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Editor's foreword

Solid-state physics is now a well-established ingredient of the majority of undergraduate physics courses, and it is now possible to give a coherent picture of the chemical composition and structure and of the electrical and thermal properties of condensed matter at a microscopic level. The study of the surfaces of solids often receives little attention in spite of the great importance of the subject for physicists, metallurgists, materials scientists, and electronic engineers. The neglect is to some extent understandable; only in the last decade or so has it been possible to make properly reproducible physical measurements on clean surfaces, and our understanding of the 'surface state' is still much more tenuous than our knowledge of the solid state. Yet it is partly for that reason that surface science is worthy of the attention of science and technology undergraduates; the field is in a state of rapid development, rival theories for various phenomena still abound, and there is the right blend of controversy and consensus to give the student the feeling for what scientific research activity is really like.

Professor Prutton's book emphasizes the physical aspects of the subject — it reviews the physical techniques that are now available to give reliable diagnostics of crystal surfaces — yet it should also have wide interdisciplinary appeal. Case studies of the application of these techniques to important technological surfaces convey clearly the present state of the art. A general background of solid-state physics or chemistry is a necessary prerequisite, but no sophisticated mathematics is needed. The book is suitable as a text for a final-year undergraduate course in physics, chemistry, materials science, or electrical engineering and is ideal initial reading for anyone setting out to do research in this area or wishing to have a general view of the field.

The solid state by H. M. Rosenberg (OPS 9) provides an ideal base for Professor Prutton's book, though the more qualitative background given in *Atoms in contact* by B. R. Jennings and V. J. Morris (OPS 5) is sufficient for much of the material.

J.A.D.M.

Preface to the second edition

In bringing the book more up to date, after the seven years of intense international activity in all aspects of surface science which have passed since I wrote the first edition, I have been faced with an even larger number of difficult choices as to just what to omit. In the spirit of the first edition I have tried to keep the book short in order to reduce the costs so that students could actually afford to buy it. Inevitably, this has resulted in omitting descriptions of techniques and results which will be dear to many people's hearts. Thus I have left out discussion of electron and photon stimulated desorption, and the impact of modern surface methods upon the understanding of catalytic and corrosion processes and I have cut down quite ruthlessly what is a really gargantuan literature on angle-resolved photoemission. Of course, I hope that, by doing so, I have achieved an interesting and reasonable balance of topics and that the references cited will lead usefully into the formidable literature of the subject.

I am particularly grateful to Dr. R. G. Forbes of the Department of Physics, University of Aston in Birmingham who took the trouble to write to me with a number of useful and constructive criticisms about the first edition. I have incorporated most of his suggestions. Also, I am grateful to Dr. J. A. D. Matthew for critical reading of the new material in this edition and Rhona Adams for her secretarial help. Dr. A. Joshi, Perkin-Elmer, Mountain View, California kindly provided the beautiful Auger micrographs in Fig. 2.14.

September 1982

M.P.

Preface to the first edition

The last ten years have seen an enormous growth in many aspects of surface science. Physicists, chemists, and metallurgists have directed their attention to measuring and understanding phenomena at surfaces, all with a view to being able to describe processes which are scientifically interesting or technologically significant. The technological drive required to understand the processes of catalysis and oxidation and to help manufacture semiconductor devices with higher yields has boosted activity in the field enormously. As this book is written this pressure has resulted in the application of a wide variety of new techniques to surface problems but, as yet, it is too early to see whether real progress will be made in understanding such complex processes as catalysis and corrosion. Nevertheless, large strides have been made both in the development of sophisticated techniques with appropriate sensitivities for surface studies and in the initial stages of the understanding the application of these techniques to the measurement of the properties of the surface of simple solids.

This book is based upon a lecture course for final-year Physics undergraduates and new postgraduates. It is intended not to be so comprehensive that the student could read it and go away and start research, but rather to act as a broad introduction to a large subject. Thus, an attempt has been made to describe why surface studies are important scientifically and technologically, what techniques are available and how they compare with each other and with bulk methods, and what types of problems have been and are being tackled. Chapters 2 and 3 are concerned mainly with techniques for the determination of what kinds of atoms are present on a surface and how they are arranged in space in relation to each other. Chapter 4, 5, and 6 then deal largely with selected case studies of particular systems chosen so as to illustrate the application of the techniques to problems concerning respectively the electronic, vibrational, and adsorptive properties of surfaces. The references given to further reading are mainly to other books or to review papers, but it is hoped that this will be sufficient to provide a useful entry to the large literature of surface work.

In order to fit the material into the length available, very many uncomfortable choices have been made. Different kinds of emphasis can be found in G. A. Somorjai's book (*Principles of surface chemistry* (1972), Prentice-Hall, New Jersey), where more weight is given to interactions

x Preface

of gases with surfaces and in J. M. Blakely's book (*Introduction to the properties of crystal surfaces* (1973), Pergamon Press, Oxford), where more attention is devoted to the thermodynamics of surfaces.

I am very pleased to be able to acknowledge the help given me by many colleagues. Drs J. A. D. Matthew, A. Chambers, and T. E. Gallon have read the whole manuscript painstakingly and have contributed many valuable points as well as countering my pedantry. Christine Upton typed the manuscript flawlessly in spite of much other work and constant interruptions. Alan Gebbie drew most of the figures for me.

Colleagues in other laboratories supplied original drawings for some of the figures; I am grateful to Professor W. Roberts, University of Bradford, for Fig. 2.7; Dr. F. Grønlund, University of Copenhagen, for Fig. 3.12; Dr. R. Reid, New University of Ulster, for Fig. 3.14(a); Dr. J. May, Eastman-Kodak Inc., New York, for Fig. 3.14(c); Professor E. W. Müller, Pennsylvania State University, for Fig. 3.19; Dr. D. W. Bassett, Imperial College, for Fig. 6.14; and Dr. H. Montagu-Pollock for Fig. 4.5.

M. PRUTTON

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1. Introduction

All the properties of a piece of bulk material are determined by the number and types of atoms it contains and by their arrangement in space with respect to each other. Some properties can be related in a straightforward manner, both theoretically and experimentally, to the chemical composition and to the crystal structure by using the large body of understanding provided by the band theory of solids (e.g. Rosenberg 1975). Thus, for instance, the division of crystalline solids into insulators, semiconductors, and conductors, the explanation of the relationship between thermal and electrical properties, and the occurrence of both Hall and magneto-resistance effects can all be satisfactorily explained within the framework of the band theory of solids.

It may be less straightforward to relate other properties to a theoretical model of a solid, and a more empirical approach may have to be adopted. One example of such a property is the ferromagnetism of some metals. This depends upon small differences between large interactions in the solid, and demands a difficult and sophisticated theory for its explanation. Mechanical creep and fatigue failure are examples of phenomena requiring an understanding of faults which occur in crystalline solids and the way in which they move in response to applied forces. Again, the theoretical description of these processes is difficult. Nevertheless, these properties are still determined in principle provided that the composition and structure of the material are sufficiently well defined.

The subject of surface physics is the study of the chemical compositions and atomic arrangements at the surfaces of solids and the theory and observation of their mechanical, electronic, and chemical properties. As in the study of bulk solids, the ultimate objective is the establishment of understanding of the relationships between the properties, the composition, and the structure. There are many reasons for expecting that a solid surface will have different properties from the bulk material and these provide an incentive for the physicist to enquire and try to understand. Equally important, there are many processes of technological significance which depend upon the use of solid surfaces and which may be improved in some way if the role of the surface could be fully understood.

In this book the surface is thought of as the top few atomic layers of a solid. In many older books on surface chemistry or metallurgy the

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surface is regarded as the top 100 nm or so of the solid. The larger distance was determined more by the techniques that were available at that time than by any more basic physical consideration.

The reasons for the expectation that a surface will have different properties from the bulk of the solid may be understood by considering a surface formed by cutting through the solid parallel to a chosen plane of atoms. If the atoms are not disturbed from their bulk equilibrium positions by this operation then the surface can be said to be a *bulk exposed plane* (Fig. 1.1(a)). Such a plane shows the minimum disturbance

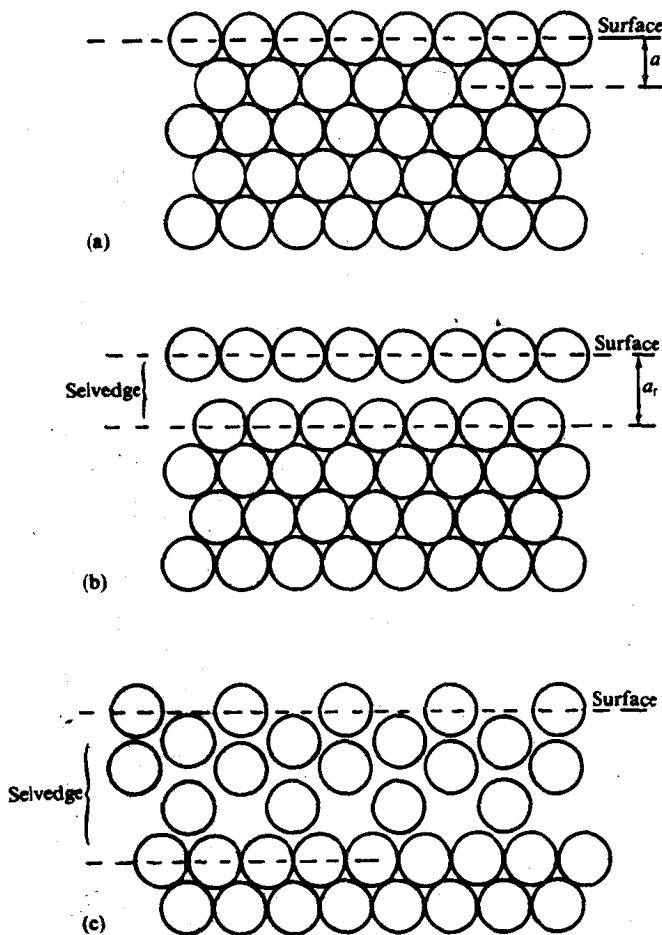


FIG. 1.1. Rearrangement of atomic positions at a solid surface. Hexagonal close-packed atoms. (a) The bulk exposed plane; (b) relaxation of the surface plane outwards; (c) reconstruction (hypothetical) of the outer four atomic planes.

of the solid arising from the formation of the surface. Even so, because many electronic properties of the bulk depend upon the three-dimensional periodicity of the potential inside the solid, the loss of periodicity in one dimension due to the existence of the surface will result in a change in the electronic states near and at the surface and so surface electronic properties different from bulk (Chapter 4). Also, the lack of nearest neighbours on one side of the surface atoms may make available chemical bonds which 'dangle' into the space outside the solid and which will be available for chemical reactions (Chapter 6).

It is more likely that the disturbance caused by terminating the solid in a surface, particularly the disturbance due to the absence of the bonding force of nearest neighbours on one side of the surface atoms will result in new equilibrium positions for the atoms in and near the surface. The simplest change of this kind is the *relaxation* illustrated in Fig. 1.1(b). Here, the separation of the surface plane from the next plane of atoms happens to be drawn so as to be greater than the corresponding separation in the bulk solid. This deviation from the bulk spacing may continue, in decreasing magnitude, as one probes deeper into the solid. The surface region over which there is a deviation from the bulk lattice spacing is referred to as the *selvedge*. Relaxation retains the symmetry of the atomic arrangement parallel to the surface but changes the spacings normal to the surface. It may result in changed properties for the surface because, for instance, it could create an electric dipole moment in the selvedge. A more extreme disturbance occurs when the surface atoms rearrange themselves into a structure with symmetry altogether different from the bulk solid. This phenomenon is called *reconstruction*, an example of which is shown in Fig. 1.1(c). This reconstruction modifies the symmetry near the surface and will affect all the structure sensitive properties of the surface—the atomic vibrations, and chemical, optical and electronic behaviour.

Many different kinds of processes which are of great scientific and technological interest occur at surfaces. The variety amongst these processes is very large, a fact which accounts for the wide spread of disciplines involved in surface physics. A few of them are listed below in order to give some view of the incentives for surface investigations.

1. *Thermionic emission*. By raising the temperature, sufficient kinetic energy can be imparted to electrons at the top of the conduction band in a metal for them to be ejected from the surface into the vacuum. This process is known as thermionic emission and is important in many electronic devices and most particularly for the source of electrons in oscilloscope tubes and electron microscopes. The number of electrons which can be obtained by thermionic emission is a function not only of the material but also of the presence of chemical contaminants (the cleanli-

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ness) of the emitting face and of its crystallographic orientation. The attempt to understand the factors controlling electron emission is an important part of surface physics which is described at greater length in Chapter 4.

2. *Crystal growth.* The development of methods for growing large single crystals of a wide variety of solids has been crucial to the extension of solid-state physics from the simplest band models and to the ability of electronic engineers to design semiconducting devices. The processes of crystal growth generally involves the deposition of atoms upon single-crystal surfaces under such conditions that the arriving atoms can diffuse about and build up the three-dimensional periodic array. Thus, the physics of the energetics and kinetics of adatoms upon single-crystal surfaces is fundamental to an understanding of crystal growth. Some of this type of surface physics is described in Chapter 6.

3. *Chemical reactions.* Many chemical reactions involve interactions between different kinds of atoms across a surface or interface. Even the simplest processes, when viewed at an atomic level, are not fully understood in these terms. One particularly important example is the corrosion of metals or a simple extreme case of corrosion – oxidation. The way in which a clean metal surface is converted to a bulk oxide when exposed to an atmosphere of oxygen must be understood before interpretation of corrosion in more complicated atmospheres is unambiguous. Some simple examples of oxidation on low-index metal faces are described in Chapter

4. *Catalysis.* The presence of surfaces of a particular metal during a chemical reaction can sometimes cause marked increases in the speed of the reaction (Bond 1974). This catalytic action is technologically important but is the subject of a largely empirical literature. It is one of the longer-term aims of surface studies to throw some light upon the way in which complex practical catalytic systems operate, particularly with a view to finding more economic catalysts than metals like platinum.

5. *Colloids.* Micrometre-sized particles of a solid suspended in a liquid – a colloidal suspension – form an interesting and useful chemical system. Many of its special properties arise from the large surface area of the particles and an understanding of its behaviour must rest upon a knowledge of the role of this surface.

6. *Semiconductor interfaces.* Many semiconducting devices depend crucially upon phenomena that occur at a surface or interface. A junction between *p*-type and *n*-type material; a junction between a metal oxide and a semiconductor (MOST devices); the junction between a metal contact and a semiconductor – all three involve the formation of a surface and the preparation upon it of another material. The chemistry

and structure of the surface and the way in which these change as the second material is added will affect the electronic properties across the interface. Some of these matters are described in Chapter 4.

7. Brittle fracture. Some metals and alloys have enormous mechanical strengths when under continuous load. However, they can often be broken by the sudden application of a much smaller load; this phenomenon is called brittle fracture and it can be quite an embarrassment! It appears to be due to the migration of impurity atoms to the grain boundaries in a solid which become weak regions under impact. The application of surface techniques to the study of this impurity segregation at grain boundaries may help to provide understanding of the problem and may even lead to the discovery of means for inhibiting the diffusion and so preventing brittle fracture in some materials.

Three different factors have played a part in the rise to the current level of interest in surface physics. In the first place, the theory of both the electronic band structure and the chemical bonding in simple bulk solids has been sufficiently successful that theoreticians and experimentalists have been encouraged to attempt to extend the theory. This extension is being explored in two directions simultaneously — the properties of more complicated ionic and molecular bulk solids and the properties of defects in solids. Amongst the defects the most obvious is the occurrence of a two-dimensional surface bounding a three-dimensional periodic structure. Secondly, the technological pressures mentioned above have become more urgent, and, because techniques became available which could throw light upon the relevant problems, interest has grown in trying to use some of the surface physics as it evolves.

The third is technical rather than historical, but it is nevertheless crucial. It is the development, in association with the interest in space research, of techniques for the achievement of ultra-high vacuum (UHV). This level of vacuum is one in which the rate of impingement upon the surface being studied of molecules from the ambient residual atmosphere in the vacuum chamber is negligible in the time required for the observations. The kinetic theory of gases (e.g. Yarwood 1967) shows that the amount of gas hitting unit area of a surface per unit time is given by:

$$Z = bp(M_r T)^{-\frac{1}{2}} \quad (1.1)$$

where p is the ambient gas pressure above the surface, M_r is the relative molecular mass of the gas, and T its thermodynamic temperature, and b is a universal constant. It is usual to write the incident flux density Z in the units molecules $\text{m}^{-2} \text{s}^{-1}$, and consequently the value of b is written in one of the forms:

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$$\begin{aligned}b &= 2.63 \times 10^{24} \text{ molecules m}^{-2} \text{ s}^{-1} \text{ K}^{\frac{1}{2}} \text{ Pa}^{-1} \\b &= 2.63 \times 10^{26} \text{ molecules m}^{-2} \text{ s}^{-1} \text{ K}^{\frac{1}{2}} \text{ mbar}^{-1} \\b &= 3.51 \times 10^{26} \text{ molecules m}^{-2} \text{ s}^{-1} \text{ K}^{\frac{1}{2}} \text{ Torr}^{-1}.\end{aligned}\quad (1.2)$$

All three pressure units (Pa, mbar, and Torr) are concurrently in use and hence b is given here for each of these units.

In a conventional vacuum system using diffusion pumps and elastomer gaskets the pressure is normally about 10^{-6} Torr and (1.1) shows that this corresponds to approximately 3.0×10^{14} molecules of nitrogen arriving each second on each square centimetre of a surface at room temperature. Since an atomic monolayer corresponds to about 10^{15} atoms cm^{-2} (inter-atomic distances being about 0.3 nm) such conditions result in nitrogen arrival rates of a monolayer every 3 s assuming that every molecule sticks to the surface. Since many experiments take longer than a few seconds this represents an unacceptable level of contamination of a surface. Ultra-high vacuum is now generally regarded as the region below 10^{-9} Torr. (1.1) shows that, at room temperature, 10^{-10} Torr corresponds to nitrogen arrival rates of 3.8×10^{10} molecules s^{-1} , or about 1 monolayer in about 8 hours. At this pressure the mean free path between collisions of molecules of the ambient atmosphere would be about 50 000 km.

The techniques required to achieve ultra-high vacua are reviewed in many textbooks (e.g. Redhead 1968; Yarwood 1967). A diagram of the type of UHV system found in many surface physics laboratories is shown in Fig. 1.2, and Fig. 1.3 is a general view of a multiple-technique system in the author's laboratory. The important features of such systems are as follows.

1. The vacuum chamber and its associated pipework are normally fabricated of argon-arc welded or vacuum-braided stainless steel. This material corrodes very slowly and has low rates of outgassing of absorbed gas.
2. The vacuum joints are made with metal instead of elastomer gaskets. Gold O rings or flat copper rings are normally used here. The use of metal gaskets avoids release of organic contaminants, reduces leakage of water vapour from the atmosphere into the system, and allows the baking described in (3).
3. The whole chamber assembly is designed so that it can be heated to above about 520 K while the vacuum pumps operate. This 'baking' of the system results in accelerated desorption of water vapour (and other gases) from all internal surfaces. When the system is cooled back to room temperature the ultimate pressure attainable is thus substantially reduced.
4. The pumps provided to evacuate the chamber are often ion pumps, titanium sublimation pumps, and, for initial pumping from atmospheric

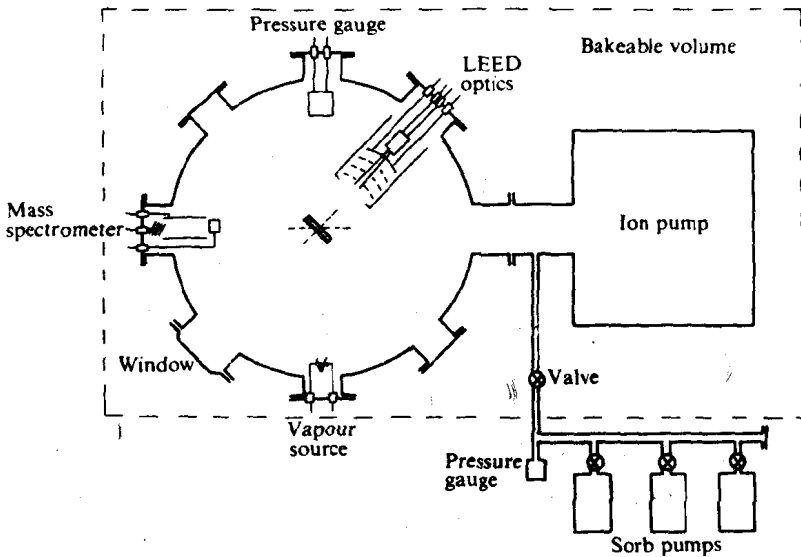


FIG. 1.2. Arrangement of vacuum components in a typical UHV system for surface studies.

pressure, sorption pumps. These three techniques avoid the use of any organic materials. Very well-trapped diffusion pumps filled with special fluids can be used where special problems arise – an important case being to pump away large throughputs of noble gases which are only very slowly removed by ion or titanium sublimation pumps.

5. The choice of materials used inside the vacuum chamber is made carefully to avoid high vapour pressures. Stainless steel, molybdenum, and tantalum are in common use for fabricating parts, oxygen-free high-conductivity copper is often used as a conductor, glass and high-density ceramics such as alumina (Al_2O_3) are used as insulators, and silver as a material to line bearings because it is such a soft metal.

Properly designed UHV systems reach the low 10^{-10} Torr range on a routine basis, and better pressures are possible with great care. Because of the time required to achieve UHV (10 – 24 hours) experiments are often designed to allow several *in situ* operations on the sample surface and several *in situ* types of measurement (Fig. 1.3). The sample itself is normally mounted on some kind of manipulator which may allow various combinations of translation and rotation of the sample in the experimental geometry, electrical isolation, heating, cooling and *in situ* cleavage as a means of preparing a clean single-crystal surface.

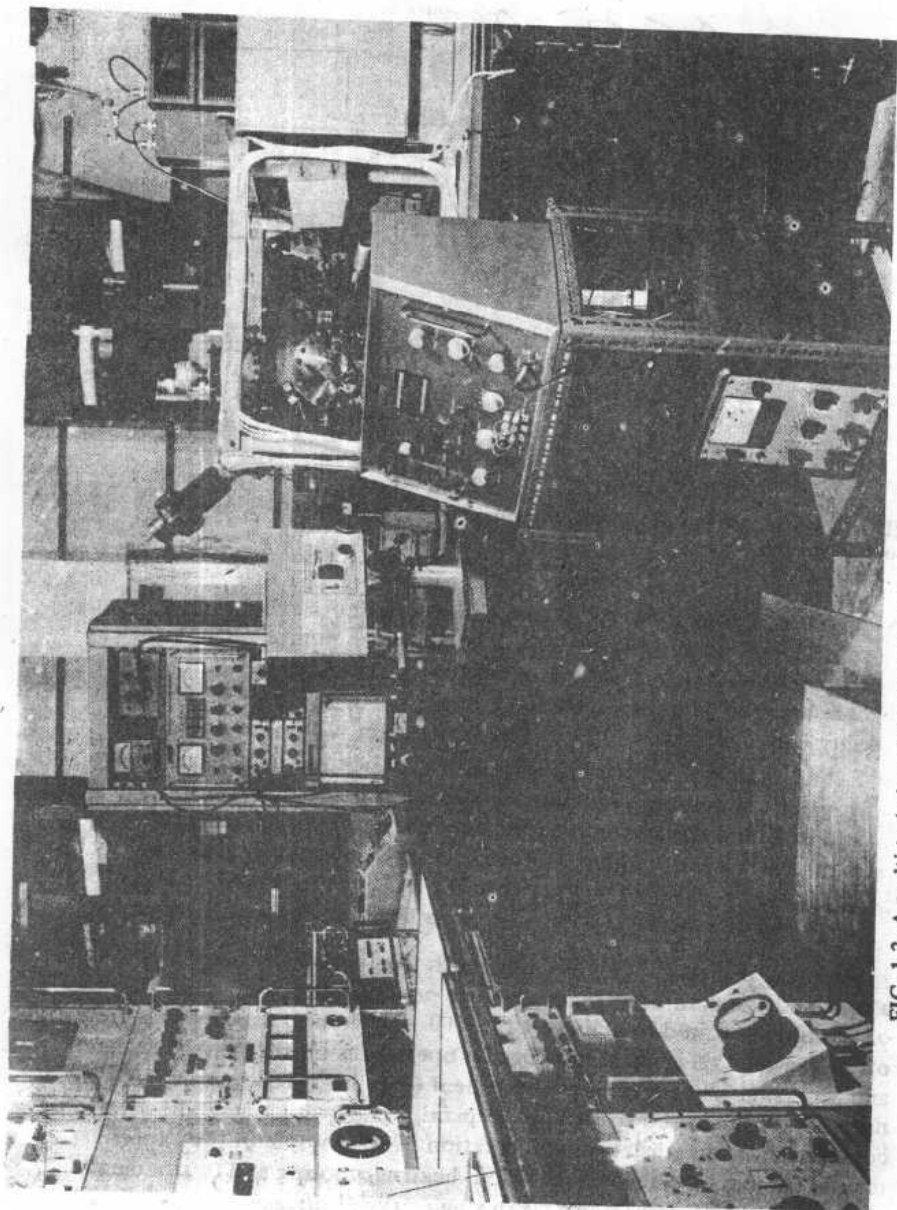


FIG. 1.3. A multi-technique UHV system in use for surface studies and equipped for LEED, RHEED, mass spectroscopy, Auger electron spectroscopy, *in situ* optical absorption, and vacuum evaporation.

Having placed a sample for study in the vacuum system and having achieved a UHV environment for it the next step is often to attempt to obtain an atomically clean surface upon which to conduct experiments. Each crystal face of each material presents its own individual cleaning difficulties, and many man-months of effort can be expended in discovering how to produce a clean surface upon which to start study. This is not the place for a detailed summary of techniques and their applicability but an idea of some of the possible approaches is given in the following list.

1. In some cases the act of achieving UHV environment simultaneously cleans up the surface for study. For example, the cleavage face of mica and the (100) cleavage faces of the alkali halides (NaCl, LiF, NaF, KCl, etc.) can be cleaned in this simple way.

2. As will be seen in Chapter 2, common contaminants on many surfaces are oxygen, carbon, and sulphur which are chemically bound (chemisorbed) to the surface of the material under study. Sometimes these can be removed by heating the sample *in situ*, whereupon the contaminants may desorb into the vacuum as volatile oxides, sulphides, or carbides or may dissolve into the solid leaving a negligible level of contamination behind. Temperatures near to the melting point of the sample material may be required to realize reasonable rates of removal of these contaminants. An example of this method is the removal of oxygen and carbon from the (111) surface of silicon. On heating for 1 or 2 minutes at 1370 K the surface carbon dissolves into the silicon leaving behind sub-monolayer levels of contamination.

3. If the chemisorbed contaminants cannot be removed by heating alone they can sometimes be removed by heating in an atmosphere which produces a volatile compound of the contaminant. Thus, surface oxides can sometimes be removed by reduction in a hydrogen atmosphere.

4. More stubborn contaminants can be physically knocked off the surface by bombardment with noble gas ions (e.g. Ar^+ , Ne^+) (Redhead 1968). This is usually effective in removing contaminants but is often accompanied by disturbance of the surface atoms of the sample material. For instance, carbon and sulphur contamination can be removed from (100) surfaces of nickel monoxide by bombardment with 200 eV Ar^+ ions, but the nickel monoxide surface is disordered in the bombardment. The surface can be reordered by annealing but this can result in the re-appearance of contaminants by diffusion out of the bulk of the crystal — so-called surface segregation. A combination of bombardment and anneal conditions has to be found empirically which cleans up the surface and allows re-ordering without unacceptable contamination.

5. Some materials cleave naturally on particular crystal faces when struck with a blade in a direction parallel to that face. This property can

be exploited to prepare clean surfaces *in situ* and is simple and direct. Examples are (100) alkali halide faces, (111) faces of materials like calcium fluoride, and even some materials like silicon and beryllium which will cleave at liquid-nitrogen temperatures. However, this method is limited to a few faces of a small number of materials.

6. Evaporation on to a suitable substrate can be used *in situ* to prepare thin films of polycrystalline or single-crystal type whose clean surfaces can be the subject of subsequent study. The contamination on the substrate can be 'buried' by the deposited film which may then be acceptable for clean surface studies. The growth of oriented single-crystals by this technique is a process known as epitaxy and is described in Chapter 6.

The criteria for deciding if a clean surface had been realized in practice used to be based upon the repeatability of an observation between many samples of the same material prepared in the same way. Although this approach has to be resorted to occasionally it is now more usual to have *in situ* assessment based upon one of the techniques of electron spectroscopy described in Chapter 2.