Chapter 2

An introduction to surface science

Metal surfaces play a number of roles in modern industries, from heterogeneous catalysis [6] to magnetic recording [7]. To advance such processes and technologies it is vital to characterise the surfaces from structural, electronic and compositional points of view. This chapter serves as a brief introduction to the structure of metal surfaces, addressing topics such as the reconstruction and relaxation of the surface region, as well as alloying, thin film growth and oxidation. The cleaning of metallic and semiconductor surfaces will also be discussed very briefly by way of introduction to the work presented in the experimental chapters of this thesis.

2.1 Crystalline structures and surfaces

2.1.1 Bulk crystalline structures

Crystalline materials consist of atoms arranged in a three-dimensional periodic array, with all crystal structures based on one of fourteen Bravais lattices [8]. The three directions which form the crystalline axes, and their associated repeat distances define a *primitive unit cell*, which when reproduced indefinitely, in combination with symmetry operations, will give the long-range crystal structure [1, 2].

The orientation of a crystal plane is given by its *Miller indices*, which are defined as the set of reciprocals of the fractional intercepts which the plane makes with the crystallographic axes. These intercepts are expressed in terms of the unit distances a, b and c along the three axes. In the cubic system, the [hkl] direction is perpendicular to the (hkl) crystallographic plane. Some examples are shown in figure 2.1. In the study of crystalline surfaces, the bulk structure is terminated along a chosen plane. The metallic surfaces investigated in this thesis are all low index surfaces (i.e. low Miller indices - (100), (110) and (111)).
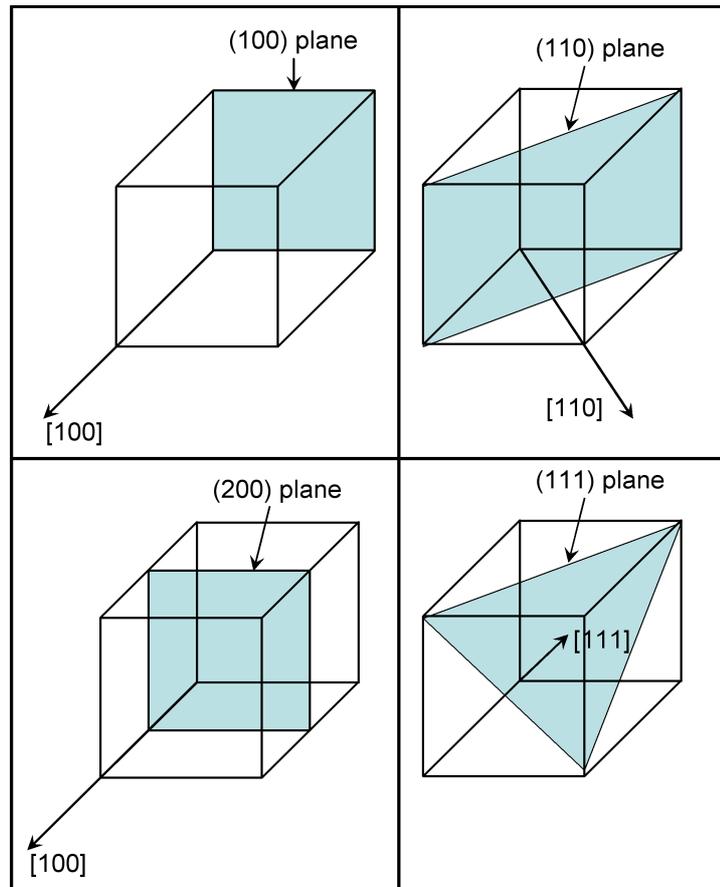
Figure 2.1: An illustration of the (100), (110), (111) and (200) crystal planes found within a simple cubic structure.

2.1.2 Surface structure

A surface is essentially an extreme imperfection in the three-dimensional periodicity of a crystalline structure. Whilst the 3D periodicity is destroyed, the 2D periodicity parallel to the surface is generally retained. The study of the surface structure is the investigation of the atomic arrangement in the vicinity of the surface, a region known as the *selvedge*. The crystal can then be considered to consist of a substrate which possesses the bulk crystalline structure and the selvedge, in which atoms may adopt different sites from those of the bulk material. The selvedge is crystalline in terms of the retention of the bulk periodicity parallel to the surface. However, some changes in the structure perpendicular to the surface plane are likely and possible reasons for this will be discussed below. All crystalline surfaces can be described by just five Bravais

nets and a small number of symmetry operations [1].

If the surface layers of a crystalline material are structurally different from the bulk, the structure at the surface may be disordered, ordered and commensurate with the substrate or ordered and incommensurate with the substrate. When the surface is ordered, the Bravais net can be related to the Bravais lattice of the underlying structure by a simple vector construction [9]. However, a more convenient notation was proposed by Elizabeth Wood in 1964 and has become the conventional method of describing surface structures [10]. The notation defines the ratio of the surface and substrate meshes together with the angle through which the surface mesh must be rotated in order to align the primitive translation vectors with those of the substrate mesh. This leads to a generic system of notation for surfaces of the form:

$$X\{hkl\}(p \times q)R\phi° - A \tag{2.1}$$

In this notation, X is the substrate material with a surface plane of *hkl*, whilst *p* and *q* are factors relating the surface and bulk meshes. $R\phi$ is the angle through which the surface mesh must be rotated to align with the bulk mesh. Such a change in the surface structure may be caused by the adsorption of species *A* to the surface. This notation can be used in cases where the surface and bulk meshes are of the same type, but not if the surface possesses a different Bravais net to the bulk structure. Figure 2.2 presents some generic examples of the Wood notation. One example of note is the $(\sqrt{2} \times \sqrt{2})$R45° surface. For easier visualisation, this is more commonly referred to as the c(2×2) surface which is $\sqrt{2}$ times larger than the unit mesh.

2.1.3   Reconstruction and relaxation at the surface

The atomic coordination and electron distribution is inevitably different from the bulk at the surface. To minimise the free energy of the surface, changes to the atomic structure can occur by the relaxation and/or the reconstruction of the atomic layers in the near-surface region. Firstly, if the changes in the structure leave the 2D surface unit mesh unchanged with respect to the bulk structure then the surface is said to be *relaxed*, with a (1×1) unit cell. In this case the change in structure effects the interlayer spacings along the surface normal. The atoms at the surface are still in
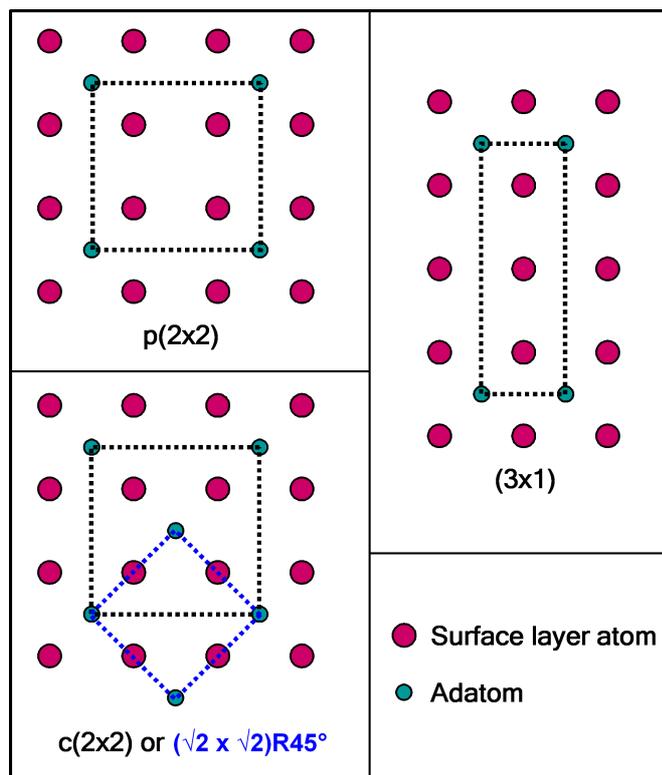
Figure 2.2: Examples of the use of the Wood notation. Shown here are p(2×2), (3×1) and c(2×2) or ($\sqrt{2} \times \sqrt{2}$)R45° overlayer structures on an fcc(100) surface.

registry with the bulk structure, but show expansions or contractions of a few % in the interlayer spacings relative to the bulk. Most clean metallic surfaces possess this characteristic, which can be observed using LEED and ion scattering techniques (for some examples, see the reviews of van der Veen [11] and Rodriguez [12]).

The surface structure can also change by a rearrangement of atoms in the surface plane such that the new surface unit cell has dimensions larger than the bulk. This is known as a *reconstruction*, with atoms at the surface no longer necessarily in registry with the bulk structure. Many semiconductors metals exhibit reconstructed surfaces, such as the Si(111)-(7×7) [13] and the clean Au(110)-(1×2) surfaces [11]. Again, the main driving force behind surface reconstructions is the minimisation of the surface energy. The simple reconstructions can often be explained in terms of minimising the number of dangling bonds by bond formation between adjacent atoms. For example, the formation of a Si(100) surface requires that the bonds between the Si atoms are

broken, leaving two dangling bonds per surface Si atom. To reduce the number of dangling bonds, adjacent Si atoms form dimer pairs, resulting in a two-domain (2×1) reconstruction on the (100) surface. Adsorption on to clean metal surfaces can also induce a reconstruction, such as during the oxidation of the Cu(110) surface [11]. In this case, significant mass transport leads to the formation of Cu-O chains in the [100] direction, a process driven by the larger strength of the Cu-O bond compared to that of the Cu-Cu bond [14].

2.2 Adsorption on metallic surfaces

In this thesis, a series of experiments have been performed to investigate the effects of the adsorption of oxygen atoms and the deposition of Pt atoms on to clean Pt, Ni and Cu low-index surfaces, in addition to the cleaning of InN surfaces via the adsorption and desorption of atomic hydrogen. In this section, the basic principles and effects of the adsorption of gaseous species on to metallic surfaces are discussed, as well as the theoretical aspects relating to thin film growth and alloy formation.

2.2.1 Physisorption and chemisorption

An atomic or molecular species which is weakly bound to the surface via Van der Waals forces is said to be *physisorbed*. No strong bonds between the adsorbate and substrate are formed and so the adsorbate may be easily desorbed from the surface. Physisorption produces virtually no change to the electronic and structural properties of the substrate material, with a snapshot of the surface taken at any time during the physisorption showing a neutrally charged surface. The process usually occurs at or near the condensation point of the gas and does not require any activation due to the lack of the formation of a chemical bond. Physisorption is also a non-dissociative, reversible process, the results of which are generally independent of the geometry of the surface and can lead to the formation of several layers of the physisorbed species.

By contrast, chemisorption involves the establishment of a chemical bond between the adsorbate and the substrate. This arises from a higher heat of adsorption

and as this increases, the bond strength also increases. Chemisorption requires a rearrangement of the electron density at the surface and leads to bonds which can range from mostly ionic to completely covalent in character. The process requires an activation energy and typically occurs at higher temperatures than corresponding physisorption processes. Chemisorption often leads to the dissociation of the adsorbate molecules and is typically an irreversible process. There is also a marked dependence on the surface geometry, although the chemisorption process is generally limited to a coverage of a few monolayers [15]. Chemisorption leads to significant changes in the atomic and electronic structure of the near-surface region, therefore lending itself to investigation using techniques such as XPS, LEED and CAICISS.

The rate at which particles are adsorbed on to a surface, R_{ads}, is largely dependent on a parameter known as the *sticking coefficient, S*, in conjunction with the flux of adsorbate atoms (per unit area), *F*, such that:

$$R_{ads} = S.F \tag{2.2}$$

The flux of incident particles, *F*, is given by the Hertz-Knudsen equation:

$$F = \frac{P}{(2\pi mkT)^{1/2}} \tag{2.3}$$

where *P* is the partial pressure of the adsorbate in the gas phase, *m* is the mass of the adsorbate species, *k* is the Boltzmann constant and *T* is the temperature. The sticking coefficient, *S*, is dependent on the adsorbate-substrate combination, but must lie in the range $0 < S < 1$ and is dependent on many factors, the foremost of which are the existing coverage of the adsorbate, θ, and any energy barrier to further adsorption which may exist. Therefore, in general:

$$S = f(\theta)exp\left(\frac{-E_a}{RT}\right) \tag{2.4}$$

where E_a is the activation energy for adsorption, *f(θ)* is a function of the existing adsorbate coverage and *R* is the gas constant. Combining the expressions for *S* and *F* with equation 2.2 gives:

$$R_{ads} = \frac{f(\theta)P}{\sqrt{2\pi mkT}}exp\left(\frac{-E_a}{RT}\right) = \frac{dN_{ads}}{dt} \tag{2.5}$$

where N_{ads} is the number of atoms adsorbed on the surface in a period of time, t. Therefore, if S is constant (generally true at low coverages), then:

$$N_{ads} = SFt \tag{2.6}$$

Equation 2.6 is particularly useful, allowing the calculation of the adsorbate coverage, the sticking coefficient, or the period for which the surface will stay relatively free from contamination. Commonly in both physisorption and chemisorption experiments, the quantity of gas to which the surface has been exposed is quoted in *Langmuirs* (*L*), where $1\,L = 10^{-6}$ torr s exposure. This unit of exposure is used extensively throughout this thesis.

2.2.2 Oxidation of metallic surfaces

Oxidised metal surfaces are the natural state of the material and have a number of applications, including gas sensors, fuel cells and in microelectronics [16]. In general, the process of oxidation begins with the physisorption and/or chemisorption of an oxygen-containing species (atomic O, O_2, H_2O, etc) on the surface. The exact results of exposing the surface to oxygen depend on a wide range of parameters, including the oxygen species, adsorbate concentration, substrate temperature, the differential heats of adsorption and the propensity for oxide formation. Transition metals with several empty states in the outermost d electron shell, such as Fe, W and Mo, are very reactive towards the dissociative adsorption of oxygen, with dissociative sticking probabilities close to unity [17]. In these cases the reaction is irreversible, with the formation of a surface oxide at low temperatures and bulk oxide at higher temperatures. However, towards the right of the periodic table, the corresponding oxides become less stable resulting in the reversible dissociative adsorption of O_2, and at low temperatures the adsorption of molecular O_2 [18, 19].

The work in this thesis focusses on oxidation as a result of the adsorption of atomic oxygen on the surface, initially forming a chemisorbed layer. As the coverage of oxygen increases, it becomes energetically favourable for oxygen atoms to diffuse into the metal substrate, forming an oxide structure. Continued exposure can lead to the penetration of O deeper into the substrate, producing a metal-oxide film.

The formation of a three-dimensional oxide tends to progress via a reconstruction of the surface and the formation of a two-dimensional surface oxide layer. Lanyon and Trapnell suggested that this proceeds via a place exchange, or substitutional mechanism [20]. A schematic of this mechanism is shown in figure 2.3. Initially the oxygen atoms are chemisorbed on the surface (figure 2.3(a)), before an exchange occurs between a chemisorbed oxygen atom and a metal atom in the surface layer (figure 2.3(b)). The re-establishment of metal atoms on the surface allows further oxygen to be adsorbed, with the heat liberated during the chemisorption process providing energy for further exchange in the surface region (figure 2.3(c)). This model has been applied by several groups to explain the initial oxidation of a range of metallic surfaces [21–28].
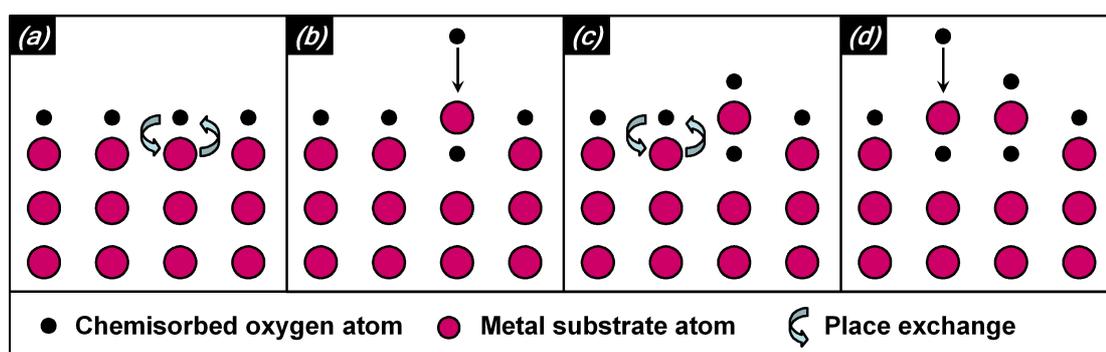

Figure 2.3: The initial stages of oxide formation on a metallic surface. (a) The process begins with the chemisorption of oxygen atoms on the surface. Metal and oxygen atoms then exchange places in the structure. (b) Oxygen is then adsorbed on the metal atom at the surface, with the liberated heat of adsorption leading to (c) further place exchanges. The process continues in (d) with further adsorption of oxygen on the surface.

However, Fehlner and Mott proposed that as the surface coverage increases to around 1 ML, the exchange mechanism becomes less favourable [28]. An activation energy is required to break the metal-metal bonds, as well as the bonds between the chemisorbed oxygen atoms and the metal atoms. If exchanges are to continue at higher coverages, there must be some force which lowers the activation energy, possibly in the form of an image potential due to the oxygen nucleus on the surface. However, it has recently been shown that at some critical coverage, θ_c^{thd}, the transition between a chemisorbed layer and oxide formation becomes thermodynamically favourable [29],

because the heat of oxide formation is higher than the heat of adsorption. This leads to the penetration of oxygen atoms into the substrate, producing oxide films which are several atomic layers thick. Below θ_c^{thd}, the differential heat of adsorption is higher than the differential heat of oxide formation, confining the adsorbed atoms to chemisorbed sites on the surface.

In this description of the oxidation process, one issue remains unaddressed in that it is extremely unlikely that the process occurs uniformly across the surface. Oxide nucleation is an activated process and therefore tends to originate at defects within the structure, as these points possess a high chemical potential and lead to the formation of oxidised islands. This effect was observed by Muñoz-Márquez and co-workers during the oxidation of the Ni(111) surface [30]. Nucleated islands tend to grow and merge until a near complete oxide layer has been formed. The rate of growth of the islands depends on the sticking coefficient of the oxygen to the surface, the rate of diffusion of the oxygen atoms across the surface and the efficiency of the incorporation of the O atoms into the oxide structure. Once a continuous oxide layer has been formed, the oxygen atoms and the metal substrate are separated by a barrier (i.e. the oxide layer), and therefore further oxidation can only proceed if substrate atoms are able to diffuse to the surface through the oxide layer. Therefore the mass transport through the oxide layer is also an important factor in the rate of metal oxidation. A more detailed discussion of these processes, with examples, is presented in a review by Lawless [15].

2.2.3   The need for ultra-high vacuum

Sub-monolayer quantities of contamination on the surface can lead to significant changes in the electronic, chemical and structural properties of the surface. Therefore, the surface must be kept clean for the duration of any experiment, which requires pressures in the low 10^{-10} mbar regime (i.e. ultra-high vacuum (UHV)). Ion scattering experiments often take several hours to complete and therefore the Warwick modular CAICISS system typically requires a base pressure of 2×10^{-10} mbar.

2.2.4 Ion bombardment and annealing

The carbides and oxides formed in the near-surface region on exposure of the surface to the atmosphere must be removed in vacuum before the surfaces can be studied. The preparation of clean single crystal metal surfaces studied in this project was performed in UHV using an ion bombardment and annealing (IBA) process specific to each of the surfaces investigated. Typically, Ar^+ ions with energies of 0.5 - 5 keV are incident on the sample surface at incidence angles of around 30°-60° with respect to the surface plane. Such ions have a large screened Coulombic interaction cross-section with the surface atoms, so the initial collision leads to a cascade through the neighbouring region of the structure. If this cascade intersects the surface, atoms at the surface are ejected, or *sputtered*, from the sample. The sputtering process causes significant damage to the surface and sub-surface regions, with an amorphous layer several angstroms thick produced in most cases. These defects can be removed by annealing to temperatures sufficiently high to induce reordering or recrystallisation within the sample. During the annealing process, the defects and dislocations tend to migrate to the surface where they combine or dissipate, restoring the overall physical order of the structure. This may also lead to the segregation of impurities to the surface, often necessitating the use of several IBA cycles to prepare a clean, well-ordered surface.

2.2.5 Atomic hydrogen cleaning

The covalent nature of binary III-V semiconductor materials means that they are prone to selective etching as well as electronic and structural damage when exposed to heavy noble gas ions. Hence, ion bombardment and annealing procedures are inappropriate, necessitating the development of an alternative method of cleaning the surface. One such technique involves exposing the surface to thermally generated atomic hydrogen. The hydrogen atoms are extremely reactive and remove the hydrocarbons and oxides on the surface, with the reaction products being more readily desorbed at relatively low temperatures (below the dissociation temperature of the bulk material). This approach has also been shown to be successful on a range of materials,

including InAs [31], GaAs [32, 33], InP [34], GaSb [31] and InSb [31], producing clean, well-ordered surfaces.

The InN(0001) films investigated in Chapter 8 were prepared using atomic hydrogen cleaning (AHC), since IBA leads to In-rich surfaces [35]. In addition, the surface cannot simply be annealed at a high temperature [36], as the dissociation temperature of InN is lower than that of the native oxide (In_2O_3). The results of the AHC process depend on the degree of exposure to the atomic hydrogen flux, as well as the temperature of the surface during the process. Excessive temperature or H* exposure can have drastic consequences for the surface structure, but if the correct parameters are applied, the removal of contaminants from the InN surface is thought to proceed as follows:

$$In_2O_3 + 4H^* \rightarrow In_2O + 2H_2O$$
$$In_2O + 2H^* \rightarrow 2In + H_2O$$
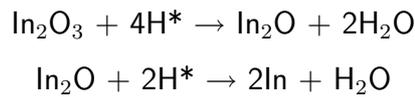
2.3   Thin film growth and alloy formation

As well as the study of clean surfaces and the results of the adsorption of gaseous species on the surface, the experimental chapters of this thesis also focus on the deposition of Pt on the clean Cu(100), Ni(110)-(3×1)-O and NiO(110) surfaces. Therefore, it is important to understand the factors which will dictate the outcome of these depositions which can lead to the formation of thin Pt films on the surface or the formation of an alloy with the substrate. The following sections outline some of the basic physics and chemistry of thin film growth and alloy formation, which is used to gain an understanding of the experimental observations presented in later chapters. For more details the reader is referred to the texts by Ohring [8], Woodruff [37] and Venables [38].

2.3.1   Thin film growth

The deposition of one metal on the substrate of a second metallic species in order to form a thin film depends on many different parameters [39, 40]. The lattice

constant of the adsorbed atoms may be significantly different to the substrate atoms, leading to a mismatch and strain in the near-surface region. The adsorbate atom may also be found to readily react with the substrate material, forming an alloyed surface. However, in many cases thin films of the adsorbed species can be grown directly on to a metallic substrate with no alloying or intermixing. The deposition rate and substrate temperature can usually be controlled during the deposition process, but several other kinetic and thermodynamic properties can also influence the final outcome of the growth procedure. According to Young's equation (equation 2.7) [41], the thermodynamic behaviour of thin films is determined by the interface energy, γ_i, in addition to the surface energies of the substrate, γ_s, and the adlayer, γ_a.

$$\Delta\gamma = \gamma_a + \gamma_i - \gamma_s \tag{2.7}$$

Depending on the relationship between the interface and surface energies, three growth modes are possible in idealised growth conditions (shown in figure 2.4):

- $\Delta\gamma \leq 0$ for all adlayers $\Rightarrow$ Frank-Van der Merwe (layer-by-layer).

- $\Delta\gamma \leq 0$ for a limited number of layers $\Rightarrow$ Stranski-Krastanov (2D $\rightarrow$ 3D).

- $\Delta\gamma > 0$ $\Rightarrow$ Volmer-Weber (3D islands).

For example, deposition of Pt on different substrates leads to different growth modes. When deposited on the Fe(100) surface, layer-by-layer growth of a Pt film results for coverages up to 11 ML [42]. On the MgO(100) surface, the deposition of Pt results in the growth of Pt islands in the Volmer-Weber growth mode [43]. The Stranski-Krastanov growth mode is observed following the deposition of Pt on the Si(100) surface [44]. This trend is explained by the relative surface energies of the substrates, with the Fe(100) surface having a surface energy of 2.43 Jm^{-2} [45], the Si(100) surface 1.36 Jm^{-2} [46] and the MgO surface 1.20 Jm^{-2} [47]. The substrate with the lowest surface energy leads to Volmer-Weber growth, whilst the highest surface energy gives layer-by-layer growth. More relevant to this thesis, Pt has a higher surface energy (1.65 Jm^{-2} for the Pt(100) surface) compared to the Cu(100) surface (1.28 Jm^{-2}). In the (110) case, Pt(110) (1.75 Jm^{-2}) has a higher surface energy than Ni(110) (1.73
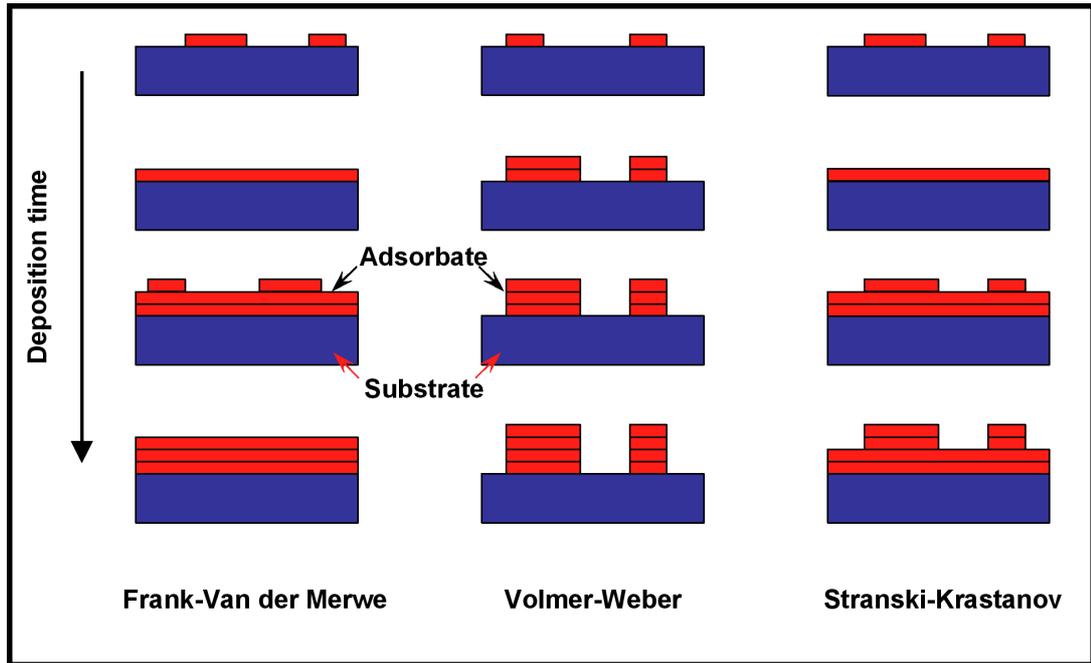
Figure 2.4: Schematic illustration of the three main thin film growth modes. The Frank-Van der Merwe growth mode occurs when $\Delta\gamma \leq 0$ for all layers, whilst the Volmer-Weber growth mode occurs when $\Delta\gamma > 0$. In the intermediate case, where $\Delta\gamma \leq 0$ for a limited number of adlayers, the Stranski-Krastanov growth mode occurs.

Jm^{-2}) [60]. Therefore, γ_a - γ_s is positive in both cases and Volmer-Weber growth should be expected, unless Pt is incorporated into the substrate structure.

There are some issues which should be raised when considering this approach as the primary factor governing the growth mode. The interface energy is often poorly defined and set to zero. However, a non-negligible positive interface energy can result from a mismatch in the structures of the substrate and adsorbate, resulting in strain in the surface region. A negative interface energy can have a profound effect on the morphology of the resulting film, promoting growth in the Franck-Van der Merwe or Stranski-Krastanov modes, allowing the first one or two layers of a film to be completed, even if γ_s is smaller than γ_a (which would lead to Volmer-Weber growth if $\gamma_i = 0$). The interface energy is usually determined using bulk heats of alloy formation and is often only an order-of-magnitude estimate [48]. The surface energies can also be problematic, with accurate determination of the surface energy of the adlayer proving

difficult due to strain in the surface region. In addition, these considerations are only generally true for growth in an equilibrium state whereas growth, by its very nature, is a dynamic process. In order to guarantee the desired growth mode, particularly layer-by-layer, the adsorbate is often deposited in conditions far from equilibrium. Therefore, the deposition and growth of a metal-metal system can often yield some unexpected results.

2.3.2   Alloy formation

A range of factors can lead to the formation of an alloy structure in the surface region instead of the growth of a thin film [40]. Firstly, the relative miscibilities must be considered. The formation of a thin film structure is generally the case for metallic species which exhibit low miscibilities. Hence, the degree of intermixing between adsorbate and substrate atoms is very low, without annealing to high temperatures. However, for a more miscible combination, the adatoms can diffuse into the substrate, producing an alloy in the near-surface region. Alloy formation usually occurs via an exchange mechanism, with atoms in the adsorbed layer swapping places with atoms in the substrate to form the alloy. It has previously been shown that alloy formation following the deposition of Pd on Cu(100) [49] and Mn on Cu(100) [50] is, at least in part, due to the high miscibility of the adsorbate and substrate species.

It has also been shown that interfacial alloying is favoured if the interface energy is negative for the system [41]. In such cases, the surface tends to minimise energy by maximising the area of the interface at the surface. This necessitates a rearrangement of the atoms in the surface region, with the dissolution of some of the adatoms into the outermost layer(s) of the substrate material along with the diffusion of substrate atoms to the surface, producing an alloyed surface layer. Examples of this process include the sub-monolayer deposition of Ag on the Pt(111) surface [51]. An alloy in the near-surface region can be produced even if the interface energy is positive, provided that the system possesses a negative heat of alloy formation. In this case, it is again energetically favourable to have an alloy in the outermost layers of the structure. This effect has been observed in the case of Au deposition on the Ag(110)

surface [48, 52].

Other examples exist where it is favourable to have certain bonding arrangements at the surface to lower the surface energy of the system, again producing an alloy structure. If species B is adsorbed on to a substrate of species A, it may be more favourable to have A-B or A-A bonding at the surface than the B-B bonding which would exist at the surface of a thin film structure. This explanation has been used to describe the formation of an alloy following the deposition of Au on the Ni(110) surface [53]. Alternatively, if the adsorbate and substrate have a significant lattice mis-match, the diffusion of adatoms into the substrate may occur in order to lower the strain at the interface, an effect cited for the formation of an alloy in the near-surface region following the deposition of Ge on the Si(001) surface [54] and following the deposition of Pd on the Cu(111) surface [55].

Arguably the most common form of alloy formation is the minimization of the surface energy by the diffusion of the substrate material into the adlayer [56], as shown in figure 2.5. This phenomenon occurs when the surface energy of the substrate material is less than that of the adsorbed species. Therefore, in order to minimise the surface energy, atoms from the substrate diffuse into the adsorbed layer(s), forming an alloy in the surface region. This effect has been seen in many systems, including the multilayer deposition of Pt on Ni(111) [57], Pt on Co(0001) [58] and Mn on Au(100) [59].

In this thesis, the room temperature deposition of Pt on to Cu and Ni surfaces has been studied. Pt has a high surface energy (1.650 Jm^{-2} for the Pt(100) surface) compared with both the Cu(100) surface (1.28 Jm^{-2}) and the Ni(100) surface (1.58 Jm^{-2}) [60]. In the case of the (110) surfaces, Pt has a surface energy of 1.75 Jm^{-2} whilst Ni has a surface energy of 1.73 Jm^{-2}. The heats of alloy formation are also negative in both the Pt-Cu and Pt-Ni cases (-0.54 eV for Pt deposition on Cu, -0.28 eV for Pt deposition on Ni) [60]. Therefore, provided there is sufficient energy to initiate the diffusion of the Cu and Ni atoms into the Pt adlayer at room temperature, alloy formation in the near-surface region is likely in all the cases studied.
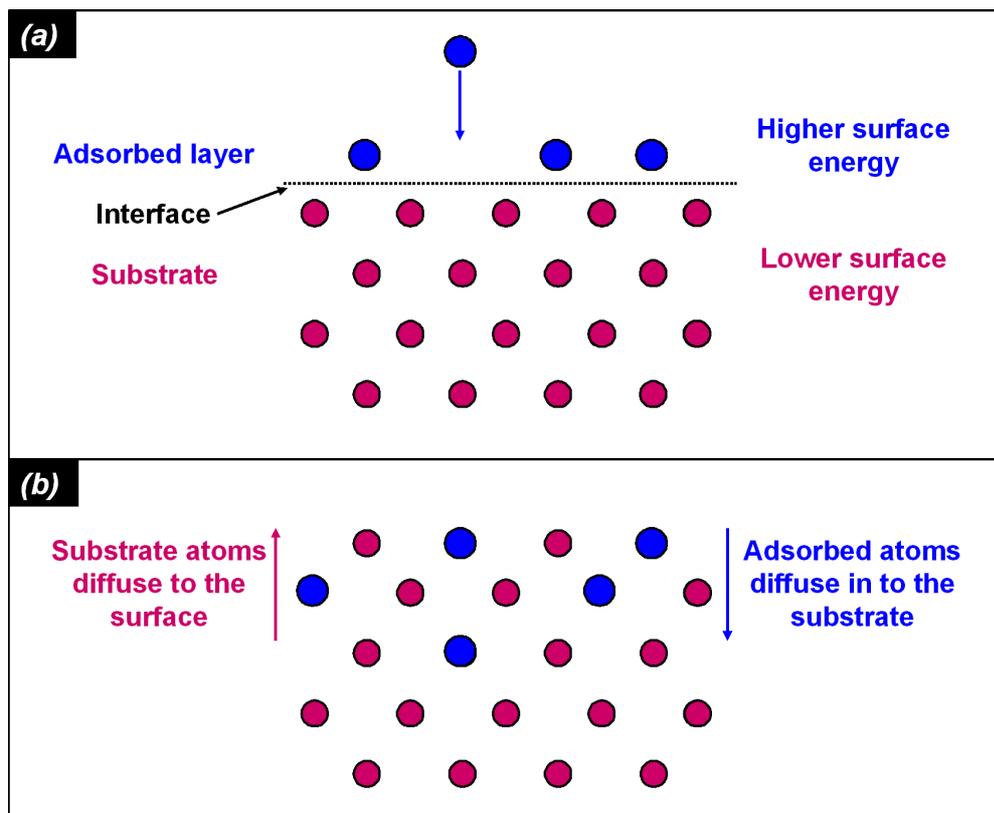
Figure 2.5: An illustration of the formation of an alloy in the surface region following the deposition of a metallic adsorbate (blue atoms) on to a metal surface (deep pink atoms) in the case where the substrate possesses the lower surface energy. (a) shows the initial adsorption of the deposit to the surface. However, due to the lower surface energy of the substrate, some of the substrate atoms near the interface diffuse to the surface, (b), leading to the formation of an alloy in the near-surface region.

2.3.3   Computational methods

The outcome of the deposition process can be simulated using a range of computational methods which have been developed in recent years. Such models generally fall into one of the following categories - *ab-initio* methods such as density functional theory (DFT) [61, 62], kinetic Monte Carlo calculations [63, 64], the BFS model [65, 66] (which can be used in Monte Carlo simulations [67]), the embedded atom method (EAM) [60, 68] and molecular dynamics simulations [69]. Whilst none of these methods have been used in this thesis to predict the outcome of the Pt deposition experiments, it is interesting to outline some of the simulation codes which

could perform this task.

DFT calculations are based on the observation that the total energy of an assembly of atoms is a function of the total electron charge density [61, 62]. It is possible to replace the many-electron solution to the Schrödinger equation by an exactly equivalent set of self-consistent one-electron equations (the Kohn-Sham equations [70]). This allows the decomposition of the many electron problem into a system of non-interacting electrons moving in an effective potential generated by the nuclei and the other electrons of the system. Iterative methods are then used to compute the electric field of an assembly of atoms with fixed atomic coordinates. The procedure yields a total energy for a particular system configuration. By allowing the atomic coordinates to vary, it is possible to find the minimum total energy configuration of systems consisting of several hundred atoms using a modern high performance workstation.

The kinetic Monte Carlo (k-MC) method can be used to firstly identify the mechanisms of adsorption and diffusion of the adatom on the surface. For low growth rates, the adatoms are assumed to be statistically independent. The initial adsorption site is selected, and if that site is unoccupied then the adatom is adsorbed in that site. Otherwise, the adatom jumps to one of the surrounding sites until it locates a vacant one. The rate at which each diffusion event occurs is then characterized by a jump activation barrier and an attempt rate. This method has been successfully applied to the study of film morphologies in both the low and high temperature deposition regimes [8, 61].

For a given atomic distribution, BFS computes the configurational energy of formation by means of a perturbation theory-based approach [65, 66]. Ground state structures of alloys are therefore obtained by optimizing the atomic distribution via Monte Carlo simulations. This method is distinguished from other techniques by the fact that there is no restriction on the number and type of elements to be considered, and no limitation on the crystallographic structure. The method has been successfully applied to the study of many bulk alloy and surface alloy systems [65, 66].

In molecular dynamics Newton's equations of motion are solved for all the atoms in an ensemble using an interatomic potential to calculate the forces. The method

computes the position and velocity of every atom in the system at time intervals which are short compared to the lattice vibration period. However, the short steps ($\sim$ 1 femtosecond) means that high deposition rates are required to analyse the system in a reasonable period of time. The unrealistically high deposition rates may therefore predict a more kinetically trapped structure than is likely to occur in practice.

Finally, in the EAM method, the energy required to embed the adsorbed atom into the local substrate electron distribution is calculated. Several other electronic and thermodynamic parameters are then taken into consideration in order to find the most favourable structure following the adsorption [60]. Whilst the EAM method has been applied to many surface alloy systems [60, 71–74], it can also be applied to a range of other phenomena, including the structure of liquid metals [75], dislocation propagation [76] and fractures [77], as well as to more directly related properties such as surface energy [78] and alloy segregation [79]. At some point in the future, it would be interesting to apply some of these codes to the systems studied in this thesis to gain more insight into the alloying process.