Chapter 1

Introduction

1.1 Motivation

With the drive of the modern world towards smaller, more efficient materials for electronic devices and industrial processes, the surfaces of such materials become ever more important. The surface science industry of the early 21^{st} century consists of a vast array of techniques which can provide a complete understanding of the surface chemical, electrical and structural properties. With such a wide range of techniques, information to be gathered and materials to be studied, surface science is poised to potentially become one of the most important fields in modern science.

Cleaving a material in air often leads to a suitable surface, but such a surface survives for only a fraction of a second before atmospheric contaminants are adsorbed on to it. This has the potential to drastically change the atomic structure, chemical composition and electronic properties of the surface. To better understand the characteristics of surfaces, the majority of surface science experiments are carried out in ultra-high vacuum (UHV). Since the 1960s, UHV equipment has been developed which enables the preparation of clean, well-ordered surfaces at pressures of 10^{-9} mbar or less. Pressures in this region provide an environment where the surface will remain free from contamination for a period of several hours, suitable for carrying out experiments using typical surface science techniques. Many of the techniques themselves require UHV conditions, otherwise the probing particles (e.g. ions, electrons) would interact with residual gas atoms and molecules, rendering the experimental information useless.

Understanding the characteristics of the adsorption of oxygen on to metallic surfaces is of key importance in processes such as the oxidation of NH_3 to produce nitric acid and the various reactions which take place inside vehicle exhaust systems. Metal oxide films have also been identified for application in items such as gas sensors and microelectronic devices. It has also been established that the oxidation of metals changes the chemical nature and atomic structure of the surface and near-surface region, therefore producing a surface with interesting structural and chemical characteristics. However, in the oxidation of many metallic surfaces, the maximum oxygen coverage which can be achieved and the structural properties of the surface region of the metal oxide remain unknown. In this thesis, three modern surface science techniques (coaxial impact collision ion scattering spectroscopy (CAICISS), low energy electron diffraction (LEED) and X-ray photoelectron spectroscopy (XPS)) have been used to study the oxidation of the Pt(111) and Ni(110) surfaces in order to deduce the characteristics of the oxidation of these surfaces.

The adsorption of one metallic species on to a substrate of a second metal can lead to either the growth of a thin film of the deposited metal, or to the formation of a surface alloy between the adsorbate and the substrate. Both possibilities yield materials which differ both chemically and structurally from bulk single crystals, and may have uses in many areas of industry. The effects of the deposition of Pt on the Cu(100), Ni(110)-(3×1)-O and NiO(110) surfaces are reported in this thesis, with an emphasis on the atomic structure and chemical composition in the surface region, as well as the determination of whether an alloy or a thin Pt film has been formed.

1.2 Modern surface science techniques

Over the years, a vast range of techniques have been developed for studying solid surfaces [1–4]. Presented below is a brief review of some of the most widely used techniques in modern surface science. The main techniques used for the experimental work presented in this thesis, namely CAICISS, LEED and XPS, will be discussed in more depth in chapter 3.

1.2.1 Diffraction techniques

The main techniques in this area involve the diffraction of electrons or photons. Of the electron diffraction techniques, LEED is easily the most commonly used in surface science [1]. LEED provides the opportunity to study the structure and periodicity of the surface. Because of their low energy ($\sim$ 100 eV), the electrons have a short penetration depth when compared to incident X-rays. Therefore only information from the topmost layers is obtained. The principles of LEED will be described further in chapter 3, with the technique used extensively throughout this thesis.

X-rays have a far smaller scattering cross-section, leading to penetration much further into the bulk of the material when compared to incident electron techniques. However, the diffraction of X-rays incident at grazing angles with respect to the surface has been successfully applied to many materials systems by measuring the intensity of the diffracted beams as a function of azimuthal angle in order to determine the surface structure [1].

1.2.2 Electron spectroscopies

Information relating to the chemical and electronic nature of surfaces is often obtained by the stimulated emission of electrons from surfaces. The emitted electrons have a kinetic energy which is characteristic of their binding energy within the material and can therefore be used to give information on the chemical environment of atoms in the surface region. Electron spectroscopies, such as XPS and Auger electron spectroscopy (AES), can be used to determine the coverage of an adsorbed material, to look for changes in binding energies as a result of deposition or adsorption, or to confirm the surface is free from contamination. The surface specificity of these techniques originates from the short mean-free-path of the emitted electrons, with scattered electrons contributing only to the background signal.

Generally in XPS and AES the core levels of the atoms in the surface region are studied. To investigate the nature of the bonding of a chemisorbed atom to the surface, the valence band levels are typically investigated with techniques such as ultraviolet photoelectron spectroscopy (UPS). Here, a lower excitation energy ($\sim$ 1-50 eV) is used to ensure the emission of the less tightly bound valence electrons.

Incident electrons can also be used to investigate the vibrational and electronic properties of the surface by the use of techniques such as high resolution electron energy loss spectroscopy (HREELS). This non-invasive technique can be used to observe vibrational modes due to adsorbates and their particular bonding configuration on the surface, as well as to investigate properties such as charge carrier concentrations and carrier mobility in doped semiconductor materials.

In the work reported in this thesis, XPS has been extensively used to study the chemical environment of atoms in the near-surface region, as well as to determine the amount of Pt deposited on to various metallic and metal oxide surfaces. HREELS has also been used to compliment the XPS and CAICISS data recorded during the study of the cleaning of the InN(0001) surfaces using atomic hydrogen.

1.2.3 Incident ion techniques

Ion scattering techniques offer a combination of structural and compositional information from the near-surface region [1, 3]. One of the main advantages in using charged particles is that they can be easily accelerated to a desired energy, steered and focussed on to the sample surface. The nature of the information obtained from an ion scattering experiment is highly dependent on the energy of the incident ions, which can be divided into three broad regimes - low energy (1-5 keV), medium energy (50-500 keV) and high energy (>1 MeV). The first ion scattering experiments were carried out at high energies and are now classified under the banner of Rutherford backscattering (RBS). However, the depth penetration is large at such energies and the technique often provides poor energy resolution. To improve the surface specificity the energy of the incident ions must be lowered. Medium energy ion scattering (MEIS) is one option, provided the incident beam is aligned along a major crystallographic direction. However, both MEIS and RBS require large, complicated and expensive equipment and hence the popularity of these techniques is somewhat limited.

Low energy ion scattering is truly surface specific (as will be demonstrated in chapter 3). The ions have a very short penetration depth (a few atomic layers), with the scattered particles having a much improved energy resolution with respect to ion scattering experiments at higher energies. Originally developed by Aono, CAICISS is a further development on the low energy ion scattering theme, with the incident and scattered directions being coaxial. The advantages of this geometry will be discussed in chapter 3, with the technique providing the main results from the systems investigated in this thesis.

1.3 Thesis outline

The main content of this thesis is divided into three introductory chapters and three experimental chapters. Several aspects of solid surfaces are discussed in chapter 2, including the differences between the structures of the surface region and the bulk material (relaxations and reconstructions). The chapter also looks at thin film growth and alloy formation mechanisms, as well as the adsorption of gaseous species on to solid surfaces. Chapter 3 introduces the Warwick modular CAICISS system and the other surface science techniques which have been used to generate the data presented in this thesis. The chapter begins with an overview of the experimental setup, before moving on to discuss the theoretical aspects of ion-surface interactions. The chapter concludes with a brief discussion of the principles of LEED and XPS. Chapter 4 presents a discussion of the different approaches to the simulation of low energy ion scattering data in order to obtain a quantitative understanding of the structural and compositional characteristics of the surface region. The principles of the FAN simulation software used to analyse CAICISS data are outlined, in addition to the process required to compare the experimental data to the spectra generated by FAN.

Chapter 5 focusses on the structure of the clean Pt(111) surface and the results of the adsorption of atomic oxygen on the surface. CAICISS, XPS and LEED will be used to investigate the atomic structure and composition of the near-surface region during the oxidation process and following subsequent annealing of the structure once an oxygen saturation coverage has been reached. Chapter 6 commences with the investigation of the structure of the clean Cu(100) surface using CAICISS. Following this, CAICISS, LEED and XPS will be used to investigate the atomic structure and composition of the near-surface region during a series of Pt depositions on the surface, in order to establish whether a thin Pt film or a Cu-Pt surface alloy is formed. Chapter 7 follows a similar theme. However, on this occasion the Pt will be deposited on to Ni(110) surfaces which have been exposed to different amounts of oxygen. Finally, Chapter 8 will summarize the experiments whilst also discussing some outstanding theoretical and experimental issues which should be addressed to enhance the capabilities of CAICISS experiments at Warwick. Included are proposed changes to the experimental setup, a brief discussion of the ion-atom interaction potential with a focus on the cases studied in this thesis, in addition to a brief discussion of the determination of the polarity of wurtzite InN(0001) surfaces using CAICISS and proposed experiments to which the technique is ideally suited.