



Structural and chemisorption properties of metallic surfaces and metallic overlayers
by Mingde Xu

A thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in
Physics

Montana State University

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Abstract:

For many years the study of the modification of surface structure has been an amazing topic that interests surface scientists. In order to extend the understanding of modified metallic surfaces in the field of electronic and atomic structure of adsorbate covered surfaces, two bimetallic systems (Pd on Al(110) and Ni on W(110)) and the hydrogen interaction with two clean metal surfaces (Nb(110) and W(110)) have been studied using various surface analytical techniques. The results for the Pd/Al system show that the Pd film grows on Al(110) in a layer-by-layer mode. The binding energies of the Pd 4d electrons for a very thin Pd film are very similar to that for an atomic-like state. The film behaves as a free and unsupported overlayer. The Pd 4d states begin to evolve into a bulk-like electronic structure at a coverage of 2.5 ML. No evidence of CO chemisorption on the Pd films of less than 2.5 ML coverage is observed, while thicker film readily chemisorb CO. In the study of Ni on W(110), it is observed that the initial growth of Ni occurs in a double-layer mode, which is very different from results reported by others. The Ni film grows in a coincidence structure with the W(110) substrate. It turns into the structure of bulk Ni at a coverage of 7.7 ML. No noticeable modification of W(110) substrate structure is observed.

Hydrogen adsorption on both Nb(110) and W(110) surfaces results in structural changes on both surfaces. For the Nb(110) surface, exposure to hydrogen induces two stages of change, an initial abrupt change due to chemisorption at the surface, and then a gradual change due to the absorption of hydrogen into the bulk. A structural model which explains these changes is consistent with the proposed surface-hydride formation model. For the W(110) surface, the structural change ends at a H₂ exposure of 400 L. The change can be attributed to either enhancement of the vibration amplitude of W surface atoms or a lateral shift of W surface atoms parallel to the surface with equal domains of W atoms shifted to the left and to the right. Prior to the studies of hydrogen interaction with these two surfaces, studies of the clean surfaces were carried out. The results are also reported in this thesis.

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To Lihui Lao
and my parents

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ABSTRACT

For many years the study of the modification of surface structure has been an amazing topic that interests surface scientists. In order to extend the understanding of modified metallic surfaces in the field of electronic and atomic structure of adsorbate covered surfaces, two bimetallic systems (Pd on Al(110) and Ni on W(110)) and the hydrogen interaction with two clean metal surfaces (Nb(110) and W(110)) have been studied using various surface analytical techniques. The results for the Pd/Al system show that the Pd film grows on Al(110) in a layer-by-layer mode. The binding energies of the Pd 4d electrons for a very thin Pd film are very similar to that for an atomic-like state. The film behaves as a free and unsupported overlayer. The Pd 4d states begin to evolve into a bulk-like electronic structure at a coverage of 2.5 ML. No evidence of CO chemisorption on the Pd films of less than 2.5 ML coverage is observed, while thicker film readily chemisorb CO. In the study of Ni on W(110), it is observed that the initial growth of Ni occurs in a double-layer mode, which is very different from results reported by others. The Ni film grows in a coincidence structure with the W(110) substrate. It turns into the structure of bulk Ni at a coverage of 7.7 ML. No noticeable modification of W(110) substrate structure is observed.

Hydrogen adsorption on both Nb(110) and W(110) surfaces results in structural changes on both surfaces. For the Nb(110) surface, exposure to hydrogen induces two stages of change, an initial abrupt change due to chemisorption at the surface, and then a gradual change due to the absorption of hydrogen into the bulk. A structural model which explains these changes is consistent with the proposed surface-hydride formation model. For the W(110) surface, the structural change ends at a H₂ exposure of 400 L. The change can be attributed to either enhancement of the vibration amplitude of W surface atoms or a lateral shift of W surface atoms parallel to the surface with equal domains of W atoms shifted to the left and to the right. Prior to the studies of hydrogen interaction with these two surfaces, studies of the clean surfaces were carried out. The results are also reported in this thesis.

CHAPTER 1

INTRODUCTION

What is the structure of metal surfaces? What is the new structure after some modifications on the surfaces? For the past decade studies of the modification and chemical properties of metallic surfaces have gained increasing interest for surface scientists. It is well known that the physical and chemical properties of metallic thin films differ considerably from those of the bulk material itself¹⁻³. For example, the uptake rate of hydrogen on Nb and Ta surfaces can be significantly enhanced by the deposition of a thin Pd film on the surfaces³⁻⁵. A monolayer thick Pd film on Au¹, Ta³ or Nb⁴ does not chemisorb CO while thicker Pd films do. A film of fcc iron grown on copper surfaces may be either ferromagnetic or antiferromagnetic depending on the crystallographic surface on which the growth occurs.⁶⁻⁸

The studies of bimetallic systems include the study of metallic film epitaxy, the morphology of the overlayer, the adsorption site, the electronic properties and the chemical properties of the system and the diffusion behavior of the films. Over the course of the past two decades, studies of hundreds of bimetallic systems have been made. A partial list of the systems studied can be found in the review article by Argile and Rhead.⁹ In these studies various routinely used surface analytical techniques have been extensively applied, such as Auger electron spectroscopy

(AES), Low energy electron diffraction (LEED) and Reflected high energy electron diffraction (RHEED), Transmitted electron microscopy (TEM), Secondary electron microscopy (SEM), X-ray photoemission spectroscopy (XPS), Ultra-violet photoemission spectroscopy (UPS), Electron energy loss (ELS), Thermal desorption spectroscopy (TDS), work function change ($\Delta\phi$), Ion scattering spectroscopy (ISS) and others.

The morphological properties of film growth are mostly studied using Auger electron spectroscopy and X-ray photoemission spectroscopy. In the case of vapor-deposited thin films a classification of three basic growth modes has been proposed by Bauer.^{10,11} They are named after their original investigators: Frank and van der Merwe¹² (FM mode, layer-by-layer growth), Stranski and Krastanov¹³ (SK mode, layer growth up to one or a few monolayers followed by island growth) and Volmer and Weber¹⁴ (VW mode, island growth). Apart from these basic growth patterns, in some systems, alloying and surface compound formation are observed.^{15,16} This is caused by the reaction of substrate and adsorbate atoms in the surface layer and the dissolution of the adsorbate into the substrate. It is also reported that there exists evidence for two metastable growth modes, the "simultaneous multilayer" growth (SM) and "monolayer plus simultaneous multilayer" growth (MSM).^{9,17}

The geometric structure of the overlayer is usually studied by LEED and other techniques. The evolution of the structure of the adsorbate is traced with increasing deposition. It is found that in some systems, such as Pd on Nb¹⁸, the film experiences a phase transition, going from commensurate to incommensurate.

Information concerning the electronic properties of the adsorbate-substrate complex is primarily derived from $\Delta\phi$, ELS, UPS and XPS measurements of the

adsorbate-substrate system as a function of adsorbate coverage. The electronic structure of the overlayer system always plays an important role in the chemical properties of the system and governs the geometric structure of the adsorbate and substrate.

Besides the study of metals adsorbed on metals, studies of the electronic and atomic structure of clean metal surfaces and studies of the chemisorption properties on metal surfaces also attract a lot of attention. Numerous theoretical calculations^{19,20} and experiments^{21,22} have been done to investigate the electronic properties and the band structure of clean metals. The interest in transition metals is based on the magnetic properties, such as the magnetic ordering in non-equilibrium geometry. For example, it has been conclusively demonstrated that films of fcc iron are ferromagnetic if the lattice constant is large enough²⁰. Of particular importance is the atomic structure of the surface. It is observed that the termination of a metal crystal by a surface significantly alters the neighbor coordination of surface atoms relative to that of bulk atoms. The changes in coordination cause the surface-region conduction-electron distribution to be different from that of the bulk, and this difference can lead to further modification of the surface's crystallography.²³⁻²⁵ The two basic kinds of surface structure change are reconstruction -- surface atoms are displaced relative to the bulk terminated positions parallel to the surface plane, and relaxation -- atoms relax inward or outward perpendicular to the surface plane. For example, a multilayer relaxation is found to exist for some clean metal surfaces in both theoretical and experimental investigations.^{24,25}

In the field of heterogeneous catalysis a great deal of work has been done to study the gas-metal interaction.²⁶ For example, in relation to the synthesis of ammonia and of hydrocarbons, studies of the chemisorption and decomposition of

ammonia on metal surfaces and of hydrocarbon adsorption on metal surfaces were undertaken. By virtue of its single valence electron, hydrogen is considered as the simplest chemically reacting adsorbate. The motivation to investigate hydrogen-surface interaction phenomena also arises from other aspects. In the field of material science and metallurgy, hydrogen is known to be a major factor in embrittlement and fracture phenomena.²⁷ Another aspect is the use of certain alloys or intermetallic compounds to dissolve and store gaseous hydrogen.²⁸

Early studies of the interaction of hydrogen with metals were undertaken primarily to understand the thermodynamics and kinetics of the adsorption process.²⁹ Most of the studies concentrated on measuring heats of adsorption, lateral interaction energies, activation energies for desorption and diffusion, accommodation and sticking probabilities, entropies of adsorption and heats of solution of hydrogen in the bulk. Later, the chemical and physical bonding mechanisms and surface structure modifications with hydrogen adsorption were studied. The hydrogen induced work function change, the hydrogen adsorption site and the two-dimensional phase and phase transitions in physisorbed and chemisorbed hydrogen systems have been actively studied although much more needs to be done. For some metal substrates, such as Ni(110),³⁰⁻³² W(100)^{33,34} and W(110)^{35,36}, the adsorbed hydrogen creates a pronounced substrate reconstruction at some critical coverage of hydrogen. It is then of great interest to explain the nature of the microscopic interaction responsible for these transitions.

In the work of this thesis, a few interesting systems of metal on metal and hydrogen interaction with metal surfaces have been investigated. In chapter 2 a few surface analysis techniques used in this work are briefly reviewed and the experimental setups are discussed. In chapter 3, AES and UPS studies of the growth, electronic structure and chemisorption properties of thin Pd films on

Al(110) are described. Al(110) was chosen because of the interest in adsorbates on simple metal substrates. The overlayer system of Ni on W(110) was studied because of the interest in the magnetic properties of thin Ni films. The results are presented in chapter 6. The interaction of hydrogen with two transition metal surfaces (Nb and W) was studied using high energy ion scattering and channeling techniques in order to characterize the H-induced surface structure changes. The results are presented in chapters 4 and 5.

For convenience, some of the acronyms frequently mentioned in this thesis are listed below.

AES - Auger electron spectroscopy

CMA - Cylindrical mirror analyzer

FM - Frank-van der Merwe

HEIS - High energy ion scattering and channeling

HMA - Hemispherical mirror analyzer

HREELS - High resolution electron energy loss spectroscopy

LEED - Low energy electron diffraction

ML - Monolayer

MSM - Monolayer plus simultaneous multilayer

PES - Photoelectron spectroscopy

RBS - Rutherford backscattering spectroscopy

RGA - Residual gas analyzer

ROI - Region of interest

SBD - Surface barrier detector

SE - Surface enhancement

SP - Surface peak

SK - Stranski-Krastanov

SM - Simultaneous multilayer

UHV - Ultra-high vacuum

UPS - Ultra-violet photoelectron spectroscopy

UV - Ultra-violet

VW - Volmer-Weber

XPS - X-ray photoelectron spectroscopy

CHAPTER 2

EXPERIMENTAL METHOD

Introduction

In the process of studying the electronic and atomic structure and chemical properties of solid surfaces and interfaces, it is important to understand the experimental facilities, the various analytical techniques, and the procedure for obtaining a clean surface. In this chapter, the surface analysis techniques, the ultra high vacuum(UHV) chambers and the instrumentation used in this thesis work are described, followed by a brief discussion of sample preparation.

Analysis Techniques

Since a full description on various surface analytical techniques can be found in quite a number of publications³⁷ only brief explanations of a few techniques used in this work (AES, UPS, XPS, LEED and HEIS) are discussed here.

Auger Electron Spectroscopy

Early studies of the energy distribution of secondary electrons emitted from a solid sample irradiated with slow electrons showed some small characteristic

peaks which were ultimately attributed to Auger electrons. Since 1967, the use of Auger electron spectroscopy has become a fundamental tool for surface analysis. One of the most important steps in the experimental development was the introduction of a cylindrical mirror analyzer (CMA) to detect Auger electrons. With the use of the CMA, the sensitivity, energy resolution and signal to noise ratio were improved so that detection of surface impurities with concentrations as low as 0.001 monolayer became possible.

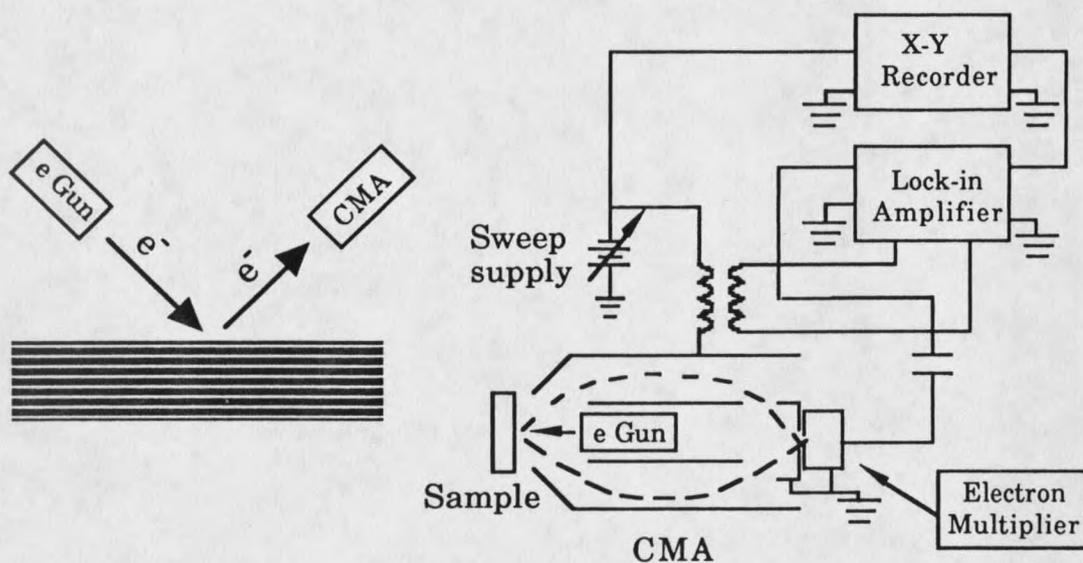


Fig. 1. Schematic of Auger electron spectroscopy with the use of CMA.

In principle any type of radiation which is able to ionize the inner shells of atoms can be used to induce Auger electron emission, but the most common and convenient source used at present is an electron beam. Fig. 1 shows schematically the Auger spectrometer with the arrangement of the CMA analyzer. In general the number of emitted Auger electrons, N , is measured as a function of electron kinetic energy, E . A further development is to use a differentiation technique to enhance the Auger signals relative to the background. The differentiation is done

by the use of a lock-in amplifier with a modulation voltage applied to the analyzer. Shown in Fig. 2 are the AES spectra for a clean Al surface and for a thin Pd film on clean Al. The Auger electrons are analyzed using the CMA with a pass energy of 25 eV and are collected by the electron multiplier. The signals are recorded on the X-Y recorder as a function of electron kinetic energy. The spectra show the characteristic peak for Al at an energy of 68 eV (LVV) and Pd near 330 eV (MNN). There is no sign of a peak for O Auger electrons which would be located at an energy of 503 eV if sufficient O were present.

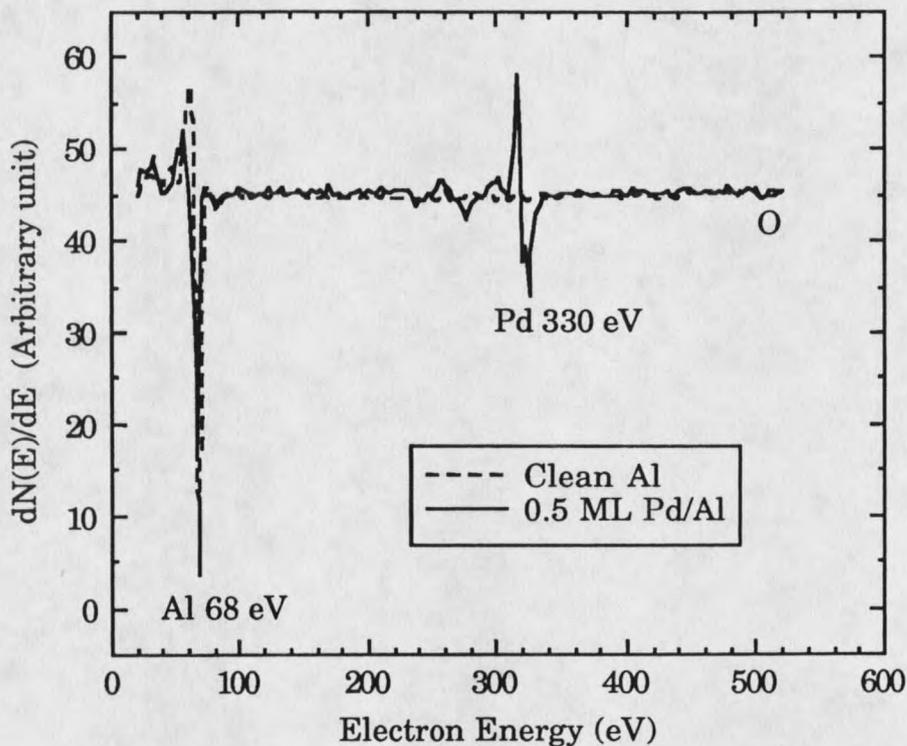


Fig. 2. AES spectra for clean Al(110) and 0.5 ML Pd/Al(110) (1ML=1.43Å).

The incident radiation ionizes the atom by exciting one of the core level (inner shell) electrons. The core hole is then filled by an outer electron, which releases energy that makes it possible to excite a second electron in the outer shell. This excited electron is called an Auger electron. Because of the discrete nature of the energy levels of the atom this Auger electron leaves the atom with a characteristic kinetic energy. For the XYZ Auger transition a hole is first excited in the X shell, and is then filled by a transition from a higher level, the Y shell. The energy gained from this transition is transferred to the electron emitted from a state in the Z shell. The energy of the emitted Auger electron is given by $E_{XYZ} = E_X - E_Y - E_Z - U_{\text{eff}}$, where E_X , E_Y and E_Z are the relevant core binding energies, and U_{eff} reflects the fact that extra energy is required to remove the electron from state Z in the presence of a hole in Y. As an example a KLL Auger electron is emitted from the L shell following a transition of another L shell electron to the K shell. Since every element has its own characteristic set of energy levels the excited Auger electron for that element possesses a characteristic kinetic energy. Owing to the extensive Auger studies for various elements, the energies of Auger electrons for different types of Auger transitions for the various elements can be readily found in the handbook of AES.³⁸ It is then possible to characterize the elements in one sample by checking the kinetic energy of the various Auger electron peaks. By measuring the intensities of the Auger electron peaks a quantitative analysis can be used to infer the concentration of each element in that sample. In the case of thin film studies, by measuring the intensities of the adsorbate and substrate Auger electron emission it is possible to determine the film thickness and to characterize the film growth morphology, as described later in this chapter.

X-ray Photoemission Spectroscopy

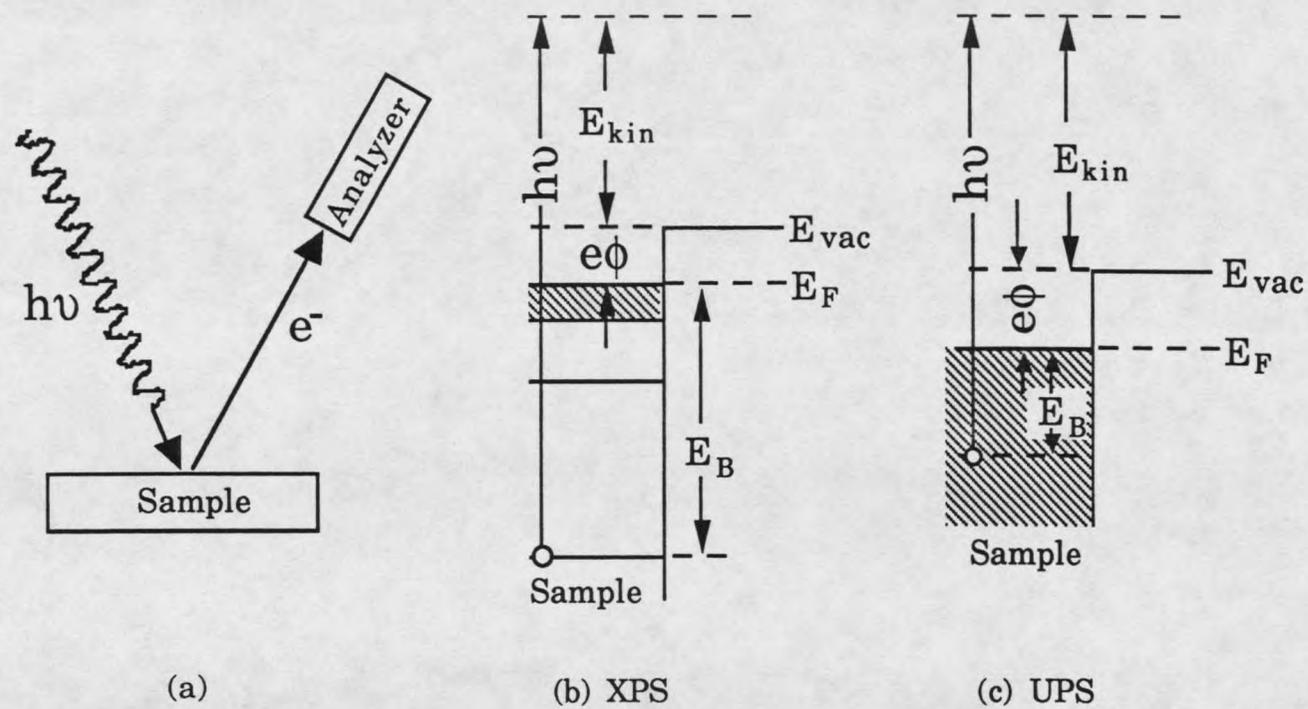
XPS, also called ESCA (electron spectroscopy for chemical analysis), makes it possible to determine the electronic binding energies in atoms and to deal in detail with various applications in surface analysis. The basic elements for X-ray photoemission spectroscopy include a light source (radiation of Al K_{α} (1486.6 eV) or Mg K_{α} (1253.6 eV) in our lab), an electron energy analyzer and a detecting system as illustrated in Fig. 3(a).

In XPS the number of X-ray excited photoelectrons is measured as a function of the kinetic energy, E_{kin} , of the photoelectron, or the binding energy, E_{B} . The relationship of E_{kin} and E_{B} is given by

$$E_{\text{kin}} = h\nu - E_{\text{B}} - e\phi \quad (1)$$

where $h\nu$ is the incident photon energy and ϕ is the work function of the solid. A typical spectrum for a Ni film on W(110) is shown in Fig. 4.

Because the electrons in each element have characteristic core-level binding energies,³⁹ it is straightforward to identify the elements in a sample by determining the binding energies of the various core-level photoelectron peaks in the spectrum. With a quantitative analysis one is also able to determine the concentration of each element in a sample by measuring the intensities of the characteristic photoelectron peaks, as in the procedure used in AES. Another useful quantitative technique in XPS is to determine the core-level chemical shift. The core-level electron binding energies for a certain element are subject to variation (typically by a few eV) depending on the chemical state, such as oxidation, etc. Measurements of the chemical shift can provide valuable information for studying the chemistry of molecules, solids and surfaces.



$$E_{kin} = h\nu - E_B - e\phi$$

Fig. 3. Schematic of photoemission spectroscopy (PES).

