Doctoral Thesis

Ballistic electron emission microscopy on low dimensional structures

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Ballistic Electron Emission Microscopy on Low Dimensional Structures

A dissertation submitted to the
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presented by

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Kurzfassung


Im zweiten Teil dieser Arbeit wurden selbst-organisierte Ge Inseln auf (100) orientierten Si-Substraten untersucht. Da Ge eine 4.2% höhere Gitterkonstante als Silizium aufweist, wächst es im sogenannten Stranski-Krastanow Modus, d.h., es kommt zur spontanen Ausbildung von facettierten Ge Inseln auf einem sogenannten 'Wetting-Layer', sobald eine kritische Bedeckung erreicht ist. Die Ausdehnung dieser Inseln liegt im Nanometerbereich. Um diese Inseln in ein Bauteil zu integrieren, ist es unumgänglich, sie in eine
Abstract

In this work two different kinds of nanoscale structures were investigated. In the first part we focused on the fabrication of epitaxial cobaltdisilicide wires on silicon(111) substrates. Metallic nanostructures have been attracting great interest in the last years, for both interesting new physical properties and applications in sub-μm-devices. Especially metallic silicides are highly interesting materials because of their excellent compatibility with silicon technology. Due to the progressing reduction of feature size the optical lithography techniques reached their limit, so new lithography techniques with resolution below 70 nm have to be found. Line widths smaller than 30 nm can be achieved with scanning probe lithography techniques but also with focused ion beams (FIB), but these techniques are rather slow and cannot -except FIB- be used for parallel processing. In this work we present a new approach for patterning CoSi₂ films by making use of self organized growth of Si on top. The growth kinetics at low coverages of silicon on CoSi₂(111) has been investigated by scanning tunneling microscopy (STM). By adjusting coverage and deposition temperature we succeeded in growing an array of Si lines parallel to the silicide surface steps, whose width was determined by the wafer miscut. Using the selective etch-rate of HF the Si wires can be used as an etch mask for the fabrication of epitaxial CoSi₂(111) lines. Line widths below 100 nm across the entire three-inch substrate were easily obtained without needing any lithography techniques.

In the second part self organized germanium islands on (100) oriented silicon substrates were investigated. Due to its high lattice mismatch of 4.2% relative to silicon Ge grows in the so called Stranski-Krastanow mode, i.e., the spontaneous formation of nanoscaled faceted islands takes place on top of a wetting layer, once a certain coverage has been reached. For any application the islands must be embedded in a crystalline Si matrix. Since alloying and Ge segregation can strongly modify the island morphology, the growth parameters must be carefully adjusted. After developing an appropriate growth procedure, Ge islands embedded in a 10 nm thick Si matrix were first investigated by STM. The buried islands cause a significant deformation of the Si surface. From the surface distortion, the strain distribution
could be calculated. In a second step the buried Ge islands were investigated by ballistic electron emission microscopy (BEEM). For that purpose a thin epitaxial cobalt disilicide layer has to be deposited on top of the Si/Ge/Si heterostructure. The larger of the buried islands affect the growth kinetics of the silicide layer in such a way, that holes with varying depth and lateral size are formed. Their density was small enough, however, that BEEM measurements could be performed on the planar surface in between. We succeeded for the first time to detect buried Ge dots exclusively by means of BEEM. The islands influence linear interfacial defects such that they form rectangles instead of the straight lines found before at cobalt-disilicide/silicon(100) interfaces. The line defects are an accumulation of point defects, most probably vacancies. Therefore they diffuse preferably into regions with compressive strain. So they accumulate into misfit dislocations or at the border of the inhomogeneous strain field caused by buried Ge dots. The interfacial Schottky barrier is lowered due to these interfacial defects, so they could best be detected at lower voltages near the onset of the BEEM current. They act as markers for the position of the buried structures. At higher energies a decreased BEEM current through the Ge islands was observed. This contrast can be attributed to a lower electron-hole pair generation rate caused by the lower density of states effective mass of the Ge holes. With these BEEM measurements we could verify a real shape transition of the islands. Before overgrowth they were oriented parallel to the <100> surface directions, afterwards they are rotated by 45°.
Chapter 1

Ballistic Electron Emission Microscopy

1.1 Introduction

The formation of semiconductor interfaces and their characterization has been a topic of great interest in solid state physics for many years. Surface sensitive techniques can be used to investigate the initial stages of interface formation, but the study of electronic properties of completed interfaces relies on traditional electrical probes, such as current-voltage or voltage-capacitance measurements [1], or on optical methods as internal photoemission [2]. All these techniques are spatially averaging, such that local variations of interface properties are hard to access. In 1988 Kaiser and Bell found a different approach for the investigation of metal/semiconductor interfaces. Ballistic electron emission microscopy (BEEM) [3] was developed out of scanning tunneling microscopy (STM) [4] utilizing the original set-up in a three electrode configuration. As in the STM, a tunneling current is maintained between a sharp metallic tip and a metallic or semiconducting sample by applying a bias voltage. One of the main advantages of this technique is a resolution of interface properties comparable to that of the STM (down to 1 nm). The carriers injected into the sample can have a kinetic energy up to a few electron Volts (eV) depending on the tip bias, and travel ballistically until they undergo a scattering event. A typical BEEM sample
Figure 1.1: Scheme of the set-up of a BEEM experiment: hot carriers are injected into a metal base layer by the tip of a STM. A fraction of the carriers crosses the Schottky barrier at the interface to the semiconducting substrate and gives rise to the collector current $I_c$ measured with help of the metallic back electrode. In our experimental set-up base and collector are virtually grounded, in contrast to 'conventional' STM set-ups where usually the tip is connected to ground.

consists of a metal base layer grown on top of a semiconducting substrate. When the thickness of the base layer is smaller than the mean-free path for scattering, many of these hot carriers may propagate through the metal film and reach the interface. If their energy is above the Schottky barrier height and if conservation laws restricting total energy and momentum parallel to the interface are satisfied, these carriers contribute to the BEEM or collector current $I_c$ measured with the help of an ohmic back contact. From the variation of the BEEM current with position and tip bias, information about the local electronic structure of the base layer and the base/substrate interface is obtained. In particular the effect of structural defects, which can sometimes also be identified by means of STM topography scans, on the electronic properties of the sample (e.g., Schottky barrier height), can be studied with high resolution.

By varying the voltage between tip and base, the energy distribution of the hot carriers can be controlled, and spectroscopy of interface carrier transport
Figure 1.2: (a)/(b) Energy diagrams for BEEM of a metal base-semiconductor collector Schottky barrier system without (a) and with (b) applied tunneling voltage $V_t$. In the case of (b), electrons within an energy higher than the Schottky barrier height $\Phi_B$ can cross the interface. (c) Example of a theoretical spectrum. Such a spectrum displays a threshold corresponding to the interface barrier height $\Phi_B$.

may be performed. Fig. 1.2(a)/(b) shows the energy diagram of a metal base/n-type semiconductor collector Schottky barrier system without/with applied tunneling voltage $V_t$. Fig. 1.2(c) displays the simplest spectrum that may be obtained with BEEM, when electrons are injected into the base. For tunneling voltages less than the interface barrier height between base and substrate, none of the injected electrons have a total energy equal to or greater than the barrier height, and the measured collector current will be zero. As the tunneling voltage $V_t$ is increased to values in excess of the barrier height $\Phi_B$, i.e., $eV_t > \Phi_B$, some of the hot electrons cross the interface into the semiconductor conduction band, and a collector current is observed. The location of the threshold in the spectrum is defined by the interface barrier height $\Phi_B$. The magnitude of the current above the threshold and the spectral shape also yields information on interface transport. A spectroscopy of the valence band structure may also be performed with BEEM utilizing hot holes as a probe. The theory describing the spectra and the different configuration using electrons/holes on n/p-doped substrates will be discussed in the following section.
1.2 Configurations of BEEM

In order to collect the carriers overcoming the interface barrier, a doped semiconducting substrate is used. A n-doped substrate is used for collecting electrons, since the band bending accelerates the carriers away from the interface. Analogously a p-doped substrate is used for detecting hot holes. In the usual forward BEEM mode (Fig. 1.3 (a), (b)) the same kind of carriers is collected as the ones emitted by the tip. The most 'comfortable' configuration is forward BEEM on n-semiconductors. The energy distribution of the electrons transmitted into the base is peaked at the Fermi-level of the tip, indicated by a grey area above the base in Fig. 1.3(a). As soon as the applied bias voltage corresponds to the barrier height, a large number of electrons is available for being collected in the substrate. In the reverse mode for n-doped substrates (see Fig. 1.3(c),) only majority carriers generated by inelastic scattering events contribute to the BEEM current $I_c$. The energy and momentum distribution of the carriers reaching the interface will therefore be broader compared to forward BEEM experiments and as a consequence the signal will be smaller. In the forward mode on p-doped samples, the

![Energy diagrams of BEEM in the forward/reverse configuration for electron (a)/(c) and hole injection (b)/(d). The energy distributions of the carriers in the base and in the collector are indicated by gray areas.](image)

Figure 1.3: Energy diagrams of BEEM in the forward/reverse configuration for electron (a)/(c) and hole injection (b)/(d). The energy distributions of the carriers in the base and in the collector are indicated by gray areas.
energy distribution of the hot holes is peaked at the Fermi level of the base (Fig. 1.3(b)), and the transmitted carriers stem from the low energy tail, so only a small number may be transmitted over the Schottky barrier into the collector. Here a larger signal is possible for the reverse mode, since the injected electrons are again peaked at the Fermi level of the tip (Fig. 1.3(d)), and at higher energies the number of the holes generated by electron-hole generation can exceed the number of holes transmitted in the forward mode at the same absolute value of $V_f$ [6].

1.3 The basics of BEEM

One of the main motivations for ballistic electron emission microscopy was the possibility to determine locally resolved the Schottky barrier height of metal-semiconductor contacts. As shown in Fig. 1.2(c), this may simply be done by determining the threshold of a measured spectrum. But one has to take into account that the magnitude of the collector current $I_c$ is usually in the range of some pA, often even lower, as it rises from zero in the threshold region. Since measurements of such small signals are always affected by noise, the determination of $\Phi_B$ is only possible within a large error range unless many spectra are averaged. The knowledge of the power law describing the shape of the spectra near the threshold allows a more accurate fit and therefore increases the accuracy of measuring $\Phi_B$.

In order to obtain an analytical model for the shape of the BEEM spectrum near the onset, one can describe the BEEM process by four independent steps [5, 3, 7].

- Tunneling from the tip to the metal film, resulting in an energetic and angular distribution of the carriers in the surface region of the metal.

- Transport of the carriers through the metal film. Elastic and inelastic scattering may lead to a broadening of the initial tip-emission characteristics and secondary carrier generation may take place. If band structure effects are also taken into account, which can lead to a fo-
cusing of the carriers within the film [8, 9, 10], this step can no longer be assumed to be independent.

- Transmission across the metal/semiconductor interface which depends, e.g., on conservation of lateral momentum and energy.

- Transport inside the semiconductor, where back-scattering can occur, or impact ionization can lead to secondary carrier generation.

Under the suggested separation one can write the following general expression for the BEEM current \( I_c \):

\[
I_c(V_i) = \int_{-\infty}^{\infty} dE \int_{IBZ} d\mathbf{k}_\parallel D(V_i, E, \mathbf{k}_\parallel) [E(E, \mathbf{k}_\parallel)] T(E, \mathbf{k}_\parallel) \rho(E) \]  

(1.1)

The integration is performed over the energy \( E \) measured with respect to the base Fermi level and over the component of the carrier wave vector \( \mathbf{k}_\parallel \) parallel to the interface inside the first 2D interface Brillouin zone (IBZ) of the metal-semiconductor junction. \( D(V_i, E, \mathbf{k}_\parallel) \) is the distribution of the hot carriers arriving at the metal surface after tunneling from the tip (section 1.3.1). The change of the distribution due to the transport through the film is considered in \( P(E, \mathbf{k}_\parallel) \) (section 1.3.2), and the transmission coefficient \( T(E, \mathbf{k}_\parallel) \) considers energy and momentum conservation which have to be fulfilled for carrier entrance into the semiconductor (section 1.3.3). Inelastic processes, as carrier multiplication due to impact ionization, are considered in \( \rho(E) \) describing the transport within the semiconductor (section 1.3.4). Here no momentum dependence has been considered, since changes in \( \mathbf{k}_\parallel \) will not affect the transport within the substrate.

### 1.3.1 Tunneling injection of carriers

The simplest approximation can be made by assuming a planar tip, so that planar tunneling theory can be applied. This approximation is sufficiently well suited to obtain the energy distribution of the tunneling current, while the angular resolution depends more critically on tip shape and surface morphology [11]. A scheme of the tunneling process is shown in Fig. 1.4. An external voltage is applied to the tip while the sample is connected to ground.
1.3. The basics of BEEM

The sign of \( V_t \) is negative, when electrons are injected from tip to sample, which is the configuration used for BEEM measurements in our set-up (see Fig. 1.1). The two electrodes are separated by a potential barrier of width \( d_G \). The barrier height is given by the average of the two work functions, \( \Phi_{\text{av}} = (\Phi_T + \Phi_M)/2 \), when no tunneling voltage is applied. Applying a (negative) bias decreases the mean barrier height for forward tunneling by \( +eV_t/2 \), when the approximation of a triangular barrier shape is used (see Fig. 1.4). In the Wentzel-Kramers-Brillouin (WKB) approximation [11], which assumes

\[
\Phi_T = \Phi_T - eV_t/2
\]

the wavelength of the electrons to be small compared to the spatial extension of the potential variations, i.e., the width of the tunneling gap \( d_G \), the distribution of the tunneling current \( D(V_t, E, k_\parallel) \) depends only on the (imaginary) normal component of the electron momentum in vacuum \( k_{\perp}^{\text{vac}} \), the densities of states of the tip and the metal, \( \rho_T \) and \( \rho_M \), the respective Fermi distribution functions, and the applied tip bias \( V_t \). The energy \( E \) is measured with respect to the sample Fermi level \( E_F \) and the temperature was chosen to be \( T=0 \) K.

\[
D \left( E, V_t, \vec{k}_\parallel \right) = \rho_T(E + eV_t)\rho_M(E) \exp \left( i\vec{k}_\perp^{\text{vac}} d_G \right) \right|^2 \tag{1.2}
\]

In the following a free-electron like dispersion relation for tip and metal will be assumed characterized by an effective carrier mass \( m \). So the kinetic
energy of the electrons can be written $E = E_\perp + E_\parallel - E_F$ with $E_\perp = \hbar^2 k_\perp^2 / 2m$ and $E_\parallel = \hbar^2 k_\parallel^2 / 2m$. For tunneling only the component perpendicular to the surface, $E_\perp$, associated with the motion normal to the tunneling barrier is relevant and can be rewritten as:

$$E_\perp = E - \hbar^2 k_\parallel^2 / 2m + E_F$$  \hspace{1cm} (1.3)

So Eq. 1.2 changes to:

$$D(E, V_t, k_\parallel) = \rho_T(E + eV_t, k_\parallel) \rho_M(E, k_\parallel) \times \exp \left( -\frac{\hbar}{m} \left[ \Phi_{eF} - \frac{eV_t}{2} - (E - \frac{\hbar^2 k_\parallel^2}{2m}) \right] d_G \right)$$  \hspace{1cm} (1.4)

Eq. 1.3 with Eq. 1.4 reveals the tunneling current $I_t$ as exponentially decreasing for energies $E_\perp$ lower than the maximum possible energy $eV_t$, and for angles $\theta = \arctan(k_\parallel / k_\perp)$ deviating from normal injection. The tunneling current will therefore always be dominated by states with the highest energy and the smallest, i.e., zero parallel momentum. This is especially important for BEEM using holes as injected carrier species (compare with Fig. 1.3(d) and (e)). Thus it is convenient to define an energetic ($\Delta E$) and angular ($\Delta \theta$) width, at which the exponent in Eq. 1.2 is reduced by one and the tunneling probability by a factor of $1/e$. Both values give a definition of the so called injection cone (IC) predicted by this free-electron theory. More elaborate calculations predict $\Delta E$ to be between 0.2-0.5 eV [12], which is in acceptable agreement with the planar tunnel theory. Since $\Delta E$ and $\Delta \theta$ are the parameters determining the injection cone IC, it is convenient to rewrite Eq. 1.4 to:

$$D(E, \theta) \propto \exp(E / \Delta E) \cdot \exp(-\theta^2 / 2\Delta \theta^2)$$  \hspace{1cm} (1.5)

In 1985 Tersoff and Hamann [12] developed a more sophisticated model taking into account the finite lateral extension of the tip by modeling it as a spherical s-wave function. They found the tunneling current to be proportional to the local density of states (LDOS) at the position $\vec{r}_0$ of the tip above the sample, i.e. $I_t \propto \rho_M(\vec{r}_0, E_F)$. It has to be considered that this
1.3. The basics of BEEM

formula is reasonable for values of the tunneling voltage in the mV range as they are typical for pure STM experiments. In the case of BEEM the bias exceeds easily the value of some V! Taking that into account (see Appendix A) $I_0$ is then proportional to the integral of the LDOS over the whole energy range where tunneling is possible (Eq. 1.6).

\[
I \propto \int \limits_{E_F}^{E_F+eV} dE \rho_S(\vec{r}_0, E) \rho_S(\vec{r}_0, E) = \sum \nu |\Psi_{\nu}(\vec{r}_0)|^2 \delta(E_{\nu} - E) \tag{1.6}
\]

1.3.2 Transport through the metal film

On propagating through the metal film, the injected hot carriers may be scattered by optical and acoustical phonons, electrons and localized impurities. Scattering at phonons will result in only minor energy losses on the order of 10 mV, which is usually not significant for BEEM, where the typical energy of the hot carriers is in range of some eV. They may undergo many scattering events and still have enough energy to cross the Schottky barrier at the interface. So phonon scattering can be regarded as a quasi-elastic process. Much more important is the influence on the spatial distribution. Further elastic scattering may occur at lattice defects, where the carriers also pick up a random amount of lateral momentum. These elastic processes lead to a broadening of the momentum distribution of the ballistic carriers, increasing the opening angle of the injection cone and can strongly influence the magnitude and shape of the BEEM current, and the spatial resolution of BEEM measurements [14]. BEEM measurements are often performed at 77 K, which reduces the influence of phonons, and thin films of excellent crystalline quality are used as base. So this kind of scattering processes may safely be neglected. Another source of elastic interaction is the reflection at the interface itself, i.e., standing wave formation due to reflection at the CoSi2/Si(111) interface has been observed [13].

Concerning inelastic scattering events, only the electron-electron interaction has to be considered, since energies up to 10 eV are still too low for plasmon excitations [16]. If the kinetic energy $E_k$ of the injected carriers is only
slightly higher than the barrier height $\Phi_B$, then the probability to cross the interface is very small after scattering, since the typical loss of energy due to an inelastic scattering event is about $2/3E_k$ [15]. It is therefore unnecessary to follow the path of the scattered carriers, because they will not contribute to the BEEM current. Hence the influence of inelastic scattering can simply be described as an attenuation of the BEEM current, with a damping term proportional to $d/\lambda_{inel}(V_i)$, where $d$ is the thickness of the film and $\lambda_{inel}(V_i)$ the energy dependent mean-free-path. Undergoing an inelastic scattering event, a ballistic carrier may suffer an energy loss between $E$ and zero, therefore the number of final states available for that carrier will be proportional to $E$, when a constant density of states is assumed. The number of secondary carriers, generated by the inelastic interaction with the ballistic carrier, will depend linearly on the energy loss. Therefore the total scattering probability will be proportional to $E^2$.

$$P(E, \bar{E}_i) = \exp\left(-\frac{d}{\lambda_{inel}(V_i)}\right) \approx \exp\left(-cE^2\right) \quad (1.7)$$

At higher voltages ($|V_i| > 2.5$ eV) scattered and generated secondary carriers may have sufficient energy to cross the interfacial barrier and dominate the BEEM current. That explains the theoretical underestimation of the mean-free-path at higher energies.

At lower voltages transport should be ballistic in thin defect-free epitaxial films and no scattering events should take place. This is also proved by the observation of quantum interference effects [17], which can only occur when the coherence of the carrier beam is conserved. The transport of a free electron with isotropic mass within the metallic base can be modeled by the propagation of a three dimensional wave-package [20]. As the wave package propagates through the film, it gets broader. For time $t \to \infty$ the opening angle of the beam within the layer approaches:

$$\tan(\theta/2) = \frac{(\Delta k_{||})/2}{m_\perp} \frac{m_\perp}{m_\parallel} \quad (1.8)$$

In the case of an isotropic mass the opening angle in real space is equal to the opening angle in momentum space. Until recently, this free-electron model was applied to all investigated BEEM systems, no band structure effects
were taken into account. E.g., an in-plane mass $m_\parallel$ much larger than the perpendicular mass $m_\perp$ would result in a less pronounced spreading of the carrier beam and therefore in a better resolution. In the limit of $m_\parallel = \infty$, no spreading at all would take place and therefore the resolution would be independent of the base layer thickness! Of course, this calculation performed by T. Meyer [20] does not adequately describe transport in CoSi$_2$ or in any other metal, but it shows clearly, that band structure effects cannot be neglected for an accurate description of transport within the base layer. The success of imaging interfacial point defects [21] and interfacial misfit dislocations [22] at the CoSi$_2$(111)/Si(111) interface was rather surprising. Although the thickness of 2.7 nm of the CoSi$_2$(111) film was very small, free-electron theory could not explain the resolution of 1 nm at the CoSi$_2$(111)/Si(111) interface. The opening angle of 40° predicted by classical BEEM theory [7] for that case would never allow such a resolution. Recently, K. Reuter and co-workers published a new theoretical approach for hot electron propagation in CoSi$_2$(111) taking into account the empirical tight binding band structure of the material. They predicted a focusing of the BEEM current along the $<1\bar{1}1>$ direction in these films [9], which should result in a thickness-independent resolution. This focusing effect could be verified experimentally for electrons by Meyer et al. [10]. Expanding the theory by taking into account the valence band structure of CoSi$_2$ they predicted a similar hole focusing effect and confirmed it also by experiments. With the 'classical' BEEM theory [7] such a resolution, and especially its thickness independence, could never be explained.

1.3.3 Transmission across the interface

Transmission across the metal semiconductor interface is described by the transmission probability $T(E,k_\parallel)$. We assume a perfectly smooth interface without any lateral structure, so that conservation of $E$ and $k_\parallel$ has to be expected. A carrier will then be transmitted when a corresponding state with the same $E$ and $k_\parallel$ exists within the semiconductor. Since crystalline periodicity can be expected on both interface sides, the problem of matching states can be reduced to the first interface Brillouin zone (IBZ). In the case
of a direct semiconductor with a parabolic band structure the conduction band minima (CBMs), resp. valence band maxima (VBMs) will be located in the zone center, i.e., at $k_{\parallel}=0$. Reaching the BEEM onset, where $E=\Phi_B$, only states with $k_{\parallel}=0$ will be available for transmission. With increasing tunneling voltage states with $k_{\parallel} \neq 0$ will be available too, when $E_{\parallel} \leq E-E_\perp$ with $E_\perp=\Phi_B$. The so called critical angle cone (CAC) lying around the zone center with an opening angle $\alpha_C$ is then given by [24]:

$$\sin^2 \alpha_C = \frac{m_t}{m_m} \frac{e|V_t|-e\Phi_B}{E_F + e|V_t|}$$

(1.9)

where $m_t$ and $m_m$ are the transverse masses of the semiconductor and the metal. In the case of an indirect semiconductor, the CAC will located around some $k_{\parallel} \neq 0$. Since tunneling favors states with small $k_{\parallel}$, one expects a much smaller BEEM current in such a metal-semiconductor system.

$\alpha_C$ and $\theta$ are parameters strongly influencing the BEEM resolution. If scattering and band structure effects are neglected, then $\theta$ determines the 'spot' size of the carrier beam impinging on the interface and $\alpha_C$ the 'hole', where the beam can shine through (see Fig. 1.5). So in the classical BEEM theory the minimal resolution will be $\approx d \cdot \theta$. Close to the threshold, where $\alpha_C < \alpha$, the resolution may improve to $\approx d \cdot \alpha_C$. But one has to consider, that in the case of a perfect interface, there would be nothing there to resolve. As soon as the interface symmetry is broken, i.e., by point defects or dislocations, these features will act as scattering centers and therefore the conservation of $k_{\parallel}$ will no longer be fulfilled.

![Figure 1.5: Injection (IC) and critical angle cone (CAC) in the electron picture of BEEM](image)
Until now the barrier maximum was assumed to be located at the metallurgical interface. But due to the image potential, acting on carriers near the metal-semiconductor interface, a lowering of the original barrier height by ΔΦ takes place. Simultaneously the maximum height of the barrier is shifted by the amount of x_m into the semiconductor [1]. By assuming a linear variation of the uncorrected potential (see Fig. 1.6), x_m and ΔΦ can than be described as follows, where ε_s is the static permittivity of the semiconductor and ε the electric field strength:

\[ x_m = \sqrt{\frac{q}{16\pi\varepsilon_s \varepsilon}} , \quad \Delta\Phi = \sqrt{\frac{q\varepsilon}{4\pi\varepsilon_s \varepsilon}} \]  (1.10)

### 1.3.4 Transport within the semiconductor

Using the picture of an abrupt barrier directly located at the interface, any current changing processes within the semiconductor might be neglected. As soon as the carriers have entered the semiconductor, they will, due to the band bending, be accelerated away from the interface instead of traveling back into the base. Additionally, since there is no further \( k_{||} \) filtering in the collector, any elastic scattering event will be without influence onto the final BEEM signal. Inelastic electron-electron scattering will not influence the BEEM signal shape and magnitude till \( E - \Phi_B \approx E_{Gap} \). So \( S(E) \) can be set to 1, i.e. the transport within the collector can be ignored for the analysis of

![Figure 1.6: Potential profile without (dashed line) and with influence of the image force.](image-url)
the BEEM spectra near the threshold. Considering the image force effect, as shown in Fig. 1.6, the potential barrier maximum will be located about $x_m=2.5$ nm away from the interface. Elastic and inelastic processes taking place in the region in front of the barrier maximum can influence the transport. Optical phonon back-scattering was found to affect mostly the BEEM current by reducing the effect of quantum mechanical reflections at the interface [26]. This explains why often a quadratic behavior of experimental BEEM spectra has been observed.

1.3.5 Conclusion

Taking into account the results of the sections 1.3.1, 1.3.2, 1.3.3 and 1.3.4, we can now develop a simple power law for the BEEM spectra near the threshold region. Using that effective mass approximation, the BEEM current near the threshold can finally be described by:

$$I_C(V_t) = R \cdot (e \cdot |V_t| - \Phi_B)\alpha$$  \hspace{1cm} (1.11)

with $\alpha=5/2$ taking into account quantum mechanical reflections [7], and $\alpha=2$, when they are neglected [3, 5]. Detailed calculations can be found in the reviews of Bell [25] and Prietsch [7]. As a more elaborate work taking into account also band structure effects, the publications of Reuter et. al. are highly recommended [8, 9, 33].
Chapter 2

Experimental

2.1 Sample preparation and growth

2.1.1 Introduction

The system in which the samples were grown and investigated consists of three chambers. The MBE chamber, a commercial VG80 MBE system, for growth, a middle chamber connected with the load lock for introducing the samples into the system and equipped with a high temperature heating stage, and the STM chamber. The base pressure during growth was between $10^{-11}$ mbar and $10^{-10}$ mbar. Two Temescal electron beam evaporators were used as sources for silicon and cobalt, a Knudsen cell for germanium. The growth rates for Si and Co were monitored using quartz balances calibrated by growing a thick reference film and weighing it. The amount of the deposited germanium was controlled by reflection high energy electron diffraction (RHEED), since the thickness dependent change in morphology is coupled with a change in the RHEED pattern. The growth temperature was monitored with a thermocouple mounted in the middle of the heating plate positioned above the rotatable sample stage. The thermocouple was calibrated by measuring the radiation emitted from a heated Si wafer with an infrared pyrometer. The samples were rotated during growth to minimize thickness fluctuations. A shadow mask was connected to the sample stage to obtain a diode area of 0.5 cm$^2$ necessary for BEEM measurements. The
crystal quality was controlled routinely by observing the RHEED pattern. All samples were grown on well oriented 3 inch silicon substrates. They were chemically cleaned and before growth the native oxide was removed from the surface by thermal desorption.

2.1.2 BEEM samples

BEEM samples have to be designed in a special way. In order to measure the interfacial barrier between a semiconductor and a metal, the semiconductor must exhibit a rather low doping level, otherwise an ohmic contact would be formed at the interface. On the other hand an ohmic contact is needed on the rear side of the sample to collect the BEEM current. Fig. 2.1 shows the layer structure for a CoSi$_2$/Si(100) BEEM sample. By depositing 10 nm of metallic CoSi$_2$ at the rear side of a degenerately doped silicon wafer of n$^+$- or p$^+$-type, the ohmic back contact essential for the detection of the BEEM signal is formed. As depicted in Fig. 2.1, a gold spring is pressed at the back side at of the sample to collect the BEEM signal. On top of the substrate a 300 nm thick undoped silicon layer is deposited, on which the silicide layer is grown by stoichiometric codeposition of Co and Si through the shadow mask.
2.1. Sample preparation and growth

Fixed at the sample stage. Thus the potential decays approximately linearly from the metal/semiconductor interface to the doped substrate in contrast to the parabolic variation depicted in Fig. 1.3. In order to minimize current leakage due to thermally activated currents across the Schottky barrier and due to defects in the diode, the diode area has to be reduced to a minimum, to keep the noise in the measured BEEM-current as low as possible. But the STM contact spring, as shown in Fig. 2.1, has also to be placed within the diode area. As a compromise between these two needs the diode is rhombic-shaped with an area of 0.5 cm². In addition all BEEM measurements were performed at low temperatures (here T=77 K) in order to minimize the noise in the BEEM-current as much as possible.

2.1.3 CoSi₂(100) growth

For all BEEM experiments degenerately n-doped (As, 5 mΩcm) Si(100) substrates were used. The chemically pre-cleaned 3 inch wafers were outgassed at a temperature of 500°C for 1-2 hours. For the removal of the silicon oxide the substrate was annealed at 800°C for 4 min while a small silicon flux was maintained. In RHEED a sharp 2x1 pattern appeared upon oxide desorption. After reducing the temperature to 700°C a 240-300 nm thick silicon buffer was grown while rotating the sample stage. The silicide was grown in a special template technique. At T=50°C 1.5 Å of Co were deposited at a rate of 0.3 Å/s followed by the codeposition of additional 1.5 Å of Co with the same rate and 5.3 Å of Si with a rate of 1.05 Å/s, which corresponds to a stoichiometric relation. The resulting amorphous template layer crystallized during a 5 min annealing step at ~ 300°C, observable in a change of the originally featureless RHEED image to a $\sqrt{2} \times \sqrt{2}$ pattern. The final silicide thickness was reached by a second codeposition of 6 Å of Co at a rate of 0.3 Å/s and 20 Å of Si at a reduced rate of 0.95 Å/s. The at first poorly crystalline layer was covered with additional 2 Å of Si. The desired surface and crystal quality was obtained by a second annealing step up to a temperature of 550°C. If during heating up the 3$\sqrt{2} \times \sqrt{2}$ RHEED pattern, characterizing the Si rich surface phase, disappeared, additional small amounts of Si were deposited. With this procedure mostly pin-hole free CoSi₂(100)/Si(100) films
with smooth interface and surface [31] are obtained. The same growth procedure was used for the silicide if instead of a simple silicon layer a Si/Ge/Si heterostructure was overgrown.

2.1.4 CoSi$_2$(111) growth

The self organization of silicon on CoSi$_2$(111) layers was studied by means of STM, so no degenerately doped Si(111) substrates were needed. The preparation and the outgassing were performed as described in section 2.1.3. After outgassing the temperature was raised to $T = 850^\circ$C for 4 min while a small Si flux was maintained to reduce the SiO$_2$ present on the surface. The 1x1 RHEED pattern changed to 7x7 when the temperature was lowered below 700°C. Then the 240 nm thick silicon layer was grown and annealed briefly at $T = 800^\circ$C. The surfaces obtained in this way were clean, 7x7 reconstructed and had a parallel arrangement of surface steps. Onto such a clean Si surface, Co and Si were co-evaporated at a rate of 0.3 Å/s and 1.05 Å/s for Co and Si, respectively, while the sample temperature was kept as low as 60°C. The total amount of Co deposited was 8 Å resulting in a silicide thickness of 30 Å. After the deposition the film was annealed in several steps up to a final temperature of about 650°C while the surface structure was monitored by RHEED. Additional silicon was supplied if the surface underwent a transition to the Co-rich surface structure, a process which can be identified by the observation of 2x2 reconstructed areas in RHEED. The growth procedure described above is known to result in smooth CoSi$_2$(111) layers, featuring an unreconstructed surface. The strain in these films is relaxed by the formation of a quasi-hexagonal network of partial dislocations. If strain relaxation is not desired, the films can be grown in a different way: Prior to co-evaporation of Co and Si, a Co template layer of 1.5 Å thickness was deposited at a rate of 0.3 Å/s onto the clean Si surface. The films grown following this procedure feature a much lower dislocation density, which is typically given by the step density present on the silicon surface due to the wafer miscut. Since the surface of strained CoSi$_2$/Si(111)layers is predominantly 2x1 reconstructed, which reduces the diffusion of Si, all of the films used for the study of self organization of silicon are grown without a Co template.
2.2 Measurement Set-Up

2.2.1 The STM

Since the STM chamber is attached to the same UHV system as the MBE, all samples could be investigated without exposing them to air. So no oxidation or surface contamination affect the measurement quality. After cooling down to room temperature, the samples were transferred into the STM. For BEEM measurements the sample and the microscope itself are cooled down to 77 K by filling two cryostats, in which the microscope and the sample stage are mounted, with liquid nitrogen. When exclusively STM measurements were performed, then the system stayed at room temperature allowing a faster change of samples. The microscope used for STM and BEEM is a home built Besocke walker [34]. Fig. 2.2(a) shows a photograph of the microscope from below, Fig. 2.2(b) a schematic sketch of the STM during measurement. The microscope consists of a macor head (H) in which four piezo tubes are mounted. The three outer ones carrying the microscope head (only two are visible in Fig. 2.2) with ruby balls at the ends are used for the coarse approach. The piezo tube in the middle is used for scanning. The tip is directly mounted at its end (see Fig. 2.2(a)). The sample (W) mounted in a ring shaped sample holder (WH) is placed directly onto the thick isolating ground plate (P) consisting of oxidized Si. The gold spring for the BEEM back contact (BS) is fixed into a small cavity within the plate. The microscope head is placed inside a metal cage (C). The three isolating Macor feet (F) stand directly on the sample surface. The tunneling contact is established by a gold spring (SS) fixed to the metal cage. This front contact and the STM-tip are located on the isolated diode area, which was formed by using a shadow mask during the growth of the base layer. The coarse approach piezos are standing on a segmented ring consisting of three planes inclined with a slope of 0.5 mm/120°. By applying a sawtooth voltage to the three coarse approach piezos, they move up or down these planes. In that way the whole microscope head is rotated and the tip screws forward or backwards from the sample surface. The entire sample and microscope arrangement is hanging on three stainless steel springs, which are fixed to
Figure 2.2: (a) Microscope cage with the microscope inside photographed from below. (b) Schematic drawing of the microscope during measuring. SP: scanning piezo tube with the tip mounted on top, F: macor feet, C: metallic cage, SS: gold contact spring for STM measurements, WH: sample holder, W: sample wafer, CP: piezo tubes for coarse approach with small ruby balls at the end, BS: gold contact spring guaranteeing an ohmic back contact for BEEM, P: insulating oxidized Si plate.

the top flange of the STM chamber. In normal operation the microscope is suspended by the springs inside a small chamber made from gold plated copper, which is in contact with the inner liquid nitrogen cryostat and thus cooled to 77 K. After inserting a new sample into the microscope, it is mechanically coupled to the bottom of the inner cryostat, in order to stabilize the sample temperature. For the measurement, the microscope is decoupled to reduce mechanical vibrations.

2.2.2 Data acquisition

The commercial Omicron control unit used for the STM and BEEM experiment is connected to a HP UNIX workstation by an IEEE-448 interface exhibiting two additional analog-to-digital converters (ACD's), one of which is used for BEEM. The measurement parameters can be set by a STM control program, which is also used for displaying STM and BEEM images during scanning and for performing several kinds of spectroscopy measurements. The amplifier electronics should be located as near as possible to the STM in order to reduce the pickup of electrical noise by the STM and BEEM.
2.2. Measurement Set-Up

signals. Therefore the first pre-amplifier stages for tip- and collector-current are mounted within the STM chamber. Since the STM itself suffers relatively often a drastic change of temperature from room temperature to 77 K and back, the pre-amplifier electronics is mounted underneath the top flange where the temperature is relatively stable. Fig. 2.3 displays the diagram of the pre-amplifier circuit. In the usual STM experiments the tunneling tip is virtually grounded. For BEEM measurement, however, $V_t$ has to be applied to the tip and also the tunneling current $I_t$ has to be measured there. Since the STM amplifier is also connected to the tip, the non-inverting input of the operational amplifier (OPA 111 BM) has to be set to the tip bias $V_t$ and the supply voltages have to be shifted by $V_t$. With this configuration the operational amplifier can still work in the middle of its range and $I_t$ can be detected simultaneously. The tunneling current is amplified by a factor of $10^5$, i.e., the resistance $R_d$ has a value of 100 MΩ. The noninverting input of the BEEM-operation amplifier (an OPA 128LM) is connected to ground.

Figure 2.3: Schematics of the in-situ amplifier circuit. The back contact of the sample is virtually grounded. The supply voltages of the tip-current amplifier are varied along with the tip bias in order to keep the amplifier in its optimal operation point.
Thus the sample back-contact is virtually grounded. The BEEM-current is also amplified by a factor of $10^8$ by the in-situ pre-amplifier. As mentioned before, the BEEM current is in the range of some pA, in contrast to the tunneling current which is usually set in the nA range. So further amplification and filtering is needed to improve the signal-to-noise ratio. Outside the vacuum chamber the BEEM signal is first low-pass filtered to reduce the noise level. Then it is amplified by another factor of 100 and offset corrected before it is fed into the STM control unit. The low cut-off frequencies of the filters used (9 Hz and 100 Hz for imaging and spectroscopy, respectively) make it imperative to work at slow scanning speeds while doing BEEM.

BEEM images are measured in the constant current (CC) mode, which is also the standard mode for recording STM topography images. While the tip is scanning over the surface (x,y-plane), the feedback loop adjusts the height $z$ of the tip in order to keep $I_t$ constant. The changes in height give information about the topography provided that the surface is chemically homogeneous. Simultaneously the collector current $I_C$ is recorded coupling topography and transport information.

Ballistic electron emission spectroscopy (BEES) was mostly also performed in the CC mode: the surface is scanned with a fixed tunneling current $I_t$ and a stabilization tunneling voltage $V_{Stab}$. At each point of the topography scan $V_t$ is then varied (between ± 2mV and ± 6V) and $I_c(V_t)$ recorded.

Scanning tunneling spectroscopy (STS) was mainly performed in the constant height (CH) mode measuring $I_t$ as a function of $V_t$. The tip is fixed at a certain height by setting the values of $I_{Stab}$ and $V_{Stab}$. In this way the local density of states (LDOS) of the sample surface can be determined.
Chapter 3

Self organization of Si on CoSi$_2$(111) films

3.1 Fabrication of epitaxial silicide wires

Self organization in epitaxial growth offers an easy and inexpensive way to fabricate ordered arrays of nanoscale structures, interesting both for their special physical properties and for the fabrication of devices. In heteroepitaxy it has been suggested to grow wires of one material running along the surface steps of a substrate made from another material in step-flow growth mode. The arriving adatoms would diffuse to the next upward step of the surface and nucleate there. By repeatedly depositing wire material and substrate material the formation of stacked wires embedded in the substrate material should occur (see, e.g., [37]). It is crucial for this procedure, that the diffusion of both materials is sufficiently fast, so that step-flow growth can be reached. In this work we suggest a different method to fabricate epitaxial CoSi$_2$ wires on a Si(111) substrate by a combination of self organized growth of silicon and an ex-situ wet-chemical etch, where Si is used as a mask. The Si mask formation is only possible because the diffusion of Si on the silicide surface is much faster than on Si itself. As a consequence the step-flow growth mode can be reached at temperatures as low as 350°C. This is crucial because the CoSi$_2$/Si(111) films used as a substrate, are not stable at temperatures much higher than 600°C, which are required to reach step-flow growth in Si/Si(111)
homoepitaxy. In STM experiments we have determined the temperature dependency of the diffusion length for Si/CoSi₂. For these experiments we used our STM in the conventional manner working at room temperature. It is well known that CoSi₂/Si(111) films can be epitaxially overgrown with thick silicon films (d ≥ 50 nm) of good quality, and devices have been fabricated out of CoSi₂/Si/CoSi₂ sandwich structures [38]. Contrary to this, little is known about the nucleation process and the early stages of Si growth on the silicide surface. The silicide films used for this STM study of the initial stages

![Figure 3.1: STM topography image of the surface of a 2.8 nm thick CoSi₂/Si(111) film. A hexagonal network is formed by misfit dislocations with \( \vec{b} = a/6 < \overline{211} > \), two of which are marked with a black arrow. (\( V_t = -2 \) V, \( I_t = 3 \) nA, gray scale range \( \Delta z = 0.75 \) nm)](image)

of epitaxial Si overgrowth were grown such, that the surface is predominantly unreconstructed as described in section 2 [27]. The unreconstructed phase of the surface is more preferable, since the 2x1 reconstruction, present on strained CoSi₂, was found to hinder surface diffusion. The strain in the silicide was relaxed by the introduction of a network of interfacial dislocations with \( \vec{b} = a/6 < \overline{211} > \). In our experiments we did not observe any influence of these dislocations on Si diffusion as long as the diffusion length is about the average step width. At higher temperature, where large islands with diameters above the step width appear, some of them nucleate on top of such dislocations. Fig. 3.1 shows the surface topography of a 2.8 nm thick CoSi₂ film. The hexagonal network of dislocations shows up on the unreconstructed surface as smooth surface steps. The surface steps of the silicide were again nearly parallel. The step height is 0.31 nm, which corresponds to the height of 1 bilayer (BL) of silicon. Onto these surfaces, we deposited Si at temperatures
3.1. Fabrication of epitaxial silicide wires

ranging from 200°C to 430°C and rates from 0.017 nm/s to 0.105 nm/s.

Figure 3.2: STM topography image of the surface of a 3 nm thick CoSi$_2$/Si(111) film after the deposition of 0.5 nm of Si. The dotted lines indicate the position of the silicide steps, bounding terraces A and B. On the wider terraces both steps are decorated (B). For narrower terraces (A) only the upwards step is decorated. The width of the silicon line is determined by the width of the terraces and can be quite small (arrow). ($V_t=2$ V, $I_t=0.2$ nA, gray scale range $\Delta z=2.5$ nm.)

In Fig. 3.2 a STM topography scan of a CoSi$_2$/Si(111) sample after deposition of 0.5 nm of Si at a rate of 0.1 nm/s and a substrate temperature of 350°C is shown. The silicon has obviously accumulated along the surface steps of the silicide. The average terrace width was about 90 nm. No island formation is observed. Most of the Si lines are bounded by an abrupt and straight step on one side, and a rougher step on the other. The straight step is positioned where the underlining silicide surface step is located. The rough step edge represents the growth front at the end of the deposition time. For most silicide steps, the Si is found to grow only on the lower terrace of the silicide (see, e.g., terrace A), but sometimes it also decorates the upper terrace (see terrace B). It is evident, that the wider a terrace, the more likely nucleation on the down-step becomes. The critical terrace width $w_{\text{crit}}$, at
which decoration of up- and down-steps starts to occur, is a measure for the diffusion length of Si. Actually the diffusion length $d \approx 2w_{crit}$, because adatoms are being reflected by a down-step and have to cross the terrace twice, before they attach to the up-step. Another interesting feature visible in Fig. 3.2 is the fact, that the fraction of the terrace which is covered by Si is nearly constant. An especially narrow terrace is indicated by an arrow. The Si line following the up-step is getting thinner as the terrace width decreases. Thus only material deposited on the same terrace contributes to the Si line. By choosing a substrate of higher misorientation the terrace width and consequently the width of the Si lines can be reduced at the same average coverage. The fraction of the terrace covered by silicon is controlled by the amount of material deposited. Earlier it was mentioned, that a total of 0.5 nm of silicon were deposited onto this particular sample. This is more than a bilayer of silicon and still only about half of the surface is covered. The

![Figure 3.3:](image)

(a) The fuzzy line is a line section taken across a terrace of the CoSi$_2$ surface displayed in Fig. 3.3(b), bounded by an up-step at $x=0$ nm and a down-step at $x=100$ nm. Si has accumulated at the left up-step. The smoother line displays the result of an analytical simulation of growth, assuming perfect diffusion of adatoms on the silicide and sticking on the silicon. (b) STM topography image of the same sample displayed in Fig. 3.2. The white rectangle marks the position were the cross section of Fig. 3.3(a) has been taken. ($V_t=2$ V, $I_t=0.2$ nA, gray scale $\Delta z=2.5$ nm.)
3.1. Fabrication of epitaxial silicide wires

reason for this can be found from line sections like the one shown in Fig. 3.3, taken in the direction orthogonal to a surface step. The profile shows silicon attached to an up-step on the left hand side, whereas the down-step on the right hand side is not decorated. The Si line is found to be always at least 2 bilayers high, which explains why only half of the surface is covered. On top of this Si base layer there are silicon islands, which are one bilayer high. The smoother line plotted in Fig. 3.3 along with the surface profile was obtained by a simple analytical approach. The simulation assumes perfect diffusion on the silicide and no diffusion at all on top of the silicon. Adatoms diffusing to the down-step of Fig. 3.3 are reflected and atoms hitting the up-step stick to it. Furthermore it is assumed, that if an atom meets a site, which is already occupied by silicon atoms, it hops on top of the latter until the thickness of 2 BL is reached. Although this is a very crude model it nicely fits the surface profile, which suggests that the assumptions are basically correct: the diffusion on silicide is much faster than on silicon, the adatoms are likely to jump onto the first bilayer which forms and almost all adatoms are reflected at a down-step. Note that the model does not take into account adatoms diffusing on the upper terrace located at x≤0 Å and not being reflected. However, the amount of additional material is quite small and knowing that about half of the adatoms will be traveling towards the down step, we can conclude that the probability for reflection is indeed very close to one. The detailed description of the analytical approach can be found in Appendix B. The large

Figure 3.4: AFM topography image of the sample shown in Fig. 3.2 after a brief HF-etch. Only the silicide below the silicon lines remains on the sample surface.
diffusion lengths of Si/CoSi$_2$ at temperatures far below the maximum annealing temperature of the silicide are essential for the self ordered growth of silicon, since there is no danger of pinhole formation or intermixing effects. By using the silicon wires as etch-mask, the fabrication of thin CoSi$_2$ wires is easily feasible. Immediately after removing the structure shown in Fig. 3.2 from the UHV environment, it was etched in 5\% HF for 15 s. In this etching step the silicon lines acted as a mask and only stripes of epitaxial CoSi$_2$ remained on the wafer. Since HF attacks also silicon oxide, the etch has to be performed as fast as possible, i.e., before the Si lines are fully oxidized. Another solution would be to keep the sample under an inert gas, which was not possible with our system configuration. Fig. 3.4 shows an AFM-image of the sample after the etching. The measured corrugation of the CoSi$_2$ lines is about 4.5 nm corresponding to the thickness of the epitaxial silicide film.

3.2 Diffusion length of Si on CoSi$_2$(111)

When a lower value for the substrate temperature is chosen during Si deposition, the diffusion length decreases and islands nucleate also in the middle of the silicide terraces. As an example a STM image of a silicide surface onto which 0.2 nm of Si were deposited at $T = 235^\circ C$ is shown in Fig. 3.5. On this sample silicon has attached to both sides of the surface steps (one step is indicated by a dashed line). In addition islands have nucleated on the terraces (arrows). In this smaller scale image the difference in diffusion length of the two materials is clearly visible: on top of the Si terraces, which have formed on the silicide, there are small, closely packed silicon islands. Surprisingly the step from the silicide to the first Si terrace is only 1 bilayer high here.

Contrary to the samples grown at higher temperature the second bilayer has thus not been completed. After a brief annealing step at $T = 570^\circ C$ the second bilayer was found to be present on the entire terrace. This indicates, that the activation energy for the hopping of adatoms adsorbed at the border of a terrace onto the first bilayer is higher than the activation energy for diffusion on the silicide surface. In order to quantify the difference in diffusion length for Si on the CoSi$_2$(111) surface compared to Si on Si(111), the island
3.2. Diffusion length of Si on CoSi$_2$(111)

Figure 3.5: STM topography image of a sample, where 0.2 nm of silicon were deposited on a 3 nm thick CoSi$_2$ film at T=235°C. The boundary of the silicon islands features a one bilayer step. ($V_t=2.5$ V, $I_t=0.2$ nA, gray scale range $\Delta z=2.2$ nm.)

density $n$ was measured as a function of temperature.

Fig. 3.6 displays topography images of 3 nm thick CoSi$_2$ films, where 0.5 nm of Si were deposited with a much smaller rate of 0.016 nm/s. The deposition temperature was 200°C for Fig. 3.6(a), and 250°C for (b). Although the temperature difference of 50 degrees is rather small, an extreme difference in the island distances can be observed. The results for two different deposition rates are plotted in Fig. 3.7. The average island spacing $n^{-1/2}$, also called diffusion length, can be read from the scale on the right hand side of the plot. The data for Si/Si(111) was taken from [39] and extrapolated from a growth rate of 0.2 ML/min. to 0.1 nm/s to allow for a direct comparison with the measurements made for Si/CoSi$_2$(111) (plotted as o) deposited at the same rate. Obviously there is not much difference in the temperature dependence of the island density for the two types of substrates. At a given
Figure 3.6: STM topography images of 3 nm thick CoSi$_2$ films, where 0.5 nm of silicon were deposited with a rate of 0.016 nm/sec. The growth temperature was $T=250^\circ$C for (a) and $T=200^\circ$C (b). (a): $V_t=2.5$ V, $I_t=0.2$ nA. (b): $V_t=3$ V, $I_t=0.2$ nA. The gray scale range is 2.0 nm for both images.

temperature, however, the island spacing is larger by more than two orders of magnitude for silicon deposited on CoSi$_2$. According to classical nucleation theory [40] for 2D islands and complete condensation, the island density $n$ depends on the growth rate $R$ and temperature $T$ like

$$n \sim \left( \frac{R}{\nu} \right)^{i/(i+2)} \exp \left( \frac{E_{eff}}{kT} \right), \quad E_{eff} = \frac{E_c + iE_d}{i + 2} \quad (3.1)$$

$E_c$ is the energy gained by the formation of the stable critical cluster, which contains $i$ adatoms. The activation energy for diffusion is denoted by $E_d$ and $\nu$ is a typical atomic vibration frequency. The slope of the curves in Fig. 3.7 gives the effective activation energy $E_{eff}$. The size of the critical cluster is obtained from fitting the rate dependency of $n$ to a power law. Our data suggests a value of $i=3$ atoms in the critical cluster. From this and the slope of the $n$ vs. $1/T$ curves, we obtain an estimate for the activation energy for diffusion of $E_d=0.95 \pm 0.1$ eV. This value depends heavily on the choice of the cluster binding energy $E_b$, which we have set equal to the energy $E_b=1.7$ eV of a Si-Si bulk bond. It is very difficult to make a comparison with $E_d$ found for Si/Si(111) epitaxy, because both higher and lower values can be
3.2. Diffusion length of Si on CoSi$_2$(111)

Figure 3.7: Island density as a function of inverse growth temperature. For the measurements denoted by (●) a deposition rate of 0.016 nm/s was used. Silicon was deposited at a rate of 0.105 nm/s for the samples marked with (○). The data for Si/Si(111) (△) is taken from [30] and extrapolated to a rate of 0.105 nm/s.

found in literature. Voigtländer et al. deduce a value of $E_d=0.75\pm0.2$ eV [39], Nakahara and Ichikawa found $E_d=2$ eV [41] and Latyshev et al. suggest $E_d=1.3\pm0.2$ eV [42]. The experimentally well defined quantity is the effective activation energy $E_{eff}$. In their experiments Latyshev et al. observed a dependence of $E_{eff}$ on growth rate $R$, with higher values for small $R$ (3 eV at 2.3 ML/min) and lower values for high $R$ (1.3 eV at 1.2 ML/s). The data of Voigtländer results in about $E_{eff}=1.06$ eV at a deposition rate of 0.2 ML/min, which contradicts the measurements of Latyshev, but might be suitable as a lower limit to $E_{eff}$ for Si/Si(111). The slope found in Fig. 3.7 results in $E_{eff}=0.91\pm0.03$ eV for silicon diffusion on the surface of CoSi$_2$, which is slightly lower than for Si/Si(111). Still most of the difference in the island densities stems from the pre-exponential factor and not from a different temperature dependence.
Chapter 3. Self organization of Si on CoSi$_2$(111) films
Chapter 4

BEEM at the CoSi$_2$/Si system

4.1 Introduction

CoSi$_2$ is a metallic silicide exhibiting the unique advantage of a cubic fluorite (CaF$_2$) structure closely related to the diamond structure of Si, with a lattice mismatch of only -1.2% at room temperature [27]. These properties allow the fabrication of thin epitaxial layers on Si(111) and Si(100), making this silicide an ideal prototype to study a metal-semiconductor interface by means of BEEM, which has been done extensively during the last years [26, 17, 21, 35]. For studying the properties of a MS interface, the (111) system was the more promising one, since the more stable CoSi$_2$(111) surface exhibits two different structures, a 2x1 and an unreconstructed 1x1. The 2x1 is strain induced [28] and can be avoided by an appropriate growth technique. The 1x1 can usually not be resolved under BEEM scanning conditions, so no surface induced atomic scale contrast can influence the BEEM images. Since the main goal of this work is not to investigate the silicide/silicon interfaces, but to detect buried heterostructures on Si(100), BEEM has only been performed on samples with a (100) surface. Therefore we will mainly focus on CoSi$_2$(100), except in the case of the electronic interface structure, in order to point out the differences resulting for the transport across the two kinds of interfaces. Fig. 4.1 shows the experimentally determined attenuation length $\lambda(E)$ of epitaxial CoSi$_2$(100) films, where spectra taken on the two different surface reconstructions were averaged. The details about
Chapter 4. BEEM at the CoSi$_2$/Si system

Figure 4.1: Attenuation lengths $\lambda(E)$'s measured in constant height (CH) and constant current (CC) BEEM mode. The CH mode data were fitted by a phenomenological form taken from Ref. [26, 19, 17, 21].

the experiments and the theory used to determine $\lambda(E)$ for both epitaxial orientations can found in the work of E.Y. Lee et. al [36]. On contrast to CoSi$_2$(111) films, where at low voltages (about 1 V) $\lambda(E)$ can be as high as 10 nm, the attenuation length for CoSi$_2$(100) films is much smaller. But with increasing voltage, i.e., energy, $\lambda(E)$ decreases faster for (111) oriented films, so the limit at high voltages is for both orientations about 2.5 nm.

4.2 Interface structure

For thin CoSi$_2$ films on Si(100) several epitaxial orientations are possible [29]. In MBE growth two of them have been observed:

A: CoSi$_2$(100)/Si(100):\{100\}$_{CoSi_2}$\parallel (100)$_{Si}$ with a\textless 010 \textgreater $\text{CoSi}_2$\parallel a[010]$_{Si}$

B: CoSi$_2$(110)/Si(110):\{110\}$_{CoSi_2}$\parallel (100)$_{Si}$ with 5\textcdot a\textless 010 \textgreater $CoSi_2$\parallel $\sqrt{2}$\textcdot a[010]$_{Si}$

Using a special growth technique (details see in section 2) the formation of grains of wrong orientation (B) can be avoided resulting in a homogeneous
4.3. Surface structure

Concerning the surface, no unreconstructed phase exists for CoSi$_2$(100) in contrast to the (111) oriented films. Two different surface reconstructions, $\sqrt{2} \times \sqrt{2}R45^\circ$ and $3\sqrt{2} \times \sqrt{2}R45^\circ$ have been first observed in RHEED studies by Yalisove et al. [30], which can be transformed into each other by depositing one monolayer (ML) of Si or Co, respectively, followed by a short anneal at $450^\circ$. They are therefore often called the 'Co-rich'($\sqrt{2} \times \sqrt{2}R45^\circ$) and the 'Si-rich'($3\sqrt{2} \times \sqrt{2}R45^\circ$) silicide surfaces. These two reconstructions have been confirmed later by STM measurements. In Fig. 4.3 a STM topography image shows the reconstructions atomically resolved. Since the reconstructions differ concerning the available electronic states, they will surely influence the momentum and/or energy distribution of the injected carriers. As a consequence, the BEEM current will also be influenced by these surface features and one has to take care to separate surface and interface effects.
4.4 Electronic properties

Many first principles band structure calculations of CoSi$_2$ have been performed, among others by Mattheiss and Hamann [32] using the method of linear augmented plane waves (LAPW). Fig. 4.4(a) displays the so calculated band structure, Fig. 4.4(b) shows the well known band structure of silicon. The Fermi surface of the silicide is composed of three constant energy surface sheets labeled $h_7$, $h_8$ and $h_9$, belonging to bands 7, 8 and 9 centered around $\Gamma$, which are the relevant ones in the energy range about the threshold (from -1eV to +1.5 eV) concerning BEEM (Fig. 4.4(b)). In order to find out if there are matching states for a given energy $E$, we will project the Si band structure onto the interface Brillouin zone (IBZ). In Fig. 4.5 the first Brillouin zone of Si for the bulk (left) and the interface (right) are sketched. A carrier, with an energy higher than $\Phi_D$, can only be transmitted if a corresponding state exists at the semiconductor side. In silicon all six conduction band minima (CBM) are located in the $<100>$ direction, 0.983 Å$^{-1}$ away from the zone center $\Gamma$. In the case of the Si(111) interface, none of the CBMs is projected into the IBZ center, they are 0.8 Å$^{-1}$ away from the $\Gamma$ point (see
4.4. Electronic properties

Figure 4.4: (a) Band structure of bulk CoSi$_2$ crystallized in the CaF$_2$ structure. (b) Band structure of silicon. (c) The Fermi surface of CoSi$_2$ is formed by three hole sheets $h_7$, $h_8$ and $h_9$. 
Chapter 4. **BEEM at the CoSi$_2$/Si system**

Figure 4.5: Bulk (left) and interface (right) Brillouin zones of silicon. The position of the conduction band minima are indicated by gray ellipsoids. Irreducible wedges appear dashed in the IBZs.

Fig. 4.5 on the lower right side and Fig. 4.4(b)). Since the extrema of the bands 7, 8 and 9 of CoSi$_2$ are centered at Γ and therefore the states with the lowest energy will be projected onto the $\Gamma$ point of the IBZ, a reduced BEEM current has to be expected for electrons with an energy only slightly higher than the Schottky barrier height, since the tunneling process favors carriers with a $k_\parallel$ near zero. Only carriers picking up an additional lateral momentum due to scattering might have a chance to pass the interface. For Si(100) (see Fig. 4.5 upper right side), two CBMs project onto $\Gamma$, so electrons with $k_\parallel$ around zero will find matching states in the Si substrates as soon as their energy exceeds the Schottky barrier height, i.e., the onset of the BEEM spectra will surely mark the height of the Schottky barrier formed at the interface. In the case of hole injection, the situation is much simpler. Since all silicon valence band maxima (VBM) are centered at the $\Gamma$ point for Si(100) and Si(111) (Fig. 4.4(b)), they will be projected onto $\Gamma$ independent of the substrate orientation.
4.5 BEEM contrasts at CoSi$_2$/Si(100) samples

In order to detect semiconducting nanostructures embedded within the silicon below the silicide base, the features associated with surface and interface effects of the latter have to be well known.

4.5.1 Surface related contrasts

The CoSi$_2$(100) surface exhibits two different surface reconstructions as has been mentioned in 4.3, the $3\sqrt{2} \times \sqrt{2}$ and the $\sqrt{2} \times \sqrt{2}$, both oriented in the $<100>$ directions of the surface. Unfortunately for BEEM experiments, they can be resolved atomically up to 2 V, and even at higher voltages the characteristic rows of the $3\sqrt{2} \times \sqrt{2}$ are easy to distinguish and therefore influence the BEEM image. Different surface structures exhibit different work functions $\Phi(V_t)$ due to the charge transfer into surface states. If this charge transfer is responsible for that change of $\Phi$, it must hence depend on the polarity of the applied voltage. As has been shown by Sirringhaus [18], the $3\sqrt{2} \times \sqrt{2}$ exhibits at $V_t > 0$ a work function smaller by $\Delta \Phi \approx 0.2$ V when compared to the $\sqrt{2} \times \sqrt{2}$. So the tip-surface distance $z$ is larger 0.2 Å than on the $\sqrt{2} \times \sqrt{2}$. According to planar tunneling theory the width of the energy distribution $\Delta E$ is determined by $z$ and $\Phi$:

$$\Delta E \propto \frac{\hbar}{\sqrt{2m}} \frac{\sqrt{\Phi}}{z} \propto \Phi$$

since $\sqrt{\Phi} z =$ const for the constant current mode. Therefore due to the sign change of $\Delta \Phi$ with the polarity of the tip the energy distribution is broader for $V_t < 0$, but sharper for $V_t > 0$. As a consequence $I_C$ is smaller on the $3\sqrt{2}$ (see Fig. 4.6) and the shifted lines appear darker at negative and positive bias in the BEEM image as it is clearly visible in Fig. 4.6.

4.5.2 Interface related contrasts

The contrasts in BEEM related to the CoSi$_2$/Si(100) interface are always due to Schottky barrier height inhomogeneities. The actual barrier height $\Phi_B$ is
Interfacial misfit dislocations

The monolayer step height at the surface of Si(100) is $a/4=0.135$ nm. By contrast, the CoSi$_2$(100) surface has a step height of $a/2=0.27$ nm. Due to that fact, the introduction of misfit dislocations with a Burgers vector $\vec{b}=a/4<111>$ is favored at interfacial steps. In the topography images they show up as smooth surface steps $a/4$ in height. In BEEM images a change of the BEEM current $I_C$ at the location of the dislocation core can be observed. In forward BEEM measurements on CoSi$_2$/n-Si(100) samples (see section 1.2) an increase of $I_C$ on top of these dislocations can be observed, on p-doped samples a decrease. By performing ballistic electron emission spectroscopy (BEES) the change of $\Phi_B$ can be determined. Fig. 4.7 displays on the left side simultaneously taken STM and BEEM images. In the topography image the smooth surface step is clearly visible. One can also see that
4.5. BEEM contrasts at CoSi$_2$/Si(100) samples

Figure 4.7: STM and BEEM images of a 3 nm thick CoSi$_2$ film on a n-doped Si substrate along a misfit dislocation (left side) taken at $V_t=-2$ V and $I_t=3$ nA. The dislocation is marked with a black, resp. white dashed line. At the right side the square root of the BEEM spectra taken along (circles) the dislocation and away from the dislocation (squares) are displayed.

A change of the surface reconstruction is induced by the strain field of the dislocation, which often happens and also influences the BEEM contrast. In the BEEM image the dislocation line is associated with a higher $I_C$, so that this region appears brighter, although the $3\sqrt{2}$ contrast is overlapping. The Schottky barrier height $\Phi_B$ was determined by taking BEEM spectra along the dislocation and on an undisturbed area. We assumed a quadratic dependence of the BEEM current as a function of the tunneling voltage according the model of Kaiser and Bell [3, 5], i.e., $I_C(V_t)=R\cdot(e^{-|V_t|/\Phi_B})^2$. The onset of $I_C$, which determines the barrier height, was determined by taking the square root of $I_C$ and fitting it linearly. Away from the dislocation $\Phi_B$ was found to be $0.74\pm0.04$ eV. Within the dislocation the barrier was reduced by 0.1 eV to $0.64\pm0.04$ eV. So here, in contrast to the CoSi$_2$/Si(111) system [18], the increase of $I_C$ is caused by a decrease in barrier height. Therefore an increase of $\Phi_B$ has to be expected for a CoSi$_2$/p-Si interface along such a misfit dislocation. The left side of Fig. 4.8 shows the STM and BEEM image (forward mode, i.e., $V_t>0$) of a dislocation under a $\sqrt{2}$ reconstructed surface. Since no reconstruction change is induced in this particular case,
Chapter 4. BEEM at the CoSi$_2$/Si system

Figure 4.8: STM and BEEM images of a 2 nm thick CoSi$_2$ film on a p-doped Si substrate taken at $V_1=2$ V and $I_t=3$ nA along a misfit dislocation (left side). The dislocation is marked with a black, resp. white dashed line. At the right side the square root of the BEEM spectra taken along (circles) the dislocation and away from the dislocation (squares) are displayed.

The deformation of the surface can better be seen. In the BEEM image the decrease of $I_C$ along the defect is marked by the darker gray shade along the line. The barrier heights were determined in the same way as has been described for the n-doped samples. $\Phi_B$ was found to be $0.38\pm0.4$ eV. The sum of the barrier heights on n- and p-doped samples should give the band gap of Si, which is about 1.1 eV, as is indeed the case. On top of the dislocation the barrier was increased, as has been predicted, up to $0.42\pm0.03$ eV. Again the sum of the barrier heights on top of dislocations is equal to the band gap of Si. Although these defects may mask other interesting features at the interface, they are rather easy to recognize in both, topographic and BEEM images.

Interfacial line defects

Fig. 4.9 displays the topography and the BEEM image of a 3 nm thick silicide film deposited on a n-Si substrate. The BEEM image exhibits linear features with increased $I_C$, which are not correlated with any surface deformation.
These lines are running along the $<110>$ directions and exhibit a length

Figure 4.9: STM and BEEM images of a 3 nm thick CoSi$_2$ film on a n doped Si substrate ($V_t$=-2 V, $I_t$=3 nA). Interfacial line defects are marked with black arrows within the BEEM image. Images are taken from Ref. [35].

between 50-200 nm and they start and begin abruptly, i.e., they do not start/end at screw dislocations as the misfit dislocations and they neither form a continuous network [35]. The contrast cannot be caused by some extended interface defect, because no correlated feature can be found on the homogeneously $3\sqrt{2}$ reconstructed surface. Additionally, no other linear defects - besides the misfit dislocations - could be found in any TEM images at the interface of CoSi$_2$/Si(100) samples. The influence on $\Phi_B$ is similar to that of the dislocations. Fig. 4.10 displays the square root of BEEM spectra taken on top of such linear defects and in defect free regions. A decrease of 0.1 eV, from 0.75 eV on a defect free area down to 0.65 eV on top of the line defects has been determined [35].
Figure 4.10: Square root of BEEM spectra measured on top of linear defects (crosses) and in neighboring defect free regions (circles). Taken from Ref.[35].
Chapter 5

Ge islands embedded in a Si matrix

5.1 Introduction

Semiconductor nanostructures have attracted a lot of interest in the last years due to the fundamental change of electronic and optical properties compared with bulk material [44]. One of the most elegant ways to obtain such small structures is the spontaneous formation of defect-free and fully coherent islands in the early stage of strained layer epitaxy [45, 46, 48, 47]. After deposition of only a few coherent monolayers on the lattice-mismatched substrate, an array of islands is formed with a rather uniform size distribution. The discrete energy-spectrum of quantum dots renders them extremely interesting for the development of lasers and even for quantum computers [49]. For device applications as well as for measurements of electronic properties, these mesoscopic structures have to be embedded in a matrix material. This procedure is not trivial at all since during overgrowth a dramatic change of shape and chemical composition and, as a consequence, of electronic properties may occur. As noticed by several researchers, Ge dots tend to change shape while the overlayer is grown, resulting in pronounced flattening [50, 52, 51]. In addition, the dots may change their composition and, as demonstrated for small Ge clusters, even dissolve completely [51]. The physical mechanisms responsible for these modifications appear to be related to the elastic strain
relaxation of the dots and the surrounding matrix and to surface segregation (see, e.g., [52]). Three dimensional confinement of carriers can occur not only within the dots, but also in the host-material due to strain. Strain induced carrier confinement has been observed in In$_x$Ga$_{1-x}$As quantum wells [53], where InP dots, grown on top of a thin GaAs capping layer act as stressors. Schmidt et al. [54] observed a red shift in photoluminescence (PL) spectra of stacked layers of carbon-induced buried Ge dots, caused by electron confinement in the strained Si matrix above the buried islands. In the past, scanning probe methods have been used mostly to study the nucleation and structural aspects of quantum dot formation, with few exceptions, such as ballistic electron emission microscopy (BEEM), from which some spectroscopic information on InAs dots has been obtained [55]. Recently many studies have been performed on the nucleation and overgrowth of quantum dots. Ge dots on Si(100) were investigated with scanning tunneling microscopy (STM) [64], atomic force microscopy (AFM) [65], transmission electron microscopy TEM [66] and low energy electron microscopy (LEEM) [67]. Cross-sectional STM (XSTM) has been applied to InAs quantum dots embedded in GaAs and the strain in growth direction and the band gap of the InAs dot has been compared with the one of the GaAs matrix [68]. In this work a scanning tunneling microscopy (STM) and ballistic electron emission microscopy (BEEM) study on Ge dots embedded in a silicon film is presented. For the STM study the STM was used in the conventional configuration at room temperature. The deformation of the silicon cap-layer caused by the buried Ge islands was measured and from the surface deformation the lateral strain above a quantum-dot has been calculated. For the BEEM measurement additionally a thin silicide film on top and a thicker silicide on the back side have been grown, acting as base and ohmic back contact, respectively.

5.2 Stranski-Krastanow growth of Ge dots on Si(100)

Ge on Si(100) is a model Stranski-Krastanow system, where after the formation of a thin wetting layer of well defined thickness 3 dimensional (3D)
islands appear. The first STM studies on this topic were presented by Mo 

et.al [45]. They discovered a 3D metastable cluster phase forming after the deposition of 6 ML of Ge at a substrate temperature of 500°C. The so called hut-clusters are epitaxial, defect-free and strictly \{105\} faceted Ge islands.

In Fig. 5.1 the STM topography image of such a hut cluster is displayed. The hut clusters are always oriented along the \(<100>\) directions of the silicon surface and exhibit usually a rectangular base area, but also species with a quadratic base can be found. On the side facets of the island the surface is reconstructed in a way, that results from dimer-rows running alternatingly in \(\langle011\rangle\) and in \(\langle01\bar{1}\rangle\) directions on neighboring ML terraces [45]. The hut clusters can be 2-4 nm high, their base length is under 100 nm. The size can be adjusted within a certain limit by varying the growth temperature. At about 500°C a new kind of island appears [69, 64]. These so-called ‘domes’ are larger than the hut-clusters, especially in height, and their side facets are much more complicated, exhibiting \{113\} and \{102\} as well as \{105\} facets [64] planes. Fig. 5.2 shows a topography image of a sample exhibiting a bimodal island distribution. For the STM as well as the BEEM experiments, the growth conditions were adjusted to obtain that bimodal island
Figure 5.2: 3-dimensional representation of a STM topography scan showing Ge islands grown on a Si(100) substrate at T=525°C. The hut-clusters are labeled (H), the coexisting domes D. The tunneling parameters were set to $V_t=-2.1\, V$, $I_t=0.65\, nA$.

distribution. The samples were grown by molecular beam epitaxy (MBE) and the substrates prepared as described in section 2.

For the STM experiments lightly p-doped (7-12 Ω cm), well oriented ($±0.05°$) Si(100) wafers were used, on which a 240 nm thick undoped silicon buffer layer was grown, exhibiting the usual 2x1 reconstructed surface as verified by reflection high energy electron diffraction (RHEED). 6 ML of germanium were deposited from a Knudsen-cell at a rate of 4 ML/min while the sample temperature was kept at 500°C. After a 5 min anneal the samples were cooled to room temperature and transferred to the STM. A topography image of such a sample is given in Fig. 5.3(a). Hut-clusters -some with quadratic base but most of them elongated- are indicated by H, and domes are denoted by D. The latter are of similar base size, but two to three times higher due to their higher indexed side facets. Typical dimensions of the hut clusters are a width of 30-40 nm and a height of 3-4 nm, whereas the domes are between 6 and 10 nm high. Fig. 5.3(b) displays the profiles of a dome
5.3  Embedding of Ge dots within a Si matrix

For the Si-overgrowth the substrate temperature was quenched down to 310°C and 3 nm of Si were deposited from the electron gun evaporator at a rate of 0.05 nm/sec. Three additional Si layers 2 nm each and one final layer 1 nm in thickness were grown with the same growth rate at 350°C, 390°C, 470°C and 550°C, respectively. In order to improve the surface quality the sample was then annealed during 5 min at 550°C. After cooling down to room temperature the sample was transferred to the STM chamber attached to the same UHV system. In case of BEEM experiments silicide layers were grown as described above before the transfer to the STM chamber. The growth procedure was developed both, to minimize shape transitions of the Ge dots and to produce a capping layer of good crystalline quality and a smooth sur-
Figure 5.4: Topography image of the same sample shown in Fig. 5.3 after deposition of 10 nm of Si onto the Ge islands. \(V_t=3\) V, \(I_t=0.5\) nA, gray scale range corresponds to \(\Delta z=0.78\) nm. By comparing the average density of the different dot-induced features we attribute the most prominent bulges with a shallow rectangular hole (indicated by A) on top to the domes. The hut clusters induce most probably the numerous smaller 'bumps' (indicated by B, C and D.)

face. Since it is known that during overgrowth flattening of the islands and at least partial alloying occur [51, 52], cross-sectional TEM images were taken to verify that the Ge dots were still present within the Si matrix. Indeed a flattening of the islands could be observed in the TEM images, such that the formation of a SiGe alloy is very probable.

5.4 STM experiments

In Fig. 5.4 a STM topography image of the same sample already measured before capping (see Fig. 5.3) is shown after the growth of the 10 nm thick silicon cap-layer. Most conspicuous are rectangular 'holes'. In this case the surface deformation is so strong, that the Si surface step structure is heavily influenced by the strain. In the hole indicated by A in Fig. 5.4 one can see a bulge caused by a buried dot. The average density of these holes of \((3.5 \pm 0.7) \times 10^9 cm^{-2}\) fits very well the density of domes observed on uncovered samples, i.e., \((4.4 \pm 0.75) \times 10^9 cm^{-2}\). Some smaller surface
5.4. STM experiments

'bumps' have been found, labeled with B, D and C (with decreasing height) in Fig. 5.4. Here the surface deformation leads only to step pinning. With \((3.5 \pm 0.2) \times 10^{10} \text{cm}^{-2}\) the density of these features exceeds the density of holes and correlates with the hut cluster density of \((3.5 \pm 0.2) \times 10^{10} \text{cm}^{-2}\) observed before. The maximum curvature of the surface was measured to be higher in the center of the 'holes' (region labeled by A in Fig. 5.4 than on the bumps present in the more planar regions (B, C and D). We can therefore conclude that larger Ge islands induce a larger outward bending of the growing surface, which in turn must cause higher lateral strain in the Si growing on top of the island. At higher temperatures Si adatoms diffuse away from the strained parts of the sample surface \([52]\) leading to the formation of 'holes'. On top of the smaller Ge islands (hut-clusters) the strain in the growing Si film is smaller and only step pinning (B, C and D) is found to occur.

5.4.1 Approximating surface strain

Fig. 5.5(a) displays the topography of a larger overgrown germanium dot. The step structure of the Si surface is heavily affected by the strain, so that the surface protrusion is bound by two incomplete Si surface steps of one ML height. The Si surface exhibits homogeneously a rather unusual 4x2 surface reconstruction instead of the 2x1 reconstruction typical for a clean, defect-free Si surface \([74, 75]\). We attribute this feature to small amount of Ge which might be present on the surface inducing a static buckling of the dimers resulting in a 4x2 reconstruction. No 2x8 reconstructed surface dominated by vacancy lines has been found, which is characteristic for a Ge-rich surface \([72]\). For an exact determination of the surface bending above the dot the surface step structure around it has to be 'removed' somehow from the measured profile above such a surface distortion. Fig. 5.4(b) displays the 'step-corrected' surface of Fig. 5.4(a). The correction has been performed by adding the needed multiple of a ML height within the hole to the topography image. The contour lines, marking positions of equivalent height, reveal that the surface deformation is of nearly exact circular symmetry. Measurements performed on other buried dots exhibit sometimes a very small aberration from the circular shape of the surface deformation towards a rectangular one,
Figure 5.5: (a) STM topography image of a surface protrusion caused by a germanium island below a 10 nm thick silicon cap-layer. The gray scale range is 0.5 nm. (b) Same image as (a) after subtraction of surface steps. Some contour lines are drawn to emphasize the circular symmetry of the surface distortion. Between adjacent contours the height difference is 0.1 nm.

parallel to the <100> directions. For this reason the elastic anisotropy could be neglected for the following first approximation of strain modeling [73]. A step-corrected height profile taken across the 'hole' in Fig. 5.5 is presented in Fig. 5.6. The height of the surface deformation is 0.35 nm, more than twice as high as a Si monolayer step. The peak height of the surface 'bumps' varies between 0.05 nm and 0.1 nm and their cross-sections are of similar shape as the one shown in Fig. 5.6.

The surface deformation was calculated according to Hu [70], describing the displacement caused by a thermal inclusion in a 3D semispace \( z \geq 0 \). The displacement caused at a point \((x, y, z)\) in an elastic medium by a point source of volume \(dx'dy'dz'\), located at \((x', y', z')\), can be described by the displacement vector \(\vec{d}^*\).

\[
\vec{d}^* = \frac{\delta(1+\nu)}{4\pi(1-\nu)} \left( \frac{\vec{R}_1}{R_1^3} + \frac{(3-4\nu)\vec{R}_2}{R_2^3} - \frac{6z(z+z')\vec{R}_2}{R_2^3} \right) \\
- \frac{2\vec{k}}{R_2^3} [(3-4\nu)(z+z') - z] dxdydz',
\]

(5.1)

where \(\vec{k}\) is a unit vector in z direction and \(\vec{R}_1 = (x-x', y-y', z-z')\),
Figure 5.6: Line-section across step-corrected surface protrusion shown in Fig. 5.5 (a) (open circles). The connecting line shows the surface protrusion calculated according to the model of Hu [70]. The lower part of the graph shows the in-plane strain component $\varepsilon_{xx}$ derived from this calculation.

$\vec{R}_2 = (x - x', y - y', z + z')$. $\nu$ is the Poisson ratio of the stressed medium, $\delta$ (here $\delta = 0.04$) describes the lattice mismatch of the included volume in relation to the matrix material. To calculate the effect of an embedded island of finite volume, one has to integrate such point sources over the given island volume. By performing this integration for a square based hut-cluster with 40 nm base length covered by 10 nm of Si, a maximum surface distortion above the center of the buried dot of 0.15 nm has been calculated (see Fig. 5.7(c)). Therefore the protrusion of 0.35 nm height measured on the 'hole' in Fig. 5.5 has to be caused by a buried dome. This is confirmed by the fact that the density of these features is equal to the density of the domes measured before. The calculated deflection of 0.15 nm is still too high compared with the measured surface deformation between 0.05 nm and 0.1 nm of the smaller surface bumps, which we attributed to buried hut-clusters. The fact that the measured surface deformation has circular symmetry [see e.g. Fig. 5.5(b)], while the calculated contours for an intact faceted hut-cluster [Fig. 5.7(a)] still show a slight deviation from circular shape, is an indication that the facets of the Ge islands are changed during overgrowth. Since the exact shape and composition of the buried dots is unknown, a point source
Figure 5.7: (a) Contour plot of the calculated surface deformation caused by a Ge hut-cluster embedded in Si. The geometry used is shown in (b): a square based pyramid (gray) with a base length of 40 nm and a height of 4 nm is embedded in a 10 nm thick Si film. (c) The surface deformation along the x-axis is indicated in (b).

(described by the term $u_x^*$ in Eq. 5.1) with the lattice-mismatch of Ge with respect to Si was assumed to cause the surface deformation. With this simplification a surprisingly good agreement between measured and calculated surface deformation could be achieved (see Fig. 5.6). The parameters used to reproduce the surface profile (a volume of $dx'dy'dz' = 5.452 \times 10^3 nm^3$ and a depth of $z'=16.57$ nm) cannot be directly interpreted as island volume and position. But it is possible, using these parameters, to determine the strain at the silicon surface. The in-plane strain component $\varepsilon_{xx}$ is shown in Fig. 5.6. In the center of the Ge islands the tensile strain was determined to be 0.02, half the value of the tensile strain measured for Si layers grown coherently on Ge substrates. The strain tensor can be determined by deriving $u_x^*$ of Eq. 5.1. This result correlates well with previous measurements of the elastic strain relaxation in Ge hut-clusters, where the apex was found to have the lattice constant of bulk Ge [71].
5.4.2 Conclusion

The strain distribution around islands embedded in a matrix material is of great interest. We have found evidence for directed diffusion of Si away from the strained surface regions on top of a buried Ge island. Directed diffusion of Ge towards regions with lower strain has been identified by Tersoff et al. [88] as the driving force for self-alignment of islands in stacked island-multilayers [66]. In the case of stacked carbon-induced germanium-island multilayers in silicon a spatially separated confinement for holes and electrons has been suggested recently [54] to account for a red-shift in PL-spectra.

5.5 BEEM experiments

5.5.1 Introduction

For an application of buried Ge nanostructures in a device, their transport properties must be investigated. There are several effects, which might influence the transport, i.e., confinement of electrons in the strained Si matrix around the dots and confinement of holes in the dots themselves, scattering at the two additional interfaces, etc. For this purpose ballistic electron emission microscopy (BEEM) and ballistic electron emission spectroscopy (BEES) measurements have been performed. For BEEM, a metallic base is needed.
on top of the buried Ge dots. We succeeded in growing a thin epitaxial CoSi$_2$ layer on top of the buried islands. The samples were grown as described in section 2. A STM image of such a complete Si/Ge/Si heterostructure with buried dots and a 3 nm thick CoSi$_2$ layer on top is displayed in Fig. 5.8. One can see that the surface is only slightly affected by the underlying structure. The film exhibits an atomically smooth surface, sometimes interrupted by holes about 50 nm in diameter. From their number density it is likely that they are located on top of some of the larger dome-shaped islands (compare with Fig. 5.4), but some of them might also be pinholes, which easily form during the annealing step of the CoSi$_2$ layer. Since there are but a few of these holes on a \( \mu \text{m} \) scale, which is far below the densities of domes and hut clusters determined on uncapped samples, they are not expected to affect BEEM measurements significantly. High resolution transmission electron microscopy (HRTEM) images were made of a cross-section of the sample of Fig. 5.8 in order to confirm that the buried islands still exist below the completed heterostructure. As one can see in Fig. 5.9, the Ge clusters (C) have indeed been perfectly covered by planar Si and CoSi$_2$ films, opening the possibility for performing BEEM- and BEES measurements on these buried structures. The thickness of 10 nm chosen for the Si layer represents a compromise between the requirement of flat surfaces and shallow depth of the nanostructures, the latter being dictated by the limited mean free path of hot carriers in Si. The HRTEM images confirm also that a shrinking of the Ge islands has taken place during overgrowth, since no covered dot higher

![CoSi$_2$](image)

Figure 5.9: Cross-sectional HRTEM image of a Si/Ge/Si heterostructure with a 3 nm thick epitaxial silicide on top.
5.5. **BEEM experiments**

than 4 nm has been found.

Having verified the existence of the Ge islands after capping them with 10 nm of silicon and 3 nm of silicide, similar samples could be investigated by means of BEEM and BEES. Fig. 5.10 displays a memory aid of the sample structure, the fabrication of which is explained in section 2, along with a sketch of the measurement set-up. The samples were transferred *in situ*

![Diagram](image)

Figure 5.10: Design of the Si/Ge/Si/CoSi$_2$ heterostructure. The samples were grown on n-Si(100) oriented substrates.

after growth into the STM/BEEM chamber in order to avoid oxidation and contamination of the surface. They were cooled down to 77 K to improve the signal-to-noise ratio of the BEEM measurements.

### 5.5.2 Motivation

Several BEEM experiments on buried semiconducting islands have been performed before. Self-assembled InAs dots embedded in a GaAs matrix were investigated by BEEM, using a thin polycrystalline gold layer as base electrode [55]. An enhanced BEEM current through the dots was observed as a consequence of a lower onset of the interfacial barrier attributed to the strain in the GaAs capping layer on top of the buried dots. BEEM experiments on GaSb dots embedded in GaAs [56], also using a polycrystalline base layer, reveal a conduction band offset between the dots and the surrounding matrix. It was also possible to observe resonant tunneling through a quantized
state in InP quantum dots in a double barrier heterostructure [57]. All these
measurements have in common that the embedded dots are still clearly vis-
able in the topography image, i.e., their position and density could easily be
identified even by STM. In contrast to that, in our case, only some of the
higher domes seem to influence the surface by causing shallow holes in the
silicide base. In most cases no surface feature is present to indicate the exact
position of buried Ge islands.

The motivations for our experiments were therefore as follows:
• The first question to be answered is, if detection of the buried islands
solely by BEEM is possible at all. As can be seen in Fig. 5.8 the majority
of the buried islands cause no surface feature helping to find their position
underneath the silicide. A second unfavorable fact is the alignment of the
Ge and the Si band structures. Fig. 5.11 shows the band-offset expected

![Figure 5.11: Design of the Si/Ge/Si/CoSi₂ heterostructure. The samples
were grown on n-Si(100) oriented substrates.](image)

for fully strained Ge islands embedded within an undoped Si matrix grown
on a p⁺-doped (a) and a n⁺-doped substrate (b). We assumed the islands
to be alloyed at least with 15% of silicon, since alloying takes place during
overgrowth [52, 51]. According to calculations of VanDeWalle [78] the band
gap of the islands E\(_{G,G Ge}\) for such a Ge concentration is reduced to a value
of 0.33 eV due to the compressive biaxial strain, causing not only a shift
but also a splitting of the degenerate hole bands. Most of the offset takes
place within the valence band, where \(\Delta E_V \simeq 0.7\) eV. In principle it is possi-
5.5. **BEEM experiments**

Deborah to detect such structures due to resonant tunneling features within the BEEM signal [61, 62, 63]. But in forward BEEM on p-doped samples the energy distribution is not sharp. This fact would extremely complicate the measurements, since sharp features within the electronic sample structure might be impossible to observe. The offset in the conduction band is almost negligible. Applying strictly the calculations from Ref. [78], a type II alignment will occur with an offset of \( \Delta E_C \approx 0.02 \text{ eV} \), which is in good agreement with recent publications [58, 59], but some researchers claim also to have found evidences for a type I alignment [60]. The sign of the offset in the conduction band is hence still under debate, but since its magnitude is small it has been neglected in Fig. 5.11. Therefore it might be hard or even impossible to detect any change in the BEEM signal. So for both substrate doping types difficulties for the BEEM measurements have to be expected. Since the signal is the highest possible in the case of forward BEEM on n-doped substrates (see section 1), we decided to use that BEEM configuration.

- The early stages of epitaxial overgrowth of germanium nano-crystals, \{105\} faceted hut-clusters and mostly \{113\} faceted domes, with silicon have been investigated recently by scanning tunneling microscopy (STM) [51]. These studies reveal that with increasing Si-coverage a dramatic change of shape takes place, i.e., a drastic decrease of the height combined with the formation of new facets, such that the islands appear to be rotated by 45° with respect to the uncapped hut clusters. In case the BEEM signal is only affected by the buried dots, it would be possible to clarify whether the rotation is real or just the result of new facets formed by attached Si atoms.

5.5.3 **BEEM results**

**Detection of the buried Ge islands**

Fig. 5.12 displays the topography image (a) and the simultaneously measured BEEM image (b) of such a sample. With 3.4 nm the gray scale range of \( \Delta z \) is larger than usual for CoSi_2(100) films due to the holes caused by some of the larger Ge islands. Also the step structure is slightly affected, but besides these facts it is a ‘normal’ silicide surface. Surprisingly, one can see in the
Figure 5.12: (a) STM topography image of a 3 nm thick CoSi$_2$ layer on top of a Si/Ge/Si heterostructure. (b) Simultaneously recorded BEEM image. (a) $V_t=-2 \text{ V}$, $I_t=2 \text{ nA}$, gray scale range $\Delta z=3.4 \text{ nm}$. (b) gray scale range $\Delta I_C=13.5 \text{ pA}$. 

BEEM image many rectangular bright features oriented along the $<110>$ directions of the surface. From their size and their density each one of these features is most probably associated with a Ge dot underneath. There are also some additional straight lines running along the $<110>$ directions causing the same contrast in the BEEM image. By performing locally resolved ballistic electron emission spectroscopy (BEES) the interface barrier was determined in the center of the buried dot, at the surrounding line defects and at a defect free area. Fig. 5.13(b) displays the averaged values of the spectra taken on the above mentioned regions. Fig. 5.13(a) the square-root of $I_C$, used to determine the Schottky barrier height $\Phi_B$ according to the quadratic power law of Kaiser and Bell [3]. On the defect-free region and in the center of the line defect, i.e., the center of the dot, the Schottky barriers were $\Phi_B=0.73\pm0.02 \text{ eV}$ and $\Phi_B=0.73\pm0.01 \text{ eV}$, respectively. On the line defect the barrier was decreased with $\Phi_B=0.66\pm0.07 \text{ eV}$. The larger error for the line-defect region can simply be explained by the fact that less spectra could be averaged. This corresponds within the error bars to the values determined for the line shaped defects at simple CoSi$_2$/Si(100) interfaces and the corresponding defect-free areas, respectively [35].
5.5. BEEM experiments

These linear defects are not associated with any topographic contrasts. Therefore they cannot be correlated with extended defects such as dislocations, found also at the CoSi$_2$/Si(100) interface (see section 4.5). Although there should be no correlations between the line defects and the misfit dislocations, they cause exactly the same decrease in the Schottky barrier height, i.e., from 0.74 eV to 0.64 eV. The only explanation for these phenomena is the presence of atomic defects at the CoSi$_2$/Si(100) interface responsible for the decrease of the interfacial barrier. In the case of vacancies they would be attracted from regions with compressive strain, as is the case, e.g., in the center of a misfit dislocation. In the previous chapter the strain field at the Si-surface above buried Ge islands was determined. As can be seen in Fig. 5.6, the in-plane strain $\varepsilon_{xx}$ changes its character from tensile in the center to compressive at the border of the dots.

We are therefore tempted to associate the rectangles visible in Fig. 5.12(b) with point defects which have diffused into the strain field above the dots, and which lower the Schottky barrier height at the silicide/Si interface. A similar effect has been observed at CoSi$_2$/Si(111) interfaces, where point defects diffuse into the core of misfit dislocations because of the compressive strain there [21]. In that case, however, the Schottky barrier height was found to be unaffected by the presence of point defects. This is in fact not
surprising, because there the point defects are so highly localized that any potential variations would be completely screened irrespective of the degree of barrier height lowering at the metallurgical interface [79]. The line defects act now as markers for the position of the Ge islands, since the strain field of the Ge dots forces them to form rectangles. Although the edges of the rectangles are parallel to the <110> direction, one cannot conclude that the dots are oriented likewise, since their strain field is nearly perfectly circular (see Fig. 5.5 and 5.7) and the <110> direction is also the preferred orientation of these lines at pure CoSi₂/Si(100) interfaces.

**Transport through the Si/Ge/Si heterostructures at high energies**

The position and density of the Ge dots could hence be determined by BEEM by means of the rectangular line defects. In order to obtain information about the real shape and size of the islands, a change in the BEEM signal related only to the buried Ge islands is needed. As we have seen, this is not the case in the near threshold region of the BEEM signal, i.e. from $V_t \sim -0.8$ V to $V_t \sim -2$ V. We have increased therefore the tunneling bias up to the maximum limited by the supply, i.e., up to -6 V. At such high energies the transport through the structure is less influenced by the differences in the Schottky barrier height at the CoSi₂/Si(100) interface, and more sensitive to events taking place in the dots themselves. Fig. 5.14(b) shows again the image of a BEEM measurement performed with $V_t = -2$ V. As discussed above, the positions of the buried dots are clearly marked by bright rectangles, but also some additional line defects can be seen. The same area was scanned with a tunneling bias of $V_t = -6$ V. The topography and the BEEM image are displayed in Fig. 5.14(c) and (d), respectively. Now dark rectangles can be seen exactly within the borders of the bright markers observed before, always exhibiting a slightly smaller area. Since this decrease in the BEEM signal is definitely coupled with the rectangular line defects, which has only been observed above buried islands, we can attribute these features unequivocally to the Ge dots. In order to find out more about the transport at different tunneling voltages, locally resolved BEES has been performed. The tip was
5.5. BEEM experiments

Figure 5.14: (a)(b) STM topography and BEEM image of a 3 nm thick CoSi$_2$ layer, on top of a Si/Ge/Si heterostructure at low voltage. (c)(d) STM topography and BEEM image of the same area as displayed in Fig. 5.14(a) scanned with higher tunneling bias. ((a) $V_t = -2$ V, $I_t = 3$ nA, gray scale range $\Delta z = 1$ nm. (b) gray scale range $\Delta I_C = 12$ pA. (c) $V_t = -6$ V, $I_t = 1$ nA, gray scale range $\Delta z = 1$ nm. (d) gray scale range $\Delta I_C = 8$ pA.)

scanned with a so-called stabilization voltage $V_{Stab}$ and a fixed tunneling current $I_t$. At each pixel spectra were taken at a fixed lateral position of the tip by varying the tunneling voltage while keeping the feed-back loop on, and the BEEM current $I_c$ was measured as a function of the tunneling bias. Since the topography is measured simultaneously, we can attribute a spectrum to each pixel of the STM- and the BEEM-image. Fig. 5.15(a)-(h) displays images of the collector current at various bias voltages taken from the local spectra. The topography (not shown) was atomically flat besides the step marked with a white dashed line in Fig. 5.15(a). At lower voltages (Fig. 5.15(a)-(c)) the line defects dominate the transport. The bright lines can clearly be seen. But at -2.5 V (also Fig. 5.15(c)) the area within the bright rectangle seems to darken, i.e., it exhibits a smaller BEEM current. With increasing tunneling voltage the contrast of the line-defects becomes weaker, while the difference between the decreased BEEM current within
Chapter 5. Ge islands embedded in a Si matrix

Figure 5.15: BEEM images of the same area various tunneling voltages $V_t$, but with the same tunneling current $I_t=2$ nA. The BEEM contrasts $\Delta I_c$ are, as $V_t$, denoted below the according images.

The rectangle relative to the surrounding area becomes larger. In order to display the change of the BEEM signal quantitatively a few spectra from the center of the dot were averaged, to avoid the influence of the line defects, and compared with an average of spectra taken on an area as far away as possible from a buried Ge islands. It can clearly be seen in Fig. 5.16, that the BEEM current stemming from a region with only silicon underneath starts to exceed the BEEM current of the region with a Ge dot underneath at $V_t=-2.5$ V. The contrast increases with increasing tunneling voltage. Since the contrast appears at a rather high carrier energy, it is very probable that it is related to inelastic processes. Ludeke et. al. [80] determined the quantum yield of electron-hole pair generation in Si by means of BEEM. They compared the results with a theoretical calculation performed by R.C. Alig [81]. The theory is applicable over the wide range of energies needed for that kind of BEEM results. The observed rapid increase of $I_C$ beyond 2.8 eV was attributed to carrier multiplication generated by impact ionization [82]. The process is ionizing, since it takes place near the metal-semiconductor interface, where
5.5. BEEM experiments

Figure 5.16: 30 spectra taken in the center of the dot (black squares) and 40 spectra taken in a region without Ge island underneath (open circles) were averaged. ($V_{Stab}=-3$ V, $I_t=2$ nA.)

the intrinsic electric field separates electrons and holes. For n-doped samples the hole is swept towards the interface where it is neutralized, whereas the electron moves into the semiconductor and contributes to the BEEM current. At first sight one may expect an even larger BEEM current through the Ge rich regions, because of the smaller band gap there. Fischetti et al. developed a full band structure theory of high field transport and impact ionization of electrons and holes in Si and Ge [83]. They indeed found the impact ionization rate for Ge slightly increased relative to the rates for Si at the same energy and temperature. But we have to take into account, that the Ge islands are included within a silicon-matrix exhibiting a 4.2% smaller lattice constant, i.e. the islands will be strained to a certain extent. A change of structural parameters will of course affect the band structure and the density of states of the material and therefore also the impact ionization rate. According to Ref. [81] the impact-ionization rate $r(E)$ can be described analytically by

$$r(E) = \frac{2\pi}{\hbar} |M|^2 \frac{V^2 \Delta}{8\pi^2} \left( \frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \frac{2\pi(E - E_{th})^{\frac{3}{2}}}{105} \quad \text{for } E > E_{th} \quad (5.2)$$

$E$ denotes the energy of the impinging electrons, which has to be larger than the threshold energy $E_{th}$. $|M|^2 = |H_j|^2$, where $H_j$ is the matrix element
of the screened Coulomb interaction for all states $j$, and $m$ is the density of states effective mass. $V$ denotes the semiconductor volume and $\Delta$ the atomic volume per electronic state. $|M|^2$ depends only weakly on the initial carrier energy [84] and can therefore be ignored in a rough first approximation, also $V$ and $\Delta$ should not change that much the final result.

The crucial parameters left are the threshold energy $E_{th}$ and the density of states effective mass $m$. Let us first concentrate on the influence of $E_{th}$. Czajkowski et al. [85] have deduced the impact ionization threshold for GeSi alloys and strained layers over the full range of composition from empirical pseudopotential band structure calculations. They determined the threshold for electron initiated processes in pure Si to be $E_{th,Si}=2.3$ eV, and for a unstrained Ge$_{85\%}$Si$_{15\%}$ alloy $E_{th,Ge}=1.8$ eV, not differing that much from the onset for pure Ge although the band structure of the alloy is expected to be silicon-like [78] (the threshold energies here are given with respect to the valence band maximum at $\Gamma$). In the case of unstrained Ge islands we would have to expect a similar impact ionization rate as displayed in Fig. 5.17 and

Figure 5.17: Electron-initiated impact ionization rate as a function of kinetic energy of the primary ionizing particle in Ge (left side) and Si (right side) calculated with a full-band-structure theory of high-field transport and impact ionization of electrons. The conduction band minima are taken as reference points for the kinetic energy. Details of the calculations and the noted references can be found in Ref. [83]. The figure was kindly provided by M. V. Fischetti.

$$E_{th} = 2.3 \text{ eV} \quad \text{for pure Si}$$

$$E_{th} = 1.8 \text{ eV} \quad \text{for Ge}_{85\%}\text{Si}_{15\%}$$
consequently a larger BEEM current compared to regions with pure silicon. But in our heterostructure the islands are bi-axially strained, i.e., compressed in the xy-plane. From the STM experiments we know, that the covering Si is also strained to a certain extent, such that in principle we cannot assume simple homogeneous stress. Confining ourselves nevertheless to strictly bi-axial stress, the threshold $E_{\text{th,Ge}}$ for the islands will decrease to $E_{\text{th,Ge,xy}}=1.4$ eV, and in the $z$ direction, i.e., perpendicular to the substrate-plane it will increase to $E_{\text{th,Ge,z}}=2.5$ eV [85]. Injection of STM favors electrons with $k_\parallel=0$, i.e., $k$-vectors parallel to $z$. But at higher energies, as is the case for our BEEM experiment, also carriers with a non zero $k_\parallel$ are possible. Furtheron, electron-phonon interactions cannot be ignored, which will change $k_\parallel$. Since the energy loss for creating a phonon is only some 10 meV, an electron can easily create an electron-hole pair even after such an interaction. So we cannot conclude that the increased threshold in the $z$-direction alone dominates the ionization rate. We also have to consider, that an increased threshold energy cannot explain the increasing difference for the BEEM current with increasing tunneling voltage $V_t$ (see Fig. 5.16). Since with increasing energy the value of $E_{\text{th}}$ in the last term of Eq. 5.2 become less and less important, this difference should become correspondingly smaller. The second parameter to be considered is the density of states effective mass denoted by $m$ in Eq. 5.2 which should be rewritten as $m_e^2m_h^{3/2}$, where $m_e$ and $m_h$ are the averaged electron and hole masses, respectively. Manku et.al [86] calculated the effective mass of light and heavy holes, $m_{e,LH}$ and $m_{e,HH}$ for SiGe alloys for a Ge content between 0% and 30%. They found a drastical decrease with increasing Ge content. The same is probably true for the effective mass of the spin-split-off band which should also taken into account for the averaged density of states effective mass of the hole bands $m_h$. For such a high Ge content as present in our buried islands, a further decrease of $m_h$ can be expected. Even if the electron density of states effective mass of the electrons, $m_e$, was about the same as that for Si and assuming $E_{\text{th,Ge}} < E_{\text{th,Si}}$, a smaller impact ionization rate can hence result within the buried dots. Also the increasing contrast at higher energies can be explained, since the factor $m_h^{3/2}$ will dominate, because $(E - E_{\text{th}})^{3/2}$ will then differ less for Si and Ge. A similar experimental behavior has also been reported by Niu et. al [87], who
observed a reduced impact ionization rate within the SiGe layer of a SiGe HBT transistor compared to Si. They also attributed this observation to the reduced density of states effective mass, since in their device configuration the alloy threshold energy is smaller than that of Si.

For a qualitative comparison for the impact ionization rates in unstrained Si, unstrained Ge and the buried and therefore strained Ge dots, the impact ionization rate within the buried Ge structure has to be calculated. As a first attempt, the impact ionization for a thin Si$_{0.15}$Ge$_{0.85}$ alloy layer, fully strained to the lattice constant of Si, was calculated by M.V. Fischetti using the same method as mentioned above. The results are displayed in Fig. 5.18. We chose an alloy layer as model for the buried Ge islands to take into account, that during overgrowth the latter were were alloyed to a certain extent. As has to be expected, the ionization rate ($r$) of the strained alloy exhibits a lower threshold than the unstrained Ge due to the reduced band gap. But the
dependence on $r$ of the kinetic energy is much smaller, resulting in a cross-over with the $r$ of Si at a kinetic energy of about 3.5 eV. Above that electron energy less secondary carriers should be produced within the Ge dots than in the surrounding Si matrix, resulting in a lower BEEM current $I_C$. In the BEEM experiments, a reduced BEEM current above an energy of 2.5 eV has been observed (see Fig. 5.16). But one has to take into account, that in BEEM experiments the reference point is the Fermi level of the base, whereas in Fig. 5.18 the energy is referred to the conduction band minimum within the semiconductor. The Ge dots a located near the silicide/Si interface. Their the conduction band within the semiconductor is about 0.74 eV above the Fermi level of the base due to the Schottky barrier formation. Hence from Fig. 5.18 we would expect the BEEM spectra to cross at about 4 eV. This is in reasonable agreement with our experimental results, in view of the crude assumption used for the true Si/Ge/Si heterostructure.

5.5.4 Conclusion

We have investigated Ge hut clusters and domes embedded in a Si matrix by means of BEEM. These islands could be detected by BEEM alone, even in the absence of any surface feature revealing their position. At low voltages, the position and rough size of the dots follow from the observation of rectangular shaped line defects resulting from the trapping of point defects within the compressive strain field at the border of the buried islands. At high voltages the dots could directly be detected due to a reduced BEEM signal through the Ge rich regions compared to the surrounding Si matrix. We attribute the decrease in the BEEM signal to a decreased impact ionization rate, which is related to the decrease of the density of states effective mass. Furtheron we could confirm that a real shape transition, i.e. a rotation of the dots by 45° takes place.
Summary

In the first part of this work we have investigated the early stages of Si/CoSi$_2$(111) heteroepitaxy by means of STM and found a very much enhanced diffusion length compared to Si/Si(111) homoepitaxy. At low temperatures silicon can be grown in quasi-step-flow mode, where upon the steps of the silicide surface are decorated by silicon wires at least 2 bilayers in height. The width of the wires can be adjusted by varying coverage and wafer mis-cut. Using the deposited silicon as a mask in a wet-chemical etching step, CoSi$_2$ wires are obtained.

In the second part we investigated Ge dots embedded within a Si matrix by means of STM and BEEM. We have established a growth sequence to embed Ge quantum dots within a thin epitaxial Si layer with a reasonable flat surface and determined the in-plane strain from the measured local surface deflection. By adding a thin epitaxial CoSi$_2$ layer on top of the structure, BEEM measurements could be performed. We succeeded in detecting the buried islands solely by BEEM due to two different mechanisms. At lower energies line-defects consisting of accumulated point defects act as markers for the position of the dots. At higher energies a reduction of the BEEM signal due to a lower impact ionization rate gave us direct information about the size of the buried dots confirming that they rotate by $45^\circ$ during overgrowth.

Outlook

Concerning the fabrication of CoSi$_2$-wires, it can be expected that by carefully adjusting wafer mis-cut and growth parameters, lines of nanometric width, much below the line widths achieved until now, can be grown using this procedure, allowing for measurements of 1 dimensional transport in epitaxial metallic wires. Also the fact, that CoSi$_2$ films are superconducting at sufficiently low temperatures [43] could provide for interesting measurements. Another issue we will address in the near future is Si overgrowth of structured CoSi$_2$ films.

An outstanding BEEM experiment on the Si/Ge/Si for the future will be to perform similar experiments on p-doped samples, where the band aligne-
ment of Ge might be detected due to resonant tunneling features within the BEEM signal. In order to overcome the problem of the broad energy distribution of the injected holes, highly p-doped diamond tips might replace the metallic tungsten tips used until now [90]. Another goal will be, to find an appropriate surfactant for the CoSi$_2$ surface, forcing the surface to be unreconstructed. The removal of the ever present surface reconstructions might allow BEEM measurements of a resolution comparable to that at the CoSi$_2$/Si(111) interface.
Chapter 5.  Ge islands embedded in a Si matrix
Appendix A

T-H model for higher voltages

In the STM-theory of Tersoff and Hamann [12] the tunneling current for small tip bias is proportional to the LDOS of the sample:

$$I_t \propto \rho_s(r_0', E_F)$$  \hspace{1cm} (A.1)

In the following we deduce an expression, which is valid also for the larger tip bias required for BEEM measurements. Following Bardeen’s formalism [89] we write the tunneling current as:

$$I_t = \frac{2\pi e}{\hbar} \sum_{\mu, \nu} f(E_\mu + eV_t)[1 - f(E_\nu)] |M_{\mu\nu}|^2 \delta(E_\mu - E_\nu)$$  \hspace{1cm} (A.2)

Energies are measured with respect to the lower edge of the sample energy-band, and the tip voltage $V_t$ is defined negative for electron injection from tip to sample. Tip and sample are made of the same material with a work function $\phi$ and a Fermi-energy $E_F$. The index $\mu$ counts states in the tip, whereas sample states are denoted by $\nu$. An energy-diagram is shown in Fig. A.1. The tip wave function $\psi_\mu$ decays into the gap region in the same way it would decay into a potential step of height $\Phi - eV_t/2 - (E_\mu - E_F)$. In analogy to [?] a spherical wave function is defined for the tip:

$$\Psi_\mu = \frac{c_t}{\sqrt{\Omega_t}} \kappa_\mu R e^{\kappa_\mu R} \frac{\exp(-\kappa_\mu |\vec{r} - \vec{r}_0|)}{\kappa_\mu |\vec{r} - \vec{r}_0|}$$  \hspace{1cm} (A.3)

where $\vec{r}_0$ is the position of the center of the tip, $R$ is the tip radius and

$$\kappa_\mu^2 = \frac{2m}{\hbar^2}(\Phi - eV_t/2 - (E_\mu - E_F)).$$
Figure A.1: Energy diagram for electron tunneling from tip to sample. Tip states (Energy $E_{\mu}$) couple to sample states (Energy $E_{\nu}$). All energies are measured with respect to the lower band edge of the sample.

The potential step for the sample wave function is $\Phi - eV_t/2 - (E_{\nu} - E_F)$ high. Assuming no variation of $|\Psi_{\nu}(x,y,z)|^2$ along the surface (x,y-plane) we set:

$$\Psi_{\nu} = \frac{a}{\sqrt{\Omega_s}} \exp(z\sqrt{\kappa_{\nu}^2 + k_{||}^2}) \exp(i\vec{k}_{||} \cdot \vec{x}).$$

The in-plane wave vector $\vec{k}_{||}$ and the in-plane position vector $\vec{x}$ both are two component vectors and

$$\kappa_{\nu}^2 = \frac{2m}{\hbar^2}(\Phi - eV_t/2 - (E_{\nu} - E_F)).$$

The tunneling matrix is calculated according to Bardeen:

$$M_{\mu\nu} = \frac{\hbar^2}{2m} \int d\vec{S} \cdot (\Psi^*_\mu \nabla \Psi_{\nu} - \Psi_{\mu} \nabla \Psi^*_\nu)$$

where the integration is carried out over a plane $S$ between tip and sample. From Eq. A.2 it is clear that only matrix elements are needed where $E_{\mu} = E_{\nu}$. In that case the values of $\kappa_{\mu}$ and $\kappa_{\nu}$ are identical too, and we obtain the same
expression as the one given in [12] with $\kappa_{\nu}$ substituted for $\kappa$:

$$M_{\mu\nu} = \frac{\hbar^2}{2m} \frac{e_t}{\sqrt{\Omega_i}} 4\pi R e^{k_{\nu} R} \Psi_{\nu}(\mathbf{r}_0) \tag{A.6}$$

In the low temperature limit the expression for the tunneling current in Eq. A.2 simplifies to:

$$I_t = \frac{2\pi e}{\hbar} \sum_{E_{\nu},E_{\mu} \in \{E_F, E_F - eV_t\}} |M_{\mu\nu}|^2 \delta(E_{\mu} - E_{\nu}) \tag{A.7}$$

This is simplified even more under the assumption, that the tip density of states is constant:

$$I_t \propto \int_{E_F}^{E_F - eV_t} dE \sum_{\nu} e^{2k_{\nu} R} |\Psi_{\nu}(\mathbf{r}_0)|^2 \delta(E_{\nu} - E) \tag{A.8}$$

The exponential term is slowly varying with energy if the tip radius $R$ is small compared with the sample-tip distance or if $e|V_t| \ll \Phi$. In those two cases we can obtain the desired formula:

$$I_t \propto \int_{E_F}^{E_F - eV_t} \rho_s(\mathbf{r}_0, E) dE \tag{A.9}$$

with the sample local density of states (LDOS) given by:

$$\rho_s(\mathbf{r}, E) = \sum_{\nu} |\Psi_{\nu}(\mathbf{r})|^2 \delta(E_{\nu} - E)$$

The tunneling current is thus in a first approximation proportional to the LDOS integrated over the energy range, where tunneling between tip and sample is allowed. The derivative of the tunneling current with respect to the tip bias is then proportional to the local density of states:

$$\frac{dI_t}{dV_t} \propto \rho_s(\mathbf{r}_0, E_F - eV_t) \tag{A.10}$$

For forward tunneling the barrier between tip and sample becomes lower as soon as a voltage is applied. As a consequence the tunneling current will
increase exponentially with increasing bias. Since the quantity of interest is the surface LDOS in the absence of the tip, this monotonic increase in measured $\frac{dI}{dV_t}$ spectra with applied voltage is often compensated for by defining the 'experimental LDOS' as the normalized tunneling conductance [76]:

$$LDOS = \frac{\frac{dI_t}{dV_t}}{I_t/V_t}$$  \hspace{1cm} (A.11)
Appendix B

Simulation of Si wire growth on CoSi$_2$(111)

In Fig. B.1 a sketch for wire growth of Si on CoSi$_2$ is displayed. At a terrace of width $W$ atoms arrive with a constant rate $\phi$. The current width of the Si wire is denoted with $x_G$, the thickness with $d(x)$. One gray square corresponds to an atom. The four squares shaded in a darker gray mark the place where the first nucleation takes place. For the simulation of the growth of silicon wires on (111) oriented layers, as described in section 3, several assumptions have to been made:

- The terrace width $W$ is at most twice the diffusion length of Si at the growth temperature used.

- Under the prevailing growth conditions the completion of the first two bi-layers occurs on such a short time scale, that the minimum observed thickness ($h$) amounts to 4 ML of Si.

- The diffusing adatoms are always reflected by the down step and will diffuse to the silicon. In case the second bilayer is completed they will nucleate at the border denoted with $x_G$ in Fig. B.1. Otherwise they will jump up and help finishing the double bilayer.

- The first nucleation takes place directly at the up step and the height of that nucleus is also given by $h$. 
Appendix B. Simulation of Si wire growth on CoSi$_2$(111)

Figure B.1: Schematic diagram for the growth of a Si-wire on CoSi$_2$(111). $x_G$ denotes the current width of the Si wire, $W$ the step width, $\Phi$ the constant rate given in bilayers per second.

- Atoms impinging directly on the silicon part have a 100% sticking probability.

First we evaluate an expression for the width of the wire as a function of time and rate. At the time $t$ the width of the Si wire is denoted with $x_G$. At the time $t'=t$, with $\Delta t=(t'-t)$ $x_G$ can be described by:

\[
\begin{align*}
  t' > t : x'_G &= x_G + \frac{1}{2}(W - x_G) \cdot \Phi \cdot \Delta t \\
  \Delta x_G &= \frac{1}{2}(W - x_G) \cdot \Phi \cdot \Delta t
\end{align*}
\] (B.1)

The factor $\frac{1}{2}$ comes from the fact, that the Si wires are at least two bilayers high and the rate $\Phi$ is given in bi-layers per second. The second part of Eq. B.1 can be rewritten as:

\[
\begin{align*}
  dx_G = \frac{1}{2}(W - x_G) \cdot \Phi \cdot dt
\end{align*}
\] (B.2)

By substituting $(W-x_G)$ with $y$ and $dx_G$ with $-dy$, the following simple differential equation is obtained:
By solving the equation and resubstituting \( y \) with \( (W-x_G) \), \( x_G \) can be described as a function of time \( t \) and rate \( \Phi \):

\[
x_G = W \left[ 1 - \exp \left( \frac{-\Phi \cdot t_{\text{end}}}{2} \right) \right]
\]  

\[(B.4)\]

For the determination of \( x_G \) only the amount of silicon deposited on the originally bare part of the silicide terrace is considered, i.e., \( W - x_G \). The data we can extract from the STM experiments are the height \( d(x) \) and the width \( x_G \) of the Si wires (i.e., the cross-sections), the rate \( \Phi \) and the total time \( t_{\text{end}} \) are measured during deposition of the Si. To compare experiment and our analytical approach, it is useful to calculate the wire thickness as a function of the distance from the up-step, where the first nucleation takes place, and the current total width \( x_G \). Thus calculated and measured cross-sections can be compared.

While the growth front advances from some point \( x \) at time \( t_x \) to its final position \( x_G \) at time \( t_{\text{end}} \) the layer at \( x \) is exposed to the constant flux \( \Phi \). The thickness at \( x \) will therefore be given by:

\[
d(x) = h + \Phi \cdot (t_{\text{end}} - t_x)
\]  

\[(B.5)\]

According to Eq. B.4 the time can be expressed as a function of \( x \):

\[
t = -\frac{2}{\Phi} \ln \left( \frac{W - x}{W} \right)
\]

\[(B.6)\]

With \( t = t_x \) at \( x \) and \( t = t_{\text{end}} \) at \( x_G \), we finally get from Eq. B.5:

\[
x > x_G : d(x) = 0
\]

\[
x < x_G : d(x) = h \cdot \left( 1 + \ln \left( \frac{W - x}{W - x_G} \right) \right)
\]
Appendix B. Simulation of Si wire growth on CoSi$_2$(111)
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Presentations

- STM and BEEM studies of buried Ge islands on Si(100), Swiss physical society meeting, Bern, Switzerland, February 27, 1998 (talk)

- Schottky-barrier lowering at defects studied by BEEM, 24th international conference on the physics of semiconductors, Jerusalem, Israel, August 2-7, 1998 (poster)

- Schottky-Barrier variations at the CoSi2/Si(100) interface studied with BEEM, Institute of solid state electronics, TU-Vienna, Austria, September 10, 1998 (invited seminar talk)

- Fabrication of CoSi2 nano-wires by self organized mask formation and wet chemical etching, 10th Euro MBE workshop, LesArc, France, March 28 - April 1, 1999 (talk)

- Si surface band gap shift on top of buried Ge quantum dots, 7th International conference on the formation of semiconductor interfaces, Goeteborg, Sweden, June 21-25, 1999 (talk)

- Direct observation of buried Ge islands by ballistic electron emission microscopy, 18th general conference of the condensed matter division of the european physical society, March 13-17, 2000, Montreux, Switzerland (poster)
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