Chapter 1

Introduction

1.1 The Surface

The surfaces of solids are unique and unusual. When a surface is formed, the order present within the bulk of the solid is suddenly and dramatically broken. The removal of symmetry in one dimension results in a high number of dangling bonds and free energy. Not surprisingly the minimisation of this free energy often induces a change within the near surface region. This change may be a simple relaxation—in which the spacing of the top few atomic layers changes whilst maintaining the 2D periodicity—or, more radically and usually the case for semiconductors, a reconstruction producing a new 2D unit cell at the surface. These two possibilities are represented in a much simplified manner in Figure 1.1. Although such a reconstruction can strain the lattice this is more than compensated for in the reduction of the free energy derived from the associated removal of the dangling bonds. The changes at the surface of a material mean that the surface may have greatly different properties to the bulk. The technological importance of surfaces cannot be overstated. Examples of areas where the surface plays a main and vital role include the interaction of metals with semiconductors, catalytic reactions, the growth of crystals, and a myriad of others [1-7].

Despite the rearrangement of the surface to reduce the free energy, many surfaces remain unstable and readily react. This results in the potential for even small amounts of contamination interfering with the interface under investigation. Of course, even without this aspect, in order to study surfaces in their pristine condition then it is necessary to control the environment in which they are prepared and studied. At atmospheric pressure a surface is effectively instantly covered in many layers of adsorbates. Even at a pressure of around

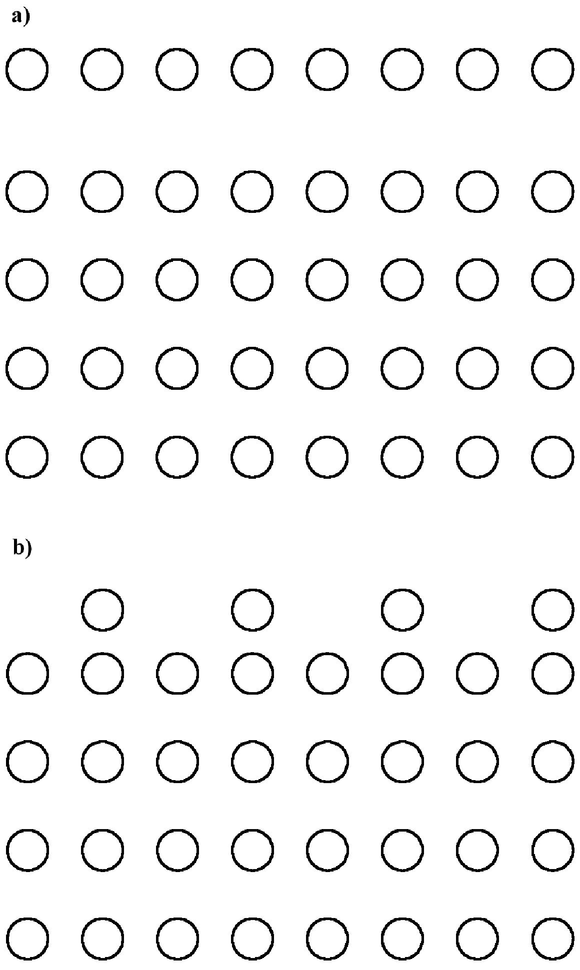

Figure 1.1: Simplified side view of a) a surface relaxation in which the atomic spacing changes near to the surface; b) a surface reconstruction, in which the atomic arrangement reconfigures to produce a new two-dimensional unit cell.

10^{-6} mbar it only takes around one second for one ML of gas molecules to cover the surface. It is necessary to reduce the pressure to the UHV regime of pressures less then 10^{-9} mbar to study surfaces. This increases the time for which the surface remains “clean” to the order of a few hours allowing experiments and analysis to be performed.

The changes at the surface of a material mean that the surface may have greatly different properties to the bulk. Not only is the structure different but the electronic and magnetic properties are also likely to differ. In the case of semiconductors the surface can cause electronic states to appear within the band gap, with wavefunctions localised perpendicular to the surface. These surface states can have important implications for the interaction of the surface with overlayers grown on it.

1.2 Techniques of Surface Science

A wide and varied range of techniques have been developed to aid in the studies of surfaces and the near surface region. The range of available instrumentation is ever increasing. Some techniques, such as LEED, have been successfully used for decades. Others, such as STM, have come to define the more modern era of surface science. Yet other techniques such as RBS owe much to the original experiments and ideas that led to an understanding of the atomic nature of matter.

The surface sensitivity required of these techniques is achieved in a variety of ways. Chemical sensitivity to some element known to be present only at the surface gives an obvious method. Some techniques rely upon geometry, either of the experimental arrangement—such as in RHEED or SXRD—or of the crystal under study, such as in MEIS. Various spectroscopy techniques rely upon the small escape depth of electrons to ensure sensitivity only to the surface region. Other techniques, such as STM, may probe only the surface by their very nature.

In isolation, each technique can reveal much, but surface science often relies on the interplay between numerous experimental methods. Some techniques have become almost standard for surface science, such as LEED, STM, and AES. Others are less common, such as UPS and EELS. Still others are limited by their need for large experimental facilities, such as SXRD, MEIS and more. Many excellent references have been written on surface science techniques and the field in general. See for example Woodruff & Delchar [3], Prutton [1], Zangwill [4].

1.2.1 Scanning Tunnelling Microscopy

The STM has risen to great prominence since its invention in the early 1980s [8-11]. The power of the STM lies in its ability to give direct, real space information about the surface on the atomic scale [12-14]. STM involves bringing a very fine metallic probe tip into almost contact with the conducting surface of interest. The appliance of a bias voltage between the tip and surface results in a measurable tunnelling current which depends on the separation between the two. More details of STM may be found in the next chapter. Often the information from STM relates directly to the surface structure. It is necessary to be cautious in the interpretation of STM images, however, as electronic effects can play a large or dominating role. At times this can make STM images difficult to interpret or even misleading. However, the electronic nature of STM can also be harnessed to provide further information. By examining the variation of the tunnelling current with bias voltage—a technique known as scanning tunnelling spectroscopy—the surface electronic structure may be studied. This is especially useful if a normal STM image is acquired at the same time such that each point at which STS data is taken can be related to an atomically resolved surface feature.

STM is also restricted to non-insulator surfaces. This has led to the development of a number of related techniques such as AFM [11, 15, 16] where the tunnelling current of STM is replaced with the van der Waals interaction between a probe tip and the surface (this is normally detected by measuring the deflection of a cantilever on which the probe tip is mounted), and other derivatives. STM and STS are further discussed in Section 2.2.

1.2.2 Low Energy Electron Diffraction

LEED has become a mainstay of the surface science laboratory. In this technique a collimated beam of electrons with energy in the region of around 20–300 eV falls onto the surface. At this energy the de Broglie wavelength of the electrons is comparable to the atomic spacing within the crystal and diffraction occurs. The diffraction pattern formed consists of a pattern of spots which contract toward the specular spot as the beam energy increases. As the scattering cross-section of the electrons is high and the mean free path small within the energy range involved, the technique is surface sensitive. The LEED pattern gives information about the reconstruction of the surface (see Section 2.3 for details). The spacing between the spots (as a function of beam energy) is inversely related to the 2D lattice spacing. Also, the symmetry of the LEED pattern reveals the symmetry of the surface. LEED has the power that it may act as a quick diagnostic tool to reveal to some extent the cleanliness of a surface (as the surface sensitive nature ensures that even a small layer of contamination degrades the LEED pattern) and any surface reconstruction before using another technique. This, and the fact that it is a fairly simple task to set up LEED equipment in any well equipped surface science laboratory, have led to LEED being one of the most widely used techniques; it is rare indeed to find a piece of surface science apparatus not equipped with a basic LEED.

The disadvantage of LEED lies mainly in that it gives little immediate information about the position (or types) of the atoms within the unit cell. For instance different atom configurations which share the same periodicity will give rise to superficially the same LEED pattern. LEED may be used as a quantitative crystallographic method but this is more complicated [17]. The high scattering cross-section means that multiple elastic scattering events contribute to the scattered beams, and a simple kinematic scattering theory fails. The use of LEED in a quantitative manner requires careful and painstaking measurement of the variation of the intensity of the LEED spots as a function of incident electron energy, to produce so called I(V) curves. This must then be followed by further time consuming computer simulations of the I(V) curves resulting from a number of trial structures. Comparison between experiment and simulation then proceeds in an interactive process. This of course assumes that some starting trial structure can be arrived at first. LEED is further discussed in Section 2.3.

1.2.3 Reflection High Energy Electron Diffraction

In RHEED a beam of electrons with energy typically in the range 10–100 keV is made to fall on the surface at a very grazing angle. Diffraction streaks are then observed on a fluorescent screen much as spots are for LEED (though there is no need for the screen to be raised to high voltage nor to screen secondary electrons as the energy of the diffracted electrons is already sufficient to cause florescence much higher than the background). The spacing of these streaks can reveal the lattice parameters. RHEED has the disadvantage that the scattering geometry must be changed, by rocking the sample or rotating about the surface normal, in order to obtain the full 2D diffraction pattern. It is also affected by the roughness of the surface. Due to the grazing angle small bumps in the surface can detract from the pattern, though this is often actually useful in determining the quality of the surface. RHEED is useful in that the RHEED pattern may be observed during sample preparation and the deposition of adsorbates. It therefore often forms a diagnostic tool in thin film growth.

1.2.4 Medium Energy Ion Scattering

MEIS is relatively lesser known technique. It offers surface and near surface sensitive structural information. Ions (usually H^+ or He^+) are accelerated to around 100 keV and focused onto the surface. Those scattered from the surface are detected over a range of angles and energies. In this way MEIS is an enhancement of RBS and is related to the techniques of HEIS in which the ions are of much higher energy (about 2 MeV) and somewhat less so to LEIS which involves energies of only a few keV. MEIS has advantages over techniques such as LEED in that it supplies easily interpreted real space information and can distinguish mass separated elements. It is not however overly sensitive to lighter elements. Structural analysis still requires computer simulation and MEIS also has the disadvantage of requiring a dedicated ion source at a large scientific facility. A further discussion of MEIS may be found in Chapter 3.

1.2.5 Surface X-Ray Diffraction

As is the case in RHEED, SXRD employs a grazing incidence and exit geometry. A 2D lattice of rods is produced, observed by rotating the sample about the surface normal until the detector cuts each rod. By then observing the change in intensity of the rod as the exit angle is varied the out of plane atomic displacements can be determined. Although the technique can give superior angular resolution than electron diffraction the intensities of the diffracted beam can be much smaller. The intensity of X-ray therefore needed for SXRD restricts its use to synchrotron radiation sources.

1.2.6 X-Ray Photoelectron Spectroscopy

X-rays are made to fall on the surface, ionising an electronic shell and ejecting a photoelectron. The energy of the photoelectron is given by

$$E_k = h\nu - E_B - \Phi \tag{1.1}$$

where $h\nu$ is the energy of the incident X-ray and E_B is the initial binding energy of the electron, and Φ is the work function of the surface. XPS is therefore a chemically sensitive probe of the surface. Further the energy resolution is high enough to detect the small shifts in energy due to the chemical state of the atom.

1.2.7 Ultraviolet Photoelectron Spectroscopy

UPS is related to XPS. In the case of UPS though the incident photons are not sufficiently energetic to ionise core level electrons and so this technique is a probe of the valence states. UPS is commonly used in investigating the surface band structure. By looking at the angles at which the photoelectrons are produced, a technique known as angle resolved UPS, the initial **k** state of the electrons may be found and a band map drawn. The interpretation of UPS spectra is somewhat complicated. The mean free path for electron–electron scattering varies rapidly at low kinetic energies and electrons from closer to the Fermi energy have a smaller mean free path than those from the bottom of the conduction band. Also if an electron is ejected with low kinetic energy the probability of photoemission is affected by the density of states available to the photoelectron.

1.2.8 Auger Electron Spectroscopy

Like UPS and XPS, AES involves analysing the energy of emitted electrons. A beam of high energy (typically in the region of 3–5 keV) electrons is caused to fall on the surface. The incident electron may remove a core level electron from the atom, leaving the atom in a highly excited state. The atom may then relax via the transition of a second electron from a less tightly bound shell to fill the core level hole. The energy liberated by this transition ejects a third, Auger electron, which is then detected.

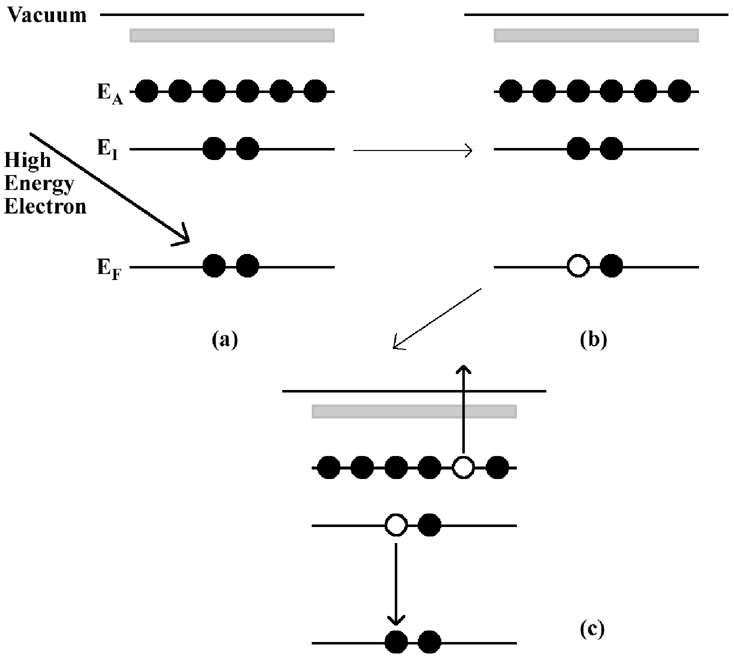

Figure 1.2: The Auger process. A high energy electron removes a core level electron from the atom (a), leaving an excited state (b). The atom relaxes via a less tightly bond electron filling the core level hole. The energy liberated causes the ejection of a third, Auger electron (c).

The process is illustrated in Figure 1.2. The kinetic energy of the Auger electron is given by

$$E_{KE} = E_F - E_I - E_A \tag{1.2}$$

where E_I is the initial energy of the electron filling the core hole, E_F is the final energy of this electron and E_A is the binding energy of the Auger electron. Note that the final energy of the Auger electron is therefore independent of the incident electron beam (indeed sometimes X-rays may be used to initiate the same process; AES lines are present in XPS spectra).

The initial ionisation of a core level electron is non-selective and may be in various shells. There are also then a number of different electrons which may fill the resultant core level hole. This number of possible Auger transitions results in a characteristic spectrum of peaks at various energies of the ejected Auger electron. AES is hence chemically sensitive.

AES has the advantage that it is fairly simple to perform. Standard LEED optics may be adapted to act as an electron energy analyser in use with AES. The technique is very sensitive to small coverages and gives a useful indication of the cleanliness of a surface. It is a complex technique to use in a fully quantitative manner however. By focussing the electron beam and sweeping it across the surface, spatially resolved AES can be achieved (this is known as a scanning Auger microscope).

1.2.9 Electron Energy Loss Spectroscopy

A beam of monoenergetic electrons is scattered from the surface and the energies of the scattered electrons analysed. There will be specific energy losses due to the excitation of particular processes within the solid. These losses will appear as peaks at a fixed energy from the primary energy. The largest features are normally due to surface and bulk plasmon losses but it is possible to detect losses due to other processes, including the excitation and ionisation of core level electrons in the solid (which gives an elemental identification). High resolution EELS allows the detection of the losses due to the vibrational states of absorbed molecules, which can be used to identify those molecules.

1.2.10 Surface Extended X-ray Fine Structure

If the absorption coefficient of a beam of X-rays transmitted through a solid is plotted as a function of incident X-ray energy then fine structure is observed. Absorption edges occur when the X-rays reach sufficient energy to excite a new core level. At energies above these edges the absorption coefficient is seen to oscillate–the extended X-ray fine structure. These oscillations are due to photoelectrons excited by the X-rays. The photoelectrons are backscattered by the neighbouring atoms and then interfere with the outgoing photoelectron wave. A constructive interference causes an increase in the X-ray absorption coefficient while a destructive interference causes a corresponding decrease in the absorption coefficient. As the energy of the incident X-rays changes so the energy of the photoelectrons, and hence their wavelength, changes. The interference moves from constructive to destructive to constructive, causing the observed ripple in the absorption coefficient.

If there is an atomic species on the surface (and only the surface) then it may be studied by tuning to the relevant, atom specific absorption edge. If this is not the case then surface sensitivity must be gained by indirectly observing EXAFS oscillations. The X-ray absorption is linked to the formation of core holes so a process reliant on this formation may be used to probe the absorption coefficient. For instance the yield of Auger electrons will vary in a way related to the absorption coefficient. The small escape depth of these electrons then gives surface sensitivity and the technique is known as surface EXAFS. SEXAFS has the disadvantage that a bright, monochromatic X-ray source such as that produced by monochromated synchrotron radiation is needed. It does give information on the chemical environment of the absorber, including the bond lengths and coordination number.

1.3 Metal–Semiconductor Interfaces

The metal–semiconductor interface is of interest both from a fundamental science perspective and in terms of technological importance [18-20]. Not only is the interface the initial contact to the semiconductor device but its electronic properties are important within the device.

When a metal and semiconductor are brought into contact charge flows between the two in order to equalise the Fermi levels. In the case of an *n*-type semiconductor the contact is Ohmic if the metal workfunction, φ_m, is less than the semiconductor workfunction, φ_s. If $\varphi_m > \varphi_s$ then the contact is rectifying, with a "Schottky" barrier height given by

$$\Phi_{SB} = \varphi_m - \chi \tag{1.3}$$

where χ is the semiconductor electron affinity. This situation is illustrated in Figure 1.3.

Unfortunately, this simplistic description rarely applies to the experimental results [21]. The above model assumes that during the interface formation the local semiconductor band structure is free to move with respect to E_f since the Fermi level is within the band gap (which lacks electronic states). The presence of surface states within the band gap of the semiconductor "pins" the Fermi level so that it is no longer free to move. This results in Equation 1.3 no longer being valid. Indeed, if the Fermi level is pinned then

$$\Phi_{SB} = E_c - E_f \tag{1.4}$$

and the barrier may be independent of the metal involved.

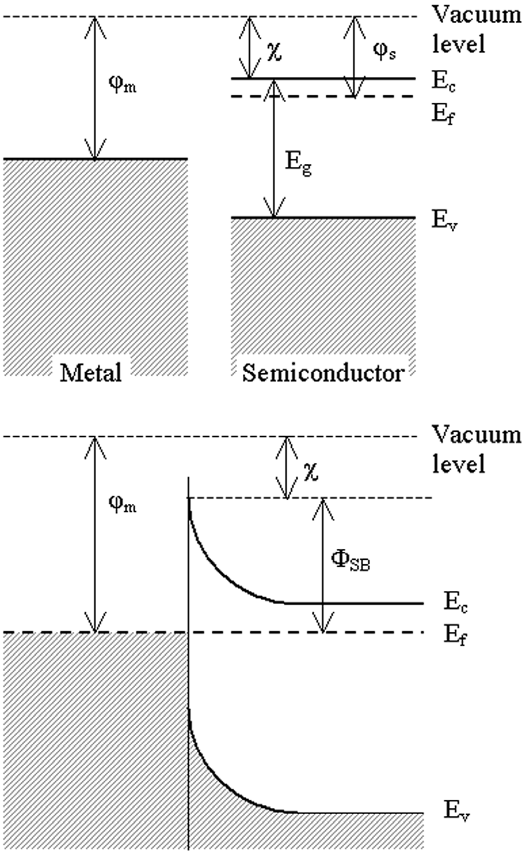

Figure 1.3: Formation of a Schottky barrier, Φ_{SB}, for an n-type semiconductor in contact with a metal. The Schottky barrier forms, and the junction is rectifying, if the metal wor function, φ_m, is greater than the semiconductor workfunction, φ_s. E_v is the top of the valence band, E_c the bottom of the conduction band and E_f the Fermi level. The band gap of the semiconductor, E_g is also indicated.

Driven by technological uses the investigation of metal–semiconductor interfaces has been intense. The formation and epitaxial growth of metal silicides on semiconductor surfaces offers potential technological benefits and growth on the group IV semiconductors, and Si in particular, offers easy integration with current technology [22-24].

In practice the interface of metal and semiconductor is a complex region affected by the interplay of chemistry, disorder, defects and other factors [25]. Clearly it is important to have an atomistic understanding in the low coverage regime in order to fully understand the growth processes involved. Investigation of the low coverage regime gives insight into the amount of intermixing of the surface semiconductor and the metal, as well as the abruptness of the interface. Exact atomic arrangement also becomes increasingly important as the drive towards miniaturisation and nanotechnology continues.

1.4 Materials Studied

1.4.1 Two Dimensional Rare Earth Silicides

The growth of RE metals on Si has, over the past few years, attracted much attention. REs have been found to form a number of novel structures on Si, depending on the substrate orientation and preparation conditions. Monolayer coverages of RE have been shown to form self ordered nanowire arrays on Si(100) [26-30]. On the Si(111) surface perhaps the most interesting structure found is the much studied "two-dimensional" silicide formed by the trivalent RE metals.

Two-dimensional RE silicides are formed when one monolayer of RE is deposited onto the clean 7 × 7 reconstruction of Si(111) and subsequently annealed to around 500 ºC (see for example Ming *et al.* [31], Spence *et al.*, [32], Kitayama *et al.* [33]). The anneal causes a reconstruction of the surface layers. A 1 × 1 LEED pattern is observed after the formation of such a silicide. A single atomic layer of RE metal is located above the substrate in so called T4, three fold hollow sites. The silicide is terminated by a bulk like bilayer of Si, the orientation of which is rotated by 180º with respect to the bulk substrate orientation, Figure 1.4. This form of silicide has been shown to occur for most of the trivalent REs and may have useful technological applications. Unusually low Schottky barrier heights of 0.2–0.3 eV on *n*-type Si have been recorded for the silicon–RE silicide interface [34-38]. Further study is required to fully understand these interesting structures, both in terms of their electronic properties and as a possible novel growth template.

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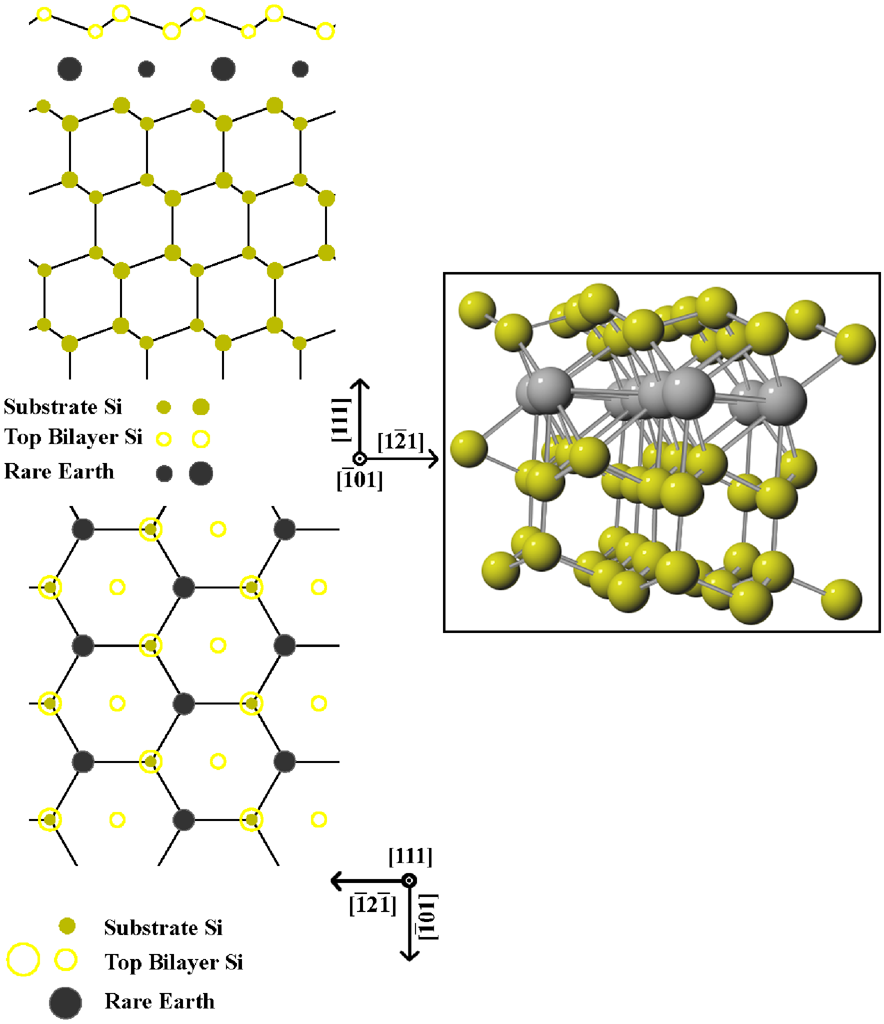

Figure 1.4: Structure of the 2D RE silicides. The RE forms a single atomic layer situated in T4 sites above the bulk Si. The silicide is terminated by a bulk-like Si bilayer, rotated by 180° with respect to the bulk. Top: Side view. Bottom: Top view (i.e. along the surface normal). Inset: Ball and stick model of the surface.

The large mass separation between RE and Si makes this an ideal system for MEIS study. The structure is made even more ideal by the heavy RE residing beneath the top Si bilayer. Analysing the MEIS signal from the RE allows a simple determination of the positions of the atoms within this bilayer. A MEIS analysis of the Tm 2D silicide is described in Chapter 4. A more general discussion of MEIS studies of all these 2D silicides is presented in Chapter 5.

MEIS does not reveal any information about the less well understood electronic nature of this interface. Here STM and in particular STS can produce atomically resolved electronic data. STS data obtained from the Ho 2D silicide is presented and discussed in Chapter 7.

1.4.2 Iron Silicides

The growth of Fe on Si has been studied for many years and with a wide variety of techniques [39-43]. Its study has risen in prominence again in recent years with the advent of spin electronics ("spintronics") [44, 45] and the possible role of Fe in spin injection into the semiconductor substrate [46]. The β-phase has attracted particular attention due to its semiconducting properties and good lattice match with Si (+2 % for CsCl structure [47]). The phase diagram for Fe coverage and anneal temperature is however complex [48] and little is known of the exact atomic configuration of some phases. In order to understand such complex systems it is useful to study the initial growth of the metal on the clean Si(111) 7 × 7 surface, in the monolayer (ML) coverage regime.

At monolayer coverage it is known that a 1 × 1 LEED pattern may be formed after a moderate anneal. This evolves to a 2 × 2 pattern after a higher temperature anneal [49]. It is thought from ISS [50] and STM [51] experiments that the 2 × 2 reconstruction is due to Si adatoms. The complete structure of this phase, and the 1 x 1 phase, is unknown. The differing masses of Si and Fe allow the elements to be resolved in a MEIS experiment. As MEIS is a powerful quantitative structural technique a structural determination for both the 1 × 1 and 2 × 2 phases may be presented. They are found to be very similar, with the 2 × 2 indeed caused by a ¼ ML of Si adatoms, as discussed in Chapter 6.

1.4.3 Metal Growth on 2D Rare Earth Silicides

As mentioned above, the novel Si bilayer termination of the 2D RE silicides may form an interesting growth template. It is an intriguing possibility that the presence of the single atomic layer of rare earth immediately beneath this bilayer may act as a barrier to diffusion of metal overlayers into the bulk. The growth of Fe silicides particularly suffers from interdiffusion of the Si and Fe causing a rough interface. Chapter 7 shows an initial investigation of Fe growth on Ho 2D silicide. MEIS offers a valuable tool for studying this system as all three elements are well separated in mass and the signal from each may be independently considered. MEIS also offers a simple to interpret indication of the quality of the interface in an initial investigation.

References

1. M. Prutton, *Introduction to Surface Physics*, Oxford University Press (1994)

2. D. A. King and D. P. Woodruff, eds. *The Chemical Physics of Solid Surfaces and Heterogenous Catalysis.* , Elsevier Scientific Publishing: Amsterdam.(1993)

3. D. P. Woodruff and T. A. Delchar, *Modern Techniques of Surface Science*, Cambridge University Press (1986)

4. A. Zangwill, *Physics at Surfaces*, Cambridge University Press (1988)

5. R. A. Stradling and P. Klipstein, eds. *Growth and Characterisation of Semiconductors.* , Hilger: Bristol.(1990)

6. G. Attard and C. Barnes, *Surfaces*, Oxford University Press (1998)

7. J. B. Hudson, *Surface Science: An Introduction*, Butterworth-Heinemann (1992)

8. G. Binnig, H. Rohrer, Ch. Gerber and E. Weibel, *Phys. Rev. Lett.* **50** 120 (1983)

9. G. Binnig and H. Rohrer, *Surf. Sci.* **126** 236 (1983)

10. H. -J. Guntherodt and R. Wiesendanger, eds. *Scanning Tunneling Microscopy.* , Springer-Verlag: Berlin.(1992)

11. R. Wiesendanger, *Scanning probe microscopy and spectroscopy : methods and applications*, Cambridge University Press 637 (1994)

12. Ph. Avouris and I. -W. Lyo, *Studying surface chemistry atom-by-atom using the scanning tunneling microscope*, in *Chemistry and Physics of Solid Surfaces*, p. 371, Springer-Verlag: Berlin (1990)

13. N. D. Lang, *Phys. Rev. B* **34** 5947 (1986)

14. W. D. Schneider, *Surf. Sci.* **514** 74 (2002)

15. S. F. Alvarado, *Surf. Rev. Lett.* **2** 607 (1995)

16. G. Binning, C. F. Quate and Ch. Gerber, *Phys. Rev. Lett.* **56** 930 (1986)

17. J. B. Pendry, *Low Energy Electron Diffraction: The Theory and Its Application to Determination of Surface Structure*, Academic Press (1974)

18. S. P. Muraka, *Silicides for VLSI Applications*, Academic Press (1983)

19. H. von Känel, *Mater. Sci. Rep.* **8** 193 (1992)

20. J. Derrien, J. Chevrier, V. Le Thanh, T. E. Crumbaker, J. Y. Natoli and I. Berbezier, *Appl. Surf. Sci.* **70/71** 546 (1993)

21. G. Margaritondo, *Rep. Prog. Phys.* **62** 765 (1999)

22. A. H. Reader, A. H. van Ommen, P. J. W. Weijs, R. A. M. Wolters and D. J. Oostra, *Rep. Prog. Phys.* **56** 1397 (1993)

23. F. M. d'Heurle, *J. Electron. Mater.* **27** 1138 (1998)

24. S. P. Murarka, *Intermetallics* **3** 173 (1995)

25. E. H. Rhoderick and R. H. Williams, *Metal-Semiconductor Contacts*, Oxford Science Publications (1988)

26. C. Ohbuchi and J. Nogami, *Phys. Rev. B* **66** 165323 (2002)

27. J. Yang, Q. Cai, X. -D. Wang and R. Koch, *Surf. Sci.* **526** 291 (2003)

28. Y. Chen, D. A. A. Ohlberg and R. Stanley Williams, *J. Appl. Phys.* **91** 3213 (2002)

29. C. Preinesberger, S. K. Becker, S. Vandré, T. Kalka and M. Dähne, *J. Appl. Phys.* **91** 1695 (2002)

30. R. Ragan, Y. Chen, D. A. A. Ohlberg, G. Medeiros-Ribeiro and R. Stanley Williams, *J. Cryst. Growth* **251** 657 (2003)

31. L. Ming, L. Grill, M. G. Ramsey, F. P. Netzer and J. A. D. Matthew, *Surf. Sci.* **375** 24 (1997)

32. D. J. Spence, S. P. Tear, T. C. Q. Noakes and P. Bailey, *Phys. Rev. B* **61** 5707 (2000)

33. H. Kitayama, S. P. Tear, D. J. Spence and T. Urano, *Surf. Sci.* **482-485** 1481 (2001)

34. K. N. Tu, R. D. Thompson and B. Y. Tsaur, *Appl. Phys. Lett.* **38** 626 (1981)

35. H. Norde, J. de Sousa Pires, F. Pesavento F. d'Heurle, S. Petersson and P. A. Tove, *Appl. Phys. Lett.* **38** 865 (1981)

36. M. H. Tuilier, G. Gewinner, C. Pirri, P. Wetzel, D. Bomont and O. Heckmann, *J. Phys. IV* **4** 187 (1994)

37. S. Vandré, T. Kalka, C. Preinesberger and M. Dähne-Prietsch, *Phys. Rev. Lett.* **82** 1927 (1999)

38. S. Vandré, T. Kalka, C. Preinesberger and M. Dähne-Prietsch, *J. Vac. Sci. Technol. B* **17** 1682 (1999)

39. J. de la Figuera, A. L. V. De Parga, J. Alverez, J. Ibanez, C. Ocal and R. Miranda, *Surf. Sci.* **264** 45 (1992)

40. W. Raunau, H. Niehus, T. Schilling and G. Comsa, *Surf. Sci.* **286** 203 (1993)

41. A. L. V. De Parga, J. de la Figuera, C. Ocal and R. Miranda, *Ultramicroscopy* **42-44** 845 (1992)

42. T. Ehara, S. Nakagomi and Y. Kokubun, *Solid-State Electron.* **47** 353 (2003)

43. H. T. Lu, L. J. Chen, Y. L. Chueh and L. J. Chou, *J. Appl. Phys.* **93** 1468 (2003)

44. G. A. Prinz, *Science* **282** 1660 (1998)

45. M. Oestreich, *Nature* **402** 735 (1999)

46. H. J. Zhu, M. Ramsteiner, H. Kostial, M. Wassermeier, H. -P. Schönherr and K. H. Ploog, *Phys. Rev. Lett.* **87** 016601 (2001)

47. K. A. Mäder, H. von Känel and A. Baldereschi, *Phys. Rev. B* **48** 4364 (1993)

48. H. von Kanel, N. Onda, H. Sirringhaus, E. Muller-Gubler, S. Goncalces-Conto and C. Schwarz, *Appl. Surf. Sci.* **70/71** 559 (1993)

49. U. Starke, W. Weiss, M. Kutschera, R. Bandorf and K. Heinz, *J. Appl. Phys.* **91** 6154 (2002)

50. U. Kafader, P. Wetzel, C. Pirri and G. Gewinner, *Appl. Surf. Sci.* **70/71** 573 (1993)

51. A. L. Vazquez de Parga, J. de la Figuera, C. Ocal and R. Miranda, *Europhys. Lett.* **18** 595 (1992)