High-Resolution Studies of Silicide-films for Nano IC-Components

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Abstract

The function of titanium- and nickel-silicides is to lower the series resistance and contact resistivity in gate, source and drain contacts of an integrated circuit transistor. With decreasing dimensions, the low resistivity C54 TiSi2 is not formed and stays in its high resistivity phase C49. It was found that a layer of niobium interposed between titanium and silicon, which is supposed to promote the C54 phase, led to the formation of the high resistivity C40 (Ti, Nb)Si in both small and large contacts.

Increased interest in Si1-xGe_x layers led to the inclusion of the Ni-Si-Ge system in this project. The interaction between nickel and poly-Si1-xGe_x was found to be different from nickel and poly-silicon in the meaning of the phases formed during high temperature annealing. High-resistivity NiSi2 was formed at 750°C, but nickel and Si1-xGe_x formed no disilicide. A massive out-diffusion of germanium from the NiSi2 Ge_x resulted in agglomeration at lower temperatures than for NiSi. This was ascribed to the larger enthalpy of formation for nickel reacting with silicon than with germanium. Ternary phase diagrams, with and without the disilicide phase, were calculated. According to the tie lines, NiSi2 Ge_x will be in thermodynamic equilibrium with Si1-xGe_x when u is smaller than x. This was confirmed experimentally, where a balanced germanium concentration in NiSi2 Ge_x and Si1-xGe_x stabilized the germanosilicide. When nickel interacted with strained and relaxed silicon-germanium it was established that a strained substrate led to a morphologically unstable NiSi2 Ge_x. The germanosilicide was highly textured on both (001) and (111) substrates. The texturing was explained by the absence of Ni(SiGe)2, which forced NiSiGe to reorient so as not to resemble a digermanosilicide at the film/substrate interface. NiSi2 Ge_x,18 formed on p-Si1,18Ge_x,18 in CBKs grew laterally under the SiO2, defining the contact hole. The contact resistivity extracted by 3D modelling was 5×10−6 Ωcm².

Keywords: thin films, titaniumsilicide, nickel-germanosilicide, ternary phase diagram, textured germanosilicide, high resolution materials analysis

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The author’s contributions

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"Av de angivna legeringarna med silicider hava de med nickelsilicid de ojämförligt bästa mekaniska egenskaperna. Dessa senare ställa sig därtill fördelaktigast ur framställningssynpunkt. Legeringarna med kromsilicid åter hava utom goda mekaniska egenskaper det lägsta elektriska ledningsmotståndet. Största tekniska betydelsen ha därför dessa legerings-system med nickel- resp. kromsilicid."

V. Christiansen, Teknisk tidskrift 1931
1. Introduction

In 1961 the integrated circuit was born; four years later Gordon Moore predicted its future development. At that time, a chip consisted of 30 transistors and Moore anticipated that the transistor density per chip would double each year into the next decade [1]. The transistor is the most significant of all semiconductor components and is the building block in all modern electronics. A typical example is the microprocessor for today’s PCs, which includes more than a billion transistors. To understand how small some parts must be in order to fit so many transistors in one chip we can relate the size to a human hair, which is about 100µm thick. The most recent transistors have features less than 1/1000 of this and are continually shrinking. The most widely used is the Metal Oxide Semiconductor Field Effect Transistor (MOSFET), Fig. 1, which is a three-terminal structure with an input (source), output (drain) and a control terminal (gate) [2]. The active part of such a transistor is the channel below the gate where the current flows from source to drain. The gate has the role of controlling the current-flow. In order to make the current flow more easily through the whole structure low series resistance is desirable. To build the rest of the component a range of different materials must be deposited until a chip is built up with a metal wiring to the transistor. The current will flow from the surface electrode and through the wiring down into the transistor. To enter the transistor the electrons pass a metal contact, which usually consists of Al/TiW and through a silicide layer, indicated in Fig.1 by NiSi(Ge), into the underlying silicon. That is where this thesis comes in. The silicide decreases the series resistance in the source/drain region and the contact resistivity of the gate electrode [3].

Figure 1. A cross-section of a MOSFET
The contact resistivity is in fact one of the greatest obstacles for continued downscaling, where digital circuit development proceeds towards smaller dimensions by following the 2004 International Technology Roadmap for Semiconductors (ITRS) [4].

This thesis deals with the formation of low resistivity silicides intended for the next generation of transistors, where the semiconductor performance is pushed even further by the use of strained epitaxial Si, epitaxial- and poly-
Si$_{1-x}$Ge$_x$ layers. It is a thesis, which by in-depth materials studies of the silicides, promotes a way for others to implement these basic material results into integrated circuits of the future. It is organized as follows; in chapter 2, the background of silicides is overviewed. Chapter 3 presents characterization tools and how the silicides are evaluated with respect to phase formation, electrical properties, degradation and texturing. The fourth chapter begins with a short TiSi$_2$ introduction and the effect of an interposed niobium layer on silicide formation. It mainly deals with the formation and thermodynamical stability of the ternary Ni-Si-Ge system, as well as the morphological stability with respect to substrate properties. This is followed by a study of the NiSi$_{1-x}$Ge$_x$ preferential orientation induced by germanium on single-crystalline substrates and ends with the integration of NiSi$_{82}$Ge$_{18}$ into Cross-Bridge Kelvin (CBK) contact structures. Conclusions together with future recommendations are given in chapter 5.
2. Silicide background

Silicides were introduced as early as the 1960s for ohmic and rectifying contacts to silicon and later to reduce the series resistance in poly-silicon lines. The first depositing techniques were based on direct deposition of the silicide onto the poly-silicon. The methods used were (a) sputtering from a composite target, (b) chemical vapor deposition, (c) co-evaporation of metal and silicon and (d) sputtering from one metal and one silicon target simultaneously. These techniques are used in the so-called POLYCIDE process where the silicide is deposited on a sheet of poly-silicon and afterwards, the lithography step together with etching form the structure needed. However, the silicide will only be present in the gate while the source and drain will still consist of silicon and have a higher series resistance. Today most silicides are formed by the self-aligned process (SALICIDE), where metal is evaporated or sputtered on silicon at the pre-formed gate, source and drain regions (MOSFET) followed by a thermal anneal to form the silicide. The most common silicides used in microelectronics are MoSi$_2$, WSi$_2$, TiSi$_2$, CoSi$_2$ and NiSi [5,6]. The three latter, with lower resistivity, are the most important today and are formed with the SALICIDE process [2,3,7].

The most commonly used since the 1980s is TiSi$_2$ with the crystallographic notation C54. It is the thermodynamically stable phase with an orthorhombic structure and low resistivity of 13-20 $\mu\Omega$cm [7]. A preceding metastable phase exists, which also has TiSi$_2$ composition but considerably higher resistivity between 60-80 $\mu\Omega$cm. It is called the C49 phase [8]. The high resistivity phase has been found to be stable in restricted geometries as the C49-C54 transition at 850°C is hindered [9,10,Paper I]. There are, however, ways around this problem. One of them is to alloy titanium with a refractory metal (rm) Nb, Ta, Mo or W or implant the rm into the silicon [11,12]. An alternative is to introduce a thin rm layer between titanium and silicon before thermal annealing. The rm-silicide will promote the C54 formation by a template effect. Niobium, for example, will lead to the formation of a template phase called C40 (hexagonal) NbSi$_2$ or (Ti,Nb)Si$_2$ [13]. The (001) of C40 (Ti,Nb)Si$_2$ is very similar to the (001) of C54 TiSi$_2$, consequently the latter grows with the former as a template phase. Another method to enhance the C54 formation is to pre-amorphize the silicon prior to titanium deposition [14]. The mechanism behind the increased amount of C54 is likely to be because the C49 grain size will be reduced and conse-
quent the number of C49 triple grain boundaries where C54 nucleates will increase [15].

The successors of TiSi2 are CoSi2 and NiSi, of which the first is widely used and the second is still in its development stage or in early production [16,17,18]. Cobalt disilicide forms at 700°C via a mixed nucleation-diffusion process, compared to the C54 TiSi2 formation, which is nucleation controlled. The small geometry problem seems less for CoSi2 than for TiSi2. It has been reported that the sheet resistance increases for gate lengths below 40 nm for CoSi2 while NiSi keeps its low resistance, at least down to 30 nm [19]. The main advantages of NiSi are low resistivity, low formation temperature, low silicon consumption and that the low resistivity phase formation is possible also with Si1-xGex. Nickel monosilicide formation takes place at 450-500°C when rapid thermal annealing for 30s is employed [Paper III]. The NiSi is the desired low resistivity phase (ρ = 11-15 μΩcm), but is not thermodynamically stable. At temperatures around 750°C the stable NiSi2 forms with a resistivity of 30-45 μΩcm [Paper II]. Agglomeration of NiSi at temperatures as low as 550-600°C is another problem; the film has to be continuous in order to obtain low sheet resistance. By adding platinum to nickel or by implanting BF2, it is possible to reduce the degradation and extend the temperature window for NiSi [20,21].

The introduction of poly-crystalline, or strained as well as relaxed epitaxial Si1-xGex layers in MOSFETs leads to several new challenges depending on the metal used. The desired low resistivity phase forms at a lower temperature when titanium reacts with Si1-xGex than when it reacts with silicon. Titanium and germanium do not form the C49 phase; instead, C54 forms directly, which is a great advantage. This is also true for germanosilicides formed from Si1-xGex, at least down to 20 at. % germanium [22]. The disadvantage is that the thermodynamic equilibrium dictates that germanium will out-diffuse from Ti(Si1-xGex)2 on Si1-xGex to form openings of Si1-yGey, where y is greater than x [23,24]. The consequence is that the sheet resistance increases in the discontinuous Ti(Si1-xGex)2, where u is less than x. When Co reacts with Si0.8Ge0.2 the formation temperature increases by about 200°C compared to when Co reacts with silicon [25]. This effect could be a reason for not choosing Co as the metal because a high annealing temperature can introduce defects in a strained Si1-xGex layer. Nickel-germanosilicide is a very promising candidate for the future. It has a similar formation temperature as NiSi and the Ni(Si1-xGex)2 formation is suppressed [Paper II, III, 16,17]. Germanium out-diffusion is however, extensive at high temperatures, which will lead to a discontinuous film. There are ways to stabilize the germanosilicide either by alloying nickel with platinum or by utilizing the fact that the NiSi1-xGex must be in thermodynamic equilibrium to the underlying Si1-xGez to prevent germanium out-diffusion [20, Paper III].
3. Materials characterization

3.1 Introduction to characterization

To study the silicide formation between a metal and silicon over large areas or in components, there is a range of different techniques of which some have been used. Usually, the first thing to study is the phase formation at different annealing temperatures. The reaction is monitored by four-point probe sheet-resistance measurements combined with X-ray diffraction (XRD). For components, contact resistance can be measured in cross-bridge Kelvin structures and sheet resistance in van der Pauw structures [28]. To study the phase formation in components as well as in thin films, transmission electron microscopy (TEM) and electron diffraction (ED) techniques are needed. TEM in combination with energy dispersive X-ray spectroscopy (EDX or EDS) are used for morphological and compositional studies of both thin films and components. There is also the possibility of using scanning electron microscopy (SEM) but it has lower lateral resolution than the TEM and is therefore not suitable for elemental or phase analysis of cross section samples with very thin, 25-80 nm, silicide films. Further, XRD pole figures were employed to resolve silicide texture on different substrates.

3.2 Electrical characterization

3.2.1 Sheet resistance

The sheet resistance measurement can be used to roughly characterize thin film properties like morphology or phase formation. The different phases are related to a specific resistivity, $\rho$ (\(\Omega\)\text{-cm}), which will effect the sheet resistance. A continuous film of a certain phase have a well defined sheet resistance value, while an agglomerated structure of the same phase have a much larger resistance. Sheet resistance has the unit $\Omega$/square. A common sheet resistance measurement is made with the four-point probe technique, in which four identical probes are arranged collinear at identical spacings, as shown in Fig. 2. This technique has been used in most of the papers to monitor the silicidation.
Figure 2. Schematic sketch of a collinear four-point probe. A current (I) is carried through the two outer probes 1 and 4 and the voltage drop (U) is measured over the two inner poles, 2 and 3.

The resistance is calculated from the relation between U, R and I where all series, contact and spreading resistances are neglected. To calculate the resistivity a correction factor is needed to correct for the probe location near edges, sample thickness, sample size and temperature [28]. The expression for calculating $\rho$ is shown in Eq. 3.1 where $t$ represents the thickness of the formed silicide. The correction factor used in the equation is valid for samples of infinite lateral size.

$$\rho = \frac{\pi}{\ln(2)} \frac{U}{I} t$$  \hspace{1cm} (3.1)

3.2.2 Contact resistance

Contact resistance measurements are crucial to characterize the specific contact resistivity in geometrically restricted components. In these experiments, the so-called cross-bridge Kelvin (CBK) structure was relied on for the contact resistivity, $\rho_c$, measurements [29]. The process of making the CBK is described in Ref. 30. A simple 1D analysis gives $\rho_c$ by measuring the contact resistance ($R_c$) which is multiplied by the nominal contact area (A). The $R_c$ is acquired from so-called I-V plots where the current (I) is drawn between pad 1 and 3 and the voltage drop (V) is measured between pad 2 and 4 in Fig. 3. The overlap between the leads that is always present around a contact hole due to processing errors is seen in Fig. 3. The assumption from the 1D model is that all current flows through the front edge of the contact hole. At high current densities, the overlap makes it possible for the current to find its way around
the front edge of the contact-hole and enter the contact from the sides. The phenomenon is called current crowding. With a log \( R_c \) vs. log \( A \) curve the current crowding effect will be present as a curve bending for smaller contact areas. In the ideal case, the curve is a straight line of slope -1.

![Figure 3. The four-terminal CBK structure used for \( \rho_c \) measurements. The conductor drawn with a broken line is made of highly doped poly-Si(Ge) and the other conductor drawn with a continuous line is Al/TiW. The intersection with the shaded area consists of silicide.](image)

Two-dimensional or even 3D modeling takes care of the current crowding by considering the overlap in relation to the contact width [31]. The 3D model has no restrictions in topology whereas the 2D model is simplified by considering the silicide thickness as constant.

### 3.3 X-ray diffraction

X-rays have a short wavelength in the range of atomic spacings due to a high energy. When such X-rays interact with atoms in a crystalline sample they will be scattered. Bragg’s law describes the scattering, see Eq. 3.2. It includes the incident wavelength \( \lambda \), the order of the reflection \( n \), the atomic plane spacing \( d \) and the scattering angle \( \theta \).

\[
n \lambda = 2d \sin \theta \quad (3.2)
\]

The material that is used to generate X-rays sets the wavelength of \( \lambda \). Copper is frequently used where \( \lambda_{\text{average}} = 1.5418 \) Å. The standard XRD application is crystal phase determination in the \( \theta-2\theta \) geometry. Materials that are textured are best characterized by XRD pole figure measurements. This set-up also utilizes the \( \theta-2\theta \) geometry and by the sample tilt and rotation, it
is possible to find diffracting planes that are not parallel to the sample surface [32].

3.3.1 θ–2θ phase and composition determination

The θ–2θ-coupled geometry is described by that the incident and reflection angles are maintained equal to one another during the measurement, so that a 2θ movement of the detector accompanies a θ tilt of the sample. By measuring intensity and specific peak positions given in 2θ or d and comparing these to tabulated reference values, it is possible to identify the phases present in the sample. XRD is also a tool for texture analysis, of preferentially oriented grains, as well as compositional analysis of compounds that follow Vegard’s law, [33, 34].

3.3.2 XRD pole figure

Textured or epitaxial silicides are commonly formed on single-crystalline substrates of different orientations. With regular θ–2θ XRD measurements it is possible to determine how a film is textured by comparing intensities of identified peaks to tabulated reference intensities. A larger relative intensity than the tabulated value indicates that a large number of these planes are parallel to the surface. In Papers V and VI, θ–2θ were not sufficient in order to explain the texture found in the NiSi0.8Ge0.2 film formed on both (001) and (111) substrates. By using the XRD pole-figure set-up it was possible to resolve the, in some cases very complicated, orientation of these silicides. The advantages of these measurements are; the extra degrees of freedom compared to θ–2θ make it possible to determine the texture types in a sample, only minor sample preparation has to be done and by using parallel-beam optics a very large sample volume can be analyzed, which improves statistics [32]. The Philips X’pert system with CuKα (average wavelength 1.5418 Å) radiation is set-up for pole figure measurements by using point focus on the primary side (incident) and an X-ray lens that creates a semi-parallel beam, which can be adjusted by slits. The secondary (diffracted) side consists of a parallel plate collimator with 0.27 mm spacing, an analyzing crystal (NiC) and the X-ray detector. The main advantage of this system is the high X-ray intensity that gives faster scans.
In Fig. 4 the pole figure geometry is defined. The angles given are essential for understanding the acquisition. The θ–20 angles set the geometry of the type of XRD technique used. Sample rotation and tilt angles are given by φ and χ, respectively. Measurements on a thin film are made with a fixed 20 angle chosen from a strong film peak separated from both other film peaks, as well as substrate peaks that can be very strong and thereby damage the detector. A film peak that is slightly separated, from a substrate peak, in 2θ is generally beneficial when it comes to determining film vs. substrate orientation in the same measurement [Papers V, VI].

3.4 Electron microscopy

In all investigations, TEM and Scanning TEM (STEM) were invaluable tools for studying the microstructure of the materials. Primarily imaging, diffraction and energy dispersive spectroscopy were utilized to determine silicide morphology, orientation, phase and compositional variations. Scanning electron microscopy (SEM) was used to inspect surface topography and contact structures from a top view. By combining STEM and EDS, imaging and elemental analysis were performed at nanometer resolution [35].

3.4.1 Imaging and electron diffraction in the TEM

A TEM can be used for imaging when high spatial resolution is needed and for detecting other signals generated by the interaction between an electron...
beam and a sample. As an electron travels through a thin specimen, there is
the probability that the electron will interact with the material. The nonuni-
form distribution of electrons that pass the sample contains both crystallo-
graphic and chemical information, Fig.5. Elastic scattering, with no loss of
energy, is in the forward direction called diffraction. The scattering is differ-
ent from that of X-rays, which are scattered by an interaction between the
electromagnetic field of the incoming X-ray and the negatively charged elec-
trons. In the sample, incoming electrons are scattered by both the electrons
and the nucleus of the atoms. By electron diffraction, it is possible to get
crystallographic information about lattice spacings, crystal symmetry, crystal
orientation etc, which makes phase identification possible. Electron diffrac-
tion follows Bragg’s law shown in Eq. 3.2.

Figure 5. Signals generated from the electron interaction with a TEM specimen.

TEM is usually performed with an incoming parallel beam on the sample.
The beam is formed by the magnetic lenses and the image is recorded on
either negative film or by a CCD-camera. The magnification is set by the
lens system. With an objective aperture inserted in the back focal plane the
direct or diffracted beam can be enabled for imaging. The former technique
is called bright field, the latter dark field. There are two major diffraction
techniques in TEM; selected area electron diffraction (SAD) and convergent
beam electron diffraction (CBED). SAD is performed with a parallel beam
and the selected area aperture. It is suitable for “large” sample areas when
several grains are analyzed at the same time. The aperture has a limited
smallest spatial size due to the spherical aberration of the objective lens. This
technique is therefore not applicable when very small grains are to be ana-
yzed. Instead, it is possible to use the CBED technique where the electron
beam is focused to a small probe with a size of 10nm or less.
High-resolution TEM (HRTEM) can be acquired by detecting the phase difference between several electrons that have been scattered in the sample lattice. This phase-contrast is enhanced by defocusing the image where only certain lattice spacings from the crystalline sample will be visible. By using the small spatial wavelength given by a field emission electron gun and high acceleration voltage, a high spatial resolution can be achieved.

3.4.2 STEM and EDS

STEM differs from TEM by using a different acquisition technique. In STEM it is based on a scanning convergent beam and separate detectors for direct or scattered beams. The magnification is set by the size of the sample area scanned by the nm-sized probe. STEM imaging can be done with so-called Z-contrast utilizing the fact that atoms with higher Z scatter to larger angles. By using the high angle annular dark field (HAADF) detector, it is possible to detect the more incoherently scattered electrons. From an image taken of a NiSi$_{0.8}$Ge$_{0.2}$-Si$_{0.8}$Ge$_{0.2}$ structure shown in Fig. 6, it is evident how the elements are distributed, while Z differs for nickel, silicon and germanium (Z$_{\text{Ni}}$=58.7, Z$_{\text{Si}}$=28.1 and Z$_{\text{Ge}}$=72.6).

Figure 6. Contrast between layers with different atomic weight are shown by Z-contrast imaging in STEM mode.

STEM combined with EDS is a powerful tool for quantifying concentration variations. The incoming electron beam will excite atoms and when they return to their ground state, by filling the core hole with an electron from an outer state, energy will be emitted. This is in the form of an Auger electron or an X-ray photon; the latter process dominates for heavier elements. The emitted photon has a specific energy that is related to the element and from which energy state it originates. By detecting the X-rays (photons) with re-
spect to their energy and count rate, it is possible to plot the number of counts vs. energy. A spectrum of energies is thus found for a compound consisting of several elements. These energy values are tabulated and each element can be identified and quantified. EDS is used in both SEM as well as in TEM. SEM/EDS generate X-rays from a volume as large as 1µm³. This is obviously too much for analyzing structures which are merely ten to a couple of hundred nm thick. By carrying out EDS analysis on a cross section TEM sample it is possible to benefit from the high lateral resolution, activating around $5 \times 10^{-7}$ µm³. By running in STEM mode, the beam is already converged to a small spot and it is therefore just to position the beam on an interesting feature and acquire the EDS spectrum. There are also software routines that make it possible to acquire elemental maps, line scans and multiple spot analyses with drift control of the specimen. In quantitative microanalysis, as we have used the EDS for, it is important to have standard specimens with known composition. A standard sample is used to establish the so-called Cliff-Lorimer factor $k_{AB}$ of a binary system of elements A and B in the Cliff-Lorimer Eq. 3.3:

$$\frac{C_A}{C_B} = k_{AB} \cdot \frac{I_A}{I_B} \quad (3.3)$$

$$C_A + C_B = 100\% \quad (3.4)$$

In these equations $C_A$ and $C_B$ represent the concentration of each element in weight percentage, Eq. 3.4, $I_A$ and $I_B$ are the integrated peak intensities from the EDS spectrum. This can easily be extended for a ternary system by including element C. The Cliff-Lorimer equation is a simplification where only the effect of $Z$, i.e. the atomic mass, is considered; absorption and fluorescence effects are neglected while the sample is considered to be thin [26]. It is important to acquire EDS data under exactly the same conditions from sample to sample as the $k$ factor will vary otherwise. The NiSi phase determined by XRD and Si$_{0.77}$Ge$_{0.23}$ determined by HRXRD were used as standard samples [32].
4. Silicide formation

4.1 Silicide properties

Binary silicides have been studied for many years and there are many reliable data. Well-established phase diagrams for Ni-Si and Ni-Ge, which are important for the calculations of the ternary Ni-Si-Ge phase diagram, are shown in Fig. 7 [36]. Nickel together with silicon forms several phases that are stable at room temperature, namely Ni$_3$Si, Ni$_{31}$Si$_{12}$, Ni$_2$Si, Ni$_3$Si$_2$, NiSi and NiSi$_2$. This is in contrast to Ni and germanium that form Ni$_3$Ge, Ni$_2$Ge, Ni$_3$Ge$_3$ and NiGe. The most important difference between the two systems is the absence of the NiGe$_2$ phase. This will have a decisive influence on the ternary Ni-Si-Ge system. Another difference is the lower melting points of the germanides, as well as that of germanium, which indicates low activation energy for reactive diffusion of nickel. The large difference in enthalpy ($\Delta H$) energies between silicide and germanide indicate a more stable formation of the former, due to a more negative value [37, Table 1]. A difference in enthalpy leads to unstable NiSi$_{1-x}$Ge$_x$ on Si$_{1-x}$Ge$_x$, while nickel reacts with silicon rather than with germanium [Papers II-VI]. Most of the corresponding silicides and germanides share the same crystal structure. The most common is the orthorhombic structure, where all three axes of the unit cell are of different length and the angle between them is 90°. They are often indexed so that the c-axis is the longest, the a-axis is next and the b-axis is shortest. All crystal data were found in Refs. 38 and 39. An important issue for micro-electronic components with a thin substrate is the silicon consumption during silicide formation. Nickel mono-silicide, which is the low resistivity phase, consumes less silicon during the formation than TiSi$_2$ and CoSi$_2$ [40]. Compared to CoSi$_2$, it consumes about 20% less silicon for the same silicide thickness. Additionally, the resistivity of NiSi is roughly 15% lower so for equal silicon consumption the sheet resistance of CoSi$_2$ becomes about 40% higher. In Table 1 some silicide and germanide crystal structures, thermodynamic and electrical properties are given.
Figure 7. Binary phase diagrams for Ni-Si and Ni-Ge
Table 1. Silicide and Germanide properties

\[ \Delta H_{\text{for}} = \text{formation enthalpy}, \ T_{\text{for}} = \text{formation temperature}, \ T_m = \text{melting temperature}, \ DDS = \text{dominant diffusing species}, \ \rho = \text{resistivity}, \ t_{\text{Sil}} = \text{formed silicide thickness}, \ t_{\text{Si}} = \text{consumed silicon thickness} \]

<table>
<thead>
<tr>
<th>Silicide</th>
<th>Cell parameters (Å)</th>
<th>Crystal structure</th>
<th>(\Delta H_{\text{for}}) (kJ/gram-atom)</th>
<th>(T_{\text{for}}) (°C)</th>
<th>(T_m) (K)</th>
<th>DDS (µΩ·cm)</th>
<th>(t_{\text{Sil}}/t_{\text{Si}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiSi(_2) (C49)</td>
<td>3.562 13.531 3.550</td>
<td>orthorhombic</td>
<td>?</td>
<td>350-700</td>
<td>Si</td>
<td>60-80</td>
<td>1.05</td>
</tr>
<tr>
<td>TiSi(_2) (C54)</td>
<td>8.252 4.783 8.540</td>
<td>orthorhombic</td>
<td>45</td>
<td>750</td>
<td>1813</td>
<td>Si</td>
<td>15-20 1.1</td>
</tr>
<tr>
<td>NbSi(_2) (C40)</td>
<td>4.797 6.592</td>
<td>hexagonal</td>
<td>46</td>
<td>650</td>
<td>2223</td>
<td>Si</td>
<td>50-60 1.08</td>
</tr>
<tr>
<td>Ni(_3)Si</td>
<td>4.99 3.72 7.06</td>
<td>orthorhombic</td>
<td>48</td>
<td>200-325</td>
<td>1580</td>
<td>Ni</td>
<td>24 1.64</td>
</tr>
<tr>
<td>NiSi</td>
<td>5.233 3.258 5.659</td>
<td>orthorhombic</td>
<td>45</td>
<td>250-400</td>
<td>1265</td>
<td>Ni</td>
<td>11-15 1.2</td>
</tr>
<tr>
<td>NiSi(_2)</td>
<td>5.406</td>
<td>cubic</td>
<td>31</td>
<td>750-800</td>
<td>1298</td>
<td>Ni</td>
<td>34 0.98</td>
</tr>
<tr>
<td>Ni(_2)Ge</td>
<td>5.113 3.830 7.264</td>
<td>orthorhombic</td>
<td>37</td>
<td>250</td>
<td>780</td>
<td>Ni</td>
<td>23 1.57</td>
</tr>
<tr>
<td>NiGe</td>
<td>5.381 3.428 5.811</td>
<td>orthorhombic</td>
<td>32</td>
<td>300-450</td>
<td>1123</td>
<td>Ni</td>
<td>? 1.18</td>
</tr>
<tr>
<td>NiGe(_2)(^a)</td>
<td>10.830 5.763 5.762</td>
<td>orthorhombic</td>
<td>?</td>
<td>700(^a)</td>
<td>573(^a)</td>
<td>? 70</td>
<td>1.99</td>
</tr>
<tr>
<td>CoSi(_2)</td>
<td>5.365</td>
<td>cubic</td>
<td>33</td>
<td>650</td>
<td>1600</td>
<td>Co</td>
<td>15 0.97</td>
</tr>
<tr>
<td>Si</td>
<td>5.431</td>
<td>cubic</td>
<td>1687</td>
<td>-</td>
<td>10(^3) - 10(^{10})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ge</td>
<td>5.658</td>
<td>cubic</td>
<td>1211</td>
<td>-</td>
<td>10(^3) - 10(^{8})</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)Formed under high pressure 5.5 GPa, decomposes to NiGe + Ge at 300°C
4.2 Titanium silicide formation

Until recently, titanium was the most widely used silicide in transistors. It was found that when gate length decreased to about 0.25µm the formation of the low resistivity TiSi$_2$ phase was inhibited [3,12,14,41]. The interaction between 30nm Ti and Si(001) after rapid thermal annealing (RTA) at temperatures between 600-1050 °C is shown by the sheet resistance measurement in Fig. 8(a). In the temperature interval 600-700°C a high resistance is measured. The sudden drop at 750°C is related to the C54 TiSi$_2$ formation and the increase at 950°C to its agglomeration.

![Graph showing sheet resistance vs. temperature](image)

**Figure 8.** (a) The sheet resistance is plotted as a function of the annealing temperature; the step 25°C up to 750°C is then increased to 50°C between each measured sample.(b) XRDs on samples with TiSi$_2$ formed at 700°C, 750°C and 1050°C. At the lower temperature, the C49 TiSi$_2$ phase dominates while at higher temperatures only the C54 TiSi$_2$ is present.

To verify the different phases, three samples annealed at 700 °C, 750 °C and 1050 °C were chosen for XRD measurements. According to the diffractionograms in Fig. 8(b) the phases formed at 700°C are C49 and a minor part C54 TiSi$_2$, at 750°C the whole silicide has transformed into the C54 phase. The sample annealed at 1050°C is also in the C54 phase while it is thermodynamically stable. A 30 nm thick titanium film would theoretically result in a 70nm C49 TiSi$_2$ film or a 73 nm C54 TiSi$_2$ film if all of it is reacted with silicon [40]. By applying Eq. 3.1, the resistivity is calculated to be $\rho_{C49} = 70 \ \mu\Omega\cm$ and $\rho_{C54} = 18 \ \mu\Omega\cm$, which is in the interval given in Refs. 2 and 3. The agglomeration, which starts at 950°C, is exemplified by the sample annealed at 1050°C shown in Fig. 9, where bright areas are agglomerated silicide and dark areas are silicon.
4.2.1 Contacts with TiSi\textsubscript{2} and the influence of niobium

To form C\textsubscript{54} TiSi\textsubscript{2} in contact structures, RTA is usually carried out in two temperature steps. This is to prevent the so-called bridging-effect that occurs when silicon diffuses into titanium, and forms a silicide outside the contact, which can create shortcuts between gate and source/drain [3]. The first low temperature anneal forms the C\textsubscript{49} phase. After removal of remaining titanium, another RTA is done at a higher temperature in which the C\textsubscript{54} phase nucleates. Nucleation of the latter phase will take place in triple grain boundaries of C\textsubscript{49}, but not all of the triple grain boundaries will act as nucleation sites for C\textsubscript{54}. When the silicon area of the contact is reduced, fewer active triple grain boundaries will be present after C\textsubscript{49} formation. Eventually there will be so few nucleation sites that the C\textsubscript{54} formation will be stopped, see Fig. 10.

![Figure 9](image1.png)

*Figure 9. Scanning electron micrograph of a sample annealed at 1050°C where bright areas are agglomerated C\textsubscript{54} TiSi\textsubscript{2} and dark areas the underlying silicon.*

![Figure 10](image2.png)

*Figure 10. Phase transformation proceeds over a large area, while it is hindered in a small area.*
Usually a coexistence of the two phases is uncommon in small contacts. Despite that, it was found in Paper I that the two phases C49 and C54 can coexist in 25µm² contact holes, Fig. 11. A thorough TEM investigation that included CBED analysis revealed nine C49 and 14 C54 grains in a contact where high resistance was measured. The mechanism behind the interrupted C54 formation is likely to be because agglomeration forces made the C54 lose its contact with the remaining C49 grains and their transformation was hindered. In small 0.5µm² CBK contacts, the C49 phase was present while in another 25µm² contact the silicide was transformed to the C54 phase.

Figure 11. A cross-sectional micrograph with inserted magnifications together with diffraction patterns shows the coexistence of C49 and C54 TiSi₂ in a 5µm CBK contact.

To promote the TiSi₂ formation, an interposed thin layer of niobium was deposited on the poly-silicon before titanium deposition. In theory, an RTA at 750°C would lead directly to a (Ti, Nb)Si₂ with the C54 structure without forming the C49 phase first [13,30]. The explanation is the lattice stacking similarity between C40 NbSi₂ and C54 TiSi₂ where the latter (001) will be parallel to the former (001) and thus grow on it with the orientation and mismatch illustrated in Fig. 12.
Figure 12. Unit cell lattices of the (001) from both C40 NbSi2 (left) and C54 TiSi2 (right) illustrating the mismatch between niobium and titanium atoms. Large atoms indicate metal and small atoms silicon.

It has been shown that this so-called “template” effect works on both single-crystal silicon and poly-silicon [13,30]. In 0.5 µm² and 25µm² CBK contacts in Paper I the C40 (Ti,Nb)Si2 phase persisted and no switch to C54 was found. The possible reasons are explained in three ways. First of all, a too thick niobium layer compared to the titanium layer thickness led to C40 (Ti,Nb)Si2 phase formation. Secondly, the silicon diffusion through (Ti,Nb)Si2 compared to TiSi2 could have been strongly retarded and made the silicide thin. A third reason is connected to the epitaxial stability of the top C40 TiSi2 which gained its stability through the underlying C40 (Ti,Nb)Si2.

4.3 The Ni-Si-Ge system

4.3.1 Formation kinetics and thermodynamics

The formation kinetics of silicides can be classified into two groups; diffusion- or nucleation-controlled [42,43]. The former means that the mass supply of dominant diffusing species (DDS) (metal or silicon) controls the reaction rate in the growing phase. The latter is valid for reactions at rather high temperatures, when the gain in Gibb’s free energy from forming a new phase is small compared to the process of forming a new surface. A basic study on diffusion couples can be done with a metal film deposited on a silicon or Si1-xGe substrate, Fig. 13. By thermal annealing at a certain temperature for a certain time a silicide with a measurable thickness is formed. The dependence on the thickness vs. time is established. For diffusion-controlled reactions, the relation is called parabolic as it follows Eq. 4.1.
Figure 13. Planar NiSi formation from Ni to the Ni$_2$Si phase which decomposes into NiSi and Ni that reacts with silicon to form NiSi. The first reaction consumes about 18 nm silicon and totally 36 nm silicon is consumed to form 44 nm NiSi.

\[ L^2 = D \cdot t \]  \hspace{1cm} (4.1)

In Eq. 4.1 \( L \) is the silicide thickness, \( D \) is the diffusivity of the DDS through the formed layer and \( t \) the time. An assumption is that there is only one planar growing phase at a time. If simultaneous growth occurs, the other phases also have to be considered and the expression would not be as simple.

Fick’s law of diffusion, Eq. 4.2, expresses the dependence of the growth rate vs. temperature. By combining Eqs. 4.1 and 4.2 the activation energy for diffusion \( Q \) can be extracted [44].

\[ D = D_0 \cdot \exp \left( -\frac{Q}{kT} \right) \]  \hspace{1cm} (4.2)

The DDS during NiSi formation has been extracted by several different experiments. A noble gas (Xe) can be implanted in the silicon substrate followed by metal deposition and silicidation [45]. If the remaining Xe is found at the silicide-silicon interface, it is likely that the DDS is silicon. If Xe is found on the surface, the DDS is metal. Similar experiments using radioactive nickel isotope or a Pt/Ni structure can also deduce the DDS during NiSi formation [46, 47]. From Paper IV the DDS of the reaction between nickel and thin silicon capping layers on top of Si$_{0.8}$Ge$_{0.2}$ was also established for the Ni-Si$_{0.8}$Ge$_{0.2}$ reaction. The formation of the silicide protruded through twice the thickness of the surface silicon layer into the underlying Si$_{0.8}$Ge$_{0.2}$ without a large amount of germanium diffusion towards the surface, Fig. 14.
Figure 14. TEM cross-section showing the non-uniform silicide formed from 20nm Ni/15nm Si/80nm Si<sub>0.8</sub>Ge<sub>0.2</sub>. Results from an EDS line scan through the film are shown to the right. A detectable Ge concentration was measured in the NiSi formed from the top Si layer.

This confirms that nickel really is the DDS during Ni<sub>2</sub>Si and NiSi formation. However, the silicide is indeed diffusion medium for silicon and germanium due to the low but detectable germanium concentration in the upper half of the silicide that was formed from pure silicon. An inverted substrate structure with nickel on thin Si<sub>0.8</sub>Ge<sub>0.2</sub>/Si shows the same behavior, germanium stays relatively still in the silicide compared to nickel [Paper IV].

The nucleation process has been described in detail in Ref. 43, therefore only some key issues are addressed here. By nucleation barrier calculations, it is possible to find out if a reaction is diffusion- or nucleation-controlled, i.e. dictated by mass-transport or the ability to nucleate. For the reaction between nickel and silicon to form Ni<sub>2</sub>Si, NiSi and NiSi<sub>2</sub>, both diffusion and nucleation controlled phase transitions exist. The reactions are

\[
2Ni + Si = Ni_2Si \quad (4.3)
\]

\[
Ni_2Si + Si = 2NiSi \quad (4.4)
\]

\[
NiSi + Si = NiSi_2 \quad (4.5)
\]

By thermodynamic calculations, it can be shown that the diffusion of the DDS is the limiting parameter for film growth in reactions 4.3 and 4.4, while in reaction 4.5 the nucleation is limiting. The free energy change is calculated from the difference between the free energy of the products and the free energy of the reactants. The driving force for a reaction to take place is that the free-energy change from one phase to another is negative. The free
energy change ($\Delta G_{\text{tot}}$) in relation to enthalpy change ($\Delta H$) and entropy change ($\Delta S$) at a certain temperature, $T$(K), is given by Eq. 4.6.

$$\Delta G_{\text{tot}} = G_{\text{products}} - G_{\text{reactants}} = \Delta H - T\Delta S \quad (4.6)$$

Due to the lack of reliable data for the constituents in Eq. 4.6, $G$ is often approximated with the value of $H$ and the disorder term $S$ is neglected. With the $H$ values from Table 1, the free energy change is calculated to be -144, -29.6 and -4.6 kJ per gram-atom respectively for the reactions 4.3-4.5. The free energy per unit volume of these three free energies calculates to $G_v$ with respective indices. Assuming that a growing nucleus is spherical in shape with radius $r$ and that the surface energy is $\Delta \sigma$, the following energy equation expresses the total free energy change for the nucleation.

$$\Delta G = \frac{4}{3} \pi r^3 \Delta g_v + 4 \pi r^2 \Delta \sigma \quad (4.7)$$

In Eq. 4.7 there is a volume part as well as a surface part that will work against each other. Note that $\Delta g_v$ has a negative sign. The maximum value for $\Delta G$ is often called $\Delta G^*$ and the critical radius $r^*$ for nucleation can be found by taking the derivative of Eq. 4.7 with respect to $r$ and setting $d(\Delta G)/dr = 0$ which gives Eq. 4.8. By combining Eq. 4.7 and Eq. 4.8, the free energy of nucleation $\Delta G^*$ is found in Eq. 4.9.

$$r^* = -2 \frac{\Delta \sigma}{\Delta g_v} \quad (4.8)$$

$$\Delta G^* = \frac{16}{3} \pi \frac{\Delta \sigma^3}{\Delta g_v^2} \quad (4.9)$$

The rate of the nucleation follows Eq. 4.10 where the first exponential term is related to nucleation and the second exponential term corresponds to diffusion.

$$\dot{\rho}^* = \text{const.} \cdot \exp\left(-\frac{\Delta G^*}{kT}\right) \cdot \exp\left(-\frac{Q}{kT}\right) \quad (4.10)$$

A large $\Delta g_v$ value thus leads to a small $\Delta G^*$ and a high probability of nucleation, so therefore the nucleation step will not be the constraint in the reaction i.e it will be diffusion-controlled like 4.3 and 4.4. On the other hand
in the case of a small value for $\Delta g$, where $\Delta G^*$ is large, nucleation limits the reaction. A typical example of a nucleation-controlled reaction is the NiSi$_2$ nucleation from NiSi and Si, which is indicated by the free energy value calculated above.

### 4.3.2 Thermodynamic equilibrium for Ni-Si-Ge

While the Ni-Si system is already well known, the work was concentrated on the Ni-Si-Ge system that was not so well explored. The Si-Ge system forms a nearly ideal binary solid solution. By adding nickel, a ternary alloy is created.

$$Ni_2Si_{1-x}Ge_x + Si_{1-x}Ge_x = 2NiSi_{1-x}Ge_x \quad (4.11)$$

The gain in free energy when the germanium concentration is 20%, is calculated for the formation of $2NiSi_{0.8}Ge_{0.2}$ to be -27 kJ/gram-atom in reaction 4.11. The lower driving force is likely the explanation why NiSi$_{1-x}$Ge$_x$ forms at about 50 °C higher temperature than NiSi.

The NiSi$_{1-u}$Ge$_u$ shares the same orthorhombic structure as NiSi and it has been found that the cell-parameters $a$, $b$ and $c$ vary linearly with $u$ following Vegard’s law, in Eq. 4.12, which relates the cell parameters of NiSi$_{1-u}$Ge$_u$ to $u$ [34].

$$a = 5.24 + 0.19u$$
$$b = 3.25 + 0.16u \quad (4.12)$$
$$c = 5.68 + 0.15u$$

Nickel-digermanide does not exist as a stable phase and the entropy of mixing between silicon and germanium in NiSi$_{1-x}$Ge$_x$ enhances the free energy of it. Combined these two facts reduce the driving force for NiSi$_2$ formation, which already was low. From experiments, it was found that the NiSi$_2$ formation was hindered in NiSi$_{1-u}$Ge$_u$ alloys [Papers II, III, V]. It was also found that the germanium concentrations were not equal in a formed NiSi$_{1-u}$Ge$_u$ and the adjacent Si$_{1-x}$Ge$_x$ at higher temperatures, $u$ was less than $x$. The difference was found to severely worsen the morphology of the germanosilicide film. A thorough investigation, which included XRD and TEM/EDS measurements of compositional changes as well as theoretically calculated phase diagrams, was conducted.

Nickel reacted with poly-Si and poly-Si$_{0.42}$Ge$_{0.58}$ by rapid thermal annealing (RTA) in the temperature range 400°C – 850°C for 30s. The XRDs for the interaction between nickel with poly-silicon after RTA are shown in Fig. 15(a). In the temperature range 400°C – 700°C, NiSi and Si peaks can be
identified [48,49,50]. At temperatures from 750 °C the NiSi peaks have disappeared and NiSi2 has formed, although hidden in the substrate peaks. In Fig. 15(b) XRDs of NiSi1-uGeu formed on poly-Si0.42Ge0.58 are shown. Throughout the whole temperature range, the mono-germanosilicide peaks are present. At low temperatures, u is equal to 0.58 according to Eq. 4.12. Between 550°C and 700°C the NiSi1-uGeu peak positions there is a large shift towards smaller lattice spacings. Smaller lattice spacing is related to a lower germanium concentration in the NiSi1-uGeu. In analogy, the shoulder “S” shows that besides the original Si0.42Ge0.58 a new Si1-xGex with x larger than 0.58 has formed [Paper II]. Furthermore, germanium is found to suppress disilicide formation even at high temperatures up to 850°C where the mono-germanosilicide peaks remain. An XTEM in Fig. 16 shows the totally agglomerated germanosilicide formed at 650°C, with only 20% germanium as revealed by EDS. In Paper II, XRD and EDS measurements of NiSi1-uGeu and Si1-xGex compositions were plotted vs. annealing temperature, see Fig. 17, for the reaction between nickel and poly-Si0.42Ge0.58. From 450°C to 600°C the compositions were fairly constant, following the original Si0.42Ge0.58. At higher temperatures, the germanium out-diffusion from the NiSi1-uGeu resulted in a new Si1-zGez, with z>0.58. EDS and XRD both showed the same tendency in composition variation, although the statistics of the EDS measurement are limited.
Figure 15. The phase formation for nickel reacting with (a) poly-Si and (b) poly-
Si$_{0.42}$Ge$_{0.58}$ is shown. The double arrowhead in (b) indicates a decreased germanium
concentration in NiSi$_{1-u}$Ge$_u$. The shoulder S show that a Si$_{1-x}$Ge$_x$ with x>0.58 has
formed at temperatures above 500°C.
Figure 16. XTEM showing the agglomerated NiSi$_{0.8}$Ge$_{0.2}$ formed from the reaction between nickel and poly-Si$_{0.42}$Ge$_{0.58}$ at 650°C.

Figure 17. A comparison made between XRD and EDS measurements showing the atomic composition of NiSi$_{1-u}$Ge$_{u}$ and Si$_{1-z}$Ge$_{z}$ after annealing Ni/poly-Si$_{0.42}$Ge$_{0.58}$ samples.
In order to be able to explain the behavior of the system, approximate ternary phase diagrams were calculated for the region limited by NiSi-NiGe and Si-Ge as outlined in Ref. 24 [Paper II]. One of these calculated isothermal ternary phase diagrams at 600°C is shown in Fig. 18. The tie lines connecting NiSi-NiGe with Si-Ge show the equilibrium concentrations of the NiSi$_{1-u}$Ge$_u$ and Si$_{1-u}$Ge$_u$. A three-phase region including NiSi$_2$, NiSi$_{0.92}$Ge$_{0.08}$ and Si$_{0.55}$Ge$_{0.45}$ indicates that according to thermodynamics the disilicide phase can form. However, it was found by XRD and EDS analysis that NiSi$_2$ did not form in the samples in the presence of germanium [Papers II, III].

![Figure 18. Calculated ternary phase diagram of the Ni-Si-Ge system.](image)

By neglecting the disilicide phase, the calculations were made simpler and more useful pseudo phase diagrams could be constructed as follows. The total free energy change of a system going to thermodynamic equilibrium is described by equilibrium equations [Paper III, 51]. By treating NiSi$_{1-u}$Ge$_u$ as an ideal solid solution its free energy can be calculated by

\[ \Delta G_{\text{NiSiGe}}(u,T) = (1-u)\Delta H_{\text{NiSi}}(T) + u\Delta H_{\text{NiGe}}(T) + \frac{1}{2}RT[(1-u)\ln(1-u) + u\ln u] \]  

(4.13)

The enthalpy in Eq. 4.13 varies linearly with the value of $u$, which is the germanium concentration in the germanosilicide. The half factor in front of the entropy term is due to the fact that the entropy of mixing only concerns the silicon and germanium atoms in the germanosilicide. The gas constant is denoted R and the temperature T is in Kelvin. The germanosilicide will in-
teract with adjacent Si$_{1-x}$Ge$_x$ by an exchange of silicon and germanium atoms. The entropy of mixing determines the free energy of the silicon-germanium, while pure elements are considered.

$$\Delta G_{\text{SiGe}}(x, T) = RT\left[(1 - x) \ln(1 - x) + x \ln x\right]$$ (4.14)

Hereby the total free energy of the system before further heat treatment is described by the sum of Eqs. 4.13 and 4.14 with one-gram atom of each element. The motion of germanium atoms from NiSi$_{1-u}$Ge$_u$ into Si$_{1-x}$Ge$_x$ is balanced by the motion of silicon atoms in the other direction in order to reach thermodynamic equilibrium. If $w$ germanium atoms go from the germanosilicide into germanium, the balance will be fulfilled if $w/2$ atoms of silicon go the other way, since the Si$_{1-u}$Ge$_u$ part of NiSi$_{1-u}$Ge$_u$ only constitutes half of the atoms in a system with one gram-atom in Eq. 4.15.

$$\text{NiSi}_{1-u} \text{Ge}_u + \text{Si}_{1-x} \text{Ge}_x \Rightarrow \text{NiSi}_{1-u+w} \text{Ge}_{u-w} + \frac{\text{Si}}{x+\frac{w}{2}}$$ (4.15)

The total free energy after equilibrium of a system with a total of one gram-atom, i.e. a half gram-atom of each compound, is described as

$$\Delta G_{\text{tot}}(u, x, w, T) = \frac{w}{2} \left[\Delta H_{\text{NiSi}}(T) + \Delta H_{\text{NiGe}}(T)\right] + \frac{1}{4} RT\left[(1 - u + w)\ln(1 - u + w) + (u - w)\ln(u - w)\right] + \frac{1}{2} RT\left[(1 - x - \frac{w}{2})\ln\left(1 - x - \frac{w}{2}\right) + \left(x + \frac{w}{2}\right)\ln\left(x + \frac{w}{2}\right)\right] - \frac{1}{4} RT\left[(1 - u)\ln(1 - u) + u \ln u\right] - \frac{1}{2} RT\left[(1 - x)\ln(1 - x) + x \ln x\right]$$ (4.16)

A plot of $\Delta G_{\text{tot}}$ vs. $w$, gives the minimum free energy at a certain $w$ and thus the equilibrium compositions. An initial composition is assumed to define the $x$ and $u$ values. For instance, if $u = x = 0.2$ and $T = 600^\circ\text{C}$ the equilibrium will be found at $w = 0.18$ according to the graph in Fig. 19(a) where Eq. 4.16 has been plotted. The resulting NiSi$_{0.98}$Ge$_{0.02}$ is in equilibrium with Si$_{0.71}$Ge$_{0.29}$ as can also be seen from the marked tie-line of the pseudo ternary phase diagram in Fig. 19(b) calculated for this material system. Equation 4.16 solved analytically gives $w = 0.181$. 

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Figure 19. In (a) the free energy minimum is shown at equilibrium $w$ of the starting composition $\text{NiSi}_{0.8}\text{Ge}_{0.2}$ and $\text{Si}_{0.8}\text{Ge}_{0.2}$. The pseudo ternary phase diagram in (b) shows the tie lines and highlights the evolution to equilibrium.

The thermodynamic equilibrium makes it possible to control the agglomeration of $\text{NiSi}_{1-u}\text{Ge}_u$ on $\text{Si}_{1-x}\text{Ge}_x$. To verify if a film and substrate in thermodynamic equilibrium are stable, a sacrificial $\text{Si}_{1-y}\text{Ge}_y$ layer with low germanium concentration can be deposited on top of the $\text{Si}_{1-x}\text{Ge}_x$ layer, $x$ is larger than $y$. The value of $z$ is tailored from the known value of $x$ and is taken from the phase diagram, where a tie line describes the equilibrium compositions for $\text{NiS}_{1-y}\text{Ge}_y$ in contact with $\text{Si}_{1-x}\text{Ge}_x$. The upper layer will be consumed by silicidation and form a $\text{NiS}_{1-y}\text{Ge}_y$ in direct contact with $\text{Si}_{1-x}\text{Ge}_x$, see Fig. 20.

Figure 20. By using bi-layer structure, the $\text{NiSi}_{1-u}\text{Ge}_u$ with low germanium concentration can be thermodynamically stable to $\text{Si}_{1-x}\text{Ge}_x$, where $x>y$.

Thus, the agglomeration driven by the thermodynamic effect is inhibited. For an underlying layer with $x=0.23$, the sacrificial layer should contain less than 2% germanium according to the tie line. Depositing a $\text{Si}_{1-y}\text{Ge}_y$ layer with such low germanium concentration might not be necessary. Instead, a pure silicon layer was deposited on top of the $\text{Si}_{0.77}\text{Ge}_{0.23}$ and it was found that the film was indeed more stable on this type of substrate structure. Another observation made by XTEM/EDS was that a small amount of germanium dissolved in the NiSi at higher temperatures. From sheet resistance measurements in Fig. 21 on different samples, it is clear that the NiSi agglomeration
is reduced on a Si/Si$_{1-x}$Ge$_x$ structure compared to on a relaxed Si$_{1-x}$Ge$_x$. A Si(001) substrate is also compared as a reference. Even at 550°C a small increase in $R_s$ shows that agglomeration of the NiSi$_{1-u}$Ge$_u$ has started. The sample with a silicon-cap does not start to agglomerate until 700-750°C. It actually follows the curve of Si(001) until 750°C, where the silicide completely disintegrates. The NiSi transforms to the NiSi$_2$ phase at 750°C and the lowered sheet resistance at high temperatures comes from the increase in film volume, which makes the silicide continuous.

![Figure 21](image.png)

*Figure 21.* Sheet resistance measurements for 20 nm Ni reacted with different substrates to study the effect on agglomeration for the bi-layer structure.

### 4.3.3 The role of substrate strain

Silicon and germanium have the same diamond crystal structure. Their atomic radii differ somewhat and germanium has the largest radius. The unit cell-parameter of silicon is 5.431 Å and for germanium it is 5.658 Å. As silicon and germanium form an almost ideal binary solid solution, it is possible to grow an epitaxial Si$_{1-x}$Ge$_x$ layer on Si, Fig. 22(a). Due to the lattice mismatch, the grown Si$_{1-x}$Ge$_x$ will no longer have its cubic crystal structure but rather a tetragonal one, Fig. 22(b). The grown Si$_{1-x}$Ge$_x$ layer will be under compressive strain and has a critical maximum thickness depending on the germanium concentration. The layer will therefore store elastic energy that can be released. As the critical thickness is exceeded, misfit dislocations will form at the Si$_{1-x}$Ge$_x$/Si interface and eventually a totally relaxed Si$_{1-x}$Ge$_x$ is formed.
In (a) the two bulk lattices for silicon and silicon-germanium are shown. In (b) the epitaxially grown SiGe will keep the silicon cell parameters in the interface plane but the third cell parameter will increase perpendicular to the interface due to the compressive strain.

The silicide agglomeration is not only controlled by thermodynamic equilibrium. Surface and interface energies are as important. By a study of different strained single-crystalline (sc)-, relaxed sc- and poly-Si$_{1-x}$Ge$_x$ it was concluded that strain plays a major role in the morphological stability of germanosilicides [Paper III]. In Fig. 23(a), a poly-Si$_{0.7}$Ge$_{0.3}$ and a strained-Si$_{0.7}$Ge$_{0.3}$ are compared. They have essentially the same character although the poly-Si$_{0.7}$Ge$_{0.3}$ seems to be a little less stable. This is in contrast to nickel interacting with sc-silicon or poly-silicon, where the silicide is more thermally stable on the former. In the reaction between nickel and poly-silicon, the NiSi start to diffuse via poly-silicon grain boundaries all the way down to the Si-SiO$_2$ interface [52]. In poly-silicon the agglomeration is driven by the reduction of poly-silicon grain boundaries to minimize the grain boundary energy, and is enhanced by NiSi diffusion. The driving force for NiSi agglomeration on single crystalline substrates is the reduction of surface-energies, which leads to grain-grooving. The other driving force is the consumption of NiSi grain boundaries i.e. grain growth [3]. Different strain levels in Si$_{0.8}$Ge$_{0.2}$ substrates impose a difference in the driving force for agglomeration of NiSi$_{0.8}$Ge$_{0.2}$, see Fig. 23(b). The germanosilicide formed on the substrate with the largest strain will degrade at a lower temperature compared to the samples with less strain. Although the three different samples display a low resistance at 550°C, it is revealed in Fig. 24(a) that NiSi$_{0.8}$Ge$_{0.2}$ formed on strained-Si$_{0.8}$Ge$_{0.2}$ has started to agglomerate, while that on relaxed-Si$_{0.8}$Ge$_{0.2}$ shown in Fig. 24(b) is smooth.
Figure 23. Sheet resistance measurements for germanosilicide formed on (a) strained- and poly-Si$_{0.7}$Ge$_{0.3}$ and (b) relaxed-, partially relaxed- and strained-Si$_{0.8}$Ge$_{0.2}$

Figure 24. XTEM on (a) NiSi$_{0.8}$Ge$_{0.2}$ formed on strained Si$_{0.8}$Ge$_{0.2}$ at 550°C where agglomeration has started although it is not seen from sheet resistance measurements. In (b) a more uniform NiSi$_{0.8}$Ge$_{0.2}$ formed on relaxed Si$_{0.8}$Ge$_{0.2}$ at 550°C is shown.

A larger mechanical strain thus induces the agglomeration by increasing silicon and germanium diffusion so the nearby NiSi$_{1-u}$Ge$_u$ can act as a diffusion media. Silicon and germanium diffusion is otherwise quite slow in the temperature range for silicidation [53,54]. The interface energy is also likely to be reduced by the germanium segregation to the grain boundary between the formed NiSi$_{1-u}$Ge$_u$ and the original Si$_{1-x}$Ge$_x$. If one compares a strained or a relaxed Si$_{1-x}$Ge$_x$ interface to NiSi$_{1-u}$Ge$_u$, the strained interface would have the lowest interface energy. By replacing some of the silicon atoms at the Si$_{1-x}$Ge$_x$ surface to germanium atoms, compressive stresses between Si-Si atoms are relieved with the somewhat larger germanium atom. This process will reduce the interface energy even further. Thus, the energy balance at triple points of two silicide grains separated by a grain boundary and the substrate-silicide interface will change. By decreasing the interface energy $\gamma_i$ between silicide and substrate and assuming that there is no difference in grain-boundary energy $\gamma_{gb}$, the resulting $\theta_i$ angle will increase and the silicide agglomerates, Fig. 25 [55,56, Papers III, IV].
4.3.4 Silicide texture

Epitaxial NiSi₂ forms on a single-crystalline silicon substrate while it shares almost identical cubic crystal structure with a 0.5% cell-parameter difference. Epitaxial NiSi, NiGe as well as NiSi₁₋ₓGeₓ also form on (111) substrates. However, the same perfect lattice matching found with NiSi₂ does not exist [Paper VI, 57,58,59].

A recent publication addresses a new type of off-normal fiber-texture for silicides on single crystalline substrates, called axiotaxy. It was found for NiSi as well as for other silicides on Si(001) [60]. Axiotaxy is based on an alignment between closely spaced silicide and silicon lattice planes. In the case of NiSi and Si, the NiSi (112), (211), (202) and (103) can be parallel to Si(220) planes. Their respective lattice spacings are 1.98 Å, 1.92 Å, 1.92 Å and 1.78 Å for the NiSi planes, and 1.92 Å for Si(220). The NiSi(211) that matches the substrate exactly will align edge to edge to the Si(220). This is also true for NiSi(202), which has an identical lattice spacing. The other silicide planes can, however, also match the Si(220) by tilting a few degrees until the projected lattice spacing matches 1.92 Å of Si(220). In that case, silicide and silicon planes will not be exactly parallel to each other, see Fig. 26. An X-ray beam with high intensity and a 2D area detector is necessary to evaluate this type of texture. The resolution and intensity of an ordinary XRD pole figure system seems to be inadequate to resolve this type of texture.

![Figure 25. Triple point of interface energy balance between silicide and substrate.](image)

**Figure 25.** Triple point of interface energy balance between silicide and substrate.

![Figure 26. Axiotaxy for NiSi(211) or (202) grains as well as a (112) grain.](image)

**Figure 26.** Axiotaxy for NiSi(211) or (202) grains as well as a (112) grain.
Germanium clearly affects the germanosilicide texture that will be of very different character on (001) and (111) substrate orientations. When NiSi(Ge) forms on poly-Si or poly-Si$_{1-x}$Ge$_x$ it will be of random orientation. For NiSi(Ge) the strongest XRD peaks are in the interval of about 1.6Å-2.9Å. In Fig. 27, four diffractograms are shown when 20 nm nickel has reacted with Si(001), Si$_{0.80}$Ge$_{0.20}$(001), Si(111) and Si$_{0.80}$Ge$_{0.20}$(111) at 500°C for 30s, respectively. The first one with NiSi on Si(001) displays no or minor texture (axiotaxy) whereas NiSi on Si(111) displays three strong peaks indicating texture. These are NiSi(111)/(102), NiSi(200) and NiSi(011)/(002). Germanosilicides formed on Si$_{0.80}$Ge$_{0.20}$ substrates are highly textured where the NiSi$_{0.80}$Ge$_{0.20}$(013)/(020) peaks are dominant on Si$_{0.80}$Ge$_{0.20}$(001) while the NiSi$_{0.80}$Ge$_{0.20}$(200) peak is strong on Si$_{0.80}$Ge$_{0.20}$(111).

Figure 27. 0–20 XRD showing the silicide formation at 500°C for 30s on Si(001), Si(111) and Si$_{0.8}$Ge$_{0.2}$(111) substrates.

Pole figure measurements of these silicides gave additional information regarding the texture. In Figs. 28(a) and 28(b) the preferential oriented NiSi$_{0.80}$Ge$_{0.20}$ formed on Si$_{0.80}$Ge$_{0.20}$(001) is shown from two different plane measurements. The pole figure in Fig. 28(a) is acquired from the NiSi$_{0.80}$Ge$_{0.20}$(112) peak, with a lattice spacing well separated from other planes. In Fig. 28(b), the NiSi$_{0.80}$Ge$_{0.20}$(011)/(002) is used. The silicide has a
fiber-like texture according to the two rings at $\chi = 25^\circ$ and $73^\circ$, in Fig. 28(a). It is a proof that the silicide (013) is parallel to the substrate (001). By using a simulation program for crystallography that can handle stereographic projections, it is possible to show that there are four different types of (112) planes, namely (112), (1-12), (11-2) and (1-1-2) that will diffract from each grain. The relatively large FWHM of about 8°, together with the four diffracting (112), will produce a pole figure that gives the impression of an almost completely fiber-textured germanosilicide. This is, however, not the case. By measuring pole-figures for other planes in the crystal, a more complex germanosilicide texture arises. The 3D pole figure in 28(b) for NiSi$_{0.80}$Ge$_{0.20}$(011)/(002) will add additional information regarding the texture. The ring found in the (011)/(002) pole figure is divided into four segments, each consisting of three peaks, which is called a triplet in Paper V.

![Figure 28. XRD pole figures for NiSi$_{0.80}$Ge$_{0.20}$ where (a) (112) shows an apparent fiber-like textured germanosilicide and (b) (011)/(002) reveals that the texture is rather in segments.](image)

The center peak of the triplet was assigned to the fact that the directional alignment between NiSi$_{0.80}$Ge$_{0.20}$[100] and Si$_{0.80}$Ge$_{0.20}$[100] and [010] was avoided. The grains will therefore be forced to reorient themselves to an orientation lying in between [100] and [010] which is in a [110] of the substrate. The orientation of the two outer members of the triplet was found to originate from pairs of grains with a lateral alignment along their mutual grain boundary.

The pole figure recordings on silicide formed on Si(111) and Si$_{0.80}$Ge$_{0.20}$(111) showed an epitaxially aligned film indicated by discrete peaks in Fig. 29. NiSi has formed with NiSi (001), (100) and (102) parallel to Si(111) calculated from the peak positions in Fig. 29(a). In Fig 29(b) there are twelve peaks all originating from the measured NiSi$_{0.80}$Ge$_{0.20}$(112). The peak positions reveal that only NiSi$_{0.80}$Ge$_{0.20}$(100) is parallel to Si$_{0.80}$Ge$_{0.20}$(111). The number of silicide peaks reflects the three-fold symme-
try of the Si(111) surface so that NiSi_{0.80}Ge_{0.20}[001] is parallel to Si_{0.80}Ge_{0.20}<0-11>.

Figure 29. The pole figure for (a) NiSi and (b) NiSi_{0.80}Ge_{0.20} formed on (111) substrates. NiSi has three different epitaxial orientations indicated by the multitude of peaks while NiSi_{0.80}Ge_{0.20} has one epitaxial orientation.

On pure silicon (111) substrates, the silicide to silicon lattice matching is always within a few percent, whereas for NiSi_{0.80}Ge_{0.20} on Si_{0.80}Ge_{0.20}(111) a 15% lattice mismatch is found. In the sample with 20% germanium the epitaxial alignment is uniquely of the type NiSi_{0.80}Ge_{0.20}(100) parallel to Si_{0.80}Ge_{0.20}(111). In Fig. 30 an HRXTEM is shown which is acquired along the Si_{0.80}Ge_{0.20}[-110]. This germanosilicide grain is, according to the Fourier transforms to the right in the image, oriented in such way that NiSi_{0.80}Ge_{0.20}(100) is parallel to Si_{0.80}Ge_{0.20}(111) and NiSi_{0.80}Ge_{0.20}[001] is parallel to Si_{0.80}Ge_{0.20}[0-11].

Figure 30. The HRXTEM image shows the (200) oriented germanosilicide formed on (111) silicon-germanium. The insets show the orientation of NiSi_{0.80}Ge_{0.20} and Si_{0.80}Ge_{0.20}. 

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The crystal orientations for Ni$_{1-x}$Si$_x$ formed on Si$_{1-x}$Ge$_x$(001) or (111) [Papers V, VI] are thus totally different from the axiotaxially or epitaxially aligned NiSi formed on Si(001) or (111) [60, Papers V, VI]. We explain the difference in epitaxial alignments between NiSi and NiSi$_{0.80}$Ge$_{0.20}$ by the fact that the Ni(SiGe)$_2$ phase does not form according to phase diagrams [Paper II]. The NiSi$_{0.80}$Ge$_{0.20}$ will then orient in such a manner that an atomic configuration at the germanosilicide-substrate interface that resembles the Ni(SiGe)$_2$ is avoided [Paper VI].

4.3.5 NiSi$_{0.82}$Ge$_{0.18}$ integration in contacts

The last step was to integrate the germanosilicide in a component for electrical characterization. The CBK structure was chosen as it is suitable for contact resistance measurements. The contact resistivity was extracted between NiSi$_{0.82}$Ge$_{0.18}$ and P$^+$-Si$_{0.82}$Ge$_{0.18}$. The contacts were characterized by SEM from a top view and by XTEM to verify the germanosilicide morphology and composition. From SEM measurements of contacts, it was found that the germanosilicide had probably grown under the oxide laterally into the Si$_{0.82}$Ge$_{0.18}$. In Fig. 31, two contacts of a 1×1 µm$^2$ nominal size are shown. The left figure shows the contact area after removing all layers except the Si$_{0.82}$Ge$_{0.18}$. The right figure shows the contact after all metal has been removed while the SiO$_2$ is left and defines the size of the contact opening. By comparing their respective sizes, which is larger for the left contact, it could mean that the germanosilicide grew laterally under the SiO$_2$.

![Figure 31. SEM top-view images of nominally 1µm large contact holes. In the left image only the Si$_{0.82}$Ge$_{0.18}$ remains after the other layers have been etched away. In the right image, the overlying SiO$_2$ is still left.](image)

To verify the lateral formation, an XTEM sample of a 0.5×0.5 µm$^2$ contact was imaged and analyzed with EDS. From Fig. 32 the nonuniform growth of the NiSi$_{0.82}$Ge$_{0.18}$ was measured to be about 55nm.
Figure 32. An XTEM image shows the 0.5µm CBK contact. The germanosilicide has grown laterally in under SiO₂, which increases the total contact area.

Either the 2D model or the 3D model can be used to extract the contact resistivity. It was found that the 2D model, in this special case, was not accurate enough. The lateral and nonuniform growth leads to this inaccuracy, but by applying the 3D model there were no restrictions on the silicide topology. The resistivity was underestimated by roughly 35% using the 2D model compared to the 3D model [Paper VII]. The extracted resistivities presented in Fig. 33 differ for square and rounded contacts. The reason could be that reactive ion etching that defined the contact hole in SiO₂, damaged the underlying Si₀.₈₂Ge₀.₁₈. It is concluded that the lowest contact resistivity value obtained, 5×10⁻⁸ Ωcm², satisfies the ITRS roadmap until 2010 [4].

Figure 33. A comparison between models for extracting the contact resistivity of the CBKs where: (a) uses the SEM top-view areas and the 2D model without considering the lateral silicidation, and (b) the corrected contact areas and the 3D model. The two different slopes are for small circular (upper left) and larger square contacts (lower right), respectively.
5. Conclusions and future work

This thesis deals with the silicide materials that are to be integrated into small contact areas in future components. Both TiSi$_2$ and NiSi have been discussed, but the thesis is primarily concentrated on the Ni-Si-Ge system. The latter has been investigated with respect to its formation and stability properties by phase diagram calculations and substrate strain effects. The investigation also included an analysis of the germanosilicide texture on single-crystalline substrates induced by germanium. It ends with a paper that addresses the germanosilicide electrical properties in CBK contacts.

The first investigation on TiSi$_2$ growth in CBK contacts showed its inability to form the low resistivity C54 phase in small contacts, even with an interposed layer of niobium that should enhance the C54 nucleation. The major contribution from Paper II was that no high resistivity Ni(Si,Ge)$_2$ formed in the presence of germanium. We also calculated approximate iso-thermal ternary phase diagrams for Ni-Si-Ge, both with and without NiSi$_2$, as according to thorough XRD and TEM analysis, disilicide was not present in the sample. Dictated by the thermodynamic equilibrium between NiSi$_{1-u}$Ge$_u$ and Si$_{1-x}$Ge$_x$, a germanosilicide with low germanium concentration will form adjacent to silicon-germanium with higher germanium concentration. Consequently, these diagrams can be used to make NiSi$_{1-u}$Ge$_u$ that is thermodynamically stable to the Si$_{1-x}$Ge$_x$ substrate. Reacting nickel with bi-layer structures of Si and Si$_{1-x}$Ge$_x$ indicates that nickel is indeed the DDS. These bi-layer structures also showed that the sequence as well as thickness influenced the silicide texture. The very pronounced texture in germanosilicides formed with a top Si$_{1-x}$Ge$_x$ was thought to be decided by an epitaxial relation on Si$_{1-x}$Ge$_x$(001) substrates due to the apparent matching in cell parameters. The study based on XRD pole figure measurements revealed something else: the NiSi$_{1-u}$Ge$_u$ (013) was found to be preferentially parallel to Si$_{1-x}$Ge$_x$(001) and no or minor lattice matching existed. It is likely an effect of avoiding an interface symmetry, which resembles atomic positions of the NiGe$_2$ phase. From electrical characterizations it was found that the mono-germanosilicide phase formed in CBK contacts and that the extracted contact resistivity was sufficiently low to comply with the 2004 ITRS roadmap until the year 2010.

In the future, a textured germanosilicide might have consequences for the formation in small contacts where one grain covers the whole length across the source/drain. NiSi is known to have highly anisotropic thermal expansion coefficients [61] and it has been seen by IBM that NiSi formed on Si(001) is
degraded due to stresses imposed by thermal annealing [62]. NiSi$_{1-x}$Ge$_x$, which is preferentially oriented, might not suffer from this effect if it aligns in order to minimize the stresses in the interface. The preferential orientation of the NiSi$_{1-x}$Ge$_x$ might also have an influence on the Schottky barrier height (SBH), which is known to vary with orientation for silicides epitaxially grown on silicon [63]. With a randomly oriented silicide film, an averaged SBH to the silicon is measured due to the great number of different silicide orientations that face the substrate. The SBH for NiSi$_{1-x}$Ge$_x$ to poly-Si$_{1-x}$Ge$_x$, Si$_{1-x}$Ge$_x$(001) or Si$_{1-x}$Ge$_x$(111) can be different due to the inherently different polycrystalline, “fiber”-textured and epitaxial silicide orientations. More studies on the influence of doping elements are also needed for the Ni-Si$_{1-x}$Ge$_x$ reaction. It was found that when nickel reacts with poly-SiGeC, a more temperature stable germanosilicide formed, although the carbon concentration is less than one percent [64]. The alloying of nickel with platinum prior to annealing also leads to a uniform film even at higher temperatures. Platinum also lowers the SBH between Ni(Pt)Si and silicon and should therefore also be tested in the Ni-Si-Ge system.

This silicide-materials study will add knowledge on how to stabilize germanosilicides formed on silicon-germanium. Efforts must, however, still be made in order to investigate the effects of germanosilicide texturing as well as the lateral NiSi$_{1-x}$Ge$_x$ growth found in contact holes. nickel-germanosilicides will likely be implemented in the next generation of CMOS components as soon as all the stability problems are solved.
Summary of appended papers

Paper I.
The hindered C54 TiSi₂ formation in 0.7µm CBK contacts was verified by XTEM and CBED. In larger contacts, the C54 phase formed although coexistence with the C49 phase was established in a highly doped 5µm contact. The coexistence of the two phases was probably due to C54 grain agglomeration hindering the consumption of the remaining C49 grains. The so-called template effect in the presence of a thin niobium layer between titanium and poly-silicon was absent. Instead, a C40 (Ti, Nb)Si₂ phase formed with no C54 being present. There were three possible reasons for this behavior: a too thick niobium interlayer, strongly retarded silicon diffusion through the (Ti,Nb)Si₂ and an epitaxial stabilization of upper part of the TiSi₂ silicide to the underlying thermodynamically stable C40 (Ti, Nb)Si₂.

Paper II.
Nickel-germanosilicide and NiSi layers formed by nickel interacting with poly-Si and polySi₀.₄₂Ge₀.₅₈ at 500°C for 30s are found to be uniform and continuous. An increased annealing temperature led to an agglomerated NiSi and eventually at 750°C the high resistivity NiSi₂ phase formed. A massive out diffusion of germanium is measured by both XRD and XTEM/EDS from the original NiSi₀.₄₂Ge₀.₅₈ at elevated temperatures. The germanium concentration in the germanosilicide was only about 10% after an 850°C anneal. At the same time, the surrounding Si₁₋ₓGeₓ region increased its germanium concentration to about 80%. The disilicide phase was absent even at high temperatures in samples with germanium present. The major contribution of this paper was the calculated iso-thermal ternary phase diagrams for Ni-Si-Ge. Two separate diagrams were calculated, of which the first type included the NiSi₂ phase. The absence of a Ni(SiGe)₂ phase in our samples made it possible to calculate new more realistic phase diagrams without Ni(SiGe)₂.

Paper III.
This paper considers the morphological stability of NiSi₁₋ₓGeₓ and the influence of strain in epitaxial Si₁₋ₓGeₓ. Several different germanium concentrations were used, as well as different strain levels. These results were compared to NiSi₁₋ₓGeₓ formed on poly-Si₁₋ₓGeₓ. Four different mechanisms were found to promote agglomeration. Compositional equilibrium between
NiSi$_{1-x}$Ge$_x$ and Si$_{1-x}$Ge$_x$ dictated by thermodynamics was determined as a major cause for agglomeration on both epitaxial and poly crystalline substrates. The mechanical strain in the epitaxial Si$_{1-x}$Ge$_x$ layer increasing agglomeration at lower temperatures was also a major factor. Grain grooving of NiSi$_{1-x}$Ge$_x$ applied to both epi- and poly-substrates but was found to be less important. The fourth mechanism was the poly-Si$_{1-x}$Ge$_x$ grain growth accelerated by nickel. To reduce the thermodynamic effect of agglomeration, a NiSi was formed from a sacrificial silicon layer deposited on Si$_{0.77}$Ge$_{0.23}$. The NiSi and Si$_{0.77}$Ge$_{0.23}$ should be in thermodynamic equilibrium according to the phase diagram in Paper II and it was shown that the germanosilicide was indeed stabilized at higher temperatures. It was also found that nickel must be the DDS during the reaction due to the fact that germanium stays relatively still in the silicide.

Paper IV.
This paper aimed at finding the critical parameters for silicide texturing in the presence of germanium. Reacting nickel with Si/Si$_{1-x}$Ge$_x$ stacks of different sequences and thickness lead to large differences in texture. A thicker top Si layer leads to more randomly oriented germanosilicide grains, while increased texturing was found when a top Si$_{1-x}$Ge$_x$ layer with increasing thickness was used. Bi-layers of NiSi and NiSi$_{1-x}$Ge$_x$ formed epitaxially on each other. Nickel diffusion dominated over silicon or germanium diffusion during silicide formation. The germanium often used as tracer element for DDS determination was found to stay relatively still in the silicide formed.

Paper V.
The resulting NiSi$_{1-x}$Ge$_x$ formed on epitaxial Si$_{1-x}$Ge$_x$(001) is highly textured with its (013)/(020) parallel to the substrate surface according to $\theta$–$\omega$ XRD. This is in contrast to more randomly oriented NiSi formed on Si(001). The b and c axis are equally long about 5.43Å, both lying in the surface plane of Si$_{1-x}$Ge$_x$(001). Cell parameters of the orthorhombic NiSi$_{1-x}$Ge$_x$ are $a$=5.28Å, $b$=3.28Å and $c$=5.71Å. Thus if the NiSi$_{1-x}$Ge$_x$(020) is parallel to Si$_{1-x}$Ge$_x$(001) a fairly good matching would occur between germanosilicide and substrate lattices. XRD pole-figure measurements surprisingly show that NiSi$_{1-x}$Ge$_x$(013) is the plane parallel to Si$_{1-x}$Ge$_x$(001) where no apparent matching is found. Those pole-figures also indicated a fiber-textured germanosilicide. Peaks were found to exhibit fourfolded symmetry reflecting the same symmetry as the substrate surface. The absence of a Ni(SiGe)$_2$ phase at elevated temperatures leads to the conclusion that the NiSi$_{1-x}$Ge$_x$ avoids an orientation where the interface between germanosilicide and substrate would resemble the nonexistent NiGe$_2$. 

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Paper VI.
As a follow up study to Paper V the same type of texturing as on (001) substrates were expected also for (111) substrates. Instead epitaxial NiSi with three different silicide planes (002), (200) and (102) parallel to Si(111) formed. In samples with 5% germanium, a multitude of different epitaxial alignments results in a complex pole figure. When NiSi$_{0.8}$Ge$_{0.2}$ form on Si$_{0.8}$Ge$_{0.2}$(111) only one epitaxial orientation NiSi$_{0.8}$Ge$_{0.2}$(200) exists. Of special interest is the (200) orientation. In the silicon sample the silicide aligns with the substrate with 2-3% mismatch, compared to NiSi$_{0.8}$Ge$_{0.2}$(200) that rotates 30° in the surface plane and the mismatch to the underlying substrate increases to 15%. The interface between (200) oriented NiSi and Si resembles the atomic configuration of NiSi$_2$. NiGe$_2$ as well as Ni(SiGe)$_2$ are not observed in earlier studies. A "repulsive" effect thus reorients the germanosilicide to a metastable epitaxial orientation as soon as germanium enters the substrate. The terraced substrate surface of the Si$_{1-x}$Ge$_x$ samples did not affect the germanosilicide orientation.

Paper VII.
To finalize the study on Ni-germanosilicide this paper examines the electrical properties of NiSi$_{0.82}$Ge$_{0.18}$ to p$^+$Si$_{0.82}$Ge$_{0.18}$. It was found to grow not only vertically in CBK contact holes but also laterally under the SiO$_2$. TEM and SEM investigations were necessary in order to apply the 3D model for extraction of the contact resistivity that varied with contact geometry, round or square. The lowest contact resistivity was extracted to be $5 \times 10^{-8} \Omega \text{cm}^2$. 
Acronyms

CBED Convergent beam electron diffraction
CBK Cross-Bridge Kelvin
CMOS Complementary metal oxide semiconductor
DDS Dominant diffusing species
ED Electron diffraction
EDS Energy dispersive spectroscopy
FWHM Full width at half maximum
HAADF High angle annular dark field
HRTEM High-resolution transmission electron microscopy
IC Integrated circuit
MOSFET Metal oxide semiconductor field effect transistor
RTA Rapid thermal annealing
SAD Selected area diffraction
SEM Scanning electron microscopy
STEM Scanning transmission electron microscopy
TEM Transmission electron microscopy
XRD X-ray diffraction
XTEM Cross-sectional transmission electron microscopy
Sammanfattning (in Swedish)

Den svenska titeln på denna avhandling är "Högupplösande studier av silicidfilm för nano IC-komponenter". Högupplösande innebär att de instrument som har använts i arbetet är i någon mån just det. Transmissions-elektronmikroskopet (TEM) med vilket man kan nå en rumsupplösning på några få Ångström är det huvudsakliga verktyget i flera av artiklarna som ingår. TEM kombinerat med diffraction för fas- och kristallorienteringsbestämning är en av de tekniker som är använd. Svep-TEM (STEM) tillsammans med energidispersiv spektroskop (EDS) är ett kraftfullt verktyg för att bestämma sammansättningar elektrontransparenta tunna (10-100nm) prover. Andra "högupplösande” verktyg är svepelektronmikroskop (SEM), 0–20 röntgendiffraction (XRD), polfigur XRD samt olika elektriska mätningar. Silicid är en förening mellan metall och kisel, i avhandlingen har TiSi2 och NiSi studerats. I detta fall ingår även nickel-germanosilicid som bildas då kisel-germanium reagerar med nickel. Dessa silicider används till transistorer inom mikro/nanoelektroniken t ex för att reducera kontaktresistivitet och serieresistansen i styre, kollektor och emitter hos en fält-effekt transistor.

Detta arbete avhandlar dels försök att bilda TiSi2 med låg resistivitet i komponenter med små elektriska kontakthål ned till 0.5 µm². Det avhandlar även det ternära material systemet Ni-Si-Ge, där grundläggande materialstudier med avseende på fasbildning, termodynamik, agglomeration, substratets inverkan och textur till slut leder fram till en färdig kontakt vars kontaktresistivitet har bestämts.

TiSi2 är sedan 1980-talet den mest använda siliciden för mikroelektroniktillämpningar. Den finns i två olika faser som båda är av ortorombisk kristallsstruktur och kallas C49 och C54. Den första är termodynamiskt metastabil och bildas vid 700 °C värmebehandling i 30s och har hög resistivitet 60-80 µΩcm. Däremot C54 som bildas vid ca 750 °C är termodynamiskt stabilt och har låg resistivitet från 15 till 20 µΩcm. I och med att transistorerna blir mindre så har TiSi2 näst sin begränsning. Vid kontaktstorlekar mindre än 0.25 µm² bildas inte C54 fasen utan C49 kvarstår. Detta beror på att C54 har svårt att kämbilda. Kärbildningen sker främst i trippelkorngränser i C49 fasen. När kontaktstorleken minskar ändra ned till C49 korngrek så reduceras antalet korngränser och följaktligen bildas ingen C54 fas. Det finns exempel på hur man kan modifiera processningen av siliciden och genom detta bildas C54. Ett sätt som har undersökts i detta arbete är genom att deponera ett tunt niob skikt mellan titan och kisel. Med hjälp av sin kristallstruktur, C40 i NbSi2 form, ges C54 ett ”mönster” att växa på. Kristallplanet (001) i
C40 är väldigt likt (001) i C54 detta gör att NbSi₂ som bildas redan vid 650°C leder till C54 TiSi₂ tillväxt utan att C49 fasen bildas. I de Cross-Bridge Kelvin (CBK) kontakter med TiSi₂ som analyserades, bildades C54 helt eller delvis i 25 µm² kontakthål men i de mindre 0.5 µm² endast C49. I kontakterna med (Ti,Nb)Si₂ bildades C40 fasen i samtliga, dvs. den förvandrade C54 uteblev helt, enligt XTEM mätningar. Tre skäl till detta kan vara: en för tjock niob film, kiseldiffusionen genom (Ti,Nb)Si₂ kan vara upp till 100 gånger längsammare än genom TiSi₂ och att en epitaxiell upplinjning mellan underliggande C40 (Ti,Nb)Si₂ gjorde att TiSi₂ på ytan förblev i C40 fas.

Efterföljande undersökningar inriktades på Ni-Si-Ge. Den första artikeln handlar om när nickel reagerar med poly-Si och poly-Si₀.₄₂Ge₀.₅₈ i temperaturintervallen 450 °C – 850 °C. Nickelmonosilicid som är läggersistiv bildades i den första reaktionen upp till 700 °C. Vid 750 °C bildades den höggersitiva fasen NiSi₂, till skillnad mot protvet med Si₀.₄₂Ge₀.₅₈ substrat där det inte bildades någon disilicid ens vid 850 °C. Det fanns även skillnader för de ”låga” temperaturerna. När nickel reagerade med Si₀.₄₂Ge₀.₅₈ vid temperaturer över 600 °C fann vi med hjälp av XRD och EDS en kraftig utdiffusion av germanium från NiSi₁₋ₓGeₓ och samtidigt att en ny Si₁₋ₓGeₓ bildades med x större än 0.58. Genom att beräkna ternära fasdiagram kunde de experimentella resultaten knytas till teoretiska. I nästa artikel studerades töjda- och relaxerade- Si₁₋ₓGeₓ filmers reaktion med nickel. Töjningsgraden befanns vara av avgörande betydelse för hur mycket den bildade NiSi₁₋ₓGeₓ filmen agglomererade. Enligt beräkning av ytvännan gjorde germanium att ytvännan sänktes i gränsyntan mellan NiSi₁₋ₓGeₓ och Si₁₋ₓGeₓ. Detta leder enligt beräkningar till ökad agglomerering. Genom att använda fasdiagrammen som fastslades i artikel II kan sammansättningen i ett övre Si₁₋ₓGeₓ lager skräddarsys för att när det reagerar med nickel bildar en NiSi₁₋ₓGeₓ i termodynamisk jämvikt med underliggande Si₁₋ₓGeₓ. Med x=0.23 ska z vara 0.02 vilket approximerades med 0%. Ett tunn kiselag reagerade med nickel och bildade NiSi ovanpå Si₀.₇₇Ge₀.₂₃ som enligt mätningar var stabilare än en NiSi₀.₇₇Ge₀.₂₃ bildad från Si₀.₇₇Ge₀.₂₃. Den bildade siliciden på enkristallina substrat visade upp en kraftig textur så fort som germanium fanns med i substratet. Enligt polfigurmätningar kombinerad med simuleringar kunde det fastställas att NiSi₀.₈Ge₀.₁₃(013) var parallell med Si₀.₈Ge₀.₂(001) samt att NiSi₀.₈Ge₀.₁₂(200) parallell med Si₀.₈Ge₀.₂(111). Skålet tros ligga i att NiSi₁₋ₓOₓ föröker undvika ett kristallografiskt läge som gör att gränsyntan mot Si₁₋ₓGeₓ liknar den, i närvaro av germanium, icke funna disilicidfasen. I den sista artikeln där NiSi₀.₈₂Ge₀.₁₂ bildades på p⁺-Si₀.₈₂Ge₀.₁₈ i en CBK kontakt, visade det sig att germanosiliciden bildades både vertikalt och även lateralt under oxiden som definierar kontakthål. Genom att modellera kontakten hormetliga geometri i en s.k. 3D modellering kunde den lägsta kontaktresistiviteten bestämmas till 5×10⁻⁸ Ωcm² vilket uppfyller den ”Roadmap” som gäller till år 2010.
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