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Chapter 1

Introduction

1.1 Why are surfaces important?

The Nobel Prize winner Wolfgang Pauli's statement, 'God made solids, but surfaces were the work of the devil!' emphasizes the diabolic nature of surfaces. Surfaces are external borders of the materials to the external world, and by exploring surfaces one can investigate the material. However, surface properties deviate significantly from the bulk solid state: this is why surface studies are both puzzling, misleading and quite exciting! At a fundamental level, surfaces are of great interest as they can be considered special defects of the bulk material. Introduction of the surface breaks an ideal periodicity in three dimensions, leading to structural changes, introduction of new electronic and vibrational states. In the last few decades, new and exciting surface properties have been explored in nanomaterials, low-dimensional structures in electronic and photonic devices and other numerous applications.

The most widely claimed motivations for surface science are in understanding the processes in heterogeneous catalysis. The mechanisms of surface reactions, product formations and the nature of its adsorption are very important questions that can be addressed with surface sensitive techniques. One would infer the rate limiting steps and reactive adsorption sites, and activation energies. These studies lead to more effective or cheaper catalysts; many such catalysts are based on precious metals, such as platinum and palladium. Real catalysts frequently consist of nm-sized (1–100 nm) metal particles deposited on the internal surface of a more or less inactive porous support. The complexity of such systems in combination with relatively high (atmospheric) reactant pressures, typical for practical catalysis, hinders the application of surface science methods to their full potential and makes it difficult to interpret the measured reaction kinetics on the basis of kinetic data for single-crystal samples [1]. One difficulty in relating surface science measurements to those in catalysis is that real catalysis performs under significantly higher pressure conditions. The difference in pressures of 8–11 orders of magnitude between the two may result in different behavior. The 'pressure gap' is beginning to close as many

technologies have been developed to use atmospheric and high-pressure *in situ* cells in combination with different incident probes.

Many recent studies have focused on the relationship between nanoparticle size, and shape [2], decoration with organic molecules [3] and achieving desired materials' functionalities, taking into account specific surface chemistry, molecular assemblies and connecting structure–property relationships. Notable similar experiments on adsorption of gases and surfactant adsorption on surfaces were conducted a century ago by Irving Langmuir with his experiments on gas adsorption on surface planes of glass, mica and platinum metal [4]. Shortly after, Langmuir and Katharina Blodgett explored two-dimensional (2D) monomolecular films and found the way to form a monomolecular layer of amphiphilic compound on the liquid (water) surface and then transfer it to a solid substrate. Their work became the foundation of the Langmuir–Blodgett method widely used in the production of electronic devices, rheology. The measurements of the adsorption of gases in multiple layers by Brunauer, Emmet and Teller [5] laid the foundation of a current standard BET method to determine the specific surface area of materials. Due to developments in the methods to characterize structure, electronic properties and surface layer energies, we now have a much better understanding of these structures and phenomena.

A different area of applications of surface studies is related to surface chemistry and the fabrication of semiconductor devices. Some significant milestones in this field should be mentioned. C J Davisson and L H Germer used vacuum tubes in electron diffraction work (Nobel Prize in 1937). In the 1950s, John Bardeen, William Shockley and Walter Brattain (Bell Labs) invented the transistor (Nobel Prize in 1956). In the formation of a p–n junction in transistors, for instance, the formation of metal–semiconductor junctions with desirable properties is strongly influenced by the chemical interactions between the metal and semiconductor. In the 1960s, the first electron and Auger spectroscopy instruments were developed. Grover and Goldstein marked a distinction between a 'real' surface and a 'clean' surface.

Many devices are fabricated on single-crystal materials; however, the surface may rearrange its atomic position relative to a simple extension of the bulk structure. For instance, the Si (001) surface is the most widely used in the semiconductor industry. The bulk-terminated surface is not stable and can be reconstructed to a 'superlattice' (to be described in section 3.2). Similarly, a clean Si (111) surface reconstructs to a (7×7) structure, seven times larger than the bulk. A proper quantitative under-standing of this complex reconstruction was proven to be one of the key problems of surface science in the 1960s and 1970s, which was finally solved with the develop-ment of vacuum-based techniques and scanning tunneling microscopies (by Binnig and Rohrer in 1986).

This book focuses on several analytical techniques that have contributed, and will further contribute, to the understanding of such problems. We will discuss the basic physical principles of the techniques, their limitations and examples of applications for surface analysis. Before we do that, we need to define the basic 'rules of the

game': if surface structure and composition has to be characterized at an atomic level, the surface must remain constant over the time of the measurement.

1.2 Ultra-high vacuum science and technology

Studies of crystal surfaces are challenging in part because of the necessity to perform experiments under vacuum or, even better, under ultrahigh vacuum (UHV) conditions. Why do we need UHV? The kinetic theory of gases can be used to show that at a pressure of 10^{-6} Torr, it takes ~1 s to form one molecule thick layer (1 ML) if we assume a sticking coefficient of 1. So, for reasonable measurement times, at pressure $p = 10^{-10}$ Torr, it is going to take ~10^4 s or ~2.75 h to form 1 ML. Pressures in 10^{-7}–10^{-10} Torr are described as being at UHV range, and the technology to obtain and maintain these vacuum levels took a long time to develop. Note that the SI unit of pressure is Pascal, Pa: 1 Pa = 1 N m^{-2} = 7.5×10^{-3} Torr = 10^{-2} mbar. In surface science, Torr units have been historically widely used.

There are three interrelated concepts to define vacuum (all related to pressure): molecular density (n, the number of molecules per unit volume), mean free path (λ, average distance between molecular collisions), and time to monolayer (ML) formation, τ_{ML}. Mean free path (average distance traveled between collisions) depends on the size of the molecule, and molecular density (or pressure), and can be expressed by the following equation:

$$\lambda = \frac{1}{\sqrt{2}\,\pi d^2 n} \tag{1.1}$$

where d is the molecular diameter in cm, and n is the number of molecules per cm^3. For air at room temperature, the mean free path (in cm) can be found as approximately $\lambda \sim 0.005/p$ (with p in Torr). With the different molecular masses of gas species taken into account, similar dependencies can be estimated and plotted for typical molecules in vacuum, as illustrated in figure 1.1.
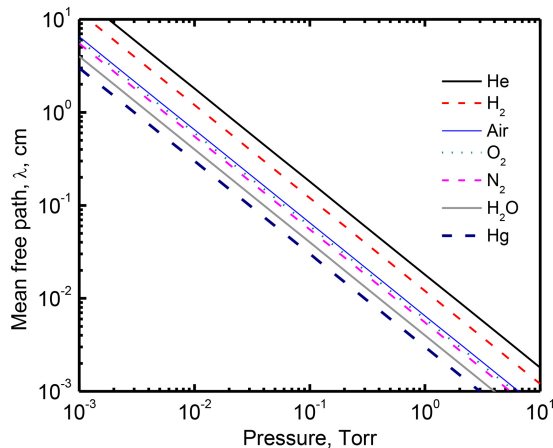

Figure 1.1. Mean free paths for different gases in vacuum.

Table 1.1. Major molecular species at normal atmospheric conditions and in ultra-high vacuum. Data taken from references [6, 7].

Component	Atmosphere		Ultra-high vacuum partial pressure (Torr)
	Percent by volume	Partial pressure (Torr)	
N_2	78.1	5.9×10^2	2×10^{-11}
O_2	20.9	1.6×10^2	–
H_2O	1.57	1.2×10^1	1.3×10^{-10}
Ar	0.93	7.05	6×10^{-13}
CO_2	0.033	2.5×10^{-1}	6.5×10^{-11}
Ne	1.8×10^{-3}	1.4×10^{-2}	5.2×10^{-11}
CH_4	2.0×10^{-4}	1.5×10^{-3}	7.1×10^{-11}
H_2	5.0×10^{-5}	3.8×10^{-4}	1.8×10^{-9}
CO	–	–	1.4×10^{-10}
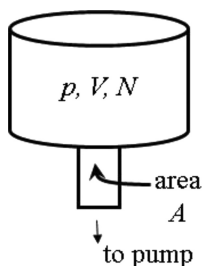
Figure 1.2. Schematic diagram of a vacuum chamber connected to a pump.

Notably, the variety of molecular species will be different when we start pumping out the vacuum chamber, initially at ambient conditions, to a certain level of vacuum, as shown in table 1.1. It is common to use apparatus in the form of large steel chambers with different equipment bolted on using 'knife-edge' flanges that provide a seal by compressing copper or Viton® gaskets. The chambers are pumped out using a combination of vacuum pumps, such as turbomolecular pumps, ion pumps or cryopumps, backed by mechanical or dry forepumps. When an ultra-high vacuum level (better than 10^{-7} Torr) is achieved, the main contributors are often H_2, H_2O, CO and CO_2.

What does determine the vacuum system ultimate (base) pressure and performance? Vacuum system performance is determined by system design (volume, conductance, surface, materials), gas load, Q (surface outgassing and contaminations), system materials (diffusion and permeation), external and internal leaks, as well as pumping speed, S. When molecules strike or pass through an orifice of area A and enter the pump (figure 1.2), the function of the pump is to keep molecules from returning to volume, V.

In order to understand how one can attain ultra-high vacuum conditions, let us consider the parameters relevant to a pumping vacuum chamber. First, we can consider a large ensemble of molecules that occupy a constant volume of the vacuum chamber. We can then apply the ideal gas law:

$$pV = NkT \tag{1.2}$$

where p is pressure, V is volume, N is the number of molecules, k is Boltzmann's constant, $k = R/N_A = 1.38 \times 10^{-23}$ J K^{-1}, and T is temperature. Assuming that T and V are constant, we take the derivative with respect to time, giving

$$\frac{\mathrm{d}p}{\mathrm{d}t} = -\frac{kT}{V}\frac{\mathrm{d}N}{\mathrm{d}t} \tag{1.3}$$

The molecules move in random directions and the average velocity of the molecules is zero (as many molecules are moving in opposite directions to the others). However, the average speed is not zero. Starting from the internal energy U, which can be calculated as consisting of the kinetic energies of the N molecules:

$$U = N\left(\frac{1}{2}m\langle v^2\rangle\right) = \frac{1}{2}N\left(\langle v_x^2\rangle + \langle v_y^2\rangle + \langle v_z^2\rangle\right) = \frac{3}{2}Nm\langle v_x^2\rangle \tag{1.4}$$

The number of collisions with the wall or with area A per unit time is calculated as follows. Consider the number of molecules with x-component of velocity v_x that strike an area A in a time interval $\mathrm{d}t$ is the number of molecules contained in a cylindrical volume $V = Av_x\mathrm{d}t$. If the number of molecules per unit volume is N/V, the number of collisions in time $\mathrm{d}t$ will be half of the total number of molecules in the cylinder, as half of the molecules are moving to the right and half to the left:

$$N_{\mathrm{coll}} = \frac{1}{2}\frac{N}{V}Av_x\mathrm{d}t \tag{1.5}$$

From equation (1.2), we can express the molecular density, n:

$$\frac{N}{V} = \frac{p}{kT} = n \tag{1.6}$$

If we remove the number of molecules per unit time with K as the statistical capture coefficient ($0 < K < 1$):

$$\frac{\mathrm{d}p}{\mathrm{d}t} = -\frac{1}{2}n\frac{kT}{V}KAv_x \tag{1.7}$$

Combining (1.7) and (1.6) gives us

$$\frac{\mathrm{d}p}{\mathrm{d}t} = -\frac{1}{2}\frac{p}{kT}\frac{kT}{V}KAv_x = -\frac{1}{2}\frac{p}{V}KAv_x \tag{1.8}$$

Let us substitute $v_x A K/4 = S$, pumping speed with units of volume/time. Then

$$\frac{dp}{dt} = -p\frac{S}{V} \tag{1.9}$$

A relevant number to consider is a maximum pumping speed for a 1 cm^2 orifice is

$$S(1 \text{ cm}^2) = \frac{4.64 \times 10^4 \times 1 \text{ cm}^2 \times 1}{4} = 11.5 \text{ l s}^{-1}.$$ Now, for a gas leakage inside the enclosed volume

$$\frac{dp}{dt} = \frac{L}{V} \tag{1.10}$$

where L is the leakage rate into the system and for both leakage and pumping:

$$\frac{dp}{dt} = -p\frac{S}{V} + \frac{L}{V} \tag{1.11}$$

At equilibrium, when the leakage rate is the same as the pumping speed $\frac{dp}{dt} = 0$, therefore $p_{eq}\frac{S}{V} = \frac{L}{V}$. Equation (1.11) can be written as

$$\frac{dp}{dt} = -\frac{S}{V}(p - p_{eq}) \tag{1.12}$$

Finally, integrating (1.12) leads to

$$p = p_{eq} + (p_i - p_{eq})\exp\left(-\frac{S}{V}t\right) \tag{1.13}$$

And for $p_i \gg p_{eq}$

$$p = p_i \exp\left(-\frac{S}{V}t\right) \tag{1.14}$$

In real cases, we do not pump through ideal orifices: we need to consider throughput through any conducting element (tube, elbow, etc). We can define conductance, C, as throughput, Q divided by the pressure difference:

$$C = \frac{Q}{p_1 - p_2} \tag{1.15}$$

The conductance is determined by the geometry of the element and is approximated by $C \sim D^3/L$—for a long tube, $C \sim D^2$ (for a zero-length orifice). At steady-state UHV, conductance is constant. When pumping through conducting elements we can apply Ohm's law analog, Q is an analog of current, $\Delta p \sim$ voltage, $C \sim$ conductivity. The effective pumping speed, S, in a chamber connected by conductance C to a pump having pumping speed S_p is given by

$$\frac{1}{S} = \frac{1}{S_p} + \frac{1}{C} \Rightarrow S = C\left[\frac{1}{1 + \frac{C}{S_p}}\right] \tag{1.16}$$

Effectively, conductance reduces pumping speed!

While many vacuum pumps are capable of operating in the 10^{-10}–10^{-11} Torr range, an important step in obtaining UHV is the 'bake' of the whole vacuum system. In the absence of external leaks, the lowest achievable pressure is limited by the outgassing of the inner walls and other surfaces inside the vacuum chamber. This outgassing is mostly due to desorption of weakly adsorbed gases, such as water or hydrocarbon, from these surfaces. The desorption rate is increased during heating at temperatures of ~150 °C for 12–24 h, and on subsequent cooling to room temperature the outgassing rate is lower by several orders of magnitude. Obviously, all of the components and materials in the vacuum chamber must be stable at these temperatures.

What are the general materials considerations to be used in UHV experiments? Vapor pressure is a function of temperature (watch for alloys containing materials with high vapor pressure at working temperature). Typically, all components must be non-magnetic as many surface techniques involve low-energy electrons; as will be described later in this book, electrons can easily be deflected by weak electrostatic and magnetic fields. Many materials that are acceptable in high vacuum (~10^{-6} Torr), such as adhesives, rubber, and Tygon®, are not acceptable in UHV and must be replaced by nylon, Teflon®, silver epoxy, neoprene, or Viton®.

Ultra-high vacuum conditions ensure that a surface is not influenced by the arrival of residual gas molecules within a time frame when the measurement is done. However, for many surface studies it is necessary to start with a clean surface, i.e. a surface which contains no more than a few percent of an atomic layer species other than those in the underlying bulk solid. The main methods used to achieve this is *in situ* cleaning, including cleavage in UHV, heating in vacuum or in a reduced-pressure gas environment, ion bombardment to remove surface contaminations, or a combination of bombardment and heating. For instance, inert gas (Ar, Ne) bombardment can be used to remove layers of surface contaminations by sputtering. The physics of this process, important parameters, and the sputtering yields will be discussed in chapter 7. After ion bombardment, a surface is left in a heavily damaged state. In order to illuminate this damage, the ion bombardment treatment is followed by a heating (annealing) step. During the heating step the diffusion rates are increased and surface order is restored, however, segregation of impurities is not uncommon. This is why, in practice, the sputtering and bombardment steps need to be repeated several times to ensure proper clean surface preparation.

It sounds like vacuum technology is just dealing with flanges, valves and vacuum pumps, but this is also science and technology that enables our high-tech society. Vacuum equipment is utilized for a large number of processes and products, such as light bulbs, microwave and electron tubes, thermos flasks and vacuum-packed coffee. Vacuum technology is essential in the production of computer chips, high-purity metals and various nanometer-scale devices.

1.3 Exercises

1. Calculate the time required for a N_2 molecule to travel a distance equal to its mean free path in a vacuum of 10^{-3} Torr at 300 K.

2. Suppose a $60 \, \text{l s}^{-1}$ turbo pump is connected to a chamber via a straight pipe 3 cm in diameter and 30 cm long. What is the effective pumping speed?

3. A UHV chamber with a volume of $0.8 \, \text{m}^3$ is pumped through a circular tube with a diameter of 20 cm and a length of 20 cm. The ion pump used has a pumping speed of $100 \, \text{l s}^{-1}$. The end pressure reached after baking out the chamber is 7×10^{-11} Torr. What is the gas desorption rate from the walls of the UHV chamber at steady state?

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