A3.10 Reactions on surfaces: corrosion, growth, etching and catalysis

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A3.10.1 INTRODUCTION

The impact of surface reactions on society is often overlooked. How many of us pause to appreciate integrated circuitry before checking email? Yet, without growth and etching reactions, the manufacturing of integrated circuits would be quite impractical. Or consider that in 1996, the United States alone consumed 123 billion gallons of gasoline [1]. The production of this gasoline from crude petroleum is accomplished by the petroleum industry using heterogeneous catalytic reactions. Even the control of automobile exhaust emissions, an obvious environmental concern, is achieved via catalytic reactions using ‘three-way catalysts’ that eliminate hydrocarbons, CO and NO\textsubscript{x}. The study of these types of surface reactions and others is an exciting and rapidly changing field. Nevertheless, much remains to be understood at the atomic level regarding the interaction of gases and liquids with solid surfaces.

Surface science has thrived in recent years primarily because of its success at providing answers to fundamental questions. One objective of such studies is to elucidate the basic mechanisms that control surface reactions. For example, a goal could be to determine if CO dissociation occurs prior to oxidation over Pt catalysts. A second objective is then to extrapolate this microscopic view of surface reactions to the corresponding macroscopic phenomena.

How are fundamental aspects of surface reactions studied? The surface science approach uses a simplified system to model the more complicated ‘real-world’ systems. At the heart of this simplified system is the use of well defined surfaces, typically in the form of oriented single crystals. A thorough description of these surfaces should include composition, electronic structure and geometric structure measurements, as well as an evaluation of reactivity towards different adsorbates. Furthermore, the system should be constructed such that it can be made increasingly more complex to more closely mimic macroscopic systems. However, relating surface science results to the corresponding real-world problems often proves to be a stumbling block because of the sheer complexity of these real-world systems.

Essential to modern surface science techniques is the attainment and maintenance of ultrahigh vacuum (UHV), which corresponds to pressures of the order of $10^{-10}$ Torr ($10^{-13}$ atm). At these pressures, the number of collisions between gas phase molecules and a surface are such that a surface can remain relatively contaminant-free for a period of hours. For example, in air at 760 Torr and 298 K the collision frequency is $3 \times 10^{23}$ collisions cm\textsuperscript{-2} s\textsuperscript{-1}. Assuming a typical surface has $10^{15}$ atoms cm\textsuperscript{-2}, then each surface atom undergoes $\sim 10^8$ collisions per second. Clearly, a surface at 760 Torr has little chance of remaining clean. However, by lowering the pressure to $10^{-10}$ Torr, the collision frequency decreases to approximately $10^{10}$ collisions cm\textsuperscript{-2} s\textsuperscript{-1}, corresponding to a collision with a surface atom about every $10^5$ s. Decreasing the pressure is obviously a solution to maintaining a clean sample, which itself is crucial to sustaining well characterized surfaces during the course of an experiment.

Modern UHV chambers are constructed from stainless steel. The principal seals are metal-on-metal, thus the use of greases is avoided. A combination of pumps is normally used, including ion pumps, turbomolecular pumps, cryopumps and mechanical (roughing) pumps. The entire system is generally heatable to $\sim 500$ K. This ‘bakeout’ for a period of
10–20 h increases gas desorption rates from the internal surfaces, ultimately resulting in lower pressure. For further reading on vacuum technology, including vacuum and pump theory, see [2, 3].

The importance of low pressures has already been stressed as a criterion for surface science studies. However, it is also a limitation because real-world phenomena do not occur in a controlled vacuum. Instead, they occur at atmospheric pressures or higher, often at elevated temperatures, and in conditions of humidity or even contamination. Hence, a major thrust in surface science has been to modify existing techniques and equipment to permit detailed surface analysis under conditions that are less than ideal. The scanning tunnelling microscope (STM) is a recent addition to the surface science arsenal and has the capability of providing atomic-scale information at ambient pressures and elevated temperatures. Incredible insight into the nature of surface reactions has been achieved by means of the STM and other in situ techniques.

This chapter will explore surface reactions at the atomic level. A brief discussion of corrosion reactions is followed by a more detailed look at growth and etching reactions. Finally, catalytic reactions will be considered, with a strong emphasis on the surface science approach to catalysis.

A3.10.2 CORROSION

A3.10.2.1 INTRODUCTION

Corrosion is a frequently encountered phenomenon in which a surface undergoes changes associated with exposure to a reactive environment. While materials such as plastics and cement can undergo corrosion, the term corrosion more commonly applies to metal surfaces. Rust is perhaps the most widely recognized form of corrosion, resulting from the surface oxidation of an iron-containing material such as steel. Economically, corrosion is extremely important. It has been estimated that annual costs associated with combating and preventing corrosion are 2–3% of the gross national product for industrialized countries. Equipment damage is a major component of the costs associated with corrosion. There are also costs related to corrosion prevention, such as implementation of anti-corrosive paints or other protective measures. Finally, there are indirect losses, such as plant shutdowns, when equipment or facilities need repair or replacement.

Most metals tend to corrode in an environment of air and/or water, forming metal oxides or hydrated oxides. Whether or not such a reaction is possible is dictated by the thermodynamics of the corrosion reaction. If the reaction has a negative Gibbs free energy of formation, then the reaction is thermodynamically favoured. While thermodynamics determines whether a particular reaction can occur or not, the rate of the corrosion reaction is determined by kinetic factors. A number of variables can affect the corrosion rate, including temperature, pH and passivation, which is the formation of a thin protective film on a metal surface. Passivation can have a tremendous influence on the corrosion rate, often reducing it to a negligible amount.

Since metals have very high conductivities, metal corrosion is usually electrochemical in nature. The term electrochemical is meant to imply the presence of an electrode process, i.e. a reaction in which free electrons participate. For metals, electrochemical corrosion can occur by loss of metal atoms through anodic dissolution, one of the fundamental corrosion reactions. As an example, consider a piece of zinc, hereafter referred to as an electrode, immersed in water. Zinc tends to dissolve in water, setting up a concentration of Zn\(^{2+}\) ions very near the electrode.
The term *anodic dissolution* arises because the area of the surface where zinc is *dissolving* to form $\text{Zn}^{2+}$ is called the *anode*, as it is the source of positive current in the system. Because zinc is oxidized, a concentration of electrons builds up on the electrode surface, giving it a negative charge. This combination of negatively charged surface region with positively charged near-surface region is called an electrochemical double layer. The potential across the layer, called the electrode potential, can be as much as $\pm 1$ V.

In moist environments, water is present either at the metal interface in the form of a thin film (perhaps due to condensation) or as a bulk phase. Figure A3.10.1 schematically illustrates another example of anodic dissolution where a droplet of slightly acidic water (for instance, due to $\text{H}_2\text{SO}_4$) is in contact with an Fe surface in air [4]. Because Fe is a conductor, electrons are available to reduce $\text{O}_2$ at the edges of the droplets. The electrons are then replaced by the oxidation reaction of Fe to Fe$^{2+}$ (forming Fe$\text{SO}_4$ if H$_2$SO$_4$ is the acid), and the rate of corrosion is simply the current induced by metal ions leaving the surface.

![Figure A3.10.1](image)

*Figure A3.10.1* (a) A schematic illustration of the corrosion process for an oxygen-rich water droplet on an iron surface. (b) The process can be viewed as a short-circuited electrochemical cell [4].

Corrosion protection of metals can take many forms, one of which is passivation. As mentioned above, passivation is the formation of a thin protective film (most commonly oxide or hydrated oxide) on a metallic surface. Certain metals that are prone to passivation will form a thin oxide film that displaces the electrode potential of the metal by $\pm 0.5$–$2.0$ V. The film severely hinders the diffusion rate of metal ions from the electrode to the solid–gas or solid–liquid interface, thus providing corrosion resistance. This decreased corrosion rate is best illustrated by anodic polarization curves, which are constructed by measuring the net current from an electrode into solution (the corrosion current) under an applied voltage. For passivable metals, the current will increase steadily with increasing voltage in the so-called active region until the passivating film forms, at which point the current will rapidly decrease. This behaviour is characteristic of metals that are susceptible to passivation.

Another method by which metals can be protected from corrosion is called alloying. An alloy is a multi-component solid solution whose physical and chemical properties can be tailored by varying the alloy composition.
For example, copper has relatively good corrosion resistance under non-oxidizing conditions. It can be alloyed with zinc to yield a stronger material (brass), but with lowered corrosion resistance. However, by alloying copper with a passivating metal such as nickel, both mechanical and corrosion properties are improved. Another important alloy is steel, which is an alloy between iron (>50%) and other alloying elements such as carbon.

Although alloying can improve corrosion resistance, brass and steel are not completely resistant to attack and often undergo a form of corrosion known as selective corrosion (also called de-alloying or leaching). De-alloying consists of the segregation of one alloy component to the surface, followed by the removal of this surface component through a corrosion reaction. De-zincification is the selective leaching of zinc from brasses in an aqueous solution. The consequences of leaching are that mechanical and chemical properties change with compositional changes in the alloy.

As an example of the effect that corrosion can have on commercial industries, consider the corrosive effects of salt water on a seagoing vessel. Corrosion can drastically affect a ship’s performance and fuel consumption over a period of time. As the hull of a steel boat becomes corroded and fouled by marine growths, the performance of the ship declines because of increased frictional drag. Therefore, ships are drydocked periodically to restore the smoothness of the hull. Figure A3.10.2 shows the loss of speed due to corrosion and marine fouling between annual drydockings for a ship with a steel hull [5]. As corrosion effects progressively deteriorated the hull and as marine growth accumulated, the ship experienced an overall loss of speed even after drydocking and an increased fuel consumption over time. It is clear that there is strong economic motivation to implement corrosion protection.

![Figure A3.10.2](image)

**Figure A3.10.2** The influence of corrosion (C) and marine fouling (F) on the performance of a steel ship drydocked annually for cleaning and painting [5].

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Surface science studies of corrosion phenomena are excellent examples of in situ characterization of surface reactions. In particular, the investigation of corrosion reactions with STM is promising because not only can it be used to study solid–gas interfaces, but also solid–liquid interfaces.

**A3.10.2.2 SURFACE SCIENCE OF CORROSION**

**(A) THE ROLE OF SULFUR IN CORROSION**

STM has been used to study adsorption on surfaces as it relates to corrosion phenomena [6, 7]. Sulfur is a well known corrosion agent and is often found in air (SO$_2$, H$_2$S) and in aqueous solution as dissolved anions (HSO$_3^-$) or dissolved gas (H$_2$S). By studying the interaction of sulfur with surfaces, insights can be gained into the fundamental processes governing corrosion phenomena. A Ni(111) sample with 10 ppm sulfur bulk impurity was used to study sulfur adsorption by annealing the crystal to segregate the sulfur to the surface [8]. Figure A3.10.3 shows a STM image of a S-covered Ni(111) surface. It was found that sulfur formed islands preferentially near step edges, and that the Ni surface reconstructed under the influence of sulfur adsorption. This reconstruction results in surface sites that have fourfold symmetry rather than threefold symmetry as on the unreconstructed (111) surface. Furthermore, the fourfold symmetry sites are similar to those found on unreconstructed Ni(100), demonstrating the strong influence that sulfur adsorption has on this surface. The mechanism by which sulfur leads to corrosion of nickel surfaces is clearly linked to the ability of sulfur to weaken Ni–Ni bonds.

![STM image of early stages of sulfur segregation on Ni(111)](image)

**Figure A3.10.3** STM images of the early stages of sulfur segregation on Ni(111). Sulfur atoms are seen to preferentially nucleate at step edges [8].

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(B) ANODIC DISSOLUTION IN ALLOYS

This weakening of Ni–Ni surface bonds by adsorbed sulfur might lead one to expect that the corrosion rate should increase in this case. In fact, an increased anodic dissolution rate was observed for Ni$_2$Fe (100) in 0.05 M H$_2$SO$_4$ [2]. Figure A3.10.4 shows the anodic polarization curves for clean and S-covered single-crystal alloy surfaces. While both surfaces show the expected current increase with potential increase, the sulfur-covered surface clearly has an increased rate of dissolution. In addition, the sulfur coverage (measured using radioactive sulfur, $^{35}$S) does not decrease even at the maximum dissolution rate, indicating that adsorbed sulfur is not consumed by the dissolution reaction. Instead, surface sulfur simply enhances the rate of dissolution, as expected based on the observation above that Ni–Ni bonds are significantly weakened by surface sulfur.

![Figure A3.10.4](image)

**Figure A3.10.4** The effect of sulfur on the anodic polarization curves from a Ni$_{0.25}$Fe(100) alloy in 0.05 M H$_2$SO$_4$. $\theta$ is the sulfur ($^{35}$S) coverage [6].

The nature of copper dissolution from CuAu alloys has also been studied. CuAu alloys have been shown to have a surface Au enrichment that actually forms a protective Au layer on the surface. The anodic polarization curve for CuAu alloys is characterized by a critical potential, $E_c$, above which extensive Cu dissolution is observed [10]. Below $E_c$, a smaller dissolution current arises that is approximately potential-independent. This critical potential depends not only on the alloy composition, but also on the solution composition. STM was used to investigate the mechanism by which copper is selectively dissolved from a CuAu$_3$ electrode in solution [11], both above and below the critical potential. At potentials below $E_c$, it was found that, as copper dissolves, vacancies agglomerate on the surface to form voids one atom deep. These voids grow two-dimensionally with increasing Cu dissolution while the second atomic layer remains undisturbed. The fact that the second atomic layer is unchanged suggests that Au atoms from the first layer are filling...
in holes left by Cu dissolution. In sharp contrast, for potentials above \( E_c \), massive Cu dissolution results in a rough surface with voids that grow both parallel and perpendicular to the surface, suggesting a very fast dissolution process. These \textit{in situ} STM observations lend insight into the mechanism by which Cu dissolution occurs in CuAu\(_3\) alloys.

The characterization of surfaces undergoing corrosion phenomena at liquid–solid and gas–solid interfaces remains a challenging task. The use of STM for \textit{in situ} studies of corrosion reactions will continue to shape the atomic-level understanding of such surface reactions.

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**A3.10.3 GROWTH**

**A3.10.3.1 INTRODUCTION**

Thin crystalline films, or overlayers, deposited onto crystalline substrates can grow in such a way that the substrate lattice influences the overlayer lattice. This phenomenon is known as epitaxy; if the deposited material is different from (the same as) the substrate, the process is referred to as heteroepitaxy (homoe epitaxy). Epitaxial growth is of interest for several reasons. First, it is used prevalently in the semiconductor industry for the manufacture of III/V and II/VI semiconductor devices. Second, novel phases have been grown epitaxially by exploiting such phenomena as lattice mismatch and strain. These new phases have physical and chemical properties of interest to science and engineering. Finally, fundamental catalytic studies often focus on modelling oxide-supported metal particles by depositing metal films on oxide single crystals and thin films and, in many cases, these oxide and metal films grow epitaxially.

When considering whether growth will occur epitaxially or not, arguments can be made based on geometrical considerations, or row matching. This concept is based on the idea that the overlayer must sit on minima of the substrate corrugation potential to minimize the interaction energy. For example, consider the illustration of epitaxial growth in figure A3.10.5 where an fcc(111) monolayer has been overlaid on a bcc(110) surface [12]. Figure A3.10.5(a) shows that the overlayer must be expanded or contracted in two directions to obtain row matching. Figure A3.10.5(b) shows, however, that rotation of the overlayer by 5.26\(^\circ\) results in row matching along the most close-packed row of the lattices. Epitaxial growth clearly provides a pathway to energetically favourable atomic arrangements.

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Figure A3.10.5 An fcc(111) monolayer (full circles) overlaid onto a bcc(110) substrate (open circles). (a) fcc[011] parallel to bcc[001]. (b) 5.26° rotation relative to (a). The lattice constants were chosen to produce row-matching in (b) [12].

The influence of the substrate lattice makes it energetically favourable for two materials to align lattices. On the other hand, if two lattices are misaligned or mismatched in some other way, then lattice strain may result. This lattice strain can lead to a metastable atomic arrangement of the deposited material. In other words, an overlayer can respond to lattice strain by adopting a crystal structure that differs from its normal bulk structure in order to row-match the substrate lattice. This phenomenon is known as pseudomorphology. For example, Cu (fcc) deposited on a Pd(100) surface will grow epitaxially to yield a pseudomorphic fcc overlayer [13]. However, upon increasing the copper film thickness, a body-centred tetragonal (bct) metastable phase, one not normally encountered for bulk copper, was observed. This phase transformation is due to a high degree of strain in the fcc overlayer.

Another example of epitaxy is tin growth on the (100) surfaces of InSb or CdTe (a = 6.49 Å) [14]. At room temperature, elemental tin is metallic and adopts a bct crystal structure ('white tin') with a lattice constant of 5.83 Å. However, upon deposition on either of the two above-mentioned surfaces, tin is transformed into the diamond structure ('grey tin') with a = 6.49 Å and essentially no misfit at the interface. Furthermore, since grey tin is a semiconductor, then a novel heterojunction material can be fabricated. It is evident that epitaxial growth can be exploited to synthesize materials with novel physical and chemical properties.

A3.10.3.2 Film Growth Techniques

There are several design parameters which distinguish film growth techniques from one another, namely generation of the source atom/molecule, delivery to the surface and the surface condition. The source molecule can be generated in a number of ways including vapour produced thermally from solid and liquid sources, decomposition of organometallic...
compounds and precipitation from the liquid phase. Depending on the pressures used, gas phase atoms and molecules impinging on the surface may be in viscous flow or molecular flow. This parameter is important to determining whether atom–atom (molecule–molecule) collisions, which occur in large numbers at pressures higher than UHV, can affect the integrity of the atom (molecule) to be deposited. The condition of the substrate surface may also be a concern: elevating the surface temperature may alter the growth kinetics, or the surface may have to be nearly free of defects and or contamination to promote the proper growth mode. Two film growth techniques, molecular beam epitaxy (MBE) and vapour phase epitaxy (VPE) will be briefly summarized below. These particular techniques were chosen because of their relevance to UHV studies. The reader is referred elsewhere for more detailed discussions of the various growth techniques [15, 16 and 17].

MBE is accomplished under UHV conditions with pressures of the order of ~10^{-10} Torr. By using such low pressures, the substrate surface and deposited thin films can be kept nearly free of contamination. In MBE, the material being deposited is usually generated in UHV by heating the source material to the point of evaporation or sublimation. The gas phase species is then focused in a molecular beam onto the substrate surface, which itself may be at an elevated temperature. The species flux emanating from the source can be controlled by varying the source temperature and the species flux arriving at the surface can be controlled by the use of mechanical shutters. Precise control of the arrival of species at the surface is a very important characteristic of MBE because it allows the growth of epitaxial films with very abrupt interfaces. Several sources can be incorporated into a single vacuum chamber, allowing doped semiconductors, compounds or alloys to be grown. For instance, MBE is used prevalently in the semiconductor industry to grow GaAs/Al_{x}Ga_{1-x}As layers and, in such a situation, a growth chamber would be outfitted with Ga, As and Al deposition sources. Because of the compatibility of MBE with UHV surface science techniques, it is often the choice of researchers studying fundamentals of thin-film growth.

A second technique, VPE, is also used for surface science studies of overlayer growth. In VPE, the species being deposited can be generated in several ways, including vaporization of a liquid precursor into a flowing gas stream or sublimation of a solid precursor. VPE generates an unfocused vapour or cloud of the deposited material, rather than a collimated beam as in MBE. Historically, VPE played a major role in the development of III/V semiconductors. Currently, VPE is used as a tool for studying metal growth on oxides, an issue of importance to the catalysis community.

The following two sections will focus on epitaxial growth from a surface science perspective with the aim of revealing the fundamentals of thin-film growth. As will be discussed below, surface science studies of thin-film deposition have contributed greatly to an atomic-level understanding of nucleation and growth.

**A3.10.3.3 THERMODYNAMICS**

The number of factors affecting thin-film growth is largely dependent upon the choice of growth technique. The overall growth mechanism may be strongly influenced by three factors: mass transport, thermodynamics and kinetics. For instance, for an exothermic (endothermic) process, increasing (decreasing) the surface temperature will decrease (increase) the growth rate for a thermodynamically limited process. On the other hand, if temperature has no effect on the growth rate, then the process may be limited by mass transport, which has very little dependence on the substrate temperature. Another test of mass transport limitations is to increase the total flow rate to the surface while keeping the partial pressures constant—if the growth rate is influenced, then mass transport limitations should be considered. Alternatively, if the substrate orientation is found to influence the growth rates, then the process is very likely kinetically limited. Thus, through a relatively straightforward analysis of the parameters affecting macroscopic
quantities, such as growth rate, a qualitative description of the growth mechanism can be obtained. The growth of epitaxial thin films by vapour deposition in UHV is a non-equilibrium kinetic phenomenon. At thermodynamic equilibrium, atomic processes are required to proceed in opposite directions at equal rates. Hence, a system at equilibrium must have equal adsorption and desorption rates, as well as equal cluster growth and cluster decay rates. If growth were occurring under equilibrium conditions, then there would be no net change in the amount of deposited material on the surface. Typical growth conditions result in systems far from equilibrium, so film growth is usually limited by kinetics considerations. Thermodynamics does play an important role, however, as will be discussed next.

Thermodynamics can lend insight into the expected growth mode by examination of energetics considerations. The energies of importance are the surface free energy of the overlayer, the interfacial energy between the substrate and the overlayer, and the surface free energy of the substrate. Generally, if the free energy of the overlayer plus the interface energy is greater than the free energy of the substrate, then Frank–van der Merwe (FM) growth will occur [18]. FM growth, also known as layer-by-layer growth, is characterized by the completion of a surface overlayer before the second layer begins forming. However, if the free energy of the overlayer plus the interface energy is less than the free energy of the substrate then the growth mode is Volmer–Weber (VW) [18]. VW, or three-dimensional (3D), growth yields 3D islands or clusters that coexist with bare patches of substrate. There is also a third growth mode, called Stranski–Krstanov (SK), which can be described as one or two monolayers of growth across the entire surface subsequently followed by the growth of 3D islands [18]. In SK growth, the sum of the surface free energy of the overlayer plus interface energy is initially greater than that of the substrate, resulting in the completion of the first monolayer, after which the surface free energy of the overlayer plus interface energy becomes greater than that of the substrate, resulting in 3D growth. It should be stressed that the energetic arguments for these growth modes are only valid for equilibrium processes. However, these descriptions provide good models for the growth modes experimentally observed even under non-equilibrium conditions.

**A3.10.3.4 NUCLEATION AND GROWTH**

The process of thin-film growth from an atomic point of view consists of the following stages: adsorption, diffusion, nucleation, growth and coarsening. Adsorption is initiated by exposing the substrate surface to the deposition source. As described above, this is a non-equilibrium process, and the system attempts to restore equilibrium by forming aggregates. The adatoms randomly walk during the diffusion process until two or more collide and subsequently nucleate to form a small cluster. A rate-limiting step is the formation of some critical cluster size, at which point cluster growth becomes more probable than cluster decay. The clusters increase in size during the growth stage, with the further addition of adatoms leading to island formation. Growth proceeds at this stage according to whichever growth mode is favoured. Once deposition has ceased, further island morphological changes occur during the coarsening stage, whereby atoms in small islands evaporate and add to other islands or adsorb onto available high-energy adsorption sites such as step edge sites. For an excellent review on the atomic view of epitaxial metal growth, see [19].

Experimentally, the variable-temperature STM has enabled great strides to be made towards understanding nucleation and growth kinetics on surfaces. The evolution of overlayer growth can be followed using STM from the first stages of adatom nucleation through to the final stages of island formation. The variable-temperature STM has also been crucial to obtaining surface diffusion rates. In such cases, however, the importance of tip–sample interactions must be considered. Typically, low tunnelling currents are best because under these conditions the tip is further from the surface, thereby reducing the risk of tip–sample interactions.
Much effort in recent years has been aimed at modelling nucleation at surfaces and several excellent reviews exist [20, 21 and 22]. Mean-field nucleation theory is one of these models and has a simple picture at its core. In the nucleation stage, an atom arriving at the surface from the gas phase adsorbs and then diffuses at a particular rate until it collides with another surface adatom to form a dimer. If the dimers are assumed to be stable (so that no decay occurs) and immobile (so that no diffusion occurs) then, as deposition proceeds, the concentration of dimers will increase approximately linearly until it is roughly equal to the concentration of monomers. At this point, the probability of an atom colliding with a dimer is comparable to the probability of an adatom colliding with another adatom, hence growth and nucleation compete. Once the island density has saturated, i.e. no more clusters are being formed, then the adatom mean free path is equal to the mean island separation and further deposition results in island growth. At coverages near 0.5 monolayers (ML), islands begin to coalesce and the island density decreases.

This simple and idealistic picture of nucleation and growth from mean field nucleation theory was found to be highly descriptive of the Ag/Pt(111) system at 75 K (figure A3.10.6) [23]. Figure A3.10.6 shows a series of STM images of increasing Ag coverage on Pt(111) and demonstrates the transition from nucleation to growth. At very low coverages ((a) and (b)), the average cluster size is 2.4 and 2.6 atoms, respectively, indicating that dimers and trimers are the predominant surface species. However, when the coverage was more than doubled from (a) to (b), the mean island size remained relatively constant. This result clearly indicates that deposition at these low coverages is occurring in the nucleation regime. By increasing the coverage to 0.03 ML, the Ag mean island size doubled to 6.4 atoms and the island density increased, indicating that nucleation and growth were competing. Finally, after increasing the coverage even further (d), the mean island size doubled again, while the island density saturated, suggesting that a pure growth regime dominated, with little or no nucleation occurring.

Growth reactions at surfaces will certainly continue to be the focus of much research. In particular, the synthesis of novel materials is an exciting field that holds much promise for the nanoscale engineering of materials. Undoubtedly, the advent of STM as a means of investigating growth reactions on the atomic scale will influence the future of nanoscale technology.
Figure A3.10.6 A series of STM images for Ag/Pt(111) at 75 K showing the transition from nucleation to growth [23]. Coverages (θ) and mean island sizes (n) are indicated.

A3.10.4 ETCHING

A3.10.4.1 INTRODUCTION

Etching is a process by which material is removed from a surface. The general idea behind etching is that by interaction of an etch atom or molecule with a surface, a surface species can be formed that is easily removed. The use of a liquid to etch a surface is known as wet etching, while the use of a gas to etch a surface is known as dry etching. Wet etching has been employed since the late Middle Ages. The process then was rather simple and could be typified as follows. The metal to be etched was first coated with a wax, or in modern vernacular, a mask. Next, a pattern was cut into the wax to reveal the metal surface beneath. Then, an acid was used to etch the exposed metal, resulting in a patterned surface. Finally, the mask was removed to reveal the finished product. Modern methods are considerably more technologically advanced, although the general principles behind etching remain unchanged.
Both wet and dry etching are used extensively in the semiconductor processing industry. However, wet etching has limitations that prevent it being used to generate micron or submicron pattern sizes for GaAs etching. The most serious of these limitations is called substrate undercutting, which is a phenomenon where etch rates parallel and perpendicular to the surface are approximately equal (isotropic etching). Substrate undercutting is much less prevalent for silicon surfaces than GaAs surfaces, thus wet etching is more commonly used to etch silicon surfaces. Generally, when patterning surfaces, anisotropic etching is preferred, where etch rates perpendicular to the surface exceed etch rates parallel to the surface. Hence, in cases of undercutting, an ill defined pattern typically results. In the early 1970s, dry etching (with CF$_4$/O$_2$, for example) became widely used for patterning. Dry methods have a distinct advantage over wet methods, namely anisotropic etching.

A form of anisotropic etching that is of some importance is that of orientation-dependent etching, where one particular crystal face is etched at a faster rate than another crystal face. A commonly used orientation-dependent wet etch for silicon surfaces is a mixture of KOH in water and isopropanol. At approximately 350 K, this etchant has an etch rate of 0.6 μm min$^{-1}$ for the Si(100) plane, 0.1 μm min$^{-1}$ for the Si(110) plane and 0.006 μm min$^{-1}$ for the Si(111) plane [24]. These different etch rates can be exploited to yield anisotropically etched surfaces.

Semiconductor processing consists of a number of complex steps, of which etching is an integral step. Figure A3.10.7 shows an example of the use of etching [25] in which the goal of this particular process is to remove certain parts of a film, while leaving the rest in a surface pattern to serve as, for example, interconnection paths. This figure illustrates schematically how etching paired with a technique called photolithography can be used to manufacture a semiconductor device. In this example, the substrate enters the manufacturing stream covered with a film (for example, a SiO$_2$ film on a Si wafer). A liquid thin-film called a photoresist (denoted ‘positive resist’ or ‘negative resist’, as explained below) is first placed on the wafer, which is then spun at several thousand rotations per minute to spread out the film and achieve a uniform coating. Next, the wafer is exposed through a mask plate to an ultraviolet (UV) light source. The UV photons soften certain resists (positive resists) and harden others (negative resists). Next, a developer solution is used to remove the susceptible area, leaving behind the remainder according to the mask pattern. Then, the wafer is etched to remove all of the surface film not protected by the photoresist. Finally, the remaining photoresist is removed, revealing a surface with a patterned film. Thus the role of etching in semiconductor processing is vital and it is evident that motivation exists to explore etching reactions on a fundamental level.
A3.10.4.2 DRY ETCHING TECHNIQUES

It has already been mentioned that dry etching involves the interaction of gas phase molecules/atoms with a surface. More specifically, dry etching utilizes either plasmas that generate reactive species, or energetic ion beams to etch surfaces. Dry etching is particularly important to GaAs processing because, unlike silicon, there are no wet etching methods that result in negligible undercutting. Dry etching techniques can be characterized by either chemical or physical etching mechanisms. The chemical mechanisms tend to be more selective, i.e. more anisotropic, and tend to depend strongly on the specific material being etched. Several dry etch techniques will be briefly discussed below. For a more comprehensive description of these and other techniques, the reader is referred to the texts by Williams [26] or Sugawara [27].
Ion milling is a dry etch technique that uses a physical etching mechanism. In ion milling, ions of an inert gas are generated and then accelerated to impinge on a surface. The etching mechanism is simply the bombardment of these energetic ions on the surface, resulting in erosion. The energy of the ions can be controlled by varying the accelerating voltage, and it may be possible to change the selectivity by varying the angle of incidence.

Plasma etching is a term used to describe any dry etching process that utilizes reactive species generated from a gas plasma. For semiconductor processing, a low-pressure plasma, also called a glow discharge, is used. The glow discharge is characterized by pressures in the range 0.1–5 Torr and electron energies of 1–10 eV. The simplest type of plasma reactor consists of two parallel plates in a vacuum chamber filled with a gas at low pressure. A radio frequency (RF) voltage is applied between the two plates, generating plasma that emits a characteristic glow. Reactive radicals are produced by the plasma, resulting in a collection of gas phase species that are the products of collisions between photons, electrons, ions and atoms or molecules. These chemically reactive species can then collide with a nearby surface and react to form a volatile surface species, thereby etching the surface.

Reactive ion etching (RIE) is distinguished from plasma etching by the fact that the surface reactions are enhanced by the kinetic energy of the incoming reactive species. This type of chemical mechanism is referred to as a kinetically assisted chemical reaction, and very often results in highly anisotropic etching. RIE is typically performed at lower pressures (0.01–0.1 Torr) and is used industrially to etch holes in GaAs.

Dry etching is a commonly used technique for creating highly anisotropic, patterned surfaces. The interaction of gas phase etchants with surfaces is of fundamental interest in understanding such phenomena as undercutting and the dependence of etch rate on surface structure. Many surface science studies aim to understand these interactions at an atomic level, and the next section will explore what is known about the etching of silicon surfaces.

A3.10.4.3 ATOMIC VIEW OF ETCHING

On the atomic level, etching is composed of several steps: diffusion of the etch molecules to the surface, adsorption to the surface, subsequent reaction with the surface and, finally, removal of the reaction products. The third step, that of reaction between the etchant and the surface, is of considerable interest to the understanding of surface reactions on an atomic scale. In recent years, STM has given considerable insight into the nature of etching reactions at surfaces. The following discussion will focus on the etching of silicon surfaces [28].

Figure A3.10.8 schematically depicts a Si(100) surface (a) being etched to yield a rough surface (b) and a more regular surface (c). The surfaces shown here are seen to consist of steps, terraces and kinks, and clearly have a three-dimensional character, rather than the two-dimensional character of an ideally flat, smooth surface. The general etching mechanism is based on the use of halogen molecules, the principal etchants used in dry etching. Upon adsorption on silicon at room temperature, Br₂ dissociates to form bromine atoms, which react with surface silicon atoms. Then, if an external source of energy is provided, for example by heating Si(100) to 900 K, SiBr₂ forms and desorbs, revealing the silicon atom(s) beneath and completing the etching process. Depending upon the relative desorption energies from various surface sites, the surface could be etched quite differently, as seen in figure A3.10.8(b) and figure A3.10.8(c).
Figure A3.10.8 Depiction of etching on a Si(100) surface. (a) A surface exposed to Br₂ as well as electrons, ions and photons. Following etching, the surface either becomes highly anisotropic with deep etch pits (b), or more regular (c), depending on the relative desorption energies for different surface sites [28].

Semiconductors such as silicon often undergo rearrangements, or reconstructions, at surface boundaries to lower their surface free energy. One way of lowering the surface free energy is the reduction of dangling bonds, which are non-bonding orbitals that extend (dangle) into the vacuum. Si(111) undergoes a complex (7 × 7) reconstruction that was ultimately solved using STM. Figure A3.10.9(a) shows an STM image of the reconstructed Si(111) surface [29]. This reconstruction reduces the number of dangling bonds from 49 to 19 per unit cell.

The (7 × 7) reconstruction also affects the second atomic layer, called the rest layer. The rest layer is composed of silicon atoms arranged in triangular arrays that are separated from one another by rows of silicon dimers. Figure A3.10.9(b) shows the exposed rest layer following bromine etching at 675 K [29]. It is noteworthy that the rest layer does not reconstruct to form a new (7 × 7) surface. The stability of the rest layer following etching of (7 × 7)-Si(111) is due to the unique role of the halogen. The silicon adlayer is removed by insertion of bromine atoms into Si–Si dimer bonds. Once this silicon adlayer is gone, the halogen stabilizes the silicon rest layer by reacting with the dangling bonds, effectively inhibiting surface reconstruction to a (7 × 7) phase. Unfortunately, the exposure of the rest layer makes etching more difficult because to form SiBr₂, bromine atoms must insert into stronger Si–Si bonds.
Figure A3.10.9 STM images of Si(111) surfaces before (a) and after (b) etching by bromine at 675 K. In (a) the \((7 \times 7)\) reconstructed surface is seen. In (b), the rest layer consisting of triangular arrays of Si atoms has been exposed by etching [28]. Both images show a \(17 \times 17 \text{ nm}^2\) area.

Si(100) reconstructs as well, yielding a \((1 \times 2)\) surface phase that is formed when adjacent silicon atoms bond through their respective dangling bonds to form a more stable silicon dimer. This reconstructed bonding results in a buckling of the surface atoms. Furthermore, because Si–Si dimer bonds are weaker than bulk silicon bonds, the reconstruction actually facilitates etching. For a comprehensive discussion on STM studies of reconstructed silicon surfaces, see [20].

Si(100) is also etched by \(\text{Br}_2\), although in a more dramatic fashion. Figure A3.10.10 shows a STM image of a Si(100) surface after etching at 800 K [28]. In this figure, the dark areas are etch pits one atomic layer deep. The bright rows running perpendicular to these pits are silicon dimer chains, which are composed of silicon atoms that were released from terraces and step edges during etching. The mechanism by which Si(100) is etched has been deduced from STM studies. After \(\text{Br}_2\) dissociatively adsorbs to the surface, a bromine atom bonds to each silicon atom in the dimer pairs. SiBr\(_2\) is the known desorption product and so the logical next step is the formation of a surface SiBr\(_2\) species. This step can occur by the breaking of the Si–Si dimer bond and the transfer of a bromine atom from one of the dimer atoms to the other. Then, if enough energy is available to overcome the desorption barrier, SiBr\(_2\) will desorb, leaving behind a highly uncoordinated silicon atom that will migrate to a terrace and eventually re-dimerize. On the other hand, if there is not enough energy to desorb SiBr\(_2\), then the Br atom would transfer back to the original silicon atom, and a silicon dimer bond would again be formed. In this scenario, SiBr\(_2\) desorption is essential to the etching process.
Figure A3.10.10 STM image (55 $\times$ 55 nm$^2$) of a Si(100) surface exposed to molecular bromine at 800 K. The dark areas are etch pits on the terraces, while the bright rows that run perpendicular to the terraces are Si dimer chains. The dimer chains consist of Si atoms released from terraces and step edges during etching [28].

Another view of the Si(100) etching mechanism has been proposed recently [28]. Calculations have revealed that the most important step may actually be the escape of the bystander silicon atom, rather than SiBr$_2$ desorption. In this way, the SiBr$_2$ becomes trapped in a state that otherwise has a very short lifetime, permitting many more desorption attempts. Preliminary results suggest that indeed this vacancy-assisted desorption is the key step to etching Si(100) with Br$_2$.

The implementation of tools such as the STM will undoubtedly continue to provide unprecedented views of etching reactions and will deepen our understanding of the phenomena that govern these processes.

A3.10.5 CATALYTIC REACTIONS

A3.10.5.1 INTRODUCTION

A catalyst is a material that accelerates a reaction rate towards thermodynamic equilibrium conversion without itself being consumed in the reaction. Reactions occur on catalysts at particular sites, called ‘active sites’, which may have different electronic and geometric structures than neighbouring sites. Catalytic reactions are at the heart of many chemical industries, and account for a large fraction of worldwide chemical production. Research into fundamental aspects of catalytic reactions has a strong economic motivating factor: a better understanding of the catalytic process
may lead to the development of a more efficient catalyst. While the implementation of a new catalyst based on surface science studies has not yet been realized, the investigation of catalysis using surface science methods has certainly shaped the current understanding of catalytic reactions. Several recommended texts on catalysis can be found in [31, 32 and 33].

Fundamental studies in catalysis often incorporate surface science techniques to study catalytic reactions at the atomic level. The goal of such experiments is to characterize a catalytic surface before, during and after a chemical reaction; this is no small task. The characterization of these surfaces is accomplished using a number of modern analytical techniques. For example, surface compositions can be determined using X-ray photoelectron spectroscopy (XPS) or Auger electron spectroscopy (AES). Surface structures can be probed using low-energy electron diffraction (LEED) or STM. In addition, a number of techniques are available for detecting and identifying adsorbed species on surfaces, such as infrared reflection absorption spectroscopy, high-resolution electron energy-loss spectroscopy (HREELS) and sum frequency generation (SFG).

As with the other surface reactions discussed above, the steps in a catalytic reaction (neglecting diffusion) are as follows: the adsorption of reactant molecules or atoms to form bound surface species, the reaction of these surface species with gas phase species or other surface species and subsequent product desorption. The global reaction rate is governed by the slowest of these elementary steps, called the rate-determining or rate-limiting step. In many cases, it has been found that either the adsorption or desorption steps are rate determining. It is not surprising, then, that the surface structure of the catalyst, which is a variable that can influence adsorption and desorption rates, can sometimes affect the overall conversion and selectivity.

Industrial catalysts usually consist of one or more metals supported on a metal oxide. The supported metal can be viewed as discrete single crystals on the support surface. Changes in the catalyst structure can be achieved by varying the amount, or "loading", of the metal. An increased loading should result in a particle size increase, and so the relative population of a particular crystal face with respect to other crystal faces may change. If a reaction rate on a per active site basis changes as the metal loading changes, then the reaction is deemed to be structure sensitive. The surface science approach to studying structure-sensitive reactions has been to examine the chemistry that occurs over different crystal orientations. In general, these studies have shown that close-packed, atomically smooth metal surfaces such as (111) and (100) fcc and (110) bcc surfaces are less reactive than more open, rough surfaces such as fcc(110) and bcc (111). The remaining task is then to relate the structure sensitivity results from single-crystal studies to the activity results over real-world catalysts.

Surface science studies of catalytic reactions certainly have shed light on the atomic-level view of catalysis. Despite this success, however, two past criticisms of the surface science approach to catalysis are that the pressure regimes (usually 10^{-10} Torr) and the materials (usually low-surface-area single crystals) are far removed from the high pressures and high-surface-area supported catalysts used industrially. These criticisms have been termed the "pressure gap" and the "materials gap". To combat this criticism, much research in the last 30 years has focused on bridging these gaps, and many advances have been made that now suggest these criticisms are no longer warranted.
A3.10.5.2 EXPERIMENTAL

(A) BRIDGING THE PRESSURE GAP

The implementation of high-pressure reaction cells in conjunction with UHV surface science techniques allowed the first true in situ postmortem studies of a heterogeneous catalytic reaction. These cells permit exposure of a sample to ambient pressures without any significant contamination of the UHV environment. The first such cell was internal to the main vacuum chamber and consisted of a metal bellows attached to a reactor cup [24]. The cup could be translated using a hydraulic piston to envelop the sample, sealing it from the surrounding UHV by means of a copper gasket. Once isolated from the vacuum, the activity of the enclosed sample for a given reaction could be measured at elevated pressures. Following the reaction, the high-pressure cell was evacuated and then retracted, exposing the sample again to the UHV environment, at which point any number of surface science techniques could be used to study the ‘spent’ catalyst surface.

Shortly thereafter, another high-pressure cell design appeared [35]. This design consisted of a sample mounted on a retractable bellows, permitting the translation of the sample to various positions. The sample could be retracted to a high-pressure cell attached to the primary chamber and isolated by a valve, thereby maintaining UHV in the primary chamber when the cell was pressurized for catalytic studies. The reactor could be evacuated following high-pressure exposures before transferring the sample back to the main chamber for analysis.

A modification to this design appeared several years later (figure A3.10.11) [36, 37]. In this arrangement, the sample rod can be moved easily between the UHV chamber and the high-pressure cell without any significant increase in chamber pressure. Isolation of the reaction cell from UHV is achieved by a differentially pumped sliding seal mechanism (figure A3.10.12) whereby the sample rod is pushed through the seals until it is located in the high-pressure cell. Three spring-loaded, differentially pumped Teflon seals are used to isolate the reaction chamber from the main chamber by forming a seal around the sample rod. Differential pumping is accomplished by evacuating the space between the first and second seals (on the low-pressure side) by a turbomolecular pump and the space between the second and third seals (on the high-pressure side) by a mechanical (roughing) pump. Pressures up to several atmospheres can be maintained in the high-pressure cell while not significantly raising the pressure in the attached main chamber.

The common thread to these designs is that a sample can be exposed to reaction conditions and then studied using surface science methods without exposure to the ambient. The drawback to both of these designs is that the samples are still being analysed under UHV conditions before and after the reaction under study. The need for in situ techniques is clear.

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Figure A3.10.11 Side view of a combined high-pressure cell and UHV surface analysis system [37].

Figure A3.10.12 Side view of the high-pressure cell showing the connections to the UHV chamber, the turbomolecular pump and the gas handling system. The differentially pumped sliding seal is located between the high-pressure cell and the UHV chamber [37].
Two notable \textit{in situ} techniques are at the forefront of the surface science of catalysis: STM and SFG. STM is used to investigate surface structures while SFG is used to investigate surface reaction intermediates. The significance of both techniques is that they can operate over a pressure range of 13 orders of magnitude, from $10^{-10}$ to $10^3$ Torr, i.e. they are truly \textit{in situ} techniques. STM has allowed the visualization of surface structures under ambient conditions and has shed light on adsorbate-induced morphological changes that occur at surfaces, for both single-crystal metals and metal clusters supported on oxide single crystals. Studies of surface reactions with SFG have given insight into reaction mechanisms previously investigated under non-ideal pressure or temperature constraints. Both SFG and STM hold promise as techniques that will contribute greatly to the understanding of catalytic reactions under \textit{in situ} conditions.

\textbf{(B) BRIDGING THE MATERIALS GAP}

Single crystals are traditionally used in UHV studies because they provide an opportunity to well characterize a surface. However, as discussed above, single crystals are quite different from industrial catalysts. Typically, such catalysts consist of supported particles that can have multiple crystal orientations exposed at the surface. Therefore, an obstacle in attempting surface science studies of catalysis is the preparation of a surface in such a way that it mimics a real-world catalyst.

One criterion necessary for using charged-particle spectroscopies such as AES and EELS is that the material being investigated should be conductive. This requisite prevents problems such as charging when using electron spectroscopies and ensures homogeneous heating during thermal desorption studies. A problem then with investigating oxide surfaces for use as metal supports is that many are insulators or semiconductors. For example, alumina and silica are often used as oxide supports for industrial catalysts, yet both are insulators at room temperature, severely hindering surface science studies of these materials. However, thin-films of these and other oxides can be deposited onto metal substrates, thus providing a conductive substrate (\textit{via} tunnelling) for use with electron spectroscopies and other surface science techniques.

Thin oxide films may be prepared by substrate oxidation or by vapour deposition onto a suitable substrate. An example of the former method is the preparation of silicon oxide thin-films by oxidation of a silicon wafer. In general, however, the thickness and stoichiometry of a film prepared by this method are difficult to control. On the other hand, vapour deposition, which consists of evaporating the parent metal in an oxidizing environment, allows precise control of the film thickness. The extent of oxidation can be controlled by varying the O\textsubscript{2} pressure (lower O\textsubscript{2} pressures can lead to lower oxides) and the film thickness can be controlled by monitoring the deposition rate. A number of these thin metal oxide films have been prepared by vapour deposition, including SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, MgO, TiO\textsubscript{2} and NiO [38].

MgO films have been grown on a Mo(100) substrate by depositing Mg onto a clean Mo(100) sample in O\textsubscript{2} ambient at 300 K [39, 40]. LEED results indicated that MgO grows epitaxially at an optimum O\textsubscript{2} pressure of $10^{-7}$ Torr, with the (100) face of MgO parallel to the Mo(100) surface. Figure A3.10.13 shows a ball model illustration of the MgO(100) overlayer on Mo(100). The chemical states of Mg and O were also probed as a function of the O\textsubscript{2} pressure during deposition by AES and XPS. It was found that as the O\textsubscript{2} pressure was increased, the metallic Mg\textsuperscript{0} (L\textsubscript{2,3}VV) Auger transition at 44.0 eV decreased while a new transition at 32.0 eV increased. The transition at 32.0 eV was assigned to a Mg\textsuperscript{2+} (L\textsubscript{2,3}VV) transition due to the formation of MgO. When the O\textsubscript{2} pressure reached $10^{-7}$ Torr, the Mg\textsuperscript{2+} feature dominated the AES spectrum while the Mg\textsuperscript{0} feature completely diminished. XPS studies confirmed the LEED and AES results, verifying that MgO was formed at the optimal O\textsubscript{2} pressure. Furthermore, the Mg 2p and O 1s XPS peaks from the MgO film had the same binding energy (BE) and peak shape as the Mg 2p and O 1s peaks from an MgO single crystal. Both AES and XPS indicated that the stoichiometry of the film was MgO. Further annealing in O\textsubscript{2} did
not increase the oxygen content of the film, which supports the fact that no evidence of Mg suboxides was found. This MgO film was successfully used to study the nature of surface defects in Li-doped MgO as they relate to the catalytic oxidative coupling of methane.

Figure A3.10.13 Ball model illustration of an epitaxial MgO overlayer on Mo(100) [38].

The deposition of titanium oxide thin-films on Mo(110) represents a case where the stoichiometry of the film is sensitive to the deposition conditions [41]. It was found that both TiO$_2$ and Ti$_2$O$_3$ thin-films could be made, depending on the Ti deposition rate and the O$_2$ background pressure. Lower deposition rates and higher O$_2$ pressures favoured the formation of TiO$_2$. The two compositionally different films could be distinguished in several ways. Different LEED patterns were observed for the different films: TiO$_2$ exhibited a (1 × 1) rectangular periodicity, while Ti$_2$O$_3$ exhibited a (1 × 1) hexagonal pattern. XPS Ti 2p data clearly differentiated the two films as well, showing narrow peaks with a Ti 2p$_{3/2}$ BE of 459.1 eV for TiO$_2$ and broad peaks with a Ti 2p$_{3/2}$ BE of 458.1 eV for Ti$_2$O$_3$. From LEED and HREELS results, it was deduced that the surfaces grown on Mo(110) were TiO$_2$(100) and Ti$_2$O$_3$(0001). Therefore, it is clear that vapour deposition allows control over thickness and extent of oxidation and is certainly a viable method for producing thin oxide films for use as model catalyst supports.

Metal vapour deposition is a method than can be used to conveniently prepare metal clusters for investigation under UHV conditions. The deposition is accomplished using a doser constructed by wrapping a high-purity wire of the metal to be deposited around a tungsten or tantalum filament that can be resistively heated. After sufficient outgassing, which is the process of heating the doser to remove surface and bulk impurities, then a surface such as an oxide can be exposed to the metal emanating from the doser to yield a model oxide-supported metal catalyst.

Model catalysts such as Au/TiO$_2$(110) have been prepared by metal vapour deposition [42]. Figure A3.10.14 shows a STM image of 0.25 ML (1 ML = $1.387 \times 10^{15}$ atoms cm$^{-2}$) Au/TiO$_2$(110). These catalysts were tested for CO oxidation to compare to conventional Au catalysts. It is well known that for conventional Au catalysts there is an optimal Au cluster size (~3 nm) that yields a maximum CO oxidation rate. This result was duplicated by measuring the CO oxidation rate over model Au/TiO$_2$(110), where the cluster sizes were varied by manipulating the deposition
amounts. There is a definite maximum in the CO oxidation activity at a cluster size of approximately 3.5 nm. Furthermore, investigation of the cluster electronic properties using scanning tunnelling spectroscopy (STS) revealed a correlation between the cluster electronic structure and the maximum in CO oxidation activity. Pd/SiO₂/Mo(100) model catalysts were also prepared and were found to have remarkably similar kinetics for CO oxidation when compared to Pd single crystals and conventional silica-supported Pd catalysts [43]. These results confirm that metal vapour deposition on a suitable substrate is a viable method for producing model surfaces for UHV studies.

Figure A3.10.14 STM image of 0.25 ML Au vapour-deposited onto TiO₂(110). Atomic resolution of the substrate is visible as parallel rows. The Au clusters are seen to nucleate preferentially at step edges.

Another method by which model-supported catalysts can be made is electron beam lithography [44]. This method entails spin-coating a polymer solution onto a substrate and then using a collimated electron beam to damage the polymer surface according to a given pattern. Next, the damaged polymer is removed, exposing the substrate according to the electron beam pattern, and the sample is coated with a thin metal film. Finally, the polymer is removed from the substrate, taking with it the metal film except where the metal was bound to the substrate, leaving behind metal particles of variable size. This technique has been used to prepare Pt particles with 50 nm diameters and 15 nm heights on an oxidized silicon support [44]. It was found that ethylene hydrogenation reaction rates on the model catalysts agreed well with turnover rates on Pt single crystals and conventional Pt-supported catalysts.
A3.10.5.3 ATOMIC-LEVEL VIEWS OF CATALYSIS

(A) NH₃ SYNTHESIS: N₂ + 3H₂ ↔ 2NH₃

Ammonia has been produced commercially from its component elements since 1909, when Fritz Haber first demonstrated the viability of this process. Bosch, Mittasch and co-workers discovered an excellent promoted Fe catalyst in 1909 that was composed of iron with aluminum oxide, calcium oxide and potassium oxide as promoters. Surprisingly, modern ammonia synthesis catalysts are nearly identical to that first promoted iron catalyst. The reaction is somewhat exothermic and is favoured at high pressures and low temperatures, although, to keep reaction rates high, moderate temperatures are generally used. Typical industrial reaction conditions for ammonia synthesis are 650–750 K and 150–300 atm. Given the technological importance of the ammonia synthesis reaction, it is not surprising that surface science techniques have been used to thoroughly study this reaction on a molecular level [45, 46].

As mentioned above, a structure-sensitive reaction is one with a reaction rate that depends on the catalyst structure. The synthesis of ammonia from its elemental components over iron surfaces is an example of a structure-sensitive reaction. Figure A3.10.15 demonstrates this structure sensitivity by showing that the rate of NH₃ formation at 20 atm and 600–700 K has a clear dependence on the surface structure [47]. The (111) and (211) Fe faces are much more active than the (100), (210) and (110) faces. Figure A3.10.16 depicts the different Fe surfaces for which ammonia synthesis was studied in figure A3.10.15. The coordination of the different surface atoms is denoted in each drawing. Surface roughness is often associated with higher catalytic activity, however in this case the (111) and (210) surfaces, both of which can be seen to be atomically rough, have distinctly different catalytic activities. Closer inspection of these surfaces reveals that the (111) and (211) faces have a C₇ site in common, i.e. a surface Fe atom with seven nearest neighbours. The high catalytic activity of the (111) and (211) Fe faces has been proposed to be due to the presence of these C₇ sites.
Figure A3.10.15 NH₃ synthesis activity of different Fe single-crystal orientations [32]. Reaction conditions were 20 atm and 600–700 K.
Figure A3.10.16 Illustrations of the surfaces in figure A3.10.15 for which ammonia synthesis activity was tested. The coordination of the surface atoms is noted in the figure [32].

It is widely accepted that the rate-determining step in NH$_3$ synthesis is the dissociative adsorption of N$_2$, depicted in a Lennard-Jones potential energy diagram in figure A3.10.17 [46]. This result is clearly illustrated by examining the sticking coefficient (the adsorption rate divided by the collision rate) of N$_2$ on different Fe crystal faces (figure A3.10.18) [48]. The concentration of surface nitrogen on the Fe single crystals at elevated temperatures in UHV was monitored with AES as a function of N$_2$ exposure. The sticking coefficient is proportional to the slope of the curves in figure A3.10.18. The initial sticking coefficients increase in the order (110) < (100) < (111), which is the same trend observed for the ammonia synthesis catalytic activity at high-pressure (20 atm). This result indicates that the pressure gap for ammonia synthesis can be overcome: the kinetics results obtained in UHV conditions can be readily extended to the kinetics results obtained under high-pressure reaction conditions.
Further work on modified Fe single crystals explored the role of promoters such as aluminium oxide and potassium [49, 50 and 51]. It was found that the simple addition of aluminium oxide to Fe single crystal surfaces decreased the ammonia synthesis rate proportionally to the amount of Fe surface covered, indicating no favourable interaction between Fe and aluminium oxide under those conditions. However, by exposing an aluminium-oxide-modified Fe surface to water vapour, the surface was oxidized, inducing a favourable interaction between Fe and the Al₂O₃. This interaction resulted in a 400-fold increase in ammonia synthesis activity for Al₂O₃/Fe(110) as compared to Fe(110) and an activity for Al₂O₃/Fe(110) comparable to that of Fe(111). Interestingly, aluminium-oxide-modified Fe(111) showed no change in activity. The increase in activity for Al₂O₃/Fe(110) to that of Fe(111) suggests a possible reconstruction.
of the catalyst surface, in particular that Fe(111) and Fe(211) surfaces may be formed. These surfaces have C₇ sites and so the formation of crystals with these orientations could certainly lead to an enhancement in catalytic activity. Thus, the promotion of Fe ammonia synthesis catalysts by AlₓOᵧ appears to be primarily a geometric effect.

The addition of potassium to Fe single crystals also enhances the activity for ammonia synthesis. Figure A3.10.19 shows the effect of surface potassium concentration on the N₂ sticking coefficient. There is nearly a 300-fold increase in the sticking coefficient as the potassium concentration reaches ~1.5 × 10¹⁴ K atoms cm⁻². Not only does the sticking coefficient increase, but with the addition of potassium as a promoter, N₂ molecules are bound more tightly to the surface, with the adsorption energy increasing from 30 to 45 kJ mol⁻¹. A consequence of the lowering of the N₂ potential well is that the activation energy for dissociation (E* in Figure A3.10.17) also decreases. Thus, the promotion of Fe ammonia synthesis catalysts by potassium appears to be primarily an electronic effect.

Figure A3.10.19 Variation of the initial sticking coefficient of N₂ with increasing potassium surface concentration on Fe(100) at 430 K [50].

(B) ALKANE HYDROGENOLYSIS

Alkane hydrogenolysis, or cracking, involves the dissociation of a larger alkane molecule to a smaller alkane molecule. For example, ethane hydrogenolysis in the presence of H₂ yields methane:

\[ \text{C}_2\text{H}_6 + \text{H}_2 \rightarrow 2\text{CH}_4. \]

Cracking (or hydrocracking, as it is referred to when carried out in the presence of H₂) reactions are an integral part of petroleum refining. Hydrocracking is used to lower the average molecular weight (MW) of a higher MW hydrocarbon mixture so that it can then be blended and sold as gasoline. The interest in the fundamentals of catalytic cracking reactions is strong and it has been thoroughly researched.
Ethane hydrogenolysis has been shown to be structure sensitive over nickel catalysts \[43\], as seen in Figure A3.10.20 where methane formation rates are plotted for both nickel single crystals and a conventional, supported nickel catalyst. There is an obvious difference in the rates over Ni(111) and Ni(100), and it is evident that the rate also changes as a function of particle size for the supported Ni catalysts. In addition, differences in activation energy were observed: for Ni(111) the activation energy is 192 kJ mol\(^{-1}\), while for Ni(100) the activation energy is 100 kJ mol\(^{-1}\). It is noteworthy that there is overlap between the hydrogenolysis rates over supported Ni catalysts with the Ni single crystals. The data suggest that small Ni particles are composed primarily of Ni(100) facets while large Ni particles are composed primarily of Ni(111) facets. In fact, this has been observed for fcc materials where surfaces with a (111) orientation are more commonly observed after thermally induced sintering. The structure sensitivity of this reaction over Ni surfaces has been clearly demonstrated.

![Figure A3.10.20](image)

**Figure A3.10.20** Arrhenius plot of ethane hydrogenolysis activity for Ni(100) and Ni(111) at 100 Torr and \(H_2/C_2H_6 = 100\). Also included is the hydrogenolysis activity on supported Ni catalysts at 175 Torr and \(H_2/C_2H_6 = 6.6\) \[43\].

The initial step in alkane hydrogenolysis is the dissociative adsorption, or ‘reactive sticking’ of the alkane. One might suspect that this first step may be the key to the structure sensitivity of this reaction over Ni surfaces. Indeed, the reactive sticking of alkanes has been shown to depend markedly on surface structure \[52\]. Figure A3.10.21 shows the buildup of surface carbon due to methane decomposition \((P_{methane} = 1.00 \text{ Torr})\) over three single-crystal Ni surfaces at 450 K. The rate of methane decomposition is obviously dependent upon the surface structure with the decomposition rate increasing in the order \(111 < 100 < 110\). It can be seen that, initially, the rates of methane decomposition are
similar for Ni(100) and (110), while Ni(111) has a much lower reaction rate. With increasing reaction time, i.e. increasing carbon coverage, the rate over Ni(110) continues to increase linearly while both Ni(111) and (100) exhibit a nonlinear dependence. This linear dependence over Ni(111) may be due to either the formation of carbon islands or a reduced carbon coverage dependence as compared to Ni(111) and (100).

**Figure A3.10.21** Methane decomposition kinetics on low-index Ni single crystals at 450 K and 1.00 Torr methane [43].

Hydrogenolysis reactions over Ir single crystals and supported catalysts have also been shown to be structure sensitive [52, 54 and 55]. In particular, it was found that the reactivity tracked the concentration of low-coordination surface sites. **Figure A3.10.22** shows ethane selectivity (selectivity is reported here because both ethane and methane are products of butane cracking) for n-butane hydrogenolysis over Ir(111) and the reconstructed surface Ir(110)-(1 × 2), as well as two supported Ir catalysts. There are clear selectivity differences between the two Ir surfaces, with Ir(110)-(1 × 2) having approximately three times the ethane selectivity of Ir(111). There is also a similarity seen between the ethane selectivity on small Ir particles and Ir(110)-(1 × 2), and between the ethane selectivity on large Ir particles and Ir(111).
Figure A3.10.22 Relationship between selectivity and surface structure for n-butane hydrogenolysis on iridium. (a) Illustrations of the Ir(110)-(1 × 2) and Ir(111) surfaces. The z-axis is perpendicular to the plane of the surface. (b) Selectivity for C2H6 production (mol% total products) for n-butane hydrogenolysis on both Ni single crystals and supported catalysts at 475 K. The effective particle size for the single crystal surfaces is based on the specified geometric shapes [43]. □ Ir/Al2O3, □ Ir/SiO2.

The mechanisms by which n-butane hydrogenolysis occurs over Ir(110)-(1 × 2) and Ir(111) are different. The high ethane selectivity of Ir(110)-(1 × 2) has been attributed to the ‘missing row’ reconstruction that the (110) surface undergoes (figure A3.10.22). This reconstruction results in the exposure of a highly uncoordinated C7 site that is sterically unhindered. These C7 sites are capable of forming a metalloccyclopentane (a five-membered ring consisting of four carbons and an Ir atom) which, based on kinetics and surface carbon coverages, has been suggested as the intermediate for this reaction [56, 57]. It has been proposed that the crucial step in this reaction mechanism over the reconstructed (110) surface is the reversible cleavage of the central C–C bond. On the other hand, the hydrogenolysis of n-butane over Ir(111) is thought to proceed by a different mechanism, where dissociative chemisorption of n-butane and hydrogen are the first steps. Then, the adsorbed hydrocarbon undergoes the irreversible cleavage of the terminal C–C bond. It is evident that surface structure plays an important role in hydrogenolysis reactions over both nickel and iridium surfaces.

(C) CO OXIDATION: 2CO+O2 → 2CO2

The oxidation of CO to CO2, which is essential to controlling automobile emissions, has been extensively studied because of the relative simplicity of this reaction. CO oxidation was the first reaction to be studied using the surface science approach and is perhaps the most well understood heterogeneous catalytic reaction [58]. The simplicity of CO oxidation by O2 endears itself to surface science studies. Both reactants are diatomic molecules whose adsorption...
on single-crystal surfaces has been widely studied, and presumably few steps are necessary to convert CO to CO₂. Surface science studies of CO and O₂ adsorption on metal surfaces have provided tremendous insight into the mechanism of the CO–O₂ reaction. The mechanism over platinum surfaces has been unequivocally established and the reaction has shown structure insensitivity over platinum [59], palladium [55, 59, 60] and rhodium surfaces [61, 62].

Although dissociative adsorption is sometimes observed, CO adsorption on platinum group metals typically occurs molecularly and this will be the focus of the following discussion. Figure A3.10.23 illustrates schematically the donor–acceptor model (first proposed by Blyholder [63]) for molecular CO chemisorption on a metal such as platinum. The bonding of CO to a metal surface is widely accepted to be similar to bond formation in a metal carbonyl. Experimental evidence indicates that the 5σ highest occupied molecular orbital (HOMO), which is regarded as a lone pair on the carbon atom, bonds to the surface by donating charge to unoccupied density of states (DOS) at the surface. Furthermore, this surface bond can be strengthened by back-donation, which is the transfer of charge from the surface to the 2π* lowest unoccupied molecular orbital (LUMO). An effect of this backbonding is that the C–O bond weakens, as seen by a lower C–O stretch frequency for adsorbed CO (typically ~2100 cm⁻¹) than for gas phase CO (2143 cm⁻¹).

![Figure A3.10.23](image)

Figure A3.10.23 Schematic diagram of molecular CO chemisorption on a metal surface. The model is based on a donor–acceptor scheme where the CO 5σ HOMO donates charge to surface unoccupied states and the surface back-donates charge to the CO 2π LUMO [58].

Ultraviolet photoelectron spectroscopy (UPS) results have provided detailed information about CO adsorption on many surfaces. Figure A3.10.24 shows UPS results for CO adsorption on Pd(110) [58] that are representative of molecular CO adsorption on platinum surfaces. The difference result in (c) between the clean surface and the CO-covered surface shows a strong negative feature just below the Fermi level (E_F), and two positive features at ~8 and 11 eV below E_F. The negative feature is due to suppression of emission from the metal d states as a result of an anti-resonance phenomenon. The positive features can be attributed to the 4σ molecular orbital of CO and the overlap of the 5σ and 1π molecular orbitals. The observation of features due to CO molecular orbitals clearly indicates that CO molecularly adsorbs. The overlap of the 5σ and 1π levels is caused by a stabilization of the 5σ molecular orbital as a consequence of forming the surface–CO chemisorption bond.
Figure A3.10.24 UPS data for CO adsorption on Pd(110). (a) Clean surface. (b) CO-dosed surface. (c) Difference spectrum (b-a). This spectrum is representative of molecular CO adsorption on platinum metals [58].

The adsorption of O₂ on platinum surfaces is not as straightforward as CO adsorption because molecular and dissociative adsorption can occur, as well as oxide formation [58]. However, molecular adsorption has been observed only at very low temperatures, where CO oxidation rates are negligible, hence this form of adsorbed oxygen will not be discussed here. UPS data indicate dissociative adsorption of O₂ on platinum surfaces at temperatures >100 K, and isotopic exchange measurements support this finding as well. The oxygen atoms resulting from O₂ dissociation can be either chemisorbed oxygen or oxygen in the form of an oxide. The two types of oxygen are distinguished by noting that oxide oxygen is located beneath the surface (‘subsurface’) while chemisorbed oxygen is located on the surface.

Experimentally, the two types of oxygen are discernible by AES, XPS and UPS. In general, it has been found that as long as pressure and temperature are kept fairly low, the most likely surface oxygen species will be chemisorbed. Therefore, when formulating a mechanism for reaction under these general conditions, only chemisorbed oxygen needs to be considered.
The mechanism for CO oxidation over platinum group metals has been established from a wealth of data, the analysis of which is beyond the scope of this chapter. It is quite evident that surface science provided the foundation for this mechanism by directly showing that CO adsorbs molecularly and O$_2$ adsorbs dissociatively. The mechanism is represented below (* denotes an empty surface site):

$$\text{CO} + {}^* \leftrightarrow \text{CO}_{\text{ad}}$$

$$\text{O}_2 + 2^* \rightarrow 2\text{O}_{\text{ad}}$$

$$\text{O}_{\text{ad}} + \text{CO}_{\text{ad}} \rightarrow \text{CO}_2 + 2^*.$$ 

The first step consists of the molecular adsorption of CO. The second step is the dissociation of O$_2$ to yield two adsorbed oxygen atoms. The third step is the reaction of an adsorbed CO molecule with an adsorbed oxygen atom to form a CO$_2$ molecule that, at room temperature and higher, desorbs upon formation. To simplify matters, this desorption step is not included. This sequence of steps depicts a Langmuir–Hinshelwood mechanism, whereby reaction occurs between two adsorbed species (as opposed to an Eley–Rideal mechanism, whereby reaction occurs between one adsorbed species and one gas phase species). The role of surface science studies in formulating the CO oxidation mechanism was prominent.

CO oxidation by O$_2$ is a structure-insensitive reaction over rhodium catalysts [61, 62]. Figure A3.10.25 illustrates this structure insensitivity by demonstrating that the activation energies over supported Rh catalysts and a Rh(111) single crystal (given by the slope of the line) were nearly identical. Furthermore, the reaction rates over both supported Rh/Al$_2$O$_3$ and single crystal Rh (111) surfaces were also remarkably similar. Thus, the reaction kinetics were quite comparable over both the supported metal particles and the single crystal surfaces, and no particle size effect (structure sensitivity) was observed.

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Figure A3.10.25 Arrhenius plots of CO oxidation by $O_2$ over Rh single crystals and supported Rh/Al$_2$O$_3$ at $PCO = PO_2 = 0.01$ atm [43]. The dashed line in the figure is the predicted behaviour based on the rate constants for CO and $O_2$ adsorption and desorption on Rh under UHV conditions.

The study of catalytic reactions using surface science techniques has been fruitful over the last 30 years. Great strides have been made towards understanding the fundamentals of catalytic reactions, particularly by bridging the material and pressure gaps. The implementation of in situ techniques and innovative model catalyst preparation will undoubtedly shape the future of catalysis.

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