

**Studies of Thin Metal Silicides
on Silicon (111)**

Ian Matthew Scott

Submitted for the Degree of Doctor of Philosophy

University of York

Department of Physics

September 2004

Abstract

This work describes the study of RE/Si(111) (RE – rare earth) and Fe/Si(111) surfaces by means of medium energy ion scattering (MEIS), scanning tunnelling microscopy (STM) and scanning tunnelling spectroscopy (STS).

The Tm/Si(111) surface has been studied by means of MEIS. Data has been obtained from the 1×1 surface reconstruction formed at monolayer rare earth coverage. The data have been compared to simulations for a model based on the known structures of other RE silicides. The structure of the Tm silicide formed has been seen to fall into this class of structure. This investigation has led to a re-evaluation of the determination of the structural parameters for this model. A trend in the structural parameters has been revealed across the rare earth series.

The electronic structure of the rare earth silicide surface has been investigated. STS has been performed on the Ho silicide 1×1 surface. A lack of distinction between inequivalent sites has been observed and the data found to be in broad agreement with what is known of the electronic structure of these RE silicides.

A MEIS investigation has been made of the initial growth of Fe on the Si(111) 7×7 surface. Two phases have been found to form depending on anneal temperature. At anneal temperatures of around 300°C a 1×1 phase is formed and at higher anneal temperatures a 2×2 phase is found. Data have been obtained from three scattering geometries. The data indicate that both phases are structurally very similar. A CsCl-type structural model is proposed, the 2×2 phase being formed by a Si adatom overlayer.

The use of the RE silicide as a growth template has also been briefly investigated by MEIS. The deposition of Fe onto the Ho silicide surface has been found to disrupt the structure and progressive annealing failed to reorder the system.

Contents

Contents	3
List of Figures.....	8
List of Tables	18
Acknowledgements	19
Declaration.....	20
Publications	20

1 Introduction 21

1.1 The Surface	21
1.2 Techniques of Surface Science	23
1.2.1 Scanning Tunnelling Microscopy	24
1.2.2 Low Energy Electron Diffraction.....	24
1.2.3 Reflection High Energy Electron Diffraction	26
1.2.4 Medium Energy Ion Scattering	26
1.2.5 Surface X-Ray Diffraction	27
1.2.6 X-Ray Photoelectron Spectroscopy	27
1.2.7 Ultraviolet Photoelectron Spectroscopy.....	27
1.2.8 Auger Electron Spectroscopy.....	28
1.2.9 Electron Energy Loss Spectroscopy.....	29
1.2.10 Surface Extended X-ray Fine Structure	30
1.3 Metal–Semiconductor Interfaces	31
1.4 Materials Studied	33
1.4.1 Two Dimensional Rare Earth Silicides	33
1.4.2 Iron Silicides	35

1.4.3	Metal Growth on 2D Rare Earth Silicides	36
	References	36
2	Experimental Aspects	41
2.1	The Daresbury MEIS Facility	41
2.2	Scanning Tunnelling Microscopy	44
2.2.1	General Principle.....	44
2.2.2	Theory	47
2.2.3	Scanning Tunnelling Spectroscopy.....	50
2.2.4	Apparatus	51
2.3	Low Energy Electron Diffraction.....	53
	References	58
3	Medium Energy Ion Scattering.....	60
3.1	Introduction	60
3.2	The Technique of MEIS.....	61
3.2.1	Shadowing and Blocking	61
3.2.2	Kinematic Scattering.....	64
3.3	Simulation of Scattering Curves	69
3.3.1	Hitting and Detection Probabilities.....	69
3.3.2	Calculation of Probabilities: The Standard Method.....	71
3.3.3	Calculation of Probabilities: Tromp and van der Veen's Method 72	
3.3.4	Connection of Ingoing and Outgoing Ion Tracks	75
3.3.5	Tracking of Ions: The Single Row Approximation.....	76
3.3.6	Tracking of Ions: The Complete Crystal Method	76

3.3.7	Multiparameter Simulations.....	78
3.4	Comparison of Simulation with Experimental Data.....	78
	References	79

4 MEIS Investigation of Thulium Silicide 82

4.1	Introduction.....	82
4.2	Experimental Details.....	82
4.3	Results and Discussion.....	87
4.3.1	Experimental Results and Analysis.....	87
4.3.2	Computer Simulations.....	89
4.3.3	Re-examination of Best Fit Model.....	94
4.4	Conclusion	97
	References	99

5 Structural Trends and the Influence of R-factors 101

5.1	Introduction.....	101
5.2	A Possible Trend.....	103
5.3	The Possible Influence of the R-factor.....	106
5.4	Re-examination of MEIS Structural Results.....	107
5.5	Examining the R-Factor	109
5.5.1	The Influence of the Low Angle Blocking Dip	109
5.5.2	Alternative R-Factors	112
5.5.3	Performance of the R-factors	114
5.5.4	Errors in the Results	118
5.5.5	Conclusion	120

5.6	Conclusion	121
	References	123

6 MEIS Study of the Initial Growth of Fe on Si(111) 125

6.1	Introduction	125
6.2	Experimental Details.....	126
6.3	Results and Discussion.....	127
6.3.1	Experimental Data.....	127
6.3.2	Possible Models	133
6.3.3	Optimising Structural Parameters	134
6.4	Conclusions	139
	References	140

7 Studies of the 2D Silicide Surface 143

7.1	Introduction	143
7.2	STS of 2D Holmium Silicide	143
7.2.1	Introduction	143
7.2.2	Experimental	144
7.2.3	Scanning Tunnelling Microscopy	145
7.2.4	Scanning Tunnelling Spectroscopy.....	146
7.2.5	Spatially Resolved Spectra.....	148
7.3	Initial MEIS Study of Fe Growth on 2D Holmium Silicide	151
7.3.1	Introduction	151
7.3.2	Experimental	151
7.3.3	Results and Discussion.....	152

7.4 Conclusion 155
 References 155

8 Conclusion 158

8.1 MEIS Study of Thulium Silicide 158
 8.2 Structural Trends in 2D Silicides 159
 8.3 R-factor Analysis of MEIS Data 160
 8.4 Iron Growth on Si(111) 161
 8.5 Studies of the Silicide Surface 162
 8.5.1 Iron Growth on 2D Silicides 162
 8.5.2 STS of 2D Silicide 162
 8.6 Future Work 163

Glossary 165

List of Figures

- Figure 1.1: Simplified side view of a) a surface relaxation in which the atomic spacing changes near to the surface; b) a surface reconstruction, in which the atomic arrangement reconfigures to produce a new two-dimensional unit cell.22
- Figure 1.2: The Auger process. A high energy electron removes a core level electron from the atom (a), leaving an excited state (b). The atom relaxes via a less tightly bond electron filling the core level hole. The energy liberated causes the ejection of a third, Auger electron (c).....28
- Figure 1.3: Formation of a Schottky barrier, Φ_{SB} , for an n-type semiconductor in contact with a metal. The Schottky barrier forms, and the junction is rectifying, if the metal work function, ϕ_m , is greater than the semiconductor workfunction, ϕ_s . E_v is the top of the valence band, E_c the bottom of the conduction band and E_f the Fermi level. The band gap of the semiconductor, E_g is also indicated.32
- Figure 1.4: Structure of the 2D RE silicides. The RE forms a single atomic layer situated in T4 sites above the bulk Si. The silicide is terminated by a bulk-like Si bilayer, rotated by 180° with respect to the bulk. Top: Side view. Bottom: Top view (i.e. along the surface normal). Inset: Ball and stick model of the surface.34
- Figure 2.1: Schematic diagram of the Daresbury MEIS facility beam line. Ions are produced by a duoplasmatron source and accelerated to around 100 keV. The ion beam is then focused and collimated before entering the scattering chamber.41
- Figure 2.2: Schematic diagram of the Daresbury MEIS facility user end station. The ion beam enters at the main scattering chamber. Sample preparation is performed in a separate chamber and sample storage and fast entry is also available.42

- Figure 2.3: The torodial electrostatic analyser and 2D detector produce the 2D data sets in MEIS experiments. Ions entering the detector are bent through 90° before hitting a set of channel plates which amplify the charge so it may be detected by the 2D detector plate.44
- Figure 2.4: The general operation of the scanning tunnelling microscope in constant current mode. As the tip is scanned across the surface its z-position is adjusted to maintain a constant tunnelling current. This results in the tip following the contours of the surface.....45
- Figure 2.5: The model tip used in the calculations of Tersoff and Hamann [13, 14]. The tip is taken as a spherical potential well of radius R , centred at \mathbf{r}_0 a distance d above the surface.....47
- Figure 2.6: Qualitative description of the reciprocity principle. Probing surface s states with a tip d state is equivalent to probing d states with a tip s state...49
- Figure 2.7: Bias condition dependence of STM imaging, in the case of the Si(111) 7×7 surface. (a) Unoccupied states with the sample biased at +1.5 V. (b) Occupied states with the sample biased at -1.5 V. The unit cell is marked in each case. Note that in the case of (b) a difference is clear between the faulted and unfaulted half of the unit cell, whilst in (a) the two halves appear the same. From Avouris & Wolkow [16].....50
- Figure 2.8: Schematic diagram of the STM 1 system. The STM is housed in a UHV side chamber attached to a UHV sample preparation chamber equipped with LEED, AES and deposition sources.....52
- Figure 2.9: Schematic diagram of AFM/STM systems used. The UHV STM side chamber may be isolated from the main UHV sample preparation chamber. Samples may be quickly exchanged in and out of the system using a load lock.....52
- Figure 2.10: Simple diffraction in 1D. Constructive interference occurs when the Bragg condition is met, i.e. path difference $d=n\lambda$, λ being the electron wavelength and $n=\dots-2,-1,0,1,2,3,\dots$54
- Figure 2.11: The Ewald sphere for elastic scattering in 2D. The bragg condition $\mathbf{k}_i-\mathbf{k}_s=\mathbf{g}$ is met whenever the sphere crosses a reciprocal lattice rod.55

- Figure 2.12: An example LEED pattern [24], showing the diffraction pattern from the clean Si (111) 7×7 surface with incident electron energy of 40 eV. Note that the periodicity of the surface is immediately apparent.....56
- Figure 2.13: Typical LEED apparatus. Electrons are diffracted from the sample and accelerated between the grid G1 and the fluorescent screen. The grids G2 and G3 filter out the lower energy, inelastically scattered electrons to reduce the background. It is often the case that the fluorescent screen is deposited on a window so that the pattern may be viewed through the glass to avoid the problems with the screen being obscured by the sample mountings.....57
- Figure 3.1: Shadowing. By aligning the ion beam along a low index crystallographic direction, the atoms deeper in the crystal are effectively shadowed from the beam.62
- Figure 3.2: Blocking. Scattered ions are blocked in their path back out of the crystal by atoms closer to the surface in a process analogous to the initial blocking. A shift in atomic position results in a shift in the angular position of a blocking feature.....63
- Figure 3.3: The kinematic factor k^2 as a function of scattering angle for two target masses of 28 amu and 168 amu, calculated for the case of H^+ ions. .64
- Figure 3.4: An example MEIS spectra (taken from the Tm 2D silicide system, see Chapter 4 for details). This spectrum demonstrates many of the features of a typical MEIS spectrum. The signals from scattering from the Si and Tm are well separated due to the mass difference between the two elements. The Tm scattering signal shows the characteristic fall in counts at increasing scattering angle due to the Rutherford scattering cross-section. The drop in energy with increasing scattering angle is most evident in the Si scattering signal. The Tm scattering signal shows clear evidence of ions being blocked at specific scattering angles. The detection around a major crystallographic direction is evidenced by the bulk blocking feature.....65

- Figure 3.5: The energy loss due to inelastic scattering becomes greater the deeper the ion penetrates. An ion entering the crystal with energy E_0 and being scattered at a depth d from the surface exits with energy given by Equation 3.9.....67
- Figure 3.6: Basic double alignment scattering. Open circles indicate equilibrium positions of atoms, filled circles the thermally displaced positions in the crystal snapshot. The ion enters parallel to the z_1 -axis, scatters from atom A and exits parallel to the z_2 -axis..... 70
- Figure 3.7: Schematic of the standard scheme for determining hitting probabilities. The ion enters at \mathbf{r}_0 and scatters from each atom in turn before colliding with the atom located at $\mathbf{r}_0 + \Delta\mathbf{n}$. Note the z' -axis is the z -axis of the Tromp and van der Veen method. 72
- Figure 3.8: Schematic of Tromp and van der Veen's scheme for determining hitting probabilities. The ion enters along the z -axis and is scattered by each atom in turn until passing through the i^{th} layer at $\Delta\mathbf{n}$, $\delta\mathbf{r}_i$ from the i^{th} atom. This scheme is related to Barrets by a simple coordinate transform (see Figure 3.7). 73
- Figure 3.9: In the complete crystal method an auxiliary lattice can be constructed by grouping atoms with (nearly) identical x -, y - or z -coordinates. This can then be used to track the ion through the crystal. As each atom occupies one auxiliary lattice point, and each lattice point contains zero or one atoms, only four auxiliary lattice points need be checked for potential collision partners. 77
- Figure 4.1: Structure of 2D rare earth silicides. The RE forms a single atomic layer located in T4 sites above the bulk Si. The silicide is terminated by a bulk-like Si bilayer (Si_1 and Si_2) which is rotated by 180° with respect to the bulk. a) side view, b) the view along the surface normal (i.e. top view).83

- Figure 4.2: The origin of the blocking dips in the Tm signal in the two scattering geometries indicated. a) $[\bar{1} 00]/[\bar{1} 11]$ b) $[1\bar{1} \bar{1}]/[100]$. The arrows indicate the origin of the blocking features labelled in Figure 4.5. Refer to Figure 4.1 for further details of the structure (note that in this figure only those atoms within the scattering plane are shown). Notice that ϵ depends only on Si₂..85
- Figure 4.3: Typical MEIS spectra from the Tm silicide for the two experimental geometries employed (left $[\bar{1} 00]/[\bar{1} 11]$; right $[1\bar{1} \bar{1}]/[100]$). The separation of the Tm and Si signals, and the bulk blocking features are all clearly visible. The Tm signal shows decreased intensity at scattering angles at which blocking has occurred.....86
- Figure 4.4: The comparison of a simulation of bulk terminated Si (111) to the experimental angular cross section through the bulk scattered ion signal, with angular offset applied. Matching the position of the bulk blocking feature allows the angular scale to be calibrated correcting for any mechanical offset of the analyser. (a) $[\bar{1} 00]/[\bar{1} 11]$ (b) $[1\bar{1} \bar{1}]/[100]$88
- Figure 4.5: The corrected angular cross section through the Tm signal for the (a) $[\bar{1} 00]/[\bar{1} 11]$ geometry and (b) $[1\bar{1} \bar{1}]/[100]$ geometry. The curves have been corrected for the angular offset and the fall off in counts due to Rutherford scattering cross section, and scaled to an arbitrary value. Also shown for comparison purposes is the experimental cross section through the Ho signal from a 2D Ho silicide [5]. The similarity of the two curves indicates the structures are very alike, as expected. The small fluctuations within the curves are experimental noise. The labelling of blocking dips refers to Figure 4.2.90
- Figure 4.6: Ball and stick representation of the Tm 2D silicide surface, showing the bond lengths of Table 4.1.....92

- Figure 4.7: Comparison between experimental data and the simulated scattering curve for the initial structural solution for 2D Tm silicide (note that for ease of display the curves have been corrected for the fall off in counts due to the Rutherford scattering cross-section). The experimental data has been freely scaled to the simulation. (a) $[\bar{1}00]/[\bar{1}11]$ (b) $[1\bar{1}\bar{1}]/[100]$. The labelling of blocking dips refers to Figure 4.2. Note the poor match of the 57° (ϵ) blocking feature in the $[\bar{1}00]/[\bar{1}11]$ geometry.93
- Figure 4.8: Comparison between experimental data and the simulated scattering curve for the final model for two-dimensional Tm silicide (again corrected for Rutherford scattering cross-section). The experimental yield is freely scaled to the simulation. (a) $[\bar{1}00]/[\bar{1}11]$ (b) $[1\bar{1}\bar{1}]/[100]$. The $\sim 57^\circ$ (ϵ) dip position is now visually a better fit.95
- Figure 4.9: Ball and stick representation of the Tm 2D silicide surface, showing the bond lengths of Table 4.2.96
- Figure 4.10: Comparison between experimental data and simulation for the “by eye” fit, corrected for Rutherford scattering cross-section. (a) $[\bar{1}00]/[\bar{1}11]$ (b) $[1\bar{1}\bar{1}]/[100]$. The $\sim 57^\circ$ (ϵ) dip position has been further improved.98
- Figure 5.1: (a) RE–Si bond lengths in bulk rare earth silicides. (b) Ionic radii of rare earth metals. Both show a decreasing trend across the series. 102
- Figure 5.2: Comparison of experimental MEIS scattering curves for 2D rare earth silicides. This feature is due to the blocking of scattered ions by the Si_2 atoms and directly reflects the Si_2 –RE bond length (the blocking dip labelled ϵ in the previous Chapter). Curves have been scaled to an arbitrary yield and then offset for clarity. 104
- Figure 5.3: Comparison of experimental MEIS data for 2D rare earth silicides. The blocking dip shown is due to blocking of scattered ions by the Si_1 atoms (the blocking dip labelled δ in the previous Chapter). Curves have been scaled to a common arbitrary yield and then offset for clarity. 105

- Figure 5.4: Contribution of each point to the total R-factor. Note the significance of the lowest angle dip. The dashed line shows similar contributions for the simulation of the final solution. 110
- Figure 5.5: Contribution of each point to the total R-factor when the Rutherford scattering cross section is not taken into account. This eliminates the added weight given to lower angles due to the additional number of counts. The depth of the lowest angle dip is still the most important factor. 110
- Figure 5.6: Contributions to the R-factor when discounting the lowest angle dip from the calculation of the R-factor. This produces a much better fit to the higher angle dips than that shown in Figure 5.4 and Figure 5.5. 112
- Figure 5.7: Comparison of (a) the original Tm silicide MEIS scattering curve and (b) the “flipped” version. The inset shows a typical LEED I-V curve [10]. The Pendry R-factor was originally designed to deal with peaks rather than dips. The flipped data may be considered qualitatively more like the LEED data for which the Pendry R-factor is standard. 117
- Figure 5.8: The structural trend in the $\text{Si}_2\text{-RE}$ bond length across the rare earth series. This plot is derived from the structural model determined using R_{Pflip} . Other methods of determining the best fit model show is a similar trend. 122
- Figure 6.1: Bulk phase diagram for Fe silicide. After von Kanel et al. [15]. The FeSi system exhibits many phases in the bulk dependent on the precise Fe:Si composition and sample preparation. 125
- Figure 6.2: Typical MEIS spectra from the FeSi 1×1 phase. Left to right: $[\bar{1} 00]/[\bar{1} 11]$, $[1\bar{1} 0]/[100]$, $[1\bar{1} \bar{1}]/[100]$. The Fe signal shows clear blocking dips. 128
- Figure 6.3: Typical MEIS spectra from the FeSi 2×2 phase. Left to right: $[\bar{1} 00]/[\bar{1} 11]$; $[1\bar{1} 0]/[100]$; $[1\bar{1} \bar{1}]/[100]$. The spectra are very similar to those observed for the 1×1 phase (Figure 6.2). 129

Figure 6.4: Comparison of scattering curves from the 1×1 and 2×2 phases. $[\bar{1}00]/[\bar{1}11]$ geometry. The scattering curves from the two phases are extremely similar, indicating that their structures are very alike. See also Figure 6.5 and Figure 6.6.	131
Figure 6.5: Comparison of scattering curves from the 1×1 and 2×2 phases. $[\bar{1}\bar{1}0]/[100]$ geometry. See also Figure 6.4 and Figure 6.6.....	132
Figure 6.6: Comparison of scattering curves from the 1×1 and 2×2 phases. $[\bar{1}\bar{1}\bar{1}]/[100]$ geometry. See also Figure 6.4 and Figure 6.5.....	132
Figure 6.7: The proposed structural model for the initial Fe silicide growth. Side view showing the scattering plane. Note that the 2×2 phase is shown; the 1×1 phase is proposed to be identical but without the ordered Si overlayer, Si_{ad} . Inset: Ball and stick model of the surface—the model on the right has the bulk Si removed for clarity.....	134
Figure 6.8: Origin of the blocking features. Note how the adatoms are mainly shadowed from the scattered ions. Red lines indicate the incident ion directions, green lines the origin of the observed blocking dips Top: $[\bar{1}00]/[\bar{1}11]$ Bottom: $[\bar{1}\bar{1}0]/[100]$ and $[\bar{1}\bar{1}\bar{1}]/[100]$ —as ions are detected around $[100]$ in both cases the same blocking dips are observed, although at different scattering angles.	135
Figure 6.9: Ball and stick model of the surface, showing the bond lengths detailed in Table 6.1.....	136
Figure 6.10: Comparison of simulated and experimental scattering curves for the final structural model. The $[\bar{1}00]/[\bar{1}11]$ geometry.....	137
Figure 6.11 Comparison of simulated and experimental scattering curves for the final structural model. The $[\bar{1}\bar{1}0]/[100]$ geometry.....	138
Figure 6.12: Comparison of simulated and experimental scattering curves for the final structural model. The $[\bar{1}\bar{1}\bar{1}]/[100]$ geometry.....	138
Figure 7.1: Theoretical band structure of RE 2D silicide [4]. Note the hole pocket at the $\bar{\Gamma}$ point.	144

Figure 7.2: Atomically resolved STM image of the 2D Ho silicide surface. Imaged acquired at a bias voltage of 2V, tunnelling current 2nA. $\sim 10 \text{ nm} \times$ $\sim 3 \text{ nm}$	145
Figure 7.3: Inequivalent sites on the 2D silicide surface. Top: atomically resolved STM image, bias voltage 2 V, tunnelling current 2 nA. $\sim 5.0 \text{ nm} \times \sim 3.6 \text{ nm}$. Bottom: Schematic top view of the surface.	146
Figure 7.4: Typical plot of tunnelling current, I , versus bias voltage, V , averaged from equivalent sites on the atomically resolved 2D silicide surface close to zero applied voltage.	147
Figure 7.5: The LDOS is better represented by a plot of $(dI/dV)/(I/V)$ versus bias voltage. Arrowed are features corresponding to bands in the 2D silicide band structure	148
Figure 7.6: STS spectra from three inequivalent sites on the atomically resolved 2D Ho silicide surface. Arrowed are features corresponding to bands in the 2D silicide band structure.....	149
Figure 7.7: Comparison of STS from a region of 2D silicide and various sites within the Si(111) 7×7 unit cell.	149
Figure 7.8: The sequence of MEIS spectra from Fe deposition on Ho 2D silicide. $[1\bar{1}0]$ incident direction with detection around $[100]$. a) As deposited b) After anneal to $\sim 550 \text{ }^\circ\text{C}$ c) After anneal to $\sim 700 \text{ }^\circ\text{C}$. The inset shows the Ho scattering signal from the 2D silicide before Fe deposition. The surface is initially disrupted and increasing annealing simply causes diffusion of the Fe and Ho into the bulk substrate.....	153
Figure 7.9: Scattering cross section through the Ho (top) and Fe (bottom) signals of spectra shown in Figure 7.8. a) As deposited b) After anneal to $\sim 550 \text{ }^\circ\text{C}$. Inset: The scattering curve through the Ho signal before Fe deposition. The lack of blocking features in the Ho and Fe signals indicate a lack of order at the surface.	154

- Figure 8.1: Side view of the Tm 2D silicide structure indicating the bond lengths. Bulk Si has been omitted for clarity. The silicide consists of a single RE layer beneath a bulk-like Si bilayer. The bilayer is rotated by 180° with respect to the bulk. 159
- Figure 8.2: Side view of the Fe silicide, showing the 2×2 Si adatom layer and indicating bond lengths. Bulk Si has been omitted for clarity. The silicide is a CsCl-type structure with, in the case of the 2×2 phase, an additional layer of Si adatoms in a 2×2 arrangement. 161

List of Tables

Table 4.1: Structural parameters for the initial best model for the Tm silicide under discussion. The Si ₁ –Tm bond length is thought to be underestimated while the Si ₁ –Si ₂ bond length is overestimated.....	94
Table 4.2: Structural parameters for the final model for 2D Tm silicide.....	96
Table 4.3: Structural parameters determined from a “by eye” fit.....	98
Table 5.1: Published structural results for two-dimensional rare earth silicides. Refer to Figure 4.1 for atomic labels. Techniques other than MEIS show a longer Si ₂ –RE bond length for a given rare earth.	103
Table 5.2: Bond lengths calculated from purely geometrical considerations (i.e. the measured angular position of the relevant blocking dip). Also shown for comparison are the published bond lengths.	107
Table 5.3: Revised structural parameters for 2D rare earth silicides and the corresponding subjective “by eye” fits. A general trend for a decrease in the Si ₂ –RE bond length with increasing atomic number emerges.	108
Table 5.4: Vertical separations between the Si ₁ and RE atoms as found in the original published results, from a revised study of the data and from fitting by eye. The by eye results show that it is possible to subjectively fit blocking dips of this form.	109
Table 5.5: Comparison of the best fit models derived from comparing simulated and experimental blocking curves using a variety of R-factors. Also shown are the best subjective visual fits (“By Eye”). A trend in the Si ₂ –RE bond length is apparent in the results from a number of comparison methods; notably the “by eye” comparison, R _{min} , R _{Pfip} and R _{χ-refined}	115
Table 6.1: Structural parameters for the final model. See Figure 6.7 for labels.	136

Acknowledgements

It is with pleasure that I may take this opportunity to thank those who have been of immeasurable help during the course of this work. There are inevitably far too many to fully list but some are deserving of particular mention:

Firstly I must deeply thank my supervisor, Dr. Steve Tear, for his unending patience, wisdom, encouragement and guidance during my research.

Undoubtedly this work would not exist but for his expert help.

I must also thank Dr. Paul Bailey and Dr. Tim Noakes of the Daresbury MEIS laboratory for their guidance and assistance in the work performed there.

Members of the University of York Surface Physics Group, both past and present, have always been available to suggest new ideas, offer encouragement and generally share the experience of working as part of an experimental physics group. I am grateful for all they have offered and hope I contributed in return.

In a similar vein the running of a successful laboratory relies on its technical support and I could not have hoped for better than Dave Coulthard, Richard Armitage, Pete Durkin and the rest of the Physics Department's excellent technical staff.

On a final personal note, none of this would have been possible without Rachel. She has been my strength and beacon of light through darkness, for which I am reduced to a simple, inadequate, thank you.

Declaration

The work presented in this thesis is that of the author except where the contributions of others have been acknowledged explicitly in the text or by means of references. No part of this work has been presented for any other qualification at this or at any other university.

Publications

Growth and electronic structure of holmium silicides by STM and STS, E.W. Perkins, I. M. Scott and S. P. Tear, *Surface Science* **578** 80 (2005)