Doctoral Thesis

Scanning probe microscopy on buried nanostructures

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Scanning probe microscopy on buried nanostructures

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Abstract

Structures having dimensions in the nanometer range, so called *Nanostructures* have become of increasing importance in the world of semiconductor physics during the last decade. On the one hand the feature sizes in computer chips are shrinking in the quest for higher performance (a 150 nm MOS process is currently used for processors), which triggers the need for information on the electronic properties of defects and on the mechanisms of electronic transport on a small scale. On the other hand the introduction of scanning probe techniques has provided the tools to access not only the structure of a sample on a nm scale, but also to probe its electronic properties locally. The mechanism of self-organization, found in many heteroepitaxial systems, offers an easy means to create huge numbers of nanoscale structures with interesting physical properties, resulting from their reduced dimensionality.

In this thesis two different kinds of nanostructures are investigated. First crystal-defects found at the epitaxial CoSi$_2$/Si(111) interface are studied on a nm scale by the method of ballistic electron emission microscopy (BEEM). The results obtained from measurements of hot carrier scattering at interfacial point defects of atomic size render information on structural issues but also on the ballistic transport process itself. The first direct observation of interfacial point defects trapped in the core of a dislocation is presented. The small apparent size of the point defects found in BEEM-measurements even on thick films can no longer be explained by conventional BEEM theory, but arises from electron focusing induced by the silicide band structure. Ballistic electron emission spectra measured in the close vicinity of a single point point defect show two components, which can be attributed to transitions breaking and conserving the in-plane momentum at the interface, respectively. While the scattering is clearly enhanced by the presence of a point defect, it is still present in defect-free regions. This apparent scattering probability at a perfect interface is explained by the presence of additional diverging beams in the BEEM-current distribution within the framework of a new BEEM-theory. The experimental confirmation of this new quantum-mechanical approach to hot electron propagation in a metal film is the key objective of this thesis.

The second part of the thesis is devoted to artificial nanostructures. As described in chapter 3, the Stranski-Krastanow growth of Ge on Si(100) was exploited to grow self-organized arrays of faceted, nanometric Ge islands. For any application these islands must be embedded in a crystalline Si layer, a task which turns out to be problematic, because Ge segregation and alloying
must be minimized. A method for overgrowth was established and scanning
tunneling microscopy measurements were carried out on samples containing
Ge islands embedded in a 100 Å thick Si layer. The embedded islands cause
a significant elastic distortion of the Si cap layer. From this surface defor-
mation, the strain at the Si surface was calculated and correlated with the
electronic properties of the Si surface as determined by locally resolved tun-
neling spectroscopy measurements. A reduction in the surface bandgap was
found with increasing strain, similar to the way the band structure of bulk
Si reacts to strain.
Chapter 1

Experimental

1.1 Ballistic electron emission microscopy

1.1.1 Introduction

Ballistic electron emission microscopy (BEEM) is a simple extension of the concept of the scanning tunneling microscope (STM) [1], giving access to buried interfaces. The method was first put forward by Kaiser and Bell [2, 3] in 1988. In a STM a tunneling current is maintained between a metallic tip and a metallic or semiconducting sample. The carriers injected into a sample can have a considerable kinetic energy (a few electron Volts (eV) depending on the tip bias) and travel ballistically until they encounter a scattering event. A prototype BEEM sample consists of a metal base layer grown on top of a semiconducting substrate. The base layer is grown thin enough to enable a fraction of the carriers injected by the tip to travel ballistically to the base/substrate interface. Carriers with high kinetic energy eventually cross the Schottky barrier and make up the BEEM- or collector current, which is measured using an ohmic contact to the semiconducting substrate. 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 this way the effect of structural defects, which are identified by means of STM topography scans (e.g. grains of different crystal orientation), on the electronic properties of the sample (e.g. Schottky barrier height) can be studied, but also purely interfacial defects, such as point defects, can be visualized with the high resolution of the STM. This high local resolution is the main advantage of BEEM compared to other methods,
which are used to investigate hot carrier transport. Device structures tailored
to inject hot electrons into a sample region of interest yield only information
averaged over a macroscopic sample area, which is given by the size of the
(lithographically fabricated) device. There are four different configurations
for a BEEM-experiment: In the forward BEEM modes the same kind of car¬
rier, that is injected into the sample, is collected in the semiconductor. As
an example, in the most popular BEEM configuration electrons are injected
into a sample with a collector designed for electron collection (n-type sub¬
strate). In the other forward BEEM mode, holes are injected into a metal
base, grown on top of a p-doped substrate. The energy diagrams for the for¬
ward configurations are shown in Fig. 1.2. Since in the hole BEEM geometry
the energy distribution of the holes is also peaked at the Fermi level of the
cathode, only few holes can cross the p-Schottky barrier at the interface and
the current is expected to be weaker than in an electron BEEM experiment.
In the reverse BEEM configurations only minority carriers, which have been
created in a inelastic scattering event, are collected. Compared to forward
BEEM the momentum distribution of the carriers incident on the interface
is very broad.
1.1. *Ballistic electron emission microscopy*

![Energy diagrams of BEEM in the forward configuration for electron (a) and hole injection (b). The energy distribution of the carriers in the base is indicated.](image)

1.1.2 Classical BEEM theory

In the simplest approximation [4, 5] the BEEM-process can be divided up into four separate subprocesses, which can be analyzed separately. First of all the *tunneling injection* of carriers from the tip into the base has to be modeled. This step of the BEEM-process is well covered by commonly used STM-theories. In the simplest case only planar tunneling is considered. A more sophisticated approach is the STM-theory established by Tersoff and Hamann [6]. Second the *propagation in the metal film* has to be addressed. The easiest way to treat this stage is a semiclassical free electron (or hole) model, which has been quite successful for the prediction of the BEEM current in the threshold region. Although a quantum mechanical treatment of the propagation within the very thin metal base films seems most appropriate, this task has not been addressed until very recently [7], because of its complexity. The third step in the BEEM process is the *transmission through the interface*. For epitaxial interfaces conservation of in-plane wavevector $k_\parallel$ is expected in addition to energy conservation. The fourth step, *propagation within the semiconductor*, is mostly neglected for the classical BEEM-setup, because inelastic scattering within the semiconductor is only expected for kinetic energies exceeding the gap width. For sample geometries where BEEM is applied to semiconductor heterostructures (e.g. double barrier heterostructures [8], superlattices [9], MOS structures [10]) this step has to be treated with more exactness (see e.g. [11]). In the following a more detailed discussion of the four different stages is given:
1. **Tunneling injection:** The simplest way to treat this problem is to assume planar tunneling between tip and sample. The energy diagram of this situation is shown in Fig. 1.3. An external voltage \( V_t \) is applied to the tip while the sample is connected to ground. The two electrodes are separated by a potential barrier of width \( d \). The sign of \( V_t \) is defined to be *negative*, when electrons are injected from the tip into the sample, which is the normal configuration in BEEM. For zero applied bias the height of the barrier \( \Phi \) is taken as the average of the work functions of tip and sample. As soon as a (negative) bias voltage is applied, the mean barrier height (measured with respect to the sample Fermi-level) is increased by \(-eV_t/2\). In a one-dimensional WKB-approximation the current from the tip to the sample would depend on the density of states of both materials and the transmission probability through the barrier:

\[
I_t \approx \int_{E_F}^{E_F-eV_t} dE \, \rho_t(E) \rho_s(E) \exp \left( -\frac{\hbar}{m} \sqrt{\frac{eV_t}{2} - (E - E_F) d} \right)
\]
1.1. Ballistic electron emission microscopy

Here the energy $E$ is measured with respect to the sample Fermi-level $E_F$ and the temperature was chosen to be $T = 0K$. The dispersion relation of the electron in the vacuum gap was assumed to be free electron like and characterized by a mass $m$. When extending the formula to three dimensions, free electron behavior is also assumed for the energy dependence on in-plane wavevector $k_{\parallel}$ (For the sake of simplicity the same effective mass is used here). A nonvanishing in-plane momentum reduces the energy $E_z$ associated with the motion normal to the vacuum barrier:

$$ E_z = E - \frac{\hbar^2}{2m} k_{\parallel}^2 $$

For tunneling only $E_z$ is relevant:

$$ I_t \approx \int_{E_F}^{E_F+eV_t} dE \int d\vec{k}_{\parallel} D(E, \vec{k}_{\parallel}) $$

$$ D(E, \vec{k}_{\parallel}) = \rho_t(E + eV_t, \vec{k}_{\parallel}) \rho_s(E, \vec{k}_{\parallel}) $$

$$ \times \exp \left( -\frac{\hbar}{m} \sqrt{\Phi - \frac{eV_t}{2} - \left( E - \frac{\hbar^2 k_{\parallel}^2}{2m} - E_F \right)} d \right) $$

It is evident, that at a given energy the tunneling process favors small values of $k_{\parallel}$. The tunneling factor is largest for high energy $E$ and therefore the tunneling current will always be dominated by the states with highest energy (unless of course there is a large variation in the density of states of tip or sample). This is particularly important for the hole BEEM configuration, where holes are injected by the tip (or electrons extracted from the sample). There most of the holes have an energy close to the Fermi-level of the sample, and only few of them have the high kinetic energy given by the tip-bias. In a more elaborate STM-theory Tersoff and Hamann have modeled the tip by a spherical wave function. They found that for small tip bias the tunneling current is proportional to the local density of states (LDOS) $\rho_o(\vec{r}_0, E_F)$ of the sample at the position of the tip. This formula can be extended to
higher voltages (see Appendix A), which results in:

$$I \propto \int_{E_F}^{E_p-eV_i} dE \rho_s(\vec{r}_0, E)$$

$$\rho_s(\vec{r}_0, E) = \sum_{\nu} |\Psi_{\nu}(\vec{r}_0)|^2 \delta(E_{\nu} - E) \quad (1.2)$$

The tunneling current is proportional to the integral of the LDOS over the energy-range, where tunneling is possible.

2. **Propagation in the metal:** A carrier propagating from surface to interface can reach the interface ballistically without undergoing any scattering events, or it can be scattered elastically or inelastically. Elastic (or quasi-elastic) scattering is mostly caused by interaction with phonons or crystal defects in the metal layer. Since measurements are carried out at low temperatures (here 77 K), phonon scattering is negligible. Crystal defects can be avoided by using thin films of high quality. Defect scattering lets a carrier pick up a random amount of momentum, thus changing the momentum distribution inferred by the tunneling process. Another source of elastic scattering is reflection at the interface itself. For instance the formation of standing waves in thin CoSi$_2$(111)/Si(111) films is routinely observed. Inelastic scattering is present due to the electron-electron interaction. It is stronger the higher the kinetic energy of the carrier (because more states become available to scatter into). In a BEEM experiment with an injection energy close to the threshold, the inelastically scattered electrons are not likely to cross the Schottky barrier and contribute to the collector current, because about $\frac{2}{3}$ of the kinetic energy is typically lost in an inelastic collision [12]. For higher energies secondary carriers generated in inelastic scattering events make up an increasing fraction of the BEEM-current. The experimentally observed exponential decrease of collector-current $I_c$ with film thickness $d$ is characterized by the energy-dependent attenuation length $\lambda(V_t)$:

$$I_c(V_t, d) = I_c(V_t, 0) \exp \left(-\frac{d}{\lambda(V_t)}\right) \quad (1.3)$$

In Fig. 1.4 $\lambda(V_t)$, which was determined experimentally for CoSi$_2$(111) films [13], is plotted. The attenuation length $\lambda$ becomes as small as
1.1. **Ballistic electron emission microscopy**

Figure 1.4: Attenuation length $\lambda(V_t)$ calculated from the thickness dependence of the BEEM current on unreconstructed CoSi$_2$/n-Si(111) [13] (filled circles). Films with thicknesses of 22 Å, 30 Å, 45 Å, and 75 Å were used. The solid curve is a theoretical estimate [12]. The open circles show the values of the attenuation length calculated from contrast observed at a monolayer interfacial step on the 22 Å film. They become unreliable below 2.2 V because of the quantum interference effect.

$\approx$25 Å for large tip bias, which causes a considerable variation in the BEEM-current between regions which differ in film thickness by as little as one monolayer.

While scattering of carriers is most prominent at high energies, transport at low energies in thin defect-free films should be ballistic and no collisions are expected to take place. The fact, that under these conditions quantum interference is observed, where the incoming electron wave interferes with the wave reflected at the interface, proves that the coherence of the beam is not destroyed by scattering. While it is clear that the spatial resolution at the interface is degrading at high energies, where transport is becoming diffusive, the question arises what resolution can be reached at low energies, in the ballistic transport regime. As will be shown in section 2.7 the widely applied free electron model clearly fails to give a valid description of the high lateral resolution...
observed experimentally. In Appendix B the propagation of a three dimensional wavepacket is used to model the transport in the base. In the case of free electrons the effective mass is isotropic, which causes the beam to spread in real space with the opening angle $\alpha$, given by the width of the in-plane momentum distribution $\Delta k_{||}$:

$$\tan(\alpha/2) = \frac{(\Delta k_{||})/2}{k_{\perp}}$$

(1.4)

This situation is drawn in Fig. 1.5(b). The same spreading is expected in a purely classical treatment, where a bunch of carriers with individually sharp momentum, but with a statistical distribution in $k_{||}$ of $\Delta k_{||}$ is considered. In this picture a high resolution at the surface implies a broad $k_{||}$ distribution via the Heisenberg uncertainty-principle, which in turn causes the beam to spread in the base layer, degrading the resolution at the interface. But the lateral spreading of a wavepacket with
a large $\Delta k_{||}$ is merely a consequence of the isotropic energy-dispersion. As soon as the energy dependency on lateral momentum compared to perpendicular momentum is weakened this is no longer true. This situation was modeled in the Appendix B by choosing a higher value for the in-plane effective mass $m_{||}$ than for the perpendicular mass $m_{\perp}$. The larger the value for $m_{||}$ is chosen, the less pronounced is the spreading of the beam. In the limit of $m_{||} = \infty$ (the energy is independent of $k_{||}$) the diameter of the beam is the same from surface to interface and no spreading at all is found [see Fig. 1.5(c)]. This simple example does - of course - not adequately describe the propagation in CoSi$_2$ films, but it illustrates that band structure effects are likely to have tremendous effects on hot carrier transport. Indeed the recent theoretical work on hot electron propagation, including a full quantum mechanical treatment of band structure effects has explained many experimental observations, which could not be understood with a simple free electron model. For instance the BEEM-current measured on Au/Si(111) was found to be similar in magnitude to the current observed on Au/Si(100) samples, where a huge difference was expected because of the different position of the silicon conduction band minima (CBM) for the two epitaxial orientations [2, 3, 14]. Tunneling into a free electron metal results in an electron distribution focused around $k_{||} = 0$. The Au band structure, however, forbids propagation along (111) directions, which is the preferred growth direction, and the electron distribution is found to be off-centered in the interface Brillouin zone (IBZ) [15]. At the interface the states within the Au have a similar overlap with both, states in Si(100) and Si(111) IBZ, which is why the collector currents are comparable for both substrate orientations. In real space the BEEM-current is composed of several diverging beams, which leads to a poor spatial resolution at the interface. Experimentally a higher resolution was estimated from BEEM measurements performed on samples, where a SiO$_2$ pattern had been formed lithographically before Au deposition [16]. The steep decrease of the collector current, which was observed if the tip was moved to a position above an oxide patch, was interpreted as a resolution in the range of 10-20 Å. It might, however, have originated from an geometric alignment of the electron beam shape and the facets of the oxide patches [15]. Contrary to the situation on Au/Si a focusing of the BEEM-current along (111) has been predicted for CoSi$_2$(111)/Si(111) films [7].
3. **Interface transmission:** The transmission at the metal/semiconductor interface is possible only if there are matching states in both materials. First of all, energy has to be conserved in the transition, which means that there is no transmission for energies smaller than the height of the Schottky barrier at the interface. Secondly, for epitaxial interfaces, the in-plane lattice periodicity is the same for both materials and thus conservation of parallel momentum is expected to hold, i.e., the in-plane wavevector $k_\parallel$ of metal and semiconductor states must be the same. The projection of the band structures into the interfacial plane is used to check for an overlap of states at a given energy $E$. Only if such an overlap in the interface Brillouin zone (IBZ) exists, transmission is possible at all. In the case of silicon, the six minima of the conduction band (CBM) are located about $0.983 \text{ Å}^{-1}$ away from $\Gamma$ the center of the bulk Brillouin zone along the $\langle 100 \rangle$ directions (see Fig. 1.6). For Si(100) substrates, two CBMs project into the center $\Gamma$ of the IBZ. Contrary to this, none of the CBMs projects onto $\Gamma$ when a Si(111) substrate is used. All six minima are found $0.8 \text{ Å}^{-1}$ away from...
the zone center. As mentioned before the tunneling process favors small values of $k_z$. Thus in a free electron metal in contact with Si(100) significant transmission is expected for energies slightly above the Schottky barrier height. On a Si(111) substrate, however, a much smaller collector current should be measured at the same energy, because almost no carriers have the lateral momentum required to reach the CBMs (unless they pick up momentum in a elastic scattering event). For hole BEEM the position of the silicon valence band maximum (VBM) is relevant. It is located at the center of the bulk Brillouin zone. It projects to the center of the IBZ $\Gamma$ whatever orientation of the substrate is used.

4. Propagation in the semiconductor: Once a carrier has crossed the potential maximum, it is accelerated further into the semiconductor and contributes to the BEEM-current. Scattering has no influence on the magnitude of the collector current, unless the kinetic energy is high enough to create an electron-hole pair ($E_{\text{kin}} > E_{\text{gap}}$). Quantum mechanically the transmission probability across a barrier is not equal to one for energies slightly above the barrier height. There is a finite probability for a particle to be reflected, even if its energy is high enough. Depending on whether or not this quantum mechanical reflection (QMR) is included in the model, a different dependence of the collector current $I_c$ on tip bias $V_t$ is obtained (see e.g. [5]):

$$I_c(V_t) = R(e|V_t| - \Phi_B)^\alpha.$$  \hspace{1cm}(1.5)

The exponent $\alpha$ is found to be $\frac{2}{3}$ [17] or 2 [2] with QMR included or excluded, respectively. The dependence of the current on tip bias is dictated by the opening up of the phase space, as the energy is increased.

It is important to note that the position of the potential maximum does not coincide with the metallurgical interface. As a matter of fact the potential maximum is simultaneously lowered and shifted into the semiconductor, because of the image force acting on the carrier close to the metal film. Taking a linear behavior for the uncorrected potential characterized by an electric field of strength $E$, the reduction in Schottky barrier height is $\Delta\Phi_B = \sqrt{\frac{\varepsilon E}{4\pi}}$ and the shift in position amounts to $z_m = \sqrt{\frac{\varepsilon}{16\pi\varepsilon_0}}$, with $\varepsilon \approx 12\varepsilon_0$ being the dielectric permittivity of silicon [18]. In Fig. 1.7 the corrected potential is plotted for
Figure 1.7: Potential profiles of the n-Schottky barrier for a CoSi$_2$(111) film, which is separated from an n$^+$ Si(111) substrate by a 3000 Å thick undoped Si buffer. The potential maximum is lowered and shifted into the semiconductor, when the image-force correction is introduced.

Electron-electron interaction is negligible as long as the kinetic energy is below the gap width. Optical phonon scattering in the semiconductor was found to merely reduce the effect of quantum mechanical reflection, explaining why square-law behavior is so frequently observed in experimental spectra [19].

### 1.1.3 The CoSi$_2$/Si material system

**Introduction**

CoSi$_2$ is a metallic silicide ideally suited for epitaxial growth on silicon due to its low lattice mismatch of -1.2 %. As a bulk material CoSi$_2$ crystallizes in the CaF$_2$ structure, but in epitaxial films a phase with a CsCl defect structure can be stabilized under certain growth conditions [20]. As a matter of fact in the thin CoSi$_2$(111) films used as base layers for BEEM experiments the CsCl phase is formed first and the CaF$_2$ phase is only ob-
1.1. Ballistic electron emission microscopy

Figure 1.8: STM-topography image of a 30 Å thick CoSi$_2$/Si(111) film taken at $V_t=1$ V, $I_t=0.5$ nA exhibiting both the strain induced 2x1 surface reconstruction (2 different domains in the upper right) and the unreconstructed 1x1 surface (lower left). The range of the gray scale is $\Delta z=1.3$ Å.

tained after an annealing step. The well ordered interfaces CoSi$_2$ forms with Si(111) and Si(100) make it an ideal prototype system to study the epitaxial metal/semiconductor interface by BEEM. For BEEM studies it is also very beneficial to have a material with a simple surface structure, since surface reconstructions cause variations in the tunneling distribution as the tip is scanned across the surface, which show up in BEEM images as small scale contrasts (see [21] and [22]). The surface of CoSi$_2$(111) features two different kinds of structures, which are illustrated in the atomically resolved STM image shown in Fig. 1.8: Two different domains of a 2x1 reconstruction are visible in the upper right, whereas the surface region in the lower left is unreconstructed. The 2x1 reconstruction is strain induced [23] and can be avoided by using a growth procedure, that allows the silicide film to relax the misfit strain. The unreconstructed surface is not atomically resolved at the tip conditions commonly used for BEEM measurements, such that no surface induced atomic scale contrast can be found in BEEM current images. This renders CoSi$_2$(111)/Si(111) samples highly interesting for studying the interface with high resolution. The strain field of the dislocations causes an elastic deformation of the silicide surface. In STM topography images the dislocations show up as faint protruding lines 0.6 Å in height [24].

The band structure of CoSi$_2$ has been calculated by various methods such
Figure 1.9: (a) The band structure of bulk CoSi₂ crystallized in the CaF₂ structure calculated using the LAPW method [25] and the band structure of silicon (b). The Fermi surface of CoSi₂ is shown in (c). It consists of three different sheets, which are associated with the hole bands 7, 8 and 9.
Structure of the CoSi$_2$(111)/Si(111) interface

The CoSi$_2$(111)/Si(111) interface is a type B interface, which means that the CoSi$_2$ lattice is rotated around the interface normal by 180° with respect to the silicon lattice. Just like the Co atoms within the bulk, the Co atoms at the interface are eightfold coordinated [28]. Monolayer (ML) or doublelayer steps at the interface are both coupled to dislocations in the CoSi$_2$ film. These partial Shockley dislocations are characterized by a Burgers vector of

$$\vec{b} = \frac{a}{6}(211).$$

The atomic structure of the CoSi$_2$/Si(111) interface as determined by transmission electron microscopy (TEM) is shown in Fig. 1.10. A quasi-hexagonal network of misfit dislocations is formed in partially relaxed layers, creating
a much higher step density at the interface, than the step density given by
the substrate misorientation.

**Transport across the CoSi$_2$(111)/Si(111) interface**

Transport across the interface is governed by the concept of $\vec{k}_{||}$-conservation. In order to find out, whether transport is possible at all, the states available inside the metal and inside the semiconductor must be compared. This was done by Stiles and Hamann in 1991 [29]. The result of their calculation is reproduced in Fig. 1.11. At an energy of 0.65 eV above $E_F$ (the Schottky-barrier height) the first states of the silicon CBM appear (crosses). Although quite a lot of phase space is available to silicid states, there is no overlap between silicide and silicon states. As the energy is increased gradually, the silicon CBM opens up while the phase space occupied by silicide states does not change appreciably. Only at an energy of 0.85 eV, i.e. 0.2 eV above the Schottky barrier do states with the same energy and parallel momentum exist in both the silicide and the silicon and electron transmission becomes possible. From this lack of phase space overlap a delayed onset was predicted for BEEM-spectra measured on CoSi$_2$/Si(111) [29]. A BEEM-current measured at energies lower than the delayed onset must be the result of a violation of $\vec{k}_{||}$-conservation at the interface. A situation where $\vec{k}_{||}$ is clearly not conserved is given, when the periodicity of the interface is broken by a crystal defect, e.g. a dislocation or a point defect. Such scatterers can supply parallel momentum, which is why they are expected to locally cause a higher electron transmission at low energies. Furthermore they are the only regions where a current is expected for electron energies between 0.65 eV and 0.85 eV. Defects located in the bulk of the CoSi$_2$ film, however, should not lead to an enhanced current in this energy range, because scattering can only change the population within the set of allowed states for CoSi$_2$, none of which overlaps with silicon states.
Figure 1.11: States in the irreducible wedge of the CoSi$_2$(111)/Si(111) interface Brillouin zone as a function of energy. Silicide states are drawn as open circles, silicon states as crosses. Overlapping states are marked with a filled circle. There are no overlapping states up to an energy of 0.85 eV, well above the Schottky barrier height \cite{29}.
1.2 Experimental setup

1.2.1 Sample growth

Introduction

All samples were grown in a commercial VG80 MBE system, equipped with two electron beam evaporators for Si and Co and a Knudsen cell for Ge deposition. The base pressure in the growth chamber was typically $10^{-10}$ mbar. Growth rates for Si and Co were measured using quartz balances, which were calibrated by growing a thick reference film and weighing. The sample temperature was controlled by radiation heating from a heating plate. The thermocouple, which was used to monitor the temperature, was calibrated by measuring the sample temperature with a pyrometer. Fluctuations in sample thickness were minimized by rotating the substrate during growth. Reflection high energy electron diffraction (RHEED) was routinely used to verify the sample quality during growth. Well oriented (111) or (100) 3-inch silicon wafers were used as substrates. They were chemically cleaned and before growth the native oxide was removed from the surface by thermal desorption.

BEEM samples

A typical BEEM sample is designed in a special way, which is depicted in Fig. 1.12. For the BEEM-current measurement, it is crucial to have a good ohmic collector contact to the semiconductor substrate. This is achieved by depositing a 100 Å thick metallic CoSi$_2$ layer at the back side of a highly doped silicon wafer of n$^+$ or p$^+$ type. At the same time current leakage from the base layer to the collector has to be reduced to a minimum, because it leads to noise in the measured BEEM-current. This task is accomplished by minimizing the area of the base, thus reducing both thermally activated currents across the diode and the number of defects in the diode, which might be the cause of further current leakage. Measuring at low temperatures (here $T = 77K$) is of course an additional means of reducing the noise in the BEEM-current. On the 3-inch wafer a diode with an area of about 0.5 cm$^2$ is formed by depositing the thin CoSi$_2$ base layer through a shadow mask, which is fixed to the substrate holder in the MBE growth chamber. The silicide is formed on top of a 3000 Å thick intrinsic silicon buffer deposited at high temperature on the degenerately doped substrate. Thus the potential
1.2. Experimental setup

Figure 1.12: Layer sequence of a BEEM sample. An intrinsic buffer is deposited on a highly doped substrate. The BEEM diode is formed by stoichiometric evaporation of Co and Si through a shadow mask. On the back side of the sample an ohmic contact is formed by depositing a metallic CoSi$_2$ film directly onto the highly doped substrate.

decays approximately linearly across the depletion region extending from the metallurgical interface to the degenerate substrate.

CoSi$_2$ growth

The growth of epitaxial CoSi$_2$(111) films on silicon was performed in the following way: The chemically precleaned silicon substrates are outgassed in the MBE growth chamber for 1-2 hours at a temperature of 600°C. Afterwards the temperature is raised to $T=850°C$ for 4 Min. while a small Si flux is maintained to reduce the SiO$_2$ present on the surface. The 1x1 RHEED pattern changes to 7x7 when the temperature is lowered to 800°C. Then the 3000 Å thick silicon buffer layer is grown at 700°C and annealed briefly at $T=800°C$. The surfaces obtained in this way are clean, 7x7 reconstructed and have a parallel arrangement of surface steps. Onto such a clean Si surface, Co and Si are coevaporated at a rate of 0.3 Å/s and 1.05 Å/s for Co and Si respectively, while the sample temperature is kept as low as 70-100°C. The total amount of Co deposited was varied between 6 Å and 16 Å, which results in silicide thicknesses ranging from 21 Å to 56 Å. After the deposition the film is annealed in several steps up to a final annealing temperature of about 650°C while the surface structure is verified by RHEED. Additional silicon is supplied if the surface undergoes a transition to the Co-rich surface structure, a process which can be identified by the observation of 2x2 recon-
structured 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 are grown in a different way: Prior to coevaporation of Co and Si a Co template layer of 1.5 Å thickness is 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 layers is predominantly 2x1 reconstructed, which causes unwanted surface contrast in BEEM images, most of the films used for BEEM experiments are grown without a Co template.

1.2.2 The BEEM-microscope

In order to prevent oxidation of the CoSi$_2$ surfaces, the BEEM measurements are performed in a STM chamber attached to the same UHV system as the MBE growth chamber. After growth the samples are left to cool down to room temperature. Afterwards they are transferred to the STM-chamber and cooled to liquid nitrogen temperature (77 K) for the BEEM-measurements. The Microscope used for all measurements is a home built low temperature STM, suited to accommodate 3-inch samples [30]. It was designed as a Besocke walker [31]. A schematic drawing of the microscope head is shown on the right hand side of Fig. 1.13. The sample wafer (W) is placed on a polished SiO$_2$ plate (G), into which a gold spring for the BEEM back contact has been integrated (B). The microscope head (H) is a piece of ceramics supported by three coarse approach piezos (CP). It carries the scanning piezo (SP) with the STM tip (T). The head is placed inside a metal cage (C) that is standing on the wafer surface on three insulating feet (F). Electrical contact to the base layer on the BEEM diode is made by a gold spring (S) fixed to the metal cage. This front contact and the STM-tip are located on the separate diode area, which was formed by using a shadow mask during the growth of the base layer. By applying a sawtooth voltage to the three coarse approach piezos, the entire microscope head is rotated. Since the piezos are resting on a thread, the microscope head can be moved towards the sample surface and away from it. The entire sample and microscope arrangement is hanging on three stainless steel springs, which are fixed to the top flange of the STM chamber. In normal operation the microscope is suspended by the springs
1.2. Experimental setup

Figure 1.13: The BEEM microscope: The microscope head seen from below is shown on the left. On the right there is a schematic drawing of the STM in operating position. During the measurement the metal cage (C) is standing on the sample wafer (W) with three feet (F). The wafer itself is resting on the groundplate (G) made from silicon oxide, and has an ohmic back contact (B) attached on the backside. The front contact to the base layer is made by a spring (S). The tip (T) is mounted on the scanning piezo (SP) and is approached to the sample surface.

inside a small chamber made from stainless steel, which is in contact with a 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 this chamber, in order to stabilize the sample temperature. For the measurement, the microscope is decoupled to avoid mechanical vibrations.

1.2.3 Data acquisition

The first preamplifier stages for tip- and collector-current are located in the proximity of the microscope inside UHV to minimize the pickup of electrical noise. Since the temperature of the microscope itself is frequently altered, the current amplifiers are fixed to the top flange of the STM chamber. The noninverting input of the BEEM-OPAMP (an OPA 128LM) is connected to ground (Fig. 1.14). Thus the sample back contact is virtually grounded. Contrary to the conventional STM configuration, where the tunneling current $I_t$ is measured at the tip, which is virtually grounded, and the tunneling bias is applied to the sample, in the BEEM configuration $I_t$ must be measured at the tip while also applying the tunneling bias to the tip. In order to achieve this and still operate the amplifier in the middle of its range, the noninverting
Figure 1.14: Schematic 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 at its optimal operation point.

input of the tunnel-OPAMP (an OPA 111BM) is set to the tip bias \( V_t \) and the supply voltages are shifted along with \( V_t \). The BEEM-current is amplified by a factor of \( 10^8 \) at the in-situ OPAMP. Outside the vacuum chamber low pass filtering is used to further reduce the noise level in the signal. Then it is amplified by another factor of 100 and offset corrected before it is fed into the data-acquisition 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.

The microscope is operated by a commercial STM-control unit (Omicron). The analog electronics (i.e. current feedback and piezo driver circuitry) as well as the digital ramp generators for x- and y- piezo movement are built into a separate unit which is controlled by a microprocessor of its own. This unit is connected to a HPUX workstation by an HP-IB (alias GPIB or IEEE-488) interface. A STM control program is used to set the measurement parameters and acquire STM and BEEM images as well as to perform spectroscopy.

1. In BEEM imaging mode the STM is operated in constant current (CC) mode. As the tip is scanned across the surface (x-y plane), the z-deflection of the tip and the collector current \( I_c \) are recorded simultaneously. The data is usually plotted as gray scale plots, with the gray value corresponding to a certain interval in height \( \Delta z \) or in collector
1.2. Experimental setup

current $\Delta I_c$.

2. Spectroscopy is most frequently performed in two modes: The first one is $I_t(V_t)$-spectroscopy or scanning tunneling spectroscopy (STS). In STS the tip is first stabilized at $(V_{\text{stab}}, I_{\text{stab}})$. Then the $z$-position of the tip is kept fixed (constant height (CH) mode) while the tunneling current $I_t$ is recorded as a function of tip bias $V_t$. The sample local density of states LDOS is probed in this configuration. In the second spectroscopy mode, which is ballistic-electron-emission spectroscopy (BEES), the collector current $I_c$ is recorded as a function of tip bias $V_t$, while keeping the tunneling current constant.
Chapter 1. Experimental
Chapter 2

Point defects at the
CoSi$_2$/Si(111) interface

2.1 Introduction

Ballistic electron emission microscopy still is a relatively new technique and - despite of the simplicity of the experimental arrangement - many experimental findings have not yet been reproduced by theoretical calculations. In this chapter BEEM measurements performed on epitaxial CoSi$_2$/Si(111) layers are presented with emphasis on experiments involving scattering of hot electrons by point defects of atomic size. These experiments not only provide new insight into structural processes such as diffusion and trapping of point defects at an interface, but also into the BEEM process itself contributing significantly to the understanding of hot electron transport in metals. The limits of the standard free electron model commonly used in the BEEM community are pointed out and the importance of a quantum mechanical treatment of hot electron transport, taking the metal band structure into account, is demonstrated.

2.2 Ballistic electrons in CoSi$_2$/Si(111)

2.2.1 Electron scattering

Thin films of CoSi$_2$/Si(111) are ideal for studying electron scattering effects in BEEM for a number of reasons:
1. They are grown with high structural perfection. No grains of material with a different crystal orientation are present in the films and the crystal structure is the same (CaF$_2$) in the whole layer. The formation of pinholes can be suppressed to an extent, that no pinholes are found in large scale topography scans. The structural perfection is important for the stability of the measurements, because tip switches are likely to occur if rough surfaces are scanned using high tunneling currents.

2. Most importantly a well ordered, unreconstructed surface can be obtained, which does not introduce any undesired atomic-size contrast in BEEM images. As a matter of fact no atomic resolution is observed in STM topography images at typical BEEM conditions (rather high tip bias and current).

3. Quite contrary to the defect-induced Schottky barrier height fluctuations found in CoSi$_2$ films grown on Si(100) [32], the Schottky barrier height does not change because of defects at the CoSi$_2$/Si(111) interface; The Schottky barrier height was found to be 0.67 ± 0.03 eV all over the interface.

4. It was pointed out before that none of six Si CBMs project onto the center of the IBZ (see Fig. 1.6). For low energies this must lead to a strong increase in $I_c$ at defects, where an electron is able to pick up some lateral momentum in a scattering event and reach a CBM.

Naturally the most obvious sources of electron scattering are misfit dislocations with a Burgers vector $\vec{b} = \frac{a}{6}(211)$, which are always present in the silicide films. Indeed a strong scattering contrast has been found near the core region of the dislocation [33]. Since the dislocations are located at the interface, electrons can even be scattered into states with a large $k_\parallel$, which exist in the silicon, but would be forbidden inside the silicide. In Fig. 2.1(b) a BEEM-image recorded on a 28 Å thick CoSi$_2$(111)/n-Si(111) layer is displayed. The collector current is clearly enhanced at the dislocation network. The dislocations are also visible in the corresponding topography image Fig. 2.1(a) as faint protruding lines of 0.6 Å height. This surface distortion is brought about by the strain field surrounding the dislocation core [24]. It follows a Lorentzian lineshape with a FWHM of twice the layer thickness $d$. The bright lines in the BEEM-image are much narrower and are thus related to electron scattering at the dislocation core rather than the dislocation strain.
2.2. Ballistic electrons in CoSi$_2$/Si(111)

Figure 2.1: (a) STM topography image of a 25 Å thick CoSi$_2$/n-Si(111) film measured with ($V_t = -1.7$ V, $I_t = 3$ nA). A network of interface dislocations is visible due to the elastic deformation of the sample surface. In the simultaneously acquired BEEM image (b) a strong increase of the collector current at the dislocations is observed. The ranges of the gray scales are 12 Å in the topography image (a) and $\Delta I_c = 168$ pA in (b).

field. At the tip-conditions used ($V_t = -1.7$ V) almost no contrast is observed between regions separated by a dislocation line. This changes dramatically if the tip bias is increased.

2.2.2 Thickness contrast

A scan acquired using a tip-bias of $V_t = -6$ V on the very same surface region is shown in Fig. 2.2. From the topography image it is evident that scanning at high voltages is less stable than at low bias. Nevertheless the same protruding lines due to the dislocations can still faintly be seen in Fig. 2.2(a). The BEEM-image Fig. 2.2(b), however, looks completely different from the low bias scan shown in Fig. 2.1(b). No contrast at all stemming from dislocation lines is present, but the image is made up of patches of constant collector current. Upon closer inspection, these patches correspond to the regions bounded by dislocations. It was already pointed out before, that dislocations separate regions differing at least by 1 ML in film thickness. The patches, which Fig. 2.2(b) consists of, are regions bounded by dislocations, where the film thickness is constant, but different from the thickness of all neighboring regions. The reason for this thickness contrast is the small value of the attenuation length $\lambda$ at high electron energies (see Fig. 1.4). At $V_t = -6$ V the attenuation length is $\lambda \approx 25$ Å, which makes it possible to map thickness changes as small as 1 ML [34].
2.2.3 Quantum interference

A completely different mechanism, which causes contrast in BEEM-images between regions of different film thickness, is quantum-interference. It arises because the electron wave incident on the interface and the reflected wave interfere constructively or destructively depending on the film thickness. Electron reflection at the interface is expected to occur mainly at energies, where no states are available in the center of the IBZ. Indeed the interference effects disappear for tip voltages above $|V_t| = 2$ V. Another reason why no interference is found for high voltages is the strong decrease of the attenuation length $\lambda$ with energy (see Fig. 1.4), such that the electron beam looses coherence before it has passed the film twice. Fig. 2.3 gives an example of quantum-interference contrast between regions, which are separated by dislocations and therefore differ in thickness by at least 1 ML. The topography image (a) and the corresponding BEEM image (b) were both measured during the forward scan at a tip bias $V_t = -1.2$ V. During the back scan a different voltage was applied to the tip ($V_t = -1.6$ V), which resulted in the images (c) and
Figure 2.3: (a) STM topography image of a 28 Å thick CoSi₂/n-Si(111) film measured with \( V_t = -1.2 \) V, \( I_t = 10 \) nA. The simultaneously acquired BEEM image is given in (b). (c) and (d) show topography and BEEM images measured with a different tip bias \( V_t = -1.6 \) V during the back scan. Regions separated by dislocations (labeled D) differ in thickness by 1 or 2 monolayers, which causes the quantum interference contrast evident in (b). The ranges of the gray scales are 1.9 Å in the topography images (a) and (c), and \( \Delta I_c = 270 \) pA and \( \Delta I_c = 480 \) pA in (b) and (d) respectively.

(d). The contrast between neighboring regions, which is very pronounced at low tip bias, becomes much weaker at higher bias and even undergoes a sign reversal. Such an oscillatory behavior is typical to the quantum interference effect and can also be observed in scanning tunneling spectroscopy measurements of the LDOS. In Fig. 2.4 the quantity \( (dI_t/dV_t)/(I_t/V_t) \) calculated from two \( I_t(V_t) \) spectra taken next to a dislocation are shown. This quantity is often referred to as “experimental LDOS” and is preferred to \( (dI_t/dV_t) \) because the increase in the average tunneling current, which is a consequence of the lowering of the effective tunneling barrier with high bias, is compensated by normalizing to \( (I_t/V_t) \) [35]. Both curves show an oscil-
Figure 2.4: Local density of states measured to the left (○) and to the right (•) of a dislocation in a 28 Å thick CoSi₂/n-Si(111) film. The tip was stabilized at \( V_t = -1.7 \) V, \( I_t = 3 \) nA.

Laboratory behavior up to about -1.5 V. For a two-dimensional free electron gas we expect to see steps in the density of states (DOS). The reason why the spectra show distinct peaks is that scanning tunneling spectroscopy is more sensitive to states with small \( k \parallel \) and therefore exaggerates the LDOS at the energy of a new subband.

Besides quantum interference contrast some other features in Fig. 2.3 remain to be discussed. In the BEEM images (b) and (d) many bright spots are visible in the planar regions between the dislocations. Since they do not have corresponding features in the topography images, we assume that the contrast is caused by a subsurface point defect [one of them is labeled ‘PD’ in Fig. 2.3(b)]. At first sight they seem to be distributed about the interface in a quite uniform way. After closer inspection, the density of point defects seems to be lower close to dislocation lines. Additionally, the dislocations themselves appear to have some inner structure: they look like a pearl necklace [see also Fig. 2.10]. In the upper right of the BEEM images of Fig. 2.3 the point defects are absent. As a matter of fact they are still visible,
but the contrast is both weaker and broader. The surface in that part of the image is 2x1 reconstructed [as indicated in Fig. 2.3(a) by a dashed line], which drastically changes the electron distribution injected into the film.

2.3 Ballistic holes in CoSi$_2$/Si(111)

Ballistic hole emission microscopy is by far less popular than ballistic electron emission microscopy, which is mostly due to the fact, that the energy distribution of the injected holes is peaked towards the Fermi-energy $E_F$ of the base as indicated in Fig. 1.2(b). As a consequence, the collector currents measured at a comparable magnitude of the tip bias will be significantly lower on CoSi$_2$/p-Si(111) samples compared to samples grown on a n-doped substrate. The smaller currents lead to a higher noise level in collector current images and spectra. Furthermore spectroscopic measurements are much more difficult to interpret, because the contribution of the holes with the energy given by the tip bias is less or equal than the contribution of lower energy holes. This is completely different from the situation in 'electron-BEEM', where it is quite safe to assume a narrow energy distribution of electrons at the kinetic energy $e|V_f|$. Nevertheless it is interesting to compare the results obtained in 'electron-BEEM' to the 'hole-BEEM' measurements. Scattering of hot holes should also result in a variation of the collector current as the tip is moved across an interfacial defect. The sign of this current variation should be opposite to the one found in 'electron-BEEM', because hot holes picking up $k_{\parallel}$ are no longer able to reach the Si VBM. This is indeed what was found in the measurements on CoSi$_2$/p-Si(111) samples displayed in Fig. 2.5. The upper images show topography (a) and collector-current (b) measured on a 30 Å thick sample [13]. The lower images (c) and (d) were recorded on a 56 Å thick silicide film. The length scales were chosen identical in order to facilitate a comparison between the two measurements. In the current images the black stripes indicate a lowered current at the locations, where interfacial dislocations are visible in the corresponding topography images. In the regions between the dislocations, there are also some dark spots (arrows), which are caused by hole scattering at point defects. The contrasts are, however, too weak and obscured by tip switches and mechanical vibrations to allow for a quantitative comparison of their sizes in both samples. Nevertheless it is possible to determine the size of the hole distribution arriving at the interface by looking at line sections taken orthogonal to a dislocation line. On the one
hand the contrast stemming from 1-dimensional scatterer is higher than that stemming from a 0-dimensional scattering center, on the other hand the noise level can be further reduced by averaging profiles along the dislocation line. Such line sections obtained from Figs. 2.5(c) and (d) are plotted in Fig. 2.6. The surface profile (denoted by open circles) follows nicely a Lorentzian line-shape with a FWHM of $\approx 104 \, \text{Å}$, which is about what is expected on a 56 Å thick layer from elasticity theory, predicting a Lorentzian with a FWHM of twice the film thickness [24]. The collector current (closed circles) is well fit by a Gaussian with a FWHM of $\approx 16 \, \text{Å}$. This is by far narrower than the extent of the dislocation strain field. As the size of the scattering center, the dislocation core, is of atomic dimensions, the width of the collector current contrast reflects the width of the hole beam impinging on the interface. From the classical free electron BEEM theory, the hole beam (or electron beam in the case of hot electron injection) is expected to propagate in a cone with
2.4 Interfacial point defects

The reasoning why the point defects observed in BEEM images have to be at the interface between CoSi$_2$ and Si and not within the CoSi$_2$ film itself or even within the Si, between interface and potential maximum, is quite complicated. It turns out, that the question ‘where are these point defects?’ is very closely related to another important question ‘where is the delayed onset?’. The delayed onset was briefly hinted at in chapter 1.1.3. It is the prediction made by Stiles and Hamann [29] based on their band structure calculations, that although the energy of the electrons injected by the STM tip may be higher than the Schottky barrier height (0.65 eV), no transmission of electrons into the collector should occur up to a tip bias of $V_t = -0.85$ V, if $k_\parallel$ was conserved at the interface. There was an early experimental con-
Figure 2.7: (a) BEEM-image taken at a tip voltage of $V_t=-1.2$ V. (b) BEEM-image taken shortly afterwards with $V_t=-0.8$ V. The contrast due to scattering at point defects is still visible at low tip bias, indicating that these are located at the interface and not within the CoSi$_2$-layer. (c) At $V_t=-0.7$ V the contrast caused by the point defects has disappeared in the noise (left), but can still be found by low pass filtering the image (right). The tunneling current was $I_t=20$ nA and the gray-scales vary within a range of $\Delta I_c=200$ pA (a), $\Delta I_c=40$ pA (b), $\Delta I_c=16$ pA (c, left) and $\Delta I_c=3$ pA (c, right).

firmation of such a delayed onset [36], but it could never be reproduced by other groups. On the contrary a 'normal' onset was found by others [37, 38] and in our laboratory [32]. Since the measurements in [36] were performed ex situ as opposed to our locally resolved spectroscopy performed in UHV, we are inclined to attribute the delayed onset measured earlier rather to a contaminated tip than to a band structure effect. Still the homogeneously lower onset found in our spectra, even in regions far away from interfacial defects, forces us to assume a small degree of violation of $k_\parallel$-conservation everywhere at the epitaxial interface. Nevertheless $k_\parallel$ must be conserved to a high degree, because if scattering at the interface was too dominant, no quantum interference effects could be found.

Now let us first assume, that the band structure calculations performed
2.4. Interfacial point defects

by Stiles and Hamann are correct, and that a small scattering probability at the interface prevents us from measuring the delayed onset. Although in principle scattering could take place anywhere in the film there are several arguments favoring the interpretation, that the bright spots in a BEEM-image are due to scattering centers located at the interface:

1. Surface scattering can be excluded since surface defects also show up in atomically resolved topography images.

2. The nearly uniform and exceedingly small apparent size of the defects \[ \approx 10 \text{ Å}, \text{see also Fig. 2.15} \] renders it highly unlikely that the latter are located between the metallurgical interface and the potential maximum within the silicon, because the spread of the electron beam is larger in the silicon.

3. The small correlation length for surface roughness deduced from resistivity measurements requires the presence of additional scattering centers apart from steps [39].

4. Finally, band structure calculations by Stiles and Hamann indicate also that the point defects are located right at the interface. According to these calculations there are no states in CoSi2, which match the silicon conduction band minima in the vicinity of the Schottky barrier. For this reason scattering within the CoSi2 cannot increase the transmission probability close to \( \phi_B \). It only mixes silicide states none of which is allowed to enter the Si, and can only couple to the Si CBM by a small interfacial scattering probability, as mentioned before. The BEEM contrast due to objects located in the bulk of the film should therefore vanish as the tip bias is lowered towards \( \phi_B \).

BEES taken on a subsurface point defect and in its neighborhood does not, however, reveal any diminishing contrast as the electron energy approaches \( \phi_B \). This can be seen in Fig. 2.7, where BEEM-images taken at the same location with different tip biases are shown. The point defects are clearly visible for \( V_t=-1.2 \text{ V} \) in Fig. 2.7(a). For \( V_t=-0.8 \text{ V} \) (b) the contrast due to scattering at point defects is still above the noise-level. For still lower electron energy (\( V_t=-0.7 \text{ V} \)) the scattering contrast disappears in the noise [see Fig. 2.7(c) left]. It can be made visible by low-pass filtering the image [see right hand side of (c)]. From the fact that the scattering contrast persists
even for energies only slightly above $\phi_B$, we can conclude, that the scattering center must lie at the interface itself and not in the bulk of the CoSi$_2$ layer.

### 2.5 The delayed onset

The onset of BEES spectra measured on thin CoSi$_2$ crystallized in the CaF$_2$ structure on a n-Si(111) substrate, was always determined to $0.67 \pm 0.03$ eV, which is the value expected for the Schottky barrier height. This was the case even when the spectra were recorded away from dislocations and point defects. In order to account for this phenomenon a scattering probability $\alpha$ at the perfectly epitaxial interface was postulated [32]. While $\alpha$ is obviously not zero, it still must be a small number, because quantum interference of incoming and specularly reflected electron waves is routinely observed in the same samples. Interfacial point defects are scattering centers, which also scatter electrons at the interface. Spectroscopy measurements were performed in the vicinity of a single point defect. Two spectra are plotted in Fig. 2.8 using filled symbols. One of them is an average of 14 spectra recorded on top of the point defect (diamonds) and the other was averaged in a region away from the defect (circles). The derivative of the spectra is plotted using open symbols. In the standard procedure used to determine the onset of the spectra, the square root of the measured collector current is fitted to a straight line in the onset region, which means that a quadratical dependency of $I_c$ on $(e|V_t| - \Phi_b)$ is assumed. The spectra shown in Fig. 2.8 were fitted using a two threshold model:

$$I_c(V_t) = R_1(e|V_t| - \Phi_{b_1})^2 + R_2(e|V_t| - \Phi_{b_2})^2$$  \hspace{1cm} (2.1)

In the fit, all four parameters were adjusted for each spectrum. The resulting parameters consistently showed a lower onset $\Phi_{b_1} = (0.69 \pm 0.03)$ eV, which corresponds to the Schottky barrier height, and a higher onset at $\Phi_{b_2} = (0.83 \pm 0.02)$ eV, which is the delayed onset, that was predicted by Stiles and Hamann. Also fits to the derivative of the spectra yielded the same pair of thresholds $\Phi_{b_1}/\Phi_{b_2}$. The fact that we do observe a second threshold in our spectra that corresponds to the delayed onset based on the band structure calculated by Stiles and Hamann, is an indication that these calculations are correct. This confirms our proof that the point defects are located at the interface, which relies on the correctness of the band structure calculation.
2.5. The delayed onset

![Graph showing I(V) and dI/dV curves with threshold energies.](image)

Figure 2.8: Average of 14 BEES spectra and corresponding first derivative spectra, taken on top of an interfacial point defect (diamonds) and in a defect-free area (circles). The spectra were measured with a tunneling current of $I_t = 20$ nA, and are normalized to $I_t = 1$ nA. Fits to Eq. 2.1 are indicated by the solid lines.

It is already obvious in Fig. 2.8, that the spectrum taken on top of a point defect exhibits a higher current belonging to the lower threshold. In order to visualize the weight associated with each onset as a function of position, every spectrum out of the entire data set of 100x9 spectra, that were recorded on a rectangular area with a spacing of 0.5 Å, was fitted to the two threshold model. The thresholds were fixed to $\Phi_{b1} = 0.69$ eV and $\Phi_{b2} = 0.83$ eV in this fit, because of the higher noise level encountered when fitting single spectra. The results of this fitting procedure are presented as gray scale images in Fig. 2.9. The uppermost image (a) gives the topography information recorded during the spectroscopy scan. In (b) the BEEM image recorded at the stabilisation bias $V_t = -1.7$ V is under display. The compressed shape of the point defect is a consequence of microscope drift during the acquisition of the spectra. In the images (c) and (d) the scale factors $R_1$ and $R_2$ are plotted, belonging to the lower threshold $\Phi_{b1} = 0.69$ eV and the higher threshold at $\Phi_{b2} = 0.83$ eV, respectively. It is evident, that the point defect contrast seen
2.6 Point defect diffusion

The invention of the scanning tunneling microscope (STM) has revolutionized the study of surface processes occurring during thin film growth. The anisotropy of surface diffusion in Si(100) homoepitaxial growth has been analyzed by STM [40] and the size and distribution of islands formed during growth at different temperatures has been used to extract data relevant for the nucleation process and the adatom diffusion at the surface [41]. Dendritic island growth caused by hindered adatom diffusion along step edges could be observed [42]. More recently adatom movements could be monitored in
2.6. Point defect diffusion

Figure 2.10: (a) STM-topography image of a 28 Å thick CoSi$_2$ film taken at ($V_t$=-1.2 V, $I_t$=20 nA). The bright line (D) is a 0.6 Å high protrusion caused by the strain field of a dislocation. Some surface point defects are present (S). The gray-scales range from 0 to 2 Å. (b) Corresponding BEEM-image: interfacial point defects like the one labeled (P) have been trapped in the core of a dislocation (D). There are empty (E) and occupied (O) regions in the dislocation. The gray-scales vary within a range of $\Delta I_c$=263 pA.

real time by this technique (see e.g. [43]). While the STM's potential for real space surface studies thus appears evident, this is true to a far lesser extent for buried interfaces. Since in our BEEM experiments we have resolved individual point defects at the CoSi$_2$/Si(lll) interface, we have found a way to apply BEEM to the study of diffusion processes at an interface.

In Fig. 2.3 there are dislocation lines, which seem to have some inner structure in the BEEM images. This becomes more obvious when smaller scale images, such as Fig. 2.10, are considered. In Fig. 2.10(a) a small-scale topography image featuring a single dislocation line is shown. In addition to the dislocation several surface point defects (labeled S) can be seen. As surface features may influence the energy- and momentum-distribution of the tunneling electrons (see [21]), they can be recognized in the BEEM-image
Chapter 2. Point defects in CoSi$_2$/Si(111)

Figure 2.11: Line sections taken orthogonal to the dislocation line shown in Fig. 2.10 through the points indicated E and O, respectively. The BEEM-current is enhanced at the location O, where a point defect is present (see o). The current in the line section which does not pass through a point defect (●) shows only a faint variation on a length scale comparable to the surface deformation (●). [Fig. 2.10(b)] as well. However, there are by far more point-like contrast features in the BEEM-image, which cannot be associated with a surface defect and are caused by scattering at interfacial point defects.

On closer inspection of the dislocation in Fig. 2.10(b), it is evident that the contrast is not uniform along this line. On the contrary, the BEEM current is largest at point defects which have accumulated in the core of the dislocation. This becomes even more evident from a comparison of line sections taken across the dislocation line (Fig. 2.11), either through an empty region of the core (E) or at a site occupied by a point defect (O). Hardly any scattering contrast is found at location (E), whereas I$_c$ is strongly enhanced close to (O). In view of these new results the sharp linear contrast features previously observed in BEEM images [33], can no longer be attributed to scattering at the dislocation core. The contrast must have been due to scattering at unresolved point defects accumulated in the dislocation core. The long range variation of the collector current visible across the ‘empty’ site (E) and the deformation of the surface occur on exactly the same length scale (FWHM=60 Å), which is given by the extent of the dislocation’s strain field. This long range contrast is not due to scattering at a point defect or the dislocation core but related to the strain field.

In all the BEEM-images the density of point defects is found to be lower
2.6. Point defect diffusion

close to the dislocation lines. Evaluating several images from scans made at a larger scale than that of Fig. 2.10(b), the point defect density \( n \) as a function of distance from the closest dislocation line was obtained (see Fig. 2.12). These data were fitted with a simple one-dimensional model, in which diffusion of point defects into a perfect sink at \( x = 0 \), the core of the dislocation, was assumed. A uniform concentration \( n_0 \) of point defects in the interfacial plane was taken as a starting condition, leading to the following expression for \( n \) (see Appendix C):

\[
 n(x, t) = n_0 \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right) 
\]  

(2.2)

It was further assumed that diffusion takes place during the final annealing step (after growth), during which the sample is kept at a temperature of 640°C for a time \( t \) of about five minutes. A diffusion coefficient \( D \) of \( 5.2 \times 10^{-16} \text{cm}^2\text{s}^{-1} \) and an initial point defect density of \( n_0 = 7.37 \times 10^{12} \text{cm}^{-2} \) was obtained. Summing up the missing point defects next to a dislocation line, we expect to find them trapped in the core of the dislocation at a line density of \( 0.066 \text{Å}^{-1} \). Counting all point defects in several highly resolved BEEM-images of dislocations yielded an occupation of \( 0.0626 \pm 0.01 \text{Å}^{-1} \) in very good agreement with the value derived from the fit.

The BEEM-contrast stemming from a single point defect has a width of approximately 10 Å. This width is a convolution of the actual size of the scatterer and the width of the electron beam at the interface. Since it reflects changes in tunneling and tip conditions it is merely an indicator of the width of the electron beam. The scattering object at the interface itself is considered to be of atomic size. Unfortunately, the present measurements do not render any further information about the structural nature of the point defects observed by BEEM. It is therefore a matter of speculation, whether the scattering is caused by vacancies, interstitial defects or impurity atoms. One argument in favor of identifying the point defects with vacancies is the following: When the silicide crystallizes from the as-deposited amorphous phase in the first stage of the annealing it assumes a defect CsCl-type crystal structure, in which only half of the Co-sublattice is occupied by randomly distributed Co-atoms [44, 45]. Upon further annealing this phase is transformed to the bulk-stable CoSi2 phase with the CaF2 crystal structure. It appears likely that this process will leave some Co-vacancies at the interface. Such a distribution of (presumably magnetic) defects in the Co-sublattice
Figure 2.12: Point defect density \( n \) plotted as a function of distance \( x \) from a dislocation. The solid line is a solution to the one-dimensional diffusion equation obtained by assuming a constant initial concentration of point defects and a perfect sink at \( x=0 \). The fit yields an initial density \( n_0 = 7.37 \times 10^{12} \text{ cm}^{-2} \) and a diffusion coefficient of \( 5.2 \times 10^{-16} \text{ cm}^2\text{s}^{-1} \).

at the interface could also account for the enhanced magnetic scattering observed in transport measurements performed on thin CoSi\(_2\) films [46, 47]. A vacancy can be considered a region of lowered strain and is attracted to regions of compressive strain (see e.g. [48]). An accumulation of vacancies near the core of a dislocation line is therefore energetically favorable.

### 2.7 Carrier focusing

Since the apparent size of an interfacial point defect is a convolution of the actual size of the defect and the width of the electron beam arriving at the interface, it can be used as a measure for the beam width, under the assumption that the size of the defect is so small that it can be neglected. From images such as Fig. 2.10(b) the diameter of the electron beam at the interface after propagation through a 28 Å thick CoSi\(_2\)(111) film is estimated to \((11 \pm 2) \text{ Å} \). This is very narrow compared to the value of 20 Å expected from free electron theory which assumes an electron cone with an opening angle of 40° [5]. While the commonly used model of the BEEM process fails to explain our measurements, a new theoretical model of electron transport in the base layer, which was put forward recently by Reuter et al. [7], is able
2.7. Carrier focusing

To account for the high resolution measured at the CoSi$_2$/Si(111) interface, in this new theory, the current distribution, which is injected into a half-space of CoSi$_2$(111) by means of an STM tip, is calculated as a function of depth. Both injection process and the current propagation in the silicide are treated quantum-mechanically in a Keldysh Green's function formalism, taking into account the CoSi$_2$ band structure. Current damping due to the electron-electron interaction is included by the introduction of an imaginary part in the energy distribution. This self-energy was set to $\eta = 0.05$ eV in order to reproduce the experimental values for the attenuation length $\lambda(V_t)$. The calculations were done in a LCAO basis, which for energies close to $E_F$ - could correctly reproduce the band structure calculated by the LAPW method [25]. In Fig. 2.13(a) the current distribution after propagation through a 30 Å CoSi$_2$(111) film is shown [7]. Most of the current in the silicide is flowing through a narrow channel below the tip. In Fig. 2.13(b) a cross section through the current distribution is plotted. It features a FWHM of 8.9 Å, which agrees very well with the experimentally obtained $11 \pm 2$ Å. In the theory the narrow beam width is explained by electron focusing along $\langle 111 \rangle$ directions induced by the CoSi$_2$ band structure. A resolution of 10 Å

![Diagram](image)

Figure 2.13: (a) Calculated current distribution (after [7]) in a layer parallel to the surface after propagation through a 30 Å CoSi$_2$(111) film. Injection from the tip at 1.5 eV occurred at the position marked by a white X, where the maximum current can still be found. The linear gray scale indicates current intensity at each atomic site: black maximum to white zero current. (b) displays a cut through the focused bean in the $\langle 211 \rangle$ direction from which a FWHM of 8.9 Å can be derived.
Figure 2.14: STM topography (a,c) and BEEM images (b,d) recorded on two different CoSi$_2$/n-Si(111) samples with thicknesses of 28 Å for the first sample (a,b) and 56 Å for the second sample (c,d). The tunneling parameters were set to ($V_t$=-1.4 V, $I_t$=20 nA) and ($V_t$=-1.5 V, $I_t$=20 nA) for (a,b) and (c,d) respectively. The range of the gray scales is 1.7 Å and 1.9 Å in the topography images (a) and (c), and 560 pA and 260 pA in the BEEM images (b) and (d) respectively.

After propagation through a 28 Å thick film would correspond to an electron cone with an opening angle of 20°. In the framework of the free electron model it is still possible to explain such small opening angle [33], but only as long as electron interference at the narrow tunneling channel between tip and surface is neglected, i.e. as long as the tip is assumed to be large. Since atomic resolution is regularly found in images of 2x1 reconstructed surface patches (distance between rows: 6.65 Å) the blunt tip approximation must be incorrect. However a diverging beam with an opening angle of about 40° is predicted, if electron interference at a circular opening with a diameter of 7 Å is used as a model for injection by a sharp STM tip [5]. This is completely incompatible with the resolution found in the BEEM experiment.

Thicker films were investigated by BEEM in order to clarify whether the narrow beam observed was indeed a consequence of electron focusing. Topography and BEEM-images of a 56 Å thick CoSi$_2$/n-Si(111) film are shown in Fig. 2.14(c) and (d), respectively, along with images taken on a 28 Å thick layer [Fig. 2.14 (a) and (b)]. From comparing the two BEEM images it is immediately clear that a focusing of the electron beam must indeed occur: the apparent size of the point defects is almost identical for both films, although they differ in thickness by a factor of two. Even single
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Point defects trapped in the dislocation core can still be identified in the BEEM image of the thicker film. Line sections were taken through BEEM images of point defects, in order to quantify the width of the electron beam at the interface. In Fig. 2.15 two current profiles taken from the two BEEM images in Fig. 2.14 are plotted. A Gaussian fit to the curves yields a FWHM of 10 Å for the point defect in the 28 Å thick film and 13 Å for the sample with the 56 Å thick silicide layer. The size of the electron distribution is slightly larger for the thicker film (almost within the error of about 2 Å), but the difference is far from the factor of two, that would be expected for a cone-like electron propagation. Additionally there is no way to explain the high resolution after propagation through a 56 Å thick film within conventional free electron theory. It is, however, fully compatible with the calculations by Reuter, which predict no significant change in the size of the central spot of the electron distribution even for a film as thick as 70 Å [49].

In section 2.3 a similar effect was observed, when holes were injected into a CoSi$_2$/p-Si(111) film: the apparent width of interfacial dislocations measured on a 56 Å thick film was only about 16 Å; far below the value expected

![Figure 2.15: BEEM current variation as the STM tip is scanned across an interfacial point defect. Line sections taken from the BEEM images Fig. 2.14(b) and (d) are plotted along with fits to a Gaussian. The profile denoted by (c) stems from the 28 Å thick sample. The data from the 56 Å thick silicide layer is plotted using (○). An offset was added to the curves for clarity.](image-url)
Figure 2.16: Electronic current distribution in the IBZ, \( J_t(E, k_z) \), evaluated at 1.5 eV after 30 Å film propagation. The current intensity is drawn with a linear gray scale, black representing maximum current. The ellipsoids define available Si states below 1.5 eV. The inset contains the constant energy surface sheet \( h_s \) mainly responsible for the current propagation: the shaded flat terraces point in the \((111)\) direction and correspond to the dark areas of the 2D current distribution (taken from [7]).

from free electron (or hole) theory. It is straightforward to assume a similar mechanism to be responsible for the high resolution in hole BEEM and in electron BEEM. In Fig. 2.13 the calculated real space distribution of the electron tunneling current after 30 Å propagation was shown. Fig. 2.16 gives the corresponding current distribution \( J_t(E, k_z) \) in 2D reciprocal space in a plane 30 Å below the surface. Contrary to previous statements based on planar tunneling theory the current distribution is not peaked towards the center of the interface Brillouin zone (IBZ). The states contributing most to the current are located slightly away from the zone center in a threefold symmetric arrangement. At the specific energy of 1.5 eV chosen here, the overlap between these states and the available states in the Si CBM's (dashed lines) is still small. Scattering at the interface is thus likely to enhance transmission, while a significant part of the electrons will be reflected at a perfect interface, allowing for the formation of standing waves in the silicide. Both effects have indeed been observed experimentally (see section
2.7. Carrier focusing

2.2.1 and 2.2.3, respectively). The current distribution in the IBZ bears a strong resemblance with the $k_s$ sheet of the Fermi surface, which is drawn in the inset. This surface belonging to the eighth band has approximately the same shape 1.5 eV above the Fermi-level, but the size is decreased. The flat regions shaded gray in the inset are the regions mainly responsible for current transport. The surface normal in these shaded regions points towards (111) and so does the group velocity $\vec{v}_p$. Thus the current is mainly directed along (111), explaining the small electron spot at the interface. The fact that the flat regions on constant energy surfaces are mainly responsible for ballistic carrier propagation is not that surprising. García-Vidal et al. [50] first applied Koster's fundamental analysis of bulk propagators [51] to BEEM. Koster's analysis states, that in the bulk preferred propagation directions are given by the surface normals to the flat parts of a constant energy surface. Such preferred directions of electron and hole propagation have been experimentally observed in macroscopic single crystals [52]. Koster's analysis is only strictly valid for large propagation distances, which is certainly not the case in the BEEM measurements presented here. Nevertheless, the numerically calculated current distribution agrees with Koster's analysis even after only 30 Å of electron propagation. At an energy 1.5 eV above $E_F$ there are two bands available: 8 and 9. The band dominating propagation is the one with the higher group velocity [49], which happens to be band 8.

The surprising fact, that the momentum distribution of the tunneling current (see Fig. 2.16) does not include states with $k_\parallel = 0$ must be understood as an effect arising from current damping due to the electron-electron interaction rather than a consequence of the tunneling process. At the surface, states close to $k_\parallel = 0$ are indeed populated by the tunneling process [53]. Since the constant energy surface in this region has the shape of a pyramid (compare inset in Fig. 2.16), these states propagate in three beams at a very shallow angle with respect to the surface ($\phi \approx 20^\circ$). The distance they have to travel until they reach the interface is three times larger compared to states propagating normal to the surface, and consequently they are damped much stronger. This situation is schematically drawn in Fig. 2.17. The electron-electron interaction is, however, a function of kinetic energy and the attenuation length $\lambda(E)$ increases significantly as the electron energy is lowered from $E_F + 1.5$ eV to a value below $E_F + 1$ eV (see Fig. 1.4). In exactly this energy range the $I(V)$ spectra are fitted to find the Schottky barrier height. This gives us another possible explanation for the low onset found in BEES spectra: The $k_\parallel$ nonconserving transitions found in regions seemingly away
Figure 2.17: In addition to the focused electrons traveling orthogonal to the surface, three weaker beams originate on the surface below the tip, which form an angle of 70° with the surface normal. Due to the longer distance to the interface most of the current is lost in these beams, because of the electron-electron interaction.

from the influence of point defects, could originate in scattering of electrons from these side-beams on interfacial defects. The density of point defects for example was determined to \( n_0 = 7.37 \times 10^{12} \text{ cm}^{-2} \), which corresponds to an average spacing of 37 Å. At the interface the distance of the electrons in the side-beams to the central BEEM spot would be 79 Å for a 28 Å thick film. Chances are very high, that scattering of the side-beams at a point defect is included in spectra averaged over a certain sample area, even if the central spot only illuminates defect-free regions. BEEM images have to be recorded at a tip bias exceeding 1 V to keep the signal to noise ratio tolerable, such that an eventual direct imaging of these side-beams at low energies remains impossible. Calculations of the real space current distribution for energies below \( E_F + 1.5 \text{ eV} \) are also lacking until now. But the mechanism described above could nicely explain the low onset of experimental BEES spectra, without the need to postulate a violation of \( k_z \) conservation at a defect-free epitaxial interface.

While the electron focusing has been explained in terms of the CoSi\(_2\) band structure, the experimentally found hole focusing remains to be clarified. In complete analogy to electron propagation in the silicide we examine the particularities of the band structure at energies below \( E_F \). The distribution of
2.7. Carrier focusing

Figure 2.18: Cuts through the CoSi$_2$ constant-energy surfaces [54] at an energy 1.5 eV above $E_F$ (a) and 0.5 eV below $E_F$ (b). The regions carrying the BEEM current are indicated by an arrow. In the insets the Fermi-surfaces belonging to the $h_8$ and $h_7$ bands are shown.

tunneling electrons is always peaked towards the Fermi level of the cathode, which is why for electron injection we have only considered the band structure at the maximum energy $E_F+1.5$ eV. Since holes can be thought of as electrons tunneling from sample to tip, their energy distribution has a maximum for $E_F$ and drops for lower energies (higher hole kinetic energy). For hole injection it is therefore appropriate to have a look at the constant energy surfaces corresponding to hole energies slightly above the hole Schottky barrier. In Fig. 2.18(b) a section through the surfaces of constant energy at $E_F-0.5$ eV is displayed [54]. Three bands (7, 8 and 9) are present in this energy range. The band with the highest group velocity is now band 7, a band which converges at $\approx E_F+1$ eV. The shape of the corresponding constant energy surface at $E_F$ is shown in the inset. The surface consists of eight planes standing orthogonal to the $\langle 111 \rangle$ directions, which is an ideal configuration for hole focusing. The states on the planar regions dominate the current transport and guide the current close to the $\langle 111 \rangle$ direction.
2.8 Conclusions

This BEEM investigation on interfacial point defects has helped to shed light on a variety of issues:

- First of all the high resolution images of interfacial point defects in electron- and hole-BEEM images taken on CoSi$_2$/Si(111) films as thick as 56 Å, have revolutionized the understanding of the BEEM process. The carrier focusing observed experimentally can not be explained by standard free electron BEEM theory and can only be understood in a full quantum mechanical approach to BEEM [7]. The free electron model has been questioned before by measurements showing a very similar interface transmission for Au/Si(111) and Au/Si(100) films [2, 3, 14]. The forward focused electron distribution, which is predicted by the planar tunneling model and free electron propagation, would result in a much lower interface transmission probability for films grown on Si(111), because only few carriers have the large $k_\parallel$ required to reach the Si CBMs. This discrepancy could be resolved by the same Greens function approach used to model electron focusing in CoSi$_2$(111) (see [15]). The calculated momentum distribution is lying far from the center of the IBZ and produces a similar overlap with the projections of the CBM pockets in the Si(100) and Si(111) IBZ. The calculated real space distribution has a threefold symmetry, but is diverging as the electrons propagate into the film. The shape of the electron beam at the Au/Si interface has not been experimentally observed in a manner comparable to the measurements presented here. The importance of the experiments on CoSi$_2$/Si(111) must be emphasized even more, because it is - contrary to Au/Si - a truly epitaxial, single crystalline layer system, for which $k_\parallel$-conservation at the interface can be expected to hold.

- The local spectroscopy measurements performed on a single point defect have proven the existence of a second onset in BEEM spectra, which is not afflicted by the presence of a scattering object at the interface and can be identified with the theoretically predicted delayed onset [29]. The fact that a lower onset is present in BEEM spectra, whose weight increases when a point defect is present, indicates, that scattering must occur even in perfectly epitaxial regions. An alternative explanation relies on the presence of additional electron beams.
2.8. Conclusions

directed sideways from the point of current injection. Although they are strongly damped under BEEM imaging conditions, electrons traveling at a flat angle could reach the interface at low bias and end up in the silicon CBMs by scattering at interfacial defects. This would cause an earlier onset in BEES spectra, without breaking $k_z$-conservation.

- BEEM has been established as one of the very few techniques applicable to the study of point defects located at an interface. When measuring point defect densities in the range of $10^{12}$-$10^{13}$ cm$^{-2}$, the BEEM technique has a big advantage over techniques like cross-sectional STM or TEM. By using one of these techniques it is very hard to obtain statistically relevant data on the lateral variation of point defect density, because the mean distance between two point defects appearing in the image of a cross-section is of the order of 100 Å. This is comparable to the spacing between dislocation lines of typically 400-500 Å, which would render it difficult to measure the point defect density as a function of distance from dislocation cores.

- Diffusion of point defects into dislocation cores has been postulated as a mechanism for a long time (see e.g. [55]). Here the first direct evidence for point defect diffusion into the core region of dislocations has been presented.
Chapter 2. Point defects in CoSi$_2$/Si(111)
Chapter 3

Embedding of Ge islands in Si

3.1 Introduction

One of the most interesting phenomena encountered in semiconductor physics during the last few years is self-ordered growth of nanoscale structures. Making use of the Stranski-Krastanow growth mode in lattice-mismatched semiconductor heteroepitaxy, the fabrication of arrays of small islands, acting as quantum dots, has become possible [56]. The discrete energy-spectrum of quantum dots renders them extremely interesting for the development of lasers and even for quantum computers [57]. For such applications the dots must be embedded in a semiconductor matrix. The process of burying such small nanostructures by epitaxial growth turns out to be a nontrivial problem, however. As noticed by several researchers, the dots tend to change shape while the overlayer is grown, resulting in pronounced flattening [58, 59, 60, 61]. In addition, the dots may change their composition and, as demonstrated for small Ge clusters, even dissolve completely [61]. 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. [60]). Three-dimensional confinement of carriers can not only occur within the self organized islands, but also in the surrounding material, with the islands acting as stressors, modifying the band structure by their strain field. Such strain-induced quantum-dots have been found to form in In$_x$Ga$_{1-x}$As quantum wells [62], the local strain stemming from InP islands, grown on top of a thin GaAs cap. In stacked layers of carbon-induced quantum dots the measured red shift of photoluminescence (PL)
spectra was explained by electron confinement in the strained silicon above the Ge islands [63]. 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 spectroscopic information on InAs dots has been obtained [64]. Very recently, cross-sectional STM (XSTM) has been applied to InAs quantum dots embedded in GaAs and the strain in growth direction and the bandgap of the InAs dot has been compared with the one of the GaAs matrix [65].

Here a scanning tunneling microscopy (STM) study on Ge dots embedded in a silicon film is presented. Using our STM in the conventional configuration we have measured the deformation of the silicon cap-layer caused by the buried Ge islands. From the surface deformation the lateral strain above a quantum-dot has been calculated. As will be shown below, scanning tunneling spectroscopy (STS) gave direct evidence for a lowering of the surface bandgap in the strained parts of the Si cap, which could be correlated quantitatively with the lateral strain.

### 3.2 Huts and domes

Since the pioneering work of Mo et al. [56], who presented the first STM topography images of so called Ge 'hut-clusters', the Ge/Si(100) Stranski-Krastanow growth system has attracted a lot of interest. The hut-clusters are epitaxial, defect-free and strictly \{105\} faceted Ge islands, which form under certain growth conditions, when more than a critical amount of Ge (≈3 ML) is deposited onto a Si(100) substrate. A STM topography image of such a hut cluster is presented in Fig. 3.1. The base of the hut-cluster is oriented along the \{001\} and \{010\} directions. On the side facets of the island the surface is reconstructed in a way, that results from dimer-rows running alternatingly in \{011\} and in \{011\} directions on neighboring ML terraces [56]. By choosing a higher substrate temperature during Ge deposition the size of the hut clusters can be increased to a limited degree. At the same time another kind of Ge island starts to form. These so-called 'domes' are larger than the 'hut-clusters' and feature \{113\} and \{102\} as well as \{105\} facets [66]. In the following experiments the growth conditions were chosen in a way, that resulted in a bimodal island distribution: The samples were grown by molecular beam epitaxy (MBE). The oxide was re-
3.3. Epitaxial overgrowth

In order to minimize Ge surface segregation and dissolution of the germanium islands, and at the same time to create a flat, well ordered surface a rather
complicated growth procedure was established. After the Ge deposition and a 5 min. anneal at the growth temperature of 500°C, the samples were cooled to 310°C and 30 Å of silicon were deposited at a rate of 0.5 Å/s. Three additional 20 Å thick Si layers were grown at 350°C, 390°C and 470°C. A final 10 Å Si cap was grown at 550°C. After a 5 min. anneal at 550°C the wafers were cooled to room-temperature and transferred to the STM-chamber in UHV. By cross-sectional transmission electron microscopy (TEM) performed after the STM experiments it was verified, that the germanium islands had not dissolved completely. A flattening of the islands was, however, apparent, and the formation of a SiGe alloy at the island boundaries or even in the core-region seems most likely (see e.g. [60]). In Fig. 3.3 a STM topography image of the same sample already measured before capping (see Fig. 3.2) is shown after the growth of the 100 Å thick silicon cap-layer.

Most apparent are the hole-like features indicated by black arrows. Upon closer inspection the sample surface can be seen to be bent upwards within such a 'hole' (see e.g. upper left corner of Fig. 3.3). The same kind of surface corrugation is found in regions surrounded by the circles in Fig. 3.3 and labeled A,B,C and D for decreasing amplitude of the corrugation. As a matter of fact many more very slight surface protrusions like the one indicated by D are found in the image. Their number density is comparable to the number density of the hut clusters determined before capping, i.e. $(3.5 \pm 0.2) \times 10^{10} cm^{-2}$. The density of the 'holes' $[(3.5 \pm 0.7) \times 10^{8} cm^{-2}]$ agrees very well with the number of domes, which were present prior to silicon deposition.
3.4. Approximating surface strain

Figure 3.3: Topography image of the same sample shown in Fig. 3.2 after deposition of 100 Å of silicon. A surface protrusion is found at locations where Ge islands have been overgrown. In the deeper 'holes' in the film (arrows) the surface distortion is largest, while it becomes gradually smaller at the locations surrounded by circles A, B, C and D. The range of the gray scales is 17 Å.


The maximum curvature of the surface was measured to be higher in the center of the 'holes' than on the bumps present in the more planar regions (A,B,C and D in Fig. 3.3). 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 [60] 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.

3.4 Approximating surface strain

Fig. 3.4 (a) allows for a closer look at a surface region, where a Ge island of intermediate size has been overgrown. There are two incomplete terraces bounded by ML steps close to the center of the surface protrusion. The Si surface exhibits the same 4x2 reconstruction [67] close to the buried island and away from it. In order to analyze the deformation of the surface quantitatively, the monolayer steps have been removed from the image by masking out the regions belonging to the same terrace and adding an appropriate multiple of a monolayer step, a/4, to the measured height [see Fig. 3.4(b)].
Chapter 3. Embedding of Ge islands in Si

Figure 3.4: (a) STM topography image of a surface protrusion caused by a germanium island below a 100 Å thick silicon cap-layer. The gray scale range is 5.1 Å. (b) Same image as (a) after subtraction of surface steps. Some contourlines are drawn to emphasize the circular symmetry of the surface distortion.

The contour lines added to the processed image indicate, that the surface deformation has almost perfect circular symmetry. The same procedure was applied to other images, with the result that only a slight deviation from circular contours towards a rectangular shape (with the flat side along (100) directions) can be found for some regions. We take this as an indication that the elastic anisotropy may be neglected in a first approximation for strain modeling [68].

A height profile, taken across the deformation peak in Fig. 3.4(a) and corrected for surface steps, is presented in Fig. 3.6. The height of the peak is 3.5 Å, more than twice as high as a monolayer step on Si! Most of the surface bumps are smaller: their height varies between 0.5 Å and 1 Å. Their cross-sections were, however, found to be similar in shape to the one in Fig. 3.6. Using a model described below, the surface deformation which would be expected for a Ge hut-cluster (approximated as a square based pyramid featuring 400 Å base length and 40 Å height), covered by 100 Å of Si, was calculated. The results are plotted in Fig. 3.5.

The resulting surface deflection of 1.5 Å confirms that the island below the surface region shown in Fig. 3.4 featuring a protrusion of 3.5 Å is not a hut-cluster, but a larger island of the dome type. The calculated deflection of 1.5 Å is, however, about two times bigger than the 0.5 Å to 1 Å measured
for the vast majority of surface bumps, which were previously attributed to buried hut-clusters. This can be explained only by dissolution of Ge in the Si cap-layer, which causes the buried islands to be significantly smaller than they originally were [60, 61]. Additional evidence for the presence of significant island shrinking is provided by the fact that the largest domes, which were found to be higher than 100 Å before the overgrowth, resulted in the hole-like features present in Fig. 3.3, after the deposition of only 100 Å of silicon. The actual islands embedded in the Si must therefore all be considerably smaller than 100 Å. This could be confirmed by cross-sectional TEM measurements, where no islands higher than 40 Å were observed. To calculate the surface deformation we used a model by Hu [69], describing the displacement caused by a thermal inclusion in a semispace \( z \geq 0 \). In an elastic medium featuring a Poisson’s ratio \( \nu \), the displacement vector \( \vec{u} \) at the position \((x,y,z)\) caused by a point source of volume \( dx'dy'dz' \) of a material with a lattice mismatch \( \delta \) (here \( \delta = 0.04 \)), located at \((x',y',z')\) is given by:
Figure 3.6: Line-section across the surface protrusion shown in Fig. 3.4 after subtraction of surface steps. A fit to a model describing the deformation of an elastic medium due to a point source is also plotted (continuous curve) along with the strain component $\varepsilon_{xx}$ deduced from the fit (lower curve).

\[ u^* = \frac{5(1 + \nu)}{4\pi(1 - \nu)} \left( \frac{R_1}{R_1^2} + \frac{(3 - 4\nu)R_2}{R_2^3} - \frac{6z(z + z')R_2}{R_2^2} \right) dx' dy' dz', \]

where $\hat{z}$ is a unit vector in z direction and $\vec{R}_1 = (x - x', y - y', z - z'), \vec{R}_2 = (x - x', y - y', z + z')$.

The surface distortion due to an embedded island can be found by integrating such point sources over the volume of the island (where $\delta \neq 0$). As mentioned before, this integration has been performed for a square based hut-cluster with 400 Å base length. As shown in Fig. 3.5(c) the surface was found to move upwards on top of the center of the island by 1.5 Å, which is about twice as much as the values measured for buried hut-clusters. This discrepancy is the result of the islands change of shape during silicon deposition. Also the fact that the measured surface deformation has circular symmetry [see e.g. Fig. 3.4(b)], while the calculated contours for an intact faceted hut-
3.5. Electronic surface structure

Having established the strain distribution in the Si cap above a buried dot, we are now in a position to have a look at the way in which the strain affects the electronic properties. Using scanning tunneling spectroscopy [35], we recorded spectra on the part of the surface shown in Fig. 3.4(a). One of the two spectra plotted in the inset of Fig. 3.7 was obtained by averaging 132 spectra taken within a circular spot (diameter 100 Å) on top of the surface protrusion (●). The spectrum denoted by (○) is an average of 784 spectra stemming from an unperturbed surface region located in the upper left corner of Fig. 3.4(a). From the derivative of the spectra displayed in Fig. 3.7, the Si surface bandgap was determined by fitting to a straight line close to the gap region [71]. It is evident, that the gap is reduced for the spectra taken on the highly strained Si right on top of the covered Ge dot. For the unstrained silicon the bandgap was found to be 0.45±0.05 eV, in agreement with theoretical calculations [72]. In the center of the surface deformation the gap is lowered by 0.16±0.03 eV because of the lateral tensile strain of 0.02. The states probed with negative tip bias, i.e. the conduction band states, are most affected by the strain. The same kind of analysis was carried out for islands causing a smaller surface distortion. The resulting differences in surface bandgap are plotted in Fig. 3.8 as a function of maximum tensile strain at the dot center. The measured $\Delta E_{\text{gap}}$ vs. $\varepsilon$ values agree within the
Figure 3.7: Scanning tunneling spectra of silicon recorded above (●) and away from (○) a Ge-island with the tip stabilized at $V_t = -0.5$ V and $I_t = 0.5$ nA. The original spectra are shown in the inset. The change in the surface bandgap was calculated to $0.16 \pm 0.03$ eV from fits to the derivative of the spectra.

The expected lowering of the bulk bandgap (lowest conduction band minus highest valence band energy) of Si was calculated using the deformation potentials from Ref. [73] and also plotted for comparison. The dotted line gives the variation in the surface bandgap, expected on the assumption that the relative changes in surface bandgap and bulk bandgap are the same. An intuitive understanding, as to why the bandgap of the surface states should be lowered in the presence of expansive strain, can be gained from the fact that the dimer bonds at the surface are stretched. This results in a smaller overlap of the two π orbitals of the Si dimers, which in turn causes the $\pi - \pi^*$ bonding-antibonding splitting to become smaller.
3.6 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 higher strain has been identified by Tersoff et al. [74] as the driving force for self-alignment of islands in stacked island-multilayers [75]. In the case of stacked carbon-induced germanium-island multilayers in silicon a spatially separated confinement for holes and electrons has been suggested recently [63] to account for a red-shift in PL-spectra. The strain-induced lowering of the Si surface bandgap observed here, is in agreement with the idea of electron confinement in the strained Si close to an embedded Ge dot.
Chapter 3. Embedding of Ge islands in Si

Outlook

The BEEM measurements on CoSi$_2$/Si(111) presented in this work have not only enabled the first direct observation of diffusion and trapping of point defects at an interface, but most importantly stimulated and confirmed a new theoretical approach to the BEEM process itself. While the nanometric resolution of interfacial objects found experimentally has been explained by band structure induced electron focusing, many experimental findings, such as electron interference, have not yet been theoretically treated. Numerical calculations of the exact beam shape at low electron energies could resolve the question, whether the delayed onset originates from defect scattering or from a violation of $k$ conservation at a defect-free interface. The very good agreement of the new theory with the experiments presented here suggests, that it is only a matter of time until these open questions are answered.

Having established the growth sequence to embed Ge quantum dots in a thin epitaxial Si layer with a flat surface, the way is now open to fabricate BEEM samples, by adding a thin CoSi$_2$ on top of the structure. Similar to the strain induced changes in surface electronic structure observed here, the band lineup at the interface is expected to be influenced by strain. Such changes in the electronic structure of the interface could be investigated in future BEEM experiments along with the transport properties of the buried heterostructure.
Appendix A

T-H model for higher voltages

In the STM-theory of Tersoff and Hamann [6] the tunneling current for small tip bias is proportional to the LDOS of the sample:

\[ I_t \propto \rho_s(\mathbf{r}_0, E_F) \]  \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 [76] 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 [6] a spherical wave function is defined for the tip:

\[ \Psi_{\mu} = \frac{c_t}{\sqrt{\Omega_s}} \kappa_\mu R e^{\kappa_\mu R} \frac{\exp(-\kappa_\mu |\mathbf{r} - \mathbf{r}_0|)}{\kappa_\mu |\mathbf{r} - \mathbf{r}_0|} \]  \hspace{1cm} (A.3)

where \( \mathbf{r}_0 \) 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 \( \Phi - eV_1/2 - (E_\nu - E_F) \) high. Assuming no variation of \( |\Psi_\nu(x, y, z)|^2 \) along the surface (x,y-plane) we set:

\[
\Psi_\nu = \frac{a}{\sqrt{\Omega_s}} \exp(z\sqrt{k_\nu^2 + k_\parallel^2}) \exp(ik_\parallel \cdot \vec{x})
\]  

(A.4)

The in-plane wave vector \( k_\parallel \) and the in-plane position vector \( \vec{x} \) both are two component vectors and

\[
k_\nu^2 = \frac{2m}{\hbar^2}(\Phi - eV_1/2 - (E_\nu - E_F)).
\]

The tunneling matrix is calculated according to Bardeen:

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

(A.5)

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 [6] with $\kappa_{\nu}$ substituted for $\kappa$: \[
M_{\mu\nu} = \frac{\hbar^2}{2m} \frac{c_t}{\sqrt{\Omega_t}} 4\pi R \rho_{\mu \nu} R \psi_{\nu}(\vec{r}_0) \] (A.6)

In the low temperature limit the expression for the tunneling current in eq. A.2 simplifies to:
\[
I_t = \frac{2\pi e}{\hbar} \sum_{E_{\mu},E_{\nu} \in \{E_F, E_F - eV_t\}} |M_{\mu\nu}|^2 \delta(E_{\mu} - E_{\nu}) \] (A.7)

This is simplified even more under the assumption, that the tip density of states is constant:
\[
I_t \propto \int_{E_F}^{E_F - eV_t} dE \sum_{\nu} e^{2\pi R} |\psi_{\nu}(\vec{r}_0)|^2 \delta(E_{\nu} - E) \] (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:
\[
I_t \propto \int_{E_F}^{E_F - eV_t} \rho_s(\vec{r}_0, E) dE \] (A.9)

with the sample local density of states (LDOS) given by:
\[
\rho_s(\vec{r}, E) = \sum_{\nu} |\psi_{\nu}(\vec{r})|^2 \delta(E_{\nu} - E) \]

The tunneling current is 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 proportional to the density of states:
\[
\frac{dI_t}{dV_t} \propto \rho_s(\vec{r}_0, E_F - eV_t) \] (A.10)

The tunneling barrier between tip and sample becomes lower as soon as a voltage is applied. As a consequence the decay of the sample wave function
\( \psi_\nu \) is weakened, which causes a higher value of \( \rho_s \) at a fixed position of the tip. Since the quantity of interest is the surface LDOS in the absence of the tip, this monotonic increase in measured \( \frac{dI_t}{dV_t} \) spectra with applied voltage is often compensated for by defining the 'experimental LDOS' as the normalized tunneling conductance [35]:

\[
LDOS = \frac{dI_t/dV_t}{I_t/V_t} \tag{A.11}
\]
Appendix B

3-d Gaussian wavepacket

In BEEM interfacial features can be imaged with a resolution, which is dictated by the lateral size of the electron beam impinging on the interface. In semiclassical BEEM-theory the spread of the electron beam is quantified by the angle of the tunneling cone

\[ \tan(\phi_T) = \frac{k_\parallel}{k_\perp} \]  

where the width of the tunneling momentum distribution is set for \( k_\parallel \). Quantum-mechanically we would rather look at the shape change of a three dimensional Gaussian wavepacket, as it travels from the surface to the interface. This corresponds to a free-electron model for electron transport in the metal. For our special case we assume the momentum distribution to be centered at some value \( k_\perp \) in the direction perpendicular to the interface with an uncertainty \( \Delta k_\perp \). The uncertainty in the in-plane direction we denote by \( \Delta k_x = \Delta k_y = \Delta k_\parallel \). The wave function in real space is then given by

\[ \Psi(\vec{x}, t) = \int \frac{d^3k}{(2\pi)^3} \phi(\vec{k}) e^{i(k \cdot \vec{x} - \frac{\vec{k} \cdot \vec{\phi}}{\hbar} t)} \]  

with

\[ \phi(\vec{k}) = \frac{(2\pi)^{3/4}}{\sqrt{\Delta k_x \Delta k_y \Delta k_\perp}} e^{-\frac{k_x^2}{2\Delta k_x^2}} e^{-\frac{k_y^2}{2\Delta k_y^2}} e^{-\frac{k_\perp^2}{2\Delta k_\perp^2}}. \]  

For the dispersion relation we take an effective mass approximation with two different effective masses orthogonal \( (m_\perp) \) and parallel \( (m_\parallel) \) to the interface:

\[ E(\vec{k}) = E_0 + \frac{\hbar^2(k_x^2 + k_y^2)}{2m_\parallel} + \frac{\hbar^2 k_\perp^2}{2m_\perp} \]  

\[ \Box \]
The wavefunction then factorizes into three one-dimensional problems, the solution to which can be found in a textbook [77], and we obtain:

$$|\Psi(\vec{x}, t)|^2 = \frac{8(\Delta k_\parallel)^2 \Delta k_\perp}{(2\pi)^{3/2}(1 + \Delta_\perp^2)} \sqrt{1 + \Delta_\perp^2} \times \exp\left(-2(\Delta k_\parallel)^2 \frac{x^2 + y^2}{1 + \Delta_\perp^2}\right) \exp\left(-2(\Delta k_\perp)^2 \frac{(z - v_\perp t)^2}{1 + \Delta_\parallel^2}\right)$$  (B.5)

The following abbreviations were used:

$$v_\perp = \frac{hk_\perp}{m_\perp}$$

$$\Delta_\perp = \frac{ht}{2m_\perp} (2\Delta k_\perp)^2$$

$$\Delta_\parallel = \frac{ht}{2m_\parallel} (2\Delta k_\parallel)^2$$

Equation B.5 describes a wavepacket, which travels along the z direction with a speed $v_\perp$ and is spreading on its way. The expectation value for the z-position is

$$\langle z \rangle = v_\perp t,$$  (B.6)

and the width of the wavepacket within the plane is

$$\langle \Delta x \rangle = \sqrt{1 + \Delta_\parallel^2} \cdot \frac{2\Delta k_\parallel}{2\Delta k_\parallel}.$$  (B.7)

As the wavepacket propagates along z it is getting broader and broader. For $t \to \infty$ the opening angle of the beam approaches

$$\tan(\alpha/2) = \frac{\langle \Delta x \rangle}{2\langle z \rangle} = \frac{(\Delta k_\parallel/2)}{k_\perp} \cdot \frac{m_\perp}{m_\parallel}.$$  (B.8)

In the case of an isotropic effective mass the opening angle in real space is equal to the opening angle in k-space, which is what is classically expected for a beam of individual particles with a certain distribution in lateral momentum. The situation is different however, if the energy dependence on $k_\parallel$ is much weaker than on $k_\perp$, which means that $m_\parallel \gg m_\perp$. In that case $\Delta_\parallel$ is small and the width of the wavepacket $\langle \Delta x \rangle$ does not change during the propagation through the metal film. The opening angle of the beam is zero in real space although the opening angle in reciprocal space might be large.
Appendix C

1-dimensional diffusion

We calculate one-dimensional diffusion into a perfect sink located at \( x = 0 \). The concentration of diffusing species is denoted by \( n(x, t) \) and is defined for \( x \geq 0 \) and \( t \geq 0 \). Initially the concentration is homogeneous:

\[
n(x, t = 0) = n_0 \text{ } \forall x
\]  

For later times, the boundary conditions are:

\[
n(x = 0, t > 0) = 0
\]

\[
\lim_{x \to \infty} n(x, t) = n_0
\]  

The diffusion equation is given by:

\[
\frac{\partial n}{\partial t} = D \frac{\partial^2 n}{\partial x^2}
\]  

with \( D \) being the diffusion constant. It is convenient to introduce the Laplace-transform \( \bar{n}(x, s) \) of \( n(x, t) \):

\[
\bar{n}(x, s) = \int_0^\infty n(x, t)e^{-st}dt
\]  

Applying the Laplace transform to eq.C.3 and integrating by parts we obtain:

\[
e^{-st}n(x, t)|_0^\infty + \int_0^\infty s n(x, t)e^{-st}dt = \int_0^\infty e^{-st}D \frac{\partial^2 n}{\partial x^2}dt
\]
The leftmost term is given by the initial condition eq. C.1 and the other terms can be rewritten:

\[-n_0 + s \bar{n}(x, s) = D \frac{\partial^2 \bar{n}}{\partial x^2}\]  

(C.6)

This equation is solved by

\[\bar{n}(x, s) = \frac{n_0}{s} + f(s) \exp(\pm s/Dx)\]  

(C.7)

with an arbitrary function \(f(s)\). From the boundary condition eq. C.2 follows, that \(\bar{n}(x = 0, s) = 0, \forall s\) and since \(n(x, t) \geq 0, \forall(x, t \geq 0)\), also \(\bar{n}(x, s) \geq 0, \forall(x, s \geq 0)\). Thus we obtain:

\[\bar{n}(x, s) = \frac{n_0}{s} \left[1 - \exp(-s/Dx)\right]\]  

(C.8)

Performing the reverse Laplace transform yields the final solution:

\[n(x, t) = n_0 \text{erf} \left(\frac{x}{2\sqrt{Dt}}\right)\]  

(C.9)
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The surface reconstruction usually found on clean Si(100) surfaces at room temperature is 2x1. The buckling of the dimers, which results in a 4x2 reconstruction, is most probably induced by a small amount of Ge atoms segregated to the surface. We do not, however, find the 2x8 reconstructed surface dominated by vacancy lines, which is characteristic for a Ge-rich surface (see e.g. L.W. Guo, Q. Huang, Y.K. Li, S.L. Ma, C.S. Peng and J.M. Zhou, Surf. Sci. 406, L592 (1998)).

The spectra have also been evaluated by calculating \(\frac{\text{d}I}{\text{d}V}/(I/V)\), a quantity which is proportional to the surface LDOS [35]. The spectral features are similar to those observed for a (2x1) reconstructed Si(100) surface (see e.g. R.J. Hamers, Ph. Avouris and F. Bozso, Phys. Rev. Lett. 59, 2071 (1987)) and the change of the surface bandgap as determined by the energy shifts of the \(\pi,\pi^*\) peaks next to \(E_F\) is in agreement with the value obtained by fitting \(\text{d}I/\text{d}V\) curves. Since smoothing had to be applied to the \((\text{d}I/\text{d}V)/(I/V)\) spectra, we prefer fitting the (un-smoothed) \(\text{d}I/\text{d}V\) curves.


[77] F. Schwabl, Quantenmechanik (Springer-Verlag, Berlin, 1992)
Publications and presentations

Publications


• H. von Känel and T. Meyer, Recent progress on BEEM, Ultramicroscopy 73, 175 (1998)


Presentations

- Study of the tunneling distribution in a STM experiment by means of BEEM, Swiss physical society meeting, St. Gallen, Switzerland, September 7, 1995 (talk)

- Interfacial point defects investigated by ballistic electron emission microscopy. 2nd Hasliberg Workshop on Nanoscience, Hasliberg, Switzerland, October 14-18, 1996 (poster)

- Studying interfaces on a nm scale by BEEM. E-MRS 97, Strasbourg, France. June 19, 1997 (invited talk)

- Diffusion of interfacial point defects studied by BEEM, ICFSI-6, Cardiff, Wales UK. June 23-27, 1997 (poster)

- Hot carrier scattering at point defects located at the $CoSi_2/Si(111)$ interface, Workshop on nanoscale characterization of silicide/semiconductor contacts by scanning probe microscopy, Gent, Belgium, September 24, 1998 (talk)

- Self organization in $Si/CoSi_2(111)$ heteroepitaxy, PCSI-26, San Diego, USA. January 17, 1999 (poster)

- Interfacial point defects studied by ballistic electron emission microscopy, Festkörperseminar ETH Zürich. Zürich, Switzerland, November 4th, 1999 (talk)
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