Chapter I

Introduction

The study of the physical properties of thin films has become an important subject in recent years. It is found that the physical properties of materials in the form of thin films are usually a little, and often greatly, different from those of the material in bulk. Over the years, optical and electrical studies have been made on many kinds of films: chemically deposited films, monomolecular layers, sputtered and evaporated films. At the present time, it is the evaporated films which have proved of great interest and importance. The study of evaporated films has become possible on account of the development of vacuum techniques, and the fact that the process of evaporation can be readily controlled.

The materials used for producing optical thin films by evaporation fall into two groups: (i) Dielectric and (ii) Metals. Dielectric films find wide applications in the field of multilayer filters. From the simple low reflecting low index layer and high reflecting high index layer, complicated multilayer systems have been evolved possessing impressive and useful optical properties. Low and high-pass filters can now be almost tailor-made to suit requirements. The theoretical development has almost kept pace with the development of techniques of deposition of the multilayer systems.
Thin films of metals find application in a wide variety of types of work. Electrical experiments may often be facilitated by the use of evaporated electrodes. Electrostatic charging is reduced by metallizing the offending components. The use of silver films can be made for the study of surface topography, birefringence of mica, thicknesses of thin films of few atoms thick and so forth.

**HISTORICAL**

For nearly half of this century, interest in the optical properties of thin films was largely confined to the use of reflecting films in interferometry. Their importance in this connection was considerable. The high resolving powers in such instruments as the Fabry-Perot interferometer enabled an impressive accuracy to be reached in spectroscopic work. However, little attention was paid to the study of thin films from their intrinsic interest.

Within the last twenty five years, interest in the optical and electrical properties has grown considerably. In the case of films of absorbing materials, early studies of electrical and optical behaviour showed large differences from those obtained on bulk materials. The differences were much greater than could be accounted for by considering the limitation of the extent of the material in one direction. A fairly clear picture of this
anomalous behaviour is now possible in view of the advancements, both theoretical and experimental. Electron microscopy has enabled information to be obtained directly regarding the aggregation in thin films. Piccard and Duffendack (1) and Levenstein (2) have thus obtained direct evidence suggesting that the thin film is in a somewhat disordered state, except in certain special circumstances. This low state of order accounts for many of the apparent anomalies but poses a severe problem in the development of the theoretical approach. The information obtainable by electron diffraction enables details of the crystal structure, crystal size, orientation, etc., of the material in the film to be obtained on a truly atomic scale. Thomson and Cochrane (3) have estimated the size of the crystallites in the film from the radial breadth of the diffracted beams of electrons.

The optical and electrical methods of investigation are, in a sense complimentary to the electron-optical methods, each providing information within its scale. The classical theory of film optics, developed notably by Drude (4) and very clearly expounded by Fry (5) considers the propagation of plane waves at the boundary of two optically different media, separated by a uniform film of a third medium. In the present case, the three media are: air, copper film and quartz substrate (Fig. 4B). The theory gave good agreement with experiment for films thicker than about 200 Å by assuming that the films were continuous. However, to maintain the agreement in thinner films, a marked
change of the optical properties with thickness had to be postulated. Garnett (6) showed that this change in the optical constants from those of the bulk metal could be explained by assuming that the thinner films were composed of numerous small aggregates. In the case a thin film which is usually supported on a transparent substrate, additional medium must be considered. Further, multiple reflections will take place within the film. Reflection and transmission, therefore, get modified. Two main approaches have been used:

(i) Fresnel’s formulae are applied to all possible reflected and refracted rays and the resulting geometrical progressions added.

(ii) Maxwell’s equations are solved for the appropriate boundary conditions.

From the latter point of view, a number of recent contributions have been made by Muchmore (7), Hadley and Dennison (8), F. Abeles (9), Leurgans (10) and Epstein (11). Leurgans (10) has applied the impedance concept in thin film optics, for the determination of optical constants of bulk metal. Any of the methods can become cumbersome. One has to resort sometimes to the graphical methods. Oldham (12) has prepared tables with the aid of computing machines to assist in this analysis.
Since the classic work of Minor (13), there have been many studies on optical constants of bulk copper. Important contributions have been made by Malsch (14), Tool (15), and Kretzmann (16). The polishing of the surface presented difficulties. Lowery, Wilkinson and Bor (17) showed that optical absorption of copper could be lowered by reducing the thickness of the polished layer. O'Bryan (18) obtained the optical constants from the measurements on opaque films in the same vacuum in which they were evaporated. The ultraviolet reflectivity of about 22 metals was determined photographically, down to the wave length of 450 Å by Sabine (19). A good summary of the early work is presented by Nathanson (20). Givens (21) and Bok (22) have reported contradictory results with opaque films of copper. Banning (23) reported pronounced drop in ultraviolet reflectivity of copper films when they were exposed to air. Archard, Clegg and Taylor (24) have determined the optical constants of thin films of copper with a photoelectric method of analysing elliptically polarised light. Winterbottom (25) applied the polarimetric technique to studies of oxide film formation on copper, iron and steel at elevated temperatures, using the Drude approximate analysis. Lustmann and Mehl (26) employed the method outlined by Leberknight and Lustman (27) in a study of the oxidation of copper.
In two recent papers, Schulz (28) has described an ingenious new method for measuring the optical constants of metals. The method has been applied to Ag, Au, Cu, and Al. Givens (29) reports that the opaque copper films obtained in a vacuum above 10^{-5} mms. show a disagreement at the red end of the spectrum, when compared with the previous results.

EXPERIMENTAL METHODS OF OPTICAL MEASUREMENT:

Drude (30) was a pioneer in the development of an experimental method for measuring \( n \) and \( k \). His method or some variation of it has been widely used. The method is thoroughly dealt with by Born (31). Without doubt, the Drude method is extremely sensitive. The amount and ellipticity of the light reflected by the surface of an absorbing medium depends on

(i) the optical constants of the bulk material,
(ii) special properties of a surface layer produced by polishing,
(iii) the properties of an overlying surface film, e.g., a film of oxide or of an adsorbed gas on the surface.

The ellipticity is very sensitive to (ii) and (iii), so that under favourable conditions, a film of 2 \( \AA \) thick can be detected. This sensitivity is advantageous for detecting the aging of copper films. Vaselinek (32) has discussed the limits of this polarimetric method for thin film measurements.
There are about a thousand experimental papers on the optical properties of metal, using this method.

Transmission methods have been used in the past by several workers. Prominent contributions are made by Murmann (33), Goos (34), Simons (35) and Schulz (36). These methods are less popular because of the intrinsic disadvantage, that only a limited range of thicknesses can be covered. There are other limitations as well. But with present sensitive instruments, the values of absorption index, $k ( = n k )$ can be determined and the values of $k$ so obtained come closer to those of bulk values.

Recently, the transmission method was applied to obtain the thickness of oxide layer formed on a thin aluminium film by Cabrera, Terrien and Hamon (37).

**SURVEY OF WORK ON ELECTRICAL CONDUCTIVITY OF THIN FILMS**

In recent years, a good deal of work has been done on the measurement of the resistance of thin films both experimentally and theoretically by a number of workers. An exhaustive survey has been made in the reports published by Appleyard, Fery and Bernamont (38). A theoretical discussion of the dependence of the conductivity on the mean free path of electrons is given by Sondheimer (39). A good amount of work on the electrical conductivity of thin films is reported by Eucken and Forster (40), Lovell (41), Pippard (42), Andrew (43), MacDonald and Sarlingson
From these conductivity measurements, Reinders and Hamburger (47), Borel (48) and Ells and Scott (49) have shown that evaporated thin films are not homogeneous and solid, but possess a spongy structure. Very thin layers are made up of isolated aggregates so that below a critical thickness, the resistivity is extremely high. Thicker layers have a connected structure but are still quite porous.

**PRESENT WORK:**

The present thesis incorporates a study of some of the important optical and electrical properties of semitransparent copper films deposited on quartz by the method of evaporation in vacuo. The dependence of these properties on the thickness as well as on the aging of copper films is studied. The present work involves the following experimental aspects of the problem:

(i) Design and construction of evaporation chamber for evaporation of copper in vacuo, so as to obtain uniform semitransparent films on quartz substrate.

(ii) Construction of ellipsometer with a photomultiplier tube attachment and a voltage stabiliser for the analysis of elliptically polarised light reflected by a copper film of complex refractive index \( n - ik \).

(iii) A Unicam spectrophotometer for measurement of percentage transmission from 200 m\( \mu \) to 1000 m\( \mu \).
(iv) Kohlrausch Bridge for the measurement of electrical conductivity.

(v) A multiple beam interferometer for the measurement of thickness of thin films by the method of Fizeau fringes.