1 Background and theory

1.1 Towards quantum size effects

The presentation "There is plenty of room at the bottom" given by Richard Feynman on December 26, 1959 at the annual meeting of the American Physical Society[1], serves to demonstrate the possibilities of miniaturization and is one of the leading driving forces for nanotechnology. Especially in combination with Moore's law[2], the predictions of which, relating to the increase of electronic circuit packing density on silicon chips, have held for more than for decades now. This law provides an impressive demonstration of the fact that, with features on commercial electronic circuits now reaching a line width of 65 nm, nanotechnology is rapidly advancing. Many other aspects of modern technology are also based on dimensions getting ever smaller, and increasing the storage and information density. Nobody is surprised any more by the notion that all the books ever written would fit on the head of a pin, and we have come to expect the next generation of computers to be much faster and smaller than the one before. Ever since 1989, when IBM scientist Don Eigler spelt the letters "IBM" with individual xenon atoms by using a scanning tunnelling microscope[3], it is only the atom that is the limit. Where the IBM experiment primarily served to show the possibility of manipulating individual atoms, it also indicated the limitations. To make any technologically useful object with such a method would require by far too much time. So it seemed that although we are capable of manipulating individual atoms, this will not provide the final step for Feynman's prophecy. Luckily, nature herself provides a solution here in the form of self-organization. In a way similar to how large organic molecules such as DNA are spontaneously formed from their individual molecular building blocks, atoms also tend to arrange themselves on surfaces in an ordered fashion. A recent example of how self-organization of atoms at a surface can be used to create a technologically useful object was presented by the group of Himpsel[4]. The group created a regular array of individual silicon atoms, with the possibility to store information on an atomic scale by either the presence or absence of an atom, this can be regarded as an atomic bit. For every silicon atom, 19 substrate atoms are needed in order to prevent the interaction between two individual storage sites. This yields an information density close to the theoretical limit of one bit per 1.5 nm. Figure 1.1 shows a comparison between this information density and that of a common compact disc; note that the scale of the two images differs by three orders of magnitude. Due to fundamental physical limitations the read/write speed of this atomic memory is however very low and in this respect it may not be directly technologically relevant. It may therefore be concluded

1   Richard P. Feynman, Journal of micro. sys. **1**, 1, March 1992.
2   G.E. Moore, Electronics **38**, 114 (1965).
3   D.M. Eigler and E. Schweizer, Nature **344**, 524 (1990).
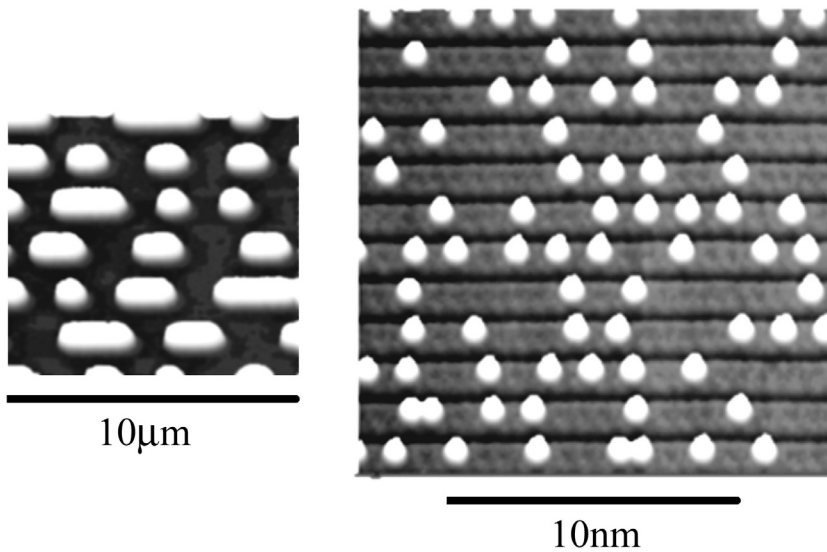4   Bennewitz *et al*. Nanotechnology **13**, 499 (2002).

Figure 1.1: Comparison between the information density of a normal CD (left) and the "atomic CD" made from individual Si atoms from Himpsel and co-workers[4] (right). Note the difference in scale between the images.

10μm

10nm

that, although for nano-*technology* there is still plenty of room at the bottom, fundamental nano-*research* today is reaching its lower limit of data storage and the manipulation of individual atoms. Hence the focus of this thesis is not to try to make even smaller structures, but the understanding of the physics governing the self organization and other processes at these length scales.

Just as the dimensions of individual atoms define the transition from nano- to atomic-scale physics, for metallic structures the electron coherence length dictates another important transition. Below this length scale the electrons will retain their phase information and can therefore no longer be regarded as a continuum or sea of electrons. This may result in many effects that are not observed in macroscopic systems, the most pronounced being the formation of standing electron waves. The first observation of these so-called quantum well states (QWS) in metals was made in 1971 by electrons tunnelling from thin lead films of around 250 Å through an oxide layer in transport measurements[5]. These and similar observations raised the interest of theoretical physicists in size dependent quantum mechanical effects in such metal films. In 1976 Schulte[6] predicted that the work function, Fermi energy, charge spilling, and electron density oscillates as a function of thickness. These calculations were performed within a jellium model, and therefore ignored the atomic structure of the metal layer. To compensate for this, Feibelman[7] included in his calculations the fact that the thickness of the layer can only increase with an integer number of atomic distances, and that the outer layers of a film relax. The general picture, however, did not change much, primarily adding the interlayer relaxation to the list of properties that will oscillate with thickness. Since most properties of a crystal depend directly on the electron distribution and density of states around the Fermi level, almost all other physical properties of the film will oscillates with thickness if this property does.

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5   R.C. Jaklevic *et al.* Phys. Rev. Lett. **26**, 88 (1971).

6   F.K. Schulte, Surf. Science **55**, 427 (1976).

7   P.J. Feibelman, Phys. Rev. B **27**, 1991 (1983); P.J. Feibelman and D.R. Hamann, Phys. Rev. B **29**, 6463 (1986).

This oscillatory behaviour, and other properties that arise from the standing electron waves in thin metal films, are generally referred to as quantum size effects (QSE). One of the most striking results of QSE is the formation of "magic" or preferred island heights and the self-organization of the metal layer into these heights, addressed in more detail below. However, the most direct manifestation of an oscillation of the electron density around the Fermi level is the variation of the conductivity of the films. For thin lead films, this has been observed both by resistance measurements in combination with reflection high energy electron diffraction (RHEED)[8] and by directly measuring the current through the layer in a four probe measurement[9]. A very intriguing QSE is the oscillation of the magnitude *and* the sign of the Hall coefficient as a function of Pb coverage[10]. This observation can only in part be explained by taking a detailed look at the band structure for a three-dimensional solid[11]. Other recently measured consequences of quantum size effects are the oscillations in the magnitude of electron phonon coupling, and in the critical temperature for superconductivity[12]. Moreover, the electronic properties directly influence the chemical reactivity of a thin film. This is nicely illustrated in a recent photoemission electron microscopy (PEEM) experiment on the oxidation of atomically flat magnesium films[13]. The reactivity is maximum when a quantum well state is close to the Fermi level and decreases when the density of states at the Fermi level is low.

Summarizing the influence of quantum size effects, one may say that they are responsible for the oscillatory behaviour of many physical properties of thin films as a function of thickness. One of the goals of the present work is to gain a better understanding of the processes involved and their causes.

1.2 Quantum well states: "textbook physics in the lab"

One of the standard teaching problems in introductory quantum mechanics is the "particle in a box", often used as a comparison for the allowed energies of electrons in a hydrogen atom. In the simplest approach, consider the potential well to be one dimensional and with infinite potential barriers. The main results is that the electrons in this well form standing waves, with a node at the barriers of the well. If the width of the well is called d, the electron wavelength λ_n can be described

8   Jalochowski *et al*. Phys. Rev. B **38**, 5272 (1988); Phys. Rev. B **45**, 13607 (1992).

9   O. Pfenningtorf, PhD thesis, Universität Hannover (2001).

10   M. Jalochowski, M. Hoffmann, and E. Bauer, Phys.Rev.Lett. **76**, 4227 (1996).

11   I. Vilfan, M. Henzler, O. Pfennigstorf, and H. Pfnür, Phys.Rev. B **66**, 241306 (2002).

12   Y-F. Zhang *et al*. Phys. Rev. Lett. **95**, 96802 (2005); Y. Guo *et al*. Science **306**, 1915 (2004).

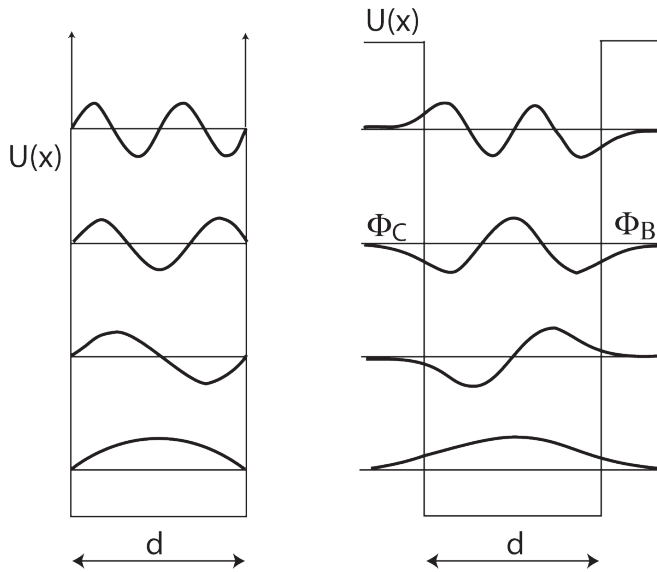13   L. Aballe *et al*. Phys. Rev. Lett. **93**, 196103 (2004).

Figure 1.2: (left) Infinite quantum well with width *d*, the first four energy levels are schematically indicated. The standing waves have their nodal points at the well boundaries. (right) Quantum well with finite potential barriers and width *d*. Spilling of the wave function is indicated by the phase shifts Φ_B and Φ_C. Figure adapted from Milun[14].

as

$$\lambda_n = 2d / n \,, \hspace{3cm} (1.1)$$

where *n* is an integer. The probability density of these standing waves is schematically depicted on the left-hand side of Figure 1.2 (adapted from Milun[14]. By taking the de Broglie relation between the wavelength and the energy *E* of an electron with mass *m* into account, one can determine the quantised energy levels in the well as

$$E_n = n^2 \frac{h^2}{8md^2} \,, \hspace{3cm} (1.2)$$

where *h* is Planck's constant. The use of infinite barriers is an approximation that does not correspond to the physical reality of thin metal films. In all the systems discussed in this work, the potential barriers are defined by the metal-vacuum interface on one side, and by the barrier between the metal overlayer and the substrate on the other. Especially the latter can be very complex, and depends on the electronic structure of the substrate and the interface properties between substrate and deposited material.

Before dealing with the complexities of electrons in an asymmetric finite potential well, it is useful to first take a closer look at the effect of exchanging the infinite barriers for finite ones. One of the most striking consequences of the quantum mechanical treatment of electrons is that of tunnelling of those electrons through or into barriers. When the barrier is lowered, the wavefunction of the
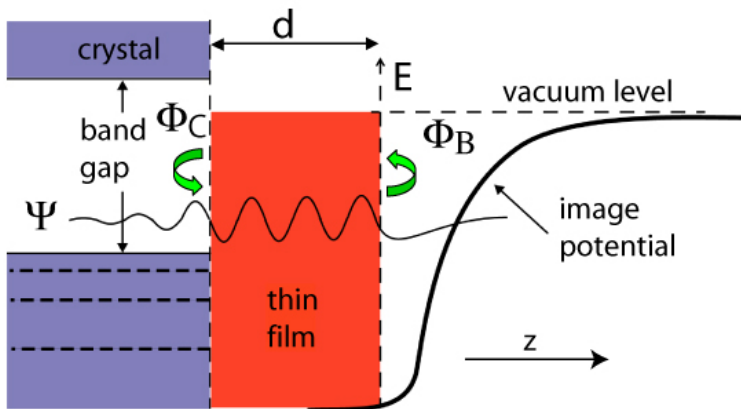
14   M. Milun, P. Pervan, and D.P. Woodruff, Rep. Prog. Phys. **65**, 99, (2002).

Figure 1.3: Schematic potential for a thin metal film on a crystal substrate. Quantum well states are formed due to the reflection of the electron wave at the image potential at the vacuum side, and the interface potential at the substrate side. Φ_B and Φ_C denote the phase shift at the vacuum and the interface, respectively. The situation for a surface state is given by $d = 0$. Figure from Echenique and Pendry[15].

electron will decay more slowly and penetrate further into the barrier. Mathematically this problem can be solved by requesting that the amplitude and gradient of the wavefunction at the boundary be continuous, i.e. the standing waves inside the well match the exponential tails outside. As can be seen in the right-hand part of Figure 1.2 this means that the wave function has extended, and that the effective width of the well is increased. From Equation 1.2 it follows directly that this will result in a lowering of the energy of the quantum well states. This dependence of the QWS energies on the height and shape of the boundary and therefore on interface conditions can be used to obtain an intuitive feeling for the processes at the interface.

Due to the asymmetry of the potential barriers, the exponential decay of the wavefunction will be different at both boundaries, and has to be treated separately. Since the exact atomic structure at the interface is usually not known, and even if it is known the resulting electron potential is difficult to describe analytically, one should look for an alternative solution of the problem. This alternative solution is provided in the form of the "phase accumulation model" first presented by Echenique and Pendry[15] for the description of surface states of metals, and later refined by Smith[16]. Because of the analogy with the motion of an electron around an atom core, it is also often referred to as the Bohr-Sommerfeld quantization rule[17]. This model states that, for standing electron waves to exist, the total phase of the electron accumulated on a complete round trip has to be equal to an integer multiple of 2π. If we now treat the tunnelling of the electrons as a phase shift at the respective interface, this can be summarized as follows:

$$2mkd_0 + \Phi_B + \Phi_C = 2\pi n, \tag{1.3}$$

15 P.M. Echenique and J.B. Pendry, J. Phys. C: Solid State Phys. **11**, 133 (1978).

16 N.V. Smith, Phys. Rev. B, **32**, 3549 (1985).

17 T-C. Chiang, Surf. Sci. Rep. **39**, 181 (2000).

where Φ_B and Φ_C are the phase shifts at the metal-vacuum and the substrate-metal interface respectively, k is the electron wavevector in the direction perpendicular to the surface, and *2mkd₀* is therefore the phase accumulated by an electron travelling back and forth through the film. The factor *md₀* arises from the fact that the thickness of the layer can only be an integer *m* times the interlayer spacing d_0. In Figure 1.3, adapted from Echenique and Pendry, the phase accumulation model is schematically illustrated. The phase shift on the vacuum side is determined by the image potential and can be calculated in the WKB approximation by[18]

$$\Phi_B / \pi = \sqrt{\frac{3.4}{E_V - E_n} - 1} \, , \tag{1.4}$$

where E_V is the energy of the vacuum level and E_n the QWS energy, both expressed in eV. The beauty of this model is that it is valid for all thicknesses; when the thickness of the layer is reduced to zero the resulting energy levels with n>0 are the image potential states and the n=0 solution is the Shockley surface state. At intermediate thicknesses the energy levels are the quantum well states previously discussed, and for very large thicknesses when $k_\perp$ becomes a valid quantum number these will merge to form the bulk band structure of the metal.

For noble metals or other substrates with a Shockley-inverted band gap along the Γ-L direction, the upper edge (L_1) has s-character and the lower edge (L'_2) has p-character, and the phase shift at the substrate-metal interface will vary accordingly. At the bottom of the band gap, the phase shift will be $-\pi$ and 0 at the top. The behaviour in between can then be described by the purely empirical formula

$$\Phi_C = 2 \arcsin \left[\sqrt{\frac{E - E_L}{E_U - E_L}} \right] - \pi \, , \tag{1.5}$$

where E_L and E_U are the energies of the lower and upper edge of the bandgap, respectively. In practice, the usefulness of this formula often proves to be rather limited and the phase shift at the substrate-metal interface cannot be predicted *a priori*. However, when the QWS energies are known from experimental data, the total phase shift can be determined as follows: consider layers with known thicknesses d_1 and d_2 and QWS with quantum numbers n_1 and n_2 at the same energy. Then subtraction of Equation 1.3 for both cases will yield

$$k_z = \frac{\pi (n_1 - n_2)}{d_1 - d_2} \, . \tag{1.6}$$

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18   E.G. McRae and M.L. Kane, Surf. Sci. **108**, 435 (1981).

In this way, the perpendicular electron wavevector k_z at energy $E_{n1,2}$ can be determined. Repeating this procedure for a wide variety of energies will give the band structure that the QWS are derived from. This band structure will be entirely free of assumptions, in contrast to the free electron final state model. Using the obtained k-values in Equation 1.3 will give the total phase shift at both interfaces, and subtraction of the Φ_B derived from Equation 1.4 will result in a value for Φ_C. One of the major practical problems in this respect is that a very extended data set is needed in order to use enough QWS that belong to different coverages but have the same energy. When these prerequisites are fulfilled, the abovementioned analysis will provide valuable results, as has been shown for aluminium films on silicon[19] where the phase shift is shown to have a profound effect on the electron wavevector in the direction perpendicular to the film. For more complex systems, the phase shift at the interface between the substrate and the overlayer will not just show a linear dependence on the binding energy as often reported[17], but also depends on the density of states of the substrate and the exact arrangement of the atoms at the interface. A more detailed description of the influence of the interface will be given in Section 1.4.

If we extend the simple results for the particle in a box model shown in Figure 1.2 to electron states confined in a metal film, the electron wavevector in the quantum well consists of the rapidly oscillating Bloch wave derived from the inter-atomic distance, modulated by the envelope wavefunction from the standing quantum well wave. The phase shifts introduced in Equation 1.3
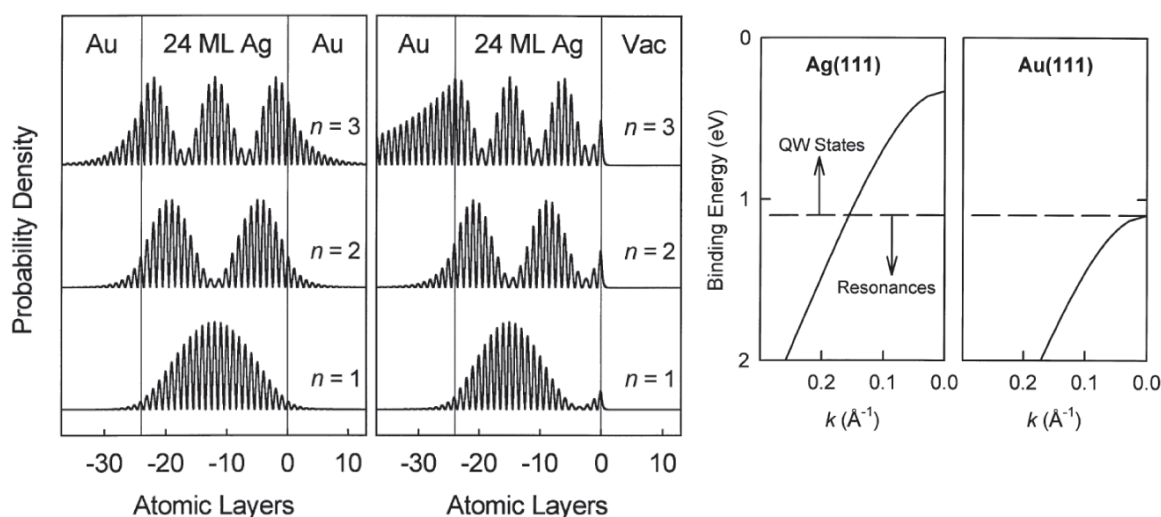

Figure 1.4: (left) Theoretical probability density for the n = 1 - 3 quantum well states in a 24 ML thick Ag(111) film sandwiched between two semi-infinite Au crystals (left hand panel), and with one Au crystal replaced by vacuum (right hand panel). The vertical lines indicate the Au-Ag and Ag-vacuum interfaces. (right) Band structure of Ag and Au along the (111) direction, QWS in the Ag overlayer can only form above the Au valence band maximum, indicated by the dashed line. Both figures from Chiang[17].

19   L. Aballe *et al*, Surf. Sci. **482-485**, 488-494 (2001).

refer to the spilling of the envelope function, therefore several wavelengths of the Bloch state of the QWS can still exist in the substrate. This is illustrated in Figure 1.4 where the theoretical probability density for the first three quantum well states of 24 layers of Ag on Au(111) is displayed, with and without a vacuum barrier[17]. Especially for the higher binding energy state (n = 3), the effect of the phase shift is quite profound. The QWS will spill several monolayers into the substrate, making the quantum well effectively much wider. This QWS is actually only just inside the band gap of the Au(111) crystal, in contrast to the two other states that are well inside this band gap, therefore the confinement is not effective. If the binding energy were a little higher, thus outside the band gap, the confinement barrier would be too low and the state would not be confined at all. For the other two states that are inside the bandgap and further from this confinement threshold, the charge spilling is less and the confinement is better defined.

So far, the influence of the reduced dimensionality on the electron wavevector in the direction perpendicular to the surface has been discussed, and it has been shown that this wavevector will be quantised. In the direction parallel to the film, the electron should not experience any influence of the confinement, and a free-electron like behaviour comparable to the bulk material is expected.
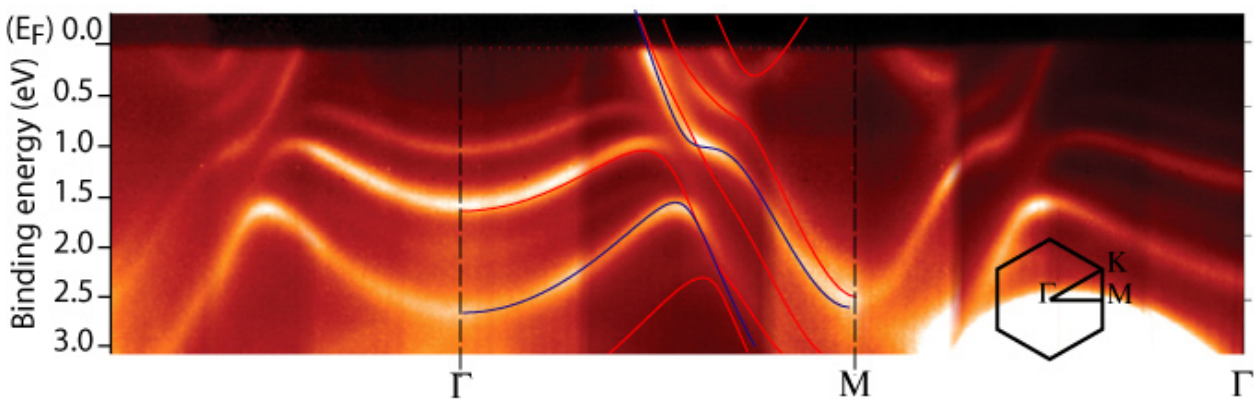

Figure 1.5: Band structure for an ultrathin Pb film on single crystal hexagonal graphite measured by photoemission along the Γ - M direction. Lighter colours indicate a higher photoemission intensity. The solid lines projected on the image show the band structure obtained by DFT calculations for a 2 and 4 ML thick free-standing Pb slab. Further details about the image and how such images are acquired are discussed in Section 3.1.1. (inset) Surface Brillouin zone for the Pb layers.

In order to obtain a feeling for the in-plane band structure, density functional theory (DFT) calculations for free standing metal slabs are very helpful. In Figure 1.5 a comparison between a DFT calculation for a free-standing Pb slab and the band structure for a film of Pb on single crystal hexagonal graphite measured by angle-resolved photoemission, is shown. Due to the negligible interaction with the substrate, the Pb layer can be regarded as a quasi free-standing slab allowing a direct comparison to the calculations. At the centre of the surface Brillouin zone (SBZ) (see inset in Figure 1.5), corresponding to the Γ point in the image, the quantization in the direction perpendicular to the film is most obvious, and this results in the individual sharp lines. For Pb these bands are derived from the $6p_z$ states. The $6p_{x,y}$ states are also quantised, and disperse downwards

halfway through the surface Brillouin zone near the M point. A further description of all features in this image will follow in Section 3.1.1. The match between calculation and measurement is striking, indicating that DFT calculations for free standing layers provide an adequate starting point for band structure determinations in quantum well systems.

1.3 Electronic growth model and self-organized growth

It has recently been shown, both in theory and experiment, that the influence of confinement on the electronic structure discussed in Section 1.2, also has a profound influence on its growth mode. This is referred to as "electronic growth", a term coined by Zhang[20] in 1998. The motivation for this model was the observation of a growth mode that could be classified as "inverse Stranski-Krastanov" growth. Regular Stranski-Krastanov growth is characterized by the initial formation of a smooth layer of the overlayer material on the substrate, followed upon further deposition by island growth. In contrast, for Ag growth on GaAs(110) at a certain critical thickness the films become atomically flat, after an initial island-like growth[21]. This rules out the influence of stress as the major driving force, as is often observed for systems with a lattice mismatch, and raises the question as to the origin of this growth mode.

The three main ingredients of the electronic growth model are quantum confinement, charge spilling, and interface-induced Friedel oscillations. Quantum confinement of electrons in the film initiates a repulsive force between the overlayer and the substrate that will try to stabilize the layer. Charge spilling results in electron transfer from the overlayer to the substrate, destabilizing the layer. Friedel oscillations are charge density oscillations in the direction perpendicular to the surface of a crystal that arise due the breaking of the translational symmetry at the surface. The general shape will be a damped sinusoidal function, where the charge density oscillations are most intense close to the surface. These oscillations result in a rearrangement of the position of the metal ions in the layers closest to the surface, which can either improve or lower the stability of the total layer. Therefore, the three above mentioned elements will compete to either make the film critically, magically, or marginally stable or completely unstable against breaking up in islands of different heights.

The characteristic measure for the film stability is the behaviour of the total energy of the layer as a function of thickness. Stable films are characterised by a second derivative of their total energy with respect to the thickness that is positive. A negative second derivative will make the films unstable, because the system can then achieve a lower total energy by breaking up into islands

20   Z. Zhang *et al*, Phys. Rev. Lett. **80**, 5381 (1998).
21   A.R. Smith *et al*, Science **273**, 266 (1996).

of adjacent coverages. The difference between magically and critically or marginally stable films is defined by the behaviour in the surroundings of the stable film. A critically stable thickness L_c can be defined when the film is stable for $L \geq L_c$ and unstable for $L < L_c$ or the other way around, indicating the first or the last stable height of the system. The magic height L_m occurs when the film is unstable at both sides of L_m. This is a regional or absolute minimum in the total energy of the layer. Films are called marginally stable in all situations that do not correspond to the stabilities described above. Figure 1.6 (from Ref. 20) shows total energy calculations for a wide variety of metals on a GaAs(110) substrate, taking all the competing influences into account.
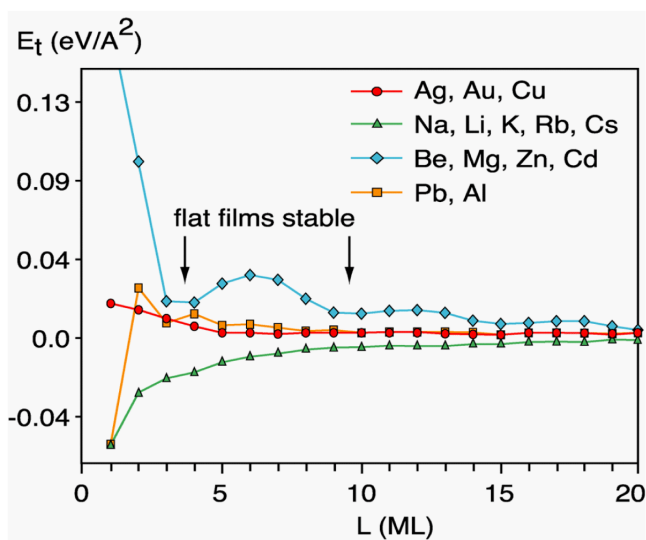

Figure 1.6: Total energy per surface area as a function of layer thickness for several classes of metals on GaAs(110). The films are stable where the curvature of the line is positive, and unstable when the curvature is negative. Figure from Zhang[20].

The fact that alkali metals cannot be grown as a smooth film at coverages larger than 1 ML on GaAs(110) is directly obvious from Figure 1.6. For all coverages the curvature is negative and all heights are unstable. The first stable height for Ag is at 5 ML, and after this the curvature remains positive for all coverages, reproducing the experimental observations[21] that triggered the development of the model. One way to determine stable thicknesses is to carefully study the growth behaviour of the film by using surface sensitive techniques. An elegant counterpart of this is to determine the stability from the destruction of the layer. For Ag films grown on Fe(100)[22] the structural stability is studied by examining the photoemission signal of a QWS for a specific layer height while annealing the system. In this way, the temperature at which the layer breaks up into islands of adjacent heights could be determined. This "bifurcation" temperature is plotted as a function of layer thickness in Figure 1.7(a) and it is clear that the 5 ML thick film is extremely stable. In a more simple manner than described above, the energy of the layer was calculated by performing a summation over all valence electrons, with (Figure 1.7(b)) and without (Figure 1.7(c)) a summation over the in-plane electron wavevectors. The energy difference between adjacent layers can be calculated as a discrete derivative
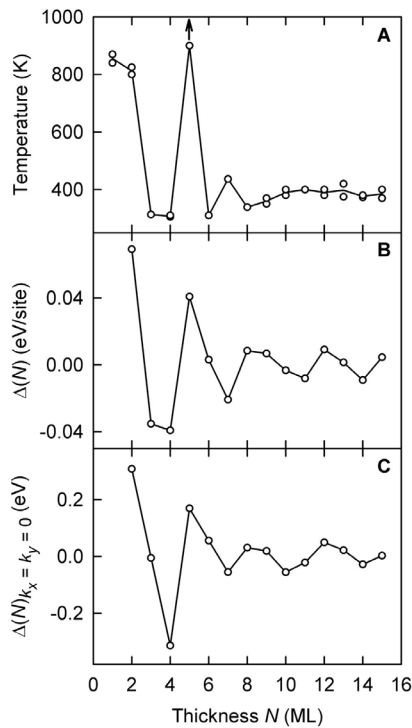
22   D.-A. Luh *et al*, Science **292**, 1131 (2001).

Figure 1.7: (a) Temperature at which the Ag layer on Fe(100) splits into adjacent island heights. The arrow for the 5 ML film indicates that this "bifurcation" temperature has not been reached. (b) Energy difference between layers per site according to Eq. 1.7, calculated for the full k range, and (c) by considering only the energies at $k_\parallel = 0$. Figure from Luh[21].

$$\Delta(N) \equiv \frac{1}{2}\big[E(N+1) + E(N-1)\big] - E(N),$$
(1.7)

where $E(N)$ is the total energy of a layer with thickness N. From the energy difference, plotted as a function of the coverage in the respective figures (a) and (b), the correlation between total energy difference and layer stability is obvious. These results also show that, to a first approximation, the total energy at the zone centre can be used as a measure for stability. The total energy at the zone centre is lowest when the highest occupied quantum well state is furthest away from the Fermi level. Whenever stability is discussed in the present work the relative position of the QWS with respect to the Fermi level is used, and systems with a density of states close to the Fermi level are considered to be less stable.

In Figure 1.6 Be and Pb are chosen as representatives for other classes of metals; the total energy of these materials shows oscillations with thickness. For a study of preferred or stable heights, this will be the most interesting behaviour because individual magic heights may be isolated. From the rapid oscillation of the total energy of Pb, it is expected that every second layer is stable/unstable. This is what was initially observed for Pb on Cu(111) by means of helium scattering[23]. It is important to realize that in helium scattering, the outmost electron density rather than the absolute position of the atoms is probed. For metallic quantum wells, the spilling of this charge into the vacuum also depends on coverage. For Pb on Si(111), a wide variety of experimental data exists where magic heights are observed. The first clear observation was made with the use of spot profile analysis low

23   B.J. Hinch *et al*, Europhys. Lett. **10**, 341 (1989).

energy electron diffraction (SPALEED) in the group of Tringides, who found that up to a coverage of 7.5 ML, lead grows primarily in 7 ML high islands on Si(111)7x7[24]. This observation was later confirmed by scanning tunnelling microscopy[25] (STM), which data showed that the islands had steep walls and flat tops. Almost just as striking as the initial observations of magic height Pb islands, is its dependence on the interface reconstruction. If the surface reconstruction of the silicon substrate is changed from (7x7) to Pb-induced (√3x√3) before deposition, the preferred height changes from 7 to 5 ML[26]. In order to understand this change, it is useful to consider the total energy calculations as a function of layer thickness for both Pb on Si(111)7x7 and on Si(111):Pb√3x√3 as displayed in Figure 1.8. The general trend of the oscillations is similar for both interfaces. However, the relative depth of the minima is different, and this is what determines the magic thickness. For the √3x√3 phase the minimum at 5 ML is lower than the one at 8 ML. For the 7x7 reconstructed interface, the relative depth of the minima is reversed, explaining the change in magic height. Some remarks concerning magic height Pb islands are necessary here. First of all in some publications the heights are measured with respect to a wetting layer (SPALEED and STM) while in others the absolute height is used (theory and photoemission). For Pb on Si(111) 7x7, the wetting layer has been determined to be one single monolayer thick[27] which is consistent with the difference between measurement and calculation in reference 26.

Substrate temperature plays an important role in the formation of magic heights, and thus needs to be taken into account. When the temperature is low enough, the mobility of the atoms is suppressed,
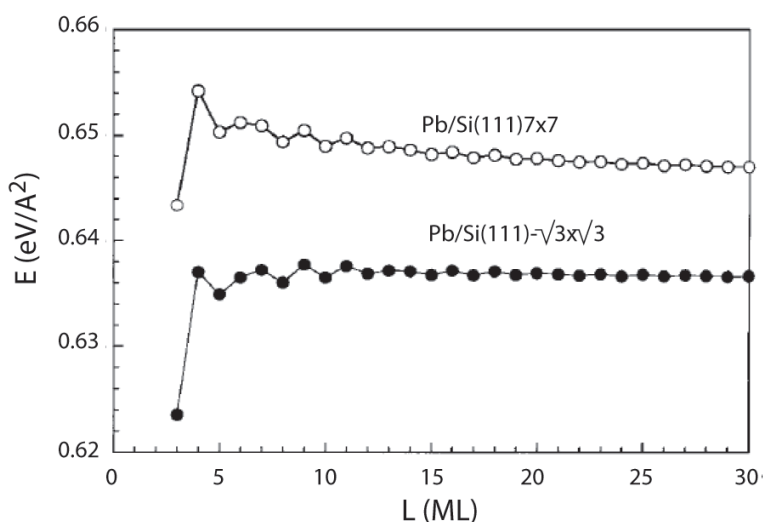

Figure 1.8: Calculated film energy vs film thickness L for the Si(111)7x7 and Si(111) √3x√3:Pb interfaces. The energy curve for the √3x√3 phase lies lower and has a lower minimum at $L = 5$ than the next minimum $L = 8$; for the (7x7) curve the order of the minima is inverted. Figure from Yeh[26].

24   K. Budde *et al*, Phys. Rev. B, **61**, 10602 (2000).

25   S.H. Chang *et al*, Phys. Rev. B, **65**, 245401 (2002).

26   V. Yeh et al, Phys. Rev. Lett. 85, 5158 (2000).

27   A. Mans, J.H. Dil, A.R.H.F. Ettema, H.H. Weitering, Phys. Rev. B, **66**, 195410 (2002).

resulting in a closed film with a narrow height distribution. At even lower temperatures this films will posses a fair amount of disorder. Above a temperature of 270 K, atom mobility for Pb will be high enough to overcome all barriers between stable and unstable heights; the electronic growth model will then no longer apply, and large clusters of a wide range of island heights form. The intermediate temperature range is where the magic height, steep-edge, flat-top islands occur. The mobility of the Pb atoms is then high enough to only form magic height islands, but too low to escape this energy minimum. The behaviour as a function of temperature depends on the substrate and the type of metal that is deposited. So far an extensive study has only been performed for Pb on Si(111)7x7, resulting in a complex phase diagram[28].

Calculating the total energy of a film by using the simple approximation of summing the QWS energies at the zone centre might not reproduce the subtle difference caused by the two different interface reconstructions mentioned above. However, this simple model does have one major advantage, i.e. it is possible to make a rough estimate of the stable and unstable heights when only the bulk band structure is known. In a quantum well, the bulk bandstructure is quantized into equal parts corresponding to the number of monolayers, as indicated in Figure 1.9 for a 8 ML thick film of Pb grown in the (111) direction. This way, the energies of the resulting QWS can be approximated, and thicknesses where the QWS are close to the Fermi level will be less stable. The position where the upper branch of the sp-band crosses the Fermi level relative to the full Brillouin zone determines the number of monolayers that are needed to add one extra QWS to the upper branch. For Pb this is at 0.46 times the distance of Γ-L, resulting in one extra QWS approximately

Figure 1.9: Schematic representation for a 8 ML thick Pb(111) film of how the QWS binding energies can be obtained by cutting up the bulk band structure along the Γ-L direction. Only in the vicinity of E_F the spacing of the QWS is regular.

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28   M. Hupalo and M.C. Tringides, Surf. Sci. **493**, 526 (2001).
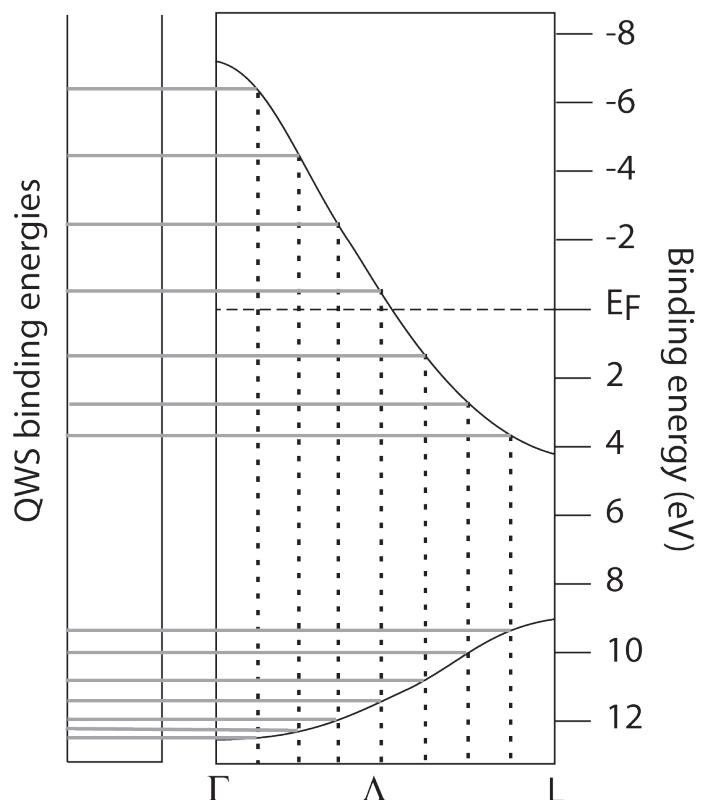
every two layers, which explains the overall trend of bilayer oscillations of stability also seen in Figure 1.6 for Pb. For layers thinner than 9 ML, the coverages with an even number of layers are more stable, between 9 and 16 ML the odd coverages are more stable. Beyond this coverage the "even" coverages are more stable again, oscillating with a period of 7 ML. This period can be explained by looking at the reduced quantum number $p = 3N - 2n$, where N corresponds to the number of atomic layers and n is the quantum number from Equation 1.3. When a branch of constant p crosses the Fermi level, the stable heights switch from even to odd or vice versa.

Self-organization is regarded as the formation of well-organized structures due to energy minimizing processes. Feynman's examples of nanoprinting or the manipulation of individual atoms to make a molecule[1], are the exact opposite of the self-organization principle discussed above. For possible technical applications, self-organization of metal or semiconductor structures on surfaces is most interesting because it could eliminate or reduce lithography steps. Electronic growth can thus be used to control the height of metallic nanostructures on surfaces, and therefore provides a self-organization pathway for the formation of such structures. Furthermore, electronic growth causes the islands to have steep edges and flat tops. Other experiments have shown that it is also possible to control the lateral size, orientation and distance of nano-objects[29].

1.4 Influence of the substrate and interface

When the size of a system is reduced, the surface-to-volume ratio increases, hence the boundary conditions become more and more important. In metallic quantum wells, the boundary is several atomic monolayers thick, causing an even larger influence of the boundaries. In the previous paragraph, the influence of the substrate-metal interface has been mathematically summarized into the phase shift at the interface. For the determination of the overall binding energy of the quantum well states, this is the correct approach; it does, however, not give any information about the physical effects taking place at the interface.

Figure 1.10 illustrates the three processes that can happen when an electron approaches an interface: (1) transmission of the electron across the interface, (2) incoherent backscattering whereby all phase information is lost, and (3) coherent backscattering. Only the last possibility will result in standing electron waves that constitute the quantum well states. In this paragraph, possible reasons why the first two processes might become important and limit coherent backscattering are discussed.

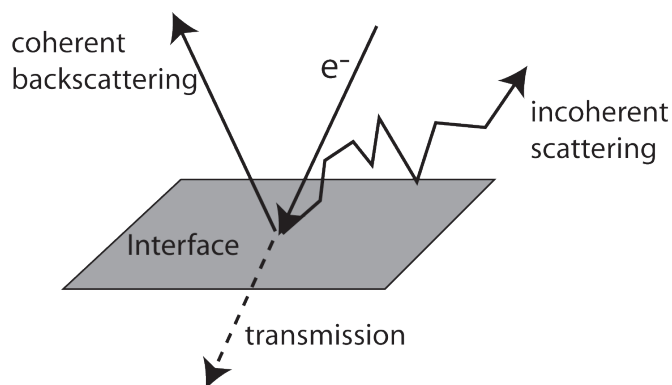29   M. Hupalo and M. C. Tringides, Phys. Rev. B **73**, 041405 (2006).

Figure 1.10: The three major events that can occur when an electron approaches an interface: (1) transmission of the electron across the interface, (2) incoherent backscattering whereby all phase information is lost, and (3) coherent backscattering. Only coherent backscattering can result in standing electron waves.

A necessary but not sufficient condition for the transmission of electrons across the metal-substrate interface is that, in the substrate, energy bands should exist that overlap with the energy of the QWS. This is the background for the common assumption that QWS can only exist within the bandgap of the substrate, and need to be referred to as quantum well resonances when they are outside the bandgap[17]. The reasoning behind this is illustrated by the $n = 3$ QWS in Figure 1.4, which is located just inside the Au(111) band gap. When the QWS moves a little lower, it can couple to the states in the substrate and will no longer be confined. That the presence of states in the substrate is not enough to allow for transmission into the substrate is illustrated for example by Al on Si(111)[19] where QWS can be seen until about 4 eV below the Fermi level, whereas the valence band maximum (VBM) of silicon and therefore the theoretical confinement threshold is located at around 0.5 eV below E_F. Similar observations have been made for other systems that do not have a perfect lattice match. This directly indicates the second condition for transmission of an electron across an interface: the interface has to provide a smooth transition from the overlayer lattice to the substrate one. For systems with a different interatomic distance, a smooth transition is nevertheless possible through some intermediate phase. This intermediate range can be a surface reconstruction of the substrate mediated by the overlayer material, or a disordered interface. An example of the first case is the √3x√3 reconstruction of Si(111) caused by Pb. On this reconstructed substrate, atomically flat layers can be grown[30]. The confinement threshold is defined by the VBM of the Si(111) and no QWS are observed outside this bandgap. On Si(111)7x7 the first layer of Pb grows with a 7x7 unit cell as well, but for higher coverages there is no well-defined crystalline structure at the interface. The electrons do, however, travel through the interface because the change in crystal structure is only gradual. This is indicated by the fact that there are again no QWS outside the silicon band gap[27]. States below the Si valence band maximum that are assigned as QWS are actually a result of the direct transition in the bulk band structure of Pb; this is obvious from the fact that the energy position does not change with coverage.

At first it seems counterintuitive that the bulk band can still be observed in a quantum well system, but this can be readily explained by considering Figure 1.4. From this figure it is clear that the wavefunction in the quantum well is composed of a rapidly oscillating Bloch wave derived from

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30   M.H. Upton et al, *Phys. Rev. Lett.* **93**, 26802 (2004).

the Pb interatomic spacing, modulated by the quantum well envelope wave function. One of the consequences of this is that in photoemission a direct transition from the QWS to the final state will occur at the same position where it would occur in the valence band in the k_z direction of the bulk crystal. This direct transition can also occur in thin films when no QWS is present at that energy position, stimulated by the disorder at the interface. Although a gradually changing interface will allow for transmission of the electron through the interface, it also limits coherent backscattering and therefore the formation of QWS. The bulk-derived Bloch wave does not depend on the interface structure; this will show up in photoemission spectra as features comparable to those for bulk Pb. This may lead to erroneous assignments of features in photoemission; in recent photoemission measurements for Pb on Si(111), broad features outside the bandgap are interpreted as QWS[27,31] although they do disperse with photon energy and do not shift with coverage.

This summarizes the two main processes that will limit coherent backscattering, and therefore adversely affect the formation of QWS. The degree of confinement of electrons depends only partly on the presence of a band gap in the substrate: it is the combination of lattice (mis)match and the electronic structure of the substrate and overlayer that matters. Controlling the interface structure is therefore an essential step towards the control of quantum wells structures.

31   M.H. Upton *et al*, Phys. Rev. B, **71**, 033403 (2005).