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THEORETICAL STUDY OF THE OXIDATION OF A PURE AND ALLOYED COPPER SURFACE
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THE OXIDATION OF A PURE
AND ALLOYED COPPER SURFACE

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Abstract

In this thesis oxidation of a pure and alloyed Cu surface was studied using density functional theory based calculations. The mechanism and energetics behind experimentally observed missing row reconstruction on a pure Cu(100) surface were studied. Examination of the formation of the missing row was approached by studying the profitableness of vacancy formation to the surface at oxygen coverages below and equal to 0.5 ML. However, an ideal surface was in all cases more favourable in energy than vacancy included structures. Therefore an additional Cu atom was added to the simulation cell to promote vacancy formation. A consequence of this on-surface Cu addition was the identifying of a new energetically favoured Cu-O-Cu chain formation. This newly identified structure is a possible transition state in the path from an ideal surface to a reconstructed one.

Copper(I)oxide formation through sub-surface adsorption was examined on a reconstructed Cu(100) surface. At low O coverage on-surface adsorption was found to be much more favoured than adsorption on sub-surface sites. However, when coverage increased to 0.75 ML structures with both on-surface and sub-surface adsorbates possessed the lowest energy. Furthermore, the diffusion barriers to the sub-surface adsorption sites were low. Both these facts support the conclusion that the transition from the reconstructed missing row structure to the copper(I)oxide takes place without any large energy effort.

The adsorption induced segregation of copper on a Ag/Cu(100) surface was studied by calculating the surface energies of slabs where the silver layer was positioned at different depths with varying O coverage. In addition, the segregation energies were also calculated with two Ag compositions. It was discovered that without oxygen adsorbates silver atoms lying on top of the surface were favoured but the surface segregation probability of Cu increases with increasing O coverage.

The same calculation procedure was expanded to study the segregation probability of five additional alloy metals with a Cu surface. Without oxygen present Mg, Al and Zn possess a weak tendency to segregate to the surface, however, V and Cr prefer to stay in the bulk. The addition of oxygen adsorbates on the surface causes the segregation of all the dopants to the top of the surface. With the Al dopant the effect of the surface orientation and the oxygen coverage were also studied. The bonds between adsorbates and the surface were strongest with the densest surface, (111), and weakest with the most opened surface, (110). Furthermore, the enrichment probability was largest in the case of the (111) surface and lowest with the (110) surface. Probability increased with increasing oxygen coverage.

Keywords: adsorption, computer simulations, copper, density functional calculations, oxidation, single crystal surfaces, surface alloy, surface reconstruction, surface segregation, transition metal alloys
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Tiivistelmä


Kupari(I)oksidin muodostumista pinnanalaisen happiadsorptiokautta tutkittiin rekonstruoituneella Cu(100) pinnalla. Pienillä happi-peitostasoihalla pinnanpäämissä adsorption havaittiin olevan huomattavasti suotuisampaa kuin pinnanalaisen adsorption. Kuitenkin heitt peiton kasvua 0,75 ML:iin rakenteet, joissa oli adsorbaatteja sekä pinnan alla että päällä, tulivat muita suotuisimmiksi. Myös lasketut energiavallat hapen diffuusiolle pinnalta pinnan alla olivat hyvin pieniä. Kaikki tulokset viittaavat siihen, että rekonstruoitunut Cu(100) pinta hapettuu helposti kupariri(1)oksidiksi.


Asiasonan: adsorptio, erilliskidepinnat, hapettuminen, kupari, metalliseos, rekonstruktio, segregaatio, tietokonesimulaatio, tiheysfunktionaaliteoria
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Abbreviations

BO Born-Oppenheimer (approximation)
CuO Copper(II)oxide
Cu2O Copper(I)oxide
DFT Density functional theory
$\psi^k_r$ Wavelike part of the electronic wave function
eV Electron volt
E Energy of the system
$E_B$ Binding energy of the adsorbate
$E_{\text{ads}}$ Adsorption energy of the O atom
$E_{\text{Ag}}$ Energy of one bulk Ag atom
$E_{\text{bulkAg}}$ Energy of the Ag alloyed Cu slab where Ag atoms lies in the third layer of the slab
$E_{\text{corr}}$ Correlation term of the total energy
$E_{\text{Cu}}$ Energy of one bulk Cu atom
$E_{\text{e-e}}$ Electron-electron interaction
$E_{\text{ext}}$ External potential energy
$E_{\text{Hartree}}$ Classical Hartree energy
$E_{\text{kin}}$ Kinetic energy
$E_{\text{O/Cu}}$ Total energy of the O covered system
$E_{\text{o}}$ Energy of oxygen molecule
$E_{\text{O-slab}}$ Energy of the adsorbate-substrate system
$E_{\text{Slab}}$ Energy of the pure metal slab
$E_{\text{Segr}}$ Segregation energy
$E_{\text{Surf}}$ Surface energy
$E_{\text{SurfAg}}$ Energy of the Ag alloyed Cu slab where Ag atoms lies on topmost layer
$E_{\text{tot}}$ Total energy of the many-electron system
$E_{\text{ideal}}$ Total energy of the ideal surface
$E_{\text{tot-\text{vac-on-surf}}}$ Total energy of the structure where there is one vacancy and one on-surface Cu atom on the simulation cell
$E_{\text{xc}}$ Exchange and correlation energy
$E_{\text{xc-LDA}}$ Exchange and correlation energy of the local density approximation
$E_{\text{xc-GGA}}$ Exchange and correlation energy of the generalized gradient approximation
$f_{\text{\text{\textit{k}}} \text{\textit{r}}}$ Cell-periodic part of electronic wave function
FCC Face-centred cubic lattice
G Reciprocal lattice vectors of the crystal
GGA Generalized gradient approximation
\( \hat{H} \) Hamilton operator
HCP Hexagonal close-packing lattice
L Langmuir (Unit of exposure), 1 L = 10^-6 torr s
LDA Local density approximation
LSDA Local spin density approximation
ML Monolayer (Unit of coverage)
\( N_{Ag} \) Number of Ag atoms
\( N_{Cu} \) Number of Cu atoms
\( N_{O} \) Number of O atoms
NEB Nudged elastic band method
PAW Projector augmented wave method
STM Scanning tunnelling microscopy
\( \hat{T}_e \) Kinetic energy of the electrons
\( \hat{T}_N \) Kinetic energy of the nuclei
\( \hat{V}_{ee} \) Potential for the repulsive interaction between electrons
\( V_{\text{ext}} \) External potential
\( \hat{V}_{Ne} \) Potential for the attractive interaction between nuclei and electrons
\( \hat{V}_{NN} \) Potential for the repulsive interaction between nuclei
VASP Vienna ab initio simulation package
XPD X-ray photoelectron diffraction
\( \theta \) Coverage
Å Ångström = 10^{-10} m
\( \varepsilon_{\text{xc}}^{\text{hom}} \) Energy-density of the homogenous electron gas per particle
\( \rho \) Electron density
\( \Psi \) Wave function
\( \psi(R,r) \) Wave function of nuclei and electrons
\( \phi(R) \) Nuclei part of the wave function
\( \phi(r) \) Electrons part of the wave function
\( \nabla \rho(r) \) Density gradient
List of original articles

This thesis consists of the following papers:


The author (Kangas) has performed all the calculations in Papers I, II and III and the majority of calculations in Paper IV. In addition, the author has also been the main writer in these four articles whilst only being partly involved in the calculations and the writing process of Paper V.
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1 Introduction

Copper metal has been utilised as a source material for thousands of years in many applications. At first copper was used to make tools, weapons and jewellery in what is known as the “Copper Age” at around 3500–2500 BC. In those days, the most important properties of copper were its high mechanical strength combined with good formability. Over the centuries copper has been utilised both as a pure metal and in alloyed form. One such example is the addition of tin to copper to form bronze which is a much stronger metal than copper. This alloying of metals was so significant historically that the resulting era was called the “Bronze Age”. Another remarkable alloy of copper is brass where copper has been alloyed together with zinc. (Aitchison 1960)

Although copper has long been used, nowadays it is still widely employed in a variety of applications. It is used, for example, in electrical wires, roofing, plumbing and coins whilst the latest application involve copper(I)oxide, Cu₂O, in the form of solar cells (Musa et al. 1998, Mahalingam et al. 2005). Furthermore, copper has been proven to possess antibacterial properties whose utilisation together with its alloys has, for example, been studied in hospitals (Noyce et al. 2007, Weaver et al. 2008).

The most important property of copper, however, is its conductivity. Copper is used as a conductor from the application of microelectronics to power lines (Dubin 2003, Wright 1917). All electrical devices contain Cu as a conductor and thus its high electrical and thermal conductivity, reasonable cost, malleability and strength makes it incomparable in these applications. Electrical devices are developing all the time and together with an increasing demand for these goods, it has led to a global increase in the consumption of copper (Moore 1965). For that reason it is understandable that the price of copper has experienced a sharp increase: at least to 5-fold during the undertaking of this thesis alone (Papp et al. 2008). The price of Cu is still very low when compared with other traditional catalyst materials such as palladium and platinum. However, it is about 4-fold when compared with the price of aluminium which is also quite a good conductor and in fact has better corrosion resistivity than Cu.

The oxidation of copper cannot be avoided since it is energetically favoured. Atomic scale knowledge of the surface is essential in order to control the oxidation of the surface or passivating it. The ability to control the oxidation process is a critical issue for example in catalytic processes where, instead of metal, metal oxides or even earlier phases during oxidation catalyses the reaction.
In this thesis phases of oxidation of a pure Cu(100) surface has been studied in Papers I, II and III. Passivation can be performed by alloying copper with other metals however these metals must be chosen so that in the presence of O atoms they segregate to the surface to react. This results in the forming of a protective oxide layer on top of the copper. In this thesis possible passivation of the copper surface has been studied in Papers IV and V.

The field of surface science is complex. Thus in the research, in addition to the structure of the surface, processes such as adsorption, diffusion and desorption on the surface and possible reconstructions and segregations of the surface during these processes have to take into account. Over the past decades there has been a great progress in both experimental and theoretical technologies used in surface science. This development has reduced the gap between experimental and theoretical studies. The most accurate experimental techniques already possess the ability to achieve atom scale accuracy whereas larger systems can be handled computationally. In many cases, the initial and final states of the surface phenomena can be observed in experiments, however by computing, energy required or released in the same phenomena can be solved. The combination of both experimental and computational results obtains the more exact picture of the progress of the phenomenon that usage of one method separately. In this thesis computed results have been analysed taking into account the present experimental results.

The structure of this thesis is organised as follows: Chapter 2 introduces the oxidising surface as the studied system whilst Chapter 3 explains the theory of the applied computational method and covers the calculation details behind the studies. Chapter 4 presents results of the oxidation of the pure Cu(100) surface and discusses these findings in the light of current scientific knowledge relating to that area. Chapter 4 also covers both studies on the formation of reconstruction on the Cu(100) surface (Paper I) and possible subsurface oxidation and Cu$_2$O formation (Papers II and III). Chapter 5 offers a discussion on the alloyed Cu surface together with an oxygen induced segregation of Cu to Ag doped Cu surface (Paper IV). Potential passivating dopant metals for Cu are also introduced in Chapter 5 (Paper V) and in conclusion, the contents and results of this thesis are summarised in Chapter 6.
2 Metal surfaces and processes on these surfaces

Many surfaces can appear flat when being studied with only human senses such as touch or eyesight. However, examining them more closely reveals the true roughness of the surface. Distances on an atom scale are normally expressed as Ångströms which correspond with $10^{-10}$ m or 0.1 nm. In this chapter, the basics of metal surfaces and interaction between oxygen and copper are introduced.

2.1 Structure of a metal surface

When simplifying we can describe atoms as spheres. In pure metals, these spheres are equal in size and are often packed together so that between atoms there is as small an amount of space as possible and all atoms have the maximal number of neighbouring atoms. These kind of organised structures are called close-packed structures. (Shriver 1994, Atkins & Langford 1994)

2.1.1 Close-packed structures

Ordered structures form a periodic lattice in which the unit cell is the smallest repeating unit. In close packed structures atoms can fill the unit cell in two distinct ways. (Housecroft & Sharpe 2005) The unit cells of these packing arrangements, the hexagonal close-packing (HCP) and the face-centred cubic (FCC) are presented in Fig. 1. This thesis concentrates on the study of copper, silver and aluminium which all have the face-centred cubic structure in which the atoms are in the corners and the centres of the faces of the cube (Somorjai 1993, Masel 1996). Deep inside the metal the forces affecting to the atoms are zero due to the high symmetry. This part of the metal are called bulk. Between the bulk and surface there is a layer in which the atoms are affected by the vicinity of the surface. This part is called selvedge.

2.1.2 Low index faces

The most reactive part of the metal is, however, the surface. Ideally, by cutting bulk metal crystal, we can obtain the so called single crystal surface which has a perfect structure without any defects (Masel 1996). The direction of the cutting determines which kind of surface is formed. Miller indices are generally used to
describe the direction of cutting by defining the points where the cutting plane crosses the x, y and z-axes of the crystal. The faces with the lowest Miller indices in the cubic lattice are presented in Fig. 2.

Fig. 1. Unit cell of a) HCP and b) FCC structure.

Fig. 2. a) 100, b) 110 and c) 111 planes in a cubic lattice.

Usually low indexed faces are used in the study of surfaces since they are the most ordered structures which have the smallest number of adsorption sites. (McCash 2007) Therefore they are the simplest faces to study. In Fig. 3 the top views of the 100, 110 and 111 faces of a FCC structure have been illustrated. This thesis mainly concentrates on the Cu(100) surface. Usually, when a metal surface is created the surface relaxes so that the topmost atom layer sinks down a few per cents from the bulk position. In some metals, a larger reconstruction of the surface is also observed. (McCash 2007)
Fig. 3. Top views of a) 100, b) 110 and c) 111 faces of a FCC structure. Topmost Cu atoms have been marked with white, Cu atoms in the second and third layer with grey and dark grey respectively.

In practice, surfaces are not as regular as single crystal surfaces: there are always defects such as steps, kinks, adatoms and vacancies on the surfaces. In addition planar terrace areas can also exist between steps. (Somorjai 1993) In Fig. 4 defects as well as adsorption sites and processes on metal surfaces introduced in Section 2.2 are illustrated.

2.2 Interaction between gas and a metal surface

When gas molecules approach a surface they can either desorb back off the surface or adsorb onto the surface. On many occasions the adsorbed molecule dissociates in this process. Coverage, $\theta$, describes the number of adsorbed atoms relative to the number of metal atoms per unit area. The unit of coverage is given as a monolayer (ML). (McCash 2007) On the surface, an adsorbate can diffuse along the surface or to subsurface sites, react with other adsorbates or desorb back to the gas phase. These surface processes were previously illustrated in Fig. 4.

2.2.1 Oxygen on a Cu(100) surface

In this thesis oxidation of a Cu(100) surface has been extensively studied. It is well known that an oxygen molecule dissociates when it approaches and adsorbs onto a surface (Junell et al. 2004, Alatalo et al. 2004). On the 100 face of a FCC metal three possible adsorption sites exists, hollow, bridge and top sites, in which the dissociated oxygen atom can lie after adsorption. Adsorption sites on the 100 surface of FCC metal are illustrated in Fig. 5. The adsorption of O atom on a Cu(100) surface is also possible at subsurface sites. Studies on these sub-surface sites are introduced in chapter 4. Two different oxidised structures have been
detected experimentally when a Cu(100) surface proceeds: Copper(I)oxide, Cu\textsubscript{2}O, also called cuprous oxide and copper(II)oxide, CuO, called cupric oxide (O’Reilly 1995).

2.2.2 Reconstruction of the surface

In some cases surface adsorption induces the reconstruction of surface atoms to minimise surface energies (McCash 2007). This is also the case with Cu(100) when oxygen coverage increases to 0.5 ML. A reconstructed Cu(100) surface has been illustrated in Fig. 6. During reconstruction Cu atoms of every fourth Cu row break off from the surface and diffuse to the step edges of the surface. Adsorbed
oxygen atoms locate on the hollow sites beside the missing rows. (Robinson & Vlieg 1990)

Fig. 6. Reconstructed Cu(100) surface at the O coverage of 0.5 ML. Every fourth Cu row is missing. Grey and black spheres represent Cu and O atoms respectively.

2.2.3 Alloying of a metal

For thousands of years, it has been well known that a metal surface can be alloyed with other metals to alter and improve the properties of the original material. Such new properties can enable the production of enhanced applications or the creation of new ones. For example, when copper was alloyed with tin during the Bronze Age, new tools and weapons were harder and more durable than the old ones made solely from copper. (Aitchison 1960)

Alloying can also be the solution to passivate a surface against oxidation. This is the case if an alloy metal reacts with oxygen to form a stable oxide layer on top of the Cu surface. For instance Al has a tendency to form a thin Al₂O₃ layer on the surface of Cu. This layer improves the corrosion resistivity of Cu since the formed oxide is more stable than the Cu surface on its own. (Lindroos et al. 1986)
2.2.4 Segregation phenomenon

As previously mentioned, passivation is possible only if alloy metals segregate to the surface to react with O atoms. Segregation generally means the redistribution of atoms between the surface and the bulk so that the total energy of a system is minimised. The possibility of segregation depends on the difference of binding energies of two similar and two different metal atoms. If the bond between two similar atoms is strong, segregation is probable. (Somorjai 1993) In cases where the adsorbate causes the segregation the driving force is the binding energy difference between different metal atoms and adsorbates. Adsorption induced segregation has been illustrated in simple terms in Fig. 7.

![Fig. 7. Adsorbate induced segregation of a single element of an alloy. White and grey circles represent different metal atoms whilst black circles denote adsorbed atoms on the surface.](image)

Probably the most well-known example of surface passivation through segregation is in stainless steel in which chromium metal segregates to the surface to react with oxygen to form a thin protective oxide layer. (Lindroos et al. 1986) In general, segregation is quite a common phenomenon in metal alloys and important since it influences properties which are needed when alloys are used, for example, in heterogeneous catalysis or applications of microelectronics. The segregation tendency of alloy metals of Cu is studied in papers IV and V.
3 Study of surface structure and processes on surfaces

The field of surface science is manifold since the structures of surfaces and processes on them include so many variables. Over the past decades there has been a great progress in experimental and computational technology as well as software algorithms and the theory of structure of matter. Therefore, it is now possible, in many cases, to define which phenomenon occurs on the surface and why they take place. Atom scale accuracy can be achieved with the most accurate experimental techniques whereas larger systems can be modelled computationally. This development has reduced the gap between experimental and theoretical studies leading to a more fruitful co-operation. To obtain a wide general view of studied problems a combination of many techniques are normally required. Advantages of computational chemistry include fairly low costs, friendliness to the environment and its speed in obtaining results compared with experimental laboratory work. Computational chemistry does not replace actual experiments but laboratory work for example could be reduced by limiting cases which have been observed to be impossible in calculations.

3.1 Electronic structure methods

Theoretical methods which use quantum mechanics to study atomistic systems are called electron structure methods. These methods are based on the Schrödinger equation which can be expressed in its time-independent form:

$$\hat{H} \psi(R, r) = E \psi(R, r)$$  \hspace{1cm} (1)

where $\psi(R, r)$ is the wave function of both nuclei and electrons, $E$ is the energy of the system and $\hat{H}$ is the differential operator representing the total energy, the Hamilton operator. The Hamilton operator consist of the kinetic energy of the nuclei, $\hat{T}_N$ and electrons, $\hat{T}_e$. Furthermore, it includes the potential part which has terms for the attractive interaction between the nuclei and electrons, $\hat{V}_{Ne}$, the repulsion of the electrons, $\hat{V}_{ee}$ and the repulsion between the nuclei, $\hat{V}_{NN}$. (Jensen 1999)

$$\hat{H} = \hat{T}_N + \hat{T}_e + \hat{V}_{Ne} + \hat{V}_{ee} + \hat{V}_{NN}$$  \hspace{1cm} (2)

Since the mass of nuclei are thousandfold compared to the mass of electrons it makes sense that the velocities of electrons are much larger than the velocities of...
nuclei. This fact allows us to separate the wave function to the nuclei part, $\phi(R)$ and the electron part $\varphi(r)$,

$$\psi(R,r) = \phi(R)\varphi(r).$$

(3)

This is called the Born-Oppenheimer (BO) approximation which leads to the vanishing of the kinetic energy term of the nuclei in the Hamilton operator. Another consequence is that the nuclei-nuclei potential remains constant. (Koch & Holthausen 2001, Seitsonen 2002) Taking the BO-approximation into account we can obtain the electronic Schrödinger equation and wave function $\varphi(r)$. The Hamilton operator can be expressed as

$$\hat{H} = \hat{T}_e + \hat{V}_{Ne} + \hat{V}_{ee} + \hat{V}_{NN}$$

(4)

The Schrödinger equation contains all the information of many electron systems. Unfortunately, it cannot be solved exactly for systems with large number of electrons and therefore many approximations have to be used. In the Hartree-Fock method the wave function is replaced with a single Slater determinant. Other examples of electron structure methods include the Møller-Plesset perturbation theory and configuration interaction method. These methods are, however, outside of the topic of this thesis and for that reason only mentioned due to their connection.

The calculations in this thesis have been performed using the most widely used code on the field of surface science the Vienna ab initio simulation package (VASP) which is based on the density functional theory (DFT) (Kresse & Hafner 1994). DFT based methods differ from other electronic structure methods since it does not solve the many-body wave function. In principle the ground state energy of the electron system is calculated from electron density.

### 3.2 Density functional theory

As mentioned the main idea in DFT is that the total energy of the electron system is a functional of the electron density, $\rho$. However, problem is that the functional connecting these two variables is unknown. (Koch & Holthausen 2001) In this section the development of DFT and the approximations behind solving the total energy have been presented concentrating on methods used in this thesis. An advantage of DFT is that electron density is a function of only three variables regardless of the size of the studied system while a wave function is a function of three variables for each electron. A consequence of DFT is that the computational
efforts needed for calculating the energetic of the system with an arbitrary number of electrons remains quite low even though the number of electrons increases. (Koch & Holthausen 2001) The idea of calculating atomic and molecular properties from the electron density appears to have arisen from the calculations of Thomas, Fermi and Dirac on an ideal electron gas in the 1920s. Walter Kohn together with Pierre Hohenberg and Lu Sham developed the DF theory in the 1960s from the base of the Thomas-Fermi theory. (Parr & Yang 1994)

### 3.2.1 Early phases of the theory

Taking into account the BO approximation introduced in section 3.1. the total energy, $E_{\text{tot}}$ for the many-electron systems can be expressed as

$$E_{\text{tot}}[\rho] = E_{\text{kin}}[\rho] + E_{\text{ext}}[\rho] + E_{\text{e-e}}[\rho]$$

(5)

where $E_{\text{kin}}[\rho]$ is the kinetic energy of the electrons, $E_{\text{ext}}[\rho]$ is the external potential energy and $E_{\text{e-e}}[\rho]$ is the electron-electron interaction energy. $E_{\text{ext}}$ can be determined as

$$E_{\text{ext}} = \int \rho(r) V_{\text{ext}}(r) \, dr$$

(6)

where $V_{\text{ext}}(r)$ is an external potential. The term for the interacting electron, $E_{\text{e-e}}[\rho]$ can be split to two parts: classical and non-classical. The classical part of this term is due to the repulsive Coulomb interaction of negatively charged electrons and can be written as

$$E_{\text{Hartree}} = \frac{1}{2} \int \frac{n(r)n(r')}{|r-r'|} \, dr' \, dr$$

(7)

The non-classical part is called exchange and correlation functional, represented by $E_{xc}$. (Jensen 1999) After the splitting of $E_{\text{e-e}}[\rho]$ the total energy can be presented in the form

$$E_{\text{tot}}[\rho] = E_{\text{kin}}[\rho] + E_{\text{ext}}[\rho] + E_{\text{Hartree}}[\rho] + E_{\text{xc}}[\rho].$$

(8)

The exchange and correlation functional includes both exchange and correlation parts. The exchange part arises from the Pauli principle which states that two electrons with parallel spins cannot occupy the same quantum state simultaneously. The correlation part is due to the fact that the prevailing spatial
position of the electron depends of the positions for other electrons. (Seitsonen 2002)

Finding the solutions for $E_{\text{kin}}$ and $E_{\text{xc}}$ has been the problem of developers of DFT. In the Thomas-Fermi method, $E_{\text{kin}}$ has been taken from the theory for non-interacting uniform electron gas

$$T_{\text{TF}}^{\text{kin}}[\rho] = C_F \int \rho \frac{3}{2} (\nabla \phi(r))^2 \, dr,$$

with $C_F = \frac{3}{10} \left(3\pi^2\right)^{\frac{2}{3}} = 2.871$ \tag{9}

and $E_{\text{xc}}$ has been replaced with $E_{\text{Hartree}}$ ignoring the term $E_{\text{xc}}$. (Parr & Yang 1994)

Later in the Thomas-Fermi-Dirac model the exchange and correlation term, $E_{\text{xc}}$, was also taken into account. However, these theories were found to be too crude and although they gave quite good results for atoms they failed to describe molecules and did not for example lead to chemical binding. (Jensen 1999, Lewars 2003)

### 3.2.2 Hohenberg-Kohn theorems and Kohn-Sham method

Although the theories behind DFT date back to the 1920s, the work of Kohn and co-workers in the 1960s developed DFT to be a very useful tool for the calculations of an electronic structure (Koch & Holthausen 2001). In 1964 Kohn together with Hohenberg published their theories which created the basis for the widely used DFT method (Hohenberg & Kohn 1964). They proved two facts for a system with a non-degenerate electronic ground state:

1. Ground-state electronic energy is determined completely by the electron density $\rho(r)$
2. The correct ground state density minimises the total energy functional

A year after the publication of Hohenberg-Kohn theorem Kohn with Sham continued the work of developing DFT by defining $E_{\text{kin}}$ and $E_{\text{xc}}$. They employed single-particle wave functions $\psi_i$ which define the density (Kohn & Sham 1965)

$$\rho(r) = \sum_i N_i |\psi_i(r)|^2,$$ \tag{10}

where $N$ is the number of electrons. The use of single-particle wave functions made it possible to calculate exactly the kinetic energy of non-interacting particles using the equation
However, in real systems electrons interact with each other. To take this into account a correction term for the kinetic energy is needed. This correction term is non-classical, like the exchange and correlation term, and therefore it is normally adsorbed to the exchange and correlation term, $E_{xc}$. This term includes all the uncertainty which DFT contains. If a solution for this term was to be known, DFT would provide the exact total energy of the system, including electron correlation.

### 3.2.3 Approximate solutions for the exchange and correlation term

The solution for the exchange and correlation term is, however, unknown and many approximate solutions have been developed. The most widely used approximation, the local-density approximation, (LDA) was also introduced by Kohn and Sham (Kohn & Sham 1965). In LDA it is assumed that locally the density can be treated as a uniform electron gas or at least it is a slowly varying function. The exchange and correlation energy of LDA at a point $\mathbf{r}$ can be expressed as

$$E_{xc}^{LDA} = \sum_{\mathbf{r}} \left[ \psi_i(\mathbf{r})^* \left( -\frac{1}{2} \nabla^2 \right) \psi_i(\mathbf{r}) \right] d\mathbf{r}. \quad (11)$$

$$E_{xc}^{LDA} = \int \rho(\mathbf{r}) \varepsilon_{xc}^{hom} (\rho(\mathbf{r})) d\mathbf{r} \quad (12)$$

where $\varepsilon_{xc}^{hom}$ is an energy-density of the homogeneous electron gas per particle. For $\varepsilon_{xc}^{hom}$ many parameterisations have been used in DFT history. VASP code uses the parameterisation of Perdew & Zunger (1981) which has been fitted to the quantum Monte Carlo results of Ceperley & Alder (1980). For spin polarised cases there is also a local spin density approximation, LSDA (von Barth & Hedin 1972). Although LDA is quite a crude approximation it works quite well in some applications but however, doesn’t achieve sufficiently accurate results in many others. Using LDA in solids the calculated binding energies are too large whilst lattice constants are too small. (Seitsonen 2002).

Many improvements to the LDA have been generated during the history of DFT. In this thesis the generalised gradient approximation, GGA, was used for the exchange and correlation functional (Perdew et. al 1992). The difference between LDA and GGA is that in the LDA exchange and correlation energy depends on the electron density but in GGA it depends, in addition to electron
density, on the derivatives of electron density taking into account the density gradients, $\nabla \rho(r)$.

$$E_{xc}^{GGA}[\rho(r)] = \int \rho(r) \nabla \rho(r) \, dx$$  \hspace{1cm} (13)

Like with LDA, there is also a spin dependent version for GGA which in this thesis has been used only for molecular oxygen.

After the work of Hohenberg, Kohn and Sham in the 1960’s methods based on DFT have improved and have gained ground in new application areas. Amongst others the time-independent DFT and finite temperature DFT have been developed. Since these methods have not been used in this thesis they are only mentioned in this connection.

### 3.3 Calculation details

The details of calculations are listed in the published papers of this thesis. In this section, the ideas behind the details used in the studies are discussed.

#### 3.3.1 Periodic boundary conditions and the slab

To keep the computational efforts reasonable, periodic boundary conditions illustrated in Fig. 8. are used in all calculations. In practice this means that used simulation cell including the slab of selected portions of the metal lattice and vacuum on top of the slab is repeated in three directions.

The surface is formed when the metal slab is repeated in two horizontal directions. As such, if a process (for example adsorption) occurs in the initial simulation cell same thing will happen in all the other replicated boxes. The repetition of the simulation cell in a vertical direction is not realistic but it could be made if the vacuum between slabs is large enough to prevent the interaction of the slabs. Furthermore, the slab has to be thick enough to prevent the artificial interaction between two surfaces. In this thesis, the surface has been mainly modelled with a metal slab that is five atoms thick. Adsorbates have been placed on one side of the slab whilst the vacuum between the slabs is about 10 Å. The error following from the height of the vacuum to the total energy is less than 0.01 eV.
3.3.2 Plane waves, k-points and cut-off energy

In DFT the total energy of the system is calculated from the electron density but as previously mentioned the single-particle orbitals produced by Kohn and Sham are used during the solving process. The calculation procedures of solving wave functions of periodic systems are demanding. Therefore reciprocal space is used to simplify these calculations. Handling of wave functions in reciprocal space is easier than in real space since waves are described with wave vectors, called k-vectors, in reciprocal space. These vectors whose direction is similar with the course of the wave point to the so called k-points.

Reciprocal lattice of a simple cubic lattice, with lattice constant $a$, is also a cubic lattice, but in reciprocal space the lattice constant is written as $2\pi/a$. Similarly to lattice vectors which determine the lattice in real space, reciprocal lattice vectors, called G-vectors, determines the reciprocal lattice. Planes which bisects these lattice vectors defines the Brillouin zones. For instance, 1$^{st}$ Brillouin zone of simple cubic structure is the area which is defined by planes that bisects the reciprocal lattice vectors that points to the nearest reciprocal lattice points.
Two dimensional cubic lattice in real and reciprocal space and the first two Brillouin zones are illustrated in Fig. 9.

Fig. 9. Two dimensional cubic lattice in real and reciprocal space. The first two Brillouin zones in a reciprocal lattice are also presented.

Real space waves are periodical which means that a similar phase of the wave always repeats after the same particular distance. Similarly in reciprocal space periodicity of the k-vectors (which describes real space waves) ensures the same value for the wave function, when the k-vector is lengthened for multiples of the reciprocal lattice constant. Therefore, all points in reciprocal space can be reduced to the k-points of the 1st Brillouin zone.

When a wave function is solved at the centre point of the 1st Brillouin zone (called Gamma-point) it has the same periodicity of the unit cell. However, at any other points of the 1st Brillouin zone the periodicity of the wave differs from the periodicity of the unit cell. Bloch’s theorem provides us a solution for this problem since it has been proven that with a periodic solid each electronic wave function can be written as

$$\psi_{n,k}(r) = f_{n,k}(r)e^{ik \cdot r},$$

where $e^{ik \cdot r}$ is a wavelike part in which $n$ is the band index, $k$ is a point in the 1st Brillouin zone and $r$ is the position vector of the point which is under
consideration. The cell-periodic part, \( f_{n,k}(\mathbf{r}) \), possesses the periodicity of a real space crystal lattice. In this thesis plane waves have been used as a basis set to describe wave functions and \( f_{n,k}(\mathbf{r}) \) is in the form
\[
f_{n,k}(\mathbf{r}) = \sum_{\mathbf{G}} c_{n,k,G} e^{i \mathbf{G} \cdot \mathbf{r}} ,
\]
where \( \mathbf{G} \) are the reciprocal lattice vectors of the crystal and \( c \) is the Fourier coefficient. Kohn Sham orbitals can be now written as a sum of the plane waves
\[
\psi_{n,k}(\mathbf{r}) = \sum_{\mathbf{G}} c_{n,k,G} e^{i (k \cdot \mathbf{G}) \cdot \mathbf{r}} . \quad \text{(Payne 1992)}
\]
Without the Bloch theorem the wave function should be calculated explicitly over several unit cells to ensure the extended periodicity. Usage of this theorem limits the calculations to one unit cell but still for each periodicity (k-point) the wave function has to be calculated.

To describe large system exactly an infinite number of k-point has to be calculated. However, it has been proven that wave functions at k-points near to each other in k-space are almost identical and for that reason it is acceptable to limit calculations and solve the wave functions only in the finite number of k-point which represents the whole k-space. (Payne et al. 1992) A number of k-points have to be chosen so that the required accuracy is reached. In this thesis the Monkhorst-Pack method is used to generate sets of k-points (Monkhorst 1976).

When a periodic system is studied the Kohn-Sham equations remain almost the same: only a summation over the k-points has to be added. The Kohn-Sham density (equation 10) becomes
\[
\rho(\mathbf{r}) = \sum_{k} \sum_{n} \psi_{n,k}(\mathbf{r})^\ast \psi_{n,k}(\mathbf{r}) .
\]
and the kinetic energy (equation 11) can be written
\[
E_{\text{kin}}(\rho) = \sum_{k} \sum_{n} \int \psi_{n,k}(\mathbf{r})^\ast \left(-\frac{1}{2} \nabla^2 \right) \psi_{n,k}(\mathbf{r}) d\mathbf{r}
\]
Plane waves are commonly used in periodic systems with periodic boundary conditions. When used, only reciprocal lattice vectors are required to be calculated for the electronic wave functions. The problem is that the number of \( G \) vectors is infinite. However, accurate results can be achieved although G-vectors
up to a particular kinetic energy, called the cut-off energy, $E_{\text{cut}}$, are involved (Honkala 2001).

### 3.3.3 Pseudopotentials

Description of the core electrons within the plane waves is computationally difficult. In chemical reactions valence electrons are active and core electrons are inert. Therefore, an approximation where core electrons with the nucleus are described within an effective potential, called pseudopotential, is commonly used to limit the computational efforts obtaining accurate results. In this thesis VASP code were used together with the Projector augmented-wave (PAW) method. This method combines the best qualities of the linear augmented-plane-wave method and plane-wave pseudopotential approach which has been studied to be reliable and efficient. (Blöchl 1994, Kresse & Furthmüller 1996, Kresse & Joubert 1999)

### 3.3.4 Nudged elastic band method

Barrier calculations have been performed using the nudged elastic band method (NEB) which is based on the transition state theory. The NEB method was first introduced by Mills & Jónsson (1994) and Mills et al. (1995) who achieved band optimisation by minimising simultaneously the forces acting on the images. Images are points selected between initial and final configurations where the energy and geometry are calculated. In the original NEB method two force components were included: perpendicular component of the true force and the parallel component of the spring force. In this thesis a NEB method with modifications by Henkelman & Jónsson (2000) and Henkelmann et al. (2000) was used. The modifications were able to generate a different way to estimate the local tangent to the elastic band whilst improving the accuracy of saddle-point energies with their climbing image insertion. NEB method based calculations with these modifications have been proven to give accurate results in the plane wave based DFT calculations.

In Fig. 10 NEB calculations have been illustrated using an energy graph with the structures of NEB images. For the initial state, an ideal surface with 0.5 ML oxygen coverage and 0.125 ML Cu coverage is used. For this NEB calculation one Cu atom from the topmost Cu layer (initial state) has been moved through the four states (images) to the top site of the Cu surface (final state). In this transition
a single vacancy site forms on the surface. The energy barrier for the transition is marked with the symbol $\Delta E$, and in this particular case is about 1.25 eV high.

Fig. 10. An example of a NEB calculation where a Cu atom from the topmost Cu layer (initial state) has been moved through the four states (images) to the top site of the Cu surface (final state). In this transition a single vacancy site forms on the surface. The energy barrier have been marked with $\Delta E$, whilst in the images white, grey and black circles represent Cu atoms in the ideal surface, Cu atoms on the surface and O atoms respectively. In addition the Cu atom which is moving in the NEB calculation has been drawn with dashed lines.
4 Oxidation of a pure Cu(100) surface

Metal surfaces oxidise since metal oxides are energetically more favoured than corresponding pure metals and molecular oxygen separately. Many metal surfaces become oxidised uniformly as predicted by the Cabrera-Mott model (Cabrera & Mott 1949). In the case of Cu(100) the oxidation process of the surface is, however, non-uniform. Papers I, II and III of this thesis concern the oxidation of a pure Cu(100) surface.

4.1 Reconstruction of a Cu(100) surface

During the oxidation process of a Cu(100) surface, the surface goes through a reconstruction where every fourth Cu row is ejected from the surface. In this chapter, background theory and results of Paper I concerning the mechanism of the reconstruction are discussed.

4.1.1 Background

When a Cu surface is exposed to oxygen gas, the oxygen atoms interact strongly with the surface in the form of adsorption. Adsorption occurs via an activated direct adsorption channel (Jaatinen et al. 2007) where O₂ molecules dissociate on the top site and atomic O adsorbs onto the hollow sites of the surface (Alatalo et al. 2004). Surface defects, especially vacancies, enhance the dissociation of O₂ molecules (Ahonen et al. 2008). Interactions between two additional O atoms or additional Cu and O atoms on the surface are repulsive, but interactions between additional Cu atoms are attractive. At low O coverage the diffusion barrier of an adsorbed oxygen atom is 0.75 eV whilst the barrier to the self-diffusion of Cu on the Cu(100) surface is 0.53 eV. As such, the presence of O atoms decreases the diffusion barrier of Cu. (Alatalo et al. 2004). At low coverages adsorbed O atoms form nanometer size c(2×2)-O structure domains which are surrounded by zigzag-shaped phase boundaries. These phase boundaries are free of oxygen. (Fujita et al. 1996)

When the average O coverage on the surface is increased to 0.34 ML the first indications of surface reconstruction appears (Kittel et al. 2001). Nano-sized c(2×2)-O domains coalesce to larger ones and start to reconstruct (Tanaka et al. 1998). In the scanning tunnelling microscopy, STM, image of Lahtonen et al. (2008) reconstructed areas are seen approximately at an average coverage of 0.4
ML. Once the Cu(100) surface has fully reconstructed dissociation and diffusion of oxygen become difficult (Jaatinen et al. 2007). Therefore, Cu atoms ejected from the surface diffuse along unreconstructed areas to step edges which transform straight edges into a more sawtoothed appearance. When reconstructed areas expands and c(2×2)-O domains decreases diffusion becomes more difficult and Cu atoms start to nucleate on the surface. (Lahtonen et al. 2008)

Reconstructed areas grow at the expense of the c(2×2)-O phase whilst at an O coverage of 0.5 ML the (\(\sqrt{2}\times\sqrt{2})R45^\circ\)-O missing row structure is completed. (Kittel et al. 2001) In this structure every fourth Cu row has broken off from the surface and O atoms are located in the hollow sites besides missing Cu rows (Robinson & Vlieg 1990). A missing row structure is illustrated in Fig. 6. Between reconstructed areas there are phase boundaries when missing rows are misaligned (Lahtonen et al. 2008). A similar reconstruction is also observed in a Ag(100) surface (Rocca et al. 2000, Loffreda et al. 2003).

Reconstruction is assumed to be induced by O adsorption. According to the results of Jensen et al. (1990) and Jakobsen & Norskov (1990) Cu-O bond formation releases much more energy than is needed to break the Cu-Cu bonds. Furthermore, Cu-O-Cu chains formed in missing row formation are energetically favourable. In a few references it has been suggested that an increase in O coverage increases the stress on the surface which leads to the formation of missing rows. (Harrison et al. 2006, Tanaka et al. 1998)

4.1.2 Results

Although there are many studies concerning the reasons for reconstruction the opposite is true about the motions of atoms when reconstruction begins. The aim in paper I was to obtain an understanding as to the atom scale development of reconstruction and predict its energy needs. Assuming that at the beginning of the missing row formation separate Cu atoms from the top layer are ejected from the surface, we calculated the surface energies for an extensive amount of structures possessing vacancy and on-surface Cu atom with different O coverage, and compared these surface energies with the surface energies of an ideal structure at corresponding O amounts. Surface energies are presented in Table 1 and have been calculated using the following equation
\[
E_{\text{surf}} = E_{O/Cu} - N_{\text{Cu}} \cdot E_{\text{bulkCu}} - N_{\text{Ag}} \cdot E_{\text{bulkAg}} - E_{\text{CuSurf}} - N_{O} \cdot \frac{E_{O_2}}{2},
\]

(19)

where \(E_{O/Cu}\) is the total energy of the modelled structure, \(N_{\text{Cu}}\), \(N_{\text{Ag}}\) and \(N_{O}\) are the numbers of those atoms in the simulation cell, \(E_{\text{bulkCu}}\) and \(E_{\text{bulkAg}}\) are the energies of bulk Cu and Ag atoms, \(E_{O_2}\) is the energy of the O\(_2\) molecule whilst \(E_{\text{CuSurf}}\) is the surface energy of the other side of the slab which was calculated by the equation

\[
E_{\text{CuSurf}} = \frac{(E_{\text{slab}} - N_{\text{Cu}} \cdot E_{\text{bulkCu}})}{2},
\]

(20)

where \(E_{\text{slab}}\) is the total energy of a clean, ideal Cu(100) slab. A reconstructed surface with coverage greater than 0.5 ML has been used in the calculations. The lower the surface energy the more favourable the structure is.

In Fig. 11 the numbering system of the calculated structures has been illustrated. Cu atoms and hollow sites of the ideal surface have been numbered and used to specify the structures in Table 1. For example in the structure vac5hol2 there is a vacancy in the place of Cu5 and an additional Cu atom on the hollow site 2.

Adsorption sites next to the vacancy were not stable and Cu atoms on these locations slid to the vacancy when relaxed. Therefore, surface energies of these structures are not presented. However, the next-nearest sites were stable. Energy differences between the ideal surface and the most favourable vacancy + on-surface Cu structures are calculated using the equation

\[
E_{\text{Diff}} = E_{\text{vac+on-surf}} - E_{\text{ideal}}
\]

(21)

where \(E_{\text{vac+on-surf}}\) is the total energy of the structure with one vacancy and one on-surface Cu atom whilst \(E_{\text{ideal}}\) is the total energy of an ideal surface. An ideal surface is more favourable than vacancy-on-surface structure if the energy difference is positive.

The smallest energy differences between ideal and comparison structures at various coverages have been illustrated in Fig. 12. Energy differences (marked with the symbol ■) for all O coverages are fairly similar, about 1 eV, which indicates that the ideal surface is clearly more favoured than vacancy + on-surface structures at a coverage between 0 ML and 0.5 ML. Therefore, the results
reported in paper I suggest that O increase does not stabilise the vacancy. These results disagree with earlier studies where reconstruction is assumed to depend on the O coverage (Harrison et al. 2006, Tanaka et al. 1998, Stolbov & Rahman 2002).

Table 1. Surface energies of the calculated structures and their resulting surface energy differences between these structures and their corresponding ideal structures.

<table>
<thead>
<tr>
<th>O coverage/ML</th>
<th>Structure</th>
<th>$E_{surf}$/eV</th>
<th>$\Delta E_{ideal}$/eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>ideal</td>
<td>3.58</td>
<td></td>
</tr>
<tr>
<td></td>
<td>vac5hol8</td>
<td>4.69</td>
<td>1.11</td>
</tr>
<tr>
<td>0.125</td>
<td>ideal</td>
<td>1.54</td>
<td></td>
</tr>
<tr>
<td></td>
<td>vac5hol8</td>
<td>2.69</td>
<td>1.15</td>
</tr>
<tr>
<td></td>
<td>vac5hol4</td>
<td>2.82</td>
<td>1.28</td>
</tr>
<tr>
<td></td>
<td>vac5hol2</td>
<td>2.90</td>
<td>1.36</td>
</tr>
<tr>
<td>0.25</td>
<td>ideal1</td>
<td>-0.37</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ideal1/vac5hol8</td>
<td>0.74</td>
<td>1.12</td>
</tr>
<tr>
<td></td>
<td>ideal1/vac5hol2</td>
<td>1.14</td>
<td>1.51</td>
</tr>
<tr>
<td></td>
<td>ideal1/vac4hol8</td>
<td>1.14</td>
<td>1.51</td>
</tr>
<tr>
<td></td>
<td>ideal1/vac4hol5</td>
<td>1.17</td>
<td>1.54</td>
</tr>
<tr>
<td></td>
<td>ideal2</td>
<td>-0.57</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ideal2/vac5hol4</td>
<td>0.88</td>
<td>1.45</td>
</tr>
<tr>
<td></td>
<td>ideal2/vac5hol2</td>
<td>1.13</td>
<td>1.71</td>
</tr>
<tr>
<td></td>
<td>ideal2/vac4hol1</td>
<td>1.13</td>
<td>1.71</td>
</tr>
<tr>
<td>0.375</td>
<td>ideal</td>
<td>-2.29</td>
<td></td>
</tr>
<tr>
<td></td>
<td>vac5hol8</td>
<td>-1.19</td>
<td>1.10</td>
</tr>
<tr>
<td></td>
<td>vac5hol1</td>
<td>-0.58</td>
<td>1.70</td>
</tr>
<tr>
<td></td>
<td>vac5hol2</td>
<td>-0.58</td>
<td>1.70</td>
</tr>
<tr>
<td>0.5</td>
<td>ideal1</td>
<td>-3.95</td>
<td></td>
</tr>
<tr>
<td></td>
<td>vac5hol2--vac5top2</td>
<td>-2.73</td>
<td>1.22</td>
</tr>
<tr>
<td></td>
<td>vac5top6</td>
<td>-2.83</td>
<td>1.11</td>
</tr>
<tr>
<td></td>
<td>vac1vac5top2top6</td>
<td>-1.49</td>
<td>2.45</td>
</tr>
<tr>
<td></td>
<td>vac5bri68</td>
<td>-2.85</td>
<td>1.09</td>
</tr>
</tbody>
</table>
Fig. 11. The numbering of atoms of the simulation cell which has been used to specify the calculated structures. In the example structure, vac5hol2, there is a vacancy in the position of the surface Cu5 and an additional Cu on the hollow site 2. (I, published by permission of Elsevier)

Fig. 12. The energy differences between the most favoured vacancy + on-surface structures and their corresponding ideal structures. In cases where the energy difference is positive the ideal surface is more favourable than the vacancy + on-surface structure.

According to our results, missing row formation did not appear to be such an obvious phenomenon although the reconstruction has proven to be an unavoidable consequence of increasing oxygen on the Cu(100) surface. In fact, it seemed that it is energetically very unlikely for Cu atoms to break off from the surface if there are no additional promoting effects other than O atoms on the surface. On account
of these results other possible promoting effects were considered. It was tested could it be possible for additional Cu atom in the simulation cell to stabilise a vacancy since it has been shown that there is an attractive interaction between Cu atoms (Alatalo et al. 2004) and also they have a tendency to agglomerate on top of the surface (Fujita et al. 1998).

In these tests, on-surface Cu atoms slid down to the vacancy even with an additional Cu atom in the cell, and similarly than in the case without an additional Cu atom the next-nearest sites were stable but still slightly higher in energy than their corresponding ideal structure. However, the most remarkable observation was the presence of a very stable structure where Cu and O atoms form Cu-O-Cu chain on the surface. This chain structure possessed an energy of about 0.5 eV lower than the corresponding ideal structure (marked with ● in Fig. 12) indicating that additional Cu stabilises the vacancy structure if a chain structure is formed. Furthermore, it is possible that Cu atoms which have already risen also promote the rising of other Cu atoms which themselves can attach to the chain. This chain structure has been illustrated in Fig. 13b together with ideal and reconstructed surfaces for comparison (Fig. 13a and Fig. 13c respectively). As shown, the Cu-O-Cu chain forms on top of the Cu row beside the vacancy. It was calculated that the energy barrier between the ideal surface with additional Cu and the chain structure was 0.5 eV.

4.1.3 Discussion

During the investigations, it was noticed that when a Cu-O-Cu chain formed on the surface it seemed like a new atom row was added to the initial surface. However, observations in recent STM studies by Lampimäki et al. (2007a) have shown no evidence of any additional rows, whereas an added row has been seen on Cu(100) in the STM study by Leibsle et al. (1995). The difference between these studies was that oxygen exposure was increased faster and the temperature was lower in the study by Lampimäki et al. A consequence of this might be that they failed to catch the possible intermediate state, the chain structure. A similar kind of added row formation has also been proven to take place during oxidation of Cu(110) (Coulman et al. 1990).

Lee & McGaughey (2011) published a similar study to the one presented in Paper I but remarkably ended up with completely different conclusions despite using the same code for their calculations. The differences between these studies can be attributed to the used pseudopotentials in addition to the used cut-off
energies and k-point meshes. In the study of Lee & McGaughey next adsorption sites from the vacancy were stable and they concluded that Cu atoms are ejected from the surface with an energy barrier of 2 eV. However, they found that the ejection of another Cu atom is energetically easier than the first ejection if the earlier ejected Cu atom lies near the second ejected Cu atom. This observation is consistent with our results which indicates that on the surface a Cu atom promotes the ejection of the Cu atom.

An explanation for the different conclusion is most probably the fact that we found two different reaction paths in these two studies. In the path identified by Lee & McGaughey the barrier of ejection is approximately 2 eV, but the process can take place without any additional Cu if the required energy is available. For the path passing through the chain structure the energy barrier is about 0.5 eV for Cu ejection, but the existence of an additional Cu atom is necessary. The computationally perceived chain formation reported in Paper I is most probably the fast intermediate state since to the best of the author’s knowledge, it is only observed in one experimental study in which oxidation of Cu(100) proceeded slowly due to the low O exposure. The total energy cost of the path within the
chain structure depends on the energies needed to break the formed added row structure. However, if there are favourable storing places for the Cu atoms, decomposition of the added row can occur without any large energy efforts.

According to experimental releasing Cu atoms diffuse to step edges where they bind next to a higher terrace of a surface. In the study of Lahtonen et al. (2008) step edges of a Cu(100) surface are seen as nearly straight lines in STM images. Step edges begin to transform into a sawtoothed appearance when small reconstructed domains appear on the surface. Diffusion occurs through unreconstructed parts where diffusion barriers are much lower than the reconstructed surface (Jaatinen et al. 2007).

Released Cu atoms start to nucleate when reconstructed domains expand resulting in the observation of rectangular nucleation centres at an O exposure of 1738 L at the junctions of c(2×2)-O domains. These nucleation centres grow as elongated islands on top of the phase boundaries between the reconstructed areas. Long sides of these islands are in the same direction of the missing rows. The results are consistent with the results presented in Paper I where larger energy releases are detected when more Cu atoms are added to the chain structure in the direction of the missing row as opposed to when Cu atoms are positioned beside the chain.

4.2 Beginning of oxide formation on reconstructed surface

The next step after reconstruction is the formation of copper(I)oxide which is only possible if oxygen atoms diffuse to sub-surface sites. In this section, results published in the Papers II and III are gathered together and are discussed in terms of background knowledge.

4.2.1 Background

According to combined temperature scanning tunnelling microscopy and quantitative x-ray photoelectron spectroscopy by Lahtonen et al., the whole surface has been reconstructed at the O exposure of 13360 L. Once the surface has been reconstructed the progress of the oxidation process is delayed. Although the O exposure has been increased, new structural signs of proceeding oxidation are not observed until the O exposure has been elevated to 9.4×10^5 L. O atoms then start to embed to sub-surface sites and so the formation of disordered Cu₂O islands commences. (Lahtonen et al. 2008, Lampimäki et al. 2007a) This
observation was surprising since according to our results in Papers II and III subsurface O atoms were favoured and barriers to O embedment were rather low.

### 4.2.2 Results

In Papers II and III profitableness of on-surface and sub-surface O adsorption with increasing O coverage on a Cu(100) surface were studied by comparing adsorption energies of modelled structures. Two types of sub-surface sites were studied as illustrated in Fig. 14: tetrahedral and octahedral sites. A tetrahedral site is between the first and the second layer under the surface bridge site whereas octahedral site is located right under the surface Cu atom in the level of the second Cu layer.

Equation 22 was used to calculate the adsorption energies of an ideal surface

$$E_{ads} = \frac{E_{O/Cu} - E_{Cu} - N_o \frac{E_{O_2}}{2}}{N_o} \tag{22}$$

where $E_{O/Cu}$ is the total energy of a oxygen covered surface, $E_{Cu}$ is the energy of a clean copper surface, $E_{o_2}$ is the energy of an oxygen molecule and $N_o$ is the number of oxygen atoms in the simulation cell. Adsorption energies on the reconstructed surface are calculated using the equation

$$E_{ads} = \frac{E_{O/\text{rec}} - E_{\text{Cu rec}} - (N_o - 2) \frac{E_{O_2}}{2}}{N_o - 2} \tag{23}$$

where $E_{O/\text{rec}}$ is the total energy of a oxygen covered surface, $E_{\text{Cu rec}}$ is the total energy of the reconstructed surface with an oxygen coverage 0.5 ML (two oxygen atoms per simulation cell), $E_{o_2}$ is the energy of an oxygen molecule in the gas phase and $N_o$ is the number of oxygen atoms in the simulation cell. Since $E_{\text{Cu rec}}$ include energies of two oxygen atoms these have been subtracted from the overall amount of oxygen $N_o$. Negative value of $E_{ads}$ indicates favoured bonding of oxygen.
Fig. 14. Studied sub-surface sites. a) top view of the tetrahedral site, b) side view of the tetrahedral site, c) top view of the octahedral site, d) side view of the octahedral site. The arrows in a) and c) show the direction of the views used in b) and d). Small spheres represent the O atoms.

Implementing a computational study with various coverage was little problematic since a Cu(100) surface reconstructs at a coverage between 0.33 ML to 0.5 ML and as a consequence the structure of the reference surface changes during calculations. In the used simulation cell it is possible to calculate the total energies of the structures at a coverage of 0, 0.25, 0.5 ML etc. In addition reference energies of clean surfaces are required (\(E_{\text{Cu}/\text{Cu}}\) in equation 22 of an ideal surface, \(E_{\text{O}/\text{Cu}_{\text{re}}\text{Cu}}\) in equation 23 for a reconstructed surface) to calculate adsorption energies for added O atoms. For that reason it is possible to calculate adsorption energies only at the coverage of 0.25 ML, 0.75 ML and higher.

In Paper II the ideal surface was used to calculate energy for O adsorption at coverages between 0 ML to 1.0 ML. However, a reconstructed surface was used to calculate the same values at coverages higher than 0.5 ML. Values calculated using different simulation cells are not comparable but it was noticed that trends in energies were similar at higher coverages in spite of the used surface. Therefore, we have the courage to make a conclusion according to the results of an ideal surface for all calculated coverages.
When O coverage was increased on on-surface sites the adsorption energy also increased indicating that there is a repulsive force between the on-surface O adsorbates. However, according to the values of sub-surface O atoms there was an attraction between sub-surface O atoms at large O coverages. Furthermore, it was also identified that there is an attraction between on-surface and sub-surface O atoms. This is because the combined adsorption energies for structures, which included only on-surface or sub-surface adsorbates, were higher than adsorption energies for a structure where the same adsorbates were on on-surface and sub-surface sites in tandem. In addition, differences between these two energies increased with increasing coverage.

Paper III concentrated further on studying high coverage O adsorption but only for a reconstructed surface. In this context, results considering the favourableness of the adsorption sites have been concluded so that results of an ideal surface at an O coverage of 0.25 ML have been reported. At a coverage of 0.5 ML the missing row structure with O atoms fixed on the hollow sites beside the missing row has been proven experimentally to be the most stable structure (Robinson & Vlieg 1990). In addition, reported results of coverage at 0.75 ML and higher have been calculated on a reconstructed surface.

Adsorption energies for a 0.25 ML coverage on the ideal surface are presented in Table 2 whilst coverages of 0.75 ML and higher for a reconstructed surface are presented in Table 3. These structures always include two oxygen atoms which correspond to the 0.5 ML O coverage of the missing row structure. Sites of O atoms added to the missing row structure are mentioned in the name of the structure listed in Table 3 and the numbers of sites refers to the numbers in Fig. 15 where the used simulation cell is illustrated.

![Fig. 15. Used simulation cell for a reconstructed surface.](image-url)
Table 2. Adsorption energies per O atom at 0.25 ML coverage.

<table>
<thead>
<tr>
<th>Ads. site</th>
<th>$E_{\text{ads}}$/atom [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top</td>
<td>-0.27</td>
</tr>
<tr>
<td>Bridge</td>
<td>-1.40</td>
</tr>
<tr>
<td>Hollow</td>
<td>-2.16</td>
</tr>
<tr>
<td>Octahedral</td>
<td>+0.14</td>
</tr>
<tr>
<td>Tetrahedral</td>
<td>+0.023</td>
</tr>
</tbody>
</table>

Table 3. Adsorption energies per O atom for reconstructed surfaces at coverages of 0.75 ML and higher.

<table>
<thead>
<tr>
<th>Ads. site</th>
<th>On/sub O</th>
<th>B/ML</th>
<th>$E_{\text{ads}}$/atom [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>hol7-3/0</td>
<td>0.75</td>
<td></td>
<td>-1.24</td>
</tr>
<tr>
<td>hol8-3/0</td>
<td>0.75</td>
<td></td>
<td>-0.35</td>
</tr>
<tr>
<td>top4-3/0</td>
<td>0.75</td>
<td></td>
<td>+1.02</td>
</tr>
<tr>
<td>octa1-2/1</td>
<td>0.75</td>
<td></td>
<td>-0.88</td>
</tr>
<tr>
<td>octa2-2/1</td>
<td>0.75</td>
<td></td>
<td>-1.23</td>
</tr>
<tr>
<td>octa4-2/1</td>
<td>0.75</td>
<td></td>
<td>-0.83</td>
</tr>
<tr>
<td>tetra24-2/1</td>
<td>0.75</td>
<td></td>
<td>-0.95</td>
</tr>
<tr>
<td>hol78-4/0</td>
<td>1.0</td>
<td></td>
<td>-0.80</td>
</tr>
<tr>
<td>hol7-octa1-3/1</td>
<td>1.0</td>
<td></td>
<td>-1.01</td>
</tr>
<tr>
<td>hol7-octa2-3/1</td>
<td>1.0</td>
<td></td>
<td>-1.12</td>
</tr>
<tr>
<td>hol7-octa3-3/1</td>
<td>1.0</td>
<td></td>
<td>-1.12</td>
</tr>
<tr>
<td>hol7-octa4-3/1</td>
<td>1.0</td>
<td></td>
<td>-0.91</td>
</tr>
<tr>
<td>hol8-octa1-3/1</td>
<td>1.0</td>
<td></td>
<td>-0.58</td>
</tr>
<tr>
<td>hol8-octa2-3/1</td>
<td>1.0</td>
<td></td>
<td>-0.82</td>
</tr>
<tr>
<td>hol8-octa4-3/1</td>
<td>1.0</td>
<td></td>
<td>-0.68</td>
</tr>
<tr>
<td>octa12-2/2</td>
<td>1.0</td>
<td></td>
<td>-1.16</td>
</tr>
<tr>
<td>octa23-2/2</td>
<td>1.0</td>
<td></td>
<td>-1.33</td>
</tr>
<tr>
<td>tetra1513-2/2</td>
<td>1.0</td>
<td></td>
<td>-0.69</td>
</tr>
<tr>
<td>hol7-octa23-3/2</td>
<td>1.25</td>
<td></td>
<td>-1.12</td>
</tr>
<tr>
<td>hol8-octa23-3/2</td>
<td>1.25</td>
<td></td>
<td>+1.88</td>
</tr>
<tr>
<td>hol78-octa1-4/1</td>
<td>1.25</td>
<td></td>
<td>-0.77</td>
</tr>
<tr>
<td>octa123-2/3</td>
<td>1.25</td>
<td></td>
<td>-1.17</td>
</tr>
<tr>
<td>tetra611254-2/3</td>
<td>1.25</td>
<td></td>
<td>-0.89</td>
</tr>
<tr>
<td>octa1234-2/4</td>
<td>1.5</td>
<td></td>
<td>-1.12</td>
</tr>
<tr>
<td>oxide-like-2/4</td>
<td>1.5</td>
<td></td>
<td>-1.17</td>
</tr>
</tbody>
</table>

At an O coverage of 0.25 ML hollow sites were clearly more energetically favourable compared to the other sites possessing an adsorption energy of -2.16 eV. Pure sub-surface adsorption was not favoured, however, for a coverage of 0.75 ML on-surface adsorption and hybrid structures (including both on-surface
and sub-surface adsorbates) have approximately the same energy. At 1.0 ML coverage the most favoured hybrid structure is over 0.5 eV lower in energy than the corresponding on-surface structure. Energy comparisons of the on-surface and hybrid structures on the reconstructed surface are presented in Fig. 16. At coverages higher than 1 ML adsorption energies are still lower than -1 eV indicating that the proceeding oxidation should be energetically beneficial.

Fig. 16. Adsorption energy comparison of hybrid and on-surface adsorption for a reconstructed surface at coverages between 0.75 ML to 1.5 ML.

Calculated energy barriers for O embedment to sub-surface sites are presented in Table 4 whose values indicated that O atoms should diffuse to the sub-surface sites quite easily. For a coverage of 0.75 ML the smallest energy barrier for the embedment of an O atom was 0.56 eV whilst corresponding values for a coverage of 1.0 ML and 1.25 ML were 0.30 and 0.33 eV respectively. These energies are small compared, for instance, with energies which are released when the same O atoms adsorb (1.24 eV – 1.17 eV). That is why the embedment of O atoms and formation of Cu₂O should take place readily after the reconstruction.

The strain in Cu lattice increases when O coverage increases in particularly on sub-surface sites. In Paper III in addition to performing tests on effects of strain which was found to be surprisingly small, the author tried to find a way to study the slab with the oxide lattice on top of the surface and the Cu lattice under
the oxide layer. However, these types of calculations were observed to be very demanding with the used calculation method.

Table 4. Energy barriers for an oxygen atom moving to a sub-surface site. In parenthesis there are initial and final sites of the moving atoms. (I, published by permission of Elsevier)

<table>
<thead>
<tr>
<th>Coverage/ML</th>
<th>Structure (moving atom)</th>
<th>$E_{\text{barrier}/eV}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.75</td>
<td>hol7→octa1</td>
<td>0.64</td>
</tr>
<tr>
<td></td>
<td>hol7→octa2</td>
<td>0.56</td>
</tr>
<tr>
<td>1.0</td>
<td>hol78→hol8octa1 (hol7→octa1)</td>
<td>0.74</td>
</tr>
<tr>
<td>20n→1on1sub</td>
<td>hol78→hol8octa2 (hol7→octa2)</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>hol78→hol7octa4 (hol8→octa4)</td>
<td>0.53</td>
</tr>
<tr>
<td>1.0</td>
<td>hol7octa3→octa23 (hol7→octa2)</td>
<td>0.33</td>
</tr>
<tr>
<td>1on1sub→2sub</td>
<td>hol8octa2→octa23 (hol8→octa3)</td>
<td>1.49</td>
</tr>
<tr>
<td>1.25</td>
<td>hol7octa23→octa123 (hol7→octa1)</td>
<td>0.38</td>
</tr>
</tbody>
</table>

4.2.3 Discussion

In agreement with our earlier mentioned results Lee & McGAughey also studied computationally oxygen embedment and the role of subsurface oxygen to oxide formation. They observed that an increase of O molecules to the sub-surface induced structural changes to the surface whose formed structures have similarities with bulk Cu$_2$O. (Lee & McGAughey 2009, Lee & McGAughey 2010) Experimentally in Yata’s studies a Cu$_2$O island formation was observed after reconstruction (Yata & Rouch 1999, Yata & Uesugi-Saitow 2002) whilst through transmission electron microscopy Yang detected triangular shaped islands. Yang further investigated the mechanism of Cu$_2$O formation and found that oxidation proceeds with the direct impingement of O atoms. Bulk diffusion also appeared to make a contribution to the growth of the Cu$_2$O islands. (Yang et al. 1997)

Studies by Yang et al. (1997) also revealed a very significant fact that surface diffusion of O atoms is a rate limiting step in this phase of oxidation. This fact explains the previously mentioned difference between our studies and the observations of Lahtonen et al. (2008). Although sub-surface oxidation is favourable at high O coverage, the progress of oxidation is delayed since surface diffusion is energetically much harder on a reconstructed than on an unreconstructed surface. Diffusion rates on the unreconstructed and reconstructed surfaces were also studied by Jaatinen et al. (2007). They agreed that diffusion on the reconstructed surface is much harder than on the unreconstructed surface.
Furthermore, they believe that adsorption of O atoms on a reconstructed surface proceeds via a trapping precursor mechanism where the energy needed for adsorption is larger than with direct adsorption on the unreconstructed surface. Although the formation of Cu$_2$O is delayed after reconstruction, disordered Cu$_2$O islands start to form at an O exposure of $9.4\times10^5$ L in the corners of ordered islands who are formed from Cu atoms during reconstruction (Lahtonen 2008). The formation of CuO, After Cu$_2$O formation, has been observed in previous publications such as O’Reilly et al. (1995). However, the formation of CuO is not included in this thesis.
5 Aligned Cu surfaces

As previously mentioned in the introduction Cu is a useful metal in many applications due to its high conductivity, however, its weakness lies in its low corrosion resistance. Since the properties of an initial metal can be altered by doping it with another metal, this chapter studies the question: could the oxidation of a Cu surface be prevented by alloying the surface?

5.1 Oxygen induced segregation of copper on top of a Ag/Cu(100) surface

In view of alloying a metal we confront a phenomenon called segregation where the components of an alloy are redistributed between the surface and the bulk. Segregation of one component is quite a common phenomenon in alloys and therefore was implemented in Paper IV which studied the oxygen induced segregation of Cu on a Ag alloyed Cu(100) surface. In this chapter a discussion about these results from Paper IV is presented.

5.1.1 Background

Hayoz et al. (1997) and Sprunger et al. (1996) have both studied the growth of Ag on a clean Cu surface by XPD and STM. Both research teams noticed that when a low coverage of Ag atoms is deposited onto a clean Cu surface the formation of a surface alloy is observed. When Ag coverage is increased, a c(10×2)-Ag layer forms on the Cu surface possessing a Ag(111)-like structure which was first observed by Palmberg and Rhodin (1968). It would be an inspiring idea if this kind of Ag layer could protect a Cu surface from oxidation. The oxidation of silver is clearly more unfavourable than the oxidation of Cu: the standard molar enthalpy of formation for Cu₂O is -168.6 kJ/mol while the same value for Ag₂O is -29.4 kJ/mol (CRC 1991). Furthermore, it was discovered that increasing the amount of Ag atoms alloyed in the Cu surface remarkably decreases the initial sticking probability of O₂ (Hirsimäki & Chorkendorff 2003). This should lead to a much slower oxidation of the surface.

However, when the alloyed Cu surface was further studied by Hirsimäki et al. observations showed that both the Ag/Cu{100} surface alloy and polycrystalline Cu(Ag) alloy oxidises almost identically with a pure Cu surface forming only Cu₂O on the surface. (Hirsimäki et al. 2005) This is possible only if the presence
of oxygen induces the segregation of Cu atoms to the surface to react with O atoms.

5.1.2 Results

In Paper IV, the main aim was to study the oxygen induced segregation of Cu to the surface of a Ag/Cu(100) alloy computationally. A simple model was developed where one layer of a Cu slab was replaced with a layer of Ag and the resulting surface energies of the slabs with varying O coverage were calculated. The Ag layer was placed, in turn, to the first, second and third layers of the Cu(100) slab. The whole slab was five layers thick and the proportion of Ag atoms was 20%. This model is considerably simplified compared to real alloys where the different metal atoms locate more randomly. However, on the grounds of the surface energies of structures with Ag layers at different depths, the favourableness of an alloying metal in surface or bulk sites could be compared. This would then allow further predictions to be made on the possible segregation facility of metals. Surface energies are shown in Table 5 and are calculated using equation 19, as presented previously in Chapter 4.1.

Table 5. The surface energies of a simulation cell where a single layer of a Cu slab is replaced by Ag at different layers for varying O coverage. The lower the surface energy the more favourable the structure is.

<table>
<thead>
<tr>
<th>E_{surf}/eV</th>
<th>Coverage/ML</th>
<th>0.25</th>
<th>0.5</th>
<th>0.75</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver in layer 0</td>
<td>2.77</td>
<td>2.42</td>
<td>-0.18</td>
<td>-0.40</td>
<td>-</td>
</tr>
<tr>
<td>1st</td>
<td>4.30</td>
<td>1.95</td>
<td>-2.52</td>
<td>-3.22</td>
<td>-4.27</td>
</tr>
<tr>
<td>2nd</td>
<td>4.13</td>
<td>2.08</td>
<td>-1.59</td>
<td>-2.86</td>
<td>-3.65</td>
</tr>
<tr>
<td>3rd</td>
<td>3.92</td>
<td>1.73</td>
<td>-2.34</td>
<td>-</td>
<td>-4.04</td>
</tr>
<tr>
<td>2nd/3rd</td>
<td>3.92</td>
<td>1.73</td>
<td>-2.34</td>
<td>-</td>
<td>-4.04</td>
</tr>
</tbody>
</table>

Furthermore, segregation energies where the energies of surface and bulk (third layer) Ag atoms were compared were calculated with Ag amounts of 5% and 20% as illustrated in Fig. 17. Segregation energies where calculated with the following equation

$$E_{\text{seg}r} = E_{\text{surf}Ag} - E_{\text{bulk}Ag}$$

where $E_{\text{surf}Ag}$ is the energy of the structure which has Ag atom/atoms on the topmost layer and $E_{\text{bulk}Ag}$ is the energy of the structure which has Ag atom/atoms in the third layer of the surface. If the calculated segregation energy is positive the
alloy metal is favoured to be in bulk but it should be noted that larger the positive value, larger the segregation probability becomes.

Fig. 17. Segregation energies of Ag doped (5% and 20%) Cu(100) surfaces as a function of O coverage over the surface. The lines are just a guide.

According to both surface and segregation energies without any oxygen adsorbates Ag atoms were clearly favoured to be in the top layer. This result is consistent with experimental data by Hayoz et al. (1997) and Sprunger et al. (1996). The coverage of 0.25 ML is considered as the turning point. Surface energy differences were small but the structure with Ag located in the second layer possessed the lowest surface energy. Segregation energy for 5% Ag was negative compared to a positive value for 20% Ag. This means that if there was a whole layer of Ag atoms on the slab the more favourable site would be bulk. However, a single Ag atom would prefer to be on the top layer.

For coverages of 0.5 ML and higher, according to both surface and segregation energies it appears that Ag atoms were favoured to be in bulk locations. Surface energy differences between structures with Ag on the surface and in bulk were high but also increased with increasing coverage. This indicates a larger facility for oxygen induced segregation. In all coverages Ag located in the
second layer had the lowest energy value. However, energy differences for structures with Ag in the third layer were not large. This result was a little surprising but probably energetically the most important task is for Cu atoms to locate on the surface. Furthermore, it might indicate that Ag atoms have the tendency to enrich to higher parts of the slab although Cu atoms are on the top layer. Segregation energies in studied compositions were positive at high coverages indicating that it is energetically more favourable for Ag atoms to be located in the bulk and for Cu atoms to react with O atoms on the surface.

At all coverages, surface energies were also calculated by dividing Ag atoms to the second and third layer. Energies of these structures were lower than if all the Ag atoms were on third layer but higher than when Ag atoms were in second layer. Since there is a size mismatch between Ag and Cu atoms larger lattice constants were also tested. It did not, however, have any influence on the trends of surface energies.

### 5.1.3 Discussion

According to the results it can be concluded that without oxygen present Ag atoms have the tendency to be located on the surface. When O coverage is increased, it becomes energetically more favourable for Cu atoms to be on the surface. The fact that surface energy differences (when Ag atoms are either on top of the surface or in bulk positions) are large and become larger when O coverage increases supports the segregation probability. Trends in segregation energies are also similar at all coverages in both compositions. However, the changes in segregation energies are stronger with higher amounts of Ag. This can be seen clearly in Fig. 17 where the graph for 20% Ag is sharper than for structures with 5% Ag. In general, although our model was simplified the results are quite clear and are in good agreement with experimental data (Hirsimäki et al. 2005).

More recent examinations by Lampimäki et al. (2007b) have revealed that the presence of Ag delays the initial states of oxidation. According to results from Lahtonen et al. (2008) this is due to the slow Cu diffusion. When Cu atoms segregate to the surface, oval-shaped Ag islands are formed which limit the diffusion of Cu. However, when oxidations proceed, strain on the Cu2O islands is higher on Ag/Cu{100} than on a pure Cu(100) surface which speeds up the oxidation leading to approximately the same oxidation rate on both surfaces. (Lampimäki et al. 2007b, Lahtonen et al. 2008)
5.2 Copper passivation by metal doping

Since promising results were obtained for an Ag/Cu(100) surface in Paper IV we wanted to expand the study to other metals. This is possible as one of the strengths of the computational study is its ease in which elements can be changed within the calculations. This way we can easily study which alloying elements could be probable for copper passivation and should be studied further.

5.2.1 Background

In Paper V, a Cu(110) surface is doped with five different metals and is analysed using the same calculation procedure from Paper IV (section 5.1). The aim of this new study is to investigate the binding strength of O atoms onto a Cu(110) surface for a coverage of 0.25 ML. Mg, Al, V, Cr and Zn were chosen as be the dopant metals since they are known to form a passive oxide when they react with oxygen. Al and Mg, whose atomic numbers are 12 and 13 respectively, are lighter than a Cu atom with its atomic number of 29. Both are sp-type metals compared to Cu which is d-type, however, V, Cr and Zn are also d-type metals. V and Cr are also lighter than Cu and are interesting dopants to research further since they are used in stainless steel. Zn differs from these two since it is heavier than Cu and its 3d and 4s orbitals are full.

Al and Mg are quite common alloy metals with Al often being used for alloying Cu, plus it has been known for a thin Al₂O₃ layer to form on top of a Cu surface. This Al₂O₃ layer has self-preparing property which prevents the continuation of oxidation of Cu. (Lindroos et al. 1986) Since Al metal, the oxidation of Al and Al doped Cu surfaces are well studied it is a good reference metal for this type of study. Therefore, Al was used to investigate more accurately the effect of surface orientation and the effect of O coverage on doped Cu surfaces. The author of this thesis was primarily responsible for these calculations and it is the reason why the text in this chapter mainly focuses on discussing the Al doped surface. However, a short conclusion of all the findings of this study is presented in this chapter’s results section.

5.2.2 Results

Without any O adsorbates on the Cu(110) surface the segregation energies of Mg, Al and Zn were negative which indicates that these metals have a tendency to
segregate on the Cu surface. Whereas, segregation energies for V and Cr were positive indicating that these metals prefer to locate in bulk. For an O coverage of 0.25 ML the binding energies of O atoms on the surfaces, where the dopant metal layers covered the Cu slab, were higher than the binding energy of the pure Cu surface. This indicates that O adsorption is more favoured if another metal, other than Cu, is on the top most layer of the surface. Binding energy difference between Zn and Cu was not large (0.46 eV). However, the other studied metals it was between 2.70 eV to 4.04 eV per O atom. These differences are so large that segregation of the dopant metal is very probable. When a dopant layer was moved deeper into the surface binding energies of O atoms decreased but the presence of the dopants still had the promoting effect of binding oxygen to the surface. Differences of binding energies were still, when the dopant layer was located in the fourth layer, 0.33 - 0.61 eV per atom.

Sub-surface adsorption was favoured only in cases where it was possible for O atoms to form bonds with the dopant metal. Structures where O atoms were bound to the four dopant metals were remarkably stable. When the dopants were placed close to the surface, binding energies were at their highest for V and Cr whereas this occurred deeper in the surface (in third or fourth layer) for Mg and Al. The behaviour of Mg and Al doped surfaces were similar on the grounds of both binding and surface energies. Furthermore, V and Cr both had similar affects upon the strength of the O adsorption. Differences between these two pairs are down to the type of metal: Al and Mg being sp-type while V and Cr are d-type. Of all the metals studied Zn was the most uneffective dopant. Even though it is a d-metal, on the contrary to V and Cr, it is a little heavier than Cu (and much heavier than Mg and Al). In addition, its 3d and 4s orbitals are full which makes it more inert.

The effect of the surface orientation on the energetic of an alloy with low index faces (100, 110, 111) of Cu were studied. The binding energies of 0.25 ML O atoms were calculated for a systems containing of a layer of Al dopant in the first, second and third layer of five layer thick Cu slab. Binding energy is defined as

\[ E_B = E_{\text{Slab}} + \frac{E_{O_2}}{2} - E_{O-\text{Slab}} \]  \hspace{1cm} (25)

where \( E_{\text{Slab}} \) is the energy of the pure slab before O adsorption, \( E_{O_2} \) is the energy of the free O molecule and \( E_{O-\text{Slab}} \) is the total energy of the adsorbate-substrate system. Binding energies are presented in Table 6.
The binding of O was much more favourable to the surface covered with Al dopants than to a pure Cu surface or surfaces where the Al atoms laid deeper. In this instance (Al layer on top of the surface) bonds of the O atoms were the strongest within the densest face, 111, of the surface and weakest within the 110 surface, where metal atoms are located further from each other. When the second and third layer were replaced with Al layer binding energies on the 111 and 100 surfaces decreased to the level of pure Cu. In the case of the 110 face binding energies also decreased when Al was deeper in the surface. However, energies were much higher than with pure Cu. This indicates that the dopant metal affects from deeper levels to surface adsorption on a 110 surface more than on the other studied surface orientations.

Table 6. The binding energies of hollow site O atoms on the Al doped Cu(110), Cu(100) and Cu(111) surfaces.

<table>
<thead>
<tr>
<th>Aluminium atoms in the layer</th>
<th>Binding energy/eV Al/Cu(110)</th>
<th>Al/Cu(100)</th>
<th>Al/Cu(111)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st</td>
<td>2.89</td>
<td>3.66</td>
<td>4.01</td>
</tr>
<tr>
<td>2nd</td>
<td>2.47</td>
<td>1.80</td>
<td>1.80</td>
</tr>
<tr>
<td>3rd</td>
<td>2.25</td>
<td>2.16</td>
<td>1.81</td>
</tr>
<tr>
<td>pure Cu</td>
<td>1.44</td>
<td>2.08</td>
<td>1.81</td>
</tr>
</tbody>
</table>

The effects of O coverage on the Al dopant where also studied by calculating the segregation energies (defined in equation 24) on the 100, 110 and 111 surfaces at the various O coverage. Results are presented in Fig. 18. In every case, the segregation energies were negative and decreased with increasing O coverage. According to these results, it can be concluded that Al has a tendency to segregate to the surface to react with O atoms which increases when O coverage also increases. The greatest decrease in segregation energies was observed for the densest 111 surface and the least with the most open 110 structure. This indicated that the segregation tendency is strongest for the densest surface orientation which decreases when the orientation is changed to a more open one.

5.2.3 Discussion

Our studies on the Al doped Cu surfaces are in excellent agreement with the x-ray photoelectron spectroscopy study by Kravchuk & Hoffman (2007). This investigation studied the effect of annealing and oxidation on the composition of
sputter-cleaned α-Cu-Al(100). Both thermal induced and oxygen induced Al segregation was found. With the combination of these both, the whole surface was covered with Al atoms. On the clean surface, only weak segregation was observed. Shen et al. (1995) attained similar results when they studied the oxidation and surface composition of an α-Cu-17%Al(100) surface with the use of ultraviolet photoelectron spectroscopy. They observed that at low O exposures O atoms react with the randomly located Al atoms on the surface. At higher exposures, Al atoms start to segregate to the surface but the low migration rate is the limiting step in the oxidation. The result, however, is that Al atoms enrich on the alloy surface to form Al₂O₃.

**Fig. 18.** Comparison of the segregation energies of Al doped Cu surfaces with various O concentration.
6 Summary

In Papers I, II and III the oxidation of a clean Cu(100) surface is studied. The oxidation of this surface has been proven experimentally to be a non-uniform process. The current overall picture of oxidation of Cu(100) is based on several experimental and computational studies. Paper I concerns the energetics of the transformation of an O covered ideal surface to a reconstructed surface. In many experiments an ideal surface transforms to a reconstructed one without any intermediate structures being observed. The computational study of Lee & McGaughey (2011) agreed with these results when they found direct path from the top layer of Cu atoms to the on-surface site with a barrier of 2 eV. In the study of Leibsle (1995) an added row structure was, however, observed when the surface was exposed to O atoms. Our result of the stable intermediated state, chain structure, is consistent with the findings of Leibsle. The path through the chain structure barrier for the Cu atom to be ejected from the Cu lattice to the surface was approximately 1.5 eV lower than in Lee’s direct path. However, this ejection required an additional on-surface Cu atom to promote the process.

Papers II and III presents energy and structural examinations of the transition from the reconstructed surface to copper(I)oxide, Cu₂O. Results of these articles have shown that when O coverage is increased to 0.75 ML and higher the mixed on-surface and sub-surface adsorption is more favoured than the pure on-surface adsorption. Furthermore, the diffusion barriers to the sub-sites are low and therefore the formation of Cu₂O should happen easily at high O coverage. However, experiments have shown that oxide formation does not start readily after the reconstruction for a coverage of 0.75 ML (Lahtonen et al. 2008, Lampimäki et al. 2007a). This disagreement is explained by the fact that the rate of adsorption and diffusion of O atoms on the reconstructed surface is very slow and these sub-processes control the rate of this phase of the oxidation process.

Papers IV and V concern the alloyed Cu surface and in the instance of Paper IV, the Cu surface was alloyed by Ag. The binding and segregation energies of alloys where Ag atoms are positioned at different heights in the slab were compared. Without any oxygen present on the surface the structure in which Ag was on top (in the first layer) was energetically the most favoured. However, for an O coverage of 0.25 ML, differences were observed between the two proportions of Ag. Cu atoms tended to segregate to the surface for 20% however for 5%, Ag segregation were not probable. For O coverages higher than 0.5 ML Cu atoms segregated to the surface to react with oxygen. These results are in
consensus with experimental results which claim that pure and alloyed Cu surfaces oxidise similarly (Hirsimäki et al. 2005).

In Paper V the study of segregation was expanded to other Cu alloys. The segregation tendency of Mg, Al, V, Cr and Zn to a Cu(110) surface was studied with and without an O coverage of 0.25 ML. Without O Mg, Al and Zn have the tendency to segregate to the surface compared to V and Cr which remained on the bulk. For an O coverage of 0.25 ML all the dopants binding energies indicated that the strongest interaction with the metal and adsorbate occurred if the dopant atom was located on top of the surface. Bonds weakened when dopant metals were moved deeper into the surface. These results combined with the fact that the binding energies were large indicate that all the studied dopants have the tendency to segregate to the surface when O atoms are present.

Furthermore, the effect of the surface orientation with the low index faces of the Cu surface and increased O coverage were studied with an Al dopant. It was observed that the bond between the O atoms and the densest surface, 111, was stronger than the bond between adsorbates and the 100 and 110 surfaces. In addition, the energy differences between structures where there was a dopant in the top or bulk layers were the largest with the 111 surface indicating the largest tendency to the segregation. However, with the most open surface, 110, the dopant metal strengthened the binding of oxygen deeper from the surface than with 111 and 100 surfaces. The segregation probability decreased with the O coverage. Finally, the results of Al segregation agreed with the experimental results of Kravchuk & Hoffman (2007) and Shen et al. (1995).

The present knowledge of the areas concerned in the Papers in this thesis has been formed according to the results of several studies, both experimental and theoretical. Experimental studies have revealed the main lines on the oxidation of Cu, however, this techniques can only observe the initial and final states of the surface processed. Computationally energetic and profitableness of the processes between these phases can be achieved and so the paths of these processes can be predicted. Papers in this thesis have successfully increased the knowledge of the oxidation of Cu. In Paper I, a new path from the ideal Cu surface to a reconstructed one was found whereas in Papers II and III, the sub-surface oxidation was illustrated to be very favoured. In Paper IV, a simple model to study the segregation of one component in an alloy was developed and tested against experimentally observed oxygen induced segregation of Cu to the surface of Ag alloyed Cu(100). In Paper V, the same model was used to study the
segregation tendency of the several other Cu alloys. Five dopant metals were identified to possess the potential for Cu passivation.
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Moore GE (1965) Cramming more components onto integrated circuits. Electronics 38


List of original articles

This thesis consists of the following papers:


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Original publications are not included in the electronic version of the dissertation.
579. Karjalainen, Mari (2011) Improving employees’ information systems (IS) security behavior: Toward a meta-theory of IS security training and a new framework for understanding employees’ IS security behavior


582. Haataja, Tatu (2011) Peroxisomal multifunctional enzyme type 2 (MFE-2): the catalytic domains work as independent units


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