Scanning tunnelling microscopy studies of silicides

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Abstract. We review the topic of scanning tunnelling microscopy (STM) studies of silicides, with an emphasis on fundamental scientific issues that can be addressed using STM and ballistic-electron-emission microscopy (BEEM). The discussion is organized according to the topics of structure (atomic scale precursors, surface reconstructions, bulk structures, interfaces) kinetics and growth (direct atomic measurement, modelling, stoichiometry, layer and island growth, phase transitions and nanoscale metallization) and BEEM (method, band structure, Schottky barrier, defect scattering, inelastic scattering and surface effects). These topics are described in general terms, then elaborated with specific examples.

1. Introduction

In this paper, we present a review of scanning tunnelling microscopy (STM) studies of silicides. The topic of silicides by itself represents a large and mature field of research that has been driven largely by the practical importance of silicides in the microelectronics industry [1, 2]. Consequently, the metallurgical behaviour of thin silicide films has been widely studied, especially using the workhorse methods of Rutherford backscattering spectroscopy (RBS) and transmission electron microscopy (TEM) [3–6]. The behaviour of the silicide–silicon interface has also been heavily studied using surface sensitive methods such as photoemission, Auger, RHEED/LEED, etc [7–11].

STM offers the opportunity to advance our understanding of the structure and kinetics of silicide systems on an atomic scale and to provide new insight into the area of heteroepitaxial thin films on a fundamental level. In this regard, it is somewhat surprising that the extent of literature on the topic of ‘STM studies of silicides’ is relatively small. This is partly due to the complexity of transition metal/silicon systems, which are strongly interacting and tend to have a complex metallurgy and hence do not provide simple ‘model systems’. This may also (ironically) be due to the very strong practical driving force for research on silicides, which tends to emphasize materials systems and bypass fundamental, atomistic issues. It is hoped that this review will help delineate some of these issues and stimulate further work along these lines.

In view of the above, we have organized this paper according to scientific topics, rather than materials systems. We do, however, limit the discussion to those metal adsorbates that are relevant to silicon technology, namely the transition metals plus copper. This excludes a large body of literature involving other metals which do not form bulk silicides, particularly Ag and Au. We recognize that there is an extensive background literature for nearly every metal/silicon system, with multiple motivations, viewpoints and techniques. We make no attempt to describe this background literature, but only to summarize and/or illustrate the particular contributions of STM. We have categorized the scientific topics as follows: structure (atomic scale precursors, surface structures, bulk structures, interfaces) kinetics and growth (direct atomic measurement, modelling, stoichiometry, layer and island growth, phase transitions and nanoscale metallization) and BEEM (method, band structure, Schottky barrier, defect scattering, inelastic scattering and surface effects). We first introduce each subtopic in general terms and then present notable examples in further detail.

2. Structure

We begin by summarizing the principal methods used to prepare silicides [1]. Most common is the solid phase or contact reaction, which proceeds by annealing a cold-deposited metal overlayer. In most practical situations (particularly for refractory metals such as Ti, Mo or W), metal is deposited on top of a native oxide layer, and epitaxy does not occur. In many other cases, most notably for Ni or Co on a ultra high vacuum (UHV) cleaned substrate, the reaction produces an epitaxial overlayer. This is called solid phase epitaxy (SPE). Recent efforts have demonstrated that epitaxy during SPE reactions can be enhanced using heavy metal or oxide interlayers [12, 13]. Epitaxial layers can be produced with greater control and flexibility using molecular beam epitaxy (MBE), whereby both metal and silicon are deposited in proper stoichiometric ratio onto a heated silicon substrate under UHV conditions. In favourable
cases, epitaxy occurs even at room temperature, perhaps with the use of ‘template layers’ [6, 10, 14]. Patterned and isolated silicide structures can be produced by a self-aligned silicide (salicide) process. Buried single-crystal silicide layers can be produced by ion beam synthesis or the closely related molecular beam epitaxy processes, which involve annealing of ion implanted or MBE buried metal layers, respectively [15–17]. Both are derivatives of the ‘mesotaxy’ process, which involves subsurface growth on silicide seed crystals [18]. Less practical, but scientifically quite interesting, are reactive deposition epitaxy (RDE), which involves metal deposition on a heated substrate, and inverted SPE, which involves silicon deposition onto a single-crystal metal surface [19].

A variety of structures result from the various reaction schemes described above. The two-dimensional (2D) structures are invariably reconstructed or relaxed, often with a unit cell larger than the substrate. This is expected in view of the strong interaction between silicon and the transition metals, which can cause drastic rearrangement of surface bonds and large strain effects, even for submonolayer coverages. The resulting surface structures are true 2D phases with distinct properties lying somewhere between the limits of surface adsorbate (adatoms on high symmetry sites) and bulk crystal (full coordination of metal atoms). For coverage above a monolayer, the system is best viewed as a three-dimensional (3D) system comprised of silicide overlayer, silicon substrate and interface. The buried interface again has distinct 2D properties. Many such systems are epitaxial, which leads to strong strain effects and the possibility of pseudomorphic or metastable structures that do not exist in equilibrium bulk systems.

STM is a powerful tool that can, in principle, provide direct structural information on an atomic scale. In practice, however, it is useful to distinguish two cases. In the first case, the structure is entirely unknown, as is typical for surface reconstructions. It is then essential to obtain corroborative information, either in the form of electronic structure theory or independent structure-sensitive measurements. In the early days of STM, ‘ball-stick (BS) theory’ was commonly employed. In BS theory, atoms are simply assigned to bumps in the STM image. Such modelling has proved to be unreliable, and is hardly useful without supporting information. In the second case, one assumes that one or more well defined silicide structures are present, and the goal becomes to correctly identify them by multiple choice. This situation is typical for partially reacted SPE growth. In this case, clues may be taken from the vacuum-exposed surfaces in the form of step heights, facet angles or surface lattice spacings. However, the permutations produced by orientation angles and buried interface structures make this a non-trivial exercise, which may or may not yield a unique answer. Regardless of exact structure identification, the STM can nonetheless provide important morphological information regarding coexisting phases, domain structure, short range order, stoichiometry and surface roughness.

### 2.1. Atomic scale precursors

The ‘initial stage of reaction’ for metals deposited on silicon has been studied for many years [20]. A principle motivation is to understand the metal–semiconductor interface, which is typically done by monitoring its evolution from bare surface to buried interface. From such studies it is clear that a reaction between metal and silicon occurs ‘spontaneously’ (meaning quickly at room temperature), and continues for several angstroms of deposited metal, being limited eventually by the interdiffusion of components [21–23]. There remains much disagreement about the structure and even stoichiometry of the resulting silicides [24–26]. STM provides new information about this old problem, mainly because it is possible to observe atomic scale precursor structures, containing possibly a single metal atom. This corresponds to the true low coverage limit or ‘initial stage’ of growth.

Ishiyama et al have identified such atomic-scale precursors in the Ti/Si(100)-2×1 system, and have studied their kinetic behaviour. A representative image is shown in figure 1 [27–29]. The bright features labelled ‘P’ correspond to a ‘pedestal’ adsorption site, while those labelled ‘V’ correspond to a Ti atom bound to a dimer-vacancy site. The structure assignments are supported by first principles electronic structure calculations from an independent group, which show that they are indeed energetically feasible and that the ‘V’ site has a lower energy, as implied by the experiment [30]. The use of ‘hot-stage STM’ allows direct observation of the conversion from ‘P’ into ‘V’ sites, as well as their diffusion properties, as we describe further in the kinetics section. The assembly of these precursors into 3D clusters, presumed to be silicide islands, was observed, but not quantified.

A very different precursor structure was reported by Bennett et al for the Co/Si(111)-7×7 system [31]. They showed that isolated Co atoms enter near-surface interstitial sites which appear in STM images as slightly ‘lower’ silicon adatoms in an otherwise undisturbed Si(111)-7×7 pattern. This is shown in figure 2. In this case, the ‘interstitial precursor’ corresponds to no reaction at all and persists until the concentration is high enough to force overlap and formation of a silicide nucleus. This behaviour is a direct realization of a concept postulated much earlier by Tu et al [32]. These interstitials do not move at 300 K, and are thus much less mobile than bulk interstitials [33], presumably due to interaction with the surface dangling bonds in the 7×7 structure. It was also observed that they prefer the ‘faulted’ half of the 7×7 structure, resulting in preferential formation of silicide islands there during later stages of the reaction. A similar preference for silicide growth on the faulted half of 7×7 has been observed for all transition metals measured to date, including Fe, Co, Ni, Pd, Ti, plus Cu and other non-transition metals as well [31, 34–37].

Interstitial structures were also inferred for the Co/Si(100) system. In this case, the first atoms deposited remain invisible, although a 2×N reconstruction forms and is already complete at 0.01 monolayer (ML) [38]. It was speculated that metal interstitials cause strain which induces the reconstruction. This is somewhat different from the case of Ni/Si(100), where a direct correlation of 2×N periodicity with Ni concentration has been established by several groups independently, using STM [39–42]. In this case, Ni atoms form an intrinsic part of the 2×N unit cell.
STM studies of silicides

Figure 1. Atomic-scale precursor structures for 0.01 Ml Ti adsorbed on Si(100)-2 × 1 at 466 K (80 × 80 Å, sample bias = +0.8 V). Individual site conversions from a pedestal site (P) to a Ti + dimer-vacancy site (V) are observed in sequential scans. (After Ishiyama [29], with permission.)

Figure 2. Interstitial precursor structures for 0.016 Ml Co adsorbed on Si(111)-7 × 7 at 300 K (75 × 75 Å, sample bias = −1.4 V). Single cobalt atoms reside in subsurface interstitial sites visible as groups (pair or triplet) of ‘depressed’ silicon adatoms. Panel B indicates the groups (black circles) and silicon adatoms on the faulted (grey) and unfaulted (white) sides of the 7 × 7 unit cell.

2.2. Surface structures

Nearly all the transition metal/silicon surfaces are reconstructed, yet model structures are published for only a few. These are shown in table 1, where we also indicate corroborative information (if available) such as surface coverage, lattice registry, electronic structure calculations, etc. We have separated silicon structures (coverage < 1 ML) from silicide structures (coverage = ‘bulk’). Beyond this tabulation, we describe a few examples in further detail to illustrate the use of STM for structural analysis on the atomic scale.

We describe first a common reconstruction, comprised of silicon adatoms back-bonded at threefold sites of a fcc(111) surface layer. Typically these adatoms are arranged in a 2 × 2 pattern, as can be seen in figure 3. This has been observed on the (111) surfaces of FeSi₂, CoSi₂ and NiSi₂ [11, 43–47]. One might argue that the adatom structure is stabilized by a reduction of the density of dangling bonds, as originally postulated by Harrison in the context of the Si 7 × 7 reconstruction [48]. Thus, the dangling bond density is 1 ML on the bare substrate but only 1/2 ML for the 2 × 2 adatom pattern. On the other hand, further reduction of dangling bond density to 1/3 ML is possible by close-packing adatoms into a √3 × √3, but this has not been observed, implying that the energy gain from removing dangling bonds is balanced by an energy cost of close packing. This energy balance, indeed, is the basis for the accepted dimer–adatom-stacking fault (DAS) model for Si(111)-7 × 7 [49]. The 2 × 2 pattern on the silicide surfaces is often imperfect, with missing or misplaced adatoms. Indeed, extended regions of ‘missing adatoms’ are commonly observed, implying that the adatom decoration involves only a minimal energy change. This is in contrast to the clean Si(111) surface, which does not show any extended regions with such a 1 × 1 structure. For these reasons, total energy calculations of this 2 × 2 adatom structure on silicide surfaces would be interesting, but they have not been done, to our knowledge.

The fcc(111) surface can also show a 2 × 1 reconstruction, at least for CoSi₂ [50]. We mention this case to illustrate two ways that STM is helpful for structure identification. First, the 2 × 1 symmetry is not evident in LEED patterns due to crossed domains, but is trivially evident using STM. Second, it was shown that the 2 × 1 is strain stabilized, since it did not occur in regions where strain-relieving dislocations formed, which were readily visible with STM.

A related example is CoSi₂/Si(100) which forms two distinct reconstructions with the same periodicity of $\sqrt{2} \times \sqrt{2}$ [51, 52]. Again STM was indispensable to distinguish these closely related structures. The CaF₂-type lattice of CoSi₂ consists of alternating (100) layers of Co and Si separated by 1.35 Å. These layers present inequivalent surfaces, with the Co-terminated one being more stable. Surface steps between equivalent terraces thus have double-layer height of 2.70 Å. On the other hand, it is possible under silicon rich growth conditions to expose the alternate plane, which also has a
Table 1. Surface reconstructions for which model structures are published. Metal coverages are independently determined except as marked by * . Silicon structures (coverage < 1 Ml) are separated from silicide structures (coverage = ‘bulk’). Determination of lattice registry and supporting corroborative methods are also listed.

<table>
<thead>
<tr>
<th>Overlayer</th>
<th>Substrate</th>
<th>((M \times N))</th>
<th>Coverage (Ml)</th>
<th>Lattice registry</th>
<th>Method(s)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Er</td>
<td>Si(111)</td>
<td>(2\sqrt{3} \times 2\sqrt{3})</td>
<td>(1/2)*</td>
<td>Y</td>
<td>STM, STS</td>
<td>[54]</td>
</tr>
<tr>
<td>Ni</td>
<td>Si(111)</td>
<td>(\sqrt{19} \times \sqrt{19})</td>
<td>(3/19)</td>
<td>Y</td>
<td>STM</td>
<td>[157]</td>
</tr>
<tr>
<td>Ti</td>
<td>Si(100)</td>
<td>Dimer-vacancy</td>
<td>(1/32)</td>
<td>Y</td>
<td>(E(k)) calc.</td>
<td>[30]</td>
</tr>
<tr>
<td>Pd</td>
<td>Si(111)</td>
<td>(\sqrt{3} \times \sqrt{3})</td>
<td>(1/3)</td>
<td>N</td>
<td>STM</td>
<td>[79]</td>
</tr>
<tr>
<td>Co</td>
<td>Si(111)</td>
<td>(\sqrt{7} \times \sqrt{7})</td>
<td>(1/7)</td>
<td>Y</td>
<td>STM, MEIS, (E(k)) calc.</td>
<td>[58]</td>
</tr>
<tr>
<td>Cu</td>
<td>Si(111)</td>
<td>‘5 \times 5’</td>
<td>(1*)</td>
<td>N</td>
<td>STM</td>
<td>[56]</td>
</tr>
<tr>
<td>Ni</td>
<td>Si(111)</td>
<td>(\sqrt{19} \times \sqrt{19})</td>
<td>(1/19)*</td>
<td>N</td>
<td>STM</td>
<td>[158]</td>
</tr>
<tr>
<td>CoSi(_2)</td>
<td>Si(100)</td>
<td>(2 \times 2)</td>
<td>Bulk</td>
<td>Y</td>
<td>STM, (E(k)) calc.</td>
<td>[51]</td>
</tr>
<tr>
<td>ErSi/1.7</td>
<td>Si(111)</td>
<td>(\sqrt{3} \times \sqrt{3})</td>
<td>Bulk</td>
<td>Y</td>
<td>STM, XPS</td>
<td>[55]</td>
</tr>
<tr>
<td>ErSi/1.7</td>
<td>Si(111)</td>
<td>(\sqrt{3} \times \sqrt{3})</td>
<td>Bulk</td>
<td>Y</td>
<td>STM, ARUPS</td>
<td>[101]</td>
</tr>
<tr>
<td>CoSi(_2)</td>
<td>Si(111)</td>
<td>(2 \times 2)</td>
<td>Bulk</td>
<td>Y</td>
<td>STM</td>
<td>[45]</td>
</tr>
<tr>
<td>Cu(_2)Si</td>
<td>Cu(100)</td>
<td>‘5 \times 3’</td>
<td>Bulk</td>
<td>N</td>
<td>STM, atom scattering</td>
<td>[99]</td>
</tr>
<tr>
<td>CoSi(_2)</td>
<td>Si(100)</td>
<td>(2\sqrt{2} \times 2\sqrt{2})</td>
<td>Bulk</td>
<td>Y</td>
<td>STM</td>
<td>[108]</td>
</tr>
<tr>
<td>CoSi(_2)</td>
<td>Si(100)</td>
<td>(2\sqrt{2} \times 2\sqrt{2})</td>
<td>Bulk</td>
<td>Y</td>
<td>STM</td>
<td>[52]</td>
</tr>
<tr>
<td>CoSi(_2)</td>
<td>Si(111)</td>
<td>(2 \times 1)</td>
<td>Bulk</td>
<td>N</td>
<td>STM, STS</td>
<td>[50]</td>
</tr>
</tbody>
</table>

Figure 3. CoSi\(_2\) islands embedded in Si(111)-7 \(\times\) 7, grown by depositing 0.26 Ml Co at 320 °C (250 \(\times\) 250 Å, sample bias = +1.5 V). An imperfect 2 \(\times\) 2 pattern of silicon adatoms occurs on most of the islands.

\(\sqrt{2} \times \sqrt{2}\) reconstruction. STM observations showed that these are distinct phases and that they occur on alternate terraces, separated by 1.35 Å steps, as expected from the crystal structure [52].

Using BS theory, one might model the CoSi\(_2\)/Si(100)-\(\sqrt{2} \times \sqrt{2}\) structure as a pattern of silicon adatoms or vacancies. Voigtländer et al have shown, however, that the outer layer is complete (containing both silicon and metal atoms) and that the STM image can highlight either metal or silicon atoms, depending on bias, as shown in figure 4 [51]. These are simulated STM images, calculated in the Tersoff–Hamann approximation: that is, tunnelling current is proportional to the energy integrated local density of states evaluated at the position of the tip [53]. Interestingly the STM image contrast can be opposite to that expected from simple density of states arguments. For example, the filled-states image at low bias (panel a) shows mainly the position of silicon atoms, even though the local density of states for the surface muffin-tin sphere is dominated by cobalt states as shown in figure 5. This is explained by the orbital character of the Si states which project further out into vacuum than the Co states in this energy range.
The erbium silicide (111) surface is an interesting case because the relevant bulk structure ErSi$_{1.5}$ is non-stoichiometric. It is a defective A1B$_2$-type structure comprised of a $\sqrt{3} \times \sqrt{3}$ ordered pattern of silicon vacancies in a (0001) plane. The Er/Si(111) surface is p(1×1) for coverage below 1 Ml and a temperature below 450°C. The (1×1) surface is modelled as a simple bulk termination with slight inwards relaxation of the surface silicon layer. At higher temperatures, the surface becomes $\sqrt{3} \times \sqrt{3}$ and this structure has been controversial. Recent efforts show that the surface layer is atomically complete, and that the $\sqrt{3}$ corrugation is due to ordered subsurface vacancies [54, 55]. The registry of the corrugation is counter-intuitive, showing protrusions above the vacancies. This was explained in terms of increased occupation of p$_z$ orbitals above the vacancies, which enhances the tunnelling current, giving the impression of ‘higher’ atoms.

Next, we mention Cu/Si(111) as an example of incommensurate overlayers. It was clear from early reports that 1 Ml Cu on Si(111) produces a $5 \times 5$ incommensurate superlattice [56]. Recent studies by Simao et al showed that annealing 2 Ml Cu on Si(111) results in the sequential growth of a first layer that is close-packed hexagonal with a lattice parameter of 5.4 times the substrate spacing $a_s$, followed by a second layer with lattice parameter 5.7$a_s$ [57]. The latter has a mosaic domain structure composed of 3.5° small-angle grain boundaries. It was argued that the layers contain different Cu–Si stoichiometries and are stabilized by strain effects. At low growth temperature, it was apparent that silicon was taken from nearby step edges to form the ‘5×5’ layer beginning from a step-down edge, but an exact stoichiometry for the reaction was not determined. For thicker overlayers, 3D crystallites formed within the 2D layers, but with no particular correlation to the 2D layers. They had multiple orientations and were presumed without discussion to be Cu$_3$Si.

As a final example, we describe Co/Si(111)-$7 \times 7$. This case illustrates the extreme rebonding that can occur in metal–silicon reconstructions. Bennett et al have shown that the $7 \times 7$ unit cell contains a single Co atom on a substitutional silicon site, with a overlying ring of six silicon adatoms of two types: bridge-bonded (four-valent) and ‘capping’ (three-valent plus dangling bond) [58]. The model and a representative STM image are shown in figure 6. These results were supported by double-alignment, medium-energy ion scattering experiments and total energy calculations [58, 59]. The calculations showed the surprising result that the cobalt derived states dominate the corrugation in filled states images, even though cobalt atoms are much farther from the tip than the Si capping adatoms. This structure is particularly interesting because it is ‘universal’ (occurring for all group 8 metals), and because it can exist in isolated units called ‘ring-clusters’ (RCs). The RCs form a 1×1 lattice gas at low coverages, but are close packed into an ordered structure ($\sqrt{7} \times \sqrt{7}$) at a saturation coverage of 1/7 Ml [60]. These RCs might well be thought of as surface molecules of silicide, since they exist as discrete units in which the bonding resembles crystalline silicide. Recent experiments using the high temperature in situ imaging capability of low energy electron microscopy (LEEM) have explored the kinetic properties of these RCs in terms of 2D phase transitions, surface diffusion and assimilation into true silicide structures [61–65].

2.3. Bulk structure identification

It is sometimes possible to identify bulk structures using STM, even though it is inherently a surface sensitive technique. The procedure is most effective if one can choose from a range of likely structures and/or orientations, and these choices must be mutually exclusive within the uncertainty of the data. Thus, one might infer crystal type and orientation from surface lattice spacings if they can be resolved, or from
the orientation of exposed facets, or most commonly from the height of surface steps. This is most effective if the terraces on each side of the step are identical so that ‘electronic structure’ effects do not alter the tip–sample separation. If dissimilar terraces are compared, one must at least verify that the height difference is largely independent of bias voltage. A further possible complication is quantum interference effects, resulting from standing waves of tunnelling current between vacuum and buried interfaces. These effects are relatively small, and are typically only visible in ‘conductance images’ [66]. We describe a few examples of bulk structure identification below.

Raunau et al have used step heights to identify $\beta$-FeSi$_2$(101)/Si(111) during SPE growth of 15 Å at 600°C [44]. In this case a second orientation, $\beta$-FeSi$_2$(110), was excluded on the basis of layer spacing. The identification of the bulk silicide phase was further supported by the observation of a bandgap of 0.85 eV, measured by STM. In the same work, it was found that FeSi forms early in the SPE reaction, and that a metastable strain-stabilized $\gamma$-FeSi$_2$ structure forms late in the reaction.

An example of measuring layer spacing between different terraces was given by Bennett et al [43]. They identified monolayer CoSi islands as intermediate structures
in the RDE reaction of 0.25 M Co on Si(111)-7 × 7 at 320 °C. The surface reconstructions were Si 7 × 7 on the substrate and 2 × 2 on the silicide island. It was argued that these reconstructions are similar (both involving Si adatoms on T4 sites) resulting in no bias dependence of the apparent layer spacing.

A further example of step height measurement is given by Stalder et al for CoSi2/Si(100) produced by MBE [52]. They show that surface steps are predominantly two monolayers high as expected from the crystal structure, which consists of alternating (100) layers of Co and Si. However, they also report monolayer steps and show that these are due to 1/4(111) dislocations at the buried interface, which are visible via the accompanying strain field. They also caution that for partially reacted overlayers multiple step heights with no obvious relation to crystal structure can occur and are likely the result of extended defects.

A good example of using facet angles to identify crystal structures is given by Stephenson and Welland for SPE of Ti/Si(100) [67]. In this case, the multiple choices include several orientations of C49-TiSi2 and C54-TiSi2. They report numerous facet orientations, but find that none agree in detail with the expected multiple choices. They point out that atomic resolution of the exposed facets would have helped greatly to identify lattice planes, but this was not possible. It was concluded that low-angle grain boundaries with multiple orientations were likely to be present at the interface. A similar unwieldy behaviour was reported for SPE of CoSi2/Si(100), where the authors showed a polar plot of the mosaic distribution of facet angles [38].

Even when the interface is properly oriented, the possibilities of stacking faults, dislocations and facetting can present a complex surface structure, such as that reported for NiSi2/Si(100) produced by SPE [68]. In this case it was argued that the multiple surface phases observed in the beginning stage of overlayer formation (low coverage) may result in significant variation in electronic transport across the interface (Schottky barrier) for thicker overlayers.

Jongyoon et al present the case of Si/Au(100), where the multiple choices of the overlayer and interface structure are not well defined [69]. This case is complicated by the presence of metastable gold silicide compounds. In the words of the authors “there is still no consensus (in the literature) about the crystal structure, lattice constant, symmetry of the crystal and even the stoichiometry of gold silicides.” Their STM observations of lattice spacings and crystal orientations are consistent with earlier work, but do not particularly diminish the confusion in this problem.

There are examples of well-defined metastable silicide structures that are stabilized in thin heteroepitaxial layers, most notably iron silicide [46,70–73]. In the case of contiguous overlayers, the particular role of STM is not evident. For monolayer island structures, however, one could expect interesting and possibly quite large strain effects to occur, due to interaction with surface reconstructions. Such effects have been suggested for islanded CoSi2 on Si(111)-7 × 7 grown by RDE [43].

2.4. Buried interfaces

The structure and electronic properties of buried interfaces are best measured with BEEM, as we describe in detail later. Here we discuss STM/AFM (atomic force microscopy) topographic measurements only.

It is possible to infer interface structures from surface measurements combined with crystallographic data. For example, for CoSi2 islands on Si(111) produced by RDE at 320 °C, it is found that the interface metal atoms have sevenfold coordination rather than the commonly observed eightfold coordination [43,74–76]. These structures correspond to (Co–Si) versus (Si–Co–Si)(111) layers at the interface, respectively, and can be distinguished by measuring the height of the free surface of silicide islands above the exposed Si-7 × 7 substrate. It was suggested that the metastable sevenfold interface is stabilized by the edge energy of the islands, which is appreciable compared with substrate interface energies for small islands [43].

Alternatively, the buried interface structure might be inferred by building up from a clean surface. For example, Pd2Si0.0001 on Si(111) is epitaxial with a 2.5% mismatched \( \sqrt{3} \) coincidence lattice. In addition, there is a well defined \( \sqrt{3} \) surface structure at 1 Ml coverage, which is modelled as a slightly distorted (0001) plane of Pd2Si [77]. STM observations suggest that the \( \sqrt{3} \)-ML structure is essentially retained at the interface as the multilayer silicide is formed. This hypothesis has not been quantified, however [78,79].

It is possible to measure some aspects of interface structure directly with STM. In particular, Stalder et al have shown in elegant fashion that the strain field from interface misfit dislocations in CoSi2/Si can be seen directly in STM topographic images, as shown in figure 7 [80,81]. They report surface vertical displacements of the order 0.5 Å, with a lateral half-width similar to the thickness of the silicide overlayer, exactly as expected from calculations of the strain field based on known elastic constants and dislocation core structure.

Lastly, we mention a special \textit{ex situ} technique for determining interface structure that seems to be quite effective. Nishikawa et al have measured a 100 nm Pt film deposited on Si(111)-7 × 7 at 350 K [82]. The film was lifted off and examined \textit{ex situ} using AFM. They demonstrated atomic-level sensitivity, and correlated the AFM data with \textit{in situ} RHEED and \textit{ex situ} TEM observations. They found that various Pt, Si, silicides were formed at the interface and inferred five distinct stages of the low-temperature reaction involving changes of stoichiometry and grain structure of the silicide.

3. Kinetics and growth

STM can be used to observe and quantify kinetic processes on an atomic scale. The recent availability of commercial STMs that can operate at high temperature has spurred much activity [83,84]. Stunning results have been obtained with remarkable detail and complexity for metal-on-metal systems [85] and for silicon-on-silicon systems [86–90]. Similar results for silicides are lacking, with the few exceptions described below.

3.1. Direct atomic measurement

Ishiyama et al reported experiments for Ti/Si(100) that illustrate beautifully the capabilities of STM for kinetic
studies of silicide reactions, particularly regarding atomic-scale precursor structures [27–29]. They observed two types of atomic structures for individual Ti atoms adsorbed on Si(100): a pedestal site ‘P’ and a dimer-vacancy-attached site ‘V’, as we showed earlier in figure 1. By comparing successive scans of the same area, they found that the ‘P’ site converts either irreversibly into the ‘V’ site (type-A conversion) or reversibly into an unidentified but highly mobile state (type-B conversion). The latter is inferred because the ‘P’ sites disappear and reappear far away (outside a scan frame) at random intervals. Formation of the ‘V’ site is accompanied by the release of two Si atoms which diffuse away to form silicon islands. The temperature dependence of conversion rates for these processes as well as for diffusive motion of the ‘V’ site were measured directly from consecutive images on a heated sample, and are shown as Arrhenius plots in figure 8. The authors give a detailed description of the probable site conversion path based on the STM images coupled with these numbers, as shown in figure 9. The activation energy of $E_D = 1.8 \text{ eV}$ obtained for diffusion of the ‘V’ site is not unlike values for metal diffusion through bulk silicide [33], and is taken to reflect the strength of Ti–Si bonding even in the surface structures. On the other hand, motion of the ‘V’ site involves several atoms and it was suggested that this is likely a ‘concerted exchange’ process [91, 92]. The high mobility (unmeasured) of the invisible species is more typical of surface diffusion of an adsorbate moving between low-coordination sites.

Figure 7. Vertical displacements $\Delta z_d$ at the surface versus lateral distance $x$ for cross sections measured perpendicular to the dislocation lines for five CoSi$_2$/Si(111) layers with thicknesses $d = 21–104$ Å. Fitted Lorentzian curves are given as continuous curves.

Figure 8. Arrhenius plot of the conversion rates for type-A ($v_A$) and type-B conversions ($v_B$). Open marks represent data obtained by an interval-scan method. The activation energies and prefactors given by the least-squares fit are $E_A = 1.6 \pm 0.1 \text{ eV}$ and $v_{A0} = 10^{14} \text{ s}^{-1}$ for type A and $E_B = 1.6 \pm 0.2 \text{ eV}$ and $v_{B0} = 10^{14} \text{ s}^{-1}$ for type B. (After Ishiyama [29], with permission.)

3D islands were formed also, but not identified or studied in detail. Certainly there is much room for further work of this type.
 STM studies of silicides

Figure 9. Models for proposed site conversion paths and corresponding potential curves. The curves shown indicate the relative height of the potential along the conversion paths and a migration path between the dimer rows (labelled ‘E’). For $E_p$, $E_C$ and $E_E$, only relative heights to the measured values are estimated. The activation energy for the diffusion of vacancy site adsorption structure ($E_D = 1.8 \text{ eV}$) is also shown. (After Ishiyama [29], with permission.)

STM has been used extensively to make direct measurements of the statistical mechanics of atomic-scale structures on many different surfaces, beginning with determination of the kink energy for steps on Si(100) [93]. Analogous work has not been done for silicides. The nearest example is given by Zandvliet et al for quenched-in dimer vacancy (DV) structures for submonolayer Ni/Si(100) [41]. They fit a pair-correlation function for DVs at a single assumed freeze-in temperature (750 K) for an assumed interaction potential, and concluded that there is a near-neighbour attraction between DVs of 0.11 eV and a long-range repulsion between chains of DVs.

3.2. Modelling

One can infer diffusion rates and island binding energies by comparing measurements of island density as a function of deposition rate and temperature with theoretical models of nucleation and growth [85, 94]. In such fashion, Bennett et al have estimated the diffusivity for Co on Si(111)-7 × 7 [95]. These measurements, however, were made at a single temperature and rate without verifying the applicability of the nucleation model. Nonetheless, a nominal value for diffusivity was obtained and attributed to the motion of subsurface interstitials [96].

Shingubara et al have measured island volume versus annealing temperature during SPE of Ti/Si(111), and show Arrhenius plots of this data [36]. However, the physical interpretation of such plots is unclear, since the growth process is complex and undefined. Nonetheless, the data indicate that the growth is qualitatively different above 500 °C, and is distinctly slower for a H-passivated surface.

3.3. Stoichiometry

It has been noted in several STM studies, particularly for RDE growth, that silicide islands are sometimes accompanied by substrate ‘holes’, corresponding to the silicon consumed in the reaction [54, 57, 99–102]. This situation offers the potential for interesting ‘titration’ studies of stoichiometry, and possibly also diffusion studies of metal and/or silicon. It requires growth conditions such that flat island and hole structures are visible on a scale large enough to be identifiable as single phases but small enough to measure with reliable statistics. The volume of metal in the islands can be computed from the calibrated total dose and areal fraction, while the volume of silicon in the islands can be computed from the area and depth of the holes. This assumes that no silicon is taken from under the island (not necessarily a good assumption), and that the surface structure in the hole matches that of the nominal surface. Errors in these assumptions are minimized for multilayer structures. In such a fashion it has been determined that the $2\sqrt{3}$ surface of Er/Si(111) contains six Er atoms/unit cell, corresponding to 0.5 Ml coverage [54].

Another example is the inverted SPE system Si/Cut(100)-‘5 × 3’, where it was determined that the overlayer has a stoichiometry of Cu$_2$Si [99]. This case is separately

Figure 10. Average cluster size versus coverage for CVD and PVD growth of FeSi(100). CVD growth is characterized by large cluster sizes compared with PVD growth. Comparisons are made for equal areal coverages. Note, each data point is taken from a separate growth experiment. The lines are guides to the eye. (After Adams [98], with permission.)

Adams et al reported beautiful measurements of island density and size distribution for the growth of Fe on Si(100) and modelled the process using Monte Carlo simulations [98]. These results are shown in figure 10. They compared the behaviour of physical- versus chemical-vapour deposition (CVD) under closely matched growth conditions and concluded that the CVD growth is dominated by autocatalytic effects. Namely, the growth rate is accelerated as clusters form, either because of improved accommodation and/or increased binding energy of the clusters. It should be said, however, that the growth process involves Fe/Fe, not silicide growth, at least in the latter stages.
notable for its similarity to the (non-inverted) Cu/Si(111)-‘5 × 5’ system [100]. Both form incommensurate overlayers with nominal stoichiometry Cu$_2$Si. This suggests that the interlayer bonding is much stronger than the overlayer–substrate bonding. It is remarkable that similar incommensurate overlayers occur despite the inverted metallurgy and different substrate symmetries.

3.4. Layer and island growth

STM can be used to track reactions as an overlayer progresses through various structures including atomic-scale precursors, 2D reconstructions and overlayers, and 3D islands or multilayers. In some cases the inter-relation of structures and/or fundamental growth mechanisms can be inferred, as described below.

Wälchli et al describe the growth of Pd$_2$Si on Pd(110) by inverted SPE [19]. They use an ingenious scheme to monitor surface stoichiometry using the chemical shift of physisorbed CO as detected by IR spectroscopy. This method can distinguish amorphous from crystalline structures. They show that the silicide reaction is suppressed entirely at 140 K, while amorphous Pd$_2$Si forms at 140–320 K and crystalline Pd$_2$Si forms at $T > 320$ K as islands embedded in the Pd substrate. The silicide reaction apparently involves an exchange process whereby Pd atoms are ejected from the substrate and diffuse around to form monolayer Pd(110) islands. A further interesting point is the high mobility of Si in bulk Pd, which apparently facilitates the exchange reaction and formation of ordered embedded structures even at 320 K. Upon heating to 550 K the Pd$_2$Si islands disappear completely. It was claimed that silicon dissolves into the Pd substrate, even though Pd and Si are bulk-immiscible. It was argued that surface stress strongly enhances solubility in the surface region, as described in general terms by Tersoff [103].

Embedded islands also form in the CoSi$_2$/Si(100) system during RDE at 500 °C [38]. In this case 2D silicide islands form at low coverage (below 0.2 ML), while 3D islands form at higher coverage. The 2D islands apparently are consumed by the 3D islands, although they are not directly connected. This is an interesting example of apparent subsurface transport and reaction. A similar 2D to 3D growth occurs in the Er/Si(111) system during RDE at 500 °C, but in this case the 3D structure (ErSi$_{1.7}$) clearly grows directly from the 2D structure which shows a $(2\sqrt{3} \times 2\sqrt{3})$ reconstruction [54].

In the advanced stages of epitaxial growth, after many layers have formed, the structure is best characterized with statistical parameters such as surface roughness. This can be compared with theoretical growth models to infer atomistic details that cannot be observed directly. Even without such details, the qualitative information about surface roughness may be useful. We describe two examples below.

Scheuch et al reported measurements of surface roughness and silicide island density during MBE growth of CoSi$_2$/Si(100) with and without As as a surfactant [104]. Surface roughness was shown to follow a power-law dependence on film thickness, with a growth exponent for the bare silicide ($\beta = 0.66$) indicative of upwards step-crossing flux (layer formation), and a growth exponent for the As covered surface ($\beta = 0.2$) indicative of downwards step-crossing flux (layer formation). The latter was attributed to a reduced surface diffusion due to the surfactant effect of the As.

In a second example, the propagation of surface roughness through heteroepitaxial layers prepared by MBE was described for a multi-layer system comprised of Si(substrate)/Co$_2$Si(30 Å)/Si(500 Å)/CoSi$_2$(30 Å) [105]. The top surface was examined with STM, and the buried interfaces with x-ray diffraction and TEM. Model calculations of the x-ray truncation rod profiles showed a correlation of step structures between interfaces, called a ‘conformal roughness of adjacent interfaces’. Indeed, it was found that surface step structures were retained during growth and thereby propagated through the multilayer structure. This implies an extremely regular step flow during growth, as originally reported for room temperature MBE growth of CoSi$_2$ [14, 106].
3.5. Phase transformations

STM can provide detailed information about surface phase transformations, such as whether phases are structurally similar and/or spatially linked, as in the following examples.

Stalder et al. have shown that a CoSi$_2$ overlayer on Si(100) transforms irreversibly from the metal rich ‘C-surface’ ($\sqrt{2} \times \sqrt{2}$) to the silicon rich ‘S-surface’ (also $\sqrt{2} \times \sqrt{2}$) via an intermediate $2 \times 2$ phase at a temperature near 500 °C [52]. The transformation can be reversed by deposition of additional cobalt. STM images showed that the $\sqrt{2} \times \sqrt{2}$ structures are different reconstructions and that the $2 \times 2$ is spatially linked to the two, and is some form of intermediate structure. Indeed, model structures provide a clue to the atomistic process of this phase transformation. This case is particularly interesting since it is an example of surface segregation of silicon, which occurs for essentially all silicides due to the lower surface energy of silicon compared to the silicides [7, 107].

Another example of coupled structures was given by von Känel et al. for iron silicides on Si(111) [70, 108]. The authors first established the existence of metastable strain-stabilized $\gamma$-FeSi$_2$/Si(111). Then using STM, they showed that this structure contains subsurface vacancies, and can be viewed as a vacancy-defective FeSi$_2$ structure. Annealing was found to induce ordering of the vacancies and was taken as an intermediate step of the phase transformation from FeSi into the $\gamma$-FeSi$_2$ structure.

3.6. Nanoscale metallization

Nanoscale metallization of silicon is a recent topic of great interest. We make no attempt to review this topic, which has been summarized in several recent works [109, 110], but only mention a few examples in the context of silicides. Nanoscale features on silicon can be produced with scanned probes in several ways including: mechanical modification (scratching) [111], direct atomic manipulation [112], field evaporation [113, 114], stimulated chemical reaction [115–117] and lithography [109, 110]. The latter two are most practical and interesting for metallization of silicon and are described further below.

The group of deLozanne has explored the use of stimulated chemical reaction of organometallic precursors containing cadmium, aluminium, tungsten or nickel [118, 119]. Typical operating conditions are sample bias of +15 V and gap of 20 nm. This creates an electric field sufficient to crack the precursor gas in the gap, releasing pure metal which then reacts with the substrate. Since the sample is relatively cool, most of the deposited material remains as unreacted metal, although the initial layers presumably form a silicide. The group has demonstrated four-point resistance measurements for nickel wires using tungsten silicide contact pads, as shown in figure 11 [120]. The slight increase of resistivity at low temperature was suggested to indicate a quantum localization effect.

The lithographic approach has been studied extensively by the groups of Adams [110, 121] and Lyding [109] particularly using adsorbed hydrogen as a monolayer resist material. It has been shown that the physical mechanism for desorption of hydrogen by the STM changes from thermal desorption to electron stimulated desorption above 6 V bias and the conversion efficiency under typical conditions was measured to be $10^{-6}$ hydrogen atoms per electron [122]. Linewidths vary from 5–50 Å depending on STM tip radius, gap size and bias voltage [110, 123]. Metallization of the patterned resist then proceeds by selective area CVD. That is, a thermal CVD reaction occurs on the exposed silicon regions but not on the remaining passivated area. The reaction is reasonably but not perfectly selective [110]. Such experiments have been performed mostly with iron, but also recently with aluminium [124].

Lastly we mention recent efforts to develop a nanoscale ‘salicide’ (self-aligned silicide) process. Graf and von Känel have demonstrated the use of AFM to write oxide traces which serve as a mask for subsequent wet etching that leaves self-aligned cobalt silicide wires [125].
4. BEEM

The electronic properties of metal/semiconductor interfaces have been a subject of research for many decades. Usually, a rectifying barrier, the Schottky barrier, is formed when a metal is brought into contact with a clean semiconductor. We shall not try to cover the huge body of literature existing on the Schottky barrier problem. Instead, we focus on electron transmission through silicide/silicon interfaces, treating examples relevant to STM.

4.1. BEEM method

Kaiser and Bell have invented an extension of STM to a three-terminal transistor-like configuration, called ballistic-electron-emission microscopy (BEEM) [126]. Here, the tunnel contact is attached to a metal film, the base, which is thin enough for hot charge carriers injected from the tip, the emitter, to reach the metal/semiconductor interface. Depending on the tunnelling bias some fraction of the injected carriers may be transmitted through the interface, giving rise to a collector or BEEM current. This current is expected to remain zero as long as the injected electrons or holes do not have sufficient energy to overcome the Schottky barrier. Variations of the Schottky barrier height can thus directly be measured on a small lateral scale, by using BEEM in the spectroscopy mode (BEES), similar to what is done in scanning tunnelling spectroscopy (STS). Since BEES is usually done by measuring the BEEM current as a function of the tunnelling voltage at a fixed tunnelling current, the tip–sample separation does not remain constant in contrast to STS. The simplest BEEM theory is based on an effective mass approximation, assuming conservation of the parallel wavevector at the interface [127]. It leads to a quadratic BEES spectrum close to the threshold. A similar dependence is, however, obtained also in the absence of \( k_\parallel \) conservation, such that the spectral shape does not indicate whether or not interface scattering is present [128]. More details about BEEM can be found in a number of recent review articles [129–131].

4.2. Band structure

The most detailed theoretical studies of electron transport have been performed on the Si(111) interfaces of NiSi\(_2\) [132,133] and CoSi\(_2\) [134,135]. These two silicides are prototype systems, forming the most perfect metal/semiconductor interfaces feasible to date. They are thus ideally suited for understanding the BEEM process at a fundamental level. NiSi\(_2\) can occur with two different orientations, either aligned with the substrate lattice (A-type) or rotated by 180° around the surface normal (B-type), leading to distinctly different Schottky barrier heights [136]. Electron transmission through the two NiSi\(_2\)/Si(111) interfaces was found to differ by a factor of three. The B-type CoSi\(_2\)/Si(111) interface turned out to be a special case since there are no states with equal energy and parallel wavevector in the silicide and in the Si near to the conduction band minimum of Si. The transmission is hence expected to be
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Figure 14. STM topographic (a) and corresponding BEEM (b) images taken in the same region of a 2.8 nm CoSi2/n-Si(111) film. Tunnelling parameters in (a) and (b) were \((V_t = -1.7 \text{ V}, I_t = 3 \text{ nA})\) and \((V_t = -6 \text{ V}, I_t = 1 \text{ nA})\), respectively. The ranges of the grey scales are 0.1 nm in (a) and 185 pA in (b).

zero up to \(\sim 200 \text{ meV}\) above the Schottky barrier, as long as the parallel wavevector is conserved.

Qualitatively speaking, all of these interfaces can be considered to be strongly reflecting for electrons with energies within \(1\)–\(2 \text{ eV}\) above \(E_F\). Standing wave formation due to quantum interference is therefore expected leading to a change of the local density of states observable by STM. Kubby and Greene have directly observed the different reflectance of A- and B-type NiSi2/Si(111) interfaces by modulation spectroscopy (MS) [137]. Changes of thickness lead to image contrast as well, making it possible to identify interfacial steps as we described in earlier sections. Lee et al have quantitatively studied the 2D subband formation due to quantum interference in CoSi2/Si(111). They could correlate the peaks observed by current-imaging tunnelling spectroscopy (CITS) with the computed band structure quantized along the \(\Lambda\) line in the bulk Brillouin zone [138].

4.3. Schottky barrier

Kavanagh et al [139] and Niedermann et al [140] have studied Schottky barrier height distributions on PtSi/n-Si(100). They both find very narrow distributions with \(\Phi_b = 0.87 \pm 0.02 \text{ eV}\), independent of the details of the preparation procedure. Both used, however, low-doped substrates where screening effects in the semiconductor limit electrostatic potential variations, such that barrier height fluctuations on the scale of a few nanometres remain unobservable [141]. In contrast to the barrier height, the BEEM current was found to be correlated strongly with the grain morphology, exhibiting variations up to a factor of 50 [140]. This was tentatively attributed to different crystallographic orientations of the grains, leading to strong variations of the interfacial transmission probability.

Hasegawa et al [142] and Fernandez et al [143] studied epitaxial NiSi2/n-Si(111) films in order to search for the expected barrier height differences of A-type and B-type interfaces. Hasegawa et al used low doped substrates with Debye screening lengths far above the average size of A-type and B-type domains, of less than 100 Å, such that no barrier height differences could be seen. By contrast, Fernandez et al measured the correct barrier height differences, despite equally low substrate doping levels, thanks to the much larger grain size of their mixed A-type and B-type films.

A nice example for which spatial variations of \(\Phi_b\) can directly be correlated with defects identified by TEM is CoSi2/n-Si(111), as described by Sirringhaus et al [144]. They were able to show that \(\Phi_b\) is significantly lowered within the extent of the strain field of interfacial dislocations with Burgers vectors of \(a/4\langle111\rangle\). The same lowering of \(\Phi_b\) was found at linear defects unassociated with any topographic surface features, as shown in figure 12.

According to theory, transmission through CoSi2/n-Si(111) interfaces should differ from the examples discussed above, because of the lack of matching states for energies close to the Schottky barrier height. The onset of the BEEM current is hence expected to be delayed by \(\sim 200 \text{ meV}\), instead of occurring as usual right at the Schottky barrier height. Such a delayed onset has indeed been reported by Kaiser.
et al [145]. The result of their ex situ study carried out on 5–10 nm thick films could not be confirmed, however, by Sirringhaus et al who did their measurements in UHV on much thinner films (2–3 nm) [146]. They measured a homogeneous BEEM onset, unaffected by dislocations, with a Schottky barrier height of 0.66 eV at 77 K. In contrast to Kaiser and coworkers, Sirringhaus et al also observed a homogeneous interface transmission, apart from dislocation and surface-induced variations. Some evidence for the expected band structure effect has recently been found by the same group, however, by comparing BEES spectra taken on individual point defects with spectra taken from truly defect-free regions [147]. The results have been interpreted in terms of different momentum breaking processes which are believed to be active simultaneously. One of them stems from the expected scattering by the interfacial point defects. The other one is present even in defect-free regions and is still a matter of speculation, one possibility being scattering by some interfacial phonon mode.

4.4. Defect scattering

BEEM is a sensitive probe of interface defects. Normally, the BEEM current is reduced in the vicinity of defects. However, the reverse occurs for silicide/n-Si(111) interfaces, as originally pointed out by Fernandez et al since the Si conduction band minima are far away from the zone centre [143]. This effect can be used to image dislocations, as shown by Sirringhaus et al for CoSi2/n-Si(111) [146]. Although the scattering effect is strongest for electron transmission through (111) interfaces, it can also be observed for holes injected into p-Si(111). In this case, however, the BEEM current is reduced by scattering since transmission of holes with a narrow angular distribution is allowed in the absence of scattering [148].

BEEM images exhibiting the highest resolution of interfacial features have recently been obtained by Meyer and von Känel, who could image single point defects at CoSi2/n-Si(111) interfaces [149]. These results provided direct evidence for the trapping of point defects in the strain field of dislocations, as shown in figure 13.

4.5. Inelastic scattering

The BEEM current is sensitive not only to elastic scattering effects, but also to inelastic hot-carrier scattering in the metal film. This can be exploited to measure the exponential dependence of BEEM current on film thickness, from which the attenuation length $\lambda$ can be obtained. This has been done for PtSi/n-Si(100) by Niedermann et al [140] and Turner et al [150] who both obtained a value of 4 nm for $\lambda$ for film thicknesses below 15 nm, and for energies of the order of 1 eV above the Fermi level. Niedermann et al who extended these measurements to larger base thicknesses found the BEEM current to deviate from the simple exponential behaviour and $\lambda$ to increase to 9 nm. They speculated that this might be caused by a bilayer structure of their films.

In the simplest case the measured $\lambda$ is just equal to the ballistic mean free path $\lambda_B$ which may be written as $1/\lambda_B = 1/\lambda_e + 1/\lambda_i$, where $\lambda_e$ and $\lambda_i$ are the elastic and inelastic mean free paths, respectively [151]. For thin films this may no longer be true since, for example, quantum interference effects may start to influence the transmission to a considerable extent. This has indeed been observed on CoSi2/n-Si(111) [152] where quantum interference visible by CITS or MS affects the BEEM current as well [146].

Lee et al have made a detailed comparison of the energy dependence of $\lambda$ for CoSi2/Si(111) and CoSi2/Si(100) [153]. They found the attenuation to be anisotropic and small enough for energies $\sim$4 eV above the Fermi level to yield a measurable BEEM contrast for film thicknesses differing by one monolayer. This offers the possibility of mapping film thickness distributions by BEEM [148,153]. An example is shown in figure 14 for CoSi2/Si(111), where the STM topographic image reveals the dislocation structure and the BEEM image reveals the thickness distribution using ‘attenuation length contrast’.

A special kind of inelastic scattering spectroscopy has been developed by Bell et al [154]. It is basically an Auger process, where hot carriers of the opposite sign to the ones contributing to the BEEM current are injected into the base, generating the other type of carrier by means of inelastic scattering, as shown in figure 15. Niedermann et al have applied this reverse BEEM (RBEEM) process to PtSi/n-Si(100) [140]. They found attenuation lengths differing from the ones found for direct BEEM, from which...
they concluded that elastic and inelastic scattering events contribute differently to the observed λ in the two processes. This may be understood by taking into account the different angular distributions of hot carriers incident on the interface in BEEM and RBEEM, the latter being much more isotropic.

RBEEM has also been performed on CoSi2/p-Si(111) by Lee et al, who found the same monolayer thickness sensitivity at large tip biases as for direct BEEM [153]. The tunnelling distributions are exactly the same for direct BEEM on CoSi2/n-Si(111) and RBEEM on CoSi2/p-Si(111). From the RBEEM spectra on CoSi2/p-Si(111) Lee et al could thus get a good estimate of the extent to which the direct BEEM current for CoSi2/n-Si(111) is affected by the generation of secondary electrons in the silicide film.

4.6. Surface effects

While the primary motivation for using BEEM is to study subsurface properties with the STM, it was recognized from the beginning that surface effects can also be important [143]. It nevertheless came as a surprise when Sirringhaus et al discovered that true atomic resolution can be achieved by BEEM and RBEEM [155, 156]. This is illustrated in figure 16, for CoSi2/Si(100), where the periodic structure of the surface reconstruction is clearly visible in the BEEM image. This is a pure surface effect, stemming from the variation of the tunnelling distribution on an atomic scale. In principle, the energy and the momentum distribution of the tunnelling electrons are both affected by the surface structure. BEEM may be considered as an energy and momentum filter for electrons entering the semiconducting collector. Provided that the transport through the metal base is predominantly ballistic, the observed atomic-scale contrast can thus be qualitatively understood. Unfortunately, no theoretical calculations are available to date to interpret the images at a truly fundamental level.

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