Electronic structure of nickel nano-structures on titanium dioxide and copper : photoemission study

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ELECTRONIC STRUCTURE OF NICKEL NANO- STRUCTURES ON TITANIUM DIOXIDE AND COPPER: PHOTOEMISSION STUDY

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A thesis submitted to Nanyang Technological University in partial
fulfillment of the requirement for the degree of Doctor of Philosophy

2010

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other university or institution.

23-Feb-2010

Date

A handwritten signature in black ink, appearing to read 'Tao Junguang', written over a horizontal line.

Tao Junguang

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Summary

SUMMARY

It is very critical in the subject of surface science to discriminate the initial- and final-state effects in photoemission of supported (or isolated) metal clusters. In this thesis, Auger parameter analysis is applied to separate the contributions of the initial- and final-state effect to the binding energy shift observed. The comparison made on $\text{TiO}_2(001)$ and $\text{TiO}_2(110)$ surfaces demonstrates the importance of substrate contributions to the initial-state effect. The further analysis helps us to assign initial-state effect to a combination of eigenvalue shift in surface core-level shift and charge transfer between the Ni clusters and the TiO_2 substrates. The cluster size effect and interfacial charge transfer have a collective impact on the electronic structure of Ni clusters on the TiO_2 surfaces. The variation of the triplet atomic states in Ni satellite features can be used to trace the electron transfer mechanism when the dimension of Ni nano-clusters is modified because the Ni $3d$ electron population varies with scaling the dimension size.

The correlation enhancement of electrons in Ni nano-clusters due to the confinement in reduced dimension has been observed. Both the size and shape of nano-clusters show strong influence on the Ni $2p$ satellite structures. Apart from the 6-eV satellite, a 3-eV satellite structure emerges in Ni $2p_{3/2}$ photoemission spectra for small clusters due to the existence of ^3E and ^3T triplet states. However, the 3-eV satellite becomes weakened in larger clusters due to the increased electron population in $3d$ level, which is achieved through the electron transfer from the free-electron-like $4sp$ states to the unhybridized pure $3d$ spin down states.

We investigated the Ni electronic structure as a function of thickness on $\text{Cu}(001)$ surfaces by means of photoemission spectroscopy. The Ni thin films exhibit a different electronic structure as compared to thicker ones. A strong

Summary

thickness dependence of the correlation-induced Ni 6-eV satellite signal is observed. Through the comparison of Ni films grown on flat versus nano-structured Cu(001) surfaces, mixing of Cu atoms and Ni atoms is found to be intensified at the terrace edge region and hence a greater Cu 4s/Ni 3d interfacial hybridization effect is predicted for Ni on the nano-structured surface.

In the last part of this thesis, the interaction of nano-clustered Ni overlayer with TiO₂ substrate was studied by photoemission spectroscopy and atomic force microscopy. Ni segregates to the top surface region when the sample is cooled down to room temperature to reduce their surface energy regardless of the surface orientation. Thermal energy drives the Ni atoms diffuse inside TiO₂ lattice to form Ni²⁺-like species. The inward diffusion impelled by thermal energy is balanced by segregation when the thermodynamic equilibrium is reached. By comparing the different TiO₂ surfaces, diffusion rates along [001], [110] and [100] orientations have been predicted. Our study suggests that the diffusion is aided by the bridging oxygen atoms running along [001] direction. The variation in diffusion rate settles the understanding of Ni thin films morphology observed on several TiO₂ surfaces.

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LIST OF ABBREVIATIONS

AES	Auger Electron Spectroscopy
AFM	Atomic Force Microscopy
AP	Auger Parameter
ARXPS	Angle Resolved X-ray Photoelectron Spectroscopy
AUXPS	Angle Resolved Ultraviolet Photoelectron Spectroscopy
BE	Binding Energy
CI	Configuration Interaction
DFT	Density-Functional Theory
D-S	Doniach -Sunjić
DOS	Density of States
FM	Frank-von der Merve
FWHM	Full Width at Half Maximum
GIXD	Grazing Incidence X-ray Diffraction
KE	Kinetic Energy
LEED	Low Energy Electron Diffraction
MIGS	Metal-Induced Gap States
PES	Photoemission Spectroscopy
RBS	Rutherford Backscattering
RHEED	Reflection High Energy Electron Diffraction
RMS	Root Mean Square
SCLS	Surface Core-Level Shift
s/d IHE	s/d Interface Hybridization Effect
SEM	Scanning Electron Microscopy

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SK	Stranski-Krastanov
SMSI	Strong Metal-Support Interaction
SPM	Scanning Probe Microscopy
STM	Scanning Tunneling Microscopy
TEM	Transmission Electron Microscopy
UPS	Ultraviolet Photoemission Spectroscopy
UHV	Ultra-High Vacuum
VB	Valence Band
VW	Vollmer-Weber
XPS	X-ray Photoelectron Spectroscopy

CHAPTER ONE

INTRODUCTION

1.1 Background

Nano-materials have unique physical properties and chemical activities differing considerably from their bulk counterparts due to the confinement of electrons and the increased surface-to-volume ratio. The nano-scaled metal particles behave electronically as zero-dimensional quantum dots because the wavelength of the electrons is of the same order as the particle size itself [1]. The interplay between nano-materials and their surroundings is distinct from those properties of large bulk-like particles. One driving force for pursuing research on nano-materials is the wide range potential applications such as in quantum dots, quantum computers and devices [2; 3], chemical sensors [4] and catalysts [5].

Catalysts are widely used in large-scale manufacturing of chemicals, and also, production of fine chemicals and pharmaceuticals. Many catalytic systems consist of nano-sized metal catalysts supported on oxides. The catalytic activity is affected by the metal cluster size. As shown in Figure 1.1 [5], the size of the Au clusters substantially affects the catalytic activity for CO oxidation and the Au clusters must be smaller than 5 nm for high catalytic activity to occur. The highest

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activity happens at the average cluster size of 3 nm which decreases significantly both when the cluster size is bigger or smaller. The clusters with the size smaller than 3 nm are only one atom thick which have significantly larger band gaps, whereas clusters with size larger than 3 nm are of three atom layer or thicker which exhibit metallic properties [5]. The maximum activity falls on the clusters possessing behaviors between insulating and metallic. The size effects in catalysis over metal nano-clusters is also overlapped with the “support effects” [6] as well as the cluster shape and the their electronic structures [7]. The interaction between metals and oxide supports are of great importance in the heterogeneous catalysis. In particular, the strong metal-support interaction (SMSI) was first suggested to explain the suppression of both H₂ and CO chemisorption capacities of metal clusters supported on TiO₂ [8; 9].

Figure 1.1 CO oxidation turnover frequencies (TOFs) at 300 K as a function of the average size of the Au clusters supported on a high surface area TiO₂ support. After Ref. [5].

Photoemission spectroscopy (PES) is a very useful tool for investigating both surface electronic and chemical structures. When using PES to study metal

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clusters there are consistent observations of cluster-size-dependent binding energy (BE) shifts, showing that the core-level BE's of metal clusters on inert supports shift to higher values with decreasing cluster size [10-13]. An analysis of core-level BE shift of adsorbed atoms and molecules can be used to extract important thermochemical quantities, which are often otherwise not measurable [14]. The photoemission core-level shifts can be ascribed to configuration changes, chemical shifts, and relaxation shifts. The configuration changes are only due to changing the distribution of electrons among s , p , and d states [15]. The chemical shift is the displacement of the core level by changing in the chemical environment before an electron is removed from the level. These two contributions are intrinsic regardless of measurement techniques, thus are combined together for simplification and termed as initial-state effect. The relaxation shift describes the shift of the core-level BE caused by removal of the electron during photoemission process, which is extrinsic and is named as final-state effect. But there is substantial disagreement over the assignment of these shifts to initial- or final-state effects [12; 13; 16; 17]. It is very critical in the subject of surface science to discriminate between these effects in supported (or isolated) metal clusters, because among them, only the initial-state effect involves information of changes in the electronic structure before photoemission, and hence is directly related to nano-materials properties and is relevant for understanding other chemical process and reactions [12; 18].

The deposition of metal clusters onto well-defined oxide surfaces under the clean conditions of ultrahigh vacuum (UHV) provides a controlled method for studying fundamental details concerning clusters or films on oxide surfaces and metal/oxide interfaces. Numerous works have been performed to improve the understanding of the metal/oxide interface considerably. However, until very

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recently little was known about the electronic structure of the metal atoms that are right at interfaces and about the thermodynamic stability of these interfaces.

1.2 Motivation

There is increasing interest in nano-materials especially in metal nano-clusters grown on inert surfaces since they may give higher catalytic effect [6; 19; 20]. One of the interesting scientific and technological challenges associated with this issue is to understand how the electronic structure of nano-clusters produces the best catalytic activity. It is well known that photoemission spectroscopy (PES) is often used to deduce information on the electronic structure of molecules and solids [21]. PES senses only the top few atomic layers and, therefore, is very surface sensitive and compelling in nano-materials studies. The question of how the PE spectra of deposited nano-materials reflect their electronic structure is quite important, but answers to the question have been, and continue to be, heavily debated in the scientific community, which limits PES application in characterization of nano-materials.

The core-level BE shifts in accordance with metal cluster size, resulting from final-state effect, can be interpreted by a relaxation model. In this model, the BE shifts are attributed to variations in the extra-atomic relaxation processes. In solids, the hole state produced by photoionization is shielded by the conduction electrons and the cores of neighboring atoms. This effect lowers the energy of the final-state, resulting in a lower measured BE. Such an effect is clearly impossible for an isolated atom and reduces in clusters due to the decreased number of neighboring atoms. Thus a shift to lower BE is expected in the transition from atom to bulk metal. For supported metal clusters, this relaxation shift will also

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depend on the ability of the electrons from substrate atoms to shield the final-state hole. Quantitatively, a unit positive charge (incompletely shielded hole) will produce shift to high BE of the order $e^2/4\pi\epsilon R$ for both core and valence levels, where R is the cluster radius [13].

Compared to the final-state effect, the physics origin of the initial-state effect is more complicated due to the reasons as followed. (1) In considering the transition from a free atom to bulk metal, changes in the electronic structure or configuration with cluster size are to be expected. (2) There is a well-defined initial-state shift for surface atoms due to the lower coordination number. Since the contribution from surface atoms increases with decreasing cluster size, the surface core-level shift (SCLS) provides an additional shift in spectral weight for smaller clusters. (3) Charge transfers between clusters and the substrate may lead to either low or high BE initial-state shift, depending on the direction of charge transfer, which itself is dependent on the alignment of the Fermi level. Unfortunately, a full understanding of the contributions from abovementioned mechanisms is still missing. Hence it is of great interest to address these issues due to its importance of PES application in nano-materials characterization. In cases that the initial-state effects are dominant in BE shifts, the shifts can be used to determine interfacial charge, bonding state of interface metal atoms and interface reactions, which are important information in oxide-supported metal clusters as model catalysts.

1.3 Objectives

The main objective of this work is to make a surface science contribution to the ongoing research in the field of supported metal nano-structures. The detailed objectives can be split up into the following parts:

- (1) To develop expertise on metal nano-cluster grown on oxide surfaces and *in-*

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situ determination of their electronic structures using PES. The knowledge obtained would help to extend PES application to characterization at the nano-level. Due to tremendous technological importance of metal clusters, particularly in heterogeneous catalysis, the present work will contribute to a fundamental understanding of catalytic activity and selectivity of oxide-supported metal clusters as model catalysts.

- (2) To a somewhat lesser extent this research has been stimulated by a desire to understand the basic physics involved in the transition from discrete energy levels of free atoms to the continuous bulk metals. The new physics will also contribute to the design of new materials and the processes of modifying existing materials to obtain new functions.

1.4 Major contributions of the thesis

The major contributions achieved in this thesis are summarized as follows:

- (1) The photoemission BE shift in nano-clusters with cluster size has been understood on the basis of both the initial- and the final-state effects. The initial-state effect is demonstrated to be strongly affected by the substrate and is assigned to a combination of eigenvalue shift in surface core-level shift (SCLS) and charge transfer between the metal clusters and substrates. In considering the transition from a free atom to bulk metal, changes in the electronic structure or configuration with cluster size are to be expected. Due to the repulsive Coulomb interaction between core and valence electrons, the core-level BE is very sensitive to the valence electron configuration. The effective bandwidth for surface atoms is less than bulk atoms due to the lower coordination number of the former. The surface core shift provides an additional shift in spectral weight to low binding energy

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for smaller clusters. Charge transfers between clusters and the substrate may lead to either low or high binding energy initial-state shift, depending on the direction of charge transfer, which itself is dependent on the alignment of the Fermi level.

- (2) The Ni $2p_{3/2}$ BE's of atomic Ni on TiO₂(001) and (110) surfaces are deduced from an extrapolation of the experimental BE curves to zero Ni coverage. Compared with atomic Ni in gas phase, relaxation shifts of 7.34 eV and 7.48 eV are obtained on TiO₂(001) and (110) surfaces, respectively, which is due to d electron screening, indicating d electron-like screening effects from the TiO₂ substrates after Ni $2p$ photoionization.
- (3) The BE's of elements from both overlayers and substrates are found to be affected by the formation of interfacial dipole. The collective contribution of chemical state change from the surface oxygen and interfacial dipoles has been found - their strength and direction changing with surface stoichiometry. Our experimental results present firm and direct XPS evidence for the reversible charge transfer at the metal-oxides interface when the oxide surface stoichiometry is altered.
- (4) Correlation enhancement of electrons in Ni nano-clusters due to the confinement in reduced dimension has been observed. Both the size and shape of nano-clusters have strong influence on the Ni $2p$ satellite structures. For small Ni clusters, apart from the 6-eV satellite, a 3-eV satellite structure emerges in Ni $2p_{3/2}$ photoemission spectra due to the existence of the 3E and 3T triplet state. The intensity of the 3-eV-satellite decreases with increasing cluster size because the Ni $3d$ level is getting

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increasingly occupied in large size clusters. The increased electron population in $3d$ level is achieved through the electron transfer from the free-electron-like $4sp$ states to the unhybridized pure $3d$ spin down states, the latter being lower in energy than that of the $3d$ - $4sp$ hybridized states.

- (5) The correlation-induced 6-eV satellite energy is enhanced (~ 0.3 eV) by Ar^+ bombardment. These observations provide the basis for gauging Ni $3d$ electron population through probing the $2p$ photoemission spectra and for modifying the supported Ni nano-clusters through thermal treatment and/or ion bombardment.
- (6) The reduction of the main peak BE of Ni thin films on Cu(001) has been observed and has been attributed to the Cu $4s$ /Ni $3d$ interfacial hybridization effect (s/d IHE) as well as the narrowing of the d band with the reduction of dimensions. On the other hand, the increased satellite BE results from the combination of interface hybridization and expansion of an extended $4s$ -like state towards the vacuum.
- (7) The center of the Ni d_{xy} band is predicted to shift closer to the Fermi level with increasing Ni film thickness on Cu(001) surface [22; 23]. Enhanced satellite intensity is correlated to the narrowing of the d band with decreased film thickness. Through comparison of Ni films grown on flat versus nano-structured Cu(001) surfaces, the mixing of Cu and Ni atoms is found to be enhanced at the terrace edge region and consequently a larger s/d IHE is expected for Ni on the nano-structured surface.
- (8) Diffusion rates of Ni atoms on TiO_2 surface along [001], [110] and [100] orientation have been predicted, with the diffusion barriers of 2.25 eV, 2.27

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eV and 2.33 eV at 490°C, respectively. The variation in diffusion rate settles the understanding of Ni thin films morphology observed on several TiO₂ surfaces.

1.5 Organization of the thesis

The thesis consists of eight chapters. Chapter 1 introduces the motivation and the objectives of this work, as well as the major contributions and the organization of the thesis.

Chapter 2 provides a literature review survey on surface physics and electronic structure difference in reduced dimensional system.

Chapter 3 describes the experimental conditions of the work and the operation of the XPS machine. It also discusses the origin of various factors of the photoemission process to give the appropriate background for analyzing the data.

Chapter 4 studies the BE shifts of Ni nano-clusters on rutile TiO₂ surfaces. Auger parameter analysis is applied to separate the contributions of the initial- and final-state effect to BE shifts with cluster sizes observed. The origin of initial-state effect involving the charger transfer and SCLS are discussed. We provide direct XPS evidence for the reversible charge transfer at the metal-oxides interface when the oxide surface stoichiometry is altered.

Chapter 5 discusses the evolution of Ni electronic structure in form of nano-clusters on TiO₂ surfaces. A 3-eV satellite structure from ³F atomic state in Ni 2p_{3/2} photoemission spectra is observed due to the strong confinement in low dimensional system. The origin of the satellite is discussed in this chapter in terms of 3d level electron population and the 3d-4sp hybridization. Our observations

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show that the Ni $3d$ electron population can be probed through the $2p$ photoemission spectra.

Chapter 6 studies the evolution of Ni electronic structure in form of thin films on Cu(001) surfaces for comparison. In this chapter, photoemission spectra were measured as a function of thickness on Cu(001) surfaces. The Cu $4s$ /Ni $3d$ interfacial hybridization effect (s/d IHE) and the narrowing of the d band with the reduction of dimensions are discussed. The mixing of Cu and Ni atoms is found to be enhanced at the terrace edge region and consequently a larger s/d IHE is predicted for Ni on the nano-structured surface. Through the study of the asymmetry index, the atomic picture of the initial growth has been proposed.

In Chapter 7, the interaction of nano-clustered Ni overlayer with TiO_2 substrate is studied. Several surface orientations of TiO_2 surface have been used to obtain the differences in terms of the interfacial reaction upon thermal treatment.

Chapter 8 summarizes the conclusions of the evolution of electronic structure of supported nano-structured Ni and provides suggestions for future studies in order to better understand the interfacial properties of Ni/ TiO_2 and Ni/Cu(001).

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LITERATURE REVIEW

2.1 Introduction

This chapter provides an overall review of the fundamental knowledge of heterogeneous catalysts from the surface physics point of view that have been reported in the literature. The selected topics have been introduced in some extent including introduction to surface relaxation and reconstruction, surface states, SCLS, electronic properties of Ni nano-clusters and interfacial interaction with supported substrates.

2.2 Surface science

A solid sample is always in contact with other media via its surface, which is generally termed as a few top atomic layers of the solid with geometrical or electron structure disturbed by breaking of the translational symmetry of the crystal in the normal direction. The surface properties play many roles in the areas such as heterogeneous catalysis, microelectronics, electrochemistry, corrosion, etc. Investigations suggest that not only the type of material but also the arrangement of atoms at the surfaces can change the catalytic properties significantly for certain reactions. One example is that the dissociative sticking of methane (CH_4) is

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increased in the order $\text{Ni}(111) < \text{Ni}(100) < \text{Ni}(110)$, *i.e.* with increasing exposure of sublayer atoms [24].

2.2.1 Relaxation and reconstruction of surfaces

The surfaces are different from the truncated bulk model because the atoms located at the surfaces experience non-zero forces which are induced by the broken bonds. This will, in most case, leads to rearrangements of surface atoms to reduce the surface free energy. These phenomena have been termed as relaxation and reconstruction, both processes may occur with clean surfaces in UHV. But it is worth noting that adsorption of species onto the surface may enhance, alter or even reverse the process.

Relaxation involves a small and subtle rearrangement in the layer spacing perpendicular to the surface with no change either in the periodicity parallel to the surface or to the symmetry of the surface, see Figure 2.1 (a). For most surfaces, relaxation leads to reduction of the distance (d_I) compared to the corresponding bulk value (d_{bulk}). At the surface (of a metal) the original distribution of electrons in the Wigner-Seitz cells would lead to a highly corrugated electron distribution, which is, however, very unfavorable because of the high kinetic energy of “bent” wave functions. The charge smoothing at the surface creates an asymmetric screening of the ion cores in the first layer and a net electrostatic force, which pushes them “into” the crystal and thus reduces d_I . This has been experimentally confirmed by low energy electron diffraction (LEED), ion beam and atoms beam scattering techniques. Relatively larger contractions are observed on the most open low-index faces of metals. This seems to indicate an increase of relaxation with decreasing density of packing in crystallographic planes or, in other words, with increasing roughness of the planes.

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Figure 2.1 Relaxation (a) and reconstruction (b) and adsorbate superstructures (c) on surfaces.

Unlike relaxation, reconstruction involves a change in the periodicity of the surface structure and loss of symmetry, as shown in Figure 2.1 (b). Surface reconstructions are of importance in that they help in the understanding of surface chemistry for various materials, especially in the case where another material is absorbed onto the surface. It occurs with many of the less stable metal surfaces, but is much more prevalent on semiconductor surfaces. In the case of many semiconductors the simple reconstructions can be explained in terms of a “surface healing” process in which the number of the unsaturated dangling bonds is reduced by bond formation between adjacent atoms. The resulting structures can be rather complicated depended on the material and preparation process. Since reconstruction involves a change in the periodicity of the surface and in some cases also a change in surface symmetry, it is readily detected using surface diffraction techniques, e.g., LEED and reflection high energy electron diffraction (RHEED).

When atoms or molecules are adsorbed on a surface, the adsorbates often form ordered structures (due to their mutual interaction) which have unit cells larger than the substrate unit cell, see Figure 2.1 (c). Adsorbates will in general

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change the structure of the underlying substrate due to the adsorbate-substrate interaction. In particular, they can induce a lift of the reconstruction of the clean surface.

2.2.2 Surface defects

Figure 2.2 Schematic drawing of various defects that may occur on a solid surface.

As is the case in the bulk, the ideally perfect ordered surfaces cannot exist for entropy reasons. Defects are always found on a real surface. Depending upon the conditions under which they are prepared (cutting, polishing, etc.), various defects may be found: steps with ledges and terraces, kinks, adatoms, terrace vacancies, ledge adatoms etc., the most common of which are represented in Figure 2.2. The characterization is thus hindered by an uncertainty about the actual crystal termination. The use of single crystals enables to eliminate point defects but total elimination of dislocations is not possible. In order to avoid impurities the measurement should be carried out under UHV conditions.

2.2.3 Surface states

At the free surface of a solid, due to the weakened potential, new electronic

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states can be formed, which are called surface states. The surface states may occur in the conduction bands, valence bands, or in gaps [21]. Such surface states are spatially confined only at the atom layers closest to the surface, meaning that their wave function decays exponentially not only from the surface into vacuum, but also into the solid. The properties of free semiconductor surfaces or metal-semiconductor junction are usually explained on the basis of surface states [25]. Indeed many of the properties of interfaces containing semiconductors are intimately related to the existence of these surface states (both empty and occupied). Advances in miniaturization technologies require improved knowledge of the precise information about these local atomic and electronic structures.

2.2.4 Surface core-level shift (SCLS)

Due to the fact that the coordination number for atoms in the surface is different from that of atoms in the bulk, a smaller valence-electron density in the surface region is resulted. Thus one expects the energy of the core-level of surface atoms to be different from that in the bulk, since the chemical shift of the core-level is largely determined by the valence-electron distribution. Surface core-level shift (SCLS) is defined as the shift in the core-level BE for a surface atom relative to that of a bulk atom. It is normally small for those *sp* band metals (valence band consist essentially of *sp* bands), e.g., Al or Ag (where the *d* levels are 4 eV below Fermi level), whereas *d* band metals (having *d* electrons at or near the Fermi level) have larger values. This suggests that band narrowing is an important factor in this effect. Since the occupancy is mostly unchanged for the surface atoms, the center of the *d*-band must shift up (down) in energy for *d*-band filling less than half (more than half) to assure alignment of the Fermi level. This shift is accompanied by shifts in the core-levels. For earlier elements of the transition metals (*i.e.* less than

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half filled d -bands) the SCLS tends to be to higher BE's compared to the bulk contribution, and to lower BE's for elements where the d -band is more than half filled.

A quantitative analysis of the SCLS can be performed based on thermodynamic model of Johansson and Mårtensson [26] and Rosengren and Johansson [27]. The main assumption of their models is a fully screened final (core-ionized) state, which actually occurs in metals. For the atomic valence electron orbitals, a core of the element of atomic number Z with one electron removed from a deep lying inner shell can be replaced by a core of a $Z+1$ atom. This model is known as the *equivalent core approximation*. The chemical shift between a free atom and an atom in the metallic state is [21]:

$$E_{c,EF}^B(Z)^{atom-metal} = I(Z+1) + E_{coh}^B(Z+1) - E_{coh}^B(Z) + E^B(Z+1, Z) \quad (2.1)$$

Where E_{coh}^B is the cohesive energy, $E^B(Z+1, Z)$ is the solution energy of metal $Z+1$ in metal Z , the upper index B stands for bulk, and $I(Z+1)$ is the ionization energy of the $Z+1$ ion. By analogy, BE of an atom on a metal surface reads:

$$E_{c,EF}^S(Z)^{atom-metal} = I(Z+1) + E_{coh}^S(Z+1) - E_{coh}^S(Z) + E^S(Z+1, Z) \quad (2.2)$$

where the upper index S stands for surface. Johansson and Mårtensson [26] assumed that: $E_{coh}^S \approx 0.8E_{coh}^B$, which yields

$$\Delta^{SB} \approx 0.2[E_{coh}^B(Z+1) - E_{coh}^B(Z)] + [E^S(Z+1, Z) - E^B(Z+1, Z)] \quad (2.3)$$

The second term in Eq. (2.3) is frequently neglected because solution energies $E(Z+1, Z)$ are only small fractions of the cohesive energies $E_{coh}^B(Z+1)$ or $E_{coh}^B(Z)$. As a result, the difference between the surface and bulk BE is given essentially by the difference of two cohesive energies. With this simple approach, SCLS (Δ^{SB}) have been calculated [27] and the results for the $5d$ transition are

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shown in Figure 2.3 together with some experimental data [28]. As can be seen, this thermodynamic model predicts a trend which is in well agreement with the experiment. Since BE's are positive, a positive SCLS means that the surface component has larger BE than bulk component, which is the case for $n_d < 5$.

There has been some discussion as to whether the SCLS is an initial- or final-state effect. The model given above is based solely on an initial-state picture. Since it works so well, one can assume that the SCLS is indeed predominantly an initial-state effect, which is also confirmed by a more complex analysis. The Z-dependence of the SCLS in 5d elements have been analyzed in greater detail by Mårtensson *et al.* [28] and Anderson *et al.* [29].

Figure 2.3 Comparisons of the experimentally determined SCLS of the 5d transition metals with the results of different theoretical approaches. Only values of the close-packed surfaces are included [28].

An interesting application of a SCLS is presented in Figure 2.4, where the $4f_{7/2}$ line from a clean W(110) surface is shown and compared to data taken from

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the same surface covered with one monolayer of O, Cs, K and Na [30]. In the spectrum from the clean surface, the signal from the bulk and the surface layer are well separated. Upon covering the surface with one layer of an alkali metal very little change in W spectrum is observed.

Figure 2.4 Photoemission spectra of $4f_{7/2}$ electrons from clean and adsorbate-covered W(110). After Ref. [30].

Only if oxygen is adsorbed on the W surface does a large shift in the surface peak occur, while the bulk peak again rests at the position which it has in the clean condition. The interpretation given by Riffe *et al.* [30] for these data concludes that for alkali metals in the adsorption process, very little charge transfer occurs from the adsorbate (alkali metal) to the substrate (W metal) while the adsorption of oxygen on W occurs via charge transfer. However, more recent investigations show that these considerations are too simple. One has to take into

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account the change of the coordination of the surface layer of W relative to that in the bulk in order to analyze the core-level shifts induced by the adsorbates correctly. If this is done, one arrives at the conclusion that the commonly employed charge transfer picture for the binding of alkali atoms on a metal substrate is at low coverage a useful approximation. Further experiments by Wertheim *et al.* [31; 32] seem to support the picture of a covalent bond between the alkali metal and the transition metal substrate.

2.2.5 Work function change

Any change of the surface in terms of morphology or adsorption will be changing the work function. Thus, the work function change can be used as a fingerprint of the state the surface is in. Upon adsorption of metal, the work function of semiconductor substrate is normally decreased at low coverage due to the charge transfer from metal to substrate. A famous case is the adsorption of alkali metals. In case of semiconductor substrate, the bond is ionic and the alkali metal gives an electron to the surface. This leads to a dipole moment which opposes the spill-out of the electrons and reduces the work function. At low coverage, the dipole-dipole interaction between the alkali atoms will keep them far apart and the work function decreases linearly as a function of coverage. When increase the coverage, the adsorption gradually converts from ionic to neutral due to mutual depolarization of the dipoles and leads to a metallic bond. This depolarization on semiconductors is however, not as strong as on metal surfaces, since in latter case the slope actually reverses at high coverages (see Figure 2.5), but no on semiconductors.

Figure 2.5 Work function change upon the adsorption of K on W(110). After Ref. [33].

2.3 Electronic structures of Ni

Ni ground state in many-body $3d$ configuration interaction (CI) calculations employing the Andersen impurity model is described as a mixture of $3d^{10}$, $3d^9$ and $3d^8$ valence configurations with relative weights of 15%–20%, 60%–70% and 15%–20%, respectively [34]. In contrast, Ni atoms in gas phase exhibit both configurations of $3d^8 4s^2$ and $3d^9 4s^1$ [35]. The comparison of Ni atom photoelectron spectrum with the corresponding solid phase of Ni metal and NiO leads to the conclusion that the $3d$ orbitals in Ni metal show strong nonlocal character [35]. For Ni atoms or clusters grown on oxide substrate, this nonlocal character of $3d$ orbitals is another fingerprint to distinguish metal from oxide state when discussing the reaction. The supported atoms and clusters differ from the isolated ones by having screening channels but a full picture is still missing.

2.3.1 Ni satellite structures in PES

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The interpretation of some features of the electronic structure of nickel as determined from PES experiments remains quite controversial; the width of the observed d bands is narrower than that obtained from self-consistent band calculations and a satellite is observed about 6-eV below the Fermi level. Theoretical studies [36; 37] agree in relating these features to correlation effects within the d band, and the Hubbard model is usually considered to be an appropriate model for describing these effects. A simple perturbation theory may be useful in the absence of better approximate solution of the Hubbard model for the relevant range of parameters (number of holes, U/W). A consistent treatment of nickel should explain not only the gross features of the satellite, but also its resonant behavior [21; 38; 39], its possible polarization [21; 36; 40], the narrowing of the bands, and the small splitting between majority (spin up, more occupied) and minority (spin down, less occupied) bands. The satellite has its maximum intensity at a photon energy of 67 eV due to resonance and is unobservable small below roughly 25 eV [37].

Various interpretations have been presented over years for the 6-eV satellite. A well accepted one is schematically shown in Figure 2.6. In the final state one has two possibilities for screening: the additional Coulomb attraction produced by the core hole can now pull the conduction band so far below Fermi level (E_F) that an additional charge can be put into the $3d$ orbitals leading in a first approximation to a $3d^{10}$ configuration. This is essentially the ground state and is very similar to the ground state in copper metal, to which it corresponds in the $(Z+1)$ -approximation. Thus the main line in Ni PES always corresponds to the $3d^{10}$ valence band (VB) configuration. However, there is also possibility that the $3d$ band, although now completely below E_F is not filled by a screening electron, and

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that the screening is instead produced within the wide $4s$ band. Effectively, one then has a two-hole state: one hole is produced by the photoemission process in the core-level, and the second, which is also quite localized, is the hole in the d shell. This two-hole configuration is not the ground state. It is an excited state and the excitation energy is roughly 6-eV, in agreement with the experimental results. Note that the 6-eV satellite is also observed in the VB spectrum, in which case the main line corresponds to the $3d^94s$ configuration and the satellite to the $3d^84s^2$ configuration in atomic notation. For more sophisticated treatments of this problem see Ref. [21].

Figure 2.6 Schematic illustration of the Ni 6-eV satellite.

This charge transferred model has been challenged by Bagus and Ilton [41]. In their model for the ionic compounds, the screening of the core hole can be done through changes in covalent character of the cluster orbitals. This offers new insights into the role of charge transfer for the PES satellite structure. However, the validity of this model for the metal, like Ni, needs further evidence.

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2.3.2 Resonance behavior of the 6-eV satellite

The most convincing evidence to support the two-hole assignment for the 6-eV satellite in the VB of Ni metal comes from resonance photoemission data [21]. In fact, resonance experiments on nickel demonstrated the usefulness of this technique for the investigation of VB features in solids. Resonance photoemission means that: one excites photoemission with photons of energy very near to the absorption threshold of a core-level. Then the direct photoemission of VB electrons can interfere with Auger CVV electrons that are emitted in a super Koster-Kronig process. The intensity for the feature in the VB for with the direct photoemission process and the Auger emission overlap is given as a function of the photon energy $h\nu$ by the so-called Fano lineshape. This has been experimental observed by Guillot *et al.* [42]. A clear resonance at the Ni 3p BE, $E_B=67$ eV, was observed. At this photon energy direct photoemission from the VB may be described by (omitting the work function) [21]:

$$3d^9 + \hbar\omega \rightarrow 3d^8[4s] + e^- \quad [E_{kin} = E_{3p} - E_{sat}(valence)] \quad (2.4)$$

[4s] is a 4s screening electron. This gives rise to the 6-eV satellite. In addition, the photon energy at the 3p resonance can excite an electron out of the 3p shell into the 3d hole just above the Fermi level in Ni metal. The excited state resulting from this process can decay by an Auger process. This leads to the same final state ($3d^8[4s]$) and gives electron with the same kinetic energy as direct photoemission leading to the satellite's final-state (omitting the work function):

$$3p^6 3d^9 + \hbar\omega \rightarrow 3p^5 3d^{10} \xrightarrow{Auger} 3p^6 3d^8[4s] + e^- [E_{kin} = E_{3p} - E_{sat}(valence)] \quad (2.5)$$

These two processes, (2.4) and (2.5), overlap coherently at the threshold

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energy, giving rise to the resonant enhancement of the satellite. At higher photon energy the *MVV* Auger electrons move away from the satellite because they appear with fixed kinetic energy $[E_{3p} - E_{sat}(valence)]$ while the kinetic energy of the photoelectrons increases with $\hbar\omega$.

2.3.3 Quantum well states

When an electron is confined in small structures such as a metal thin film, the solutions of Schrödinger's equation are electron standing waves characterized by the quantum number n , which are called quantum-well states. Many electronic devices are made of thin films. The existence of the quantum well states in the metal thin films is quite important in terms of interfaces and multilayer coupling, such as, the oscillatory magnetic coupling of two ferromagnetic layers across a non-magnetic layer and giant magnetoresistance. A detailed study can help to determine the bulk band structure of the film material and the lifetime broadening of the quasiparticle [43]. Such states can be probed and therefore studied by angle-resolved photoemission.

2.4 Nano-clusters

Nano-clusters form a state of matter that intermediate between a bulk solid material and an ensemble of single atoms or molecules, which allow a study of the evolution of a physical property from the atom towards the solid. The electrons in a nano-cluster are confined to spaces that can be as small as a few atom-widths across, giving rise to quantum size effects [44]. With a decrease in metal cluster size, their abundant surface begins to play a dominant role providing a unique way to learn how metal-metal bonding, cluster shape, and packing are affected by ligands bound to the cluster surface. For a cluster of 2000 atoms a fraction of about 30% is still at the surface. This makes clusters very sensitive to their chemical

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environment. They may form very specific and very selective catalysts. Furthermore, the chemical reactivity can change by orders of magnitude from one cluster size to the next [45]. Some properties even depend on whether a particle contains an even or odd number of electrons [46]. As a consequence, clusters with different sizes have to be inspected individually.

The unique properties of nano-clusters lead to a great application in the areas where surfaces play important role, such as catalysis. In the past decades, the nano-clusters of different noble metals have been found to catalyze a wide range of reactions, which serves as a strong motivation in surface science to understand the chemistry and physics behind. Besides the key role of metallic properties, that the nano-clusters being more active and selective catalysts is due to the large percentage of metal atoms lying on the surface possessing the dangling bonds. The realization that the electronic, optical, magnetic and chemical properties of nano-clusters depend on their size enhances the interest in the area.

Moreover, the large surface to volume ratio has strong implications for cluster magnetism. The surface atoms are lower coordinated than the bulk and therefore have a more atom-like character than interior atoms and contribute more to the magnetic moment of the cluster. Thus, clusters provide not only model catalysts but also model systems for nano-electronics and nano-structured magnetism.

In metallic clusters, inter-atomic distances are shortened in the neighborhood of the most under-coordinated atoms. In a macroscopic model of a liquid droplet, this contraction of the lattice parameter may be accounted for by the effect of the Laplace pressure exerted by surface forces. It is a function of the particle radius R , of the compressibility coefficient K , of the surface tension γ and

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of the surface area A [7].

$$\frac{\Delta a}{a} = - \left(\gamma + A \frac{d\gamma}{dA} \right) \frac{2K}{3R} \quad (2.6)$$

At a more microscopic level, the surface relaxation is based on the competition between covalent energy and short-range atom-atom repulsion. This also leads to contractions of bond-length in the neighborhood of under coordinated atoms.

2.5 Interfacial interaction

2.5.1 Electronic interaction of metals with oxides

In catalysis, the clusters are supported on the surface of a support material and the interaction between them modifies many of the effects described above. Interfacial contact between a metal and an oxide can result in charge redistribution at the junction similar to the situation at the metal-semiconductor interfaces. The electronic interactions are simply driven by the principles of the system Gibbs free energy minimization and the continuity of the electric potential in a solid. Electron transfers always occur at reactive interfaces, where already existing chemical bonds are broken and new ones are formed leading to inter-diffusion over length scales of more than a single monolayer and formation of new phases with a thickness of at least one monolayer [7].

The local charge redistribution is the electron rearrangement involving a few atomic layers at the interface. Depending on the metal/oxide system, different mechanisms may be dominant in the electronic interaction [47]. A good review can be found in Ref. [7] which is brief summarized below.

2.5.1.1 Empirical correlations from dispersion force

At a metal/oxide interface, the mutual polarization of the two media gives rise to dispersion forces. The dispersion contribution, *i.e.* the van der Waals

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interaction, is quite weak compared to other interactions, such as the electrostatic interaction [47]. Therefore, it is believed that this interaction is important only in the systems consisting of a noble metal deposited on a wide band gap oxide [48].

An empirical correlation has been derived showing that the adhesion energies at metal/oxide interfaces increase as the plasmon energy of the metal increases and/or as the band gap of the oxide narrows [48]. Stoneham [49] found another empirical correlation where the optic dielectric constant (ϵ_∞) of the oxide provides a simple classifying rule. An ϵ_∞ higher than a critical value leads to wetting. Indeed oxides with sufficiently high ϵ_∞ , such as TiO_2 and Nb_2O_5 , exhibit SMSI effects in catalysis.

2.5.1.2 Image charge theory

Many phenomena associated with metal/nonmetal interfaces with a large dielectric constant mismatch can be understood in terms of image interactions due to charges in the nonmetal. The image theory assumes that the metal/oxide interaction energy originates from the attractive Coulomb force between ions in the oxide and their images in the metal. The interaction may give adhesion energy of the order of joules per square meter [47].

It is known that the VB of metal atoms supported on an ionic oxide can be distorted by the electrostatic field of the oxide. This phenomenon is called the polarization effect, and results in electron redistribution among the different components of the metal band. In the case of ultrathin metal overlayers, e.g. one monolayer of adsorbate, the binding of metals to oxides is dominated by the polarization effect, which mimics the macroscopic image charge effect.

2.5.1.3 Metal-induced gap states (MIGS)

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MIGS are produced by matching the delocalized metal wave functions with exponentially decaying oxide states in the band gap energy range at a defectless interface. The effect of the metal jellium seems to allow some states originally in the valence and conduction bands of an oxide to be pulled into the band gap of the oxide. The MIGS are associated with a smooth density of states (DOS) in the band gap and their density decays from the interface into the oxide over a length of several angstroms (Å).

2.5.1.4 Interface bonding

Formation of chemical bonds is an important mechanism for charge transfer at metal/oxide interfaces. It is known that either covalent bond or ionic bond can be established between metal atoms and surface oxygen ions or cations of oxides. The ionic character of a polar covalent bond between atoms A and B is determined by their electronegativities, X_A and X_B . The bonding charge shifted to the more electronegative atom is expressed by the relation [7]:

$$\Delta q/e = 0.16 |X_A - X_B| + 0.035 |X_A - X_B|^2 \quad (2.7)$$

Using the simple concept of Pauling's electronegativity, one can predict the direction and amount of charge transfer at metal/oxide interfaces. It is worth mentioning that formation of interface bonding strongly depends on oxide surface properties including, but not limited to, surface termination, surface reconstruction, surface impurities, and surface point defects.

2.5.2 Chemical interaction of metals with oxides

The term chemical reaction is used for those cases where mass transport occurs over length scales of more than a single monolayer or where new phases with a thickness of at least one monolayer are formed [7]. The driving force behind the mass transport in the solids is a gradient in the electrochemical potential,

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consisting of a gradient in the electrical potential and/or chemical potential. Due to the nature of the products formed at metal/oxide interfaces, the chemical interaction can be generally classified into four different groups, 1) redox reaction, 2) alloy formation, 3) encapsulation, and 4) interdiffusion.

2.6 Growth modes

2.6.1 Brief introduction to growth modes

Of major importance in modern technology are solid interfaces between overlayer and substrate. Thus it will be useful to look at the process of film growth and the underlying principles which determine the structure and morphology of particular interface. The individual atomic processes which determine film growth in its initial stages are illustrated in Figure 2.7.

Figure 2.7 Schematic representation of atomic processes involved in film growth on a solid substrate. Film atoms are shown as solid circles, substrate atoms as open circle.

Condensation and desorption processes happen simultaneously which is at equal rates in thermodynamic equilibrium. Therefore, in equilibrium, there is no net growth of a film and so crystal growth must be a non-equilibrium kinetic process. The final macroscopic state of the system depends on the route taken through the various reaction paths indicated in Figure 2.7.

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Figure 2.8 Schematic representations of three basic modes of thin film growth for different coverage θ regimes (ML means monolayer). (a) Island growth (Vollmer-Weber, VW); (b) layer-by-layer growth (or Frank-von der Merve, FM); (c) layer-plus-island growth (or Stranski-Krastanov, SK).

In general, three markedly different modes of film growth can be distinguished, as shown in Figure 2.8. In the layer-by-layer (or Frank-von der Merve, FM) growth mode, the atoms of deposited material are strongly attracted to the substrate than to themselves. Each new layer starts to grow only when the last one has been complete. In the opposite case, which the interaction between neighboring film atoms exceeds the overlayer substrate interaction, leads to island (or Vollmer-Weber, VW) growth mode. In this case, an island deposit always means a multilayer conglomerate of adsorbed atoms. The layer-plus-island (or Stranski-Krastanov, SK) growth mode is an intermediate case, as shown in Figure 2.8, after formation of one, or sometimes several complete monolayers, island formation occurs.

Auger Electron Spectroscopy (AES) and X-ray Photoemission spectroscopy (XPS) are broadly applied for studying the growth modes *in situ* due to their simplicity in application. The intensities of Auger transition (in AES) or

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core-level emission (in XPS) are measured for both substrate and adsorbate atoms. The prediction of the growth mode is thus drawn based on the plot of the intensity ratio between overlayer and substrate as a function of coverage. The standard plots are shown in Figure 2.9 for different growth mode.

Besides these spectroscopy techniques, there are other techniques important in the study of film growth that gives direct image, such as Scanning Tunneling Microscope (STM), Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) for example.

Figure 2.9 Schematic Auger line intensities (in AES) from deposit and substrate versus amount of deposited material (coverage θ) for (a) layer-by-layer (FM) growth, (b) layer-plus-island (SK) growth, and (c) island growth (VM).

2.6.2 Thermodynamic consideration of growth modes

A simple formal distinction between the conditions for the occurrence of the various growth modes can be made in terms of surface or interface tension, *i.e.* the characteristic free energy.

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Figure 2.10 Simplified picture of an island of a deposited film; γ_S , γ_F , and $\gamma_{S/F}$ are the surface tension between substrate and vacuum, between film and vacuum and between substrate and film, respectively. The angle Φ is the contact angle.

Figure 2.10 shows schematically a metal island supported on a flat oxide surface. In the simplified case with absence of surface energy anisotropies of the metal, at a point where substrate and a 3 dimensional (3D) island of the deposited film touch, a mechanical equilibrium for this system can be written by Young's equation [7]:

$$\gamma_S = \gamma_{S/F} + \gamma_F \cos \phi \quad (2.8)$$

where γ_S is the surface tension of the substrate/vacuum interface, γ_F that of the film/vacuum, and $\gamma_{S/F}$ that of the substrate/film interface. For the two limiting growth modes, layer-by-layer (FM) and island (VW), the relationship of the surface tensions reads:

$$(1) \text{ FM growth: } \phi = 0, \gamma_S \geq \gamma_{S/F} + \gamma_F; \quad (2.9)$$

$$(2) \text{ VW growth: } \phi > 0, \gamma_S < \gamma_{S/F} + \gamma_F; \quad (2.10)$$

The SK mode occurs when the interface energy increases as the layer thickness increases [50]. The increase of the interface energy can be understood by assuming a lattice mismatching between deposited film and substrate. The adjustment of the lattice of film to match the substrate happens at the expense of

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elastic deformation energy. However, at atomic level, surface energy picture is much more complex and there is no simple thermodynamic way to visualize the whole process.

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EXPERIMENTAL METHODS

3.1 Ultra high vacuum (UHV) chamber

Most measurements reported in this thesis were performed in an UHV system, maintained at a pressure below $\sim 5 \times 10^{-10}$ mbar. Residual gases adsorbing on the surface of a crystal can cause a significant error in the measurement of experimental data, thus it is crucial to maintain a sufficiently low pressure in the experimental chamber. For example, at the background pressure of 10^{-6} mbar and with a sticking coefficient of unity, the surface will be contaminated with one monolayer of the gas in approximately one second. The pressure in the 10^{-10} mbar range will keep the surface clean for approximate 10^4 seconds (nearly 3 hours). This is much longer than a typical experimental measurement time of 30 min to 1 hr.

3.2 Sample preparation

The preparation of clean and well-ordered single crystalline oxide surfaces remains one of the great experimental challenges of surface science. A variety of techniques have been used with varying degrees of success, depending on the oxide being used.

3.2.1 Methods for preparing clean and ordered sample surfaces

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Before loading into the chamber, the TiO₂ substrates were first ultrasonic cleaned by 10% nitric acid solution, followed by purity water and MOS purity acetone in sequence in order to remove residual metal particles and organics. Clean TiO₂ surfaces were obtained by repeated cycles of Ar⁺ sputtering and UHV annealing, following a known recipe [51; 52]. Both the surface cleanliness and chemical state were verified from the high-sensitivity and high-resolution XPS spectra.

The Cu(001) single crystals were mechanically polished down to a grain size of 0.1 μm before insertion into the vacuum system, then prepared by repeated Ar⁺ ion sputtering and annealing at 500 °C in the UHV chamber with base pressure < 5×10⁻¹⁰ mbar.

3.2.2 Metal overlayer deposition

Ni was deposited by an Omicron EFM3 *e*-Beam evaporator (Figure 3.1) in the UHV preparation chamber. All the deposition is done at room temperature. Most measurements are done at room temperature unless otherwise specified. The *e*-beam evaporator deposition rate had been previously calibrated by Rutherford Backscattering (RBS) measurements. The deposition rate is around 0.5 Å/min. The desired Ni thickness is achieved through the deposition time, and is also confirmed by *ex situ* cross-section TEM measurements.

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Figure 3.1 Schematic of EFM3 *e*-beam evaporator.

3.3 XPS characterization

All XPS measurements were performed using VG ESCALAB 220i-XL instrument (base pressure $<5 \times 10^{-10}$ mbar) equipped with a monochromatic Al K_{α} (1486.7 eV) X-ray source. The XPS BE was calibrated with pure gold, silver, and copper standard samples by setting the Au $4f_{7/2}$, Ag $3d_{5/2}$, Cu $2p_{3/2}$ peaks and Ni Fermi edge at binding energies of 83.98 ± 0.02 eV, 368.26 ± 0.02 eV, 932.67 ± 0.02 eV and 0.00 ± 0.02 eV respectively. All spectra were recorded in the constant pass energy mode with pass energy of 20 eV and step width of 0.1 eV.

3.3.1 Brief introduction to XPS

The physics behind XPS is the photoelectric effect discovered by Hertz in 1887 [53] and explained in detail by Einstein in 1905 [54]. After development by Siegbahn *et al.* [55] of a high-resolution spectrometer, which allowed to measure accurately kinetic energy of photoelectrons, the goal of using XPS for electronic structure investigation had been realized. Since then, XPS becomes a widely used technique for investigation of the surface of a solid sample.

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The basic elements of an XPS instrument are a light source, an electron energy analyzer and an electron detector as drawn in Figure 3.2.

Figure 3.2 Basic elements of XPS experiment.

XPS is a technique in which photons of known energy ($h\nu$) liberate electrons from samples. As currently used, the fundamental energy conservation equation is the following [56]:

$$h\nu = E_B^{Vac} + E'_k = E_B^{Fermi} + \phi_{spec} + E_k \quad (3.1)$$

in which h is Planck's constant; ν is the photon frequency; E_B^{Vac} is the BE of a given electron relative to the vacuum level, E_k is the kinetic energy as measured finally in spectrometer, which may be different from E'_k by a small contact potential difference; E_B^{Fermi} is the BE relative to the Fermi level; and ϕ_{spec} is the work function of the spectrometer. Their kinetic energy (E_k) distribution is analyzed either in a given emission direction (angle resolved XPS, ARXPS) or after an integration over all possible directions (integrated photoemission). Hemispherical analyzer is widely used nowadays for XPS because of better resolution characteristics. A schematic diagram of a hemispherical electrostatic electron energies analyzer is shown in Figure 3.3.

Figure 3.3 Hemispherical electron energy analyzer.

3.3.2 Theoretical consideration of XPS

At the heart of all theories of PES is the so-called one-step model of photoemission which treats the initial excitation step, the transport of the photoelectron to the surface and the scattering at the surface barrier as a single quantum-mechanically coherent process [21]. This approximation is designed for the high-energy photoelectron limit.

Assuming a small perturbation H' the transition probability ω per unit time between the N -electron states ψ_i (initial) and ψ_f (final) is calculated within a unified framework starting from Fermi's golden rule:

$$\frac{d\omega}{dt} = |\langle \psi_f | H' | \psi_i \rangle|^2 \delta(E_f - E_i - \hbar\omega) \quad (3.2)$$

$$\propto |\langle \psi_f | 2AP + i\hbar\nabla A | \psi_i \rangle|^2 \delta(E_f - E_i - \hbar\omega) \quad (3.3)$$

where E_i and E_f are initial and final state energy of the system, A is the vector potential and P the momentum operator $P = i\hbar\nabla$. For not too high energies (< 1 keV or so), one has large wavelength compared to the atomic distance and therefore A can be taken as constant, which leads to zero of ∇A and can be

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neglected. This is true in the crystal and in free space but not necessarily at the surface. From the Eq. 3.3, one realizes that for a constant potential (free-electron gas, for instance) there is no photoemission. This is also obvious when we think about the requirement to conserve energy and momentum at the same time.

3.3.3 Core-level photoemission spectroscopy

In core-level PES the more strongly bound electrons around the nuclei are probed, which are localized to a specific atom and are similar to the atomic orbitals. PES of core-levels can therefore give element specific information of a sample. In order to arrive at a first view of core-level photoemission, let us take a one-electron view for the initial and final state wave function. The initial state wave function is then written as:

$$\psi_i^N(R) = \phi_{i,k} \psi_{i,k}^{N-1}(R) \quad (3.4)$$

where $\phi_{i,k}$ is the single-particle wave-function of the electron to be removed and $\psi_{i,k}^{N-1}(R)$ is the properly antisymmetrized determinant of the remaining $N-1$ electrons. Similarly the final state has the form of:

$$\psi_f^N(R) = \phi_{f,E_{kin}} \psi_{f,k}^{N-1}(R) \quad (3.5)$$

where $\phi_{f,E_{kin}}$ is the wave-function of the free electron and $\psi_{f,k}^{N-1}(R)$ are the possible states for the ionic system, *i.e.* the system with one electron missing.

$$\frac{d\omega}{dt} \propto | \langle \phi_{f,E_{kin}} | AP | \phi_{i,k} \rangle \langle \psi_{f,k}^{N-1}(R) | \psi_{i,k}^{N-1}(R) \rangle |^2 \delta(E_f - E_i - hv) \quad (3.6)$$

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In the first step of evaluating the overlap integral, one can assume that the remaining orbitals are the same in the final state as they were in the initial state (frozen-orbital approximation), which renders $\langle \psi_{f,k}^{N-1}(R) | \psi_{i,k}^{N-1}(R) \rangle = \delta_{i,0}$. Under this assumption, the PES experiment measures the negative Hartree-Fock orbital energy of the orbital, *i.e.*:

$$E_{B,k} = -\varepsilon_k \quad (3.7)$$

which is also called Koopmans' binding energy. However, this is not the good approximation. One realizes intuitively that the system, after ejection of the electron will try to readjust its remaining $N-1$ electrons in such a way to minimize the total energy (relaxation process). Thus, the measured binding energy should read:

$$E_{B,k} = -\varepsilon_k - R_k \quad (3.8)$$

where R_k is the relaxation energy.

When we project $\psi_{i,k}^{N-1}(R)$ onto the eigenstates of the ionic system there will not only be overlap with the ground state but also with some of the excited states. If the system is left in an excited state there will be less energy available for the photoelectron. We now assume that the final state with $N-1$ electrons has s excited states with the wave function $\psi_{f,s}^{N-1}(R)$. The transition matrix element must then be calculated by summing over all possible excited final states yielding:

$$\frac{d\omega}{dt} \propto | \langle \phi_{f,E_{kin}} | AP | \phi_{i,k} \rangle |^2 \sum_s |c_s|^2 \quad (3.9)$$

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with $c_s = | \langle \psi_{f,s}^{N-1}(R) | \psi_{i,k}^{N-1}(R) \rangle |$. Here $|c_s|^2$ is the probability that the removal of an electron from orbital $\phi_{i,k}$ of the N -electron ground state leaves the system in the excited state s of the $N-1$ electron system. For strongly correlated systems many of the c_s are non-zero. In terms of the photoemission spectrum, this means that for $s = k$ one has the so-called *main line* and for the other non-zero c_s additional *satellite* lines occur.

3.3.4 Valence-state photoemission spectroscopy

The valence band refers to the levels occupied by electrons with low BE's, *i.e.* near the Fermi edge. The intensity in the valence band originates from both localized nearly atomic-like orbitals and non-localized hybrid-type molecular orbitals. The probed orbitals are responsible for the chemical bonds in the material thus produce much new information. In this energy region the orbitals are quite delocalized, and the valence electrons interact strongly, forming bands. Since valence band spectroscopy involves the outer shells of the atoms, the technique is generally very sensitive to the local chemical environment on the surface. Combined with theoretical calculation, angle resolved valence band spectra are used to map the band structure of single crystalline materials.

3.3.5 Three-step and one-step considerations

An intuitive and often-used way for the interpretation of PES in solids is the so-called three-step model, developed by Berglund and Spicer [57; 58]. While the three-step model makes the photoemission process quite comprehensible and easy to discuss, it is a purely phenomenological approach. It breaks up the complicated PE process into three steps: i) photoexcitation of an electron in the solid; ii) propagation of the photoexcited electron to the surface; iii) escape of the electron from the solid into vacuum, which demands conservation of the

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momentum parallel to the surface. In the one-step model one considers the excitation from the initial state into a damped final state near the surface. The one-step model of photoemission starts from a given electronic potential which is needed for the necessary construction of multiple-scattering states and propagators. This potential is taken from a separate electronic-structure calculation and must be considered as the decisive input for the one-step model. The reliability of the PES theory is thus intimately related to the “quality” of the potential for the system at hand. An illustration of the three-step model and one-step model is given in Figure 3.4.

Figure 3.4 Illustration of the three-step and the one-step model in PES. The three-step model consists of (1) photoexcitation of an electron, (2) its travel to the surface and (3) its transmission through the surface into the vacuum. In the one-step model a Bloch wave electron is excited into a wave that propagates freely in the vacuum but decays away from the surface into the solid. After Ref. [21]

3.4 Important aspects of XPS

3.4.1 Core-level line-shape

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For core-level photoemission in metal, the outgoing photoelectron is fast and therefore measures the spectral function of the core hole. This case has been treated by Doniach and Šunjić [59]. Their result is deduced by convoluting a $1/\omega^{1-\alpha}$ singularity with a lifetime width of 2γ leading to the following expression for the line shape:

$$f(\varepsilon) = \frac{\Gamma(1-\alpha) \cos \left[\frac{\pi\alpha}{2} + (1-\alpha) \arctan \left(\frac{\varepsilon}{\gamma} \right) \right]}{(\varepsilon^2 + \gamma^2)^{\frac{1-\alpha}{2}}} \quad (3.10)$$

where Γ represents the Γ -function, ε is the energy relative to the position of the maximum and α is an asymmetry parameter. The line-shape function fits the core lines of simple metals extremely well. However, its integral diverges, which is of course unphysical. A non-diverging line-shape was first suggested by Mahan [60]. The expression given by Mahan is:

$$f(\varepsilon) = \frac{1}{\Gamma(\alpha)} \frac{e^{\frac{\omega}{\xi}}}{\left| \frac{\omega}{\xi} \right|^{1-\alpha}} \Theta(-\varepsilon) \quad (3.11)$$

here ξ is the cut-off parameter with a magnitude of the order of the Fermi energy and $\Theta(\varepsilon)$ is the step function. The Doniach-Šunjić (D-S) line-shape is obtained in the limit $\xi \rightarrow \infty$. In actual applications the two line-shapes are very similar and can only be distinguished far out in the tail. Under Thomas-Fermi approximation, asymmetry parameter, α , can be used to estimate the effective charge of the photohole seen by the conduction electrons (c_p) following the equation:

$$\alpha = 0.083 r_s c_p^2 \quad (3.12)$$

where r_s is the Wigner-Seitz radius (in units of the Bohr radius) of the electron gas.

3.4.2 Background subtraction

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PES of solids always contains a background, which is formed by inelastically scattered photoelectrons. The choice of an appropriate background correction is of course of considerable importance if PES is to be used for quantitative purposes. Different models of background shape are in use: linear-type background, Tougaard background and Shirley background. A simple linear-type background can be used for fast spectra analysis, while for more accurate analysis, Tougaard background and Shirley background are suggested with the latter more popular used [61].

3.4.3 Energy resolution

The energy resolution is characterized by the full width at half maximum (FWHM), which is a convolution of ΔE_a , ΔE_x and ΔE_i :

$$\Delta E = f(\Delta E_a^2, \Delta E_x^2, \Delta E_i^2) \quad (3.13)$$

where ΔE_a is due to the analyzer, ΔE_x is the line width of the x-ray source and ΔE_i is intrinsic width related to the material. For certain instrument, ΔE_a and ΔE_x are not varied during the experiment. All the change of ΔE comes from the intrinsic lifetime broadening, ΔE_i , which is Lorentzian broadened due to the Heisenberg uncertainty principle. For solids, phonons in the lattice give additional Gaussian distributed broadening of the line.

3.4.4 The electron inelastic mean free path (IMFP)

The surface sensitivity of XPS can be judged from Figure 3.5, which gives the “universal” electron inelastic mean free path (IMFP). The IMFP is a measurement of the probability for inelastic scattering. It is determined by electron-electron and electron-phonon collisions. The IMFP at energies of interest here is determined largely by the electron-electron interaction [21]. The graph gives a qualitative view of how the mean free path varies with photoelectron

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kinetic energy and thereby gives a perspective of how the surface sensitivity of a PES experiment can be changed using a variable photon source.

Figure 3.5 A sketch of the “universal” electron mean free path as a function of kinetic energy. The data indicate a universal curve with a minimum of 2-5 Å for kinetic energies of 50-100 eV. From Ref. [21].

The IMFP can be defined as the distance over which the probability of an electron escaping without significant energy loss due to inelastic processes drops to e^{-1} of its original value. Under this definition, the escape probability (dP) originated from a layer of thickness dz at depth z detect at an angle θ with respect to the surface normal is given by:

$$dP \propto e^{-z/\lambda \cos \theta} dz \quad (3.14)$$

The total intensity, I , of a core line from the pure model material is then obtained by integrating over the exponential escape probability, P , multiplied by

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the atomic density, n , the cross section for the transition, σ , and constant C , yielding :

$$I = Cn\sigma \int_0^\infty e^{-z/\lambda \cos\theta} dz = Cn\sigma\lambda \cos\theta \quad (3.15)$$

If a completely homogenous and flat ultra thin film of a material A is deposited on the material B, the intensity measured for the core line attributed to material B will be damped due to the overlayer, since the photoelectrons must travel through an additional layer of material A. The attenuated intensity, I_B is given by:

$$I_B = C_B n_B \sigma_B \int_t^\infty e^{-z/\lambda \cos\theta} dz = I_B^0 e^{-t/\lambda \cos\theta} \quad (3.16)$$

where I_B^0 is the signal from the substrate without the overlayer; t is the overlayer thickness. The intensity for material A is given by:

$$I_A = C_A n_A \sigma_A \int_0^t e^{-z/\lambda \cos\theta} dz = I_A^\infty [1 - e^{-t/\lambda \cos\theta}] \quad (3.17)$$

where I_A^∞ is the intensity from the thick overlayer.

Plots of $\ln(1 - \frac{I_A}{I_A^\infty})$, $\ln(\frac{I_B}{I_B^0})$, or $\ln(\frac{I_A}{I_B})$, can be used to estimate the thickness of the deposited overlayer if this mean free path is known.

3.5 Atomic force microscope

The atomic force microscope (AFM) is a very high-resolution type of scanning probe microscope (SPM) with demonstrated resolution of fractions of a nanometer. It gathers the information by “feeling” the surface utilizing a sharp tip, as shown in Figure 3.6 (a), to move over the surface of a sample in a raster scan. The information it collected including the surface morphology, optical absorption, or magnetism.

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Figure 3.6 (a) Image of an AFM tip. Inset shows the close up view where the radius of curvature of the tip is typically less than 10 nm. (b) Schematic showing the working principle of the AFM.

The distance between the tip and the sample surface is so small such that atomic-range forces act between them. The interaction force between the tip and the sample can be found according to Hooke's Law. Piezoelectric elements that facilitate tiny but accurate and precise movements on (electronic) command enable the very precise scanning. Figure 3.6 (b) schematically illustrates how the AFM works. The scanner is capable of sub-nanometer resolution in x-, y- and z- directions with the z-axis conventionally taken to be perpendicular to the sample surface. Hence, the AFM is a very powerful tool for scientists to study the surfaces of materials at the nano-scale.

CHAPTER FOUR

BINDING ENERGY SHIFTS IN NICKEL CLUSTERS ON RUTILE TITANIUM DIOXIDE SURFACES

4.1 Introduction

There are consistent observations of cluster-size-dependent BE shift, showing that the core-level BE's of metal clusters on inert supports are shifted to higher values with decreasing cluster size [12; 13; 16; 18; 62-65]. The assignment of these BE shifts to initial- or final-state effects is still debated upon [12; 13; 16]. Auger parameter (AP) analysis has been found as a simple method to tell them apart [12; 18; 66; 67]. For Cu clusters grown on thin Al₂O₃ films, Wu *et al.*[66] concluded from an AP analysis that initial-state contributions are small and may be significant only for very small clusters. However, Bagus *et al.*[12; 68] showed that the initial- and final-state contributions to the BE are of comparable magnitude in the Co/Al₂O₃/NiAl(110) system and further related the initial-state BE shift to bond distance changes in the clusters.

The question of how the PES of deposited nano-particles reflects structural geometry is of equal importance [12]. Currently, the structure and morphology

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information of supported clusters on the atomic scale can be most easily accessed only by STM. However the effectiveness of this technique may, sometimes be restricted by resolution problems due to the insulating nature of materials. The answer to above question may offer an indirect but promising feasibility to study cluster growth mechanism with PES, which is especially important for insulating substrates where direct STM observation is limited. The surface structure and growth morphology of Ni grown on single crystalline TiO_2 have been well studied by STM and three-dimensional cluster growth mode was indicated [51; 52]. The contribution of lattice strain in small clusters to higher initial-state BE shift is predicted in Ref. [12]. These authors have argued that lattice strain changes the chemical bonding between the metal atoms and this change induces BE shifts.

Recently, it has also been proposed that reducible oxides are preferred for this enhanced charge transfer behavior due to the easy formation of O-rich surface terminations [6]. The initial TiO_2 surface stoichiometry is important in terms of interfacial charge transfer and is expected to show considerable effect on the value of the interfacial dipole moment, which leads to the core-level BE shifts as measured by PES.

In this work, we studied the AP evolution with different interface structures by monitoring the core-level BE and Auger peak shifts with XPS. The respective contributions of initial- and final-state effects are identified based on the AP analysis. The determination of structural geometry in Ni/ TiO_2 system by means of PES has been discussed as well.

Previously, a few discussion has been addressed regarding to the surface stoichiometry effect on the initial- and final-state effect [69]. In the second part of this chapter, we employed XPS measurement to investigate the deposition of Ni on

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TiO₂(001) with different surface stoichiometry. They are: (i) almost stoichiometric surface (A-TiO₂) achieved by annealing, (ii) lightly reduced surface with modest amount of surface oxygen vacancies (LR-TiO₂), and (iii) heavily reduced surface with vast surface oxygen vacancies (HR-TiO₂).

4.2 Ni on stoichiometric TiO₂ surfaces

4.2.1 Auger parameter (AP) analysis

The Auger parameter, α , was proposed in the early 1970s by Wagner [70; 71] as a means of correcting for charging effects observed in XPS of non-conducting compounds without the use of an internal standard. The parameter is defined as the kinetic energy (KE) difference between a set of photoelectron and Auger electron transitions for the element to be analyzed:

$$\alpha = E_K(AES) - E_K(PE) \quad (4.1)$$

where $E_K(AES)$ and $E_K(PE)$ are the KE of Auger peak and core-level, respectively. The modified one, which is more convenient for calculation and discussion, is defined as:

$$\alpha' = E_K(AES) + E_B(PE) \quad (4.2)$$

where $E_B(PE)$ is the corresponding BE of the photoemission core-level.

In the simplest approximation, as shown by Wagner [70] and Thomas [72], the shifts in core-level BE, ΔE_B , and in Auger KE, ΔE_K , are given by

$$\Delta E_B = -\Delta\epsilon - \Delta R \quad (4.3)$$

$$\Delta E_K = \Delta\epsilon + 3\Delta R \quad (4.4)$$

where the $\Delta\epsilon$ is the initial-state effect and the ΔR the final-state effect. The shift in Auger parameter reads $\Delta\alpha = 2\Delta R$, thus provides a direct measurement of the extra-atomic relaxation energy. Therefore, with this method, we are able to separate the contributions of the initial- and final-state effect to the BE shift.

Figure 4.1 Example of the Ni $L_3M_{4,5}M_{4,5}$ (LVV, CVV) and $L_3M_{2,3}M_{2,3}$ (LMM, CC'C'') Auger transitions peaks.

Holneicher *et. al.* [73] have proposed a modified Auger parameter (β), which use the CC'C'' Auger transition peak rather than the normally used CVV peak. The use of modified Auger parameter is followed by Bagus *et. al.* [18] and these authors claimed β is more accurate than α . However, we still find the advantages of using α rather than β due to the reasons given below. First, the improvement of using β is rather small, as indicated by the calculations in Bagus's paper [18], where the difference between α and β is only 0.03~0.12 eV. However, as shown in Figure 4.1, the experimental error for the peak position of CC'C'' peak is much larger than that of CVV peak, because the latter one is much sharper. Therefore, the overall accuracy is not necessary better for the use of β . Second, by

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using the modified Auger parameter, β , Ritcher *et. al.* [12] have predicted that the lattice contraction leads to higher BE value. This prediction is not consistent with SCLS measurement, where surface relaxation also leads to lattice contraction. These authors have done the calculations for the isolated clusters, which were directly correlated to their experimental results. The lack of considering the substrate effect and the experimental error as mentioned above may lead to this disagreement.

Figure 4.2 The Ni $2p_{3/2}$ core-level, Ni $L_3M_{4,5}M_{4,5}$ Auger transitions and valence band spectra as a function of Ni coverage on rutile $\text{TiO}_2(001)$ surface. Spectra are normalized to the same height to show the binding energy change.

The spectra were measured through cumulative depositions on cleaned $\text{TiO}_2(001)$. Care was taken to ensure no additional O_2 was introduced through deposition nor the duration of the analysis. Figure 4.2 shows the Ni $2p_{3/2}$ core-level,

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and the Ni $L_3M_{4,5}M_{4,5}$ Auger transitions, and the VB spectra as a function of Ni coverage on $TiO_2(001)$ substrate at room temperature. There are no visible variations in the shapes of the Ni $2p_{3/2}$ core-level and $L_3M_{4,5}M_{4,5}$ Auger transitions, apart from an increase of peak intensities with increasing Ni coverage. However, a clear shift of the Ni $2p_{3/2}$ BE to lower value has been observed with increasing Ni coverage, in conjunction with a shift of the Ni $L_3M_{4,5}M_{4,5}$ Auger transitions to higher KE's. The detailed comparison of the shifts is presented in Figure 4.3. Similar behavior has also been observed on the $TiO_2(110)$ surface.

Figure 4.3 The BE shifts of Ni $2p_{3/2}$ core-level (solid squares) and $L_3M_{4,5}M_{4,5}$ Auger transitions (solid circles) with respect to those of bulk Ni as a function of Ni coverage.

There have been extensive reports on the shift of the core-level transitions for metal clusters on insulating supports to lower BE values accompanying the size increase from small clusters to large ones and approaching bulk metal [12; 18; 63; 64; 74]. Discussion has focused on the origin of the shifts and some reports have attributed the shift to oxidation at the interface. However the heat of formation (ΔH_f^0) for TiO_2 ($-472 \text{ kJ}\cdot\text{mol}^{-1}$) is larger than that of NiO ($-240.6 \text{ kJ}\cdot\text{mol}^{-1}$) [75], so

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the interfacial reaction in forming Ni oxide is thermodynamically unfavorable at room temperature. More importantly, our spectrometer has been well calibrated, so that the interfacial reaction can be ruled out on the basis of the non-zero DOS at the Fermi edge (E_F) even at very low Ni coverage, as is seen in the VB spectra of Figure 4.2. At higher Ni coverages, strong VB metallic peaks appear with a sharp cutoff at E_F . Hence we conclude that the oxide-metal reaction is not the cause for the observed core-level BE and Auger KE shifts. Instead, we will ascribe such shifts to the effects of cluster size.

4.2.2 Initial- and final-state contributions

Previously, the BE shifts for cluster size have been explained solely by final-state screening effects [63; 64; 66]. However, many recent works [12; 16; 18] have shown that the initial-state makes large contributions to the shifts. The AP method has been used to separate the initial-state ($\Delta\epsilon$) and final-state (ΔR) contributions to the shifts [12; 18]. From the measured shifts in Ni $2p_{3/2}$ BE's and Ni $L_3M_{4,5}M_{4,5}$ Auger transition KE's, we performed an AP analysis for both $\text{TiO}_2(001)$ and (110) surfaces with the 7.5 ML Ni thickness data as the bulk reference using the method mentioned in the previous section.

By using the AP analysis, $\Delta\epsilon$ and ΔR from the Ni $2p_{3/2}$ BE shift are separated and plotted in Figure 4.4 (a) and (b) as a function of Ni thickness, respectively. From Koopmans' theorem, $\Delta\text{BE} = -\Delta\epsilon$ when only orbital energies are considered; when final-state relaxation energy is taken into account, then $\Delta\text{BE} = -\Delta\epsilon - \Delta R$ [12]. In this convention, positive $\Delta\epsilon$ and ΔR contribute to a shift to lower BE. For each of the two contributions ($\Delta\epsilon$ and ΔR), there are separate components derived from the surface core level shift (SCLS) and substrate effects. In other words, we write:

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$$\Delta\mathcal{E} = \Delta\mathcal{E}_{\text{SCLS}} + \Delta\text{CT};$$

$$\Delta R = \Delta R_{\text{SCLS}} + \Delta R_{\text{sub}}$$

where $\Delta\mathcal{E}_{\text{SCLS}}$ and ΔR_{SCLS} are the initial- and final state effect in SCLS, respectively. ΔCT is due to the charge transfer between the clusters and substrate and ΔR_{sub} is related to the conductivity of the substrate which determines the capability to neutralize the positive charge created during the photoemission process. At 0.5 ML Ni coverage, $\Delta\mathcal{E}$ values of 0.44 eV and 0.19 eV are obtained for the (001) and (110) surfaces, respectively, which indicate a strong change in effective orbital energies in small clusters. However, the larger final-state relaxation contributions ($\Delta R < 0$) result in overall shifts to higher BE.

Figure 4.4 The initial (a) and final (b) state effects contributions to the total shifts as a function of Ni coverage obtained by AP analysis for both TiO₂(001) (solid squares) and TiO₂(110) (solid triangles) surfaces.

As shown in Figure 4.4 (a), the initial state effect, $\Delta\mathcal{E}$, is sensitive to the cluster size, which agrees with work done by Mason [67]. On both surfaces, initial-state effects ($\Delta\mathcal{E}_{\text{SCLS}}$) in Ni $2p_{3/2}$ core-level BE's form part of the overall SCLS [13]. Here, the SCLS combines changes in the local DOS (positive $\Delta\mathcal{E}_{\text{SCLS}}$ leads to lower

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BE) with opposing final-state effects ($\Delta R_{\text{SCLS}} < 0$) from screening [76]. For Cu thin film on Ni(100), theoretical calculations show that the initial eigenvalue shift ($\Delta \epsilon_{\text{SCLS}}$) is +0.66 eV, while the final-state shift (ΔR_{SCLS}) is -0.30 eV leading to an overall SCLS of 0.36 eV to lower BE [76]. We note that the magnitude of ΔR_{SCLS} is half that of $\Delta \epsilon_{\text{SCLS}}$. For Ni the overall SCLS is reported to be 0.43 eV to lower BE [77-79], but no separation of initial eigenvalue and final-state contributions has been made. Nevertheless, it is fair to conclude that $\Delta \epsilon_{\text{SCLS}}$ for Ni is larger than +0.43 eV. If we use the argument that the magnitude of ΔR_{SCLS} is half that of $\Delta \epsilon_{\text{SCLS}}$ then the latter is more likely to be around +0.80 eV. For SCLS, $\Delta \epsilon_{\text{SCLS}}$ is derived from changes in the local electronic structure at surface as a result of surface lattice relaxation, *i.e.* from contraction of the first Ni interlayer spacing [80-83]. On the other hand, the BE shift to higher value ($\Delta \epsilon < 0$) for Co deposited on a thin Al_2O_3 layer was attributed to lattice strain in Ref. [12]. However, it is likely that the Al_2O_3 substrate prepared using a standard recipe would only have a thickness of about 0.5 nm [84]. Under such circumstances, electron coupling between the underlying NiAl metal and the Co adsorbates, rather than lattice strain, would be the likely reason for the BE shift to higher value [7].

The $\Delta \epsilon$ observed in small Ni clusters on both TiO_2 (110) and (001) surfaces are much smaller compared to the initial eigenvalue shift in SCLS. This implies an important opposing contribution derived from the charge transfer between the metal adsorbates and TiO_2 substrates leading to reduced $\Delta \epsilon$. The smaller $\Delta \epsilon$ in Ni found on (110) surface compared with that on (001) surface indicates larger electron transfer effects in the former. The difference in $\Delta \epsilon$ on the two surfaces is as large as 0.25 eV. By assuming eigenvalue shift ($\Delta \epsilon_{\text{SCLS}}$) for Ni surface atoms to be +0.80 eV, the electron transfer effects are estimated to be -0.36 eV and -0.61 eV

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for Ni clusters on the TiO₂(001) and (110) surfaces, respectively. The transferred charges are then calculated to be about 0.06 e and 0.10 e from Ni to the substrates [85], respectively, in good agreement with previous reports [86; 87]. Electron transfer in the order of 0.1 e/Ni atom was estimated based on spectroscopic measurements, in Ref. [87]. Therefore, we believe that charge transfer makes a significant contribution to the initial-state effect.

The final-state shifts (ΔR) obtained on TiO₂(001) and (110) surfaces at 0.5 ML are -0.84 eV and -0.52 eV, respectively. By ascribing the final-state effect to Coulomb attraction [63], ΔR can be related to the cluster size through the following equation:

$$\Delta R = \frac{\alpha e^2}{4\pi\epsilon_0 r} \quad (4.5)$$

where α is a constant with a value around 0.5 for hemisphere cluster shape [13], and r is the cluster radius. Based on Eq. (4.5), the Ni cluster sizes on (001) and (110) surfaces are estimated to be 0.85 nm and 1.38 nm, respectively. To check the reliability of our estimates, we compare these values with estimates from STM measurements performed on TiO₂(110) surface by other investigations [51; 52; 88]. Tanner *et al.* [51] have demonstrated cluster growth for Ni on TiO₂(110) and their STM measurements reveal cluster radii of about 2.0-2.5 nm at 0.3 ML coverage. With a similar coverage of 0.25 ML, Fujikawa *et al.* determined cluster dimensions of about 1.0 nm in radius and 0.7 nm in height [88]. At a relatively higher coverage of 1ML, the cluster radius was found to be 1.43 nm [52]. While the variation can be ascribed to the different deposition rate and systems used, the values fall within the range of 1.0-2.5 nm for Ni coverage of less than 1 ML. Although we did not check the cluster size by atomic resolution microscopy, our determination of the

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cluster size from the final-state contribution through Eq. (4.5) shows reliably good agreement with the reported STM measurements. This further provides us a feasible way to study metal cluster sizes indirectly through photoemission spectroscopy, especially for insulating oxide surfaces where STM may be difficult. The difference in cluster size on the two surfaces for the same Ni coverage suggests a variation of growth rate, indicating a different interaction between Ni on TiO₂(001) and (110) surfaces. From thermodynamic considerations, cluster growth (Volmer-Weber) should result when the sum of interfacial energy (γ_i) and surface free energy of the overlayer metal (γ_m) is larger than the surface free energy of the clean substrate (γ_s), *i.e.*

$$\gamma_i + \gamma_m > \gamma_s \quad (4.6)$$

When the sum is less, the film should wet. The surface free energy of Ni (2.34 J/m²) [89] is greater than that of TiO₂ surfaces, which have been calculated to be 1.46 and 0.78 J/m² for (001) and (110) surfaces, respectively [90]. On the other hand, Ni is non-reactive with TiO₂, which leads to a positive value of γ_i [86]. Thus, the left side in Eq. (4.6) is always larger than the right side for Ni on TiO₂ substrates, resulting in the cluster growth mode. Further, the surface free energy of TiO₂(110) is only about half of that of the (001) surface, so cluster growth would be more evident on TiO₂(110) than on (001) surface, sustaining larger cluster sizes for the same coverage. Thus, the variation in surface thermodynamical properties results in different cluster sizes, and finally leading to different BE shift for the same metal coverage.

When the Ni thickness exceeds 1 ML, the initial-state ($\Delta\epsilon$) contribution becomes negligible (within ± 0.10 eV), as shown in Figure 4.4. The data clearly

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demonstrates the importance of final-state contributions even at very small thickness (< 1 ML) and by the comparison of results for $\text{TiO}_2(001)$ and $\text{TiO}_2(110)$ surfaces, we assign the initial-state effect to a combination of eigenvalue shift in SCLS and charge transfer between the clusters and the substrate.

4.2.3 Annealing effect

The cluster size effect is also evident in annealed systems. Upon annealing up to 400°C , the Ni clusters agglomerate into larger ones and result in a Ni $2p_{3/2}$ BE shift towards lower value as shown in Figure 4.5. This further strengthens the view that the interface reaction between Ni and TiO_2 to form Ni oxide is unfavorable for temperatures below 400°C . The annealing-induced oxidation of Ni will be discussed later.

Figure 4.5 Ni $2p_{3/2}$ core-level BE of Ni clusters deposited on rutile $\text{TiO}_2(001)$ surface as function of annealing temperature.

4.2.4 Full-width-at-half-maximum (FWHM) variation

Beside the shift in BE, the FWHM of the Ni $2p_{3/2}$ peaks also decreases with increasing Ni coverage, as shown in Figure 4.6. Three possible mechanisms are proposed here to account for this FWHM evolution:

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The first one is the shortened lifetime of the core hole induced by the photoemission process in small clusters due to faster relaxation. The reduced lifetime produces broader peaks and a subsequent increase in FWHM.

The second reason is an energy shifted component related to modifications in the surface electronic structure [91], that decreases in intensity with increasing Ni film coverage. The reduced coordination of the Ni atoms at the peripheral of a cluster differs compared with atoms at the centre leads to an initial-state of higher BE. But as the coverage is decreased, the contributions from the peripheral atoms feature more significantly in the PE spectra [91].

The third possibility is that of non-uniform cluster sizes on the TiO_2 surfaces. If we imagine an “ideal” case in which there is no Ni adatom diffusion, the density of Ni atoms on the surface at any given time should be the same for all areas since the Ni deposition itself is uniform over the surface. Therefore, the clusters tend to grow to the same size. However, there is always adatom surface diffusion, even at room temperature. Both broad or narrow cluster size distributions have been observed experimentally by STM in many cluster growth studies [51; 52]. The broadness of the distribution depends on both diffusion rate of adatom and deposition flux. In the current study, the rate of Ni adatom diffusion is expected to be slow compared to the deposition flux since the cluster growth occurs at room temperature, and this should produce a narrow size distribution. Due to the dependence of BE on cluster size, an increase of FWHM of Ni $2p_{3/2}$ peak is obtained, although the size variation is not sufficient to induce a splitting of the peak. The size distribution effect should be more pronounced at low Ni coverages due to the stronger dependence of BE on cluster size for smaller clusters (see Figure 4.3).

Figure 4.6 The FWHM of the Ni $2p_{3/2}$ core-level peak as a function of Ni coverage deposited on rutile $\text{TiO}_2(001)$ surface. The line is drawn to guide the eyes.

4.2.5 BE shift for atomic Ni on TiO_2 surfaces

In addition to the BE shifts of metal clusters relative to the bulk metal, an interesting topic is the BE for atomic Ni. The development of synchrotron radiation facilities, which produce intense and tunable x-ray beams, offers a possibility for photoemission study of atomic Ni in the gas phase and a comparison with Ni metal in solid phase [35]. However, it is still difficult to directly measure BE of atomic Ni on a substrate surface using photoemission due to low signals. To overcome this obstacle, we propose an indirect method to obtain the Ni $2p_{3/2}$ BE of atomic Ni on TiO_2 substrate. In this method, we first measure and plot Ni $2p_{3/2}$ BE's as a function of Ni coverage. Then we fit the experimental data to a curve that is extrapolated to zero coverage to reach the atomic asymptote. Figure 4.7 shows the experimental data and fitting curves for both $\text{TiO}_2(001)$ and (110) surfaces. By using this method, the BE's of a Ni atom are deduced to be 853.69 eV and 853.55 eV on $\text{TiO}_2(001)$ and (110) surfaces, which are 7.34 eV and 7.48 eV smaller than that of atomic Ni in the gas phase (861.03 eV) [35], respectively. The

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difference in the BE is very close to the calculated relaxation shift between a free Ni atom and bulk metal due to screening by d electrons (7.3 eV) [15]. It is interesting to discuss the physical meaning behind such a close agreement. According to the theoretical model proposed by Williams *et al.* [15], the total BE shift Δ between a free Ni atom and a Ni atom on TiO₂ surface can be decomposed into contributions from configuration changes, chemical shifts, and relaxation shifts:

$$\Delta = \Delta_{\text{config}} + \Delta_{\text{chem}} + \Delta_{\text{relax}} \quad (4.7)$$

Δ_{config} is defined as the change in the core-level BE only due to a change in the electron configuration of a free Ni atom and an atom on TiO₂. The chemical shift Δ_{chem} is the displacement of core-level caused by the changes in the chemical environment before photoionization. So these two terms reflect initial-state effects. The third term Δ_{relax} in Eq. (4.7) corresponds to the BE shift caused by removal of the electron and is identified with relaxation.

Figure 4.7 The BE of the Ni $2p_{3/2}$ core-level peak as a function of Ni coverage deposited on rutile TiO₂(001) (solid squares) and (110) (solid triangles) surfaces. The curves are least-squares fits to the experimental data.

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It reflects the final-state effect. Williams *et al.*'s calculation [15] indicated that the total BE shift of Ni metal relative to a free Ni atom is largely due to relaxation shift. Therefore, it is reasonable to neglect the Δ_{config} and Δ_{chem} contributions to total shift between a free Ni atom and a Ni atom on TiO₂ surface. The relaxation shift (7.34 eV and 7.48 eV) in a Ni atom on TiO₂ tallies with 7.3 eV in Ni metal bulk, which indicates the screening charge in a Ni atom on TiO₂ is *d*-like rather than 4.5 eV expected for *s* electron screening. This agrees with Johnson and Pepper [92] for one Fe, Ni or Cu atom adsorbed on a sapphire substrate, where the authors found evidence of a hybridization between the metal *d* states and the substrate oxygen orbitals. The dissimilar relaxation shifts indicate a diverse electronic structure of the single Ni atom on different TiO₂ surfaces. The main reason for this discrepancy lies in the amount of charge transfer occurring on the two TiO₂ surfaces. As discussed above, at low coverage, the Ni atoms on TiO₂(110) experience greater charge transfer than those on the (001) surface. This results in a lower value for BE of Ni atom on TiO₂(110) surface.

4.3 Ni on different stoichiometric surfaces

4.3.1 Surfaces preparation

The three stoichiometry TiO₂(001) surfaces were prepared using the following method. The A-TiO₂ sample is achieved through cycles of Ar⁺ ion sputtering and annealing at 773 K for 30 min under UHV conditions. The Ti³⁺ was detected to be less than 3%. The LR-TiO₂ and HR-TiO₂ samples were obtained from the clean A-TiO₂ samples subsequently sputtered 20 seconds and 10 minutes under UHV conditions, respectively, to introduce some more surface defects.

4.3.2 BE shift of Ni 2*p* on different surfaces

In Figure 4.8, we compare the Ni 2*p*_{3/2} BE shifts in Ni clusters deposited on

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A-, LR- and HR-TiO₂(001) surfaces as a function of Ni coverage. We observe similar trends of peak shift for Ni 2p_{3/2} towards a lower BE value with increasing Ni deposits for all surfaces. For Ni on A-TiO₂ surface, the BE of Ni 2p_{3/2} reaches 853.32 eV at 2.0 Å Ni and keeps decreasing, at a slower rate, to 853.00 eV when the Ni thickness approaches 13.0 Å. This observation is consistent with typical cluster-size dependent core-level BE [17]. It is common to observe a cluster-size-dependent BE of metal clusters to a higher value with decreasing cluster size on inert surfaces [12; 13; 16; 18; 62-65]. Despite the similar trend, the magnitude of the BE shifts are different for the LR- and HR-TiO₂(001) surfaces as shown in Figure 4.8. The Ni 2p_{3/2} BE's approach 853.22 eV and 853.15 eV at 2.0 Å and drop to 852.99 eV and 852.92 eV when the Ni thickness reaches 13.0 Å for LR- and HR-TiO₂ surfaces, respectively. By using the method described previously as well as in Ref. [17], the BE's of Ni 2p_{3/2} at the atomic limit are 853.87 eV, 853.63 eV and 853.29 eV for Ni on A-, LR- and HR-TiO₂(001) surfaces, respectively. Compared to that on A-TiO₂ surface, the Ni 2p_{3/2} BE are reduced by 0.24 eV and 0.58 eV on LR- and HR-TiO₂, respectively. For high coverage limit (bulk limit), it is shown in Figure 4.8 that the BE's of Ni 2p_{3/2} attain the same level for A-, LR- and HR-TiO₂ within the experimental error when the Ni thickness is increased to 13.0 Å.

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Figure 4.8 The Ni $2p_{3/2}$ core-level binding energies as a function of Ni thickness on A-TiO₂ (open squares), LR-TiO₂ (open circles), and HR-TiO₂(001) (open triangles) surfaces. The solid curves are least-squares fits to the experimental data.

The BE shifts of supported metal clusters can be classified into the initial- and final-state contribution. We have used the Auger parameter analysis to separate the initial- and final-state effects [17], which has been discussed in great detail in last section. We have found that the initial-state effect is strongly affected by the substrate and is assigned to a combination of eigenvalue shift in SCLS and charge transfer between the metal clusters and substrates. Final-state effect is inversely proportional to the cluster size. With these findings in mind, we will continue to discuss the substrate effect in more detail in following.

4.3.3 Growth mode on different surfaces

It has been reported that Ni clusters bind very weakly to the stoichiometric

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TiO₂ surface [93; 94]. Therefore, the deposited Ni atoms are inclined to migrate and aggregate to form larger clusters on A-TiO₂ at the same coverage. On the reduced surfaces, the Ni particles are of a smaller size and highly dispersed on terraces [95]. This means that with an equal amount of Ni being deposited (same deposition thickness), the Ni clusters formed on the reduced surfaces will be smaller than those on the A-TiO₂ surface. Therefore, if only the final-state effect plays a role (due to differences in cluster sizes), larger BE is expected on the reduced surface at the same Ni thickness. The opposing results shown in Figure 4.8 thus suggests that the final-state effect alone cannot adequately account for the core-level shift of Ni clusters on the three kinds of TiO₂(001) surfaces. The initial-state effect especially the charge transfer must be involved.

4.3.4 Charge transfer on different surfaces

For oxide supported metal system, charge transfer is a common phenomenon taking place at the interface. Observable electron transfer has been reported to take place between Ni and reduced TiO₂ [85; 87; 96] and this charge transfer plays a significant role in enhancing CO oxidation [93; 97-99]. However, there are some disagreement on the charge transfer direction [85; 87; 96]. In Refs. [87] and [96], it was reported that 0.10~0.30 electron per Ni atom was transferred from Ni to TiO₂, while ~0.10 electron per Ni atom was found to be transferred from TiO₂ to Ni in Ref. [85]. A charge transfer of 0.10 electron per Ni would introduce ~0.58 eV BE shift [85], which is comparable to that caused by the cluster size effect.

The Ni 2p_{3/2} BE shifts for Ni deposits on the A-, LR and HR-TiO₂(001) surfaces differ, which, however, can be rationalized with the physical picture that both cluster size and charge transfer between the substrates and Ni clusters are

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involved to the BE shift. On A-TiO₂, we have proved that the Ni clusters at the initial deposition stage loses electrons to the TiO₂ substrate in the previous section. Both the cluster size effect and positively charged Ni result in the shift of the Ni 2p_{3/2} core-level spectra to a higher BE. On the other hand, reduced surfaces have a larger electron density as compared to the A-TiO₂. The Ni clusters on reduced TiO₂ surfaces preferentially nucleate on the defective sites. Thus, the electron transferred from Ni to the substrate is diminished compared to that on A-TiO₂(001) surface because the electron diffusion into the reduced surfaces is significantly suppressed by the accumulation layer. Consequently, the Ni clusters are getting less positively and even negatively charged due to the electron transfer from Ti near the defective sites to the Ni clusters. It will be useful at this point if we first present our observations about the less positively charged Ni clusters on LR-TiO₂ and the negatively charge clusters on HR-TiO₂. Generally, less positively and negatively charged Ni clusters will reduce the BE shift. Therefore, at initial coverage where charge transfer effects are strong, the Ni 2p_{3/2} BE for reduced surface will be lower than that of the A-TiO₂ as evidenced in Figure 4.8. This is a strong indication that the charge transfer between Ni clusters and TiO₂ substrates is heavily influenced by the surface stoichiometry. The decreasing of BE on the reduced surfaces caused by charge transfer should be larger than the apparently observed values (0.24 and 0.58 eV, for LR- and HR-TiO₂, respectively) due to smaller cluster size. Based on Figure 4.8, the cluster size effect still dominates over the charge transfer effect. Even in the HR-TiO₂ case, the BE is positive shifted for small clusters.

The major difference on the annealed surface and reduced surfaces lies in their oxygen vacancies density. Reduced TiO₂ surfaces, via sputtering, will have

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more surface oxygen vacancies. This leaves excess electrons around the newly created vacancies. These electrons are not localized to any particular surface atom and they are therefore still active in reaction and bond formation. Therefore, when Ni is deposited on the reduced surface as compared to that of the A-TiO₂, the charge transfer equality will be affected. Electrons from the defective sites may result in a less positively or even negatively charged Ni clusters, which decrease their core level BE. This has been schematically illustrated in Figure 4.9. As shown in Figure 4.9, the distinct initial surface band bending and the potential barrier created are strongly accounted for the variation in charge transfer process for different surfaces. The initial surface band bending direction and relative magnitude shown in Figure 4.9 is also consistent with the measured O 1s BE's for the clean surfaces (no Ni deposition).

Figure 4.9 Schematic of charge transfer mechanism for Ni on A-TiO₂, LR-TiO₂, and HR-TiO₂.

4.3.5 BE shift of O 1s on difference surfaces

Charge transfer between Ni clusters and TiO₂ substrate produces interfacial dipoles. To gain more insight of this influence, the BE's of O 1s are presented as a

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function of Ni coverage for A-, LR- and HR-TiO₂(001) substrates in Figure 4.10. The BE evolution of O 1s rather than Ti 2p has been used because of the nature of the Ti 2p spectra on the reduced surfaces. Due to the presence of surface defects such as Ti³⁺, the resulting spectrum is overly broad and it is therefore more difficult to obtain an accurate Ti 2p BE position. However, the Ti 2p BE position can be obtained accurately for the annealed surface. We have therefore used the Ti 2p of the annealed sample to verify that the shift observed for the O 1s is an accurate reflection of the interface electrostatics as identical shifts are observed for both the Ti 2p and the O 1s BE. For the A-TiO₂ and LR-TiO₂, at initial deposition stage (< 2.0 Å), the BE of O 1s increases with increasing Ni coverage before it decreases slightly at higher coverages. This trend was only observed on the A-TiO₂ and the LR-TiO₂ surfaces. Instead, for the HR-TiO₂ surface, only a monotonically decrease of the O 1s BE was observed. The reasons are detailed following.

For A-TiO₂ and LR-TiO₂(001) surfaces, electrons transfer from Ni clusters to TiO₂ substrates upon Ni deposition. This charge transfer process introduces downward band bending, as shown in Figure 4.9, which increases the BE's of substrate elements when referred to Fermi level. The upward shift of O 1s BE at initial deposition stage is consistent with this band bending effect for A-TiO₂ and LR-TiO₂(001) surfaces. It is reasonable that the influence of the band bending will decrease with increasing Ni thickness. Based on the Figure 4.10, it reaches saturation around 2.0 Å. As seen in Figure 4.10, the O 1s BE's move to lower BE side at high Ni coverage (> 2.0 Å) with the similar slope for all surfaces. It has been well known that an insulator-to-metal transition occurs when the metal cluster size increases. On the other hand, for metal/nonmetal interfaces with a large dielectric constant mismatch, image charge will generate in metal when a core hole

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is created in the substrate [7] during the photoemission process. The generation of the image charge will lower the system energy, resulting in an enhancement of the kinetic energy of the outgoing electrons, therefore, a reduction in BE. We therefore propose that an insulator-to-metal transition of Ni clusters takes place at the thickness of 2.0 Å on TiO₂ surfaces, which introduces the image charge interactions at Ni/TiO₂ interfaces. For HR-TiO₂ surface, the initial surface band bending is downward, which creates a potential barrier preventing the electron from flowing in. The monotonically downward shift of O 1s BE on this surface indicates an inversed charge transfer direction, *i.e.* from TiO₂ to Ni, which reduces the magnitude of initially downward band bending (see Figure 4.9). The decreased slope at higher coverage for HR-TiO₂ surface indicates that the image charge effect is weaker than the band bending effect.

Figure 4.10 The O 1s BE shifts as a function of Ni thickness on A-TiO₂ (solid squares), LR-TiO₂ (solid circles), and HR-TiO₂(001) (solid triangles) surfaces. The straight lines drawn for the HR-TiO₂ are the least-squares linear fits to the experimental data. Note the different scales.

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Due to the charge transfer, interfacial dipoles should form. The interfacial dipoles are different for Ni dispersed on the three different TiO₂ surfaces. Thus, the oxidization state of Ni cluster depends on the substrate surface treatment. In particular, the amount of electron transferred from Ni increases with decreasing O vacancy densities on the TiO₂ surface due to enhanced bond between Ni and O for the annealed support. This implies that the transferred electrons may have been derived from the oxygen anions via Ni-O²⁻ interactions. This also proves that the HR-TiO₂ are electron rich (formally having two excess electrons per O_{br}), whereas the annealed one is electron deficient [6]. With increasing the surface oxygen vacancies, which is negatively charged, the electron transfer from the Ni to TiO₂ is inhibited and at some certain level when the electron charge density is high enough, the electron starts to transfer from TiO₂ to Ni.

4.3.6 Work function change for Ni/LR-TiO₂ system

Figure 4.11 Variation of surface work function ($\Delta\Phi$) with Ni coverage for Ni/LR-TiO₂(001) system. $\Delta\Phi$ is defined as ($E_w - E_{w_clean}$), where E_w and E_{w_clean} are the work functions for Ni/LR-TiO₂ system and clean LR-TiO₂ surface, respectively.

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In order to further prove that Ni clusters are positively charged on LR-TiO₂ surface, the change of surface work function ($\Delta\Phi$), induced by the deposition of Ni on LR-TiO₂(001) surface was measured using ultraviolet photoelectron spectroscopy (UPS) and the results is displayed in Figure 4.11. After the initial stage, sharp decrease of the work function was observed in the submonolayer coverage regime. This behavior has often been observed for alkali metals adsorbed on transition metal oxides, and is attributed to electron transfer to the transition metal oxides and the resulting dipole layers [100]. Figure 4.11 confirms that the Ni on LR-TiO₂ transfers some amount of electrons to the substrate. After subtracting the band bending effect, an outward dipole moment of 0.27 Debye per Ni atom is found using the Helmholtz equation [101]. This dipole moment is as small as only 10% of that observed on Cs/TiO₂ interface [102]. The small dipole moment on the present interface suggests that the amount of electrons transferred through the interface is one tenth of that of Cs/TiO₂(110); probably 0.1 electron per Ni atom. Such a small ability charge transfer is attributed to the large electronegativity of Ni, which is 1.91 on the Pauling's scale, compared with 0.79 for Cs.

Improved stoichiometry upon Ni deposition evidenced in Figure 4.12 suggests that Ni preferably adsorbed upon the oxygen vacant site. Here we propose that, the oxidation of Ti is due to the charge transfer from Ti to Ni with the assistance of oxygen vacancies. The electron transfer from Ti to Ni is kinetically driven by their electronegativities, which are 1.54 and 1.91 for Ti and Ni on the Pauling's scale, respectively. The final chemical state of Ni is the combination of charge transfer between O-Ni and Ti-Ni. For Ni on HR-TiO₂, the high electron density makes interfacial interaction less favored. The energy barrier for Ni diffusing into the HR-TiO₂ is lowered, making this electron transfer process easier.

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The similar behavior was found for Fe on TiO_2 , where it has been reported that different oxidation state of Fe was found on stoichiometric and reduced TiO_2 surfaces [103]. There are Fe^{3+} and Fe^{2+} states exist on A- TiO_2 surface, while no oxidation state of Fe is found on reduced TiO_2 surface.

Figure 4.12 The XPS spectra for Ti 2p on the HR- $\text{TiO}_2(001)$ surfaces for selected Ni coverages. The thickness is specified in the figure and the vertical lines corresponding to the binding energy position of Ti^{4+} , Ti^{3+} and Ti^{2+} , respectively.

Based on the above observations, the conclusion can be drawn that the appearance of Ti^{3+} state of Ti is due to the influence the chemical environment of the oxygen atoms of TiO_2 at the defect sites. Upon Ni deposition, the electron wave function of oxygen vacancy becomes more localized due to the attraction of Ni atoms sitting on top of it, making the Ti appear as the Ti^{4+} state.

4.4 Summary

We have investigated Ni $2p_{3/2}$ BE shifts with respect to the Ni bulk metal values as a function of Ni coverage deposited on $\text{TiO}_2(001)$ and (110) surfaces at

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room temperature. The changes with different coverage have been explained using the cluster-size-dependent effects. AP analysis of photoelectron spectra indicates that both initial- and final-state effects are responsible for the shift observed in small clusters. The initial-state effect causes the shift of Ni $2p_{3/2}$ BE to lower values with decreasing size, while the final-state effect causes a shift to higher BE values with decreasing size. Screening dominates the final-state shifts in larger clusters. From the comparison of results for $\text{TiO}_2(001)$ and $\text{TiO}_2(110)$, we have demonstrated the importance of substrate contribution to the initial-state effect and further assigned the initial-state effect to a combination of eigenvalue shift in SCLS and charge transfer between the Ni clusters and the TiO_2 substrates.

An indirect method has been developed to determine the Ni $2p_{3/2}$ BE of atomic Ni on TiO_2 substrate, and the values corresponding to (001) and (110) surfaces are 7.34 eV and 7.48 eV smaller than that of atomic Ni in the gas phase, respectively. These values are very close to the relaxation shift of 7.3 eV expected from d electron screening. The foregoing investigation has contributed to a better understanding of the photoionization process of Ni atoms on TiO_2 surfaces. In addition, it also offers an indirect but feasible method to study cluster growth mechanisms by photoemission spectroscopy, which would be especially important for insulating substrates where direct STM observation is limited.

Electronic structures of Ni clusters deposited onto the stoichiometric and reduced $\text{TiO}_2(001)$ surfaces at room temperature were comparatively investigated by XPS. The cluster size effect and interfacial charge transfer have a collective impact on the electronic structure of Ni clusters on the $\text{TiO}_2(001)$ surfaces. The Ni $2p_{3/2}$ BE shift is much smaller on reduced $\text{TiO}_2(001)$ surfaces, providing the first experimental evidence for the charge transfer from the defective sites on the

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reduced $\text{TiO}_2(001)$ surface to Ni clusters. On the A- and LR- $\text{TiO}_2(001)$ surfaces, the O 1s BE exhibits an unexpectedly upward shift with the increasing Ni thickness below 2 Å, which is well understood by collective contributions of interfacial charge transfer and image charge effect. The present study shows that the charge state of Ni depends on the initial conditions of the $\text{TiO}_2(001)$ surface on which the Ni atoms are dispersed. In the case of Ni deposited on the reduced $\text{TiO}_2(001)$ surfaces, the electron diffusion into the substrate is significantly suppressed due to the presence of the electron accumulation layer. This difference in the charge state of Ni atom will affect its ability to donate electrons to the 2p orbitals of adsorbed CO molecules, and hence to dissociate CO, the latter being an important step in the methanation reaction [85; 104-106]. Our results deepen the fundamental understanding of the important Ni/ TiO_2 catalytic systems.

Remarkable drop of the work function by Ni deposition on the LR- TiO_2 surface is correlated with an electron charge transfer from Ni to TiO_2 substrate. We have evidently proved that the charge transfer is taken place from Ni to TiO_2 on the A- TiO_2 and LR- TiO_2 , while the opposite direction on the HR- TiO_2 . The supported Ni cluster properties are affected by the surface stoichiometry, therefore, the interface property must be considered when performed further analysis.

CHAPTER FIVE

EVOLUTION OF NICKEL ELECTRONIC STRUCTURE ON TITANIUM DIOXIDE SURFACES

5.1 Introduction

In strong correlated systems, the photoemission spectral features become complex and the picture directly related to DOS breaks down. Though nickel metal is itinerant ferromagnet, it shows localized d band behavior [107] and is therefore an interesting test case to study. A famous example is Ni satellite structures observed in both core level and valence band photoemission spectra [21]. The 6-eV satellite is a two-hole bound state with a $c^{-1}3d^94s^2$ final state configuration ($3d^84s^2$ for valence band), while the main line corresponds to the final state of $c^{-1}3d^{10}4s^1$ [21].

In this chapter, correlation enhancement of electrons in reduced

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dimensional Ni metal has been studied. Surface is as an inherent reduced dimension two-dimensional (2-D) system. In first part of this chapter, we performed angle resolved PES study on a Ni foil in order to compare the difference between the topmost surface and the bulk counterpart in terms of the satellite position and intensity. In the second part of the chapter, we will be focusing on the Ni nano-clusters on rutile TiO₂ single crystal surfaces in order to explore the enhanced correlation in reduced dimensional Ni system. Both size and shape of nano-clusters have been demonstrated to show effect on the Ni 2*p* satellite structures. Discussions have been addressed on the 6-eV satellite as well as a 3-eV satellite structure emerges in Ni 2*p*_{3/2} photoemission spectra due to the existence of ³F atomic state. The modification of Ni 2*p* core-level spectra upon thermal annealing and Ar⁺ ion bombardment have also been addressed. Our observations provide feasibility to gauge Ni 3*d* electron population by probing the 2*p* photoemission spectra and to modify the supported Ni nano-clusters through thermal treatment and/or ion bombardment.

5.2 Ni foil surface: enhancement of the 6-eV satellite

The well-known Ni 6-eV satellite exhibits different properties in reduced dimensional systems. Table 5.1 summarizes the angle resolved XPS (ARXPS) results performed on Ni foil. In the Table 5.1, the satellite intensity is evaluated as the ratio between satellite intensity (*I*_{sat}) and main peak intensity (*I*_{main}). In this convention, the satellite intensity is doubled when detected at a take-off angle of 15° compared to normal detection (take-off angle of 90°). As we know, the spectra at low take-off angle carry more information from surface, where the dimension is lower compared to bulk. By considering the inelastic mean free path of 1.26 nm [108], the probing thickness is about 0.98 nm at 15° take-off angle. For take-off

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angle of 40° , the probing thickness is 2.43 nm. In Table 5.1, only a small increase is found for satellite and main peak intensities ratio when the take-off angle changes from 90° to 40° . This indicates that the notable enhancement of satellite intensity due to reduced dimension occurs only with a thickness less than 2.4 nm and most likely to be about 1.0 nm. The tendency that the satellite intensity increases with decreasing take-off angle is consistent with current theoretical understanding of the origin of the 6-eV satellite [38; 109]. At the surface, the reduced atomic coordination leads to lattice contraction [110; 111] and hence the increased Coulomb correlation energy U . The increased Coulomb correlation energy U and $d-d$ electron correlation are the origin of the enhancement of satellite intensity. Since the Ni foil is in polycrystalline form, the orientation related band structure distribution can be ruled out as a reason of variation of satellite intensity at different take-off angles.

Table 5.1 Ni 6-eV satellite intensity ratios with respect to the main peak for different take-off angles, together with the BE's and FWHMs of the main and the satellite peaks.

Take-off angle (deg)	BE's of main peak (FWHMs) (eV)	BE's of sat. peak (FWHMs) (eV)	$I_{\text{sat}}/I_{\text{main}}$
90	852.91 (0.92)	858.71 (3.03)	0.16
40	852.94 (0.93)	858.74 (3.26)	0.18
15	852.96 (0.98)	858.76 (4.04)	0.32

5.3 Ni nano-clusters on rutile TiO₂ single crystal surfaces

5.3.1 Evolution of Ni 2p spectra as coverage

Figure 5.1 displays the high resolution XPS $2p_{3/2}$ spectra of Ni nano-clusters deposited on TiO₂(001) for 150 s and 900 s, respectively.

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Figure 5.1 Ni $2p_{3/2}$ XPS spectra for Ni deposited on $\text{TiO}_2(001)$. The deposition time are 150 s and 900 s, respectively, specified on the figure.

The main peaks (labeled as A) is accompanied by broad satellite features spreading at higher BE region. The main peak is identified as $c^{-1}3d^{10}4s^1$ final state, where c^{-1} is the core hole [21]. In small clusters, the modified electronic structure will shift the main peak position to higher BE's [17]. In the present work, we will focus on the evolution of Ni $2p$ satellite structures with the dimension of nano-clusters and their origin. To this end, all spectra are normalized and shifted to superimpose the Ni $2p_{3/2}$ main peaks in order to easier the comparison. The same treatment applies in other figures throughout this chapter. After this treatment, the leading edges of the main peaks are identical in shape. The satellite feature in the range of 854.0 to 865.0 eV is characterized as two components, with one at 3.0-4.0 eV higher in BE than the main peak (referred to hereafter as B) and the other one about 6.0 eV higher (referred to hereafter as C or 6-eV satellite). The satellite features labeled as B and C demonstrate the limitations of one-electron theory [35; 112; 113].

By STM measurements, the growth of Ni on TiO_2 has been demonstrated to

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be a Volmer-Weber (cluster growth) mode, forming three dimensional ($3d$) clusters even at the lowest coverage [51; 52; 88]. This agrees with the thermodynamic prediction. Furthermore, as measured by STM, the size of Ni clusters increases with increasing deposition time, *i.e.*, increasing Ni coverage [51]. The Ni cluster size distribution is controlled by the D/F ratio, where D is the diffusion rate and F is the deposition flux rate [52]. Increasing the D/F ratio will result in a lower cluster density, larger clusters and a broader size distribution [52]. The size distribution is found to be sharp and approximated as Gaussian [88] or with slight negative skew at room temperature [51], whilst at higher temperatures the skew is slightly positive [51]. Our deposition flux rate and other experiment conditions are roughly the equivalent to those of Fujikawa's experiments [88], therefore, the size distribution in our experiments would be similar as what they found, which is a sharp approximate Gaussian distribution. Thus, the change of Ni $2p_{3/2}$ spectra in Figure 5.1 can be related to the evolution of the Ni cluster size. As shown in Figure 5.1, the B component is robust only for very short deposition time, *i.e.* small clusters, while the C component does not change evidently. These phenomena are not correlated to the spin-orbit multiplet due to a considerably large separation of the Ni $2p_{1/2}$ peak from $2p_{3/2}$ in the order of 20.0 eV. All the clusters discussed here are in nanometer (nm) size range with the smallest ones possessing only several atoms [51; 52; 88]. At this size, strong quantum size effect should occur and the electronic properties are more atomic-like. For Ni atoms in gas phase, the $2p$ photoemission spectra consist of many atomic states [35; 114], while the supported atoms are different from isolated ones [17]. Accompanying the dimensionality increase, the atomic states are getting overlapped and their weight should be altered. The multiplet complexity of the Ni $2p$ spectra demonstrated above,

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especially prominent for smaller clusters, is thus originated from the change of electronic properties due to the strong $d-d$ interaction and extra-atomic screening in reduced dimensional system.

The existing of oxygen atoms in TiO_2 substrate may raise a question as to whether there is any oxidation or not. Hereby, before going into detailed discussion, it is necessary to distinguish the satellite features from the oxide peaks. Despite the fact that there is small amount of charge transfer between the Ni and TiO_2 , the oxidation process (involving mass transport) has been generally ruled out, as discussed previously as well as in Ref. [17]. In order to make the present section self-contained, we briefly summarized the reasons here: (1) the heat of formation ($\Delta_f H^0$) per oxygen atom for TiO_2 ($-472 \text{ kJ}\cdot\text{mol}^{-1}$) is larger than that of NiO ($-240.6 \text{ kJ}\cdot\text{mol}^{-1}$) [75], the interface reaction to form Ni oxide is thus thermodynamically unfavorable; (2) the work function of $\text{TiO}_2(001)$ is 2.64 eV [90], much smaller than that of Ni (5.04~5.42 eV) [115], therefore the positive end of built-in electric field at Ni and $\text{TiO}_2(001)$ interface is pointing from TiO_2 to Ni, which prevents O^{2-} anion from moving to Ni side to react [7; 116; 117]. The argument is further strengthened below in the discussion of annealing samples.

5.3.2 Ni 2p 3-eV satellite

In Ni, there is a high DOS above E_F so that there are many final states into which the electrons can scatter and a reduction of the DOS at E_F leads to weaker satellites [118]. Furthermore, it is concluded that the contribution of empty $4sp$ bands to a satellite is weak because a scattering of d electrons into sp states has low probability. The intensity of the satellite features is determined by the weight of unoccupied Ni $3d$ character and by its nature and position above E_F . The Ni $3d$ characters far above E_F produce smaller contribution to the d^9 satellites than those

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just above E_F [118; 119]. The spin momentum is conserved during the photoexcitation process. The minority spin spectrum only contribute to spin triplet final states, whereas the spin singlet final states originated from the majority spin spectrum [120]. Large p - d electrostatic interaction splits the Ni $2p$ satellites into several atomic states, with assignments of 1D , 3F , 3D , 3P , 1F , and 1P [121-123]. The location of those atomic states can be found in Figure 5.2.

Figure 5.2 PES spectra of Ni $3p$ core level. Atomic notations are indicated in the lower panel. After Ref. [123].

The peaks at 10.0 eV higher in BE than Ni $2p_{3/2}$ main peak is attributed to 1F and 1P states of the $2p^5 3d^9$ configuration (labeled as D in Figure 5.1), while they are too weak to be recognized. The well-known 6-eV satellite is attributed to the combination of 3D and 3P states, labeled as C in the Figure 5.1. The 1D and 3F states give rise to the nearest feature to the Ni $2p_{3/2}$ main peak, labeled as B, whose significant weight is governed by 3F state [120]. For the Ni bulk, due to the reduced symmetry, the 3F triplet will split into 3E and 3T . In Figure 5.1, with

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increasing the Ni coverage, *i.e.* increasing the cluster size, the dramatic change of the Ni $2p$ spectra appears as a reduction of the feature B. The enhanced 3-eV satellite is due to the increase in the d -hole number at surface [124]. The increase in d -hole number can be associated with the increase in the $3d^8$ configuration in the ground state. On the other hand, since the intensity of feature B is mostly donated by the 3E and 3T states, the intensified feature B at low Ni coverage, *i.e.* smaller cluster size, thus indicates an enhancement of the 3E and 3T states. The 3E and 3T states are triplet states caused by pure minority spin down emission. The decreased 3F state with increasing cluster size indicates a reduction of minority $3d$ hole-states, thereby an increased population of $3d$ minority electron states, in line with the fact that Ni $3d$ level is more populated when it goes from atom to bulk.

Figure 5.3 The comparison of Ni $2p_{3/2}$ XPS spectra (lower) and difference (upper) spectra between the 150 s deposited and 900 s of Ni deposited on $TiO_2(001)$. The straight lines drawn are guide for the eyes.

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Furthermore, a direct line-shape comparison of Ni $2p$ spectra of small clusters (deposition time of 150 s) with large ones (deposition time of 930 s) is displayed in Figure 5.3. Their difference spectrum is given in the upper part of Figure 5.3. In the difference spectrum, two peaks are clearly exhibited, which are located at 0.90 eV and 3.21 eV higher in BE than the main peak, respectively. The photoemission spectrum of atomic Ni can be found in reference [114]. There are no atomic states related to the 0.90 eV peak. It is introduced merely due to the broadening of the peak for smaller clusters. The noticeable peak at 3.21 eV higher than the main peak confirms the existence of 3E and 3T triplet states; with its variation argue against a non-magnetic $3d^{10}$ final-state valence configuration. The Ni 6-eV satellite is also originated from the triplet state (3D and 3P states in atomic notation) and shows some enhancement at small clusters, as shown in Figure 5.3. However, since the 6-eV satellite is highly pronounced even for Ni bulk, the change observed here is weaker compared to 3E and 3T states. We then focus on the appearance of the 3.21 eV peak, which indicates that 3E and 3T triplet states change with the dimension size. From here, we develop a way to illustrate the alternation of Ni $3d$ population using non-spin resolved photoemission method. On the other hand, the unfilled $3d$ states consist of part of pure spin down states and part of hybridized $3d-4sp$ states [40], which part would be firstly filled has not been indicated yet. The $3d-4sp$ unoccupied hybridized states are completely unpolarized, the filling of these states will generate singlet and triplet states evenly. The pure spin-down states give rise only to the triplet states in photoemission spectra. Thus the drop in intensity of the 3F state is an indication of the filling of $3d$ pure spin down states. The filling electron is original belong to free-electron-like $4sp$ states, which are randomly polarized and highly overlapped with those $3d$

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characters close to the E_F . Thus, we conclude that the unfilled $3d$ pure spin-down states is lower in energy and closer to E_F than those of the unfilled $3d-4sp$ hybridized states.

The results in Figure 5.3 imply that the 3E and 3T states are likely to be modified upon annealing and Ar^+ ion irradiation. Through STM measurement, Tanner *et al.* [51] have found that the Ni clusters annealed in UHV coarsened up to ~ 880 K, but after this temperature the metal clusters did not grow any further. The agglomeration of Ni clusters upon annealing results in a broad d band and an increased $3d$ population.

5.3.3 Evolution of Ni $2p$ 3-eV satellite upon thermal annealing

Figure 5.4 Ni $2p_{3/2}$ XPS spectra for 5 min-deposited Ni clusters annealed at 100°C and 200°C, respectively. Annealing temperature is specified on the figure.

Figure 5.4 illustrates the Ni $2p$ XPS spectra for 5 min-deposited Ni clusters, together with those annealed at 100°C and 200°C for 5 min stepwise. To gain a better understanding of the spectra change, the comparison and their difference

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between the as-deposited and the 200°C annealed is illuminated in Figure 5.5. Again, the peaks appear at 0.91 eV and 3.25 eV higher than the main peak are attributed to the broadening of the peak and variation of 3E and 3T triplet states, respectively. From Figure 5.4, the prominent drop at feature B region should be noticed at 200°C compared to the small fade at 100°C. It is suggested that, if the feature B is caused by oxidation process, the annealed clusters should present more. However, this is not evidenced as seen in Figure 5.4. Another argument may be that there are metastable oxidation states of Ni exist at the interface between Ni and TiO_2 due to the fact that Ni may be associated with the interfacial oxygen, so the peak we assigned to Ni 3E and 3T triplet states may be due to an oxide-like environment from these interfacial atoms. The heat of formation per oxygen atom for NiO and Ni_2O_3 are $-240.6 \text{ kJ}\cdot\text{mol}^{-1}$ and $-163.2 \text{ kJ}\cdot\text{mol}^{-1}$, respectively [75]. If there is any metastable oxidization state of Ni, it would be dominated by NiO rather than Ni_2O_3 . We note that the chemical shift for Ni^{2+} and Ni^{3+} is 2.0 eV and 3.5 eV, respectively [125]. If the peak we assigned to Ni 3F atomic state is due to the oxidation state of Ni, it would be the metastable state of Ni^{3+} , which is less likely due to the above evidence. Thus, we eliminates the influence of oxidation process on the feature B. Imposing these results, we deduce that the evolution of the feature B is free from the oxidation process but related to the variation of the 3E and 3T states.

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Figure 5.5 The comparison (lower) and difference (upper) spectra of Ni $2p_{3/2}$ XPS spectra between the as deposited and 200°C annealed spectrum. Annealing temperature is specified on the figure. Vertical straight lines are drawn to guide the eyes.

Thermal annealing triggers the agglomeration of the Ni clusters. The agglomeration of Ni the clusters will make the $3d$ level electrons more populated, leading to a reduction of $3d$ -hole number. As a result, the 3F triplet state decreases upon annealing, as shown in Figure 5.5. The parallel tendency as deposition-dose-based upturn of the clusters size denote that filling up the $3d$ spin-down unoccupied states is the intrinsic mechanism for populating the Ni $3d$ level when the cluster size is increased. The pronounced dip of the 3E and 3T states at 200°C is an indication that the Ni clusters become highly mobile on $\text{TiO}_2(001)$ at this temperature. Based on these, we can modify the Ni $3d$ electron population easily by thermal annealing and gauge it by probing its $2p$ photoemission spectra.

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In Figures 5.1 to 5.5, evolution of the Ni 2*p* spectral demonstrate that the modified initial electronic structure of Ni clusters due to alteration of Ni 3*d* minority electron population upon the cluster dimension is the origin of variation of ³E and ³T triplet satellite states. This also implies that the initial electronic structure of Ni cluster changed with dimension can be probed by non-spin resolved photoemission through the analysis of the ³F triplet satellite state.

5.3.4 Evolution of Ni 2*p* satellite upon Ar⁺ ion bombardment

Apart from the cluster size, Ar⁺ ion bombardment has the potential to control the shape of the nano-clusters [126]. The bombarded nano-clusters exhibit strong electronic size effects, which are not related to the surface roughness and appear only on the supported clusters.

Table 5.2 tabulates the 6-eV satellite energy and intensity ratio comparison of Ni foil, as-deposited clusters, and Ar⁺ ion bombarded clusters. The corresponding Ni 2*p*_{3/2} spectra are shown in Figure 5.6. Along with the electronic size effects induced, the shape of the Ni nano-clusters may be modified by the Ar⁺ ion bombardment. As reported for Au/TiO₂ system [126], the sputtering modifies the cluster morphology from hemispherical island to dotlike.

Table 5.2 The BE positions, differences, FWHMs and intensity ratios of Ni 2*p*_{3/2} main and satellite peaks for Ni foil, as-deposited and Ar⁺ ion bombarded Ni clusters.

	BE's of main peak (FWHMs) (eV)	BE's of sat. peak (FWHMs) (eV)	Sat. energy (eV)	I _{sat} /I _{main}
Ni foil	852.91 (0.92)	858.71 (3.03)	5.80	0.16
As deposited (30 min)	853.11 (1.00)	859.06 (2.73)	5.95	0.15
Ar ⁺ bombarded (60 s)	853.30 (1.18)	859.59 (2.96)	6.29	0.13

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Figure 5.6 Ni $2p_{3/2}$ XPS spectra for Ni foil, 30min-deposited Ni clusters, and the one after 20 s Ar^+ ion sputtering.

As the Ar^+ ion bombardment produces nano-clusters and reduces both the lateral and vertical dimensions, quantum confinement is possible in either direction. As a result, we found the 6-eV satellite displays different properties upon Ar^+ ion bombardment. In this experiment, the bombardment is performed using 3 keV Ar^+ ion (current density $\sim 5 \mu\text{A}/\text{cm}^2$) with an incident angle of 53° with respect to surface normal. Upon the ion bombardment, the ^3E and ^3T states do not change evidently. The large difference appears as the change of 6-eV satellite energy, as shown in Figure 5.6. In Table 5.2, the bulk form Ni foil has the lowest satellite energy of 5.80 eV. The satellite energy is increased by 0.34 eV upon Ar^+ ion bombardment, together with a weak drop of satellite intensity, as shown in Table 5.2. The variation of Ni $2p$ satellite energy is very interesting and has a potential use for diagnosis of chemical environment of Ni atoms, and for the electronic

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structure of the Ni alloys [127]. This change may be related to the cluster shape change induced by Ar^+ ion bombardment as in Au/TiO_2 . STM measurement would be helpful to gain more direct information of this interesting phenomenon.

5.4 Summary

In conclusion, we use XPS to study the Ni $2p$ satellite of Ni clusters on $\text{TiO}_2(001)$ as a function of Ni coverage as well as annealing and Ar^+ ion bombardment. The variation of Ni $2p$ satellite with cluster size is discussed. The Ni $2p$ spectra resulted at low coverage confirm the existence of ^3E and ^3T triplet states, with its variation argue against a non-magnetic $3d^{10}$ final-state valence configuration. We demonstrate that the narrowed d band in the reduced dimensional clusters leads to intense ^3E and ^3T triplet states in Ni $2p$ spectra due to the lowed $3d$ electron population. The electrons in $4sp$ states prefer to transfer to unhybridized pure $3d$ spin-down states, which is lower in energy level than that of $3d$ - $4sp$ hybridized states. Our results might be useful in terms of magnetic quantum dots or nanostructures to interpret their electronic structures. Due to the prominent change of the satellite features with low temperature annealing, it may be an efficient method to check other transition-metal systems where the satellite issue is still controversial. Here we suggest to carrying out a further theoretical calculations related to the Ni d - d interaction and the s - d hybridization for different size of Ni clusters on $\text{TiO}_2(001)$, which can give more insight into this problem.

CHAPTER SIX

EVOLUTION OF NICKEL ELECTRONIC STRUCTURE ON COPPER (001) SURFACES

6.1 Introduction

As one of the most important magnetic ultrathin film systems, Ni/Cu(001) has been extensively studied in terms of its magnetic properties [128; 129], growth mechanism, and electronic structure [130; 131]. The core-level photoemission spectral features of both the films themselves and the interfaces between the substrates have attracted much attention in the bid to understand their unique electronic structures that have exhibited properties such as quantum-well states [132], oscillatory magnetic coupling [133], and oscillatory superlattice conductivity [134]. However, there are some discrepancy between the theoretical calculations and experimental results. For example, theoretical calculations predict that the electronic structure of an isolated single layer of Ni(001) is very different from the bulk, with a reduced bandwidth and markedly different DOS [135-137]. Various theoretical approaches [22; 137-139] have shown that the band structure and 3d partial DOS of Ni film on Cu is different from that of bulk Ni. Pampuch *et al.* [140] reported a consistent result with theory; Mankey *et al.*, however, found

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that the electronic structure of Ni on Cu(001) disperses strongly in the perpendicular direction and are consistent with a bulk-like electronic structure within a monolayer [141]. The reason for the bulk-like behavior has been attributed to a hybridization and charge transfer effect between Ni and Cu, through which the Ni monolayer built up a bulk electronic structure [141]. More recently, Matsui *et al.* [142] performed atomic-layer resolved analysis of Ni thin film on Cu(001). They found a different electronic structure when the dimension is reduced [142], which agrees with the result reported by Pampuch *et al.* [140] and the theoretical approaches [22; 137-139]. An underestimation of the thickness by one monolayer in Ref. [141] might be sufficient to explain the differences in conclusion [140]. The charge transfer from the Cu substrate into the Ni film smoothes out the 3d electron potential barrier at the Ni/Cu interface, allowing a greater penetration of the Ni electron wave functions and subsequent hybridization with the substrate electronic structure [136].

In Ni, the *s-d* charge transfer is very sensitive to changes in the environment, such as in the Cu/Ni system, the hybridization between Cu 4*sp* and Ni 3*d* results in a decrease of Ni *d* holes number (n_h) in the minority spin channel [143]. The exchange of electron between Ni 4*s* and 3*d* level results in a change of screen strength, leading to a BE change for both the main and satellite peaks, accompanied by a difference in satellite intensity. Although many studies have been applied to understand the structure-induced difference in electronic and magnetic properties of the Ni/Cu (001) system [144; 145], very few have been applied to the understanding of changes in satellite structure and the study of the screening effect of *s* and *d* electrons as a function of Ni thickness on Cu(001).

In this chapter, we investigate the Ni electronic structure as a function of

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thickness on Cu(001) surfaces by means of PES. The thickness dependence of the correlation-induced Ni 6-eV satellite signal is addressed. A comparison has been made for Ni films grown on flat versus nano-structured Cu(001) surfaces. Based on the comparison, the mixing of Cu atoms and Ni atoms has been found to be intensified at the terrace edge region and hence a greater Cu 4s/Ni 3d interfacial hybridization effect (*s/d* IHE) is predicted for Ni on the nano-structured surface. Through the study of the asymmetry index, the atomic picture of the initial growth is proposed. The convenience and powerful of the method is discussed.

6.2 Development of electronic structure of Ni thin films

6.2.1 XPS spectra fitting procedure

All the XPS spectra are fitted using *Thermo Advantage* (version 3.44) provided by the Thermo Electron Corporation. The Ni XPS spectra include a broad leading signal with an asymmetric tail on the high binding energy side, as well as satellite signals. In order to fit these asymmetric spectra, the Shirley background is used over a range selected to include both the main and satellite peaks, which is each fit with an artificial Gaussian peak whose *Lorentz/Gaussian ratio*, tail mixing ratio, tail height and exponential tail height were all unconstrained in order to achieve an optimal least squares fitting. Following this, the spectra are redrawn with the Shirley background subtracted from the raw data. By this method, any artifact introduced by the background should be removed and the evolution of the spectra can be easily shown by direct comparison.

6.2.2 Evolution of Ni 2p spectra as thickness

The spectra in Figure 6.1 reveal the dependence of the Ni electronic structure on the overlayer thickness. We show Ni 2p_{3/2} core-level spectra of selected Ni coverages on Cu(001) at arbitrary normalization in Figure 6.1 (a). In

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this figure, all spectra present similar structures: a main peak located at around 853 eV accompanied by a broad satellite feature that spreads in a higher BE region. The variation of the Ni $2p_{3/2}$ BE's with Ni thickness is visible in the enlarged views, as shown in Figures. 6.1 (b) and (c) for Ni $2p_{3/2}$ main peaks and satellite peaks, respectively. It is seen in Figure 6.1 (b) that the Ni $2p_{3/2}$ main peak is shifted towards a higher BE value when the Ni coverage increases, while the satellite peaks display the opposite trend, as seen in Figure 6.1 (c).

Figure 6.1 Ni $2p_{3/2}$ photoemission spectra for several Ni films grown on Cu(001) (a). The thickness is specified in the figure. Enlarged views of Ni $2p_{3/2}$ main peak and satellite peak are presented in (b) and (c) respectively. The straight lines are drawn to guide the eyes.

6.2.3 BE shift of Ni $2p$ spectra

To get a better view of this evolution, the value of the BE's of Ni $2p_{3/2}$ main and satellite peaks are highlighted in Figure 6.2. As seen in Figure 6.2, when the Ni coverage increases from 1.5 ML to 8.0 ML, the BE of Ni $2p_{3/2}$ main peak

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shifts higher by 0.16-eV, approaching its bulk BE value, while the satellite peak value decreases by 0.23 eV. The Cu $2p_{3/2}$ level BE values are found to be essentially independent of the presence of Ni coverage. In Ni, the $2p_{3/2}$ main peaks and the satellite peaks are correlated to the screening of the core hole in the final state induced during the photoemission process by d and s band electrons, respectively [21]. Thus the evolution of BE's suggests that the d and s electrons screening strength are modified when the Ni coverage increases, due to the change of electronic structure and redistribution of Ni $3d$ - $4s$ electrons. Although the Cu $4s$ /Ni $3d$ interfacial hybridization effect (s/d -IHE) involves charge transfer from Cu to Ni [22; 136; 141], this interfacial hybridization makes a weak impact on Cu $2p_{3/2}$ core level BE because the Cu $2p_{3/2}$ core level is dominated by the bulk signal. However, in the very thin Ni film, the contribution of the s/d -IHE to the Ni $2p_{3/2}$ core level BE shift must be considered. This interfacial effect has a greater contribution in the case of the thin film; thus, the observed evolution of Ni $2p$ BE originates partially from this. Furthermore, when the Ni film thickness increases from 5 ML to 8 ML, the saturation trend of BE shift is found for satellite peak, which is not the case for main peak, as seen in Figure 6.2. The plausible explanations are the turn-on of spin reorientation transition (SRT) [146; 147] and the crossover in the magnetic properties due to the change of Curie temperature [148] with the increase of the Ni thickness. The SRT is connected to the enhanced orbital magnetic moments at the surface layers which are sensitive to the local bonding configuration [146] and the crossover in the magnetic properties is surprisingly sharp between 5 and 7 ML [148].

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Figure 6.2 Binding energy of Ni $2p_{3/2}$ main peaks (solid squares) and satellite peaks (solid triangles) as a function of Ni coverage.

The s/d -IHE causes the Ni $2p_{3/2}$ main peak's shift to a lower BE as a result of charge transfer to the Ni, which is consistent with Figure 6.2. Another reason accounting for the negative BE shift of the Ni $2p_{3/2}$ main peak is attributed to the narrowing of the d band in the reduced dimension system [149], which induces a combined effect of modified DOS and stronger d band screening of the core hole in the final state for thin film. Among the Ni $3d$ DOS, there are more unoccupied states in $d_{x^2-y^2}$ and d_{xy} bands above the E_F compared to that in d_{z^2} , d_{xz} , d_{yz} bands [112]. The fewer unoccupied states in d_{xz} and d_{yz} bands are due to stronger screening by the sp electrons and that the d_{z^2} orbital is involved in the hybridization of Ni sp - d_{z^2} and Cu sp [141]. The Ni $d_{x^2-y^2}$ orbital does not mix with the Cu substrate for symmetry reasons and constitutes a surface band above the E_F [22]. Although it has unoccupied states, the Ni d_{xy} band has its center

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located 0.2 eV below E_F at 1.2 ML [141]. Thus, the increasing of 3d unoccupied states (*i.e.*, holes, n_h) with the increase in Ni coverage [112] is mostly due to the increasing n_h in the d_{xy} orbital, which suggests that the center of the d_{xy} band moves upwards and closer to the E_F with increasing Ni coverage. These changes in the d_{xy} band result in a reduced screening effect of the core hole in the final state of the photoemission, leading to increased BE of Ni $2p_{3/2}$ main peak in thicker Ni films, as shown in Figure 6.2. The upwards movement of the d_{xy} band leads to a reduced BE of Ni $2p_{3/2}$ main peak. However, the observed BE for 8.0 ML is 0.16-eV greater compared to that for 1.5 ML. This suggests that the combination of s/d -IHE and the reduced screening effect dominate the upward shift of d_{xy} band by 0.16-eV, leading to a higher BE shift in total.

6.2.4 Evolution of Ni 6-eV satellite

On the other hand, the interface hybridization reduces the Ni 4s electron screening, resulting in a larger BE of the satellite peak, which is consistent with Figure 6.2. Besides the s/d -IHE, the shift of Ni $2p_{3/2}$ satellite peak BE's also reveals a variation of Ni electronic structure with increasing Ni coverage on Cu(001). In the top layer of Ni films, the number of 4s-like valence electrons is decreased due to the expansion of the extended 4s-like state towards the vacuum in an attempt to lower its kinetic energy [22]. The expansion of the extended 4s-like state towards the vacuum induces a reduced s electrons screening of the core hole in the final-state, leading to a higher BE of Ni $2p_{3/2}$ satellite peak, as evidenced in Figure 6.2. In thick films, the surface contribution is less pronounced, which results in reduced satellite BE's when the Ni coverage increases. Thus the low BE shift of the Ni satellite peak with increasing the Ni coverage originates from both the s/d -IHE and the extended 4s-like state towards the vacuum.

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Figure 6.3 Re-plot of Ni $2p_{3/2}$ photoemission spectra for several Ni films grown on Cu(001). The thickness is specified in the figure. All spectra are normalized and shifted to superimpose the Ni $2p_{3/2}$ main peak. The Shirley background has been subtracted to remove, if any, artifacts introduced by the background signal. The inset shows the enlarged view of the satellite region.

The change of satellite energy is traced back to an electronic effect arising from either the lattice strain or the interaction with the Cu substrate, which shifts the satellite positions and varies the relative intensity of final states. The difference in structure can produce different electronic and magnetic properties. Besides the BE change, the satellite intensity has also been found to decrease as the Ni

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coverage increases. To highlight the evolution of satellite intensity, the XPS spectra of Ni $2p_{3/2}$ core-level for selected Ni coverages on Cu(001) are re-organized in Figure 6.3. All spectra are normalized and shifted to superimpose the Ni $2p_{3/2}$ main peaks in order to facilitate easier comparison. The Shirley background has been removed to prevent interference from the background signal. The inset in Figure 6.3 shows the enlarged view of satellite region. It is easy to notice the dramatic change of the satellite signal. The intensity ratios between the satellite peaks and the main peaks ($I_{\text{sat}}/I_{\text{main}}$) have been presented in Figure 6.4 (a) as a function of Ni coverage.

Figure 6.4 The satellite intensity ratio ($I_{\text{sat}}/I_{\text{main}}$) (solid stars) (a) and the satellite energy (solid circles) (b) as a function of Ni coverages.

As shown in Figure 6.4 (a), the intensity of the satellite decreases gradually with increasing of Ni coverage. The intense satellite signal at low coverage is attributed to the low dimensionality of the film [107]. First-principles total-energy

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calculations find a substantial narrowing of the $3d$ band width for the Ni monolayer [143; 147; 150; 151]. It has been quantified to be 30% narrower for the free Ni(001) monolayer [151]. The narrowed d band in thin films leads to strong d - d electrons interaction, which creates a situation in which the satellite structure is enhanced: the strong d - d electrons interaction is considered to be the origin of satellite formation [107]. When the film becomes thicker, both the d electron localization and the d - d electrons interaction strength decrease, as a result of which the satellite signal becomes weakened in thicker films. The evolution of satellite energy as a function of Ni coverage is highlighted in Figure 6.4 (b), which shows the decreasing trend with increasing Ni coverage.

The changes induced in the band structure should start saturating after the Ni film reaches a certain thickness, at which the band structure starts to stabilize [112; 130]. This tendency can be seen in Figures 6.3 and 6.4. After 5.0 ML, the BE's of satellite peaks start to saturate due to the onset of $3d$ behavior of Ni film. In both of Figures 6.4 (a) and (b), the low-dimensional character starts to fade away at around 5.0 ML, indicating that the number of unoccupied d states (n_h) attains a stable value. The n_h for Ni in Ni/Cu(001) is increased by 20% from 1 ML to 5 ML [112]. The reduction of n_h for thin films is due to the hybridization of the Cu $4s$ and Ni $3d$ bands resulting in a charge transfer from Cu $4s$ to Ni $3d$ orbitals. This has also been proposed in the configuration-interaction (CI) calculation [34]. The n_h of a Ni atom of interest can fluctuate through the hybridization between the $3d$ atomic orbital of the Ni atom and the orbitals of surrounding atoms. The degree of hybridization should reduce as the thickness of Ni films increase on the Cu(001) surface, leading to the increase of n_h . As shown in Figure 6.4, the satellite intensity ratio is changed by 37% and the satellite energy is changed by only 5% when the

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Ni coverage increases from 1.5 ML to 8.0 ML. The magnitude of the narrowing of d band is very close to the change of satellite intensity, which indicates that the satellite intensity has a stronger correlation with the narrowing of d band.

6.2.5 Comparison on different Cu(001) surfaces

The electronic structure of the films can be modified by changing the growth mode [107]. It is well known that surface roughness has a dramatic effect on the magnetic properties of magnetic monolayers, which also affects the photoemission behavior. Thus, we perform a comparison between the Ni films on flat Cu(001) surface and a nano-structured one that is constructed by Ar^+ ion sputtering [152; 153]. To accentuate the different electronic structure of Ni films on these two kinds of surfaces, direct comparisons are carried out for 2.0 ML and 5.0 ML Ni films in Figures 6.5 (a) and (b), respectively. The FWHM of the fitted Ni $2p_{3/2}$ main peak that indicates the homogeneity of deposited Ni films increases from 1.03 eV to 1.09 eV on the flat Cu(001) surface and from 1.10 eV to 1.16-eV on the nano-structured surface when the Ni coverage increases from 2.0 ML to 5.0 ML, respectively. From this it can be inferred that the Ni films at the initial deposition stage should be more homogeneous on the flat surface than on the nano-structured surface. The homogeneity of Ni 2.0 ML overlayer on the flat Cu(001) surface is higher than that on nano-structured surface, revealing the stronger d - d electron interaction in this film, therefore promoting an intense correlation induced 6-eV satellite, as can be seen in the insets of Figure 6.5 (a). The main peaks of Ni $2p_{3/2}$ locate almost at the same BE value on the flat surface and on nano-structured one for 2.0 ML Ni films. For Ni on Cu(001) system, the grazing incidence x-ray diffraction (GIXD) data show that the in-plane lattice parameter is expanded even at 20 ML [154]. This induces a larger strain in the Ni films leading to a tetragonal

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structure. The lattice strain introduces modifications to the Ni electronic structures, which may affect the screening by s and d electrons. However, the essentially same BE values for Ni $2p_{3/2}$ main peak indicates that the change of d electron screening originating from this lattice strain is negligible. However, the correlation induced 6-eV satellite peak is found to be 0.33 eV higher in BE on the flat surface than that on the nano-structured surface. Quantitatively, there is a 5% decrease of satellite energy on nano-structured surface compared with that on flat surface, implying that the lattice strain has a weak effect on the s electron screening of the core hole in the final state; it is 5% weaker for 2.0 ML Ni films on the flat Cu(001) surface than that on nano-structured surface.

Figure 6.5 Comparison of Ni $2p_{3/2}$ XPS spectra of Ni films grown on a flat Cu(001) surface (open triangles) and nano-structure surface (open circles) for 2.0 ML (a) and 5.0 ML (b), respectively. The Shirley background has been subtracted to remove, if any, artifacts introduced by the background signal.

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As for the satellite intensity, apart from the Ni $d-d$ electron interaction, the s/d -IHE should be considered. The growth mode of Ni on nano-structured is similar to that on vicinal surfaces [153]. In the case of Co films, the Co 2D island shape and size differ drastically for Co evaporated onto a flat or a vicinal Cu(001) surface [155]. Deviations from ideal layer-by-layer growth are small [155]. The diameter of the island is smaller on vicinal surface than that on flat ones [155]. The growth behavior of Ni on Cu(001) is expected to be similar to that of Co. Thus, small Ni islands on nano-structured Cu(001) surface is expected. In small islands, the $d-d$ electron correlation is enhanced, which is supposed to display a more intense satellite structure. However, this is not the case as seen in Figure 6.5 (a). The observed weaker satellite intensity on the nano-structured Cu(001) surface suggests that a larger s/d -IHE is present on the nano-structured Cu(001) surface, which reduces the satellite intensity [156]. The nano-structured Cu(001) surface has more step edges, which the missing bonds occupy and the Ni patches also attach preferentially. The reduced satellite intensity on the nano-structured surface indicates that the Ni atoms accumulated at the step edge have stronger interaction with Cu atoms. However, the discussion of the s/d -IHE should be correlated with the effect of Cu incorporation within the Ni matrix during Ni deposition [107]. The importance of the hybridization between Ni $sp-d$ with Cu s electrons can also be correlated to the increase of the Ni d -hole number with increasing the Ni film thickness on Cu(001) [112]. The Ni on nano-structured Cu(001) surface has different DOS structure near the E_F compared to that on flat surface. More d -holes are created in Ni atoms on nano-structured Cu(001) surface. The d_{xy} orbital is shifted up much closer to the E_F for Ni atoms on nano-structured Cu(001) surface than those on flat surface.

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For thicker Ni films, the Ni $2p_{3/2}$ spectra are almost identical to each other on the two kinds of surfaces, as shown in Figure 6.5 (b) for 5.0 ML Ni films. At this coverage, the shape of Ni films turns out to be a $3d$ structure on both surfaces [130] and their behaviors are bulk-like. The identical Ni $2p_{3/2}$ spectra result from the formation of bulk-like properties. The difference in $d-d$ electron correlation fades away for thick Ni films. On the other hand, the Cu $4s$ wave function penetrates only about 1 Å, so that 5.0 ML is a thick enough layer to justify overlooking the interface effect.

6.3 Subsurface growth of Ni films on Cu(001) surfaces

The electronic structure and magnetic properties of ultrathin Ni films on Cu(001) surface are tailored by the interface structure down to atomic level. The initial growth mode of Ni on Cu(001) is, therefore, of essential importance in the study of this system. A most important issue in this respect is exchange between film and substrate atoms. It has been reported to modify not only the magnetic anisotropy [157], but also the transport properties through the interface drastically [158]. STM and LEED show that the growth mode of Ni is in a pseudomorphic layer-by-layer mode on Cu(001), resulting in a tetragonal, instead of a cubic, structure [130; 131]. The tetragonally distorted lattice plays a key role for the magnetic anisotropy [159-161]. Tersoff [162] predicted that the atomic size mismatch can drive the interface mixing in heteroepitaxial systems. However, due to the lack of element specificity and atomic resolution in depth direction, STM can neither detect interface mixing [130] or alloy compositions [163]. Conflicting structure models have been proposed based on quantitative LEED studies due to the very similar scattering amplitudes of Ni and Cu [131; 164; 165].

XPS is sensitive to the atom species. Besides the BE change, in transition

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metals, core-level XPS have strong asymmetry lineshape when the core hole pulls a d state below or close to the E_F . A significant asymmetry in the line-shape was observed, which was explained in terms of a single core-level component characterized by an asymmetry parameter (or singularity index). Scattering of the conduction electrons by the hole potential results in a singularity at threshold. This asymmetric shape can be satisfactorily fitted by Doniach-Šunjić (D-S) line-shape function [59]:

$$I(\varepsilon) = \frac{\Gamma(1-\alpha)}{(\varepsilon^2 + \gamma^2)^{(1-\alpha)/2}} \cos \left[\frac{\pi}{2} \alpha + \theta(\varepsilon) \right]$$

$$\theta(\varepsilon) = (1-\alpha) \tan^{-1}(\varepsilon/\gamma)$$

where Γ is the Γ function, ε is the energy measured relative to the E_F , α is the singularity index, and γ is the natural line width of the hole state corresponding to its lifetime. α is roughly proportional to the square of the DOS at E_F which enters through the calculation of the joint density of e - h pair states [166]. The alloy and disordered systems show smaller values for α compared to the pure metal [166].

In case of ultrathin Ni films on Cu(001) system, many theoretical studies on the electronic structure has been reported in last decades [22; 135; 137; 139; 143; 167-169]. The shape of the $3d$ partial DOS is found modified, compared with that of bulk Ni. The Ni $2p$ line remains asymmetry in the alloy or disordered system because the DOS at E_F remains quite high, which enable the study of the variation of α even the system is changing to alloying or mixing or disordering.

6.3.1 Data processing detail

The XPS spectra are fitted using freeware *fitt* [170] and *fitxps* [171], which allows to fit the peaks in D-S line-form. The Shirley background is used over a range selected to include both the main and satellite peaks, which is each fit with a D-S lines convoluted with a Gaussian broadening to represent the combined

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photon and instrumental broadening and a Lorentz broadening to represent the lifetime of the core hole.

6.3.2 Typical fitting results

Figure 6.6 shows a typical example of the Ni $2p_{3/2}$ fitted using two D-S lines. The background is modeled by the Shirley approach. The quality of the fit can be seen from the fit residual, which shows no systematic variation.

Figure 6.6 A typical fitting for Ni $2p_{3/2}$ spectrum of 1 ML Ni on Cu(001) surface. The black open circles are the experimental data and the red line cross them is the envelope of the fitted curves. The blue dashed line models the Shirley background. The violet and olive shadows are the main peak and satellite peak, respectively. Residual is give below in orange color.

6.3.3 Singularity index for satellite and main peaks

Table 6.1 tabulates the singularity index for both satellite and main peak of Ni $2p_{3/2}$ on flat Cu(001) surface. From the Table 6.1, we can see that the singularity index of the satellite peak remains zero within experiment error for all thickness.

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Table 6.1 Singularity index of satellite and main peak of Ni $2p_{3/2}$ on annealed Cu(001) surface.

Ni thickness (ML)	0.5	1.0	1.5	2.0
α for main peak	0.204 $\pm$ 0.005	0.204 $\pm$ 0.005	0.218 $\pm$ 0.005	0.222 $\pm$ 0.005
α for sat. peak	0.001 $\pm$ 0.005	0.001 $\pm$ 0.005	0.001 $\pm$ 0.005	0.001 $\pm$ 0.005

The singularity indices are related to the final-state and validate the sudden approximation. Since the value of singularity index is proportional to the square root of the DOS near the E_F , the nearly zero value of satellite peak validates the two hole states nature of the Ni 6-eV satellite, in which the core hole is screened by the 4s electron and the Ni 3d is pulled by the core hole deep inside the valence band [21]. This has been schematically illustrated in Figure 6.7.

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Figure 6.7 Density of states representation of the mechanism that produces the valence-band satellites in photoemission from metallic Ni. After Ref. [21].

From the figure, it can be seen that the DOS generated by $4sp$ electrons at E_F in satellite final-state is much weaker compared to that of $3d$ in main peak. This explains the small singularity index for satellite obtained in this work. Beside the singularity index, the natural Lorentzian linewidth of the main peak component has been found much narrower compared with that of satellite peak, which indicates a

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shorter lifetime of satellite peak.

The singularity indices for Ni $2p$ main peak are plotted in Figure 6.8 as a function of Ni thickness. These α values, around 0.21, are rather large due to the large DOS of d electron at E_F as demonstrated in Figure 6.7. The values obtained in present work agree well with that (0.24) reported in Ref. [166]. The disordered polycrystalline Ni presents very small α value, 0.10 [166]. Even in sub-monolayer region, the α value we obtained is much larger than 0.10. This implies that the Ni atoms deposited on Cu(001) surface form very well ordered epitaxial layer rather than disorderly distributed structure, which agrees with previous studies [22; 130; 140]. We will strengthen this point in the following sections.

Figure 6.8 Plot of singularity index of Ni $2p_{3/2}$ main peak on flat Cu(001) surface as a function of Ni coverage.

Furthermore, a variation of the singularity indices for the Ni $2p_{3/2}$ main peak can be noticed. After 1.0 ML Ni, there is a “jump” of the singularity index. This is unusual since surfaces normally have larger singularity indices which are

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related to the increase in atomic-like character for the screening response of surface atoms due to their lower coordination [172]. Therefore, a reduction of the singularity index with the increase of the Ni thickness would be naturally expected. The subsurface growth, where Ni resides below a 1 ML Cu surface layer, as proposed in [164] is a possibility to explain the unexpected “jump”. After the Ni and Cu exchanges, the Cu atoms get pushed outward by the burrowing Ni atom, the Cu atoms display a tendency to encircle existing Ni atoms. The mixed interface behaving like alloy results in a smaller singularity index when the Ni thickness is less than 1.0 ML. The increased singularity index after 1.0 ML deposits is due to the formation of the Ni film on the top of the mixed interface. For very low coverage, the Curie temperature is below room temperature, thus the system studied here are all in paramagnetic states, no phase transition occurs.

6.3.4 Ni on nano-structured Cu(001) surface

A recent molecular dynamics simulation [173] predicted that the diffusion barrier at the surface can be overcome via defect sites. We thus perform a comparison for Ni films on a nano-structured one that is constructed by Ar⁺ ion sputtering [152; 153; 174] in order to study the kinetics of Ni-Cu mixing. Table 6.2 lists the singularity index for both satellite and main peak of Ni 2p_{3/2} on nano-structured Cu(001) surface. The singularity index of the satellite peak is unchanged from flat Cu(001) surface, following the same mechanism mentioned above.

Table 6.2 Singularity index of satellite and main peak of

Ni 2p_{3/2} on nano-structured Cu(001) surface.

Ni thickness (ML)	0.5	1.0	1.5	2.0
α for main peak	0.142±0.005	0.141±0.005	0.177±0.005	0.161±0.005
α for satellite peak	0.001±0.005	0.001±0.005	0.001±0.005	0.001±0.005

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Figure 6.9 presents the α values for Ni $2p_{3/2}$ main peak on nano-structured Cu surface. As for the case of nano-structured Cu surface, the singularity index is dramatically reduced compared to that of annealed surface (see Table 6.1 and Figure 6.8). The reduction of α value suggests stronger hybridization between Ni and Cu in case of the Ni on nano-structured Cu surface driven by the defect site at the edge [23]. The nano-structured Cu(001) surface has more step edges, where the strain is larger. Tersoff [162] has shown that strain energy plays an important role in driving the mixing of Cu and Ni. Calculations concerning Ni/Cu/Ni multilayers show that energy barriers for atom exchange processes are reduced near step edges [175]. Even on the nano-structured Cu(001) surface, the singularity indices jump to larger value after the coverage of 1.0 ML. The reason should be the same as on flat surface. The drop at 2.0 ML as compared to 1.5 ML indicates the ending of layer-by-layer growth mode on this surface.

Figure 6.9 Plot of singularity index of Ni $2p_{3/2}$ main peak on nano-structured Cu(001) surface as a function of Ni coverage.

6.3.5 Modeling of subsurface growth

Based on the variation of the α values, subsurface growth of Ni has been proposed and the Cu capping layer is predicted to be only up to 1 ML. Cu has a surface free energy lower than Ni (21.6 vs. 27.3 kcal/mol) [176], the Cu atoms segregate on the top of Ni is thus energetically favorable, which leads to a floating Cu overlayer on the evaporated Ni. Figure 6.10 (a) schematically shows the subsurface growth mode. At the coverage of 0.5 ML, strong exchange of deposited Ni with the Cu atoms of the topmost layer happens. As a rule, the incorporation of a Ni atom takes place in the vicinity of the region, where the atom lands. From Figure 6.10 (a), we can see that the 0.5 ML and 1.0 ML Ni are similar to each other in terms of the surrounding bonding atoms and the depth. Thus the same α value is expected, which is the case as shown in Table 6.1 and Figure 6.8. After 1.0 ML, the Ni and Cu exchange process is limited [177]. Subsequent formation of the second Ni overlayer by layer-by-layer growth takes place. This is indicated by the increase of α value when the Ni coverage is increased up to 1.5 ML. Additional Ni atoms sitting on top of the Cu layer at 1.5 ML increases the α value. For 2.0 ML, the whole second layer consists of Ni atoms only and the Cu capping layer is totally covered by surface Ni atoms, at which the value of α reach its maximum.

Another growth mode has been proposed when the Ni is grown on the Cu(001) surface, which is the mixing growth mode, as shown in Figure 6.10 (b). The similarity of α values for 0.5 ML and 1.0 ML suggests an elimination of this growth mode. If the mixing growth presents, first, the α value would be rather small, (0.10 for disordered Ni [166]); secondly, the α value for 1.0 ML would be different from that of 0.5 ML due to their difference bonding environment. Moreover, the α value for 1.0 ML should be larger than that of 0.5 ML since there

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are more Ni atoms floating on the top.

Figure 6.10 Structure model for 2.0 ML Ni/Cu(001) of (a) subsurface growth mode and (b) interface mixing growth mode. Light (orange) and dark (blue) spheres represent Cu and Ni atoms, respectively.

To crosscheck the reliability of the data we obtained, we note the authors of Ref. [166] have found the relationship between α and the DOS following the formula: $\alpha = 0.375\rho(E_F)^2$. The total $\rho(E_F)$ is the summation of each layer. Let's denote the DOS of the top Ni layer and the layer with Cu capping layer as $\rho_{surf}(E_F)$ and $\rho_{mix}(E_F)$, respectively. Based on the value for 1 ML, we easily get the value of 0.7376 eV^{-1} for $\rho_{mix}(E_F)$. At 2 ML Ni, by considering the attenuation of the signal, the α value we got should have the following relationship with DOS:

$$\sqrt{\frac{\alpha_{2.0}}{0.375}} = \frac{1}{2}\rho_{mix}(E_F)\exp\left(-\frac{d}{\lambda}\right) + \frac{1}{2}\rho_{surf}(E_F)$$

where d is the thickness and λ is the inelastic mean free path for Ni ($12.6 \text{ \AA}$). So we obtain 0.8929 eV^{-1} for $\rho_{surf}(E_F)$. The larger value of $\rho_{surf}(E_F)$ as compared

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to $\rho_{mix}(E_F)$ agrees with the first-principles calculation [178], where it is found that the DOS at E_F in Ni gets smaller when the Ni atoms go into the sublayers.

By using these results, the α value for 1.5 ML can be derived. Only half of the Ni sublayer is covered by the second Ni layer, so the α value should have the following relationship:

$$\sqrt{\frac{\alpha_{1.5}}{0.375}} = \frac{1}{3}\rho_{mix}(E_F) \exp\left(-\frac{d}{\lambda}\right) + \frac{1}{3}\rho_{mix}(E_F) + \frac{1}{3}\rho_{surf}(E_F)$$

Using the values of $\rho_{mix}(E_F)$ and $\rho_{surf}(E_F)$, we get $\alpha_{1.5}=0.216$. This agrees well with our fitted result of 0.218. The coincidence validates our methodology and the growth mode we proposed. This growth behavior is not unique for a Ni/Cu(001) system, but also found for Ag [179], Au [180], Pd [181], Fe [182-184], and Co [185-187] grown on Cu (001). Recently, a model study on the surfactant effect of the floating substrate layer was also reported for a Ni/Ag(001) system [188].

6.3.6 The change of Cu DOS at E_F

Figure 6.11 presents the singularity indices for the Cu $2p$ as the function of Ni thickness. In case of annealed Cu surface, the α value increase after the landing of 0.5 ML Ni deposits and keep unchanged afterwards within the experiment error. This indicates the increase of DOS at E_F for Cu after the mixing with Ni atoms. This agrees with our above explanation that there are strong hybridization of Cu $4s$ and Ni $3d$ at the interface region. For nano-structured Cu surface, the enhancement of α continues up to 1.5 ML, which supports the evidence that the Cu $4s$ /Ni $3d$ interfacial hybridization is enhanced on the nano-structured surface due to the increased step edge.

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Figure 6.11 Plot of singularity index of Cu $2p_{3/2}$ main peak for flat (black solid squares) and nano-structured (red solid circles) Cu(001) surfaces as a function of Ni coverage.

It should be emphasized that the growth of ultrathin films depend both on the energetics and on various factors affecting the kinetics of the deposited atoms [177]. The driving force for the surface-confined mixing can be attributed to broken bonds at the surface and to atomic size mismatch [162]. The kinetic variables encompass the relative size of the deposited atoms and the substrate atoms, the deposition rate, the substrate temperature, the structural order of the substrate, the degree of contamination, and so on. The dependence on kinetic factors is due to nonequilibrium processes usually involved in the growth of thin films. This explains the different model proposed previously [131; 164; 165; 177].

In summary, the picture of the initial growth of a Ni on Cu(001) surface supported by the current study is a segregated subsurface Ni layer growth below a 1 ML thick Cu capping layer which behaves as a surfactant. The effect could simply be due to a direct exchange process between first- and second-layer atoms.

6.4 Valence band evolution of Ni on Cu(001) surface

Figure 6.12 reveals the dependence of the Ni $3d$ electronic structure as a function of overlayer thickness measured by UPS with the light source of HeII (40.8 eV). We show complete VB spectra of Cu(100) and up to 10 ML Ni/Cu(100) at arbitrary normalization. Regions of Ni $3d$ and Cu $3d$ emission can easily be distinguished as the pure Cu spectrum shows at photon energy of HeII no feature between 2 eV and the Fermi level. Cu $3d$ emission occurs between 2 and 4 eV. Two peaks observed for raw Cu at 2.65 eV and 3.45 eV BE's are attributed to Δ_1 band (Γ_{12}) and Δ_5 band (Γ'_{25}) [140], respectively. The shoulder at 2-eV BE is due to Cu $4sp$ emission.

For Ni spectra, the evolution of the $3d$ spectra is rather complicated. In the spectrum of 0.4 ML Ni, only one peak located at 0.75 eV BE ($\bar{\Gamma}_1$) is noticed. When the Ni coverage increases to 1.0 ML, second peak starts to appear at 0.29 eV BE ($\bar{\Gamma}_5$). The peaks at 0.75 eV BE shift its position to 0.91 eV at 2.0 ML. For the thicker Ni film (> 3.0 ML), two peaks derived from Ni $3d$ states are fixed at 1.13 eV (Γ'_{25}) and 0.37 eV (Γ_{12}) BE's. This indicates that the 3 ML Ni already shows bulk electronic structure. Only a very weak feature due to emission from the Cu $3d$ band is seen between 2 and 4 eV BE range at the Ni thickness larger of 4 ML Ni. This is a clear indication that the Cu substrate is covered almost completely by 4 ML Ni.

Figure 6.12 UPS spectra of valence band. Normal-emission spectra in the vicinity of the Brillouin-zone center of Cu(001) and selected coverages of Ni/Cu(001).

The difference between 2.0 ML with both 1.0 ML and 3.0 ML conclusively substantiates the evolution of Ni electronic structure as Ni thickness. The variation of the Ni 3d position as a function of thickness has been related to the particularly strong electron correlation effect and narrowed *d* band in low dimension for Ni thin film [140]. Besides the evolution of Ni electronic structure with thickness, the

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subsurface growth mode should be taken into consideration when sub-monolayer Ni is discussed. This helps us understand the details of the subsurface growth.

At 0.4 ML, only one peak located at 0.75 eV BE is observed. This peak ($\bar{\Gamma}_1$) is originated from Ni d_{z^2} orbital [22; 136]. The appearance of this peak thus suggests a picture that the Cu atoms are sitting directly above the Ni atoms after exchange to facilitate the formation of Ni d_{z^2} orbital. The BE position of $\bar{\Gamma}_1$ keeps invariable until 1.0 ML when the subsurface growth holds valid. The appearance of peak at 0.29 eV BE ($\bar{\Gamma}_5$) at 1.0 ML comes from the Ni bond with the Cu atoms next to its direct top in neighboring layer because the $\bar{\Gamma}_5$ is originated from Ni d_{xz} and d_{yz} orbitals [22; 136]. At low coverage, the Ni atoms are randomly separated. The opportunity to have the Cu atom next to its direct top in neighboring layer is low, thus the population of $\bar{\Gamma}_5$ peak.

6.5 Summary

In summary, by means of XPS and UPS, we have studied the electronic structure of Ni films on Cu(001) in comparison to bulk. The reduction in the BE value of the Ni $2p_{3/2}$ main peak in the thin film is strongly correlated to the s/d IHE and the narrowing of the d band in samples of reduced dimensions. However, the increased satellite BE is attributed to the combination of interface hybridization and expansion of extended $4s$ -like state towards the vacuum. The modified DOS and stronger screening due to the d band narrowing in a 1.5 ML Ni film cause the Ni $2p_{3/2}$ main peak BE to shift lower to a greater extent, by 0.16 eV, than that of a 8.0 ML film. The center of the Ni d_{xy} band is moved upwards and closer to the Fermi level when the Ni coverage is increased. A strong thickness dependence of the correlation-induced Ni 6-eV satellite signal is observed. It is found that the relative intensities of the correlation-induced 6-eV satellite peaks to main peaks

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increase when the Ni film thickness decreases. The results are explained from the viewpoint of dimension-dependent electronic structures of Ni films. The change in satellite intensity is related directly to the narrowing of the d band, since they are changed by almost the same percentage amount. Those observations corroborate the view that the dimensionality of transition metals determines mainly the character of the electronic states. Through the comparison of Ni films on flat and nano-structured Cu(001) surfaces, mixing of Cu atoms and Ni atoms is found to be enhanced at the terrace edge region and a larger s/d IHE is predicted for Ni on nano-structured surface.

Singularity indices are deduced from the measured XPS spectra and used to predict the subsurface growth of Ni. Under the current experimental conditions there are effective channels for interdiffusion of Cu and Ni atoms. The thin film growth depends very sensitively on various energetic and kinetic parameters, so the growth mode for the same system may vary widely according to experimental conditions. The discrepancies in the literature on the growth modes of Ni on Cu (001) might have originated from this reason. The exchange of atoms is spatially confined to the atomic layer adjacent to the interface, where considerable rumpling is observed near Ni atoms within the Cu matrix. In view of the delicate dependence of the physical properties of this prototype epitaxial system on the detailed structure these results have profound implications for future experimental studies and electronic structure calculations. UPS measurements help to affirm the evolution of Ni electronic structure and the subsurface growth.

CHAPTER SEVEN

GROWTH BEHAVIOR OF NICKEL ON RUTILE TITANIUM DIOXIDE SURFACES

7.1 Introduction

The interfacial interactions of metal/oxide system, which consist of interfacial charge redistribution and/or mass transport upon interface formation, are important factors to determine the performance of metal/oxide heterojunctions, particularly in nanotechnology, where the miniaturization of devices down to the nano-regime leads to an enormous increase in the density of interfaces. In experiments, especially for ultra thin metal overlayer, thickness of the overlayer, substrate orientation, and many other parameters will affect the interfacial reaction [86].

It has been found that the interaction between metals and oxide supports, so-called strong metal–support interactions (SMSI), are of great importance in heterogeneous catalysis [117; 189-194]. In particular, the SMSI was first suggested by Tauster *et al.* to explain the suppression of both H₂ and CO chemisorption capacity of metal clusters supported on TiO₂ which are reduced at high temperatures [8; 9]. Later, SMSI was widely observed in many metal/oxide

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catalytic systems [117; 191-194]. Two major factors contribute to the SMSI states are an electronic factor and a geometric factor. The electronic factor is determined by a perturbation of the electronic structure of the metal catalyst, which originates from charge transfer between the metal and the oxide, while the geometric factor results from a thin layer of reduced oxide support physically covering the metal particles (called the encapsulation or decoration model), which blocks active catalytic sites at the metal surface.

In this chapter, the thermal stability and interfacial reaction of metallic Ni layer deposited on TiO_2 surfaces have been investigated using *in situ* photoemission. Several surface orientations have been used to compare their difference in terms of the interfacial reaction upon thermal treatment. Surface morphological change and cluster structural transformation have been monitored by *ex situ* AFM.

7.2 Adsorption of Ni on TiO_2 surface at room temperature

7.2.1 Surface electronic structure of raw TiO_2

Figure 7.1 shows the comparison of UPS spectra for $\text{TiO}_2(110)$ surface under HeI and HeII radiation. Two well resolved emission features located at 7.4 eV and 5.5 eV BE's are observed when use HeI light source, which are referred to bonding and non-bonding of O $2p$ derived states, respectively. However, under HeII irradiation, only the bonding peak is well resolved. As we know, HeI has smaller energy than that of HeII, thus it provided more information from s orbital. Based on the dramatic difference shown in Figure 7.1, the following conclusion can be drawn: the O $2p$ non-bonding peak is predominant by the hybridization with Ti $4s$ orbitals, while the bonding peak is the mixture of hybridization with Ti $3d$ and $4s$, which is consistent with the previous observation [195].

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Figure 7.1 UPS spectra for UHV annealed clean $\text{TiO}_2(110)$ surface under HeI (red curve) and HeII (black curve).

Figure 7.2 shows the angle resolved UPS (ARUPS) spectra for $\text{TiO}_2(110)$ surface. As shown in the Figure 7.2, the signal from the non-bonding peak is enhanced with the decrease the take-off angle. The development of non-bonding signal indicates that the hybridization of the Ti $4s$ orbitals with O $2p$ is amplified at the surface as a result of the reduced symmetry from D_{2h} to C_{2v} [195]. Thus non-bonding signal is very sensitive to the condition of the surface O. These changes have long been associated with a reduced surface [196]. This is supported by the evidence that by comparison of the reduced surface with annealed one, the intensity of the nonbonding feature decreases with respect to that of the bonding feature.

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Figure 7.2 ARUPS spectra for UHV annealed clean $\text{TiO}_2(110)$ surface. Inset show the geometry of the measurement performed.

7.2.2 Surface electronic structure of TiO_2 with Ni

Figure 7.3 shows the UPS spectra for several Ni coverages on TiO_2 surface. As seen in Figure 7.3, the intensity of the nonbonding feature decreases dramatically with respect to that of the bonding feature after the landing of Ni deposits. Detectable density of states in the band gap induced by defect is also observed. The attenuation of the nonbonding peak and the appearance of the band gap emission after the Ni deposition follow the same trend on reduced surfaces. The reduction of non-bonding signal is associated with rehybridization upon defect formation. As discussed above, the non-bonding O $2p$ signal comes mostly from the surface oxygen atoms. The reduction of the signal implies the disturbed bonding of those surface oxygen atoms by the landing of Ni, which supports the

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conclusion of bridging O as adsorption site for Ni through which charge transfer takes place as evidenced in Refs. [96; 197; 198]. This adsorption behavior is strongly affected by the O dangling bond [197]. During the landing of the metal atoms, charger transfer takes place via the bond with the surface O, which stabilize the metal deposit [6]. Charge transfer takes place between the metal and O, as evidenced in our case.

Figure 7.3 UPS spectra for several Ni coverages on TiO₂(110) surface. Black open triangles, red open circles, green open squares represent raw surface, 1 ML Ni, and 2 ML Ni, respectively.

As shown in Figure 7.3, the non-bonding intensity keeps decreasing when the Ni coverage is larger than 1 ML. This suggests a cluster growth mode of Ni on TiO₂, because the decrease of non-bonding peak would hit its maximum value at 1 ML for layer-by-layer growth. Therefore, the growth mode and the preferred

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landing position can be easily deduced from the spectra presented in Figure 7.3.

7.3 Thermal behavior of Ni overlayer on rutile $\text{TiO}_2(110)$ surface

7.3.1 Evolution of the XPS spectra upon thermal treatment

XPS is a very powerful tool to study the reaction between Ni and TiO_2 . Figure 7.4 shows the XPS spectra of Ti $2p_{3/2}$ and O $1s$ obtained at different annealing temperature for 3 nm Ni on $\text{TiO}_2(110)$ surface. As shown in Figure 7.4, the BE's of Ti $2p_{3/2}$ and O $1s$ shifts to low BE with the increase of temperature and moves back to its original position when the sample is cooled down to room temperature. The change of BE for Ti $2p_{3/2}$ and O $1s$ are the same amount. This behavior has also been observed for pure TiO_2 substrate when annealed (results not shown). Furthermore, no obvious reduced Ti^{3+} or Ti^{2+} peaks are observed in Figure 7.4 (a). Therefore, this BE shift is purely due to the thermal effect rather than any indication of reaction.

Figure 7.4 XPS Spectra of thermal reaction of 3 nm Ni on $\text{TiO}_2(110)$ for (a) Ti $2p_{3/2}$ core-level and (b) O $1s$ measured at different temperatures. The spectra are collected at normal photoelectron emission. The dashed lines are drawn to guide the eyes.

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In Figure 7.5, we present the XPS spectra of Ni $2p_{3/2}$ and VB obtained at different annealing temperature for the same samples as mentioned above. All Ni $2p_{3/2}$ spectra shown in Figure 7.5 (a) have a main peak located around 853 eV, which is accompanied by a small peak located around 858.9 eV-the so-called 6-eV satellite due to $4s$ band screening [21]. The Ni $2p_{3/2}$ peak moves to higher BE with the increase of heating temperature, which is opposite to that of Ti $2p_{3/2}$ and O $1s$ peaks. No obvious oxidized Ni state appears until the temperatures of 600°C. This is validated from the Ni $2p_{3/2}$ core-level spectra, where the peak shape does not change until 600°C. When the sample is heated to 600°C, a small hump located at 856.3 eV (indicated by an arrow in Figure 7.5 (a)) shows up, indicating that a small fraction of the Ni atoms get oxidized. The intensity of the Ni oxidation state develops with heating temperature; however, metallic Ni still dominates at 635°C.

Figure 7.5 XPS Spectra of thermal reaction of 3 nm Ni on $\text{TiO}_2(110)$ for (a) Ni $2p_{3/2}$ core-level and (b) valence band measured at different temperatures. The arrow in (a) indicates the formation of oxidized Ni.

When the sample is cooled down to room temperature, an interesting

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phenomenon is observed from Figure 7.5 (a) that Ni oxidization peak is dramatically depressed. This is attributed to the broken of Ni-O bond due to the segregation of Ni atoms to the very top surface region of TiO₂(110) substrate when it is cooled down. The observation in VB, given in Figure 7.5 (b), supports this scenario by the enhancement of Ni 3d signal and better resolved O 2p peaks. Thus the following reaction channel has been proposed. When the sample is kept at high temperature, some Ni atoms have diffused into TiO₂ lattice, which makes it easier to form Ni²⁺-like species. The Ni²⁺-like species are those Ni atoms dissolved into TiO₂ lattice and connected with oxygen but not readily to form steady NiO lattice. The inward diffusion can be impelled by thermal energy at high temperature and balanced by segregation to reach equilibrium. The existence of diffusion channel may be opened to reduce the surface energy as thermodynamically predicted in Ref. [162]. When cooled down to room temperature, the inward diffusion channel is closed due to the discharge of thermal energy. The segregation of Ni atoms to surface depresses the formation of the Ni²⁺-like species, as shown in Figure 7.5.

The reaction of Ni and TiO₂ is thermodynamically not favorable [17; 174] at room temperature. The heat of formation (ΔH_f^0) for TiO₂(-472 kJ·mol⁻¹) is much larger than that of NiO (-240.6 kJ·mol⁻¹) [75]. However, the oxidation process is much stronger at the substitution sites than the adsorption sites [199]. At high temperature when the inward diffusion channel opens, the number of substitution sites will increase efficiently, which spurs the formation of Ni²⁺ state. However, the Ni²⁺ states produced here are different from the stable Ni oxides, as supported by the different BE for Ni²⁺ and the segregation when cooled down.

7.3.2 Evolution of the surface morphology upon thermal treatment

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Figure 7.6 shows the AFM images of 3 nm Ni thin films grown on $\text{TiO}_2(110)$ surface and annealed at several different temperature. Surface diffusion modifies surface morphology. AFM images from Figure 7.6 visibly provide us a rough picture of the whole physical process of Ni on $\text{TiO}_2(110)$ surface upon thermal treatment. The initial surface is featureless. As the annealing temperature increases, the AFM images show that the surface roughness increases and Ni 3D islands appear (see Figures 7.6 (a) and (b)). Coarsening of the cluster is evidence for the natural self-organization of the surface adatoms, where the driving force is the reduction in surface energy of the islands.

Figure 7.6 AFM images of Ni on $\text{TiO}_2(110)$ surface after annealing to different temperatures: (a) 300°C and (b) 600°C. Images are 1 $\mu\text{m} \times 1 \mu\text{m}$ in size.

The image in Figure 7.6 (a) was captured for the sample annealed at 300°C, the surface is still very flat, with a very small root mean square (RMS) of 0.21 nm. When the annealing temperature is increased to 400°C, all 2D islands were converted into 3D islands but they still stick together. At the temperature of 500°C, well separated 3D islands are formed with a dispersed size distribution. The well separated 3D islands in 500°C suggest the turn-on of the inward diffusion. When the temperature climbs up to 630°C, the quite uniform 3D islands with elongated

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shape are observed, as shown in Figure 7.6 (b). The size of the islands is bigger compared to that of 500°C. Detailed discussion on the mechanism of cluster formation is provided in Section 7.6 of this chapter.

7.4 Thermal behavior of Ni overlayer on rutile TiO₂(100) surface

7.4.1 Evolution of the XPS spectra upon annealing

Similar phenomena is also observed on TiO₂(100) surface. XPS spectra in Figure 7.7 show the thermal reaction of Ni on TiO₂(100) upon the thermal treatment. Great difference compared to the Ni on TiO₂(110) is that Ni started to be oxidized at a relative low heating temperature, 500°C, which is 100°C lower than that of Ni/TiO₂(110) system. And at 600°C, Ni is totally oxidized, as shown in Figure 7.7 (a). After sample is cooled down to room temperature, very weak metallic Ni peak reappears aside the oxidized Ni 2p_{3/2} peak. The valence band shown in Figure 7.7 (b) is consistent with the Ni 2p_{3/2} core line. The relative metallic Ni intensity is much weaker than it is on TiO₂(110) surface. The possible reason is that TiO₂(100) surface has a larger surface energy than TiO₂(110) surface so that less Ni segregated to the TiO₂(100).

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Figure 7.7 XPS spectra of thermal reaction of 3 nm Ni on $\text{TiO}_2(100)$ for (a) Ni $2p_{3/2}$ core-level; and (b) valence band measured at different temperatures. The spectra are collected at normal photoelectron emission.

In order to find out the distribution of the segregated Ni and the oxidized Ni location, ARXPS has been performed on the 600°C annealed sample. The spectra for valence band and O $1s$ are shown in Figure 7.8.

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Figure 7.8 ARXPS spectra of 600°C annealed Ni/TiO₂(100) sample for (a) valence band and (b) O 1s. The measurement is done after the sample is cooled down to room temperature. Black, red and green curves are at take-off angles of 90°, 50° and 20°, respectively.

In valence band spectra, the peaks at BE's of 4.5 eV and 1.15 eV are related to the Ni²⁺ and metallic Ni, respectively. At the take-off angle of 20°, there is a dramatic enhancement of O 1s high BE shoulder (see Figure 7.8 (b)) as well as the Ni²⁺ and metallic Ni states in valence band (see Figure 7.8 (a)). However, only weak difference is noticed for the take-off angles of 90° and 50°. According to these facts, we draw the conclusion that the segregated Ni and oxidized Ni are all located at the very top surface. By considering the inelastic mean free path of about 1 nm [108], the probing thickness is about 2 nm and 1 nm at take-off angles of 50° and 20°, respectively. Thus, the segregated Ni and oxidized Ni are concentrated in the top 1 nm surface layer.

7.4.2 Evolution of the surface morphology upon annealing

Figure 7.9 (a) shows 3 nm Ni grown on TiO₂(100) and annealed up to 300°C. Similar to that on TiO₂(110) surface, the surface is fairly smooth. When the

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sample was annealed at 400°C, both 2D and 3D islands are observed. The 3D islands are relatively smaller, around 20-30 nm in diameter, compared to those on TiO₂(110) surface at same temperature (around 80 nm). The 2D islands are found distributed along the distribution of non-uniform 3D islands, which wrap around the latter. Surprisingly, the sample annealed at 600°C displays many holes and rows at surface, as presented in Figure 7.9 (b). The 3D plot of this sample shows that the islands at the surface are in rectangle shape with longer edge along the [001] direction. The typical size of the island is 30 nm × 100 nm. The holes are formed during the segregation of Ni because the Ni islands are found mostly located next to the holes. The anisotropy of the island may be related to the difference in diffusion barrier, thus diffusion rate, along different crystal orientation. The detailed reason will be discussed in section 7.6.

Figure 7.9 AFM images of Ni on TiO₂(100) surface after annealing at (a) 300°C and (b) 600°C. Images are 1 μm × 1 μm in size.

7.5 Thermal behavior of Ni overlayer on rutile TiO₂(001) surface

Figure 7.10 shows normalized intensity spectra of Ni 2p_{3/2} and valence band of 3 nm Ni on TiO₂(001) surface. Distinctly, the thermal reaction of Ni on TiO₂(001) shown in the XPS spectra is different from both the TiO₂(110) and (100) surfaces. Figure 7.10 (a) is Ni 2p_{3/2} spectra of Ni overlayer on TiO₂(001). No

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oxidized peak is observed during the annealing process from room temperature to 490°C, at which temperature, no Ni $2p_{3/2}$ signal can be detected implying no Ni atoms (at least below the detection limit of XPS) present at the top layer of TiO₂(001) surface within about 4 nm. But when the sample is cooled down to room temperature, strong metallic Ni $2p_{3/2}$ peak reappears (see Figure 7.10 (a)).

Figure 7.10 XPS spectra of thermal reaction of 3 nm Ni on TiO₂(001) for (a) Ni $2p_{3/2}$ core-level; and (b) valence band measured at different temperatures. The spectra are collected at normal photoelectron emission. The dashed lines are drawn to guide the eyes.

Valence bands in Figure 7.10 (b) of the sample cooled down to room temperature confirm that nickel is in metallic state instead of oxidized or other state. The normalized intensity is several times higher than it is on TiO₂(110) and (100) surfaces, indicating that Ni segregates the heaviest on TiO₂(001) surface. This implies that Ni diffuses along [001] is much easier than that along [110] and [100] directions. AFM images, shown in Figure 7.11 indicates no 3D islands

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observed for Ni on $\text{TiO}_2(001)$ surface upon annealing. The flatness can be reflected by the small RMS, which are 0.13, 0.10 and 0.12 for 300°C, 400°C, and 490°C annealed samples, respectively.

Figure 7.11 AFM images of Ni on $\text{TiO}_2(001)$ surface after annealing to (a) 300°C and (b) 490°C. Images are $1\ \mu\text{m} \times 1\ \mu\text{m}$ in size.

7.6 Rationalizing the observations on different surfaces

Finally, let us rationalize our observations. As suggested different by above experimental observations, the diffusion rates along [001], [110] and [100] orientations are the major task to determine. For (001) surface, the inward diffusion is much easier so that no Ni atoms can be detected after annealing at 490°C. The flatness of the sample annealed at 490°C, as shown in Figure 7.11 (c), indicates that the inward diffusion must be much heavier than the in-plane diffusion. Thus the diffusion rate along the [001] orientation is the largest. This also helps to explain the rectangle row structures at 600°C annealed sample on (100) surface (see Figures 7.9 (c) and (d)). The longer edge formed along [001] is due to the fast diffusion rate at that direction. The in plane direction perpendicular to the [001] is [010]. Based on the size of the rectangle, the diffusion rate along [010], which is the same as [100] due to symmetry, is only 0.3 times that of [001].

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The anisotropic Ni islands shape observed in AFM results for the 630°C annealed sample on (110) surface helps us to determine the diffusion rates along [001] and [1-10] (identical to [110] by symmetry), see Figure 7.6 (d). From the shape of the Ni islands, the diffusion rate along [110] is about 0.7 times that of [001]. This qualitatively agrees with the density-functional theory (DFT) calculation results in Ref. [6] for the diffusion barriers along [001] and [1-10] directions.

In transition state theory, the diffusion time of an atom is given by

$$t = \nu_0^{-1} \exp\left(\frac{\Delta E_b}{k_B T}\right) \quad (7.1)$$

where ν_0 is called the attempt frequency, ΔE_b is the activation barrier, k_B is the Boltzmann constant, and T is the temperature. In order to estimate the activation barrier, the typical value of 10^{13} s^{-1} for the attempt frequency is used. For Ni on $\text{TiO}_2(001)$ at 490°C, the Ni would diffuse into the substrate on the order of 1 min. Thus ΔE_b is estimated to be 2.25 eV. With this value, the inward diffusion of Ni on $\text{TiO}_2(001)$ would take $3.85 \times 10^{24} \text{ s}$ at room temperature, so that its occurrence is prohibited. Therefore no oxidation is observed experimentally.

The diffusion barrier of Ni into $\text{TiO}_2(110)$ and $\text{TiO}_2(100)$ would be higher than 2.25 eV. Within the assumption that the attempt frequencies equal at all directions, the diffusion barrier along [110] and [100] are established to be 2.27 eV and 2.33 eV, respectively, at 490°C. From here, we see that a slight difference in diffusion barrier may introduce dramatic reaction at the interface upon annealing.

Figure 7.12 show the ball and stick drawing of the $\text{TiO}_2(110)$, $\text{TiO}_2(100)$ and $\text{TiO}_2(001)$ surfaces. The arrows inside the Figure 7.12 indicate the easiest diffusion direction, which is aided by the bridging oxygen atoms running along

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[001] direction. This prediction is consistent with the DFT calculation results in Ref. [6]. On $\text{TiO}_2(110)$ and $\text{TiO}_2(100)$ surfaces, the bridging oxygen atoms are exposed outside, where the Ni atoms preferentially land on. The bonding between them aligns the Ni islands elongated at that direction. On $\text{TiO}_2(001)$ surface, the surface is non-polar, and those “bridging” oxygen atoms are running into the surface. The assistance of those “bridging” oxygen thus leads to the disappearance of Ni atoms on $\text{TiO}_2(001)$ surface detected at elevated temperature. It also explains the flatness of the segregated Ni deposits observed by AFM because the diffusion is perpendicular to the surface.

Figure 7.12 Ball and stick drawing of side view of $\text{TiO}_2(110)$ (a) and $\text{TiO}_2(100)$ (b) and the top view of $\text{TiO}_2(001)$ (c) surfaces. Grey and red balls are Ti and O atoms, respectively. The black arrows indicate the easier diffusion direction. The pictures are slightly tilted to show the channel clearly.

The easiest inward diffusion of Ni on $\text{TiO}_2(001)$ surface may be also related to its small surface atom density, which is only $0.14 \text{ atoms}/\text{\AA}^2$, compared to 0.31

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atoms/ $\text{\AA}^2$ and 0.22 atoms/ $\text{\AA}^2$ for (110) and (100) surfaces, respectively. This can be easily seen from the Figure 7.13. A very open channel is structured on $\text{TiO}_2(001)$ surface, which promotes the inward diffusion.

Figure 7.13 Top view of $\text{TiO}_2(110)$ (a), $\text{TiO}_2(100)$ (b) and $\text{TiO}_2(001)$ (c) surfaces. Grey and red balls are Ti and O atoms, respectively.

The interfacial reaction is correlated to some more factors such as surface energy, interfacial charge transfer, formation of interface dipole and Schottky barrier height, etc., the details of which is beyond the scope of this thesis. Interested readers are referred to Ref. [7] and references therein.

7.7 Summary

In summary, we have studied the growth of Ni on TiO_2 by means of PES. By knowing the origin of the O 2p bonding and non-bond peak, we are able to distinguish the growth mode and landing position of Ni deposits. The Ni is landed on top of surface O, which transfers electron to latter. The behavior that the non-

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bonding peaks intensity keeps decreasing when the Ni coverage is larger than 1 ML suggests a cluster growth mode of Ni on TiO₂.

The interaction of nano-clustered Ni overlayer with TiO₂ substrate was also studied by XPS and AFM. Different interaction behavior with regard to the surface orientation is observed. No matter on which surface, Ni segregates to the top surface region when the sample is cooled down to room temperature due to the reduction of their surface energy [162]. At high temperature, the Ni atoms diffused into TiO₂ lattice to form Ni²⁺-like species, which are not readily to build steady NiO lattice. The inward diffusion can be impelled by thermal energy at high temperature and balanced by segregation to reach equilibrium. The oxidation process is much stronger at the substitution site than the adsorption sites [199]. Ni is comparatively easy to react with oxygen on TiO₂(100) surface, while the fast inward diffusion on TiO₂(001) make this difficult to detect. Based on the study on different TiO₂ surfaces, diffusion rate of Ni on TiO₂ surface along [001], [110] and [100] orientations has been predicted. By using the transition state theory, the diffusion barriers are estimated to be 2.25 eV, 2.27 eV and 2.33 eV along [001], [110] and [100], respectively. The diffusion is aided by the bridging oxygen atoms running along [001] direction. The variation in diffusion rate settles the understanding of Ni thin films morphology observed on several TiO₂ surfaces.

CHAPTER EIGHT

SUMMARY AND FUTURE WORK

8.1 Summary

The BE shifts of Ni $2p_{3/2}$ as a function of Ni coverage deposited on TiO₂ surfaces have been investigated. Auger parameter analysis is applied to separate the contribution of the initial and final state effects to the binding energy shift observed. From the comparison of results for TiO₂(001) and TiO₂(110), we have demonstrated the importance of substrate contribution to the initial state effect and further assigned the initial state effect to a combination of eigenvalue shift in SCLS and charge transfer between the Ni clusters and the TiO₂ substrates. The stoichiometry of the substrate is also found affect the overlayer BE shift. The cluster size effect and interfacial charge transfer have a collective impact on the electronic structure of Ni clusters on the TiO₂ surfaces. The present study shows that the charge state of Ni depends on the initial conditions of the TiO₂ surface on which the Ni atoms are dispersed.

Besides the BE shift, correlation enhancement of electrons in Ni nano-clusters due to the confinement in reduced dimension has been observed. Both the size and shape of nano-clusters have strong influence on the Ni $2p$ satellite

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structures. For small Ni clusters, apart from the 6-eV satellite, a 3-eV satellite structure emerges in Ni $2p_{3/2}$ photoemission spectra due to the existence of 3E and 3T triplet states. However, the intensity of the 3-eV-satellite decreases with increasing cluster size because the Ni $3d$ level is getting increasingly occupied in large size clusters. The increased electron population in $3d$ level is achieved through the electron transfer from the free-electron-like $4sp$ states to the unhybridized pure $3d$ spin down states, the latter is lower in energy than that of the $3d$ - $4sp$ hybridized states. The correlation-induced 6-eV satellite energy is enhanced by Ar^+ bombardment. These observations provide feasibility to gauge Ni $3d$ electron population by probing the $2p$ photoemission spectra and to modify the supported Ni nano-clusters through thermal treatment and/or ion bombardment.

On the other hand, when ultrathin Ni film is prepared on Cu(001) surfaces, the reduced main peak BE of Ni is found. The reason has been attributed to the Cu $4s$ /Ni $3d$ interfacial hybridization effect and the narrowing of the d band with the reduction of dimensions. The opposite BE shift in 6 eV satellite BE results from the combination of interface hybridization and expansion of an extended $4s$ -like state towards the vacuum. Through comparison of Ni films grown on flat versus nano-structured Cu(001) surfaces, the mixing of Cu and Ni atoms is found to be enhanced at the terrace edge region and consequently a larger s/d IHE is predicted for Ni on the nano-structured surface.

The interaction of nano-clustered Ni overlayer with TiO_2 substrate was also studied by XPS and AFM at elevated temperature. Different interaction behavior with regard to the surface orientation is observed. No matter on which surface, Ni segregates to the top surface region when the sample is cooled down to room temperature due to the reduction of their surface energy. At high temperature, the

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Ni atoms diffuse into TiO_2 lattice to form Ni^{2+} -like species, which are not readily to build steady NiO lattice. The inward diffusion can be driven by thermal energy at high temperature and balanced by segregation to reach equilibrium. Ni is comparatively easy to react with oxygen on $\text{TiO}_2(100)$ surface, while the fastest inward diffusion on $\text{TiO}_2(001)$ make this difficult to detect. By comparison of different TiO_2 surfaces, diffusion rates of Ni on TiO_2 surface along [001], [110] and [100] orientations have been predicted. By using the transition state theory, the diffusion barriers are estimated to be 2.25 eV, 2.27 eV and 2.33 eV along [001], [110] and [100], respectively. The diffusion is aided by the bridging oxygen atoms running along [001] direction. The variation in diffusion rate settles the understanding of Ni thin films morphology observed on several TiO_2 surfaces.

8.2 Future work

As for the BE shift of supported metal nano-structure, substrate stoichiometry is found to show some effect on it. Charge transfer is found present and the direction depends on the surface stoichiometry. It is thus interesting to prepare a surface where no charge transfer exists. On such a surface, the initial state effect would be purely from the SCLS. By successfully doing this, we are able to tell the exact value for the initial eigenvalue for the SCLS ($\Delta\epsilon_{\text{SCLS}}$), which has never been measured before.

Besides the surface stoichiometry, the dielectric constant is expected to show some effect on the BE shift observed, because the final state effect is related to the screening effect whose strength is correlated to the dielectric constant of the material. We will vary the material of the substrate to facilitate this task. Those materials should have quite different dielectric constant value. The potential ones are ZnO ($\kappa \sim 1.7\text{-}3.5$), SiO_2 ($\kappa \sim 3.9$), MgO ($\kappa \sim 9.7$), HfO_2 ($\kappa \sim 25$), TiO_2 ($\kappa \sim 110$),

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and SrTiO_3 ($\kappa \sim 475$) etc. The difference in dielectric constant will shed different light on electron screening effect. This will greatly improve our understanding in describing the final-state effect in the BE shift.

During the study of the thermal behaviors of metal film on the TiO_2 substrate, the diffusion rate is found different along different channel (orientation). The underlying physics of this phenomenon is to be answered by some careful designed experimental work as well as using first-principles calculations. Our predicted diffusion barrier should be validated or corrected by first-principles calculations. TEM is helpful in studying the inward diffusion of the Ni. It helps to identify whether the diffused species are interstitial or substantial defect and whether they are clusters or separated atoms. In future, we will perform some TEM measurement for the annealed sample to answer above questions.

On the basis of photoemission results, we found the Ni mixed with the Cu(001) at interfacial region. Considering that the interfacial alloying involves atoms movement, STM would be a benefit to consolidate the photoemission results. The question that how the interfacial mixing modifies the electronic structure as observed in our UPS studies will be further detail studied with the help of STM.

The Ni film grown on Cu(001) surface provides quantum well structure. The quantum confinement is expected to show some effect on the electronic structure of Ni film. During the previous study, we have found that the core hole lifetime of the Ni $2p_{3/2}$ is oscillating as a function of Ni thickness (not presented in this thesis). This may be related to the quantum confinement in the quantum well structure. The detail physics is interesting and will be studied in our future work.

Author's publications from this thesis:

- 1) **J. G. Tao**, L. X. Guan, J. S. Pan, C. H. A. Huan, L. Wang, J. L. Kuo, Z. Zhang, J. W. Chai and S. J. Wang “Density functional study on ferromagnetism in nitrogen-doped anatase TiO₂” *Appl. Phys. Lett.*, 95, 062505 (2009)
- 2) L. X. Guan, **J. G. Tao**, C. H. A. Huan, L. Wang, J. L. Kuo, “First-principles study on ferromagnetism in nitrogen-doped In₂O₃” *Appl. Phys. Lett.* 95, 012509 (2009).
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7) J. S. Pan, **J. G. Tao**, A. C. H. Huan, Z. Zhang, J. W. Chai, S. J. Wang, "Binding energy shift in photoemission spectroscopy study of Ni clusters deposited on rutile TiO₂ surfaces." *Appl. Surf. Sci. accepted*.

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1) H. W. Ho, B. C. Zhao, B. Xia, S. L. Huang, **J. G. Tao**, A. C. H. Huan, L. Wang, "Magnetic and magnetotransport properties in Cu and Fe co-doped bulk In₂O₃ and ITO", *J. Phys.: Condens. Matter* 20, 475204 (2008).

2) G. Z. Xing, J. B. Yi, **J. G. Tao**, T. Liu, L. M. Wong, Z. Zhang, G. P. Li, S. J. Wang, J. Ding, T. C. Sum, A. C. H. Huan, T. Wu, "Comparative study of room-temperature ferromagnetism in Cu-doped ZnO nanowires enhanced by structural inhomogeneity", *Adv. Mater.* 20, 3521 (2008).

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