

OPTICAL PROPERTIES OF THIN SOLID FILMS

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PREFACE

THE earliest recorded scientific studies on the optical behaviour of thin films were made in the seventeenth century. They appear, together with the results of a wide range of other optical experiments, in Sir Isaac Newton's early treatise on Opticks, written in a style which has a charm and fascination of its own. It is a tribute to Newton that reference to his work needs to be made (and not merely from the standpoint of historical interest) in a book written in the twentieth century. Although the mechanism of the propagation of light was in Newton's time shrouded in uncertainty, the observations made on the colours of thin films in relation to their thickness have proved useful for a long time and have formed the basis of certain of the methods of thickness measurement used at the present time.

With the development in recent years of methods of preparing thin films of materials, interest in the optical properties of films has been considerably stimulated. The wealth of information which has now become available is such as to deserve inclusion in a single volume. Although there remain many unsolved problems, the general features of the optical behaviour of thin films are now reasonably well understood. Progress in the methods of studying the structures of films continues apace, further assisting in the problems of interpretation of optical phenomena exhibited by films while developments in the field of high-speed computing are doing much to reduce the labour involved in studying the properties of multiple-film systems. The closing chapter of this book is devoted to a study of the practical applications of thin films, a field in which considerable and striking progress has been made.

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Journal of Applied Physics, vol. 14 (Table 3.1).

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Journal of Scientific Instruments, vol. 29 (Fig. 5.1).

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INTRODUCTION

certain special circumstances. The low state of order accounts for many of the apparent anomalies observed in the behaviour of thin films and poses a severe problem in the development of a theoretical approach.

1.2. METHODS OF FILM DEPOSITION

By far the most widely used method of depositing films, particularly for use in optical systems, is that of thermal evaporation and it is to this method that most attention is given in the next chapter. With no other method can so complete a measure of control be obtained. By the use of suitable shutters and diaphragms and by subtle movement of the target during the deposition of the film, practically any distribution of material on a surface may be obtained. The immediate application which springs to mind in this connection is that of producing the various aspheric surfaces which we know from geometrical optical studies to be so useful. Many such forms are extremely difficult to produce by methods other than the evaporation process—so difficult as to be of no practical interest. These and other applications of this type are discussed in the concluding chapter.

The multiplicity of variables attending the deposition process, by which such effective control may be obtained, is in some measure responsible for the lack of concordance which is so often evident in the results of thin film investigations made by different observers. Until an appreciation of the dependence of film properties on the conditions of formation of the film was obtained, little attention was directed to keeping the many important variables under control. Among the factors which are liable to influence the properties of a film are: rate of deposition, velocity of impinging atoms, structure and condition of target surface, history of film between deposition and examination, etc. Lack of information on these and the many other variables which may determine the nature of the film formed makes comparison of different workers' results very difficult. Electron-optical methods have enabled an appraisal to be made of the effect of the evaporation conditions on the structure and properties of films produced. We may now hope, therefore, for a greater degree of consistency among thin film results from different sources.

1.3. CALCULATIONS OF THE OPTICAL PROPERTIES OF THIN FILM SYSTEMS

When a beam of light traverses a stratified medium in which there are discontinuous changes in refractive index (or changes which take place in a distance small compared with the light wavelength)

multiple reflections occur. If the distances between boundaries are small so that the multiply-reflected beams are coherent with one another, then the intensity of light reflected or transmitted by the system is obtained from the algebraic sum of the amplitudes. The amplitudes to be summed are calculated from Maxwell's equations with the application of the appropriate boundary conditions. For a single film bounded by surfaces of known reflectance, the reflectance and transmittance are given by the Airy summation; this is the familiar case of the Fabry-Pérot etalon. The treatment is approximate inasmuch as it is assumed that the change of phase on reflection of the light at either side of the reflecting surfaces of the etalon is the same. In practice, where a metal reflecting surface is used, this is not true. The error is small, however, for the case where high reflectances are used and this is the usual arrangement in an interferometer. If the properties of the etalon are to be calculated from the optical constants of all the layers, instead of considering the silver layers as possessing an effective reflectance, then the problem becomes very complicated. This, however, is a case of the general problem of calculating the optical properties of a set of films, from given values of the optical constants and thicknesses.

A moment's consideration shows that the method of counting up and summing the multiple reflections is likely to be of limited appeal for systems of many layers. More elegant ways are possible. The summation may be assumed to have been effected before we arrive on the scene so that we deal with the resultant amplitude of the wave in each medium. Expressions for the reflectance and transmittance are then readily found by the application of boundary conditions to the resultant waves. In principle, the solution for any number of layers is straightforward inasmuch as the reflectance and transmittance may be calculated explicitly in terms of the parameters of the system. In practice, the expressions for R and T for more than two layers are very cumbersome or intolerably cumbersome, depending on whether the layers are transparent or absorbing. The effect of inserting complex values of the Fresnel coefficients in the innocent-looking expressions for R and T for even a single film is striking, in an unpleasant way.

The methods used in dealing with this problem are dealt with in Chapter 4. The treatments given are those which can be applied without extensive higher mathematical equipment. Although in certain instances, more elegant treatments and more compact forms are possible, these generally require a considerably greater degree of mathematical skill than that possessed by the majority of physicists.

INTRODUCTION

1.4. MEASUREMENTS ON THIN FILMS

With the increasing importance of thin film work, the need has arisen for information on the properties of films and this has necessitated the development of methods of investigation suitable for dealing with thin layers. Many early methods of measuring film thickness required a knowledge of the refractive index of the film and vice versa. Procedures now developed which enable both quantities to be determined independently have shown how great is the need for methods which are independent of the assumption that any of the properties of a film (save, perhaps, its chemical composition) are the same as those of the material in bulk.

The greatest difficulties arise in connection with films of absorbing materials and especially with those in which the absorption is high (metals). Unequivocal determination of the optical constants of such films is possible only by making measurements of the amplitude and phase of light beams transmitted by and reflected from both sides of the film. These measurements are difficult to make with high accuracy. The pitfalls of earlier methods, which were unable to give the optical constants and thickness simultaneously, are well illustrated by the alarming ranges covered by the various reported values of the optical constants. Such differences may in part have arisen from the use of unsuitable methods of measurement and in part from the fact that the optical constants of films may vary considerably with the conditions of preparation.

The violent variations with thickness of the optical constants of thin metal films have been shown to be a consequence of the aggregated nature of the films. The structure of metal films deduced from observations of the optical properties shows remarkable agreement with that observed directly by electron microscopy or deduced indirectly from electron diffraction and other experiments.

1.5. THE USES OF THIN FILMS

With the rapid development of the design of demountable vacuum systems, the number and diversity of uses of thin films have increased apace. The small vacuum evaporation plant has become an almost essential part of the furniture of the research laboratory. On an industrial scale, the vacuum evaporation system has joined the ranks of routine industrial processes even to the point of being incorporated in a continuous belt system for lens blooming. (Paradoxically, it is now more difficult for a lens-producing plant to produce an unbloomed lens than a bloomed one, the greater hardness of the

bloomed surface making the bloomed product less susceptible to scratches than is the raw glass.)

In the laboratory, thin films find application in a wide variety of types of work. Electrical experiments may often be facilitated by the use of evaporated electrodes, which make intimate contact with the surface without causing mechanical damage. The hygroscopic optical components used in infra-red spectroscopy may be protected by coating with a suitable insoluble film. Reflecting surfaces may be similarly protected against deterioration by the atmosphere. Electrostatic charging, so often the bugbear of experiments employing fine suspensions, may sometimes be reduced by metallizing the offending components; the same process applied to the fluorescent screen of a cathode-ray tube both eliminates charging troubles and results in a brighter picture. The difficulties of measuring surface temperatures are largely overcome by the use of evaporated films as thermocouples whilst the bulk of optical measurements in the near infra-red depend on the photoconducting properties of layers produced by thermal evaporation (with a certain amount of additional persuasion).

Perhaps the most striking of the many developments have been in the field of multilayer filters. From the simple low-reflecting low-index layer and high-reflecting high-index layer, magnificently complicated multilayer systems have been evolved possessing impressive and useful optical properties. Narrow transmission bands, wide bands with steep edges, low- and high-pass filters may now be almost tailor-made to suit requirements. The fact that for some filters large numbers of layers are called for is of no consequence since the development of techniques of deposition and of monitoring have not lagged behind the theoretical work.

From the large number of papers which have appeared in the last few years on the optical properties of thin solid films, it is clear that an exhaustive treatise must be of encyclopaedic proportions. In this work examples have been drawn from a field in which progress is still rapid; they give a representative picture both of the potentialities and of the limitations of thin films in relation to optical studies.

THE FORMATION OF THIN FILMS

Introduction—The thermal evaporation process—Practical methods of evaporation—The method of sputtering—Other methods of film deposition—Fundamental aspects of the condensation process

2.1. INTRODUCTION

WE shall consider in some detail the experimental aspects of the various methods of preparing films. Most attention is paid to the method of thermal evaporation since this method has been most extensively developed. It possesses many advantages over the other methods described below, not the least of which lies in the ease with which the process may be controlled. Films of high purity are readily produced and with a minimum of interfering conditions. In spite of this favourable aspect, however, results of studies of the properties of evaporated films have not always shown the consistency which would be expected. The cause of these discrepancies frequently lies not in any inherent difficulties of the method itself but more probably in a lack of control of the many experimental variables on the part of different investigators, who frequently fail to state the precise conditions under which films are prepared.

The evaporation method is not universally applicable in practice since, for high melting-point materials, it may well be impossible to deposit films without undue heating of the receiving substrate. The temperature of the substrate during deposition plays an important role in determining film structure so that any method in which this factor cannot be accurately controlled is to be avoided if reproducible results are to be obtained. For metals for which the evaporation method is unsuitable, the method of sputtering is often used. In this method, the mean source temperature at which an appreciable rate of sputtering occurs is considerably below that at which thermal evaporation at the same rate would occur so that the amount of radiation falling on the target surface is considerably less. The method of sputtering was used extensively before the development of thermal evaporation techniques, much of the early work on the fundamentals of film deposition (Section 2.6) having been carried out with sputtered materials. The current tendency is to use the

evaporation method where this can be applied rather than that of sputtering on account of the greater control of experimental conditions which is available. Also the possible influence of the considerable quantity of gas which requires to be present in the sputtering process is avoided by using the evaporation method. The method developed recently of sputtering in a magnetic field enables sputtering to be effected at much lower pressures than before.

The importance of the remaining methods quoted is mainly of a utilitarian nature. Little work has been done in studying the properties of electrolytically or chemically deposited films except in so far as the films are of some practical significance. For example, the optical behaviour of certain chemically deposited films has been examined since it is found to be possible to make non-reflecting films and highly-reflecting films by this method (Sections 7.2-3).

2.2. THE THERMAL EVAPORATION PROCESS

We first consider the conditions which must be realized in order that the deposition of a film from the vapour may take place with a minimum of interfering factors. The variables which are to be expected to have some influence on the nature and properties of an evaporated film may be summarized thus:

- (i) Nature and pressure of residual gas in chamber
- (ii) Intensity of beam of atoms condensing on surface
- (iii) Nature and condition of target surface
- (iv) Temperature of evaporation source and hence velocity of impinging atoms
- (v) Contamination by evaporated material by supporting material of source.

The residual gas

It is sometimes stated that the condition to be met for the deposition of films by the evaporation method is that the mean free path of the volatilizing atom shall be large compared with the dimensions of the system or, more specifically, with the source to target distance. Under this condition the evaporating atoms make negligibly few collisions with the atoms of the residual gas in the chamber. The following table gives the values of the mean free path of an atom of silver at various pressures of residual oxygen.

THE FORMATION OF THIN FILMS

Table 2.1

Pressure mm Hg	Mean free path cm
10^{-3}	4.5
10^{-4}	45
10^{-5}	450
10^{-6}	4500
10^{-7}	45000

For a typical laboratory system with dimensions of the order of tens of centimetres, the mean free path condition is met by working at a pressure of 10^{-5} mm Hg. There is, however, an additional and more stringent condition to be fulfilled if the influence of the residual gas on the film structure is to be reduced to negligible proportions. This concerns the rate at which residual gas atoms strike the surface of the target during the deposition of the film. On kinetic theory it is seen that the number of gas molecules at pressure p and absolute temperature T striking unit area of a plane surface in unit time is given by

$$N = p / (2\pi mkT)^{1/2} \quad \dots 2(1)$$

For oxygen at 10^{-5} mm Hg and at room temperature the value of N is 5.2×10^{15} atoms $\text{cm}^{-2} \text{sec}^{-1}$. Taking the area occupied by a single adsorbed atom of oxygen on the surface to be $\sim 1.4 \text{ \AA}^2$ it is seen that at this pressure the rate at which the residual atoms strike the target is such as to form a monomolecular layer in ~ 1 second. Since this rate of deposition is not small compared with that for the condensing material under the usual evaporation conditions, it is clear that, if interference by the residual gas is to be avoided, work must be carried out at pressures very much lower than 10^{-5} mm Hg. In this connection, it may be mentioned that, in their work on the electrical properties of thin films of the alkali metals, E. T. S. APPLEYARD and A. C. B. LOVELL¹ found it necessary to bake the target surface for 80 hours at 250°C at a pressure below 10^{-7} mm Hg before reproducible results could be obtained.

A further example is provided by the behaviour of films of aluminium prepared in a vacuum system employing a mercury diffusion pump. Such films are attacked by mercury, resulting in a breaking-up of the film. This is observed even when trapping with solid carbon dioxide and acetone is used although the vapour pressure of mercury at this temperature (-78°C) is only 3×10^{-9} mm Hg.

It is thus clear that for any work on the fundamental aspects of the condensation process a glass or silica vacuum system, preferably

without greased cone joints, which may be subjected to prolonged baking, is a necessity.

Effect of beam intensity

The influence of beam intensity is shown in a striking manner by the experiments of Wood, Knudsen and others on cadmium, silver, and mercury. The existence was shown of a critical beam density below which no condensation occurred and also of a critical substrate temperature, above which no film could be formed except at very high beam intensities. These experiments and their interpretation are discussed in Section 2.6 below.

The target surface

The effects of the target surface on the nature of the condensed film depend on the structure of the substrate, whether amorphous, polycrystalline or monocrystalline, on the target temperature, and on the cleanliness of the target. The studies of the epitaxy of condensed layers show clearly the influence of the first factor; the condensing atoms tend to take on the structure type of the underlying surface, forming amorphous layers on amorphous substrates and single-crystal layers on single-crystal substrates. This behaviour is itself markedly temperature-dependent. Films of germanium are found to be practically amorphous when deposited on a monocrystalline surface at room temperature. On raising the temperature, the film becomes polycrystalline and, at a higher temperature, monocrystalline (H. KÖNIG², L. E. COLLINS and O. S. HEAVENS³). Unless precautions are taken to maintain the target surface at a steady temperature during the deposition of a film, the adventitious rise of temperature of the surface during the evaporation may result in a film possessing any of a wide range of structure types.

In observations of the structure of antimony deposited (*a*) on a freshly-formed surface of gold and (*b*) on a surface contaminated by a film of grease, S. LEVINSTEIN⁴ found that, in the former, the film formed was continuous (within the resolution limit of some 100Å) whilst on the contaminated surface, aggregates of diameters ranging up to 1–2 μ were formed.

Influence of rate of evaporation

Variation of the rate of evaporation has the effect of varying both the intensity of the condensing beam and also the mean velocity of arrival of the atoms. Separation of these two factors is a matter of some difficulty although, since the range of temperature over which evaporation is practicable tends to be rather limited, the

available range of velocities of arrival is not large. By the use of a velocity selector, Levinstein investigated the effect of varying the beam velocity on the structure of films of gold, bismuth and antimony and found, for velocities within thermal ranges, no detectable influence on structure. This result, although negative, is of considerable value in indicating that variations in structure observed on varying the rate of evaporation result mainly from the variation of beam intensity produced. The difficult experimental problem of separating the two factors is thus removed.

Levinstein observed that low rates of evaporation of these metals tend to produce non-crystalline layers, or layers in which the crystal size is very small ($\sim 10\text{--}15 \text{ \AA}$) whereas high rates of evaporation yield films of large crystallites. Similar behaviour has been reported for chromium⁵.

Contamination by the source material

In much of the work which has been carried out on evaporated films, the method of evaporation using a boat or filament as the supporting source (see Section 2.3) has been employed. Tungsten, tantalum or molybdenum are frequently used for this purpose, since they possess high melting-points. It is known that, in certain instances, e.g. the evaporation of aluminium from a tungsten spiral, solution of the supporting material by the molten charge may occur. The resulting solid solution usually loses the charge material preferentially during the evaporation so that the film formed contains a much smaller proportion of the spiral material than does the molten charge. The extent of the contamination of germanium and silver films by these source materials has been determined by O. S. HEAVENS⁶ using radioactive tracer techniques and has been found not to exceed a few parts per million under the best conditions. It is unlikely that an impurity content of this order will influence the optical properties of films, except in the case of semi-conducting materials in the infra-red region of the spectrum. If this degree of contamination is to be avoided, other techniques of evaporation employing high frequency heating may be employed.

An exhaustive study of the influence of all the factors enumerated above on each substance to be examined would be a time-absorbing and unrewarding process. There are indications that certain of the above factors have negligibly small effect on certain properties of films. Thus Levinstein found no detectable differences in the *structures* of films deposited at different pressures of residual gas over a range extending up to 10^{-3} mm Hg. The *electrical* properties of films of germanium have, however, been found to be significantly

different for films deposited at 10^{-4} mm Hg from those formed at lower pressures. The results of P. L. CLEGG⁷ on the optical properties of silver films show little variation of the optical behaviour with rate of deposition.

2.3. PRACTICAL METHODS OF EVAPORATION

The oven

As mentioned above, for work on the fundamental aspects of the condensation process, an all-glass vacuum system, in which pressures of less than 10^{-8} mm Hg are obtainable, is the first prerequisite. The material to be evaporated must be contained in an oven so that accurate control of the temperature of the source may be effected. Since under the normal evaporation conditions the mean free path of the evaporating atoms is large compared with the dimensions of the system, and therefore with the size of the aperture of the oven, conditions of molecular streaming obtain. The intensity, I , of the beam of atoms leaving the oven in a direction making an angle θ with the normal to the orifice, is given by the cosine law.

If p = vapour pressure of the material in the oven

T = absolute temperature

A = area of orifice

r = distance of target from the oven, in the direction θ then

$$I = \frac{N_0}{(2\pi MRT)^{\frac{1}{2}}} \cdot \frac{pA}{\pi r^2} \cos \theta \quad \dots 2(2)$$

where N_0 is Avogadro's number, R the gas constant and M the molecular weight of the substance evaporating.

On a plane surface (*Figure 2.1*) at a distance y from the oven, the number of atoms arriving per unit area of the surface in a direction θ is given by

$$I_1 = \frac{N_0}{(2\pi MRT)^{\frac{1}{2}}} \cdot \frac{pA}{\pi y^2} \cos^4 \theta \quad \dots 2(3)$$

The oven is heated electrically and the temperature measured near the orifice, using a thermocouple. The relations 2(2) and 2(3) apply only under the mean free path condition stated. If the mean free path is comparable with the slit dimensions, then a cloud of vapour forms near the slit, evaporation takes place effectively from this cloud and the distribution obtained on the condensing surface is characteristic of an extended source. For an oven made from metal, the problem of obtaining an even temperature distribution is not generally difficult. There are, however, many substances

for which no suitable metal exists for use as a container of the molten charge. Thus although aluminium may be evaporated from a tungsten helix, it cannot satisfactorily be melted in bulk in a tungsten oven, on account of the rapid solution of the tungsten in the aluminium. For such materials, a refractory lining, e.g. of graphite, porcelain, quartz, thoria, etc., is required.

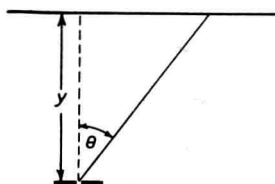


Figure 2.1

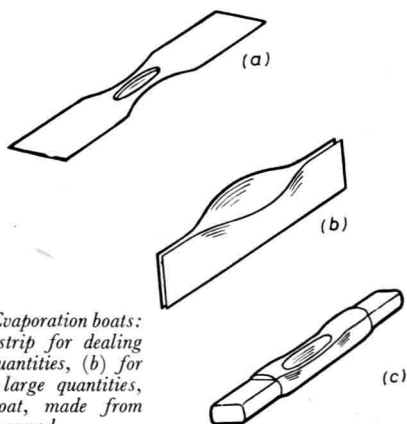


Figure 2.2 *Evaporation boats:*
(a) dimpled strip for dealing
with small quantities, (b) for
dealing with large quantities,
(c) carbon boat, made from
an arc rod

For the preparation of films under conditions where the temperature of the source need not be known with high accuracy, or for the evaporation of materials for which the use of an oven is quite impracticable, there are several simpler types of source, described below.

The strip or boat

This is perhaps the simplest of all methods of evaporation and may be employed for a wide variety of materials. A strip, or shaped boat, of high melting-point material is heated by passing a large current, the material to be evaporated being placed on the strip or in the boat. Typical forms of boat are shown in Figure 2.2. Tungsten, molybdenum and tantalum in thicknesses of about 0.1–0.2 mm are frequently used as strip materials and appear to be suitable for almost all dielectric materials (except the most refractory) and for many metals. With certain metals, particularly aluminium, solid solution of these boat materials by the molten evaporation charge is known to occur and this has the effect of weakening the boat. However, if the boat is mounted in a reasonably strain-free position, fracture may be avoided. The difficulties

occasioned by solution of the boat material may often be avoided by the use of a carbon boat which can conveniently be made from an arc rod.

Preliminary heating of the boat to drive off surface contamination is necessary; the oxides of tungsten, molybdenum and tantalum

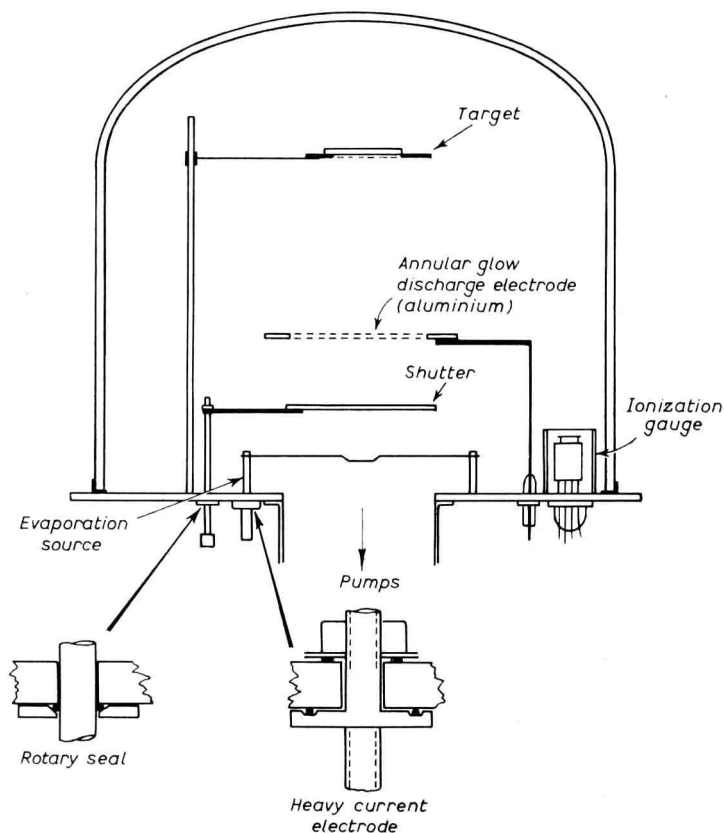


Figure 2.3 Layout of typical evaporation plant

volatilize readily at temperatures well below the melting-points of the metals. When the evaporation is started, a shutter is interposed between source and target in order to intercept the first fraction of the evaporate, which latter may contain impurities from the surface of the charge. In mounting metal strips or boats, care should be taken to avoid materials (e.g. brass screws) which may volatilize