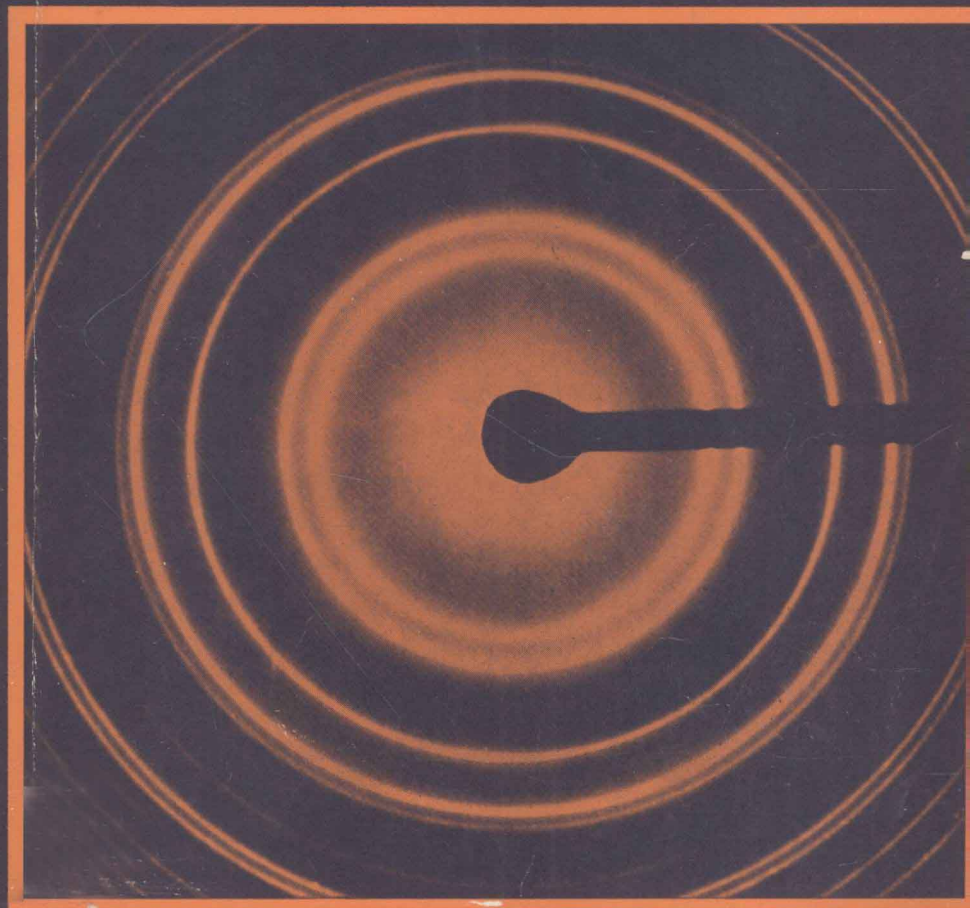# Thin Film Physics

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THIN FILM PHYSICS

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Preface

Although some nineteenth-century activity is recorded in connection with thin film studies, it was not until the middle of the twentieth century that a really substantial effort began to be devoted to this field. There are two main reasons for this. On the one hand, the experimental techniques required in order to carry out meaningful studies had not been developed. On the other hand it was found that many of the rapidly increasing demands of technology could be met in a thorough and elegant fashion by the exploitation of thin film properties.

This monograph provides a fairly extensive view of the present state of progress in a number of important areas of thin film physics. A complete book could be written on any of the chapters contained herein – in fact several such books already exist. Thus the present work is not intended to provide in-depth studies of any particular area, but rather to provide, for the general reader or for the newcomer to the field, a general background from which interests in individual directions may develop. As will be seen, the state of progress in different fields varies somewhat. In some cases, highly sophisticated models have been evolved to account for detailed and subtle behaviour of films: in others, only rather general comments are possible.

Within the last few years, the improvements in experimental techniques have begun to exercise a decisive influence on the progress of thin film physics. For the first time, experiments have become possible under very highly controlled conditions. Diagnostic techniques have been developed which enable far more direct information to be obtained than hitherto. In some of the sections of this book, the impact of these new methods is beginning to appear.

It is a pleasure to acknowledge the assistance of Drs Prutton, Chambers and Gallon, for providing the diffraction patterns for Plates I, III, V, VII and VIII, and to thank the Optical Society of America for permission to reproduce fig. 6.7.

Contents

1

Introduction

At the time of writing, a very considerable part of our industry is involved with thin films. Much of this is old-established, as in the use of electroplated films for protection or decoration. Much of it is of recent origin and involves the use of techniques which have been developed over the last few years. In one way and another most physical properties of films – optical, chemical, magnetic, electrical, etc. – are of importance in an ever widening sphere of industrial, scientific and technical applications. At the same time studies of the fundamentals of film formation and of the basic reasons for differences in behaviour between films and bulk materials are being pursued with increasing vigour. With the development of sophisticated methods of production and examination, our understanding of many of the apparent vagaries of film behaviour is steadily improving. Many of the discrepancies in our early experiments on films are now known to have arisen from factors whose influence was unknown or unsuspected. Advances in many of the necessary accompanying technologies have enabled work on films to be carried out under conditions admitting a high degree of control.

The first results of such recent developments have shown an increase in the reproducibility of results obtained on *some* thin film systems. Let us not give the impression that no problems remain to be solved in this respect. As will be seen in the discussions of the succeeding chapters, there remain several fields in which, in spite of the most careful control of conditions of preparation, wide variations in film properties result. In some cases, this characteristic remains an effective barrier to the commercial use of films in developments where it is known that great advantages could accrue.

Our problems in studying thin film systems begin before we pro-
duce the film. The structure and properties of many films are known
to depend considerably on the state of the surface on which they
are deposited. It is to be expected that this will be so for films of
average thickness corresponding to only a few atomic diameters,
and this is indeed found to be so. Sometimes, however, the influence
of the substrate makes itself felt in films of considerably greater
thicknesses than this. The way in which the crystallographic form
of films depends on substrate surface conditions is discussed in
Chapter 4.

Our initial problem, then, in dealing with film properties is one
of surface physics. We need to know exactly what kind of surface
is being used for the deposition of the film – whether it is crystallo-
graphically oriented or not; what density of dislocations or imper-
fections exists; whether any absorbed gas is present and if so, what
gas and how it is bonded to the surface; if the surface is gas-free,
then what is the spatial distribution of surface atoms of the substrate
and what is that of the electrons in the neighbourhood of the surface
atoms; what are the activation energies for desorption and surface
migration of the deposit atoms on the surface. These are typical of
the questions to which answers may be needed before an adequate
description of film properties can be made. We are, in most cases,
not able to furnish even a fraction of the answers. The reason for
this is in part, that the necessary experimental techniques for find-
ing many of the answers have only recently come into our hands.
The results of the application of some of the powerful techniques
recently developed have sometimes been surprising. Thus we had
happily assumed that the crystallographic arrangements of atoms
on the surface of a crystal would be not too violently different from
that of a parallel plane inside the crystal. We would expect that the
interplanar spacing normal to the surface may differ from that
inside the crystal. We may even imagine that the surface atoms
may be displaced along the normal to the surface by different
amounts, depending on their crystallographic position. We would
not expect to find the symmetry of the distribution of the surface
atoms to differ radically from that of the atoms inside. This, how-
ever, is precisely the kind of thing which has been observed when
the recently developed technique of slow-electron diffraction coupled
with post-diffraction acceleration has been applied. Shattering ob-

servations of this kind make it clear that, even with the clean surfaces which can be produced and maintained in the present ultra-high vacuum system, we are still some way from being able to discuss with confidence the detailed mechanics of condensation phenomena.

In studies of the early stages of film formation it is often not clear whether nucleation or growth effects constitute the dominant mechanisms determining the film structure. Macroscopically it is clear, from electron microscopy, that the film in the sense of a uniform, continuous distribution of atoms, is a rarity, if indeed it ever occurs. However, such observations are based either on films grown in what we now dismiss as 'dirty' vacua – say in the region of 10^{-5} torr – or on films which have been exposed to the air. Our only present method of examining the surface distribution of absorbed atoms under clean conditions is by the indirect method of slow-electron diffraction. Until some intrepid instrument designer produces a high-resolution electron microscope operating at a pressure of 10^{-10} torr, we must remain in semi-darkness on this point.

In this book, we shall devote most of our attention to films whose thickness is large compared with the interatomic spacing. In many cases (although not all) such films exhibit behaviour which is at most only mildly influenced by the underlying substrate, at least in the sense of being more or less independent of the effects of the binding forces to the substrate.

We shall first review the various methods by which thin films are produced, discussing the respective merits and demerits of the methods described. The range and scope of methods used to examine film properties and structures will be dealt with and will be followed by an account of the types of structure obtained under various conditions of preparation. The ensuing chapters will then deal specifically with the physical properties of films which have been the subject of study. These chapters will also include accounts of the more important applications of film systems.

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Methods of Preparation of Films

The methods commonly used to prepare thin films of solids may be classified under the following headings:

- (*i*) Electrolytic deposition, which includes cathodic and anodic deposition;
- (*ii*) Sputtering, including the more recently developed method of reactive sputtering;
- (*iii*) Deposition in vacuum from a heated source (thermal evaporation);
- (*iv*) Deposition from vapour reactants;
- (*v*) Diffusion.

In some cases, method (*iii*) may be used reactively, by introducing a gas which reacts with the evaporated material. The main characteristics of these methods are given below.

2.1 *Electrolytic deposition – cathodic films*

The method of making metal coatings by electrolytic deposition on the cathode of a cell is probably one of the oldest known methods for making films artificially. Superficially, the method is simple. Ions in the solution are impelled to the electrodes by the applied electric field. At the electrodes, the charges are neutralized and straight deposition may occur. Alternatively reactions may occur between the resultant atoms or radicals and the electrode or bath materials. The laws governing the overall process are well-known but factors governing the precise form and microstructure of films formed in this way are less well understood. As the method has

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been developed industrially, so valuable empirical techniques have been evolved which enable considerable control to be exercised, e.g. on the brightness, durability, etc. of the films. In many cases the detailed mechanisms of operation of many of the additives used are not yet well understood.

A simplified view of the electrolytic deposition process, inadequate in detail but giving an indication of the main factors influencing the process, may be seen from fig. 2.1. A double layer forms at the cathode of the system, formed by the electrons in the metal and the ions adsorbed on the surface. In this region, the dominant forces are of short range. Adjacent to this region is a diffusion layer, lying between the cathode and the main body of the electrolyte. In the latter, the electrolyte concentration is substantially constant and the transport of ions is effected by the applied electric field. In the cathode diffusion layer, the combined effects of the concentration gradient and field apply so that the motion of the ions is governed both by diffusion and by electrical forces.

From fig. 2.1 it may be deduced that such factors as temperature and state of motion of the electrolyte will, through their influence on diffusion of the ions, affect the deposition conditions. The geometry of the deposition system will play a part since this will determine the local current density. The presence of the double layer on the cathode surface means that there will be a marked selective effect on the adsorption of solution constituents. Thus a significant degree of control is available through the use of additives which exercise buffering effects or inhibit bubble formation, and through which the stress, brightness, texture and other properties of the electrodeposited surface may be determined.

2.2 *Electrolytic deposition – anodic films*

When certain metals are made the anodes of electrolytic cells, oxide film formation occurs, leading frequently to extremely hard, compact well-adhering coatings. Anodised aluminium articles have long been generally available – excellent examples of the way in which the normally highly reactive aluminium is completely protected by the anode film. The electrolytic capacitor forms another everyday example of the use of such films. In the field of electron microscopy, use has in the past been made of anodic aluminium
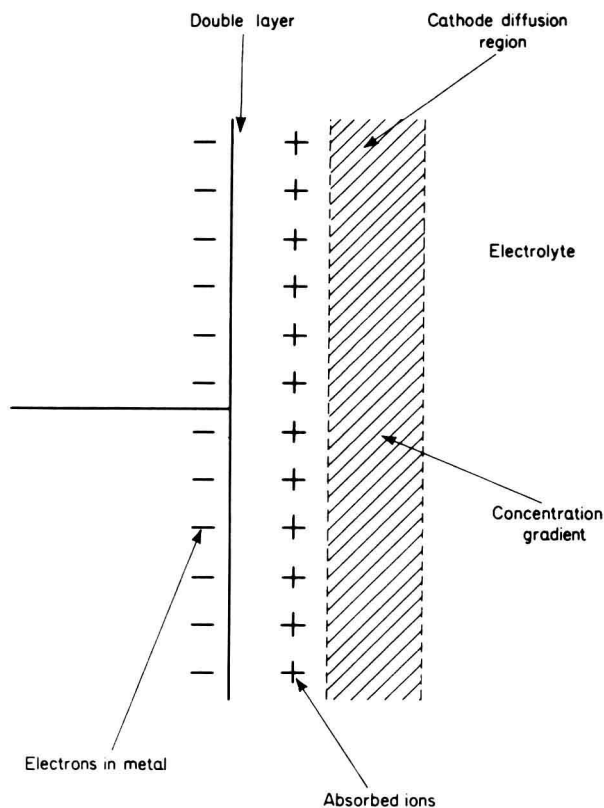
FIG. 2.1. Schematic of electrolytic cell.

oxide as a substrate for transmission electron microscopy. After removal from the metal, the oxide is self-supporting in thicknesses down to less than 10 nm and is amorphous, so that no appreciable detail is seen in the micrograph or diffraction pattern.

The metals on which anodic films may be formed are:

Aluminium	Hafnium	Tin
Antimony	Magnesium	Titanium
Beryllium	Niobium	Tungsten
Bismuth	Silicon	Uranium
Germanium	Tantalum	Zirconium

A typical current/voltage relation for the anodic process is shown in fig. 2.2. At any applied voltage, a combination of electron (leakage) current and ionic current flows although in the region OA, the ion current is negligible compared with the leakage current. Once an appreciable ion current flows, then the behaviour becomes time-dependent, since oxide film is being formed so that the barriers to current flow are changing. It is convenient to consider separately (a) growth at constant current and (b) growth at constant applied voltage.
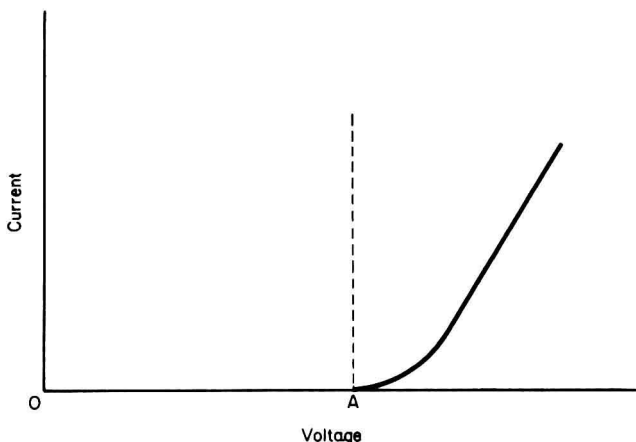

FIG. 2.2. Current vs voltage for anodic process.

It is assumed that the structure and composition of the film is constant during formation and that a constant differential field strength dV/dl is required (V = applied voltage, l = film thickness) to maintain a constant ionic current. Under conditions where the electronic leakage current is negligible, the rate of increase of film mass is proportional to the current so that, under constant current conditions, dl/dt is constant. The voltage/time relation is thus linear since

$$\frac{dV}{dt} = \frac{dV}{dl} \cdot \frac{dl}{dt}.$$

In practice a slight dependence of dV/dl on current is observed. For tantalum at $18°$ C, the value of dV/dt for a current density of 10 mA.cm^{-2} is about 3.6 volts.sec^{-1}.

In applications of the method of anodic film growth, a constant
potential is generally applied. Since the growth of the film results
in a diminished driving field, the current decreases with time. In
practice, the rate of increase of current and hence of thickness falls
to a very low value. In fact, the growth rate always remains finite,
so there is no question of the film's growing to a limiting thickness –
the film will continue to grow indefinitely. However it is found that
with, e.g. aluminium, application of a fixed voltage V to a cell
rapidly produces a film of thickness $\sim 1 \cdot 3 \ V$ nm and that the rate
of increase beyond this value is very low indeed – probably such as
to show no measurable increase over periods of the order of an
hour or two. Thus the concept of an approximate growth/voltage
constant is useful in this sense.

The detailed mechanism of film growth is one of some complexity.
The basic requirement is that of a diffusion mechanism for ions
through the film and it is generally assumed that it is the metal ions
which travel through the oxide. It is clear that the metal/oxide
interface must during growth be in a somewhat dynamic equili-
brium. Little is usually said of the way in which the film bonds to
the metal under these conditions, for the very good reason that little
is known. For discussion of the kinetics of the growth process it is
assumed that metal ions pass through the oxide by interstitial diffu-
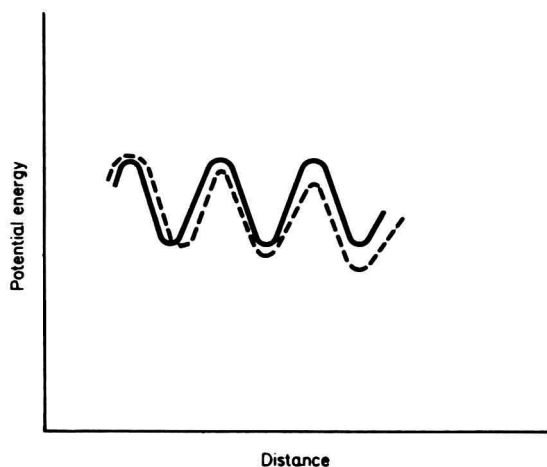sion. If it is assumed that the variation of the potential energy of

Distance

FIG. 2.3.

the ion through the lattice in the field direction is as shown in fig. 2.3, then the effect of an applied field E on the motion of an ion with a charge Ze is to reduce the zero-field barrier W by an amount $ZeaE$. The probability that an ion will surmount the barrier of height $W - ZeaE$ is given by

$$v \exp \left\{ -\frac{(W - ZeaE)}{kT} \right\}$$

so that the current density in the forward direction will be

$$i_+ = 2anv \exp \left\{ -\frac{(W - ZeaE)}{kT} \right\} \qquad 2.1$$

where n is the ion density, which is in general a function of l, and v is the oscillation frequency of the ion in the lattice. For the reverse direction, where a barrier of height $W + ZeaE$ is involved, the current is

$$i_- = 2a \left\{ n + 2a \frac{\partial n}{\partial l_a} \right\} v \exp \left\{ -\frac{(W + ZeaE)}{kT} \right\}. \qquad 2.2$$

Two extreme cases may be recognized. If $ZeaE \gg kT$ ('high-field' case), then i_- is negligible compared with i_+ so that equation 2.1 holds. If $ZeaE \ll kT$, then the net current $i = i_+ - i_-$ is given, to within this ('low-field') approximation as

$$i = 4a^2 e^{-W/kT} \left\{ \frac{nvZE}{kT} - \frac{\partial n}{\partial l} \right\}. \qquad 2.3$$

A refinement of the above simple picture is required to allow for the fact that the potential barrier to removal of the metal ion from the metal will be different from that for diffusion between interstitial sites. Thus the potential curve of fig. 2.4 is more appropriate. If we assume that v = atomic volume of the metal and Ω that of the oxide (i.e. a volume v of metal produces a volume Ω of oxide), then for unidirectional, high-field conditions, the rate of increase of film thickness for a current density i will be given by

$$\frac{dl}{dt} = \left(\frac{iv}{Ze} \right) \Omega \exp \left\{ -\frac{(W - ZebE)}{kT} \right\} \qquad 2.4$$

where $E = V/l$, the field in the oxide and l the oxide thickness. If we adopt Cabrera and Mott's (1949) criterion that the limiting growth rate is that corresponding to the addition of one atomic
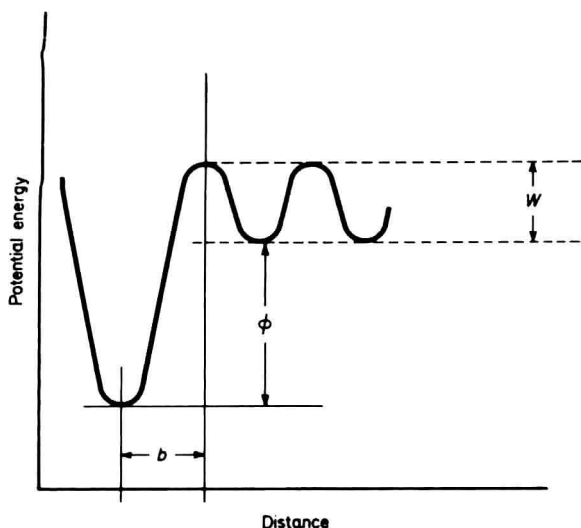
FIG. 2.4.

layer per day, so that $dl/dt \sim 10^{-13}$ cm.sec^{-1} we can determine
the limiting thickness L at which this occurs – viz:

$$L = (ZbV/kT)\left[\frac{W}{kT} - \ln(10^{-13}/A)\right]^{-1} \qquad 2.5$$

where $A \equiv Ze/iv$. Inserting plausible values for the parameters
involved in this equation, a limiting thickness for the thermal
oxidation of aluminium is about 4 nm, in reasonable agreement
with the experimentally observed thickness.

If the Mott-Cabrera theory is applied directly to the case of
anodic oxidation, it leads to predictions which accord poorly with
the experimental observations. A logarithmic law is observed
experimentally (cp. equation 2.5) but numerical values of the
constants are seriously in error. Moreover the experimental results
suggest that the term $ZebE/kT$ is independent of temperature,
implying that b varies linearly with absolute temperature. On
physical grounds, this appears unlikely.

An omission of the potential barrier theory outlined above is that
it does not take account of tunnelling at the barriers. In certain
circumstances, tunnelling may be significantly more probable than
thermal excitation over the barrier. Thus for the case of zirconium,