newer heterostructures (series 14xx) had saturation currents equal to the computed values for both, symmetrical and asymmetrical devices. For the latter, the lowest potential barrier at zero bias corresponds to the CoSi$_2$ hole barrier (see Figure 6.5).
This allowed for a direct determination of the barrier height from a single \( I-V \) curve at a certain temperature.

In Figure 6.11 the barrier determined from single reverse \( I-V \) characteristics of a 100 \( \mu \)m asymmetrical device (W1439) is shown as a function of temperature. The values are very close to the expected Schottky barrier of \( \text{CoSi}_2/p\)-Si. At low temperatures the barrier decreases suddenly which is equivalent to too large saturation currents at those temperatures. Thus small contributions different from thermionic emission are present in the dc dark current as already mentioned above. It has to be emphasized, that this ideal electrical behavior is only due to absolutely excellent heterostructure quality. Whether the H - plasma treatment of the virgin wafers or only growth conditions were responsible for this improvement of heterostructure quality cannot be concluded for sure, because of too few experiments. But it is tempting to say that the improvement in Si buffer quality by the new wafer cleaning technique has a positive influence on the heterostructure quality.

![Figure 6.12](image_url)

Figure 6.12: Barrier deduced from \( I-V \) characteristics at different temperatures of a 250 \( \mu \)m asymmetrical TIPS. The barrier lowering for negative bias can quantitatively be attributed to Schottky effect. In forward bias the barrier decreases but cannot be determined over a large range because of major deviations of the \( I-V \) characteristics caused by the large series resistance. The insert shows the temperature dependence of the saturation current, which yields a barrier \( \Phi \) of 0.50 eV.
6.6. Electrical characterization of TIPS

With the temperature dependent saturation current the Schottky barrier can be determined assuming thermionic emission theory. The saturation current determined for both bias directions was equal and yielded a barrier of 0.50 eV for a 250 μm asymmetrical TIPS (Insert Figure 6.12). With the energy band diagram in Figure 6.5 it is clear that this barrier is the CoSi₂/p-Si Schottky barrier. From I-V characteristics, measured at different temperatures, I determined the barrier as a function of bias, which is shown in Figure 6.12. At zero bias the barrier has the height of the CoSi₂/p-Si Schottky barrier of 0.50 eV and is lowered about 30 meV at -0.5 V, which is close to the theoretical value of Schottky effect which amounts to 20 meV at this point. In forward direction the current is strongly influenced by the series resistance and the determination of the barrier from I-T characteristics becomes problematic even for small bias. However, the start of the linear decrease of the barrier towards that of PtSi/p-Si according to Figure 6.5 can be seen. At the flat-band condition, which is expected to be at \( V_{FB} = 0.2 \) V, the lowest barrier is the PtSi hole barrier with \( \Phi \approx 0.3 \) eV. Experimentally this barrier is reached at \( \sim 0.15 \) V which is close to the theoretical value. From this point on the barrier should remain almost constant, which unfortunately cannot be measured by this method.

Figure 6.13: Barrier deduced from I-V characteristics at different temperatures of a 100 μm symmetrical TIPS. Barrier lowering is mainly due to Schottky effect and is more or less symmetrical reflecting the device symmetry. Fits according to eq. (6.1) are included.
For symmetrical sensor structures, the barrier determined from temperature dependent \( I-V \) measurements showed a maximum of \( \sim 0.53 \) eV at zero bias which corresponds to the \( \text{CoSi}_2/p-\text{Si} \) Schottky barrier height similar to asymmetrical TIPS (see Figure 6.13). The device symmetry is reflected in an almost symmetrical characteristics and the barrier decrease can quantitatively be attributed to Schottky effect. However, small deviations from symmetry can probably be explained by the two different silicide - silicon interfaces involved. The lower silicide has an A-type and the upper silicide a B-type interface with the intermediate silicon.

These facts let me conclude that electric current transport in TIPS is governed by thermionic emission across the barriers. The smallest barrier, which depends on the exact bias condition, determines thereby the major current transport process. Since the currents are sometimes larger than is expected for an ideal Schottky diode and deviations from ideal behavior is always observed at low temperatures, other transport processes, as e.g. carrier hopping between localized states, must be present. Schottky - barrier inhomogeneities (i.e. regions with lower potential maximum) over the device surface (e.g. defect density also on the best heterostructures is still high; single pinholes in Si can be present) can not be excluded. However, pinch - off hampers the current to flow entirely in these regions. Tung showed that the potential of an inhomogeneity present in the Schottky - barrier height, e.g. in a region with a lower barrier, is pinched - off if the defect area is small or the silicon doping is very low [159,160]. Since the intermediate Si in TIPS is low doped, pinch - off should be effective.

\( I-V \) curves could be reproduced many times for each device when the applied bias did not exceed several volts. However a too high tension or current through the device lead to irreversible deterioration of the device performance where in the worst case an ohmic behavior resulted. At low temperatures the devices were less sensible to high voltage since the current densities were then lower by orders of magnitude. I always observed a good scaling of zero - bias resistance with device area indicating that electric transport is not disturbed by edge effects.

6.6.2. C-V measurements

\( C-V \) measurements were carried out at RT with constant frequency of 1 MHz. The capacitance was thereby determined from the imaginary part of the conductance. Since TIPS devices consist essentially of two back to back connected Schottky barriers the resultant
capacitance is due to two voltage-dependent Schottky barrier capacitances connected in series. Therefore, the resultant total capacitance will increase from a zero-bias value to a maximum and then decrease monotonically with increasing bias. From the point of complete depletion of the silicon, the capacitance is the same as that for a parallel plate capacitor with the silicon acting as a dielectric [135,161]. For symmetrical structures the C-V relationship is symmetrical with respect to zero, whereas for asymmetrical structures the C-V profile is displaced and obviously not anymore symmetrical [135]. Since the silicon films are thin (<2000 Å) and undoped, they should already be depleted at zero bias thus yielding flat C-V profiles.

The measured C-V profiles of symmetrical TIPS were almost flat for bias smaller than ±1.0 V as can be seen in Figure 6.14 a). The largest devices showed some small deviations at zero bias, which is almost symmetrical about zero. According to Ref. [161] these humps indicate a maximum silicon doping of 4×10¹⁶ cm⁻³. This doping results from contamination of the silicon evaporation source and contamination of the MBE sample holder. Since the silicon is always grown with the substrate kept at ~700 °C, contamination desorbed from the hot
environment is incorporated in the growing silicon film. Dislocations in addition can also lead to a doping effect [162]. Capacitance of asymmetrical TIPS with the PtSi/Si hole Schottky barrier forward biased cannot be determined by conductance measurements, because of the rapidly increasing current. The decrease on this side is also due to the exponentially increasing current which falsifies the conductance measurements. (Figure 6.14 b))

However, as can be seen in Figure 6.14 b) for the other bias direction, the profile is almost flat as for the symmetrical devices. An increase of capacitance with device diameter is observed for both kind of TIPS. This area dependence is shown in Figure 6.15, where the zero-bias capacitance of symmetrical and asymmetrical TIPS are plotted as a function of device diameter. Since the structures should behave as a plate capacitor, the calculated capacitance, assuming the plate separation to be equal to the Si film thickness and a dielectric constant for Si of $\varepsilon = 11.9$ [88], are plotted.

$$C = \varepsilon \varepsilon_0 \pi d^2 / 4 h_{Si}$$

Figure 6.15: Area dependence of zero-bias capacitance for symmetrical (W1191; circles) and asymmetrical TIPS (W1439; squares). The lines are the calculated capacitance of a plate capacitor with the area given by $\pi d^2 / 4$, the plate separation distance equal to the silicon thickness and the dielectric constant $\varepsilon$ of silicon. Although only 11 data points are visible for TIPS made of heterostructure W1191, they represent the capacitance of 68 measured devices.

Besides the exact area dependence an excellent correspondence of the calculated values with the measured ones is observed for the symmetrical TIPS (squares). It has to be mentioned that the capacitance variation of symmetrical TIPS from different samples was less

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1) capacitance was determined in the flat region of the C-V profile
than 5 %\textsuperscript{13}, indicating homogeneous device quality over the entire wafer. For asymmetrical TIPS (circles) there is some fluctuation in the zero - bias capacitance but the area dependence as well as the absolute values correspond well with the plate capacitor model. Contamination of the Pt/Si interface introduced during photolithography or Pt deposition may explain the fluctuations of capacitance. Because this fabrication step imposed some problems, the Pt was grown rather thick in order to move the silicide/silicon interface well below the initial Si surface.

6.7. Photoelectric characterization of TIPS

6.7.1. Experimental

Although the photoelectric response of TIPS could be measured at RT, at least for very small bias, all measurements were carried out in a cryostat with the samples held at 77 K in order to get an improved signal - noise ratio. The signal of the photocurrent was measured across a calibrated load resistance with lock - in technique. The load resistance was adjusted according to the zero bias resistance of the device in order to get the optimal signal - noise ratio and with the main voltage drop across the sensor. Monochromatic light (0.5 - 1.1 eV) was chopped at frequencies of about 80 Hz which is comparable to operating frequencies of multiplexed arrays. The spectral intensity of the light source was calibrated using a Molecron pyroelectric radiometer.

6.7.2. Simulation and fitting procedure

In order to get more insight into the photoelectric measurements, the photoemission processes of TIPS were modeled in order to obtain the resulting total photocurrent. To quantitatively describe the TIPS quantum efficiency one has to modify the usual Fowler model, taking into account a) the four different photocurrents present in the TIPS structure (Figure 6.4 and Figure 6.5) and b) the wavelength dependent light absorption in both silicides (multireflection in thin films). Quantum efficiency was therefore described employing

\[ Y_{QE_{total}} = \sum_{i=1}^{4} Y_i; \quad Y_i = A_i(V) f_i,abs (hv - \Phi_{eff})^2, \quad (6.13) \]

\textsuperscript{13} The largest devices showed a 15 % variation, but this can probably be attributed to the inaccurate determination for the capacitance from conductance due to the large currents.
whilst considering the direction of the four photocurrents [92]. The $A_i(V)$ describe the relative amount of each hot carrier species and are only a function of bias applied across the TIPS. An effective potential barrier $\Phi_{\text{eff}}$ standing for the sum of Schottky barrier, image force barrier lowering and applied external voltage has to be used in the modified Fowler equation eq. (6.13).

Multireflections of light at the various interfaces and interferences in both silicides and the intermediate silicon lead to light intensities which depend strongly on the silicide and silicon film thickness. The optical system with all important parameters is drawn in Figure 6.16. The electric field vector in each film as a function of film thickness was computed using the Abeles matrix method [163] where the Fresnel reflection and transmission coefficients were calculated using the wavelength dependent complex refractive indices. The energy dependent complex refractive indices for the silicides were taken from the literature (CoSi$_2$: [164]; PtSi: [165]), while for silicon the dispersion is marginal in the IR spectral range and was set to be constant ($n_{\text{Si}} = 3.4$ and $k_{\text{Si}} = 0$) [166]. The fraction of incident light absorbed in each silicide film $f_{\text{abs}}$ was then derived employing eq. (6.2). Multireflections in the bulk silicon were supposed to be incoherent. In first order they alter the light intensities in the silicides energy independently and were, therefore, neglected [164]. It is obvious that the reflection, transmission and absorption coefficients are nontrivial functions of energy and film thicknesses.

![Figure 6.16](image_url)

**Figure 6.16:** Shown are all multilayer parameters used to compute the light absorption in both silicide films. Only the refractive indices of the silicides are complex and energy dependent. Interferences in the silicon between the two silicides were assumed to be coherent whereas in the silicon substrate they were supposed to be incoherent.
For simplicity's sake, the probability of an electron respectively hole, which is excited at a distance $x$ from the interface, to reach the interface was set constant, i.e. reflection of hot carriers in the metals was assumed to be without dispersion. Simulations of TIPS with dimensions listed in Table 6.1 indicated that this approximation has only a minor influence on the results. Simulations further evidenced that the intermediate silicon plays the role of a Fabry-Pérot cavity, where the thickness of the silicon mainly determines the respective weight and shape of the absorption in both silicide films. To fit the measured responsivities, the barriers according to the bias condition (Figure 6.5) were put into the calculation and only the $A_i(V)$ ($i = 1,...,4$) were fitted. Schottky effect corrections of the barriers have been included. The simulation of the optical system and the fitting was performed using Mathematica.

6.7.3. Photoresponse measurements

A) Symmetrical TIPS

Symmetrical TIPS have been measured with back and front illumination yielding essentially the same results. Quantum efficiencies were somewhat larger for back illumination because of refractive index matching of the Si substrate. In Figure 6.17 Fowler-plots of a 175 μm symmetrical TIPS for several bias conditions measured at 77 K are reproduced.

![Fowler plots](image)

Figure 6.17: Fowler-plots of symmetrical TIPS for different bias conditions (0.05, 0.1, 0.2 and 0.4 V) measured at 77 K (175 μm, W1433). The photoresponse is similar to a single Schottky-barrier.
At zero bias the cutoff energy corresponds to the CoSi$_2$/n-Si Schottky barrier. The signal was unfortunately too low at zero bias, because of equivalent photocurrents from both silicides. With increasing bias the photoresponse increases because the electric field in the silicon leads to enhanced carrier collection and because of the decrease of mutual cancellation of photocurrents. Simultaneously a clear decrease of the cutoff energy with increasing bias is observed. Although the dark current increases exponentially with voltage, photocurrents could be measured confidently up to voltages of ±2.0 V, reflecting the very high structural Si quality.

In Figure 6.18 the barrier, determined from Fowler - plots of a 110 μm symmetrical TIPS with a 1370 Å thick Si film, as a function of bias is plotted. Within 2 Volts the barrier drops from the initial CoSi$_2$/n-Si Schottky barrier value towards the Schottky barrier of holes. This, however, is difficult to understand. Since both silicide films are thin and of about the same thickness, light absorption in both films is roughly equal. According to the energy - band diagram shown in Figure 6.4, the photocurrent is the sum of two contributions of opposite flow direction. One current is due to holes and the other to electrons so that both contributions have the same sign. The respective weight of these two currents is extremely sensitive to the bias applied between the two electrodes.

![Figure 6.18: Cutoff energy as a function of bias across of a symmetrical TIPS measured at 77 K. (110 μm, W1191, d$_{Si}$ = 1370 Å)](image)
At zero bias the electron contribution is predominant whereas for a small bias the hole current increases dramatically. Since in fact for larger bias the potential maximum is shifted farther into the silicon, the photoexcited carriers have to reach first this potential maximum ballistically. Dissipating optical phonon interactions on these paths are possible. Different mean free ballistic path lengths of electrons and holes in Si probably may explain this change of photocurrent with bias. Similar observations have also been reported by Pahun et. al. [90], but a full explanation of this effect is still lacking.

Further the behavior is not absolutely symmetric which is probably due to the different film thicknesses or the two structurally different interfaces (lower interface: type A; upper interface: type B). As in view for intended application the asymmetrical devices are much more interesting than symmetrical ones, emphasis is put on the analysis of asymmetrical devices.

B) Asymmetrical TIPS

Asymmetrical TIPS have been measured with back illumination, i.e. through the silicon substrate, because in front illumination the 380 Å thick PtSi layer absorbed too much light and no photoresponse could be detected.

A first analysis at least for bias different from the flat-band voltage, was carried out using Fowler-plots. Although the square-root of the normalized photocurrent is drawn in Fowler-plots, the sign is respected in Figure 6.19. Above 1 eV the photoresponse is already influenced by the creation of electron-hole pairs in Si. For a single Schottky-contact, the intersection with the x-axis yields the Schottky-barrier height. However, for asymmetrical TIPS the Fowler-plots deviate markedly from a straight line. This is because at least two photocurrents over different Schottky-barriers are present. For \( V < 0.14 \) V the photoresponse is negative and for \( V \geq 0.18 \) V it is positive for all wavelengths. Inbetween these bias values the photocurrent changes its direction as a function of wavelength. This is due to the four different photoemission processes which around the flat-band voltage have comparable contributions. A detailed description of this phenomenon follows later. However, a determination of Schottky-barrier heights is still possible. For bias below \( \sim 0.16 \) V barriers of 0.5 and 0.8 eV and for bias above \( \sim 0.17 \) V of 0.35 - 0.4 eV could be deduced at different TIPS. The former barriers correspond to the PtSi/n-Si and the CoSi$_2$/p-Si Schottky-barrier and the latter to the PtSi/p-Si Schottky-barrier. The CoSi$_2$/p-Si Schottky-barrier height is in agreement with the values obtained from electrical measurements (see e.g. Figure 6.12 and
Figure 6.13. The value obtained with Fowler-Plots for the PtSi/n-Si Schottky barrier is very close to the average value determined with I-V measurements of PtSi/n-Si diodes (see e.g. Figure 6.6). Adding the Schottky barriers for holes and electrons yields the Si bandgap [134] which can roughly be demonstrated in the case of PtSi. The CoSi2/n-Si Schottky barrier height cannot be determined because the photocurrent over the much lower PtSi/p-Si barrier is predominant. Barrier heights of all measured devices scattered within ±0.05 eV around the mean values.

![Figure 6.19: Fowler plots of an asymmetrical TIPS for different bias conditions (W1439, 250 μm). For negative bias the plots differ markedly from a linear behavior. This is consistent with two photocurrents over two different barriers. Around 0.17 V the shape and the intersection with the x-axis changes dramatically.](image-url)
The main photocurrent for all bias directions stems from the PtSi because light absorption in the CoSi$_2$ is much smaller. Thus when plotting the barrier of the dominating photocurrent as a function of bias an abrupt change at the flat-band bias $V_{FB} = 0.17 \pm 0.01$ V is observed (see Figure 6.20). Thus above $V_{FB}$ photoemission of holes in PtSi and below $V_{FB}$ photoemission of electrons in PtSi is predominant. In fact the cutoff energy is switched sharply at $V_{FB}$ from 0.84 to 0.4 eV corresponding to a shift in cutoff wavelength from 1.55 to 3.1 μm. The important point is that the switching happens within only 0.01 V.

![Figure 6.20: Barrier of the dominating photocurrent (electron and holes from PtSi) as a function of applied bias measured at a 50 μm asymmetrical TIPS (W1439). At the flat-band voltage of 0.17±0.01 V the photoemission process changes abruptly. The barrier for $V < V_{th}$ corresponds to the PtSi/n-Si Schottky barrier (process 1) and for $V > V_{FB}$ to the PtSi/p-Si Schottky barrier (process 4).](image)

Although for bias slightly smaller than $V_{FB}$ the effective barrier for photoexcited holes in the PtSi is smaller than for electrons, this photocurrent is strongly suppressed. A small electric field in the silicon layer increases the effective barrier for these photoexcited holes. Only those having energies larger than the effective potential barrier can cross the barrier and be collected in the CoSi$_2$. This requires that the holes traverse the 1500 Å thick Si ballistically, since the potential maximum is near the Si/CoSi$_2$ interface. On the other hand, at high electric fields in a semiconductor, the most frequent scattering event is the emission of optical phonons [88], which determines also the saturation velocity. The optical phonon inelastic mean free path of hot electrons and holes in Si are ~76 Å and ~55 Å, respectively.
The average energy loss per phonon - electron/hole collision is about 63 meV [88]. Thus it is evident that the holes suffer many phonon collisions before reaching the potential barrier maximum. Because of the considerable energy loss of the holes, the transmission rate of hot holes is drastically reduced. In contrast the photoexcited electrons in PtSi have only to reach the PtSi/Si interface ballistically and are then accelerated towards the other silicide by the electric field in Si.

To be more accurate, the potential maximum is in reality shifted a small distance into the silicon because of the Schottky effect. Since this distance is rather small compared to the silicon film thickness, the majority of the electrons can cross the barrier. The ballistic mean path of these hot electrons in the silicide is in the range between 40 and 76 Å [146,147]. This indicates that hot carriers created within that distance from the silicide - silicon interface may escape the barrier and that reflections at the silicide - air interface do not have to be considered because of the six times thicker film thickness.

In Figure 6.22 the photoresponse of an asymmetrical TIPS for several bias conditions is shown simultaneously with fits assuming the effective barriers according to Figure 6.5. Negative photocurrents are drawn by open symbols and the positive photocurrents with the appropriate black symbols. The shape and magnitude of the photoresponse strongly depends on the applied bias. For positive bias as low as 0.18 V the photocurrent is positive over the whole measured wavelength range. At 0.17 V a phase shift of 180 degrees corresponding to a change of current direction is observed at ~1250 nm. This point of change in photocurrent direction shifts to larger wavelengths for smaller bias. At 0.15 V the photocurrent changes the direction at least two times. Below that bias, the photocurrent is negative over the whole wavelength region. This strange behavior can only be understood by taking into account all four photoemission processes. The qualitative behavior of the photoresponse as shown in Figure 6.22 could be exactly reproduced with asymmetrical TIPS having diameters between 50 and 250 μm. Also the flat - band bias could be reproduced with an accuracy better than 10 mV.

The fit procedure unfortunately was not able to fit the relative amounts of the four processes and the appropriate effective barriers simultaneously because of too many fit parameters. Since the different Schottky - barriers can be deduced from Fowler - plots, they were fixed at their proper values in the fitting procedure. For the fits of the TIPS shown by solid lines in Figure 6.22, I set the flat - band voltage to 0.17 eV and Schottky barrier heights to 0.4 and 0.8 eV in PtSi and to 0.53 and 0.65 eV for holes and electrons in CoSi₂.
respectively, for all bias conditions. The effective barriers at each bias were then set according to the bias condition shown in Figure 6.5, including the Schottky effect. This model fits well to all photoresponse measurements even for the one measured at 0.15 V where the sign of the photocurrent changes twice. Inspection of the relative amounts of each photocurrents $A_i(V)$ obtained from fits showed that the hole and electron photocurrents of both silicides have opposite signs and processes 2 and 3 as well as 1 and 4 have the same sign (processes labeled according to Figure 6.5). This is an imperative condition of the energy-band model in Figure 6.5. The ratio of hole and electron photocurrents of PtSi is more or less constant for bias smaller than $V_{FB}$. Between 0.16 and 0.17 eV the ratio increases abruptly and remains again constant for higher bias (see Figure 6.21).

![Figure 6.21: Ratio of $A_i(V)$'s of PtSi holes and electrons as obtained from fits. (fit parameters of asymmetrical TIPS shown in Figure 6.22)](image)

This indicates that at the flat-band bias the photoemission of holes from the PtSi is switched on and for PtSi photoelectrons is switched off sharply as was suggested earlier. The analogous reverse situation is observed for the ratio of hole and electron photocurrents from the CoSi$_2$. This in turn implies that photocurrents with an opposing electric field persistent in the silicon are strongly suppressed, which was explained above to be due to optical phonon scattering. In summary this confirms that for positive bias, the photoexcited holes from PtSi and the photoexcited electrons from CoSi$_2$ are the dominant contributions of the photocurrent. Analogously for negative bias the other two photoemission processes predominate. For bias close or equal to the flat-band bias $V_{FB}$ an abrupt change between these two regimes takes
place (to within 10 - 20 mV). Thus the measurements shown in Figure 6.22 together with the parameters of the fits are in full qualitative agreement with the energy band diagram proposed in Figure 6.5 when assuming hot carrier - phonon interactions.

For a complete discussion of the photoemission processes, the possibility of photoexcitation of carriers trapped in Si deep levels should also be considered. With an optical absorption cross section of typically $10^{-16}$ cm$^{-2}$ or below, only about $10^{-5}$ of the incident light is absorbed in the Si if an optically active defect - density of $10^{16}$ cm$^{-3}$ is assumed [90]. Even with a collection efficiency of unity, the contribution remains vanishingly small. Furthermore the photoexcited free carriers have an isotropic momentum distribution. One half of the carriers should be swept by the electric field towards the silicides, thus forming a bias independent current as long as $V > V_{FB}$ or $V < V_{FB}$.

For bias around the flat - band condition the quantum efficiency is lower by approximately two orders of magnitude. A reason is the low electric field in the silicon leading to an inefficient collection of photocreated carriers. On the other hand, at larger voltages, impact ionization may possibly increase the current. Maximum quantum efficiencies as high as 10% at 1 eV and 0.1% at 0.5 eV have been measured at asymmetrical TIPS, which is comparable to values reported for Pt/Si/ErSi$_2$ TIPS (5% at 1 eV) [90]. Finally it has to be mentioned that the devices have in no way been optimized neither with optical cavities and refractive index matching layers nor by choosing ideal multilayer film thicknesses. One has to bear in mind that the low quantum efficiency in SBD and TIPS is mainly due to the restricted cone angle of momentum for carriers crossing the interface due to the requirement for conservation of parallel momentum. Because both silicides absorb light, at least the double quantum efficiency of conventional SBD should be attainable with TIPS, however.

Instead of chopping the light I tried also to modulate the bias with a small signal (amplitude 0.1 V). In order to get the maximum signal the average bias was set to the flat - band value of 0.17 V. A very small photoresponse could be measured over the whole wavelength region. In this experiment, both the photocurrent and the dark current are modulated. Because the latter is up to three orders of magnitude higher than the photocurrent, it was very difficult to measure the photocurrent properly.

For successful operation of TIPS, low dark currents are needed, which are mainly limited by the quality of the silicon. Defect and/or pinhole densities have, therefore, to be as low as possible. Some devices did not operate because of too much diffusion of dopants from the substrate into the silicon spacer.
Figure 6.22: Photoresponse of a 100 µm asymmetrical TIPS for different bias conditions (upper part bias $V > V_{FB}$ and in the lower part $V < V_{FB}$). Negative photocurrents are drawn with open symbols and positive photocurrents with the appropriate black symbols. Quantum efficiency for 0.01, 0.1 and 1% is indicated. Fits including light multirefections in the thin films, the four photoemission processes and the effective energy - band configuration are drawn with solid lines. (W1439, D6)
Apart from these problems a more technological problem was also imposed by the discontinuity of the buried silicides causing the plasma etching not to have a well defined etch stop. Contacts with silicides have then only been made by hazard. Fabrication of operating TIPS demanded therefore silicide - silicon heterostructures of excellent crystalline quality. Hence, a lot of time was devoted to the growth and characterization of silicides and silicide - silicon heterostructures in order to improve the growth process. For possible device integration in Si technology, feasibility with Si(001) should be demonstrated because this is the standard substrate orientation. However, the poor heterostructure quality achieved on Si(001) did not allow for device fabrication.

6.7.4. Detectivity

The operational requirement for an IR detector is an adequately large signal to noise ratio (S/N). If one defines an S/N for unit incident power and bandwidth at a particular wavelength, the area dependence is

\[
\frac{S}{N} \propto A^{-\frac{1}{2}}. \tag{6.14}
\]

This leads to the definition of an area - independent figure of merit, the detectivity \( D^* \) [167]

\[
D^* = \frac{SA^{\frac{1}{2}}}{N}. \tag{6.15}
\]

For analysis the only noises taken into account were the contributions of fluctuations in the background photon rate and the Johnson noise (thermal noise) of the junction resistance. Experimental data showed then that the Johnson noise limits the device performance. With a Johnson noise of \( N^2 = 4kT/R_0 \) [168], the detectivity is then

\[
D^* = S\left(\frac{R_0 A}{4kT}\right)^{\frac{1}{2}}, \tag{6.16}
\]

where \( R_0 \) is the zero - bias junction resistance, \( T \) the operating temperature and \( k \) the Boltzmann constant. In Table 6.2 the detectivity determined at asymmetrical TIPS at 1 eV and zero bias is listed.
6.7. Photoelectric characterization of TIPS

<table>
<thead>
<tr>
<th>$d$ [μm]</th>
<th>$R_0$ [GΩ]</th>
<th>$D'$ [$10^{10}$ cmHz$^{1/2}$/W]</th>
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<tr>
<td>50</td>
<td>200</td>
<td>2.7</td>
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<tr>
<td>100</td>
<td>40</td>
<td>2.3</td>
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<td>150</td>
<td>35</td>
<td>2.6</td>
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<tr>
<td>250</td>
<td>15</td>
<td>3.0</td>
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Table 6.2: Zero - bias junction resistance and detectivity $D'$, assuming dominating Johnson noise contribution, of four asymmetrical TIPS determined at 77 K, 1 eV and zero bias. $d$ is the diameter of the intermediate silicon. In agreement with theory the detectivity $D'$ is an area independent figure of merit. The zero - bias resistance correlates roughly with $d^{-2}$.

Comparable detectivities for Ir/Si/ErSi$_2$ TIPS have already been reported by Sagnes et al. [92] and for CoSi$_2$/p-Si SBD by Kurianski [121]. The detectivity is mainly determined by the area specific zero - bias resistance $R_0$, which has an exponential temperature dependence. Thus reasonable detectivities of TIPS and SBD can only be obtained at low operating temperatures, i.e. at 77 - 100 K.

6.8. Summary

A new infrared detector consisting of a metal - semiconductor - metal sandwich, was fabricated using CoSi$_2$/Si/CoSi$_2$/Si(111) and PtSi/Si/CoSi$_2$/Si(111) heterostructures. The most important feature of this device (also called TIPS) is the enormous tunability of the cutoff wavelength, which for the presented devices can be varied between 0.4 and 0.8 eV. Electric and photoelectric characterization of symmetrical and asymmetrical TIPS is in full agreement with the proposed energy band model. This model includes two back to back connected Schottky barriers with a thin undoped silicon layer in between, which is hence entirely depleted.

Electrical characterization revealed that the temperatures above ~ 150 K thermionic emission over the lowest potential barrier determines the $I$-$V$ characteristics. Barriers as determined from saturation currents of single $I$-$V$ curves or from $I$-$T$ curves were consistent with the proposed energy - band diagrams. Furthermore $C$-$V$ measurements proved the Si to be completely depleted.
Photoelectric measurements between 1 and 2.5 μm at 77 K yielded a functional dependence which can only be explained by taking into account all four photoemission processes and the exact light absorption of the thin film multilayer. Simulating and fitting the photoresponse of asymmetrical devices with these considerations yields exactly the experimentally observed characteristics. The thereby associated barriers correspond to the silicide - silicon Schottky barriers for holes and electrons of both silicides. Because of hot carrier thermalization in the silicon, probably due to optical phonon interactions, the two processes where the carriers head against the electric field, are strongly suppressed. The situation is mirrored when passing through the flat - band condition, leading to an abrupt change of the dominant photoemission processes and of the cutoff wavelength. Device quantum efficiencies comparable to conventional Schottky barrier detectors were obtained, although the TIPS have by no means been optimized with antireflection coatings and optical cavities.

Responsivity of the new sensors presented in this work can be steered whilst the cutoff energy can be tuned over 0.4 eV by an external bias. This allows a possible application of wavelength resolved, i.e. really colored, IR imaging. All the depicted characteristics combined with the possibility of monolithic integration with Si electronics offers tremendous versatility for this novel type of IR detector.

More insight in the thermalization process could be obtained by measuring asymmetrical TIPS with much thinner silicon spacers. If this silicon thickness will be comparable with the ballistic mean free path, thermalization will not anymore be significant. Thus the photoelectric TIPS characteristic will change markedly (apart from the different light absorption).
REFERENCES


APPENDICES

A: Elasticity

Classical elasticity describes the reaction of a homogeneous, macroscopic solid to the influence of external stress. For small deviations from equilibrium, elasticity can be described by a three-dimensional extension of *Hooke’s law*, which assumes restoring forces to be linearly proportional to strain. The state of stress is described with the second-rank tensor \( \sigma_{kl} \), where diagonal elements describe pure axial compression or tension and off diagonal elements shear stress. The second-rank strain tensor \( \varepsilon_{ij} \) is defined as

\[
\varepsilon_{ij} = \frac{\partial u_i}{\partial x_j},
\]

where \( \partial u_i \) denotes the displacement from the equilibrium position along the \( i \)-axis. *Hooke’s law* states that the stress \( \sigma_{kl} \) is proportional to the elastic strain \( \varepsilon_{ij} \), or conversely, that the strain is proportional to the stress. The proportionality factors are the elastic stiffness constants \( C_{kiij} \) and the elastic compliance constants \( S_{kiij} \).

\[
\sigma_{kl} = \sum_{ij=1}^{3} C_{kiij} \varepsilon_{ij} \quad ; \quad \varepsilon_{kl} = \sum_{ij=1}^{3} S_{kiij} \sigma_{ij}
\]

The elastic properties of the material are described by the 4th rank elastic stiffness tensor \( C_{kiij} \) which has 81 different elements. By taking into account tensor symmetries \( (C_{kiij} = C_{ijkl} = C_{ikji} = C_{ikji} = C_{klij}) \), only 21 independent tensor elements remain, which is the maximum number of independent elements for any medium. Crystal symmetries reduce the number of independent tensor elements further. Using *Voigt’s scheme* (replace indices \( k \) or \( i \) according to \( 11 \rightarrow 1, 22 \rightarrow 2; 33 \rightarrow 3; 23 \) and \( 32 \) \( \rightarrow 4; 13 \) and \( 31 \) \( \rightarrow 5; 12 \) and \( 21 \) \( \rightarrow 6 \)), the elastic stiffness tensor can be represented by a 6 by 6 matrix. This representation is useful for calculations, but one has always to bear in mind that the matrix elements do not transform like elements of a second rank tensor. For non-isotropic cubic systems, to which all materials analyzed throughout this work belong to, the tensor consists of the three independent elastic stiffness constants \( C_{11}, C_{12} \), and \( C_{44} \). If the coordinate frame is oriented along the three equivalent cubic symmetry directions \( \{100\} \), the elastic stiffness tensor in *Voigt’s representation* is
The elastic stiffness constants $C_{ij}$ are measured in the SI-unit Pascal (Pa) (typical elastic constants are in the range of GPa).

An often used value is the Poisson ratio $\nu$, which along [001] in a cubic system is defined as

$$\nu = \frac{C_{12}}{C_{11} + C_{12}}.$$  \hspace{1cm} (A.4)

It tells how a volume changes under uniaxial pressure, i.e. it is the ratio of lateral contraction and longitudinal extension. A Poisson ratio of $\nu = 0.5$ means that no volume changes occur under uniaxial pressure.
B: Strain evaluation

For a strained film on a substrate, the crystal axis differs by a small angle $\Delta \vartheta$ as can be seen in figure B.1 below (except the surface normal direction). With RBS angular scan measurements through a channeling direction, the absolute angles $\vartheta_s$ and $\vartheta_f$ for the substrate and film, respectively, can be determined. In the figure the situation for a cubic system under biaxial expansion (e.g. $\text{CoSi}_2 \{a_t = 5.36 \text{Å}\}$ on $\text{Si} \{a_s = 5.43 \text{Å}\}$) is shown. The film, grown coherently on the substrate, therefore shrinks in the direction perpendicular to the surface due to the Poisson effect$^1)$. The angular distortion $\Delta \vartheta$, which can be measured directly with RBS, is connected with the tetragonal/trigonal strain $\epsilon_t$ in the following way.

The lattice constants of the film are strained according to

$$ a_{\parallel} = (1 + \epsilon_{xx}) a_f \tag{B.1} $$

$$ a_{\perp} = (1 + \epsilon_{zz}) a_f \tag{B.2} $$

The angles $\vartheta_s$ and $\vartheta_f$ are then

$$ \tan(\vartheta_s) = \frac{x a_{0s}}{a_{0s}} = x \tag{B.3} $$

$$ \tan(\vartheta_f) = \frac{x a_{\parallel}}{a_{\perp}} = \frac{a_{\parallel}}{a_{\perp}} \tan(\vartheta_s) \tag{B.4} $$

Since $\vartheta_s + \Delta \vartheta = \vartheta_f$ and $\Delta \vartheta$ is small one can apply the Taylor approximation

$$ \tan(\vartheta + \Delta \vartheta) = \tan(\vartheta) + \frac{\Delta \vartheta}{\cos^2(\vartheta)} \tag{B.5} $$

$$ \tan(\vartheta_s) + \frac{\Delta \vartheta}{\cos^2(\vartheta_s)} = \frac{a_{\parallel}}{a_{\perp}} \tan(\vartheta_s) \tag{B.6} $$

And finally with $2 \sin \vartheta \cos \vartheta = \sin 2\vartheta$ and the approximation

$$ \epsilon_t = \frac{a_{\parallel} - a_{\perp}}{a_f} \approx \frac{a_{\parallel} - a_{\perp}}{a_{\perp}}, \tag{B.7} $$

it follows that

$$ \Delta \vartheta = \frac{1}{2} \left( \frac{a_{\parallel}}{a_{\perp}} - 1 \right) \sin(2 \vartheta_s) \approx \frac{1}{2} \epsilon_t \sin(2 \vartheta_s). \tag{B.8} $$

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$^1) \text{S. Hashimoto, Y. - Q. Feng, W. M. Gibson, L. J. Schowalter, and B. D. Hunt, } \text{Nucl. Instrum. Methods} \text{ B 13, 45 (1986).}$
C: Critical thickness (model by Matthews\textsuperscript{1})

In the model of Matthews the energy of a grid of misfit dislocations $E_d$ and the energy associated with elastic strain are minimized. The energy $E_d$ per unit area of a dislocation is

$$E_d = \frac{G_0 G_s}{G_0 + G_s} \frac{(\eta - \varepsilon)b}{\pi (1 - \nu)} \left( \ln \frac{R}{b} + 1 \right),$$  \hspace{1cm} (C.1)

where $h$ is the lattice misfit, $b$ is the magnitude of the dislocation Burgers vector, $R$ is the radius about the dislocation where the strain field terminates and $G_0$ and $G_s$ are the shear moduli of the film and the substrate, respectively. The energy $E_e$ per unit area associated with elastic strain $\varepsilon$ and film thickness $h$ is approximated by

$$E_e = \frac{2 G_0 (1 + \nu)}{1 - \nu} h \varepsilon^2.$$  \hspace{1cm} (C.2)

Strain energy increases linearly with film thickness in contrast to the dislocation energy. Therefore, at some thickness $h$, dislocations are favored. Minimizing the energy $E_d + E_e$ with respect to $\varepsilon$ and setting $R = h$, which is valid for $h$ less than half the separation of adjacent dislocations $S$, yields the strain

$$\varepsilon = \frac{G_s b}{4\pi (G_0 + G_s) (1 + \nu) h} \left( \ln \frac{h}{b} + 1 \right).$$  \hspace{1cm} (C.3)

The largest possible strain value $\varepsilon$ is equal to the misfit $\eta$. If the strain $\varepsilon$ predicted by eq. (C.3) is equal to or larger than $\eta$, the film will strain to match the substrate exactly, in which case $\varepsilon$ will equal $\eta$ and $E_d$ will be zero. Thus the critical thickness $h_c$ is

$$h_c = \frac{G_s b}{4\pi (G_0 + G_s) (1 + \nu) \eta} \left( \ln \frac{h_c}{b} + 1 \right).$$  \hspace{1cm} (C.4)

Equations (C.4) and (C.3) are exact for isotropic solids and for cubic crystals if the orientation is either $\{001\}$, $\{111\}$ or $\{011\}$. However, nature is kinder to us than the Matthews theory suggests, and considerably thicker films than $h_c$ predicted by eq. (C.4) can be grown in practice. This is because his theory is an equilibrium theory and in practice films are grown far away from thermodynamical equilibrium. Ball and van der Merwe\textsuperscript{2} derived alternative expressions for $E_d$ and $\varepsilon$. However, their equations are only more accurate than Matthews theory for $S < 2h$. Since this was not the case in my films, only Matthews's theory was employed.

\textsuperscript{2} C. A. B. Ball and J. H. van der Merwe in \textsuperscript{1} Chap. 27.
The forward current - voltage (I-V) characteristics of an ideal Schottky diode obeying the thermionic emission model are given by

\[ I = I_s \left[ \exp \left( \frac{eV_D}{kT} \right) - 1 \right], \quad (D.1) \]

where \( e \) is the electronic charge, \( V_D \) the voltage applied across the diode, \( k \) the Boltzmann constant and \( T \) the temperature. Practical Schottky diodes show deviations from the thermionic emission behaviour due to image force lowering or interface states. They can more closely be described by

\[ I = I_s \left[ \exp \left( \frac{eV_D}{n kT} \right) - 1 \right]. \quad (D.2) \]

The included factor \( n \) in the exponential is the ideality factor indicating the fraction of forward current caused by barrier emission compared to other mechanisms such as tunneling, recombination in the space charge region or some other mechanism. Additionally the effect of the diode series resistance \( R \), which stems from the substrate, is usually modeled as a series of a diode and a resistor with resistance \( R \) through which the current \( I \) flows. The voltage drop \( V_D \) across the diode is therefore lowered through the introduced resistance. Thus with \( V_D = V - IR \) and for \( V_D > 3 kT/e \), eq. (D.2) is approximated to

\[ I = I_s \left[ \exp \left( \frac{e(V - IR)}{n kT} \right) - 1 \right], \quad (D.3) \]

where the saturation current \( I_s \) is

\[ I_s = A A^{**} T^2 \exp \left( -\frac{e\Phi}{kT} \right). \quad (D.4) \]

\( A \) is the effective area of the diode, \( A^{**} \) is the Richardson constant and \( \Phi \) is the Schottky barrier height (\( A^{**} = 120 \text{ A cm}^{-2} \text{ K}^{-2} \) for a free electron gas\(^2\)) and \( A^{**} = 112 \text{ A cm}^{-2} \text{ K}^{-2} \) for n-Si\(^3\)).

A method to extract the series resistance \( R \) of ideal Schottky diodes (i.e., \( n = 1 \)) was first proposed by Norde\(^4\) and had been modified by Sato and Yasumura\(^5\) for the case (1 < \( n < 2 \)).

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In their paper Cheung have given a method for the extraction of the three key diode parameters \((n, R, \Phi)\) from one forward current - voltage characteristic, which is summarized below.

Rewriting of equation (D.3) in terms of current density \(J = I / A\) and \(\beta = e / k T\) leads to

\[
V = R A J + n \Phi + \frac{n}{\beta} \ln \left( \frac{J}{A^{**} \ T^2} \right) \tag{D.5}
\]

Differentiating (D.5) with respect to \(\ln(J)\) and rearranging terms one obtains

\[
\frac{dV}{d(\ln J)} = R A J + \frac{n}{\beta}. \tag{D.6}
\]

With a plot of \(dV/d(\ln J)\) vs. \(J\) one gets the resistance \(R\) from the slope and the ideality factor \(n\) from the intercept with the \(y\) - axis. To evaluate the Schottky barrier one has to define the function

\[
H(J) = V - \frac{n}{\beta} \ln \left( \frac{J}{A^{**} \ T^2} \right), \tag{D.7}
\]

which together with formula (D.5) can be written as

\[
H(J) = R A J + n \Phi \tag{D.8}
\]

Using the \(n\) value determined from equation (D.6), the intersection with the \(y\) - axis of a plot of \(H(J)\) vs. \(J\) yields the value for the Schottky barrier height \(\Phi\), while from the slope a second determination of the resistance \(R\) is obtained. However, when in a semi - logarithmic plot of current vs. voltage the linear range is small, it is advantageous to use the more sophisticated model of Werner (see Appendix E).
E: Schottky diode analysis II (Werner method)\(^1\)

J. H. Werner proposed a model of a real Schottky Diode, where, additional to the ideality factor \(n\) and the substrate series resistance \(R_s\), a shunt resistance \(R_p\) is introduced. An ideal Schottky diode should have a bias-independent reverse current, which in nature is hardly observed even when mesa structures are etched. For small forward bias the measured \(I-V\) is then also influenced by shunt currents.

![Equivalent circuit of a real Schottky diode as proposed by Werner, with a shunt resistance \(R_p\) and a series resistance \(R_s\). Further an ideality factor \(n\) is used to describe the current-voltage dependence.](image)

With this model the current-voltage equation (D.3) has to be transformed to

\[
I = I_D + I_P = I_S \left( \exp \left( \frac{e(V - IR_s)}{n k T} \right) - 1 \right) + \frac{1}{R_P} (V - IR_S).
\]  
(E.1)

Here \(I_D\) is the diode current and \(I_P\) describes the shunt current through a possible parallel resistance \(R_p\). In this model it is assumed, that the saturation current \(I_S\), the shunt and series resistance \(R_p\) and \(R_s\) and also the ideality factor \(n\) are independent of the bias \(V\). From the reverse bias characteristics for large negative bias, the shunt resistance can be derived. The current \(I_D\) through the diode can then be corrected for the shunt current as

\[
I_D = I - \frac{V}{R_P}.
\]  
(E.2)

Then for forward bias \(V_D = V - IR_S \gg 3 k T/e\) the thermionic diode current \(I_D\) is given by

\[
I_D = I_S \exp \left( \frac{e(V - IR_S)}{n k T} \right).
\]  
(E.3)

When introducing the conductance $G = dI_D/dV$, which can either be measured or calculated\(^1\), Werner proposes the following three different equations.

A) \[
\frac{G}{I_D} = \frac{e}{n k T} (1 - G R_S)
\]  
(E.4)

B) \[
\frac{1}{G} = \frac{n k T}{e I_D} + R_S
\]  
(E.5)

C) \[
\frac{dV}{d(ln I_D)} = R_S I_d + \frac{n k T}{e}
\]  
(E.6)

Equation C) (E.6) is equivalent to the Cheung formula (D.6). From each equation the series resistance $R_S$ and the ideality factor $n$ can be extracted. With the voltage, corrected for the series resistance, the saturation current and therefrom the Schottky barrier $\Phi$ can then be determined. One can compare the three results in order to test the accuracy and selfconsistency of the evaluation. In his paper, Werner concludes that equation A) (E.4) yields the most reliable and accurate values for the Schottky barrier $\Phi$, the ideality $n$ and the series resistance $R_S$.

\(^1\) The numerical determination of $G$ from the $I - V$ curve requires dc voltage steps typically of less than 1 mV in order to get the real slope of the curve.
Publications

*Structural and electrical investigation of an epitaxial metallic FeSi2-phase on Si(111)*
N. Onda, J. Henz, E. Müller, H. von Känel, C. Schwarz, R. E. Pixley

*Surface study of thin epitaxial CoSi2/Si(100) layers by scanning tunneling microscopy and reflection high energy electron diffraction*
R. Stalder, C. Schwarz, H. Sirringhaus, and H. von Känel

*Surface structures of strained epitaxial CoSi2/Si(100) layers studied by scanning tunneling microscopy*
R. Stalder, C. Schwarz, H. Sirringhaus and H. von Känel

*Surface structure of ultrathin, epitaxial CoSi2 films on Si(100) observed by scanning tunneling microscopy*
H. Sirringhaus, R. Stalder, C. Schwarz and H. von Känel

*Application of epitaxial CoSi2/Si/CoSi2 heterostructures to tuneable Schottky-barrier detectors*
C. Schwarz, U. Schärer, P. Sutter, R. Stalder, N. Onda and H. von Känel

*Epitaxial phase transitions in the iron/silicon system*
Observation and characterization of the pseudomorphic to stable phase transformation of Fe$_{1-x}$Si on Si(111)

Epitaxy of cubic iron silicides on Si(111)

Phase transitions in epitaxial silicides
C. Schwarz, S. Goncalves - Conto, E. Müller - Gubler, H. Sirringhaus and H. von Känel

Characterization of CoSi$_2$/Si/CoSi$_2$ heterostructures on Si(111) by scanning tunneling microscopy
H. Sirringhaus, C. Schwarz and H. von Känel

Epitaxial semiconducting and metallic iron silicides

Elastic and vibrational properties of pseudomorphic FeSi films
Magnetron sputter epitaxy of $Si_{1-n}Ge_n$/$Si(001)$ strained - layer superlattices
P. Sutter, C. Schwarz, E. Müller, V. Zelezny, S. Goncalves - Conto and H. von Känel

Ion channeling studies of epitaxial Fe and Co silicides on Si
C. Schwarz, N. Onda, S. Goncalves - Conto, H. Sirringhaus, H. von Känel and R. E. Pixley

New epitaxially stabilized CoSi phase with the CsCl - structure
H. von Känel, C. Schwarz, E. Müller, L. Miglio, F. Tavazza and G. Malegori
Oral presentations

*Growth and characterization of thin epitaxial CoSi₂ layers on Si(100)*
contributed talk presented at the fall meeting of the Swiss Physical Society in Chur, 
October 10 - 11, 1991

*Growth of β-FeSi₂/Si(001) by molecular beam epitaxy*
contributed talk presented at the 7th Euro-MBE, Bardonecchia, Italy, March 7 - 10, 1993

*Pseudomorphic growth of transition metal monosilicides on Si(111)*
contributed talk presented at the spring meeting of the Swiss Physical Society in Neuchâtel, 
March 24 - 26, 1993

*Strain measurements on epitaxial silicides*
contributed talk presented at the spring meeting of the Swiss Physical Society in Bern, 
March 17 - 18, 1994

*Application of silicide - silicon heterostructures to a tunable IR-detector*
contributed talk presented at the spring meeting of the Swiss Physical Society in Bern, 
March 23 - 24, 1995

Poster presentation

*Application of epitaxial CoSi₂/Si/CoSi₂ heterostructures to tuneable Schottky - barrier detectors*
presented at the VII-MBE Conference, Schwäbisch Gmünd, Germany, August 24 - 28, 1992
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languages German, French, English
DANK

An dieser Stelle möchte ich Prof. Dr. Peter Wachter herzlichst danken, dass er mich als Diplomand und später als Assistent in seine Forschungsgruppe aufgenommen hat. Somit wurde meine Forschungsarbeit sowie diese Arbeit überhaupt ermöglicht.


Herrn Prof. Dr. I. Eisele von der Universität der Bundeswehr in München danke ich für die spontane Übernahme des Korreferats.

Die Arbeit an der MBE Maschine zusammen mit Dr. R. Stalder, Dr. N. Onda, Dr. U. Kafader, Dr. E. Y. Lee und H. Sirringhaus war sehr interessant und äußerst abwechslungsreich. Ein grosser Dank geht an die STM - Spezialisten Roli und Henning, die immer sofort bereit waren ihre STM - Spitze über meine Schichten zu scanren um aufschlussreiche Bilder meiner Schichten zu liefern. Nico, der mich bereits während meiner Diplomarbeit in die Geheimnisse der elektrischen Charakterisierung dünner Filme einführte, möchte ich ganz speziell danken.

Für die aufwendigen Röntgenuntersuchungen, vor allem an der neuen CoSi - Phase, möchte ich ganz speziell unserer Französin Sylvie Goncalves - Conto danken.

Ebenso bedanke ich mich für die zahlreichen TEM und SEM Untersuchungen bei Dr. E. Müller - Gubler, H. - R. Deller und P. Wägli.

Dr. André Weber und Peter Suter vergoldeten meine Strukturen jeweils mit ihren Sputter - Apparaturen. Für die vielen guten Kontakte und Dioden möchte ich auch Ihnen von Herzen danken.

Peter Steiner hat mit seinen Messprogrammen und der überaus grosszügigen zur Verfügungstellung seines Kryostaten einen wesentlichen Beitrag zu dieser Arbeit geliefert. Die besonders angenehme Atmosphäre im Labor F5 wird mir noch lange in Erinnerung bleiben.

Ein Dank gebührt auch Urs Schärer, der im Rahmen seiner Diplomarbeit die ersten systematischen Messungen an symmetrischen TIPS gemacht hatte.
Unserem Techniker H. - J. Gübeli, der die Apparaturen immer im Schuss hielt, gebührt ebenfalls mein Dank.


Ein grosser Dank geht an Prof. Dr. H. Melchior, der mir die Infrastruktur seines Instituts für die Herstellung und der teilweisen elektrischen Charakterisierung von TIPS - Strukturen zur Verfügung stellte, sowie seinen Mitarbeitern, welche mich in die entsprechenden Prozesse einführten.

Diese Arbeit wurde dank der finanziellen Unterstützung von der FSRM (Fondation Suisse pour la recherche en microtéchnique) ermöglicht. Für die dabei verknüpfte Zusammenarbeit mit Dr. Y. Oppliger vom CSEM (Centre Suisse d'électronique et micromécanique) möchte ich mich ebenfalls bedanken.

Allen hier nicht namentlich erwähnten Personen und speziell den Mitarbeitern der Gruppe von Prof. Dr. P. Wächter möchte ich mich für die angenehme Zusammenarbeit danken.

Zuletzt geht mein Dank an meine Eltern, die mich auf meinem Werdegang moralisch und vor allem mein Studium finanziell unterstützen.


März 1995