

# 1

## Introduction

The metal oxides constitute a diverse and fascinating class of materials whose properties cover the entire range from metals to semiconductors and insulators. Their surfaces play crucial roles in an extremely wide range of phenomena. The environmental degradation of high- $T_c$  superconductors; bonding between grains of alumina in sintered ceramics; the passivation of metal surfaces against corrosion; catalysts for the partial oxidation of hydrocarbons; solid-state gas sensors for pollution monitoring and control; the failure of dielectric materials because of surface conductivity; the stability of electrode/electrolyte interfaces in fuel cells: all of these are dependent upon the properties of metal-oxide surfaces or the interfaces between metal oxides and other materials.

For all of their technological and scientific importance, our understanding of the basic physics and chemistry of metal-oxide surfaces lags a decade or more behind that of metals and semiconductors; the reasons for this are discussed in § 1.2 below. However, over roughly the past fifteen years, an ever increasing number of research groups have begun to study the properties of well characterized metal-oxide surfaces, both experimentally and theoretically. This is shown graphically in Fig. 1.1, which plots the number of papers published per year on fundamental surface-science studies of metal oxides (the data are based upon papers referenced in this book). The field is now sufficiently well-developed that it is appropriate to step back and view it in overall perspective, looking for trends in surface properties as well as details of specific materials and systems. That is the purpose of this book.

### 1.1 Technological importance of metal-oxide surfaces

Before examining in detail what has been learned about the properties of metal-oxide surfaces from experimental measurements and theoretical calculations on well-characterized single-crystal samples, which is the approach taken in this

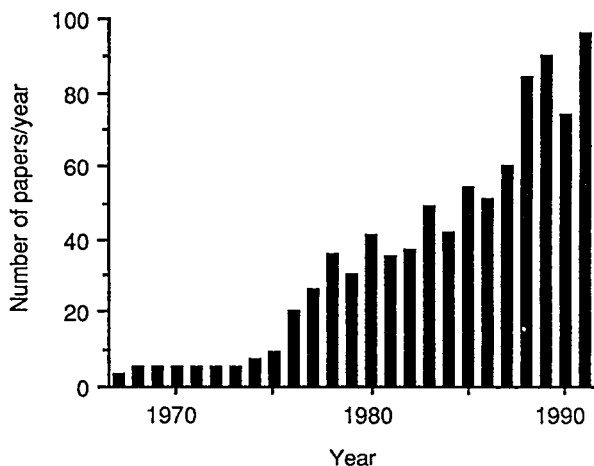


Fig. 1.1 The number of publications/year, based upon papers referenced in this book, in the area of the properties of well-characterized metal-oxide surfaces.

book, it is useful to consider some of the reasons that make oxides of technological interest, since they determine in large measure what properties are studied. The importance of metal oxides in catalysis is profound. Most commercial catalysts consist of microscopic particles of a metal supported on a high-surface-area oxide. The two most commonly used oxide supports are  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  (the former is not a metal oxide and will not be considered here), although other metal oxides are sometimes used. Metal catalysts supported on such non-reducible oxides generally exhibit little effect of the presence of the support, but in some cases either the interaction between the catalyst and the support, or the existence of complementary reactions taking place on the metal and the oxide, play an important role in catalysis. When catalyst metals are supported on reducible transition-metal oxides, strong interactions can occur that alter the catalytic behavior of the metal; this is discussed in § 7.6.

Metal oxides are also themselves catalysts for a variety of commercially important reactions. Sometimes a metal oxide is used in its pure form (e.g., bismuth molybdate for the oxidation of propene to acrolein or acrylonitrile), while in other cases the oxide is supported on another oxide, and the catalytic activity results from the interaction between the two oxides (e.g.,  $\text{V}_2\text{O}_5$  supported on  $\text{TiO}_2$  for the selective oxidation of hydrocarbons and the selective catalytic reduction of nitrogen oxides). All of these catalytic reactions proceed by complex mechanisms that involve a range of different chemical interactions; these include acid/base reactions as well as oxidation and reduction steps where lattice oxygens are lost and gained by the substrate. Chapter 6 is concerned with the chemisorption of mole-

cules on oxides, and we shall see there that fundamental understanding of chemisorption and catalysis is still in quite a primitive state. In supported systems, the interactions that take place at oxide/oxide interfaces are not at all well understood, and model systems will have to be studied in order to unravel the important aspects of the interactions and their effect on chemical reactions; research to date in this area is discussed in § 7.7.

A major landmark in the study of transition-metal-oxide surfaces occurred in 1972 with the report by Fujishima and Honda<sup>1</sup> that  $\text{TiO}_2$  could be used as a catalytic electrode in a photoelectrolysis cell to decompose water into  $\text{H}_2$  and  $\text{O}_2$ , without the application of an external voltage. The single-crystal transition-metal-oxide surface research that was stimulated by that discovery is mirrored in the increase in the number of publications in Fig. 1.1 in the mid-1970s. While not yet commercially competitive, photoelectrolysis is still an active area of research in electrochemistry (see § 6.2.5).

Another important application of metal oxides is as gas sensors. The most studied oxides for this purpose are  $\text{ZnO}$  and  $\text{SnO}_2$ . Both of these have high bulk electrical resistivity when stoichiometric, although they normally behave as n-type semiconductors due to the presence of defects or deliberate doping. The adsorption of certain molecules bends the bands at the surface, producing changes in surface conductivity large enough to be readily measured; thus the surface conductivity can be used to monitor the presence of that molecule. In some cases the sensitivity and selectivity of the material can be improved by deposition of sub-monolayers of metal on the oxide surface.

In air, oxides are the lowest free energy state for all but a few of the metals in the periodic table. Therefore much of the corrosion of metals involves the formation of (generally unwanted) oxides. Studies of metallic corrosion are most appropriately performed by beginning with the metal and following what happens to it when it is exposed to an oxidizing environment. A vast literature exists on the oxidation of metals, none of which will be discussed here. Instead we approach the phenomenon from the other direction by considering nearly perfect surfaces of metal oxides, which are often the end products of corrosion. A knowledge of the properties of those end products is a necessary prerequisite to understanding the corrosion process.

The most recent impetus for the study of oxide surfaces has been the discovery of Cu-oxide-based high- $T_c$  superconductors. Although superconductivity is a bulk phenomenon, issues of environmental degradation and electrical contacts, combined with the short coherence lengths in oxide superconductors, have raised important surface questions, and there have been some attempts to answer them by using vacuum-fractured or single-crystal samples. This is partially responsible for the larger number of papers since 1988 in Fig. 1.1.

## 1.2 Considerations in the study of oxide surfaces

There are several reasons why the study of metal-oxide surfaces lags so far behind that of metals and semiconductors. This state of affairs can be explained partly by the simple reluctance of research groups with well-established programs to enter a new field. But there are also some sound reasons for their reluctance, since the study of oxides by surface-science techniques does present a number of challenges that are more severe than those encountered with metals and semiconductors.

One major problem is that of sheer complexity. This is noticeable first of all with crystal structures. Even a relatively simple structure such as corundum ( $\alpha$ - $\text{Al}_2\text{O}_3$ ,  $\text{V}_2\text{O}_3$ , etc.) has a ten-atom primitive unit cell, while  $\text{V}_2\text{O}_5$  has fourteen atoms in its unit cell. One of the first goals of a surface-science study is to find out where the atoms are on a surface, but it is clear that the complexity of oxide structures can make this a formidable task. In fact, the number of properly determined oxide surface structures is very small.

Along with the complex crystallography comes a similarly complex combination of chemical and physical properties. Many elements, especially transition metals, display a range of possible oxidation states and hence a series of oxides with different compositions. The oxides of vanadium, for example, include not only  $\text{VO}$ ,  $\text{V}_2\text{O}_3$ ,  $\text{VO}_2$  and  $\text{V}_2\text{O}_5$ , but also a wide range of intermediate phases, some of well-defined composition such as  $\text{V}_4\text{O}_9$ , others like  $\text{VO}_x$  being essentially non-stoichiometric, with  $0.8 \leq x \leq 1.3$ . This chemical complexity has many serious implications for surface science. It means that even bulk samples of many oxides may be difficult to obtain with reproducible composition and properties; and they will often have high defect concentrations, which may dominate the physical properties of even the purest available materials. Such difficulties will be greatly exacerbated at surfaces and undoubtedly contribute to the problems in surface preparation that are mentioned below. Another consequence of chemical complexity is the wide range of chemical interactions possible with chemisorbed molecules. Surfaces with apparently similar composition, but prepared slightly differently, can have totally different properties. Most surface scientists, of course, are familiar with this type of problem, but it is generally much more severe with oxides than with metals or semiconductors.

The electronic structure of metal oxides is also much more complex than that of most metals or semiconductors. For example, the bulk electronic structure of the late 3d-transition-metal oxides lies somewhere between itinerant and localized, and neither theoretical approach – the former of which has been developed for metals and semiconductors and the latter that is used to describe molecules – is entirely appropriate. The discovery of metal-oxide high- $T_c$  superconductors has spurred a great deal of interest in the bulk electronic structure of such compounds,

but as yet no comprehensive theory exists. With so little known about the bulk electronic structure of metal oxides, it is small wonder that studies of their surface electronic properties are so far behind those of many other materials. Even when good models of electronic structure do exist, the structural complexity makes it difficult to carry out good calculations. The number of atoms per unit cell in many structures, coupled with the reduced symmetry at the surface and the necessity to calculate many unit cells to separate surface and bulk effects, means that first-principles electronic structure calculations still require a great deal of computer time.

Another difficulty with oxides is a practical one related to the experimental techniques used by surface scientists. Many of the most interesting metal oxides are very good electrical insulators. MgO and Al<sub>2</sub>O<sub>3</sub> are of tremendous importance in the ceramics industry, and both are wide-bandgap insulators that cannot be made conducting by doping or reduction. Many of the most powerful techniques of surface science involve the emission or absorption of charged particles, whether they be electrons or ions, at some point in the measurement process. Samples that have negligible bulk conductivity often cannot be studied by those techniques due to problems of surface charging. While there may be ways to circumvent that problem to some degree, the fact remains that insulators are far more difficult to study, and the range of experimental techniques that is available is smaller, than with metals or semiconductors.

The question of surface preparation is central to all surface-science investigations, and herein lies what is possibly the greatest difficulty of all. Compared with elemental solids, the preparation of nearly perfect surfaces of any compound is difficult. The establishment of geometric order on the surface is not sufficient, since the stoichiometry of the surface can differ from that of the bulk. For semiconductors such as GaAs or InSb, procedures have been developed to produce surfaces that are as nearly ideal terminations of the bulk structure as nature will allow. But the preparation of each separate crystal face of each different compound is a research program in itself. For metal oxides, this has only been done in a few cases.

Perhaps the best method by which to prepare nearly perfect surfaces is cleaving in ultrahigh vacuum (UHV). A fairly large amount of energy is dissipated in the cleaving or fracture of most materials, and that energy can cause disruption of the surface. Fractoemission studies show that photons, electrons, atoms and ions can all be liberated during fracture, so it would be naive to consider even a surface that cleaves easily to be an ideal termination of the bulk crystal structure. But cleaving or fracture is still more likely than other methods to yield well-ordered surfaces having nearly the composition of the bulk. It has recently become possible to actually look on an atomic scale at surfaces by using scanning tunneling or atomic force microscopy, but only a small amount of such work has yet been done on oxides. Hopefully in the near future it will be possible to prepare oxide surfaces



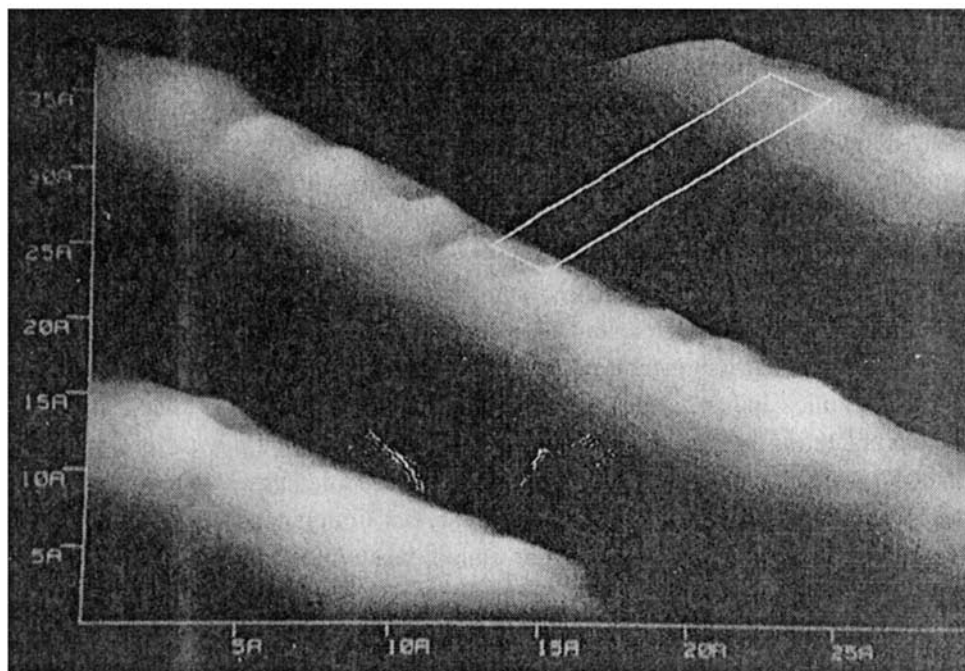


Fig. 1.2 Atomic resolution STM image of the  $\text{TiO}_2$  (100)-(1 × 3) surface, with the surface unit cell (dimensions  $3 \text{ \AA} \times 15 \text{ \AA}$ ) marked. The bright rows are ridges of atoms; this structure is discussed in § 2.3.2. [Ref. 2]

that we *know* correspond to surfaces modelled theoretically, but we are not yet at that stage.

The alternative to cleaving single-crystal surfaces is to cut samples along the desired crystal plane, polish them to remove as much roughness as possible, etch them to remove damaged layers left by the cutting and polishing processes and any surface contamination, and anneal them in UHV (or perhaps an  $\text{O}_2$  ambient) to restore the geometric order of the surface. This is the method that has been used in most studies of single-crystal metal oxides; we will refer to surfaces prepared in that way as ‘polished and annealed’, or ‘P&A’ in tables. There is no reason to believe a priori that polished and annealed oxide surfaces will have the same structure as an ideal cleaved surface; in fact, numerous results show that not to be the case. It is thus necessary to characterize the stoichiometry and geometric structure of the surface as completely as possible before meaningful interpretations of data taken on it can be made. The techniques that are currently available to accomplish that goal are far from perfect, and in some cases they may even be misleading.

The development of scanning tunneling and atomic force microscopy (STM and AFM) is inaugurating a new era in surface characterization. Figure 1.2, for exam-

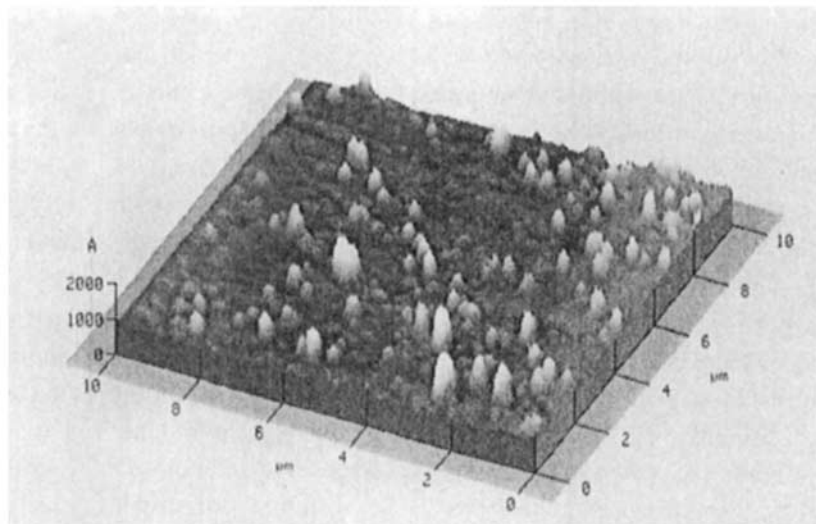


Fig. 1.3 Atomic force micrograph of a polished and annealed  $\text{TiO}_2$  (110) surface prepared in ultrahigh vacuum. [Ref. 3]

ple, shows an STM image of a reconstructed  $\text{TiO}_2$  (100) surface, in which the clearest features are rows of atoms having a spacing of  $15 \text{ \AA}$ . Less obvious, but also detectable, are individual atoms within the rows, which have a  $3 \text{ \AA}$  spacing.<sup>2</sup> Although results like this sometimes serve to confirm existing models, the ability to image surfaces on an atomic (or nearly atomic) scale has also shown the naiveté of many of our ideas concerning single-crystal surfaces. Figure 1.3 shows an AFM micrograph of a  $\text{TiO}_2$  (110) surface that was prepared by standard surface-science procedures of ion bombardment and annealing.<sup>3</sup> It exhibited good low-energy-electron-diffraction (LEED) patterns, and photoelectron spectra indicated the absence of defect-derived states in the bulk bandgap. And yet the surface is hardly defect free! Much of the experimental work discussed in this book has been conducted on surfaces that may not be much more perfect than this one, although the data are interpreted in terms of nearly perfect surfaces, containing atomically flat planes and few steps. Until more atomic scale information is available concerning the actual topography and structure of metal-oxide surfaces from the use of such techniques, it will not be possible to compare experiments with more realistic models of surfaces than has been done to date.

### 1.3 Work functions of metal oxides

One of the very important properties of a surface is its work function,  $\Phi$ , which is defined as the energy necessary to remove an electron from the Fermi level in a

material and put it at rest in vacuum an infinite distance away from the material. (Practically, ‘infinite distance’ means distances beyond which the electron potential does not change with position away from the surface; this is usually tens or hundreds of ångströms.) The work function plays a dominant role in thermionic emission, Schottky barrier formation, photoelectron emission, etc. It can be measured in several ways, including thermionic emission, the low-energy cut-off in photoelectron emission, contact potential difference measured with a Kelvin probe, and retarding potential methods.<sup>4</sup>

The work function is an extremely sensitive measure of the state of a surface. In fact, it is *so* sensitive for metal oxides that its absolute value has little significance. Differences in step or point defect densities, traces of adsorbed molecules too small to be observed by any surface spectroscopy, slight changes in surface reconstruction, etc., can cause significant changes in  $\Phi$ . Care must also be taken in comparing work functions determined by different experimental techniques, particularly if  $\Phi$  is not uniform across the surface. For example, Kelvin probe measurements give an average value of the work function for the area of the surface covered by the electrode, while measurements of the low-energy cut-off of the secondary-electron spectrum in ultraviolet photoelectron spectroscopy (UPS) and other electron spectroscopies give the minimum value of  $\Phi$  for the surface. Not only do different research groups measure different values on surfaces prepared in nominally the same manner, but a single group often obtains different values on different crystals, different cleaves, or different days. For that reason we will not stress the absolute values of work functions in this book. However, we would be remiss not to briefly summarize some of the experimental results that have been obtained on metal oxides; this is done in Table 1.1.

What do the results in Table 1.1 mean? Look, for example, at the first two entries under ZnO. Photoemission cut-off and field-emission measurements on ZnO (0001) surfaces that are both presumably atomically clean give very different values, although each measurement claims to have very small error limits. In theory, this should not be the fault of the different measurement techniques. Or look at the values for two photoemission measurements of the work function of polished and annealed SrTiO<sub>3</sub> (100), a surface that has been exhaustively studied by several groups. The very different values of  $\Phi$  indicate that variables beyond the control, or knowledge, of the researchers play a large role. In Refs. 11 and 12, it was found that differences in annealing temperature and time could change the work function of ZnO surfaces by more than 2 eV, although in other ways the surfaces were essentially the same. Thus it is very difficult to know what absolute values of work functions on metal oxides really mean. The most dangerous situation occurs when only *one* determination of  $\Phi$  has been made; people are then tempted to *believe* it! (There is a saying at the National Institute of Standards and



Table 1.1. Measured work functions of clean metal-oxide surfaces

| Oxide                              | Face                                       | Surface preparation                                      | Work function (eV) | References   |        |
|------------------------------------|--|--|--------------------|--|--------|
| <i>Non-transition-metal oxides</i> |  |  |                    |  |        |
| ZnO                                | 0001                                       | UHV cleaved  | 4.25 ± 0.05        | 5, 6   |        |
|                                    |  |  | Field evaporation  | 3.15 ± 0.15  | 7      |
|                                    |  | P&A  | 4.3 ± 0.1          | 8  |        |
|                                    |  |  | 3.9                | 9  |        |
|                                    |  |  | 3.75 ± 0.05        | 10, 11   |        |
|                                    |  |  |                    | 3.2 to 3.7, depending upon surface preparation procedure | 12     |
|                                    |  | 000 $\bar{1}$  | UHV cleaved        | 4.95 ± 0.05  | 5, 6   |
|                                    | 3.9 to 4.45, depending upon annealing temp |  |                    | 13   |        |
|                                    | Field evaporation                          |  | 4.85 ± 0.15        | 7  |        |
|                                    |  |  | P&A                | 4.6 ± 0.2  | 8      |
|                                    |  |  | 4.6                | 9  |        |
|                                    |  |  |                    | 4.35 ± 0.05  | 10, 11 |
|                                    |  |  |                    | 3.7 to 6.1, depending upon surface preparation procedure | 12     |
|                                    | 10 $\bar{1}0$                              |  | UHV cleaved        | 4.64 ± 0.05  | 5      |
|                                    |  | 4.5 to 4.7, depending upon annealing temp.               |                    | 13   |        |
| P&A                                |  | 4.37   | 14                 |  |        |
|                                    |  | 4.3  | 9                  |  |        |
|                                    |  | 4.05   | 10, 11             |  |        |
|                                    |  | 4.4 to 5.0, depending upon surface preparation procedure | 12                 |  |        |
| SnO <sub>2</sub>                   | 110  | P&A  | 7.74               | 15   |        |
| <i>Transition-metal oxides</i>     |  |  |                    |  |        |
| TiO <sub>2</sub>                   | 110  | P&A  | 5.5                | 16   |        |
|                                    |  |  | 5.3 ± 0.1          | 17–19  |        |
|                                    |  | 5.3  | 20                 |  |        |
|                                    |  | Ion bombarded  | 5.1                | 20   |        |
|                                    |  |  | 4.6                | 16   |        |
|                                    | 100  | P&A  | 5.9 ± 0.1          | 21, 22   |        |
|                                    |  | P&A, (1 × 3)   | 5.7                | 23   |        |
|                                    |  | P&A, (1 × 7), reduced                                    | 5.5                | 23   |        |
|                                    | 441  | P&A  | 4.6 ± 0.1          | 18, 19   |        |

Table 1.1. (cont.)

| Oxide                                      | Face           | Surface preparation | Work function (eV) | References |
|--|----------------|---------------------|--------------------|------------|
| SrTiO <sub>3</sub>                         | 100            | P&A                 | 4.2                | 24         |
|  |                | Ion bombarded       | 3.2                | 20         |
|  | 111            | P&A                 | 2.8                | 20         |
|  |                | Ion bombarded       | 5.2                | 25         |
| Ti <sub>2</sub> O <sub>3</sub>             | 10 $\bar{1}$ 2 | UHV cleaved         | 3.4                | 25         |
|  |                | UHV cleaved         | 3.9 ± 0.1          | 26–28      |
| V <sub>2</sub> O <sub>3</sub>              | 10 $\bar{1}$ 2 | UHV cleaved         | 4.9 ± 0.1          | 29         |
| V <sub>2</sub> O <sub>3</sub><br>(1.5% Cr) | 10 $\bar{1}$ 2 | UHV cleaved         | 4.2                | 30         |
|  |                | Ion bombarded       | 4.4                | 30         |
| $\alpha$ -Fe <sub>2</sub> O <sub>3</sub>   | 0001           | P&A                 | 5.4 ± 0.2          | 31         |
|  |                | Ion bombarded       | 4.5 ± 0.2          | 31         |
| NiO  | 100            | UHV cleaved         | 4.4 ± 0.1          | 32         |
|  |                | P&A                 | 4.65 ± 0.02        | 33         |
|  |                |                     | 4.40 ± 0.05        | 34         |
|  |                |                     | 4.35 ± 0.02        | 35         |

Technology that the only person who knows the exact temperature is the person who has only one thermometer.) Thus the data in Table 1.1 are intended more as a warning than as a source of useful information.

This is not to say that work functions of metal oxides are entirely useless. The *relative* changes in  $\Phi$  that accompany the variation of some parameter of the surface can contain a tremendous amount of information, and such changes are often used in studies of adsorption, defect creation, etc. We will discuss work function changes wherever applicable, since they can be a very sensitive measure of the response of the surface. In some cases, such as chemisorption, quantitative information can be obtained from changes in  $\Phi$ . But the absolute values will rarely be discussed, and many papers that study work-function changes do not even mention the absolute values for the reasons given above.