Cambridge University Press
978-1-107-02310-9 — Modern Techniques of Surface Science
D. Phil Woodruff
Excerpt
More Information

1

Introduction and General Background Concepts

1.1 Why Surfaces?

The growth in the study of solid surfaces and in the number of techniques available for their study has been enormous since the early 1960s. At least one reason for this has been a growing awareness of the importance of understanding surface properties, and indeed the fact that work on surfaces has had an impact on this understanding and on specific applications in the ‘real world’. At a fundamental level, surfaces are of great interest because they represent a rather special kind of defect in the solid state; much of our understanding of solids is based on the fact that they are, in essence, perfectly periodic in three dimensions. Indeed, their electronic and vibrational properties can be described in great detail using methods that rely on this periodicity. The introduction of a surface breaks this periodicity in one direction and can lead to structural changes as well as the introduction of localised electronic and vibrational states. Gaining a proper understanding of these effects is not only an academic concern as there is growing interest in the properties of low-dimensional structures in semiconductor devices, and a free surface can represent the simplest case of such a structure.

Perhaps the most widely quoted motivation for modern surface science is the goal of understanding heterogeneous catalysis. The greatly increased rates of certain chemical interactions that occur in the presence of a solid (usually powder) catalyst must result from the modification of at least one of the constituent chemicals adsorbed on the solid surface, which thereby gains an enhanced ability to interact with the other constituent(s) while in this state. One would therefore like to understand what these modifications are, whether there are new intermediate species formed, what are the rate-limiting steps and activation energies, what kind of sites on the catalyst surface are active and how these processes depend on the catalyst material. This might lead to better or cheaper catalysts; at present many such catalysts are based on precious metals such as platinum and palladium.

Cambridge University Press
978-1-107-02310-9 — Modern Techniques of Surface Science
D. Phil Woodruff
Excerpt
More Information

The problems of understanding these processes in a microscopic or atomistic way are formidable. Industrial processes frequently operate at high temperatures and pressures (i.e. many atmospheres) and the catalysts are in the form of highly dispersed powders, possibly with individual particles comprising only hundreds of atoms. Moreover, they frequently involve transition metals on oxide 'supports' that may or may not be passive, and they may include small additions of 'promoters' that greatly enhance the efficiency of the catalysts.

The scientific approach to addressing these questions, which makes the fullest use of the techniques described in this book, is to study highly simplified versions of these problems. This involves initially taking flat, usually low-Miller-index, faces of single crystals of the material of interest and studying the adsorption or coadsorption of small quantities of atoms and molecules on them in an otherwise ultra-high-vacuum (UHV) environment. The objective of this approach is to characterise the surfaces and the associated adsorption and reaction processes in fine detail so that the conditions are very well defined. It is easy to see reasons why this approach may be too far removed from applied catalytic problems to be of real value, yet even in the early 1980s some understanding of simple catalytic reactions at a microscopic level had started to emerge from these model studies (King & Woodruff, 1982). Since then, problems of increasing complexity have been explored with significant success, although there is also growing interest in trying to extend some methods to higher 'near-ambient' pressures. The objective here is to bridge the 'pressure gap' that exists in those cases in which the fundamental processes at low and high pressure have been found to differ.

Another area of interest in surface science is to understand the corrosion of materials and certain kinds of mechanical failure due to grain boundary embrittlement. One important process in these problems is of the segregation of minority ingredients (often impurities) in a solid to the free surface, or to internal surfaces (grain boundaries), when the temperature is high enough to allow diffusion through the bulk at a reasonable rate. Some specific species can find it very energetically favourable to be in one of these surface sites rather than in the bulk, so that a bulk concentration of even a few parts per million can lead to surfaces or interfaces covered with a complete atomic layer of the segregant in equilibrium. Segregation of this kind is now well established as being a cause of intergranular fracture of engineering materials. On the other hand, similar segregation to free surfaces can have the effect of improving resistance to corrosion. Studies in this broadly metallurgical area have proceeded not only by the simplified model investigations described above but also by applying surface science techniques to investigate the surfaces of 'real' materials of interest. In particular, by determining the composition of the top few atomic layers of a fractured or corroded surface, considerable information can be gained. To do this, one requires techniques which are highly surface specific in their

Cambridge University Press
978-1-107-02310-9 — Modern Techniques of Surface Science
D. Phil Woodruff
Excerpt
More Information

analytic capabilities. Coupled with a method of removing atomic layers in a reasonably controlled fashion, usually by ion bombardment, a depth profile of the surface and subsurface composition can be obtained.

A further area of application of surface studies that lies particularly close to the fundamental problems mentioned at the beginning of this section concerns the fabrication of semiconductor devices. Although there are applications for depth profiling on actual devices for the 'troubleshooting' of production problems (due to contamination or interdiffusion at interfaces), there are also problems of quite fundamental importance which lie naturally quite close to the modelling approach used in catalytically motivated research. For example, the formation of metal–semiconductor junctions with desirable properties is strongly influenced by the tendency for chemical interactions to occur between the metal and the semiconductor. Many real devices are based on well-oriented single-crystal materials, so this aspect of the modelling is no longer idealised. Moreover, in the case of semiconductor surfaces some of the simplest problems remain far from trivial to solve. Most semiconductor surfaces appear to involve some structural rearrangement of the atoms relative to a simple extension of the bulk structure. For example, the stable structure of a clean Si{111} surface reconstructs to a 'superlattice' seven times larger in periodicity than the bulk (this superlattice is a (7×7) structure in the notation described in section 1.7). A proper quantitative understanding of this complex reconstruction proved to be one of the key problems of basic surface science in the early years, but by the late 1980s a rather clear picture had emerged by the use of a combination of methods (of which high energy electron diffraction, a method not normally used in surface studies, and scanning tunnelling microscopy (STM) played a key role). Simpler reconstructions also occur at some semiconductor surfaces. Even in the case of the {110} cleavage faces of III–V compounds such as GaAs, at which there is no change in the two-dimensional periodicity of the surface, there is a rearrangement in bond angles influencing the relative positions of the Ga and As layers. Finally, it is notable that there is continuing interest in the growth of semiconductor devices by methods such as molecular beam epitaxy (MBE) that are similar to those used in surface science generally (UHV and 'adsorption' at very low rates). The surface structures formed during MBE can be very complex and highly sensitive to the stoichiometry of the uppermost layer. Growth studies also reveal that many materials will not grow in a layer-by-layer form on certain other layers. These limitations in 'atomic engineering' need to be understood properly if exotic multilayer devices are to be designed and built.

The development of atomic-scale imaging methods of surfaces as part of the surface science armoury has also led to an increasing impact in the study of nanoscience and nanomaterials. The properties of solids and surfaces on the nanometre scale (as in traditional heterogeneous catalysts but also increasingly in modern nano-engineered materials) are often fundamentally different from those of extended solids, owing to the dominance of the surface and to quantum size effects.

This book is concerned with the analytical techniques which have contributed, and should continue to contribute, to understanding these problems. It is concerned with the basic underlying physical principles of the techniques and the extent to which those principles constrain their usefulness. As such, it is not intended to be an experimental handbook for surface analysis but rather to provide the background of physical understanding that allows the techniques to be used and assessed properly. Some experimental details are given, but only to aid in understanding the strengths and limitations of individual techniques. During almost 50 years in the development of modern surface science a large number of novel methods have been explored; the focus here is on those techniques that continue to play a significant role in surface studies.

A few preliminary comments are in order regarding units. In general, SI units are adopted in this book; hence the decision in this edition to express vacuum pressures in mbar rather than torr as a unit of pressure (see section 1.3). However, this adherence to SI units will be allowed to lapse in the expression of lengths to more intuitive or convenient units. Typical samples have dimensions of ~1 cm^2, so surface coverages will be expressed in terms of a number per cm^2 rather than per m^2, while interatomic spacings and layer spacings will be expressed in ångströms, arguably a more natural unit than the nearest SI unit, nanometres (1 Å = 0.1 nm).

1.2 Ultra-High Vacuum (UHV), Contamination and Cleaning

If one is to study the properties of a surface that are well characterised at an atomic level it is clear that the composition of the surface must remain essentially constant over the duration of a measurement. In order to achieve this, the rate of arrival of reactive species from the surrounding gas phase must be low. A reasonable criterion would be that no more than a few per cent of an atomic layer of atoms should attach themselves to the surface from the gas phase in, say, an experimental time scale of about one hour. This requirement can be evaluated readily from the simple kinetic theory of gases. Thus, the rate of arrival of atoms or molecules from a gas of number density n per unit volume and with an average velocity c_a is

$$r = \frac{1}{4} n c_a \tag{1.1}$$

Equating the kinetic energy of a particle of mass m with root mean square velocity c_{rms} to its thermal energy, determined by the absolute temperature T and Boltzmann's constant k_B, gives

$$c_{\rm rms}^2 = 3k_{\rm B}T/m \tag{1.2}$$

Combining the relationship between the two velocities,

$$c_{\rm a} = (8/3\pi)^{1/2}c_{\rm rms} \tag{1.3}$$

with the fact that the pressure P is given by

$$P = nk_{\rm B}T \tag{1.4}$$

then leads to an expression for the rate of arrival:

$$r = P(1/2\pi k_{\rm B}Tm)^{1/2} \tag{1.5}$$

A convenient form of this expression, in which P is expressed in mbar, T is in K and m is substituted by the molecular weight M multiplied by the atomic mass unit, gives

$$r = 2.66 \times 10^{22}P/(TM)^{1/2} \tag{1.6}$$

with r in molecules cm^{-2} s^{-1}. For example, N_2 molecules ($M = 28$) at room temperature ($T = 293$ K) in a pressure of 1 mbar have an arrival rate of 2.95×10^{20} molecules cm^{-2} s^{-1}.

It is convenient to define a *monolayer* adsorption time in terms of the pressure. In defining this it is assumed that a monolayer, i.e. a single complete atomic layer, consists of about $(1–2) \times 10^{15}$ atoms cm^{-2} and that all molecules arriving at the surface stick and are incorporated into this monolayer. Thus, for this example, the monolayer time is about 4×10^{-6} s at 1 mbar, 4 s at 10^{-6} mbar and more than 1 hour at 10^{-9} mbar. This means that if all the gas atoms and molecules arriving at a surface in a vacuum system do indeed stick to it, then the contamination of a few per cent of a monolayer in an experimental time of 1 hour requires a low pressure of 10^{-10} mbar or better. While these are broadly worst-case assumptions, some surfaces of interest do react readily with H_2 and CO, the main ingredients of a UHV chamber, and so match these conditions. An ultra-high vacuum is therefore required to keep a surface in its clean or otherwise well-characterised condition once produced. Indeed, the need for a good vacuum can also extend to the kind of depth profiling study of technical surfaces described in the previous section. In these cases a sample is initially analysed 'as loaded' so that the surface composition is dominated by contamination from being handled in air and is uninfluenced by the quality of the surrounding vacuum in the analysis chamber. However, once surface layers have been removed in the depth profiling, the freshly exposed surface is susceptible to new contamination and must be studied in a good-quality vacuum.

Cambridge University Press
978-1-107-02310-9 — Modern Techniques of Surface Science
D. Phil Woodruff
Excerpt
More Information

A detailed discussion of the methods for achieving UHV is not appropriate to this book and can be found in many volumes concerned specifically with vacuum technology (e.g. Delchar, 1993; Chambers *et al.*, 1998; Chambers, 2005). A few points of general interest are worth noting, however. The first is that a major reason for the development of modern surface science research in the 1960s, in addition to those given in the previous section, is the commercial availability of convenient UHV components since that time and their subsequent development. Early surface science experiments were carried out in glass vacuum systems using liquid N_2 trapped Hg diffusion pumps. The surface science instrumentation had to be incorporated into these sealed glass vessels with electrical connections made through glass-to-metal seals in the containment vessel. Modern surface science studies usually involve the use of many different techniques in the same vessel, each of which may be quite sophisticated, and this is achieved by mounting each onto a stainless steel flange sealed to a stainless steel chamber using Cu gaskets or Au wire seals. This gives great flexibility and demountability for installation, modification and maintenance; it is hard to see how the current level of sophistication of some surface science experiments could have been achieved realistically with glass systems. In addition to the development of these demountable metal vessels, great use is now made of ion pumps and turbomolecular pumps, which require only electrical power to function and do not need liquid N_2 cooling and the regular attention that this implies.

The second general point regarding UHV is the constraints on fabrication methods necessary for instrumentation within the vacuum. Although one must use vacuum pumps capable of operating in the 10^{-10}–10^{-11} mbar range, an important ingredient in obtaining UHV is the need to ‘bake’ the whole system. In the absence of leaks and with suitable pumps, vacua are limited by the ‘outgassing’ of the inner walls and instrument surfaces within the chamber, mainly due to the desorption of weakly adsorbed gases from these surfaces. By heating all these surfaces the rate of desorption is increased and the surface coverage decreased, and thus the rate of desorption on the subsequent cooling to room temperature is reduced. This reduces the gas load on the pumps and thus allows lower pressures to be achieved. Typically, a stainless steel chamber with all its enclosed instrumentation is baked at temperatures of ~140–200 °C for 12–24 hours. Obviously this means that all components in the vacuum chamber must be stable and have low vapour pressures at these elevated temperatures. An additional common requirement for the experiments described in this book is that all components must be non-magnetic as many surface techniques involve low energy electrons, which are easily deflected by weak electrostatic and magnetic fields. Fabrication methods compatible with these requirements are now well established, involving mainly the use of non-magnetic stainless steel and refractory metals, together with ceramics for electrical or thermal insulation. Many materials that are acceptable in a ‘high vacuum’ (~10^{-6} mbar), such as some adhesives and plastics, are not acceptable in UHV.

While UHV guarantees that a surface should not be influenced by the arrival of ambient atoms and molecules from the residual gas phase on a time scale of the order of one hour or more, a further requirement for studies of the properties of ideal surfaces is to be able to clean them, in the vacuum system, to a level compatible with the same contamination constraints as those that define the required vacuum; i.e. one must produce a surface which contains no more than a few per cent (and preferably less) of an atomic layer of species other than those that comprise the underlying bulk solid. Generally, the surface should also be well ordered on an atomic scale. The main methods used to achieve this *in situ* cleaning are

(i) cleavage,
(ii) heating,
(iii) ion bombardment,
(iv) chemical processing.

The first of these is largely self-explanatory; for those materials which do cleave readily (e.g. oxides, alkali halides, semiconductors, layer compounds), and for studies of the surface orientation which comprises the cleavage face, surfaces can be prepared in vacuum that are intrinsically clean. Apart from the limitations on the materials and orientations that can be prepared in this way, a significant problem with the method is that it is usually only possible to cleave a single sample (even a long bar) a few times, so the surface cannot be re-prepared many times. It is also possible that cleavage may result in a heavily stepped surface. As a result, large variations in the properties of a surface (particularly the adsorption kinetics) may be obtained from one cleave to the next on many materials. Moreover, on some materials the cleavage surface is found to have a different structure from that obtained by heating to allow the surface to equilibrate; the Si{111} surface is an example of this.

Heating a surface, like heating the walls of a vacuum vessel, can lead to the desorption of adsorbed species. However, in most cases some impurities on the surface are too strongly bound to be removed by heating to temperatures below the melting point of the sample. Heating as a method of cleaning has been used mostly for W and similar high melting point materials, for which the surface oxides are flashed off below the melting point of the underlying metal. Even for these materials, however, it is unlikely that the method can be totally satisfactory owing to impurities such as C, which form exceedingly strongly bound compounds with the substrate material. Once this kind of impurity has been removed, however,

Cambridge University Press
978-1-107-02310-9 — Modern Techniques of Surface Science
D. Phil Woodruff
Excerpt
More Information

heating alone may be sufficient to regenerate a clean surface following an adsorption experiment using the more weakly bound adsorbate species. This surface regeneration by heating may be applicable to many materials for which heating alone is totally ineffective in the initial cleaning process.

The use of inert-gas (usually Ar) ion bombardment of a surface to remove layers of the surface by sputtering is by far the most widely used primary method, particularly for metal surfaces. The actual physics of this process and the yields obtained are discussed in Chapter 2. The technique is effective in the removal of many atomic layers of a surface and, even if an impurity species is far less effectively sputtered than the substrate, it can generally be removed eventually. One disadvantage of ion bombardment, typically at energies of 0.5–5.0 keV, is that the surface is left in a heavily damaged state, with many atoms statically displaced from their crystalline sites and usually also with embedded Ar atoms; the surface must then be annealed to restore the order. This in itself can create problems; as was noted in the previous section, many dilute impurity species in the bulk of a solid will segregate preferentially to the free surface so if a sample with a clean surface is heated, the diffusion rates are increased and further segregation can occur; typical segregants found in transition metals, even of very high average purity, are C and S. This then requires further ion bombardment cleaning, further annealing and so on. In practice a number of cycles (sometimes as many as ten or more) of bombardment and annealing do lead to the depletion of segregating impurities in the subsurface region and thus to a clean surface. Far fewer cycles are then required for re-cleaning the sample after adsorption studies.

The final approach of chemical cleaning *in situ* involves the introduction of gases into the vacuum system at low pressures ($\sim 10^{-6}$ mbar or less) that react with impurities on a surface to produce weakly bound species, which can then be thermally desorbed. This method is most widely used for the removal of C from refractory metals such as W that can be cleaned of most other impurities by heating alone. Exposure of such a surface to O_2 at elevated temperatures leads to the removal of C as desorbed CO, leaving an oxidised surface that can then be cleaned by heating alone.

1.3 Adsorption at Surfaces

Although several techniques described in this book are applicable to the surface analysis of a wide variety of practical materials problems, the emphasis of the presentation is on applications of the 'surface science method', i.e. studies of well-characterised low index single-crystal surfaces and adsorption of atoms and molecules on them. It is therefore helpful to define some terms and units that will be used in later chapters. The first of these is the definition of a *monolayer* of

Cambridge University Press
978-1-107-02310-9 — Modern Techniques of Surface Science
D. Phil Woodruff
Excerpt
More Information

adsorbate. One way of defining the coverage of a surface at monolayer level – i.e. of a single complete atomic or molecular layer – is in terms of the coverage of a two-dimensional close-packed layer, taking account of the atomic or molecular size. Such a definition is frequently used in studies of polycrystalline surfaces. However, on surfaces of well-defined crystallography it is generally more convenient to use a definition based on the atomic density of packing in the surface itself. Therefore, unless explicitly stated otherwise, a monolayer of adsorbed atoms or molecules will be defined as a layer having a number density equal to that of the atoms in a single atomic layer of the substrate material parallel to the surface. In the absence of reconstruction, this is, of course, the same as the number density of atoms in the top atomic layer of the substrate. Frequently the saturation of a particular adsorbate species occurs at a coverage of less than one monolayer, so the definition implies nothing about the maximum possible coverage, which depends on the adsorption system under study.

A second definition concerning adsorption studies is the need for a unit of exposure. The unit which had become firmly established in the literature is the langmuir (abbreviated as L), defined as 1 L = 10^{-6} torr s exposure. Unfortunately it is more usual nowadays for pressures to be quoted not in torr (1 torr = 1 mm mercury =1.333 mbar) but in mbar, so 1 L is often (implicitly rather than explicitly) redefined as 10^{-6} mbar s. These two definitions are not, of course, equivalent. Because of this ambiguity, exposures in this book will be given only in units of 10^{-6} mbar s. A major disadvantage of the langmuir unit (and also the unit used here, 10^{-6} mbar s) is that, as may be readily appreciated from equation (1.6), the actual number of atoms or molecules arriving at a surface in 1 L of exposure depends on the molecular weight of the gaseous species and its temperature. Table 1.1 illustrates the effect of this variation, showing the number of molecules striking 1 cm^2 of surface in 1 L with a gas temperature of 300 K. Also shown here is the coverage, in monolayers, which would result if all the molecules arriving were to stick on a Ni{100} surface, with dissociative adsorption assumed for H_2, O_2 and I_2. Despite this disadvantage of the L unit (or its mbar s equivalent), there is no doubt that it is experimentally convenient, as most researchers performing an exposure are equipped with an ion gauge (calibrated in mbar or torr) and a stopwatch! It provides a convenient unit for characterising the exposures needed to produce certain adsorption states on a surface and allows some transferability between experimenters working on the same adsorption system. It also is a unit of convenient magnitude in that, as Table 1.1 shows, 1 L corresponds to approximately one monolayer coverage if all molecules stick to the surface. A proposal for a unit based on the actual number of impinging molecules (Menzel & Fuggle, 1978) failed to gain any long-term support. One further point that is worth mentioning in the context of Table 1.1 is the question of sticking probabilities.

Cambridge University Press
978-1-107-02310-9 — Modern Techniques of Surface Science
D. Phil Woodruff
Excerpt
More Information

Table 1.1 *Effect of 1 L (10^{-6} torr s) exposure of different adsorbates at 300 K*

Incident and adsorbing species	No. of molecules arriving (cm^{-2})	Coverage on Ni{100} with unit sticking probability (monolayers)
H_2 adsorbing as H	1.43×10^{15}	1.80
O_2 adsorbing as O	3.58×10^{14}	0.44
CO adsorbing as CO	3.83×10^{14}	0.24
I_2 adsorbing as I	1.27×10^{14}	0.16

The final column of Table 1.1 was constructed assuming that all impinging molecules stick to the surface (i.e. that the 'sticking probability' is unity) independent of coverage. In fact this would represent a relatively unusual state of affairs. As the coverage increases, some molecules arriving at the surface will land at sites already occupied by adsorbed species, rather than at vacant clean surface sites. Assuming that these also stick (and then may diffuse over the surface to empty surface sites) actually involves assuming that second layer adsorption (albeit possibly more weakly bound and transient) is possible. An alternative possibility, that the molecules arriving at occupied sites are not adsorbed, leads to an average sticking probability that falls exponentially with time. This *Langmuir adsorption* is one of several possible forms of adsorption kinetics discussed in many books on adsorption (e.g. Hayward & Trapnell, 1964; Masel, 1996; Kolasinski, 2012) and will not be discussed further here. The measurement of sticking probabilities, however, will be considered in Chapter 6. Notice that exposures given in langmuirs (or in 10^{-6} mbar s) that are based on ion gauge readings of total chamber pressures are unlikely to be very reliable for any serious study of adsorption kinetics, owing to difficulties in establishing the pressure at the sample and the need for ion gauge calibration for different gases. For similar reasons, exposures determined in this way using different chambers in different laboratories may lead to variations of a factor 2 or more in the (apparent) exposures needed to obtain particular adsorption states.

Finally, in this book many examples of adsorption systems chosen to illustrate the application of specific techniques may be referred to as involving *chemisorbed* or *physisorbed* atoms or molecules. The distinction between these two types of adsorption lies in the form of the electronic bond between the adsorbate and substrate. If an adsorbed molecule suffers significant electronic modification, relative to its state in the gas phase, to form a chemical bond with the surface (covalent or ionic) then it is said to be chemisorbed. If, however, it is held to the surface only by van der Waals' forces, relying on the polarisability of the otherwise undisturbed molecule, then it is said to be physisorbed. Clearly physisorption