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First-principles Study of the Contractive Reconstruction of Gold
and Silver Monolayers on Gold, Silver, and Aluminum

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First-principles study of the contractive reconstruction
of gold and silver monolayers on gold, silver, and aluminum

Noboru Takeuchi

Under the supervision of Kai-Ming Ho
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Iowa State University

Using first-principles calculations in conjunction with modeling techniques, we have investigated the structures of Au and Ag monolayers on a number of metal surfaces. Au(100) has a $c(26 \times 68)$ surface unit cell and the reconstruction has been interpreted as the top layer transforming to a contracted hexagonal-close-packed layer, superimposed on the square lattice of the underlying substrate atoms. Similar reconstructions have been observed on the 5d fcc metals Ir and Pt, but not in the 4d Rh, Pd, and Ag. We studied the energetics of a monolayer of Au and Ag using first-principles calculations. We found that it is energetically favorable for both Au and Ag to transform from a square to hexagonal arrangement and to contract to a higher surface density, but Au gains substantially more energy than Ag. This is true both for a monolayer in isolation as well as on top of a jellium surface. We also calculated the "mismatch" energy (energy loss when the top layer loses registry with the substrate) for Au and Ag, and found that Ag has a slightly higher mismatch energy. The first-principles results thus offer a strong indication that Au(100) can reconstruct but Ag will not. The reconstruction is further studied with a 2 dimensional Frenkel-Kontorowa model, with parameters extracted from our total energy calculations. We found that it is indeed energetically favorable for the top layer of Au(100), but not for Ag, to transform to a hexagonal-close-packed structure and contract.

Au(111) has a $(22 \times \sqrt{3})$ surface unit cell, and there is strong experimental evidence that the reconstruction pattern is formed by an uniaxial contraction of the top layer of Au atoms, so that both the fcc (ABC stacking) and hcp (ABA stacking) surface sites are occupied by the surface Au atoms. The strong tendency for the Au top layer to contract has already been established. We calculated the energy for the Au atoms to occupy the high symmetry surface sites, and found that the fcc and hcp sites are almost equal in energy, the bridge site is slightly higher while the top site is very energetically unfavorable. The Au(111) surface reconstruction is simulated using a Frenkel-Kontorowa model. The lowest energy pattern is indeed a unilaterally contracted hexagonal layer, occupying both the fcc and the hcp sites. The surface band structures for the top layers occupying various sites are also studied.

Ag grows on Al(111) with the Stranski-Krastanov mode. For coverage less than 1 monolayer, Ag grows pseudomorphically on Al. For larger coverage, Ag cluster formation takes place, and the Ag monolayer is contracted. We use first-principles total energy calculations to study the energetics of Ag on Al(111) and decide under what conditions it is more favorable for Ag to grow epitaxially or to form clusters. The contraction of the Ag monolayer is considered using a Frenkel-Kontorowa model.

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Noboru Takeuchi

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CHAPTER 1. INTRODUCTION

Clean metal surfaces may have a structure that is not a simple termination of the bulk. This phenomenon, called reconstruction, indicates a change in the interatomic forces in the environment at the surface. It is important to understand the physical mechanism driving the reconstructions, and to be able to predict whether a surface will reconstruct or not. This understanding of the reconstruction, can help us understand the properties of the surface and also give information of how a clean surface interacts with absorbed atoms. Surface reconstructions are seen in all the low index surfaces of Au [1-13]. The (100) surface exhibits a $c(26 \times 68)$ pattern [1-6] the (110) surface shows a (2×1) "missing row" reconstruction [3,7], and the (111) surface a $((22 \pm 1) \times \sqrt{3})$ [1,8-13] unit cell. A common feature of all reconstructions is that the topmost layer becomes denser. Other 5d fcc metal Ir and Pt also show a similar reconstruction in the (100), and (110) surfaces, but the corresponding 4d fcc metals Ag, Rh, and Pd that have the same number of valence electrons, and similar lattice constants to their 5d counterparts Ir, Pt, and Au, do not show reconstructions in the (100) and (110) surfaces. Also, even though the (111) surface of Ag does not reconstruct, Ag on Al(111) shows a contraction when the coverage is larger than one monolayer [14].

The everyday advancement and development of computer technology is allowing

the study of newer systems using modern band theoretical methods. A few years ago, only bulk properties were possible to study using *ab initio* methods [15-36]. Today many surface geometries have been accurately determined [37-52]. However, in the case of Au, only the Au(110) (1x2) missing row reconstruction has been studied using first-principles [51]. The reason is that due to the large unit cells of the reconstructed unit cells of the (100) and (111) surfaces of Au, *ab initio* calculations are not feasible with today's computer capabilities. In this thesis, we study the complex reconstruction of the (100) and (111) surfaces of Au using first-principles total energy calculations and modeling techniques.

To completely understand the properties of a surface, we also need to know the way a surface grows. A crystal can grow in three different modes: layer by layer, forming clusters, or a combination of both. The type of growth mode can determine the properties of a surface. We study the growth of Ag on Al(111) using first-principles together with some modeling techniques.

At present, the most satisfactory approach to the one-electron description of the ground state properties of crystals is based on the local-density-functional (LDF) formalism [53]. The central quantity of LDF is the total energy, which is a variational minimum of the real ground state charge density. By accurately evaluating the ground state total energy self-consistently as a function of atomic position, we can determine surface geometries. These calculations also allow us to investigate the microscopic electronic causes of these geometries. In this thesis we use local-density-functional theory to explain the physical causes of the reconstruction or its absence in some of the (100) and (111) surfaces of Ag, Au, and Ag on Al(111).

Throughout our calculations, we use the frozen core approximation. In this

approximation, the nuclei plus the core electrons are considered as rigid ions which are assumed to be unresponsive to the change in their chemical environment.

Since the electronic properties of crystalline solids are most of the times dictated by the outermost electrons, we do not have to consider the inner electrons. The interaction of the cores and the valence electrons is then simulated by angular-momentum-dependent (non-local) pseudopotentials, which are generated using the "Norm Conserving" scheme [54]. In the pseudopotential approach, the core states are eliminated from the problem. Unlike the all electron wave-functions, the pseudo-wave-functions are smooth with no radial nodes.

The localized character of the *d* electrons makes the expansion for the wave-function in plane waves uneconomical. We use an energy independent mixed-basis set containing plane waves and Bloch sums of localized orbitals to represent the electronic wave-function. To facilitate the calculation of the total energy, a momentum space representation is used [55]. To accelerate the convergence of the self-consistent loop, we use a dielectric matrix scheme to calculate the new input potential that drastically reduces the number of iterations [56]. In our slab calculations, the interlayer distances are fully relaxed with the help of Hellmann-Feynman forces [57].

The reconstructions of the Au(100), Au(111), and Ag on Al(111) are discussed within the context of a two dimensional Frenkel-Kontorowa (FK) model [58], with parameters extracted from first-principles results. The 2D FK model describes a situation with two competing interactions: the top layer favoring a contraction to a denser arrangement, while the potential due to the substrate trying to pin the surface atoms in registry.

The properties of the *ab initio* pseudopotentials used in our calculations are

described in Chapter 2.

In Chapter 3, the formulation for the first-principles total energy calculations in solids, using a momentum-space formalism, is reviewed. A brief description of the mixed basis approach for the expansion of the electronic wave-function, and the self-consistent loop are given. In this chapter we also review briefly the Hellmann-Feynman theorem.

In Chapter 4, we study the energetics of a monolayer of Au and Ag using first-principles calculations. We find that it is energetically favorable for both Au and Ag to transform from a square lattice to a contracted hexagonal-close-packed arrangement. However, Au gains substantially more energy than Ag. This is true for both a monolayer in isolation, as well as on top of a jellium slab. Our calculations provide some insight of the microscopic origin of the difference in stability between 4d and 5d fcc metal (100) surfaces.

In Chapter 5, the (100) surfaces of the 4d and 5d fcc metals are studied using Au and Ag as prototypes. We calculate the mismatch energy (the energy loss when the top layer loses registry with the substrate) for Au and Ag and found that Ag has a slightly higher mismatch energy. The reconstruction is further studied with a 2-D Frenkel-Kontorowa model, with parameters extracted from our total energy calculations. It is found that indeed it is energetically favorable for the top layer of Au(100), but not for Ag, to transform to a contracted hexagonal-close-packed structure. The value of the contraction in the area found in our calculations agrees very well with the experimental values.

In Chapter 6, the (111) surface of Au is studied. There is strong experimental evidence that the reconstruction pattern is formed by an uniaxial contraction of the

top layer of Au atoms in such a way that both the fcc (ABC stacking), and the hcp (ABA stacking) surface sites are occupied by the surface Au atoms [13]. The strong tendency of the Au top layer to contract has already been established in Chapter 5. The energies for the top Au atoms to occupy high symmetry sites in the (111) surface are calculated. It is found that indeed the fcc and hcp sites are almost equal in energy, the bridge site is slightly higher, while the top site is very energetically unfavorable. The Au(111) surface reconstruction is then simulated using a Frenkel-Kontorowa model, with parameters determined by first-principles results. For the ground state, the surface layer contracts uniaxially along the $(1\bar{1}0)$ direction, occupying both the fcc and hcp sites. Also in this chapter, the surface band structures for the top layer of atoms occupying various sites are studied.

In Chapter 7 we study the growth of Ag on Al(111). Experimentally [14] it has been shown that Ag grows on Al(111) in the Stranki-Krastanov mode (forming layers at the beginning, and then clusters later). With the onset of cluster growth in the second layer, the monolayer of Ag is contracted. Using first-principles total energy calculations this growth is studied. It is found that indeed at the beginning Ag grows pseudomorphically, but later prefers the formation of clusters. A physical explanation is given. Also with a 2D-FK model we study the contraction for coverage of one monolayer.

CHAPTER 2. NORM-CONSERVING PSEUDOPOTENTIALS

Concepts

Even with today's computer capabilities, it is impossible to calculate the wave function for all the electrons in the solid. To study a problem, particularly in solid state physics, we have to pick out the essential factors that describe the problem, and drop out other minor effects, as long as they do not affect the solution in a significant way.

A solid can be thought of as a set of rather tightly bound spherical ions (the atomic cores) sitting in the electron cloud formed by the valence electrons. These valence electrons are responsible for almost all the ordinary physical and chemical properties. The pseudopotential was introduced to simplify electronic structure calculations by eliminating the atomic core states and the strong potentials responsible for binding them [15]. At the beginning two distinct lines of development were discernible: in one, ion pseudopotentials of enforced smoothness were empirically fitted to reproduce experimental energy bands [59]. Consequently, wave functions were only approximately described. The second one has its origin in the Orthogonalized-Plane-Wave (OPW) method for band structure calculations introduced by Herring [60]. For the wavefunctions of the electrons in the crystal he used a linear combination of core states and plane waves that he made orthogonal to the filled core states. This

approach produces wave functions that are plane wave-like except in the core region where they must have enough oscillations in order to be orthogonal to the core-state wave functions. In the late '50s Phillips and Kleinman [61] showed that Herring's wave-functions can be derived as solutions for a problem in which a repulsive potential cancels much of the core potential, producing a net weak pseudopotential. These pseudopotentials are generally strongly repulsive at the origin, making it difficult to employ Fourier analysis in solids because of the large number of basis functions required. The resulting wave functions generally exhibit the correct shape outside the core region; however they differ from the real wave-functions by a normalization factor.

Since the pseudopotential is a device to eliminate the core states from the problem, the pseudo-wave-functions need only to reproduce the true valence wave-functions in the valence region. There is no need to refer to the core states and the pseudo-wave-functions do not need to be orthogonal to the core-state wave functions. This is the idea of the "Norm-Conserving" pseudopotential developed by Hamann, Schlüter, and Chiang [54]. Their new family of energy-independent pseudopotentials have the following properties:

1. The pseudopotential must reproduce the corresponding eigenvalues from an all-electron calculation.
2. The pseudo-wave-function, after normalization, must be identical to the true valence wave-function outside a chosen "core radius" r_c
3. The integrals from 0 to r of the real and pseudo charge density agree for $r > r_c$

for each valence state (norm conservation)

$$\int_0^r \rho_{ps}(\mathbf{r}) d\mathbf{r} = \int_0^r \rho_{el}(\mathbf{r}) d\mathbf{r}, r \geq r_c, \quad (2.1)$$

4. The logarithmic derivatives of the real and pseudo-wave-function and their first energy derivatives agree for $r > r_c$.

Properties (3) and (4) are crucial for the pseudopotential to have optimum transferability among a variety of environments in self-consistent calculations in which the pseudo charge density is treated as a real physical object. Property (3) guarantees, through Gauss's theorem, that the electrostatic potential produced outside r_c is identical for the real and pseudo charge distributions.

The pseudopotential obtained in this way converges identically to the atomic Coulomb potential outside the core region for each valence state. In general pseudopotentials are not unique and are non-local operators.

Fitting Procedure for the Norm-conserving Pseudopotential

The generation of our pseudopotential is done according to the scheme of Hamann, Schlüter, and Chiang [54]. They freed the construction of the atomic pseudo-orbital from reliance on core states. The construction proceeds as follows:

1. We first choose an appropriate atomic reference configuration, which often differs somewhat from the ground state, and carry out an *ab initio* self-consistent all electron calculation using a Herman-Skillman-like program [62]. The local-density-function approximation is used, and for the exchange correlation potential we use the Hedin-Lundqvist [63] form. We retain both the potential

$V(r)$ and also $u_l(r)$, defined as r times the valence wave function with angular momentum l .

2. For each valence state l , we obtain the potential in the form:

$$V_{1,l}(r) = V(r)[1 - f(r/r_{cl})] + c_l f(r/r_{cl}), \quad (2.2)$$

where r_{cl} is the cutoff radius for each l . The restrictions are that $f(x)$ is a smooth "cutoff function" which approaches 0 as $x \rightarrow \infty$, approaches 1 at least as fast as x^3 as $x \rightarrow 0$, and cuts off for $x \sim 1$. The constant c_l is adjusted so that the nodeless solution w_{1l} of the radial Schrödinger equation with V_{1l} has energy ϵ_{1l} equal to the original eigenvalue ϵ_l . This potential converges to $V(r)$ for $r > r_{cl}$.

Property (1) of the last section is now satisfied, and the normalized function w_{1l} satisfies property (2) within a multiplicative constant,

$$w_{1l}(r) = \gamma_l u_l(r), \text{ for } r > r_c \quad (2.3)$$

3. Now we have to satisfy the norm-conserving constraint (conditions 2-4). We modify the intermediate pseudo-wave-function w_{1l} to

$$w_{2l}(r) = \gamma_l [w_{1l}(r) + \delta_l g_l(r/r_{cl})], \quad (2.4)$$

where $g_l(x)$ cuts off to zero for $x > 1$, and behaves as x^{l+1} at small x . The chosen asymptotic behavior of $f(x)$, and $g(x)$ guarantees the potential to be finite at the origin. The choice of cutoff functions used by Hamann, Schlüter, and Chiang is $f(x) = \exp(-x^c)$, and $g_l(x) = x^{l+1} \exp(-x^c)$ where c is varied in the fitting to assure the pseudo-wave-function $w_{2l}(r)$ is a smooth function.

The δ_l is determined by the smaller solution of the quadratic equation resulting from the normalization requirement of the wave function:

$$\gamma_l^2 \int_0^\infty [w_{1l}(r) + \delta_l g_l(r/r_{cl})]^2 dr = 1 \quad (2.5)$$

4. The final screened pseudopotential V_{2l} defined as that potential which produces the nodeless pseudo-orbital w_{2l} with eigenvalue $\epsilon_{2l} = \epsilon_k$, is found by inverting the radial Schrödinger equation. The result is given by:

$$\begin{aligned} V_{2l}(r) &= V_{1l}(r) + \left[\frac{1}{w_{2l}(r)} \frac{d^2}{dr^2} w_{2l}(r) - \frac{1}{w_{1l}(r)} \frac{d^2}{dr^2} w_{1l}(r) \right] \quad (2.6) \\ &= \frac{\delta_l g_l(r/r_c)}{w_{1l}(r) + \delta_l g_l(r/r_c)} \left[\epsilon_l - V_{1l}(r) - \frac{l(l+1)}{r^2} \right. \\ &\quad \left. + \frac{1}{g_l(r/r_c)} \frac{d^2 g_l(r/r_c)}{dr^2} \right] + V_{1l}(r). \end{aligned}$$

5. The final step is to obtain the ionic pseudopotential $V_{ps,l}(r)$ by unscreening $V_{2l}(r)$:

$$V_{ps,l}(r) = V_{2l}(r) - (V_H(r) + V_{xc}(r)), \quad (2.7)$$

where $V_H(r)$ and $V_{xc}(r)$ are the Hartree and the exchange-correlation potential, respectively, which can be calculated from the pseudo charge distribution.

Applications to Ag, Au, and Non-relativistic Au

We have used in our calculations non-local ionic pseudopotentials generated using the norm-conserving scheme of Hamann, Schlüter, and Chiang. These angular-momentum-dependent pseudopotentials are constructed by constraining their pseudo-wave-functions to match the ground-state, all-electron, valence-electron wave-functions

exactly outside some "core-radius", as well as reproducing the same atomic eigenvalues for the valence states. Au is a heavier atom than Ag. One then expects relativistic effects to be more important in Au than in Ag. Relativity affects mostly the core electrons, specially electrons in s orbitals which have substantial amplitudes near the atom. The effect on the valence electronic structure is a lowering of the s-like bands relative to the d-like bands. This can be understood as an effect coming from the changes in core orthogonality repulsion as relativity produces a shrinking in the orbitals of the core s electrons. In our calculations, this effect (the scalar relativistic effect) is included by constructing our pseudopotential by fitting to all-electron results obtained from solving the Dirac equation for the atom. The other relativistic effect, spin-orbit coupling, is not included in our calculations. In order to check the importance of the relativistic effects in Au, we have generated both a non-relativistic and a scalar relativistic pseudopotential for Au. The Ag, Au non-relativistic, and Au scalar relativistic pseudopotentials are shown in Figures (2.1) to (2.3). To check the transferability of our pseudopotential, we compare the eigenvalues and excitation energies for various atomic configurations above the ground state obtained from the pseudopotentials with the corresponding all-electron values. The results are listed in Tables (2.1) to (2.3). We see that the pseudopotential results reproduced the all-electron results with an error of less than 0.008 Ry for all excited configurations.

Table 2.1: Eigenvalues and excitation energies of the pseudoatom for different configurations of scalar relativistic Au. Values in parentheses denote the deviations from the corresponding all-electron results

Configuration	Eigenvalues (Ry)			Excitation energy (Ry)
	d	s	p	(ΔE_{tot})
$5d^{10}6s^1$	-0.5267 (0.0023)	-0.4502 (0.0038)	-0.0728 (-0.0023)	0
$5d^96s^2$	-0.6803 (-0.0015)	-0.5126 (0.0055)	-0.0986 (-0.0014)	0.1210 (0.0040)
$5d^{10}6p^1$	-0.6750 (0.0053)	-0.5624 (0.0058)	-0.1549 (-0.0012)	0.3908 (-0.0062)
$5d^96s^16p^1$	-0.8248 (0.0001)	-0.6188 (0.0068)	-0.1748 (-0.0007)	0.5491 (-0.0041)
$5d^86s^26p^1$	-0.9889 (-0.0070)	-0.6782 (0.0076)	-0.1959 (0.0003)	0.8065 (0.0075)

Table 2.2: Eigenvalues and excitation energies of the pseudoatom for different configurations of Ag. Values in parentheses denote the deviations from the corresponding all-electron results

Configuration	Eigenvalues (Ry)			Excitation Energy (Ry)
	d	s	p	(ΔE_{tot})
$4d^{10}5s^1$	-0.6029 (0.0003)	-0.3169 (0.0049)	-.0700 (.0002)	0
$4d^{10}5p^1$	-0.7340 (0.0034)	-0.4096 (0.0035)	-0.1385 (-.0001)	0.2561 (-0.0043)
$4d^95s^2$	-0.8644 (0.0026)	-0.4085 (0.0067)	-0.1139 (0.0004)	0.3714 (0.0050)
$4d^95s^15p^1$	-0.9827 (-0.0059)	-0.4851 (0.0022)	-0.1728 (0.0024)	0.6729 (0.0035)

Table 2.3: Eigenvalues and excitation energies of the pseudoatom for different configurations of non-relativistic Au. Values in parentheses denote the deviations from the corresponding all-electron results

Configuration	Eigenvalues (Ry)			Excitation Energy (Ry)
	d	s	p	(ΔE_{tot})
$5d^{10}6s^1$	-0.6148 (0.0000)	-0.3315 (0.0002)		0
$5d^{10}6p^1$	-0.7376 (0.0005)	-0.4159 (0.0002)	-0.1417 (0.0001)	0.2643 (-0.0001)
$5d^96s^2$	-0.8362 (-0.0052)	-0.4095 (0.0019)	-0.1154 (0.0016)	0.3536 (0.0034)
$5d^96s^16p^1$	-0.9483 (-0.0062)	-0.4841 (0.0013)	-0.1731 (0.0013)	0.6558 (0.0032)
$5d^{8.5}6s^16p^{0.5}$	-1.5983 (-0.0069)	-0.9932 (0.0032)	-0.6087 (0.0039)	1.4773 (0.0052)
$5d^86s^{0.5}6p^{0.5}$	-2.3988 (0.0089)	-1.6136 (0.0040)	-1.1586 (0.0057)	3.1223 (0.0072)

Figure 2.1: The angular-momentum-dependent (scalar relativistic pseudopotential) for Au

Figure 2.2: The angular-momentum-dependent pseudopotential for Ag

Figure 2.3: The angular-momentum-dependent pseudopotential for nonrelativistic Au

CHAPTER 3. GENERAL FORMALISM FOR TOTAL ENERGY IN SOLIDS

Local-density-functional Theory

The electronic and structural properties of the surfaces considered in this thesis are calculated with the density functional formalism [53], which is one of the most widely used methods to study the ground state property of solid state systems [64]. Hohenberg and Kohn showed that the total ground state energy of a many-electron system in the presence of an applied external potential (in our case, the valence electrons in the presence of the ionic potentials) is a unique functional of the charge density $\rho(\mathbf{r})$. In this approach, the total energy can be expressed in atomic units as:

$$E_T[\rho(\mathbf{r})] = T[\rho] + \frac{1}{2} \int \int \frac{2\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}d\mathbf{r}' + E_{xc}[\rho] + \int V(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + E_{c-c} \quad (3.1)$$

where $T[\rho]$ represents the kinetic energy of a system of non-interacting electrons of density ρ , the second term the electronic Hartree energy, the third term the exchange correlation energy, the fourth term the electron-core interaction energy ($V(\mathbf{r})$ is the external potential, in this case the potential due to the cores), and the last term represents the core-core interaction.

Within the local density approximation (LDA) the exchange-correlation func-

tional is expressed as:

$$E_{xc}[\rho(\mathbf{r})] = \int \epsilon_{xc}(\rho(\mathbf{r})) d\mathbf{r}, \quad (3.2)$$

where $\epsilon_{xc}(\rho(\mathbf{r}))$ is the exchange-correlation energy per electron of an uniform electron gas of density $\rho(\mathbf{r})$. $\epsilon_{xc}(\rho(\mathbf{r}))$ is not known exactly for an arbitrary charge density, but approximations such as the Wigner interpolation formula [65], Hedin-Lundqvist local exchange-correlation potential [63], and analytical fit to Ceperley-Alder's Monte Carlo results [66] are often used. We use in this thesis the Hedin-Lundqvist form for the exchange-correlation functional.

Hohenberg and Kohn [53] also proved a variational principle which states that the correct charge $\rho(\mathbf{r})$ minimizes the energy functional. This variational principle, together with the local density approximation and the constraint of particle conservation, results in the following set of equations (in atomic units):

$$[-\nabla^2 + V_{eff}] \psi(\mathbf{r}) = \epsilon_i \psi(\mathbf{r}), \quad (3.3)$$

$$\rho(\mathbf{r}) = \sum_{i=1}^N n_i |\psi(\mathbf{r})|^2, \quad (3.4)$$

where n_i is the occupation number of state i and N is the total number of electrons in the system.

The effective potential, V_{eff} , is given by:

$$\begin{aligned} V_{eff}[\rho(\mathbf{r})] &= V_c(\mathbf{r}) + V_H(\mathbf{r}) + V_{xc}(\mathbf{r}) \\ &= V_c(\mathbf{r}) + \int \frac{2\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' + \frac{\delta(E_{xc}[\rho(\mathbf{r})])}{\delta\rho(\mathbf{r})} \end{aligned} \quad (3.5)$$

These equations are to be solved self-consistent for the charge density $\rho(\mathbf{r})$, which in turn will determine the ground state properties of the system under consideration.

Up to this point, the density functional formalism together with the local density approximation basically reduces a many body problem to solving a set of one-particle Schrödinger-like equations.

Momentum-space Formalism for the Total Energy of Solids

A momentum-space formalism for calculating the total energy of solids designed particularly for application with the self-consistent pseudopotential method was first derived by Ihm, Zunger, and Cohen [55]. Assuming non-overlapping ion cores, Equation (3.1) can be written in atomic units as:

$$\begin{aligned}
 E_T = \sum_i n_i \langle \psi_i | -\nabla^2 | \psi_i \rangle &+ \frac{1}{2} \int \int \frac{2\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r} d\mathbf{r}' \\
 &+ \int \epsilon_{xc}(\rho(\mathbf{r})) d\mathbf{r} + \sum_{\mathbf{R}, \tau} \left[\int \rho(\mathbf{r}) V_{ps}^L(\mathbf{r} - \mathbf{R} - \tau) d\mathbf{r} \right. \\
 &\quad \left. + \sum_{i,l} n_i \langle \psi_i | V_{ps,l}^{NL}(\mathbf{r} - \mathbf{R} - \tau) \hat{P}_l | \psi_i \rangle \right] \\
 &\quad + \frac{1}{2} \sum'_{\mathbf{R}, \mathbf{R}', \tau, \tau'} \frac{2Z_V^2}{|\mathbf{R} + \tau - \mathbf{R}' - \tau'|}
 \end{aligned} \tag{3.6}$$

where the prime in the summation means the $|\mathbf{R} + \tau - \mathbf{R}' - \tau'| = 0$ term is excluded; $\mathbf{R}$ denotes the lattice vector; τ denotes the basis vector; Z_V is the effective ionic charge; and V_{ps}^L is the local part of the pseudopotential that acts equally on all the angular momentum components of the wave function. The non-local part defined as:

$$V_{ps,l}^{NL}(\mathbf{r}) = V_{ps,l}(\mathbf{r}) - V_{ps}^L(\mathbf{r}), \tag{3.7}$$

where $V_{ps,l}$ and $\hat{P}_l$ are the core pseudopotential and the projection operator for angular momentum l , respectively.

Thus, the long range part (singular part) of the pseudopotential has been isolated in to the local part, making $V_{ps,l}^{NL}$ short range.

To simplify equation (3.6), we multiply on the left of equation (3.3) by $\psi_i^*(\mathbf{r})$, integrate over $\mathbf{r}$ and sum over i , and substitute in to equation (3.1). The total energy per primitive cell becomes in reciprocal space:

$$E_T = 2 \sum_{nk}^{(occ.)} w_k \epsilon_{nk} - \Omega_{cell} \left[\frac{1}{2} \sum_{\mathbf{G}} \frac{8\pi |\rho(\mathbf{G})|^2}{|\mathbf{G}|^2} + \sum_{\mathbf{G}} \rho(\mathbf{G}) (\epsilon_{xc}(\mathbf{G}) - v_{xc}(\mathbf{G})) \right] + \frac{1}{2} \sum_{\mathbf{r}, \tau, \tau'} \frac{2Z_V^2}{|\mathbf{R} + \tau - \tau'|} \quad (3.8)$$

The first term is the sum of the occupied band energies, w_k is the weight of each sampled $\mathbf{k}$ -point, and n is the band index, Ω_{cell} is the volume of the primitive cell, and $\mathbf{G}$ denotes the reciprocal lattice vector.

In practice, some mathematical manipulations are necessary to calculate E_T from equation (3.7) because $V_{Coul}(0)$, $V_{ps}(0)$ and $\frac{1}{2} \sum_{\mathbf{r}, \tau, \tau'} \frac{2Z_V^2}{|\mathbf{R} + \tau - \tau'|}$ are individually divergent quantities. First we solve the band-structure eigenvalue problem, with $V_{Coul}(0)$ and $V_{ps}(0)$ set equal to zero. This corresponds to a constant shift of the potential. To compensate for the arbitrary shift we add $(\alpha_1 Z + \gamma_{Ewald})$ to the total Energy. γ_{Ewald} is the Coulomb interaction energy of the positive ion cores together with the neutralizing homogeneous background, and can be evaluated using the Ewald method [67]. α_1 is give by

$$\alpha_1 = \frac{N_a}{\Omega_{at}} \int (V_{ps}^L(\mathbf{r}) + \frac{2Z_V}{r}) d\mathbf{r}, \quad (3.9)$$

where N_a is the number of atoms per primitive cell and Ω_{at} is the atomic volume.

The final expression for the total energy per unit cell is:

$$E_T = 2 \sum_{nk}^{(occ.)} w_{nk} \epsilon_{nk} - \Omega_{cell} \left[\frac{1}{2} \sum_{|\mathbf{G}| \neq 0} \frac{8\pi |\rho(\mathbf{G})|^2}{|\mathbf{G}|^2} + \sum_{\mathbf{G}} \rho(\mathbf{G}) (\epsilon_{xc}(\mathbf{G}) - v_{xc}(\mathbf{G})) \right] + (\alpha_1 Z + \gamma_{Ewald}) \quad (3.10)$$

Equation (3.10) is rewritten to facilitate the self-consistent calculations as follows:

$$E_T = \sum_{nk} f_{nk} \epsilon_{nk} - \Omega_{cell} \sum_{\mathbf{G}} \rho(\mathbf{G}) V_{sc}^{in}(\mathbf{G}) + \Omega_{cell} \frac{1}{2} \sum_{|\mathbf{G}| \neq 0} \frac{8\pi |\rho(\mathbf{G})|^2}{|\mathbf{G}|^2} + \Omega_{cell} \sum_{\mathbf{G}} \rho(\mathbf{G}) \epsilon_{xc}(\mathbf{G}) + (\alpha_1 Z + \gamma_{Ewald}), \quad (3.11)$$

where f_{nk} in the first term is the weight of each state, and V_{sc}^{in} in the second term is the reciprocal space component of the input screening potential for the self-consistent band calculation given by

$$V_{sc}^{in}(\mathbf{G}) = \frac{8\pi \rho(\mathbf{G})}{|\mathbf{G}|^2} + v_{xc}(\mathbf{G}) \quad (3.12)$$

Mixed-basis Approach to the Electronic Structure

In most band-theoretical methods, the electronic wave-function is expanded in a set of basis functions and the solutions to the Schrödinger equation are obtained by variational procedures. It is important to choose a small, yet physically complete, set of functions. For the systems we are dealing with, the localized character of the d electrons makes the expansion for the wave-functions in plane waves uneconomical. In order to treat a system such as this, with atomic-like character as well as extended plane-wave-like character, an energy-independent basis set containing both plane

waves and Bloch sums of localized orbitals are used to represent the electronic wave-functions [68].

$$\psi_{n\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \sum_{\mathbf{G}} \alpha_n(\mathbf{k} + \mathbf{G}) e^{i(\mathbf{k} + \mathbf{G}) \cdot \mathbf{r}} + \sum_{jm} \beta_{jm}(n, \mathbf{k}) \phi_{jm}(\mathbf{k}, \mathbf{r}), \quad (3.13)$$

with

$$\phi_{jm}(\mathbf{k}, \mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{R}} e^{i\mathbf{k} \cdot (\mathbf{R} + \tau_j)} f_{jm}(\mathbf{r} - \mathbf{R} - \tau_j) \quad (3.14)$$

In these equations, Ω is the crystal volume, N is the number of atoms, and m is the label for the orbital on the j^{th} atom. In the case of Au we use for $f_{jm}(\mathbf{r})$ Gaussian local orbitals of the form:

$$f_m(\mathbf{r}) = N' r^2 e^{-\lambda r^2} Y_{2m}(\hat{a}), \quad (3.15)$$

to represent the localized part of the d electronic wave function, where N is the normalization constant, and λ is the Gaussian exponent.

In the case of silver, due to the fact that the 4d states are more localized than the Au 5d states, we have used for the local orbital a numerical basis of the form:

$$\begin{aligned} f'(r) &= B f(r) [1 - \exp[-\alpha(r_c - r)^2]], r \leq r_c \\ &= 0, r > r_c \end{aligned} \quad (3.16)$$

where $f(r)$ is a radial function closely related to the radial distribution of the atomic d wave function, B is a normalization constant, and α is determined variationally [32, 33].

This mixed-basis leads to the following matrix eigenvalue problem:

$$(H - ES)\Lambda = 0, \quad (3.17)$$

where H is the Hamiltonian matrix, S is the overlap matrix, and Λ is a column vector with elements $\lambda_1, \dots, \lambda_n$ corresponding to the expansion coefficients α, β in equation (3.12)

When evaluating the matrix elements involving the local orbital, if we are using the Gaussian as local orbital we make use of the on-site approximation [68], but when using the numerical basis, the "on-site" approximation becomes exact if r_c is smaller than the nearest-neighbor distance.

The valence charge density is then calculated from:

$$\rho(\mathbf{r}) = 2 \sum_{n\mathbf{k}} \theta(\epsilon_f - \epsilon_{n\mathbf{k}}) |\psi_{n,\mathbf{k}}(\mathbf{r})|^2, \quad (3.18)$$

where $\theta(x)$ is the step function and ϵ_f is the Fermi energy and is determined from the number of electrons per primitive cell, z , by the equation:

$$z = 2 \sum_{n\mathbf{k}} \theta(\epsilon_f - \epsilon_{n\mathbf{k}}) \quad (3.19)$$

In practice, the $\mathbf{k}$ summation is restricted to the irreducible part of the Brillouin zone determined by symmetry and only the part of the charge density invariant under all the space group operations is retained.

Dielectric Matrix Scheme for Fast Convergence

The one-electron wave-functions are obtained from the Schrödinger equation:

$$(-\nabla^2 + V)\psi_{n\mathbf{k}} = E_{n\mathbf{k}}\psi_{n\mathbf{k}}, \quad (3.20)$$

where the crystal potential V is constructed as the sum of three components V_{ion} , V_H , and V_{xc} . V_{ion} is the superposition of the potentials due to the bare ions on

the various atomic sites, V_H is the Hartree potential, and V_{xc} is the local exchange-correlation potential. V_H , and V_{xc} are obtained from the electronic density ρ by the following equations:

$$\nabla^2 V_H = -4\pi e^2 \rho(\mathbf{r}), \quad (3.21)$$

$$V_{xc}(\mathbf{r}) = -\beta(3/\pi)^{1/3} e^2 \rho(\mathbf{r})^{1/3} \quad (3.22)$$

where β can be a constant or a function of $\rho(\mathbf{r})$ [63, 69]. We start with an initial guess V_{in} for $V_H + V_{xc}$, and find the solution of equation (3.20). With these wave-functions we can obtain the electron density using equation (3.18) that we write here again:

$$\rho(\mathbf{r}) = 2 \sum_{n\mathbf{k}} f_{n\mathbf{k}} |\psi_{n,\mathbf{k}}(\mathbf{r})|^2, \quad (3.23)$$

where $f_{n\mathbf{k}}$ is the occupation factor and 2 is the spin factor. From this electron density, the Hartree screening potential and the exchange-correlation (Hedin-Lundvist form [63]) potential of the electrons are calculated. With these two potentials, an output potential V_{out} is constructed. Self-consistency requires that this procedure be repeated until V_{in} is equal to V_{out} . Usually this is achieved by putting in a new V_{in} constructed by mixing the old V_{in} and V_{out} as following:

$$V_{in}^{new}(\mathbf{G}) = c V_{in}^{old}(\mathbf{G}) + (1 - c) V_{out}^{old}(\mathbf{G}) \quad (3.24)$$

where the mixing coefficient, c , is a function of $\mathbf{G}$ which corresponds to screening the charge density oscillation by a Fermi-Thomas type dielectric function. However, for surface calculations, with large unit cell, the low $\mathbf{G}$ components of the potential converge very slowly and, furthermore, the various Fourier components are found to

be strongly coupled so that a simple mixing scheme like the one above is no longer adequate.

Ho *et al.* [56] devised a scheme that drastically reduces the number of iterations required to reach self-consistency in electronic-structure calculations. Suppose the input and output potentials for the n th iteration are V_{in} and V_{out} respectively. We want δV_{in} such that:

$$V_{in} + \delta V_{in} = V_{out} + \delta V_{out} \quad (3.25)$$

δV_{out} can be expressed in terms of δV_{in} using perturbation theory,

$$\delta \rho(\mathbf{G}) = \frac{1}{\Omega_c} \sum_{\mathbf{G}'} \chi(\mathbf{G}, \mathbf{G}') \delta V_{in}(\mathbf{G}'), \quad (3.26)$$

where Ω_c is the cell volume, and the susceptibility χ is given by:

$$\chi(\mathbf{G}, \mathbf{G}') = -2 \sum_{n, n', \mathbf{k}} (f_{n, \mathbf{k}} - f_{n', \mathbf{k}'}) \frac{\langle n\mathbf{k} | e^{-i\mathbf{G} \cdot \mathbf{r}} | n'\mathbf{k}' \rangle \langle n'\mathbf{k}' | e^{i\mathbf{G}' \cdot \mathbf{r}} | n\mathbf{k} \rangle}{E_{n', \mathbf{k}'} - E_{n, \mathbf{k}}} \quad (3.27)$$

We know that

$$\delta V_{out} = \delta V_H + \delta V_{xc} \quad (3.28)$$

where δV_H and δV_{xc} can be derived from equations (3.21) and (3.22). Using equations (3.24), (3.25) and (3.26) we obtain:

$$\sum_{\mathbf{G}, \mathbf{G}'} \epsilon(\mathbf{G}, \mathbf{G}') \delta V_{in}(\mathbf{G}') = V_{out}(\mathbf{G}) - V_{in}(\mathbf{G}), \quad (3.29)$$

$$\epsilon(\mathbf{G}, \mathbf{G}') = \delta(\mathbf{G} - \mathbf{G}') - \frac{1}{\Omega} \sum_{\mathbf{G}''} v_{xc}(\mathbf{G} - \mathbf{G}'') \chi(\mathbf{G}'', \mathbf{G}') - \frac{8\pi}{G^2 \Omega} \chi(\mathbf{G}, \mathbf{G}') \quad (3.30)$$

where $v_{xc}(\mathbf{G})$ is the Fourier transform of the exchange correlation interaction $v_{xc}(\mathbf{r})$, which is the functional derivative of the exchange-correlation potential:

$$v_{xc} = \frac{\delta V_{xc}}{\delta \rho} \quad (3.31)$$

Thus, given V_{out} , and V_{in} , we can obtain δV_{in} by a matrix inversion.

Since only the low Fourier components are strongly coupled, it is only necessary to calculate $\epsilon(\mathbf{G}, \mathbf{G}')$ for only few starts of reciprocal lattice vectors.

Hellmann-Feynman Forces

The use of the Hellmann-Feynman theorem helps us minimize the number of trial geometries needed to determine the equilibrium geometry, and allow us to relax all the layers simultaneously. It was first proved for the case of the all-electron problem [57], and then extended to the case of pseudopotential calculations [55]. We start with the expression for the total energy per primitive unit cell given in equation (3.11), and suppose that the position of one of the atoms in the unit cell is changed by a displacement $\delta \tau$. This change in the displacement causes a change in the total energy given by:

$$\begin{aligned} \delta E_T = & \sum_{n\mathbf{k}} (f_{n\mathbf{k}} \delta \epsilon_{n\mathbf{k}} + \delta f_{n\mathbf{k}} \epsilon_{n\mathbf{k}}) - \Omega_{cell} \left[\sum_{\mathbf{G}} \rho(\mathbf{G}) \delta V_{sc}^{in}(\mathbf{G}) \right. \\ & \left. + \sum_{\mathbf{G}} \delta \rho(\mathbf{G}) (V_{sc}^{in}(\mathbf{G}) + \frac{8\pi |\rho(\mathbf{G})|^2}{|\mathbf{G}|^2} + v_{xc}(\mathbf{G})) \right] + \delta \gamma_{Ewald}. \end{aligned} \quad (3.32)$$

because the self-consistency criteria guarantees that

$$V_{sc}^{in}(\mathbf{G}) = \frac{8\pi \rho(\mathbf{G})}{|\mathbf{G}|^2} + v_{xc}(\mathbf{G}) \quad (3.33)$$

the term involving $\delta\rho(\mathbf{G})$ drops out, and equation (3.28) becomes:

$$\delta E_T = \sum_{n\mathbf{k}} (f_{n\mathbf{k}} \delta \epsilon_{n\mathbf{k}} + \delta f_{n\mathbf{k}} \epsilon_{n\mathbf{k}}) - \Omega_{cell} \sum_{\mathbf{G}} \rho(\mathbf{G}) \delta V_{sc}^{in}(\mathbf{G}) + \delta \gamma_{Ewald}. \quad (3.34)$$

To evaluate the first term in equation (3.30) (the change in band energies) we use perturbation theory:

$$\begin{aligned} \sum_{n\mathbf{k}} f_{n\mathbf{k}} \delta \epsilon_{n\mathbf{k}} &= \sum_{n\mathbf{k}} (f_{n\mathbf{k}} \langle \psi_{n\mathbf{k}} | \delta V_{ion} + \delta V_{sc}^{in} | \psi_{n\mathbf{k}} \rangle) \\ &= \sum_{n\mathbf{k}} (f_{n\mathbf{k}} \langle \psi_{n\mathbf{k}} | \delta V_{ion} | \psi_{n\mathbf{k}} \rangle + \Omega_{cell} \sum_{\mathbf{G}} \rho(\mathbf{G}) \delta V_{sc}^{in}(\mathbf{G})), \end{aligned} \quad (3.35)$$

where δV_{ion} is the change in the ionic potential:

$$V_{ion}(\mathbf{r}) = \sum_{\mathbf{R}, \tau, l} V_{ps,l}(\mathbf{r} - \mathbf{R} - \tau) \hat{P}_l. \quad (3.36)$$

Using equations (3.30) and (3.31) we can calculate the force on each atom. This force can be divided into two terms:

$$\mathbf{F} = \frac{-\delta E_T}{\delta \tau} = \mathbf{F}_{ion} + \mathbf{F}_{el}, \quad (3.37)$$

where

$$\mathbf{F}_{ion} = -\frac{\delta \gamma_{Ewald}}{\delta \tau}, \quad (3.38)$$

$$F_{el} = -\sum_{n\mathbf{k}} (f_{n\mathbf{k}} \langle \psi_{n\mathbf{k}} | \frac{\delta V_{ion}}{\delta \tau} | \psi_{n\mathbf{k}} \rangle + \frac{\delta f_{n\mathbf{k}}}{\delta \tau} \epsilon_{n\mathbf{k}}) \quad (3.39)$$

$\mathbf{F}_{ion}$ is the ionic restoring force, and $\mathbf{F}_{el}$ is the electronic force which is made up of contributions from all the occupied states.

Calculational Procedures

In this section, we describe the calculation procedures used in the self-consistent band calculations.

1. Choose the initial position of the atoms (most of the times we use the coordinates of the atoms at the ideal bulk positions for the initial positions).
2. Solve for the eigenvalues and the wave functions via equation (3.3) in the mixed basis approach. Our basis contains plane waves with energy $|\mathbf{k} + \mathbf{G}|^2$ up to certain E_{cut} , and a set of Gaussian (for Au) or a numerical basis (for Ag) as local orbitals.
3. Determine the band occupancy for each sampled $\mathbf{k}$ -point in the irreducible Brillouin zone (IBZ), and calculate the Fermi Energy using equation (3.19).
4. The total pseudo valence charge density is calculated via equation (3.18). The charge density is expanded in reciprocal space with approximately 2300 plane waves for Au, and 8000 plane waves for Ag. From the charge density, the Hartree screening potential and the exchange-correlation energy (Hedin-Lundqvist) of the electrons is calculated.
5. At each iteration step n a new input potential for the $(n+1)$ th iteration is obtained using the dielectric matrix scheme.
6. The total ground state energy is calculated using equation (3.11).

We repeat steps 2 through 6, until self-consistency is achieved ($V_{in} = V_{out}$). After that, forces on each atom are calculated using the Hellmann-Feynman theorem. The use of Hellmann-Feynman forces minimizes the number of trial geometries needed to determine the equilibrium geometry, especially because all the layers are relaxed simultaneously.

7. With the forces calculated before, the new positions of the atoms are predicted.

Using the forces calculated from few first geometries, we deduce a force-constant matrix that couples the different layers, and guides us in choosing the new position of the atoms.

In Figure (3.1) a diagram of this self-consistency loop is shown.

CHAPTER 4. MONOLAYER CALCULATIONS

Introduction

As stated in the introduction, with the current computer capabilities, a study of the Au(100), Au(111), and Ag on Al(111) surface reconstructions using first-principles only, is not feasible because of the large unit cell of the reconstructed surface. To deal with this problem, we use first-principles total energy calculations to study some systems closely related to these reconstructions which require smaller unit cells. The understanding of these systems give us physical insights of how these reconstructions happen.

There is experimental evidence that the reconstructions of Au(100), Au(111), and Ag on Al(111) are driven mainly by atomic interactions within the surface layer. It has been known for many years [1-6] that only the top (100) layer of the 5d fcc metals Ir, Pt, and Au change from the ideal square lattice of the ideal bulk, to a contracted hexagonal-close-packed structure. The inner layers of atoms, do not reconstruct, and keep the ideal square structure corresponding to the (100) plane of an fcc metal. This kind of reconstruction is not present in the (100) surface of the 4d fcc metals Rh, Pd, and Ag. A recent experiment shows that even though Pd(100) does not reconstruct, adding one monolayer of Pt to a Pd(100) surface gives a reconstruction of the top layer of Pt [70]. The case of the Au(111) surface is similar

to the (100) surface, only the first layer changes, while the underlying layers remain unchanged in the (111) plane. Also, even though the Ag(111) surface does not show any reconstruction, a single layer of Ag on Al(111) transforms from the ideal bulk structure into a compressed structure when the coverage is larger than one monolayer. In all these cases, the contraction develops from an in-registry structure into the compressed structure, leading us to believe that the contraction is mainly a property of the top layer itself. Consequently, a lot can be learned about these reconstructions by studying the properties of atomic monolayers. For transition metals near the end of the row, the d bands are nearly completely filled, thus the d charge distribution is nearly spherical and directional effects in the bonding are not important. The main effect of the substrate is to provide an electron background through which the surface atoms on the top layer interact with one another. We can get a very good description of the interaction between the surface atoms by replacing the substrate with a jellium surface of appropriate electronic density. In this chapter we use *ab initio* calculations to study the energetics of Au and Ag monolayers in isolation, and on top of a jellium substrate.

First-principles Calculations

We have used in our calculations non-local ionic pseudopotentials generated using the norm-conserving scheme of Hamann, Schlüter, and Chiang [54]. The total energies are calculated within the local-density-functional formalism [53] with the Hedin-Lundqvist form [63] of the local exchange-correlation energy. The wave-functions are expanded by means of an efficient mixed-basis set [68] consisting in plane waves with energy $(\mathbf{k} + \mathbf{G})^2$ up to 12 Ry plus a set of localized functions centered at the atomic

sites to describe the d orbitals. For Au we use Gaussians as localized orbitals, and for Ag, due to the fact that the 4d are more tightly bound than the Au 5d states, we use for the local orbitals numerical functions which are more flexible and hence can better represent the local orbitals. The shape of the local orbitals are determined variationally. The charge density for Au is expanded with approximately 2300 plane waves corresponding to a cutoff energy of approximately 110 Ry. For the case of Ag we use approximately 8000 plane waves for the charge-density expansion corresponding to a cutoff energy of 256 Ry. For most of our calculations we use 15 k-points in the irreducible wedge of the surface Brillouin zone (SBZ). This method has been used in previous investigations of the structural properties of bulk Au and Ag, and of the reconstruction of the (110) surfaces with excellent results [32, 51].

Ag and Au Monolayers in Vacuum

Experimental results show that the reconstruction of all the three surfaces we are going to study have the common feature that only the topmost layer contracts to a denser arrangement. This feature suggests that the atomic interactions in the surface layer play the main role in the reconstruction of these surfaces. Thus, it is reasonable to study, as the first step, the behavior of a single layer of Au and Ag by itself.

Periodicity along the direction perpendicular to the monolayer is absent. As is usual in surface calculations, an artificial periodicity along this direction must be retained, so we can use the well-established tools of the pseudopotential theory to obtain the electronic structure of our system [71]. This artificial periodicity is achieved considering a unit cell consisting of a single layer of atoms exposed to an

empty space on both sides. This cell is repeated so the total system is periodic. We used 15.5 a.u. for the separation between two consecutive monolayers, corresponding to twice the bulk lattice constant (we previously had used 10.9 a.u. giving the same results). For both gold and silver monolayers, total energies are calculated for square and hexagonal structures. For each structure we have varied the lattice area and the results are fitted to the universal binding curve [72]:

$$E(a) = \Delta E E^*(a^*), \quad (4.1)$$

with $a^* = (a - a_m)/l$, $E^*(a^*) = (1 + a^*)\exp(-a^*)$, where ΔE , a_m , and l are scaling parameters. The value of ΔE is the cohesive energy per surface atom (the energy with respect to the free atom) [32], the coordinate a^* is a scaled length, a_m is the equilibrium lattice constant, and l is a scaling length related to the curvature. In Figures (4.1) and (4.2) we plot the energy change in the contraction for the Au and Ag monolayers (square and hexagonal) as a function of the percentage reduction of surface area per atom. The zero area contraction corresponds to the ideal bulk area per unit atom, and the energy gain is with respect to the energy of the square monolayer at that area. We can observe that for both Au and Ag the curve for the hexagonal monolayer gives the lowest energy, and the minimum of the energy is at an area smaller than the ideal (100) surface of an fcc structure. This means that it is energetically favorable for both Au and Ag to switch from the square lattice corresponding to the ideal fcc (100) surface to a more compacted hexagonal-close-packed arrangement. However, there are some differences between the Au and Ag cases. The area contraction for the case of Au is approximately 25%, larger than 20% corresponding to Ag. But more impressive is the difference in the gain of the

energy when contracting. Ag gains only 23 mRy, while Au gains more than 60 mRy, or about 2.5 times more energy than Ag.

The above calculations were made with 15 k -points in the irreducible surface Brillouin zone (SBZ). In order to check if this number of k -points is large enough, calculations for the Au hexagonal monolayer are repeated with 36 k -points in the SBZ. This is shown in figure (4.3) where it can be seen that the results are almost identical, giving us confidence that we can work safely with 15 k -points in the SBZ.

It is interesting to know the reason why Au gains that much energy when contracting and Ag gains so little. Some people have downplay the importance of the d -electrons in the contraction of the Au(100) surface [73]. We think that the d -electrons play a very important role determining the contraction of the Au (100) surface and its absence in Ag. The difference between Au and Ag is a stronger bonding in Au due to a higher $s - d$ hybridization. In the bulk, this stronger bonding is responsible for the bigger cohesive energies and stiffer bulk moduli in the 5d metals than in the respective 4d metals. It is also responsible for the fact that even having a bigger core radius, the 5d metals have almost the same equilibrium volume than their respective 4d counterparts. Two main factors contribute to this difference between the 5d and the 4d metals: one is that the 4d electronic wave functions are more tightly-bound, while the 5d wave functions are more extended. Ho and Bohnen [51] showed that increasing by 5% the d -part of the pseudopotential, the cohesive energy and the bulk modulus were closer to the ones of Ag. They also used this pseudopotential to explain the missing-row reconstruction for the Au(110) surface. We repeat the hexagonal monolayer calculation using this pseudopotential. In Figure (4.4) we can see that the energy gained by the Au monolayer when contracting is reduced.

The other factor that makes the bonding in the 5d metals stronger than in the 4d is the relativistic effects, that are more important in the heavier 5d elements: for example Au has 79 protons making its nucleus very heavy, compare to the lighter Ag nucleus that has only 47 protons. In a previous calculation [32] we have shown that the bulk properties of the non-relativistic Au bear a resemblance to the properties of Ag. To show the effect of relativity in our calculations, we study the energetics of the Au hexagonal monolayer, using a non-relativistic potential. In Figure (4.4) we can see that the energy gained by the Au monolayer when contracting is also reduced when the calculation is done with a non-relativistic rather than the scalar relativistic pseudopotential. In both cases (with the non-relativistic, and the pseudopotential with the d-part increased) the contraction is smaller.

Ag and Au Monolayers on Jellium

In our monolayer calculations, we have assumed that the Au top layer transforms by itself, but in reality, the top layer has a substrate of atoms underneath. In order to include the substrate effect without losing the translational symmetry in the (100) plane, we substitute the underlayers of Au (Ag) atoms by a uniform charge background of density:

$$\begin{aligned} n_+(\mathbf{r}) &= n, |z| \leq a, \\ &= 0, |z| > a. \end{aligned} \tag{4.2}$$

where n is constant, and $2a$ is the width of the jellium slab. The ionic potential due to this jellium background is the Coulomb potential due to the repeated slabs of this

uniform charge. The Fourier component of this Coulomb potential is:

$$V(\mathbf{G}) = 8\pi\rho(\mathbf{G})/G^2 \quad (4.3)$$

where $\rho(\mathbf{G})$ is the Fourier component of the charge density, and the $\mathbf{G}$ s are the reciprocal lattice vectors. The jellium approximation is reasonable because we are dealing with elements at the end of the row in the periodic table. For these elements, the d-band is full, so directional bonding is not important. The jellium density n is determined in 2 ways: (i) Taking the charge density in interstitial positions in the bulk, midway between two nearest neighbors. This method gives $r_s \sim 1.8$ and $r_s \sim 2.0$ for Au and Ag respectively; (ii) By putting a monolayer over a jellium slab and varying the charge density until the charge profile (solved self-consistently and averaged along a direction perpendicular to the surface) on the monolayer matches the one of the top layer in the slab calculation (this calculation is explained in the following chapter). This gives $r_s \sim 1.6$ and $r_s \sim 1.76$ for Au and Ag respectively.

The energy of our atom on jellium system includes the energy of the jellium substrate itself. Because we are interested in the intralayer interaction and the interaction between the monolayer with jellium we have to subtract this substrate energy. This energy is calculated separately. In Figure (4.5) we plot the energy of the jellium slab by itself as a function of area for $r_s=1.6$, 1.76 , and 1.9 . It can be seen that as one would expect, the surface energy per unit area is constant. To check our results, we also calculated the surface energy for other jellium densities and compare with the values found by Lang and Kohn [74]. This comparison is shown in Figure (4.6) where we can see that our results agree very well with Lang and Kohn's calculations. There are some small discrepancies, but they can be attributed to the fact that we are using periodic slabs for our calculation, while Lang and Kohn's results are obtained

with a semiinfinite unit cell. In Figures (4.7) and (4.8) we have used the first method to estimate the jellium density (we took $r_s = 1.9$ for both Au and Ag). We plot the energy change for the square and hexagonal monolayers on top of jellium (subtracting the jellium energy) as a function of the contraction in the area (in percentage). Figure (4.7) corresponds to Au and Figure (4.8) corresponds to Ag. The results are fitted to the universal binding curve with the energy of the single atom on jellium taken as an extra parameter. For each point in these curves, the distance of the monolayer to the jellium is determined minimizing the energy. We can observe that for both Au and Ag in the square and hexagonal structures, the energy gain when contracting is smaller than the energy gain in the case of the monolayer on vacuum. This result was expected, because before, in the vacuum, the Au and Ag monolayers did not have anything that could oppose the contraction. Now they have a jellium substrate underneath them. However, the jellium results are qualitatively similar to those of the monolayer: in both cases Au, and Ag, the hexagonal structure is more favorable than the square, but in the case of Au the energy gain by contraction is larger than in Ag.

In Figure (4.9) we have the energy gain for the Au and Ag hexagonal monolayers using the second method to determine the jellium density (that gives $r_s = 1.6$ for Au and $r_s = 1.76$ for Ag). The results are again qualitatively the same. So we can conclude that independently of the value of r_s : Both Au and Ag monolayers want to contract to a hcp structure, but the energy gain by contracting is larger in Au than in Ag.

If we examine Figure (4.9), we observe that for the Au with $r_s=1.6$ the curve of energy gain shows many wiggles. We repeat the calculation for the Au hexagonal

monolayer on jellium ($r_s = 1.6$) with 28 k-points and observe that those wiggles disappears, but the general form of the curve remains the same (Figure (4.10)).

In the above calculations the thickness of the jellium 11.6 a.u. (corresponding to a thickness of 3 layers of Au and Ag atoms), and the size of the unit cell in the (100) direction is about 31.0 a.u. To see the dependence of our calculations on the thickness of the jellium, we changed it to 13.5 a.u. (3.5 layers of atoms) for the case of Au with $r_s = 1.6$, and repeated the calculations. The results are shown in Figure (4.11), where we can see that they do not depend on the jellium thickness.

Summary

We have applied first-principles total energy calculations using *ab initio* pseudopotentials to study the behavior of monolayers of Au and Ag by itself, and on top of a jellium slab. We found that for both Au and Ag the ground state is hexagonal. We also found that both Au and Ag want to increase the surface density by reduction of the surface area per atom. However, Au gains more energy than Ag and contracts more. This results do not depend on whether the atoms are on vacuum or on top of a jellium slab, and are independent of the density of the jellium.

The difference in the behavior between Au and Ag is a weaker $s-d$ hybridization in the 4d transition metals than in the 5d. The microscopic origin for this difference can be traced to strong relativistic effects in the heavier 5d elements. Calculation with a non-relativistic potential reduces the contraction energy substantially.

Figure 4.1: Energy change per atom for square and hexagonal Au monolayers as a function of the percentage contraction of surface area per atom

Figure 4.2: Energy change per atom for square and hexagonal Ag monolayers as a function of the percentage contraction of surface area per atom

Figure 4.3: Energy change per atom for hexagonal Au monolayers as a function of the percentage contraction of surface area per atom for different number of k-points

Figure 4.4: Energy change per atom for square and hexagonal Au monolayers as a function of the percentage contraction of surface area per atom using a non-relativistic pseudopotential, and a pseudopotential with the d-part increased by 5%

Figure 4.5: Energy of the jellium slab in function of the area for different jellium densities

Figure 4.6: Comparison of surface energies of jellium slab with values found by Lang and Kohn. Black filled circles show the values of our calculation, and the line corresponds to Lang and Kohn's results

Figure 4.7: Energy change per atom for square and hexagonal Au monolayers on top of a jellium slab of $r_s = 1.9$ as a function of the percentage contraction of surface area per atom

Figure 4.8: Energy change per atom for square and hexagonal Ag monolayers on top of a jellium slab of density $r_s = 1.9$ as a function of the percentage contraction of surface area per atom

Figure 4.9: Energy change per atom for hexagonal Au monolayers on top of a jellium slab of density $r_s = 1.6$ and Ag monolayers on top of a jellium slab of density $r_s = 1.76$ as a function of the percentage contraction of surface area per atom

Figure 4.10: Energy change per atom for hexagonal Au monolayers on top of a jellium slab of density $r_s = 1.6$ using 15 and 28 k-points in the SBZ as a function of the percentage contraction of surface area per atom

Figure 4.11: Energy change per atom for hexagonal Au monolayers on top of a jellium slab of density $r_s = 1.6$ and thickness equal to 3 and 3.5 layers of Au as a function of the percentage contraction of surface area per atom

CHAPTER 5. NOBLE METAL (100) SURFACE RECONSTRUCTIONS

Introduction

Gold surfaces have been studied extensively using different experimental techniques [1-13]. In particular the Au(100) surface presents a complicated reconstruction pattern, whose main character can be simplified as a contracted hexagonal-close-packed overlayer on top of a square substrate [1-6]. The first LEED measurements of this surface [1] indicated a (1x5) reconstruction. Later LEED measurements with better resolution resolved the splitting in the LEED spots, suggesting a (20x5) rather than a (1x5) superstructure [2]. Other LEED [3] and He-scattering [4] studies suggested a larger c(26x68) unit cell. Binnig, Rohrer, Gerber, and Stoll [5] using scanning tunneling microscopy proposed a

$$\begin{pmatrix} X & 0 \\ Z & Y \end{pmatrix}$$

unit cell, where $X = 24 \pm 3$, $Y=48$ or 43 , depending on temperature, and $-5 \leq Z \leq 0$, implying an additional rotation of the overlayer over the substrate. A recent study of the temperature dependence of the Au(100) surface [6], has found a distorted hexagonal structure for $1170K < T < 970K$, and a rotated distorted hexagonal structure for $970K < T < 300K$. The (100) surfaces of other 5d fcc metals show

similar reconstructions. Ir(100) exhibits a (1x5) pattern [3], and Pt(100) shows a series of closely related patterns with a quasihexagonal unit cell, two of them are the (5x1) and (5x20) structures [2]. In the other side, the 4d fcc metals Rh, Pd, and Ag, which have the same number of valence electrons, and very similar lattice constants to their 5d counterparts Ir, Pt, and Au respectively, do not show any reconstruction in their (100) surface. We study this complicated behavior (the reconstruction of the 100 surfaces of the 5d metals, and its absence in the 4d) using Au and Ag as prototypes. At present, because of the large size of the unit cell, a complete *ab initio* study of the Au(100) surface is very difficult. Semiempirical calculations of this surface reconstruction have been made by Ercolessi *et al.* using their so called "glue model" [75], and by Dodson with the Embedded Atom Method [76]. They have shown that using phenomenological many-body potentials the reconstruction of the (100) surface of Au can be simulated, but they did not give a physical explanation of why this reconstruction occurs. The purpose of this chapter is to understand the physical mechanism that drives the reconstruction in the (100) surface of the 5d fcc metals, and to understand why similar transformations do not occur in the (100) surfaces of the 4d fcc metals. In the chapter 4 we studied the energetics of a single layer of Au and Ag on vacuum and on top of a jellium slab. We found that Au and Ag monolayers want to contract. However in the real surface, for the top layer to transform from the ideal (100) square lattice to the contracted hexagonal-close-packed structure, the energy gain by contracting has to be greater than the energy it loses because of a loss of registry with respect to the underlying layers. To have an estimate of this energy, we calculate the energy of the top layer on the ideal (100) fcc position, and the energy of the top layer shifted on top of the second layer of atoms.

With these values, and the energetics of the Ag and Au monolayers on jellium, we use a Frenkel-Kontorowa model to give a description of the contraction.

First-principles Calculations

We have used in our calculations non-local ionic pseudopotentials generated using the norm-conserving scheme of Hamann, Schlüter, and Chiang [54]. The total energies are calculated within the local-density- functional formalism [53] with the Hedin-Lundqvist form of the local exchange-correlation energy [63]. The wavefunctions are expanded by means of an efficient mixed-basis set [68] consisting in plane waves with energy $(\mathbf{k} + \mathbf{G})^2$ up to 12 Ry plus a set of localized functions centered at the atomic sites to describe the d orbitals. For Au we use Gaussians as localized orbitals, and for Ag, due to the fact that the 4d are more tightly bound than the Au 5d states, we use for the local orbitals numerical functions which are more flexible and hence can better represent the local orbitals. The shape of the local orbitals are determined variationally. The charge density for Au is expanded with approximately 2300 plane waves corresponding to a cutoff energy of approximately 110 Ry. For the case of Ag we use approximately 8000 plane waves for the charge-density expansion corresponding to a cutoff energy of 256 Ry. For most of the calculations we use 15 $\mathbf{k}$ -points in the irreducible wedge of the surface Brillouin zone (SBZ). This method has been used in previous investigations of the structural properties of bulk Au and Ag [32, 33], and the reconstruction of the (110) [51] surfaces with excellent results.

Slab Calculations

For the top layer to transform from the square lattice of the (100) unreconstructed surface to a hexagonal close packed structure, the energy that it gains by contracting must be greater than the energy it loses because of a loss of registry with the underlying layers (we call it "mismatch energy"). In our previous calculations this "mismatch energy" was not present because we always used a uniform substrate (vacuum for the monolayer calculation, and a uniform charge density for the monolayer on jellium calculation), and it has to be calculated separately. A good estimate of this mismatch energy can be calculated as following: we regard the substrate atoms as a rigid periodical potential with the same symmetry and periodicity of the atoms, and we consider the top (100) layer of atoms as interacting with this potential. The energy per surface atom of this interaction is given by:

$$E(\mathbf{R}) = \sum_{\mathbf{G}} W_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{R}}, \quad (5.1)$$

where $\mathbf{G}$'s are the 2-dimensional (2D) reciprocal lattice vectors and $\mathbf{R} = (x, y)$ is the position of an atom on the top layer.

Using first-principles we can calculate the energies of the top layer of Au and Ag atoms occupying the two sites with highest symmetry: the ideal site, corresponding to the ideal (100) fcc surface, and the shifted site, corresponding to the the atoms in the surface layer shifted on top of the atoms in the second layer. Using these energies we can expand equation (5.1) up to first order terms obtaining:

$$E(x, y) = E_0 + \frac{W}{4} \left(\cos \frac{2\pi}{a} x + \cos \frac{2\pi}{a} y \right) \quad (5.2)$$

where a is the lattice constant of the 2D square substrate lattice. $W = E(a/2, a/2) - E(0, 0)$ is the energy needed to move the top layer atoms from the most stable position

(ideal) to the most unstable position (shifted) by $(a/2, a/2)$. A three dimensional plot of this potential energy is shown in Figure (5.1).

As in the case of the monolayer calculations, we have to retain an artificial periodicity in the direction perpendicular to the surface. In order to do this, our system consists of periodic slabs of atoms, separated by empty space. Our primitive slab consists of 5 layers of atoms and an empty space equal to twice the bulk lattice constant. If we call $E(ideal)$ the energy of the ideal 5-layer slab with the surface atoms at the ideal position, and $E(shifted)$ the energy of the 5-layer slab with its top and bottom layers shifted by $(a/2, a/2)$ to the shifted position, then $W = 1/2(E(shifted) - E(ideal))$, where the $1/2$ factor is because in our slab calculations we have two surfaces. For both, the ideal, and the shifted slab calculations, all the intralayer distances are fully relaxed with the help of Hellmann-Feynman forces [57]. The use of Hellmann-Feynman forces minimizes the number of trial geometries needed to determine the equilibrium geometry, especially because all the layers are relaxed simultaneously. Using the forces calculated from few first geometries, we deduce a force-constant matrix that couples the different layers. This matrix guide us in choosing the new position of the atoms. The values found for W are 36.8 and 39.3 mRy per surface atom for Au and Ag respectively. It can be observed that the energy loss by displacing the atoms in the first layer on top of the atoms in the second layer is slightly larger in Ag than in Au. This result, together with the fact that gold gains more energy than silver by contracting offer us an explanation of why Au reconstruct and Ag does not.

From the ideal fully relaxed slab calculation, we can get the surface energy. $E_s = 1/2(E(ideal) - 5E_{bulk})$ where E_s is the surface energy, E_{bulk} is the bulk

energy, and the $1/2$ factor is again because of the two surfaces of the slab. We found $E_s = 51.5$ mRy for Au and $E_s = 42.9$ mRy for Ag. If we divide by the area of the slab and change units, we get $E_s/A = 1333 \text{ erg/cm}^2$ for Au and $E_s/A = 1110 \text{ erg/cm}^2$ for Ag, that agree very well with the values given by Somorjai [77] $\gamma = 1401 \text{ erg/cm}^2$ for Au and $\gamma = 1140 \text{ erg/cm}^2$ for Ag.

In order to test the thickness of the slab, we repeated the calculations for Au adding two layers of atoms. The results do not change very much. We found $W = 36.5$ mRy and $E_s = 52.3$ mRy.

In Table (5.1) we show the relaxation of the interlayer separation in percentage of the separation of the inner layers, for the top layer atoms occupying the top and bottom positions. We observe that there is no much difference whether we use a 5 layer atom slab or a 7 layer. By averaging relaxation of the first layer of atoms we found an outward relaxation of about 15%. No experimental data have been reported for this relaxation on the Au(100) surface, however for the Ir(100) surface, that is closely related to the Au(100) surface, Moritz [78] reported a 15% expansion of the first layer. From the final positions of the atoms in the top and bottom positions after relaxing, we can get a good estimate of the amplitude of the corrugation for the first layers of Au. The value we get for the amplitude of the corrugation of the first layer is around $0.68 \text{ \AA}$, very close to the experimental value $0.5 \text{ \AA}$ found by Rieder *et al.* using He-scattering [4], and very close to the value found by Ercolessi *et al.* [75]. For the second and inner layers, we find a very small value for the corrugation. This result differs from the calculations of Ercolessi *et al.* They found corrugations of the same order of magnitude for the first four layers. We think that this big corrugation that they calculated for atoms in the inner layers is probably due to the fact that

their model is a hard ball model.

Frenkel-Kontorowa Simulation

In the reconstruction process, the density of atoms on the surface changes. The proper quantity that governs the reconstruction is not the total energy anymore, but the surface energy. The change in the total surface energy can be written as:

$$D(q) = (d(q) + qE_s)/(1 - q) \quad (5.3)$$

where q is the fractional decrease in area per surface atom (at the ideal surface $q=0$), $d(q)$ is the energy change per atom, due to the transformation from square to hexagonal and the area contraction by a fraction q , E_s is the surface energy of a fully relaxed (1x1) surface (already calculated).

$d(q)$ can be calculated using a Frenkel-Kontorowa [58] model in two dimensions. This model describes the situation in which the top layer has a different lattice constant (and in this case, also a different symmetry) than the substrate, and consists of an elastically bounded mesh of atoms on top of a rigid periodical potential that replace the substrate atoms. Within this model the mismatch energy is given by:

$$d(q) = \sum_{ij} e(\mathbf{R}_i - \mathbf{R}_j) + \sum_i \cos \frac{2\pi}{a} x_i + \cos \frac{2\pi}{a} y_i \quad (5.4)$$

where $\mathbf{R}_i = (x_i, y_i)$ is the position of the i^{th} surface atom, and a is the lattice constant of the unreconstructed (100) surface. The first term describes the intralayer interaction and the homogeneous part of the interaction of the top layer with its substrate, and can be represented by a 2-body potential in the form of the universal

binding curve that was fitted to our hexagonal monolayer on jellium calculations. The second term describes the energy of the interaction between the surface atoms and the substrate. In the ground state the atoms rearrange in such a way that there is an equilibrium between the strain energy (first term) and the potential energy (second term) so that the total energy $d(q)$ is minimum. A one dimensional F-K model can be solved analytically in the continuum limit [58], but the 2D case cannot. To find the ground state of equation (5.4), we have to use numerical techniques. In our calculations a 2D mesh of 61x61 atoms is used. We start placing the atoms in an initial hexagonal configuration, with the total area constrained to correspond to a given contraction. The boundary atoms are fixed so this total area never changes. The positions of the atoms R_i 's are relaxed by an iterative procedure until we reach a configuration that gives a local minimum for $d(q)$. Throughout all this procedure we assume that each atom has six nearest neighbors. Our iterative method consists basically in a steepest descent method. At each step of the procedure, we calculate the value of the function that we want to minimize, in this case the total energy (strain plus potential), and its derivatives (the forces on each particle). We displace the atoms in the direction of the forces, by an amount proportional to the magnitude of the forces. The value of the constant of proportionality λ is found variationally: we change λ and calculate the energy until we found its minimum. We repeat this procedure until the force on each atom is zero. Once $d(q)$ is found, equation (5.3) can be used to find the change of the surface energy as a function of q . Results are plotted in Figure (5.2) for Au and Ag with $r_s=1.9$. It can be seen that is energetically favorable for Au to reconstruct, but not for Ag. We can also see that the contraction for Au is around 21% that agree very well with experiments (20%). At this contrac-

tion, the Au layer is basically a hexagonal layer, slightly distorted by the underlying potential (Figure (5.3)). Even though the agreement with the experiments is very good, our value for the contraction should not be taken literally. Equation (5.4) is one approximation, and the use of the monolayer on jellium is another. However the final conclusion does not depend on these assumptions, the results are qualitatively similar for different jellium densities, even with a simple monolayer (no jellium) and show that Au reconstruct, and Ag does not.

Summary

We have applied first-principles calculations together with modeling techniques to show that the top layer of Au(100) reconstruct, changing from a square lattice to a contracted hexagonal closed packed structure, while the top layer of Ag(100) does not. The most important difference between Au and Ag is that the top layer of Au gains more energy in the change from a square lattice to a contracted hcp structure. This larger gain is due mainly to a stronger participation of the d orbitals in the bonding. This is a consequence of a large $s - d$ hybridization. The origin of this difference can be traced to a "more extending" nature of the d orbitals and to relativistic effects that are very important in Au, but not in Ag. This differences are not specific to Ag and Au, but are also true in the other 4d and 5d fcc metals, so it is natural that similar reconstruction occur in the (100) surfaces of the 5d fcc metals Ir and Pt but not in the corresponding (100) surfaces of the 4d metals Rh and Pd. We showed that a surface reconstruction will occur if the energy gain by contraction is bigger than the energy loss because of a loss in registry with the substrate, so even though the Ag (100) surface does not reconstruct, it is possible for an Ag overlayer to

transform to a closed-packed arrangement if Ag is on top of a substrate that interacts less strongly with Ag. This is in fact observed experimentally in Ag on Cu(100) [79].

Table 5.1: Relaxation of the interlayer separation in % of the inner layers separation for different sizes of the slab

	5layers of Au		7layers of Au	
	bottom	top	bottom	top
Δ_{12}	-2.4	32.8	-2.1	29.0
Δ_{23}	0.0	0.0	0.0	-1.0
Δ_{12}	-	-	0.0	0.0

Figure 5.1: 3-D plot of the interaction energy between the substrate and the top layer atoms in the Au (100) surface

Figure 5.2: Surface-energy change (per surface atom) for Au and Ag as a function of the percentage area contraction

Figure 5.3: The reconstructed Au(100) surface as given by the F-K model. The filled circles denote the position of atoms in the reconstructed top layer, and the intersections of the lines denote the positions of atoms in the second layer

CHAPTER 6. AU(111) SURFACE RECONSTRUCTION

Introduction

It has been known for several years that the Au(111) surface reconstructs [5-13]. Its reconstruction was first studied by techniques like Low Energy Electron Diffraction (LEED) [3, 8], Reflection High Energy Electron Diffraction (RHEED) [9], and Transmission Electron Diffraction (TED) [10, 11]. Van Hove *et al.* [3] proposed a model of a $(p \times \sqrt{3})$ structure with $p=21-22$, supposing a contracted surface layer in only one of the three $(1\bar{1}0)$ directions. High resolution Transmission Electron Diffraction (TED) experiments conducted by Takayanagi and Yagi [11] suggested that the compression is not uniform, but localized in two transition regions where the stacking changes abruptly from ABC to ABA. Harten *et al.* studied this reconstruction with High Resolution Helium Atom Diffraction [12]. Their experiment gave more information about the ABC and ABA stacking, and the boundary regions between the two of them. They interpreted the diffraction pattern as a manifestation of a one dimensional sine-Gordon soliton-like misfit structure. However, in the same experiment, they showed that the width of the regions with ABA and ABC stacking are not equal. A single sine-Gordon model assume equally spaced solitons, and so cannot describe two regions with different widths. To solve this problem, a double sine-Gordon model was proposed by El-Batanouny *et al.* [80]. This model incorporates a pair of

solitons, allowing for the existence of ABC and ABA stacking with different domain sizes. Most of these models assume that both the hexagonal-closed-packed (hcp) site, as well as the face-centered-cubic (fcc) site, can be occupied by the surface atoms. Experimentally, this has been shown using Scanning Tunneling Microscope (STM) [13]. A necessary condition for this to happen is that the fcc and hcp sites have very similar occupancy energy for top layer Au atoms. Using first-principles total energy calculations, we found that this is indeed the case. Our results show that the two sites differ in energy only by about 1 mRy per surface atom. Another necessary condition for the Au(111) reconstruction is the tendency of the top layer to contract to a higher degree of compactness than in an ideal (111) surface layer. Our previous calculations in Chapter (3) have demonstrated that this is possible. Using the information that we have about the top layer contraction, and the energy of occupancy of various surface sites computed by total energy techniques, the surface reconstruction is described with the help of a Frenkel-Kontorowa (FK) model [58]. The STM measurements of Woll *et al.* confirmed previous models of the reconstruction, and at the same time provided images of the real space atomic arrangement of the surface with atomic resolution. The fact that the STM is giving images with atomic resolution for the surfaces of a metal is slightly surprising and may suggest the existence of surface electron states near the Fermi level that give larger corrugation than the overall charge density. We investigated the surface electronic structure of the (111) surface of Au along the Γ -M-K- Γ lines, together with the projected bulk band structure on the two dimensional Brillouin zone.

First-principles Calculations

We use in our calculations non-local ionic pseudopotentials generated using the norm-conserving scheme of Hamann, Schlüter, and Chiang [54]. The total energies are calculated within the local-density-functional formalism [53] with the Hedin-Lundqvist [63] form of the local exchange-correlation energy. The wave-functions are expanded by means of an efficient mixed-basis-set consisting of plane waves with kinetic energy $(\mathbf{k} + \mathbf{G})^2$ up to certain E_{cut} and a set of localized functions centered at the atomic sites to describe the more tightly bound orbitals [68]. For the calculation of the energies of the different sites, we use $E_{cut} \approx 12\text{Ry}$ and a set of Gaussian (determined variationally) as local orbitals. A slab consisting of 7 Au(111) layers is used to describe the surface. For the surface state calculations, to facilitate the identification of the surface states, we increase the number of Au layers to 15. In order to reduce the number of plane waves needed in our basis for the 15 layer slab, we use for the local orbitals numerical functions which are more flexible and hence can better represent the local orbitals than the Gaussians. We found that with the optimal choice of numerical functions, the cutoff energy for the plane wave expansion can be reduced to 7.5 Ry. This method has been used in previous investigations of the structural properties of bulk Au [32], and the reconstruction of the (110) [51] and (100) [52] surfaces with excellent results.

ABC and ABA Packing

The face-centered-cubic (fcc) the hexagonal-close-packed (hcp) structure represent two different ways of arranging hard spheres in a regular array to minimize the

interstitial volume. The fcc structure corresponds to a 'ABC...' packing of hexagonal layers of atoms while the hcp structure corresponds to a 'ABA...' packing [81]. For the Au(111) surface, if a continuation of the bulk structure occurs, an ABC stacking is expected (Au is an fcc metal). However, the Au(111) surface reconstruct to a $(22 \pm 1) \times \sqrt{3}$ superlattice. Previous studies of the energetics of a Au monolayer on top of an uniform substrate [52] shows that a single layer of Au atoms favors a contraction to a smaller lattice constant from the bulk value. The intrinsic tendency for the Au surface layer to contract to higher surface density is opposed by the potential of the underlying Au atoms, which tries to keep the top layer in registry (ABC stacking). However, if the energy of occupying the hcp sites (ABA stacking) is close to the energy to occupy the fcc sites, the energy cost in losing registry can be expected to be small and a contraction of the top layer can be favorable. STM experiments [13] have shown directly the occupation of both hcp and fcc sites on the surface, a good evidence that the energy of a surface atom occupying one of the sites does not differ very much from that of the other. However the two energies cannot be the same as the width of the regions with ABA stacking is different from the one with ABC stacking.

We use first-principles techniques to obtain the total energy of the top Au layer occupying the fcc (conventionally called C site) and the hcp (A site) sites (see Figure (6.1)). The energies for the top site (T in Figure (6.1)), and the bridge site (B in Figure (6.1)) are also obtained. For the fcc, hcp, and top site calculations, an evenly-spaced sampling grid of 15 k-points in the surface Brillouin zone (SBZ) (Figure (6.2)) is used for the calculation of the electronic charge density during the iteration to self-consistency. In the case of the bridge site, reduced symmetry mandates a SBZ three

times larger (see Figure (6.3)), and the sampling grid is increased to 45 k-points accordingly. All the interlayer distances are fully relaxed using forces calculated by the Hellmann-Feynman theorem. The results are summarized in Table (6.1). The energies quoted are energies per surface atom, and the zero of the energy is taken to be the energy of the top layer occupying the top site. We observe that indeed the energy of the A site is very close to the energy of the C site. The small energy difference is consistent with the observed occupation of both sites. We can also see that the energy difference between the C site and the bridge site is only about 3 mRy. This is a small number compared with the energy difference with the top site (14 mRy for the C site and 13 mRy for the A site). This fact allows a gradual shift of the atoms from the fcc to the hcp stacking through the bridge site (B), and the contraction of the surface layer in one of the $(1\bar{1}0)$ directions. The big height of the potential at the top site makes the contraction of the lattice in the $(\bar{1}12)$ direction very unfavorable. Hence, it is rather natural that the reconstruction observed is uniaxial rather than uniform contraction.

In Table (6.2), we show the relaxation of the interlayer separations in the direction perpendicular to the (111) surface (in percentages of the ideal bulk separation) for the top Au layer occupying different positions. We observe that in all cases, only the first layer shows a significant relaxation. From the vertical position of the surface atoms at the hollow sites (A or C) and the one at the bridge site, we can estimate a corrugation height of the order of 0.05 Å on the reconstructed surface. This is smaller than the 0.15 Å [13] found experimentally. However, this should not be regarded as a large discrepancy, since the corrugation, whether deduced by theory or experiment, is rather small anyway, and closer examination of published experimental data (e.g.,

Figure (2) of Reference [13]) would reveal that the 0.15 Å is more like an order of magnitude estimate.

In the above calculations, the surface is modelled by periodic slabs seven layers thick separated by an empty space of thickness equivalent to four layers. The adequacy of the vacuum spacing between the slabs has been tested. We increase the vacuum distance to six layers and repeat the calculations with the top layer of Au atoms in the fcc and bridge sites respectively. The difference in the energy per surface atom between the two sites remains the same (3.1 mRy). We have also tested the thickness of the slab. Increasing the number of Au layers to nine does not give any significant change. The interlayer distances with the top layer at the fcc and the bridge sites computed with different slab thickness and separation are compared in Table (6.3).

Frenkel-Kontorowa Model

The first-principles results shown in the previous section offer insight and useful information about the energetics of the Au(111) reconstruction that may not be obtainable with other methods. It is difficult to give a complete description of the reconstruction based on *ab initio* calculations alone, since the reconstructed surface unit cell is far too large to fit into current computers. However, a good description of the reconstruction can be obtained using a simple two-dimensional Frenkel-Kontorowa (FK) model, with parameters extracted from our first-principles results. The 2D-FK model describes a situation with two competing interactions: the top layer favoring a different scale length (in this case a uniform contraction to a smaller lattice constant), while the potential due to the substrate atoms trying to pin the surface atoms in reg-

istry. The surface will transform if the energy gained by contraction is larger than the energy lost in losing registry with the substrate atoms, and if the surface does transform, the final atomic arrangement will be governed by the interplay between the strain energy in the top layer and the potential energy due to the underlying layers.

Our previous calculation [52] show that a Au monolayer prefers a higher packing density than the arrangement of the surface atoms on a Au(111) surface with bulk lattice constant. It remains to be demonstrated that the tendency for contraction is large enough to overcome the potential due to the substrate.

Since the effect of the substrate atoms can be expressed in the form of a periodic potential with the symmetry and periodicity of the unreconstructed substrate surface (with lattice parameter of the corresponding bulk), we expand the potential energy per surface atom in a Fourier series of the form:

$$E(\mathbf{R}) = \sum_{\mathbf{G}} W_{\mathbf{G}} e^{i\mathbf{G} \cdot \mathbf{R}}, \quad (6.1)$$

where the $\mathbf{G}$'s are the 2-dimensional (2D) reciprocal lattice vectors of the substrate surface and $\mathbf{R}=(x,y)$ is the position of an atom on the top layer.

Our knowledge of the binding energies at a few high symmetry sites (top, bridge, fcc, and hcp) allows us to determine the first few terms in equation (6.1). Explicitly, we have:

$$\begin{aligned} E(x, y) = & \frac{3V_B}{4} - \frac{(V_C + V_A)}{9} \left[\cos \frac{2\pi}{a} x + \cos \frac{2\pi}{a} y + \cos \frac{2\pi}{a} (x + y) \right] \\ & + \frac{(V_C - V_A)}{3\sqrt{3}} \left[\sin \frac{2\pi}{a} x + \sin \frac{2\pi}{a} y - \sin \frac{2\pi}{a} (x + y) \right] \\ & + \left(\frac{V_C + V_A}{9} - \frac{V_B}{4} \right) \left[\cos \frac{2\pi}{a} (2x + y) + \cos \frac{2\pi}{a} (2y + x) + \cos \frac{2\pi}{a} (x - y) \right] \end{aligned} \quad (6.2)$$

where V_C is the energy at the C site, V_A is the energy at the A site, V_B is the energy at the bridge site, and the zero of the potential energy is taken to be the energy at the top site. The lattice constant of the 2D hexagonal lattice is given by 'a', and the coordinates of the atoms are expressed in terms of the basis of the substrate lattice. The Hamiltonian of the corresponding 2D FK model is:

$$H = \sum_{i,j} e(\mathbf{R}_i - \mathbf{R}_j) + \sum_i E(x_i, y_i) \quad (6.3)$$

where $\mathbf{R}_i = (x_i, y_i)$ is the position of the i^{th} surface atom. The first term describes the interaction of the top Au atoms under the average influence of the substrate, and this is the term that favors the contraction of the surface. Since the relative energy differences in occupying different positions with respect to the underlying layers are taken care by the second term in equation (6.3), the first term can be deduced by considering the energetics of a monolayer on top of a homogeneous (translationally invariant) substrate that mimic the average effect of the substrate. To this end, we use the results of our previous calculations of the energetics of a monolayer on top of a uniform background [52]. In these calculations we put a layer of Au atoms on top of "jellium", with jellium density determined by finding the charge density of Au at bulk interstitial positions, midway between two nearest neighbors. The distance of the monolayer from the jellium edge was determined by energy minimization, and the energy of the jellium slab was subtracted so our final energy describes the atomic interactions within the surface layer in the background of a decaying electron sea. Even though Au is not a free-electron-like element, the function that describes the energetics of the monolayer on jellium should give a good representation of the first term in equation (6.3) because Au has a full d-band, and directional effects are not

expected to be important in the bonding between the surface layer and the substrate.

The second term in equation (6.3) is the potential imposed on the top layer of the Au atoms by the underlying layers, and it is described in equation (6.2), with all the parameters ($V_A, V_B, \dots$ etc.) coming from our first-principles calculations. We note that $E(x,y)$, as formulated in equation (6.2), does not describe the total interaction potential energy of the top Au layer with the substrate, but rather the relative energy change as the atoms in the top layer changes from one site to another. In Figure (6.4), this relative potential energy per surface atom, $E(x,y)$, is plotted as a function of the position. The x-axis and the y-axis are chosen to be the $(1\bar{1}0)$ direction and $(\bar{2}11)$ direction respectively. Figure (6.5) shows a corresponding contour plot of the same function in the (111) plane. From these plots, the big difference in energy between the top site and the other sites is conspicuous and we can also see rather clearly low energy 'channels' spanning the fcc, bridge and hcp sites along which the top layer can contract with minimal potential energy loss. The 2D F-K model here describes a situation in which the top layer has a different preferred bond length with respect to the potential dictated by the substrate. In the ground state there should be a compromise between the strain energy (first term) and the potential energy (second term) so that the total energy is a minimum. Equation (6.3) cannot be solved analytically, and to find the ground state, we use numerical techniques. In our calculations a mesh of 119×119 atoms is used. The positions of the atoms $\mathbf{R}_i'$ s are relaxed by an iterative procedure until a configuration that gives a local minimum is reached. Initially all the atoms are placed in the fcc site (i.e., in an ideal (111) surface configuration). We find the forces that act on each atom, and then displace them in the direction of the force by an amount proportional to the

force (the proportional constant is chosen variationally). We repeat this process until the force is zero. The atomic arrangement of the ground state of our F-K simulation is shown in Figure (6.6), where the surface Au atoms are represented by filled circles, and the unreconstructed second layer atoms are shown as crosses for reference. Our results indicate that it is indeed energetically favorable for the surface atoms on Au(111) to contract to a higher packing density. The reconstructed surface pattern, as shown in Figure (6.6), agree nicely with the patterns deduced from experiments. This shows that the 2D F-K model, though simple, contains the essence of the physics underlying this particular problem. Furthermore, all the parameters needed are determined by theoretical computations. A closer examination of Figure (6.6) shows that the surface layer does not contract to form a uniformly contracted hexagonal layer, but rather, the surface atoms contract along the $(1\bar{1}0)$ direction. In fact, we may view an ideal (111) surface as composed of linear rows of atoms in the $(1\bar{1}0)$ direction, and the reconstruction causes each $(1\bar{1}0)$ row of atoms to distort into a sinusoidal-like pattern, lying above and sandwiched by two rows of atoms in the second layer. The lattice constant in the $(1\bar{1}0)$ direction is reduced by approximately 5.0% , close to the experimentally observed 4.3% contraction. With this contraction our unit cell is a $(20 \times \sqrt{3})$ superlattice.

Both the fcc and the hcp sites are occupied and the reconstructed pattern reflects a gradual shift from one site to another. This is a consequence of the fact that the fcc and hcp sites have almost the same energy of occupation and the bridge site (midway between fcc and hcp sites) is only slightly higher in energy (see Table (6.1) and Figures (6.4) and (6.5)) so that the system find it easier to contract along a $(1\bar{1}0)$ "channel", occupying the fcc, hcp and all intermediate sites (One of these

"channels" is shown in Figure (6.5)). Note that the surface does not contract in the $(\bar{1}12)$ direction, since some surface atoms would have to climb above the top site, which is very unfavorable in energy (Table (6.1) and Figures (6.4) and (6.5)). There are three equivalent $(1\bar{1}0)$ directions on the surface, so that three types of domains of equal energies can be formed on the surface, separated by domain boundaries. In our simulations, only a single domain was found since our system is relatively small in size. The 119×119 mesh is large enough to simulate the reconstruction in the local scale. Larger sample sizes will be needed to observe domain structures and algorithms like simulated annealing should be preferred over the steepest decent method used in the present calculation.

Data from He-scattering and STM experiments have lead to the conclusion that there are more surface atoms in fcc (ABC) stacking than in hcp (ABA) stacking. This is consistent with the fact that the calculated energy is lower for the fcc than the hcp sites. However, different experimental techniques did not seem to agree on the exact ratio between the size of the regions with fcc and hcp stacking. This discrepancy can at least be partly attributed to the different assumptions used in the analysis of the experimental data. Even for a direct real space imaging technique like STM, the image is a convolution of topological and electronic information.

It is interesting to resolve the reconstruction pattern from our simulation to greater detail. In Figure (6.7) we plot one row of atoms (filled circles), exaggerating the scale in the $(\bar{1}12)$ direction. The empty circles at the top represents the fcc sites in the ideal surface, and the empty circles at the bottom represent the position of the hcp sites. We observe from Figure (6.7) that the pattern is more sinusoidal-like than square-wave-like, so that it is difficult to define the "size" of regions corresponding

to fcc or hcp stacking for the pattern we have obtained. If we define, for the purpose of discussion, that sites that lie closer to the ideal fcc sites than the hcp sites belong to the region of fcc stacking, then there are indeed more atoms in the fcc than in the hcp stacking.

Surfaces States

The fact that the scanning tunneling microscope gives atomic resolution images for Au(111) is interesting since Au is a metal and the (111) surface is a compact surface, so that the charge density profile should be very smooth at a few angstroms above the surface. This suggests that there may exist surface states near the Fermi energy that have interesting nodal structures that gives the atomic resolution in STM experiments. It is also interesting to investigate the effect of the surface stacking sequence on the surface electronic structures, a topic that has rarely been considered before. In particular, we want to see the influence of the position of the layer on the existence, the energy and the dispersion of the surfaces states. We are thus motivated to calculate the surface band structure of the Au(111) surface, not only for the ideal situation with the top layer in the fcc stacking sequence, but also for the top layer atoms occupying the hcp and bridge sites respectively. For better and easier identification of the surface states or resonances, we increased the slab thickness from seven-layers (which has been fully relaxed using Hellmann-Feynman forces) to 15 layers by inserting eight extra layers (with ideal interlayer distances) in the middle of the slab. A vacuum equivalent to five atomic layers separates the periodic slabs. The self-consistent potentials are obtained by iterating with 15 k-points in the irreducible SBZ for the Au top layer at the fcc, hcp and top sites (45

k -points are used for the top layer at the bridge sites, which has less symmetry). After reaching self-consistency, the electronic band structures of the systems are calculated along the symmetry directions Γ -M-K- Γ for the fcc and hcp sites and along Γ -M1-K1- Γ -M2-K2- Γ for the bridge site (the points K1 and K2 are the same. Only the directions Γ -K1 and Γ -K2, and M1-K1 and M2-K2 are different). To facilitate the identification of the surface states, we also calculate the projected band structure for the Au(111) surface. This is done by projecting the bulk band structure of Au on to the two dimensional (111)-SBZ. Results are shown in Figures (6.8) to (6.11), where the zero of the energy corresponds to the Fermi energy. The shaded areas in the projected band structure indicate regions where bulk states can exist. For the top layer at the fcc, and hcp sites, the Hamiltonian matrix have reflection symmetry about the plane perpendicular to the (111) surface that passes along the Γ -M line. For the case of top layer atoms at the bridge site, this symmetry occurs only in the plane that passes along the Γ -M2 line but not in the Γ -M1 line. Whenever reflection symmetry exists, the electronic states with wave-vectors along these symmetry lines can be separated into two groups with even and odd symmetries, and they are plotted separately in Figures (6.8) to (6.11).

Several criteria guided us to locate the surface states and resonances in the surface band structure. Surface states usually appear as extra energy levels in the gaps of the projected bulk bands, and since a slab geometry has two surfaces, they usually occur in almost degenerate pairs (slightly split by the interaction of the surface states). The key criterion we used is to look for states with wavefunction amplitudes highly localized (more than 50%) within the first two layers of the surface. States with big amplitudes at the surface are displayed in Figures (6.8) to (6.11) as solid

or dashed lines according to the degree of localization at the surface. By comparing Figures (6.8) to (6.11), we observe that the surface band structures along the high-symmetry lines are very similar for the top layer occupying fcc, hcp, and bridge sites. Most of the surface states and resonances that exist on the surface with the top layer in fcc-stacking have corresponding surface states and resonances that exist on the surface with the top layer at the hcp and bridge sites. The dispersion of the surface states are also very similar. A closer examination reveals that even the charge density of the corresponding surface states are very much alike. As an example, we show here a surface state at Γ (the state marked as A in the plots) near the Fermi level. This surface state has been observed by photoemission experiments [82] and it is probably the one probed by STM experiments. The fact that the energy and dispersion of the surface states does not depend very much on whether the top layer is in the fcc, hcp or bridge site allows us possible comparison with the experimental results. This is shown in the inset in Figure (6.8). We observe that our calculations agree very well with the experimental results. In Figure (6.12), we plot the charge density contours of this surface state at the Γ point in the plane formed by the vectors (111) and ($\bar{1}$ 12), for the surface atoms occupying the fcc, hcp and bridge sites. The positions of the atoms are indicated by filled black circles. From the plot we see that the surface state is localized in the top two or three layers, and is indeed rather similar for the three cases considered. We may conclude that the surface electronic structure is only very weakly dependent of the position of the top layer Au atoms. We also observe that the charge density profile for this surface state becomes rather smooth at a short distance above the top layer. It is thus unlikely that we can rationalize the atomic resolution obtained by STM with the charge density corrugation of surface states near Fermi

energy. Strong tip and surface interaction or local elastic deformation of the surface by the tip may be other possible explanations that we should not overlook.

Summary

We have used first-principles calculations to obtain the energies of the top layer of Au atoms occupying the fcc, hcp, top, and bridge sites on the Au(111) surfaces. For each of the geometries considered, the atomic positions are fully relaxed with Hellmann-Feynman forces. We found that the fcc and hcp sites are almost degenerate in energy, with the hcp site higher in energy only by about 1 mRy per surface atom, thus giving concrete theoretical evidence to support the speculation that these two sites are very close in energy on the Au(111) surface. The knowledge of the energy of occupation of a few high symmetry sites allow us to extract a surface potential as seen by the top layer atoms. This surface potential energy, combined with our previous results of a Au monolayer contraction on top of a homogeneous medium (jellium surface), are cast into a Frenkel-Kontorowa model. The equilibrium configuration of this model is then found numerically, resulting in a top layer configuration very similar to the one deduced from experiments. In particular we found that the top layer indeed reconstructs, contracting along a $(1, \bar{1}, 0)$ direction by about 5%, and both fcc and hcp sites are occupied in the final configuration. The surface electronic structure of Au(111) surface is also investigated, and we found that the surface band structure is rather insensitive to the position of the top layer.

Table 6.1: Energy per surface atom for the top layer occupying different sites, using the top site as reference. Negative energies indicate higher stability

Site	Energy(mRy)
FCC	-13.8
HCP	-12.9
TOP	0
BRIDGE	-10.7

Table 6.2: Relaxation of the interlayer separation in % of the ideal layer separation for the top layer at various sites

	TOP	BRIDGE	FCC or HCP
Δ_{12}	16.2	3.7	1.5
Δ_{23}	-0.1	-0.3	-0.3

Table 6.3: Percentage relaxation of the interlayer separation for different sizes and separations of the slab

	7layers of Au		7layers of Au		9layers of Au	
	4layers of Vacuum		6layers of Vacuum		4layers of Vacuum	
	fcc	bridge	fcc	bridge	fcc	bridge
Δ_{12}	1.5	3.7	0.8	3.7	1.6	2.1
Δ_{23}	-0.3	-0.3	-0.3	-0.3	0.2	0.3
Δ_{34}	0	0	0	0	0.1	-0.1
Δ_{45}	-	-	-	-	0	0

Figure 6.1: A schematic structure of the (111) face of Au. A, C, T, and B labels atoms in the hcp, fcc, top, and bridge sites respectively.

Figure 6.2: The 2-D Brillouin zone of Au (111) for the surface atom in the fcc, hcp, and top sites. The irreducible parts of the Brillouin zones are shaded

Figure 6.3: The 2-D Brillouin zone of Au (111) for the surface atom in the bridge site. The irreducible parts of the Brillouin zones are shaded.

Figure 6.4: A 3-dimensional plot of the potential energy per surface atom experienced by the top layer as a function of the position.

Figure 6.5: Contour plot of the potential energy per surface atom in the (111) plane.

Figure 6.6: The reconstructed Au(111) surface as given by the F-K model. The crosses denote the positions of the second layer, and filled circles denote the positions of atoms in the reconstructed top layer

Figure 6.7: One row of surface atom in the $(1\bar{1}0)$ direction. The scale in the $(11\bar{2})$ direction has been exaggerated. Filled circle denote the position of the reconstructed top layer, open circles at the top denote the position of the fcc sites, and open circles at the bottom denotes the positions of the hcp sites. C and A mark the regions of ABC and ABA stacking

Figure 6.8: Surface states and resonances along high symmetry lines for Au(111) with the surface atoms at the fcc site

Figure 6.9: Surface states and resonances along high symmetry lines with the surface atoms at the hcp site

Figure 6.10: Surface states and resonances along the $\bar{M}_1$ - $\bar{K}_1$ - $\bar{\Gamma}$ - $\bar{M}_1$ direction with the surface atoms at the bridge site

Figure 6.11: Surface states along the $\overline{M}_2$ - $\overline{K}_2$ - $\overline{\Gamma}$ - $\overline{M}_2$ direction with the surface atoms at the bridge site

Figure 6.12: Contour plots of the charge density of the surface state A in the plane formed by the vectors (111) and $(\bar{1}12)$ with the top layer at (a) for the fcc site, (b) for the hcp site, and (c) for the bridge site

CHAPTER 7. STUDY OF THE GROWTH OF AG ON AL(111)

Introduction

During the past years, the study of crystal growth has become a very hot topic of research. With the advent of new experimental techniques it is possible to fabricate crystals with certain desired properties. Methods such as molecular-beam-epitaxy (MBE) allow the construction of materials one molecule at a time. New materials, with different surface properties such as work function and conductivity have been artificially created. Nowadays it is possible to deposit controlled amounts of atoms on to metallic, and semiconductor substrates, and in this way create new multilayer materials, with specific physical and chemical properties, that can be very useful in the solid state device technology. The growth mode may be two dimensional, three-dimensional, or a mixture of the two [83]. For quite sometime the growth mode has been separated in three main groups. (i) The Volmer-Weber (VM) mode, when initiated from the three-dimensional islands (cluster formation); (ii) The Frank-van der Merwe (FM) mode, when it grows by the successive addition of two-dimensional layers; and (iii) The Stranski-Krastanov (SK) when initial FM growth is followed by VW growth. However not always the crystal grow in the way we want them to do. In order to successfully create the material with the properties we are interested in, we have to understand the physics of crystal-growth, and to know under what condition

a crystal will grow in certain way.

Bauer [83] first suggested a criterion to predict the growth mode based on the free surface energies of the substrate surface σ_s , the adsorbate σ_a , and the interface σ_i :

$$\begin{aligned}\sigma_a + \sigma_i - \sigma_s &\leq 0; \text{ FM growth,} \\ \sigma_a + \sigma_i - \sigma_s &> 0; \text{ VW growth.}\end{aligned}\tag{7.1}$$

Bauer's criteria represent a zero-order approximation, and neglect many factors like the intermixing, anisotropy, strain energy of the overlayer, mismatch, etc.

The purpose of this chapter is to theoretically investigate the growth of one metal into another. We choose Ag on Al(111) because it shows a very interesting growth mode [14]. For small coverage Ag grows pseudomorphically (Its lattice constant is the same as the lattice constant of Al, i.e., contracted 0.9% with respect to bulk Ag) on the Al(111) surface. With the onset of cluster growth in the second layer, the monolayer is contracted with respect to the Al substrate. We use first-principles total energy calculations to study the growth of Ag on Al(111). We calculate the total energy of bulk Ag and Al, and the total energy of the Al(111) surface with and without adlayers of Ag. We show that indeed, the growth is of the SK mode: at the beginning the Ag layer grows pseudomorphically with respect to the Al substrate, but later prefers the cluster formation. Our calculation gives physical insight of why the Ag layer contracts only after one monolayer of coverage. Also using the information that we have about the contraction of a single monolayer of Ag on a jellium substrate, and the energy of occupancy of various surface sites computed by total energy techniques, we use a Frenkel-Kontorowa (FK) model [58] to study the contraction of the Ag monolayer.

First-principles Calculations

We use in our calculations non-local ionic pseudopotentials generated using the norm-conserving scheme of Hamann, Schlüter, and Chiang [54]. The total energies are calculated within the local-density-functional formalism [53] with the Hedin-Lundqvist [63] form of the local exchange-correlation energy. For the Al calculations, the wave-functions are expanded in plane waves with kinetic energy $(\mathbf{k} + \mathbf{G})^2$ up to a cut-off energy $E_{cut} = 12mRy$. For the calculation of Ag and Ag on Al, the wave-functions are expanded by means of an efficient mixed-basis-set consisting in plane waves with kinetic energy $(\mathbf{k} + \mathbf{G})^2$ up to a cut-off energy $E_{cut} = 12mRy$, and a set of localized functions centered at the atomic sites to describe the more tightly bound orbitals [68]. We use for the local orbitals numerical functions which are more flexible and can better represent the local orbital than the Gaussians. This method has been used in previous investigations of the structural properties of bulk Ag [32], and the study of the Ag(100) surface [52]. For most of the calculations described below, 15 $\mathbf{k}$ -point in the irreducible surface Brillouin zone (SBZ) are used.

Ag and Al Bulk Calculations

Several factors contribute to the energetics of the crystal growth. There is an interplay between bulk and surface contributions. In order to decide what kind of growth takes place, we have to compare the total energy of several bulk and surface structures. If we want to obtain meaningful results, it is important that the various calculations are done in a consistent way. Even though we have already calculated the bulk energies of Ag and Al before [32], the calculations were done using an uniform $\mathbf{k}$ -

point grid sampled in the first Brillouin zone (IBZ), corresponding to the conventional fcc unit cell. To have a consistent comparison between all the different energies, the sampling of the k -point has to be similar in all the cases. In this section, we calculate the bulk energies of Ag and Al using a k -point sampling that match the one of the surface calculations. Our unit cell consist of 3 layers of Ag or Al(111) atoms, placed in the ABC stacking, so when this unit cell is repeated in the [111] direction, the bulk is obtained. The atoms in each layer are arranged with hexagonal symmetry. The distance between successive layers is $a/\sqrt{3}$, where a is the lattice constant of Ag or Al. The reciprocal lattice vectors are given by:

$$\begin{aligned} \mathbf{K}_1 &= \frac{2\pi}{a} \left(-\frac{2}{3}, -\frac{2}{3}, \frac{4}{3} \right), \\ \mathbf{K}_2 &= \frac{2\pi}{a} \left(\frac{2}{3}, -\frac{4}{3}, \frac{2}{3} \right), \\ \mathbf{K}_3 &= \frac{2\pi}{3a} (1, 1, 1). \end{aligned} \tag{7.2}$$

In the plane formed by $\mathbf{K}_1$ and $\mathbf{K}_2$, we use 15 k -points sampled in the irreducible part of the surface Brillouin zone corresponding to a (111) surface of the fcc structure. This sampling is repeated in the $\mathbf{K}_3$ direction n times, with n an integer that we varied. In Figures (7.1) and (7.2) we show how the energy depends on n . We observe that to achieve convergency for both Ag and Al, n has to be greater than 3.

Total Energy of the Al Surface

Another quantity that we need for the study of the growth of Ag on Al is the total energy of the (111) surface of Al. We perform self-consistent local density functional calculations for the Al(111) surface. We use a unit cell consisting of 9 layer of Al atoms and 9 layer of vacuum. The forces acting on each atom are calculated

using the Hellmann-Feynman theorem, and the structure is relaxed following the direction of the forces. The use of Hellmann-Feynman forces allows the determination of equilibrium atomic positions with a small number of trial geometries. Different geometries are tried until the forces on every layer drop below $1 \times 10^{-3} \text{ Ry}/\text{\AA}$. In most of the surfaces, when the relaxation occurs, the atoms move inward. However, for the case of the Al(111) surface, LEED experiments by Nielsen and Adams found a 0.9% expansion of the first layer [84]. Previous LDA calculations by Needs [85], also show an expansion of 1%. Our calculation agrees with those experimental and theoretical results. We find a small relaxation of the first layer atoms moving outwards 1.2% with respect to the interlayer distance of the inner atoms.

Once we have found the equilibrium position of the atoms, we can calculate the Surface Energy of the Al(111) surface. $E_s = \frac{1}{2}[E(9 \text{ layer slab}) - E_{bulk}]$ where E_s is the surface energy, E_{bulk} is the total energy of the Al bulk, $E(9 \text{ layer slab})$ is the total energy of our Al(111) slab calculation, and the 1/2 factor comes because of the two surfaces of the slab. We found $E_s = 27.5 \text{ mRy/at.}$, and for the surface energy per unit area, $E_s/A = 0.052 \text{ eV}/\text{\AA}^2$, that agrees very well with the value $\gamma = 0.048 \text{ eV}/\text{\AA}^2$ using a jellium approximation quoted by Needs [85], and it is not very far from $\gamma = 0.044 \text{ eV}/\text{\AA}^2$, value found by Needs using pseudopotentials.

A calculation of a 7 layer slab of Al(111) gives $E_s = 29.7 \text{ mRy/at.}$, very close to the value found using 9 layers of Al, assuring us that 9 layers of atoms is good enough for our calculations.

Growth of Ag on Al(111)

The heat of formation ΔE is the quantity that is important deciding the kind of growth of a given material. Using the Al(111) surface and the Ag bulk as reference materials, the heat of formation is defined as follows:

$$\Delta E = E - [\theta E(Ag_{bulk}) + E(Al_{surface})], \quad (7.3)$$

with $E(Ag_{bulk})$ the total energy of Ag bulk, $E(Al_{surface})$ the total energy of the Al(111) surface, and E the total energy of the system we are considering. We note in equation (7.3) that the most negative ΔE , the most favorable the structure is. The heat of formation is the energy change in the process of the formation of the structure, starting from its initial components, the Al(111) surface and the Ag bulk.

In this section we calculate the total energy of one, two, and three layers of Ag on top of each side of an Al slab. All the Ag and Al atoms are in the ABC stacking corresponding to the fcc structure. The interlayer distances are fully relaxed with the help of Hellmann-Feynman forces. We use 9 layers of Al, and at least 5 layers of vacuum (in some cases we used 7 layers of vacuum, with no significant difference). Using these results, and the energies of bulk Ag and Al, and the energy of the Al(111) surface calculated before, we can find the heat of formation of Ag growing pseudomorphically on Al at coverages varying from $\theta = 0$ to $\theta = 3$:

By definition for $\theta = 0$, $\Delta E = 0$.

Using the result of our calculation of a single layer of Ag on Al, we can obtain $\Delta E(\theta)$, $\theta = 1$, for Ag growing pseudomorphically with respect to the Al substrate:

$$\Delta E(1) = E(1 \text{ layer of Ag on Al}) - [E(Ag_{bulk}) + E(Al_{surface})] \quad (7.4)$$

In the same, using the results of our calculations of two and three layer of Ag on Al, we can obtain $\Delta E(2)$ and $\Delta E(3)$. Generalizing for θ integer, we can write:

$$\Delta E(n) = E(n \text{ layers of Ag on Al}) - [nE(Ag_{bulk}) + E(Al_{surface})] \quad (7.5)$$

Neglecting boundary effects, $\Delta E(\theta)$ is linear between θ integer. The filled line in Figure (7.3) shows the heat of formation for Ag growing pseudomorphically on top of the Al(111) surface.

To calculate the heat of formation of Ag cluster formation on top of the Al surface, we make the assumption that the number of Ag atoms in the surface of the cluster, and in the interface is small compare with the total number of atoms in the cluster. Making this assumption, the total energy of this system is just the energy of the Al(111) surface plus the energy of the Ag bulk, giving for the heat of formation:

$$\Delta E(\theta) = 0 \quad (7.6)$$

as shown in Figure (7.3) by the x axis.

The total energy of the system consisting of Ag clusters growing on top of one layer of Ag on Al(111) is the energy of the Ag bulk plus the energy of one layer of Ag on Al(111), giving:

$$\Delta E(\theta) = E(1 \text{ layer of Ag on Al}) - [E(Ag_{bulk}) + E(Al_{surface})] \quad (7.7)$$

as shown in Figure (7.3) by the dotted line.

If the cluster growth is on top of two layers of Ag:

$$\Delta E(\theta) = E(2 \text{ layers of Ag on Al}) - [2E(Ag_{bulk}) + E(Al_{surface})] \quad (7.8)$$

as shown in Figure (7.3) by the dashed line. In Figure (7.3) the system with lower heat of formation is the most favorable. We observe that for low coverages, $\theta < 2$ the

pseudomorphic growth is more favorable than the cluster formation. For $\theta > 2$ we see that the cluster growth is more favorable than the pseudomorphic growth. So indeed Ag grows in Al(111) in the Stranski-Krastanov mode: at the beginning forming layers, but later forming clusters. So far we have not considered any contraction. This is done in the next section, but first let's examine Figure (7.3) deeply, and get more physics from there. We can observe that the slope of the line that represents the pseudomorphic growth, decreases at $\theta=1$, and $\theta=2$. This means, that the binding energy of Ag decreases as we increase the number of layers, with the Ag atoms preferring to be in the first layer rather than in the second, or third. This can be interpreted as a stronger bonding between Ag-Al than Ag-Ag. This fact gives us an explanation of why the Ag layer starts contracting only when the coverage is one monolayer: for $\theta < 1$ Ag is happy being in registry with the Al substrate, but for $\theta > 1$ the Ag atoms instead of forming a second layer of atoms, prefer to stay in the first layer, inducing its contraction, so more Ag atoms can be in contact with the Al atoms.

Contraction of the Ag Layer

A complete description of the reconstruction, using *ab initio* calculations alone is very difficult because the contracted Ag layer is incommensurate with the Al surface. However, we can give a good description of the reconstruction using a simple two-dimensional Frenkel-Kontorowa (FK) model, with parameters extracted from first-principles total energy calculations. A FK model describes the situation of the Ag atoms on the Al substrate. They are exposed to two competing interactions: the interaction of the Ag atoms favoring a contraction to a smaller lattice constant, while

being exposed to a potential due to the substrate Al, trying to pin them in registry with respect to the substrate. Depending of which interaction is stronger, the Ag layer will contract or remain with the same lattice constant of the Al substrate. Our previous calculation of the Ag monolayer on top of a jellium slab, show that the Ag atoms prefer a higher packing density than the arrangement of the surface atoms on the Al(111) surface with the Al bulk lattice constant, as shown in Figure (7.4)

The effect of the substrate atoms is expressed in the form of a periodic potential with the symmetry and periodicity of the unreconstructed Al(111) surface. The potential energy per surface atom is expanded in a Fourier series of the form:

$$E(\mathbf{R}) = \sum_{\mathbf{G}} W_{\mathbf{G}} e^{i\mathbf{G}\mathbf{R}}, \quad (7.9)$$

where the $\mathbf{G}$ s are the 2-dimensional (2D) reciprocal lattice vectors of the substrate surface and $\mathbf{R}=(x,y)$ is the position of an Ag atom. In order to have an estimate of this energy, we use first-principles techniques to obtain the total energy of the Ag atom occupying the fcc, hcp, bridge, and top sites of the Al surface. For the fcc, hcp, and top sites 15 k-points in the surface Brillouin zone (SBZ) are used. For the bridge site, the reduction of the symmetry mandates a SBZ three time larger, and the sampling of the k-points is increased to 45. For each site, all the interlayer distances are fully relaxed using Hellmann-Feynman forces. The results are summarized in Table (7.1), where the energies are energies per surface atom, and the zero of the energy is taken to be the energy of the Ag atom occupying the top site. The energies of the fcc and hcp are very similar, but as it should be, the fcc site is more stable than the hcp. The energy of the bridge site is slightly higher, while the energy of the top site is very unfavorable.

Our knowledge of the adsorption energies at these few sites, allow us to determine

few terms in equation (7.9)

$$\begin{aligned}
 E(x, y) = & \frac{3V_B}{4} - \frac{(V_C + V_A)}{9} \left[\cos \frac{2\pi}{a} x + \cos \frac{2\pi}{a} y + \cos \frac{2\pi}{a} (x + y) \right] \\
 & + \frac{(V_C - V_A)}{3\sqrt{3}} \left[\sin \frac{2\pi}{a} x + \sin \frac{2\pi}{a} y - \sin \frac{2\pi}{a} (x + y) \right] \quad (7.10) \\
 & + \left(\frac{V_C + V_A}{9} - \frac{V_B}{4} \right) \left[\cos \frac{2\pi}{a} (2x + y) + \cos \frac{2\pi}{a} (2y + x) + \cos \frac{2\pi}{a} (x - y) \right]
 \end{aligned}$$

where V_C is the energy at the fcc site, V_A is the energy at the hcp site, V_B is the energy at the bridge site, and the zero of the potential energy is taken to be the energy at the top site. The lattice constant of the 2D hexagonal lattice is given by a , and the coordinates of the atoms are expressed in terms of the basis of the substrate lattice.

Using these two interactions, we can write the FK model as:

$$d(q) = \sum_{ij} e(\mathbf{R}_i - \mathbf{R}_j) + \sum_i E(x_i, y_i) \quad (7.11)$$

where q is the fractional decrease in area per surface atom (at the ideal surface $q=0$), and $d(q)$ is the energy change per atom, due to the area contraction by a fraction q . The first term describes the interaction of the Ag atoms under the average influence of the substrate. This is the term that favors the contraction. To represent it, we use the results of our previous calculations of the energetics of a Ag monolayer on top of a jellium slab. Because Al is a free-electron like element, the jellium approximation should describe reasonably well the effect of the Al substrate on the Ag layer. In the previous calculation the density of the jellium slab was $r_s = 1.9$, close to the Al charge density $r_s = 2.0$. The 2D Frenkel-Kontorowa model describes a situation in which the Ag layer has a different preferred bond length with respect to the potential dictated by the Al substrate. The system will find its ground state configuration by

optimizing between the strain energy and the potential energy. The FK model can not be solved analytically in 2 dimension. We solve it numerically, using a 2D mesh of 120x120 atoms. The total area is constrained to correspond to a given contraction q , the R_i 's are relaxed according to equation (7.11) to determine the lowest energy configurations and the corresponding $d(q)$.

For a coverage greater than one, the Ag layer gain energy not only because of the contraction, but because more atoms can occupy the first layer. If we write the coverage as $\theta = 1 + x$, the energy of the contracted Ag layer can be written as of function of x :

$$E(x) = (1 + x)E(1 \text{ layer of Ag on Al}) + (1 + x)d(q), \quad (7.12)$$

with $1 - q = 1/(1 + x)$, and $d(q)$ as defined in equation (7.11)

The heat of formation of a contracted Ag layer on Al(111) is then given by:

$$\Delta E(x) = (1 + x)d(q) + x[E(1 \text{ layer of Ag on Al}) - E_{bulk}] \quad (7.13)$$

We found that indeed for more than one monolayer, the lattice constant of the Ag layer is contracted.

Summary

We have used first-principles total energy calculation to study the crystal growth of Ag on Al(111). We found that Ag grows in the Stransky-Krastanov mode. It starts growing forming layers (FM mode), and then forming cluster (VW mode). At the one monolayer coverage, the Ag layer contract. This sudden contraction is due to the fact that the Ag binding energy in the first layer is bigger than the Ag binding

energy in the second. This means that the Ag atoms prefer binding with the Al atoms, causing a contraction of the Ag layers so more Ag atoms stay in contact with the Al atoms.

Table 7.1: Energy per surface atom for the Ag layer occupying different sites of the Al(111) surface. The top site is used as reference. Negative energies indicate higher stability

Site	Energy(mRy)
FCC	-22.1
HCP	-20.4
TOP	0
BRIDGE	-14.1

Figure 7.1: The k-point convergence test for the total energy of the Ag bulk using a matching sampling

Figure 7.2: The k-point convergence test for the total energy of the Al bulk using a matching sampling

Figure 7.3: Energy change per atom for a Ag monolayer in close-packed arrangement as a function of the percentage contraction of surface area per atom. The reference point is the area occupied by one surface atom on an ideal (111) surface with the lattice constant of Ag. The arrow shows the ideal (111) surface area of the ideal (111) surface with the lattice constant of Al

Figure 7.4: The heat of formation for the crystal growth of Ag on Al(111) for coverage between $\theta = 0$ and $\theta = 3$

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