CHAPTER I

INTRODUCTION

1.1 General Remarks ... 2
1.2 Historical ... 4
1.3 Work Done on Bismuth Films ... 6
1.4 Work Done on Antimony Films ... 9
1.5 Scope for Present Study ... 12
1.1 GENERAL REMARKS

The remarkable difference in the properties of the material in bulk and of the same material in the form of thin film and ultra-thin film has led the scientists to investigate many interesting problems in this field. Thin film of a given element differs in most of its physical properties from that of a similar film of the same element but having slightly different thickness or prepared under slightly different governing conditions. Apart from these, a film prepared by one method possesses, in general, different physical properties from that prepared by some other method.

It should be noted that many scientists have found it more convenient to study the material in thin film form rather than in the bulk state, particularly some of its properties. The study of the properties of thin films is now becoming more important in the view of numerous applications of thin films in various branches of science and technology. A few of these are as follows:

a. in optical devices like beam-splitters, lasers and interference filters,
b. in electronic devices like thin film transistors, resistors, capacitors, printed circuits and computers,
c. in space research
Besides these, vacuum technology in recent years has achieved its higher stages and this, in its turn, is among the basic requirements for the film preparation mainly by the method of thermal evaporation. All these facts have led many scientists to focus their attention on the study of thin films.

It is found rather difficult to prepare thin films under exactly identical conditions; as a result, two thin films of the same element can hardly possess all properties which are identical or can be reproduced. There are some other factors, theoretical and experimental, which put limitations to the study of the Physics of thin films. Of course, many important facts have been collected as regards the film structure, thanks to the electron microscopy and to the Moire pattern technique.

It is the purpose of the present work to study the optical properties of thin metallic films. On the one hand, different theories that account for the same are studied and on the other hand, optical constants of thermally evaporated films of antimony and bismuth are obtained experimentally. Infinitely many reflections of light rays between the film boundaries lead to the complicated expressions for the calculation of optical constants. These are programmed for the IBM 1620 and the output data are represented graphically to enable the determination of the optical constants for any intermediate parameters.
1.2 HISTORICAL

The variation of the thin film optical constants from their bulk values was first explained by Maxwell Garnett (1). Based on some simplifying assumptions he has put forward the idea that the structure of the film is mainly responsible for such remarkable difference; the film is not merely the so-called thin "layer" of the given element but is a number of small "pieces" that group together to form the layer. The theory has received a very good appreciation and Schopper (2) applied it successfully, in its modified form, to account for the variation of optical constants with thickness. Today, the advancement of electron microscopy has made this interpretation to be more acceptable (3, 4, 5) by providing detailed picture of the film structure. It has now become clear that the film is composed of many microparticles or islands and has thus an aggregated structure that accounts for many of its properties. The degree of aggregation changes so rapidly with the decrease in the film thickness that a metallic film of thickness below 50 A.U. can be said to be semiconducting (6).

The formulae for the evaluation of optical constants of thin films based on the electromagnetic theory of light have been derived by many workers including Caballero (7), Matossi (8), Rood (9), Branes and Czerny (10), Weinstein (11), Crook (12) and others. Forsterling (13)
developed a relation for the dielectric film by summing up an infinite number of amplitudes of light rays reflected between the film boundaries. Murmann (14) generalized them for absorbing films. Vasicek (15) pointed out that Murmann-Forsterling's theory fails to account for the law of conservation of energy. He then developed in a series of papers (16-21) the modified theory based again on infinitely many reflections in the film. It must be noted that both these theories merge into one when all, but one, reflections are ignored.

The theories of thin film optics require that, in general, either of the following pairs of parameters must be measured experimentally:

a. The reflectance $R$ and transmission $T$ for the incident radiation (22-25),

b. The amplitude distortion $\tan \psi$ and phase change $\Delta$ of the radiation reflected from the film surface (26-29).

The determination of $\psi$ and $\Delta$ is based on the method of ellipsometry and the same is followed in the present work. This is a polarimetric method developed by Drude (30) and depends on the change in the state of polarization of light when it is reflected from the surface under investigation. Holmes and Feucht (31), Barakat (32) and Burge and Bennet (33) have given excellent details of
this method. Heavens (34) and Posquet and Rouard (35) have given a comprehensive review on the methods to determine the optical constants of thin film.

The variation of these constants with the film thickness and with the wavelength of incident radiation have been explained by Garnett (1) in the beginning of this century. But in the past decades they are better explained on the basis of the interband transitions of electrons (36); these transitions are sometimes responsible for abnormal variation of the optical constants. The optical transmission is often interpreted in terms of the frequency dependence of the dielectric constant of the film under investigation.

1.3 WORK DONE ON BISMUTH FILMS

The investigation on the optical properties of Bi and Sb in the visible region of electromagnetic spectrum dates back to Drude (30) in 1890. Sabine (37) studied the reflectance of the films of these semi-metals in the region of wavelength between visible and ultraviolet while Plyler and Ball (38) studied their infra-red transmission.

The measurements at low temperatures show that the layers of Bi are in a disordered state after quenching and condensation. The heat and activation energies of transition are 1.45 cal/mol. and 0.09 ev respectively. By producing Bi layers at 4°K Barth (39) could obtain lattice
state stabilized up to 200° K by adding other metals that lower the transition temperature. Takagi (40) evaporated films on crystal surfaces and showed that the film is in the liquid state below the melting point, 271° C; atomic arrangement at 110° C resembles closely that of solid Bi. Above 271° C a tendency toward close-packed structure was noted. Annealed films of Bi contained unoriented grains (41) of 10,000 to 30,000 A.U. size.

Electron diffraction measurement at room temperature (42) shows that the structure of vacuum deposited thin films of Bi is near to cubic than normally it is. The crystals do not change their structure abruptly but there occurs the structure loosening. A detailed investigation (43) showed that the structure is loosening at temperature $\theta$ which is a function of film thickness $d_1$. Microscopic grain size has no effect on $\theta$, but there was a correlation between $\theta$ and crystallographic plane that tends to orient parallel to the substrate. It is worthy of note that (44) in non-crystalline thin Bi film two structures co-exist well beyond the melting point: an expanded spherical close-packing on the one hand and a layer structure on the other. Palantik et al (45) have plotted the microstructure of Bi films as a function of the film depth and of the base temperature.

Heine (46) has noted that the band structure of Bi is such that the number of free electrons and holes
each is 1.5 per atom. A simple many-valley model has been proposed by Abeles and Meiboom (47) for the band structure to account for the galvanomagnetic effects. A number of workers have studied also the de Hass-van Alphan type of oscillations at very low temperatures (48, 49). The Fermi surface of Bi in the free electron approximation modifies (50) when the potential and spin-orbit coupling are introduced. Brown et al (51) have observed that the infra-red magnetoabsorption of Bi is due to direct interband transitions between Landau levels rather than to de Hass-van Alphan type oscillations of the Fermi level.

Diffuse X-ray reflection of evaporated Bi layers at low temperatures (52) showed disordered structure and a sharp reflection on heating. Walker et al (53) obtained a correlation between the photoelectric yield and optical properties in vacuum ultraviolet for such layers. Hodgson (54) used reflection method to measure optical constants of Bi mirror in the infra-red and obtained the number of free electrons to be 5.1 per Bi atom. On the other hand, the mean free path of conduction electrons is found to lie between 20,000 and 40,000 A.U. at room temperature. Schulz (55) has noted that Bi films become relatively transparent in the infra-red region due to low density of free electrons and this accounts for the wavelength variation of optical constants. Again, in the infra-red, the layer density for Bi remains practically the same as
its bulk value. Anomalous optical constants are observed due to lattice defects frozen-in and behave rather like those of extremely thin films.

Kent (56) evaluated the optical constants of Bi over a wide range of wavelengths and Schulz (57) studied them in the infra-red. Walker et al (58) measured experimentally the reflectance of Bi layers down to the wavelengths of 450 A.U., while the optical and electrical properties of Bi layers have been investigated by Harris and Piper (58), particularly in the infra-red.

1.4 WORK DONE ON ANTIMONY FILMS

Many investigators seem to have more interest in Sb than in Bi; a number of workers have studied in its various forms its different properties. Gimminger and Richter (60) observed structural alterations in the layer of Sb when it is being evaporated. Such structural transitions cause the electrical properties of thin films to change (61), as suggested by electron diffraction study, which corresponds to a phase transition from metastable to crystalline form. Bi and Sb, when in amorphous state, exhibit semiconductivity (62) due to the semiconducting bond. Götzberger (63) marked the peculiar dependence on film thickness of the behaviour of amorphous Sb films deposited in vacuum. At 200 A.U. thickness the film goes from amorphous to crystalline state and above 2,000 A.U.
crystallization proceeds at an explosive rate.

Electron microscope investigations by Stoyanova (61) predicted that the amorphous film of Sb (0.5 g cm$^{-2}$) has fine crystallites of 35 A.U. size. Taft and Apka (65) point out that the semiconducting state of Sb is amorphous while Rome (66) observed abnormal behaviour of the optical constants at the phase change. Local pitches appear on thermally evaporated Sb films (67) that represent a brown modification superposed on a blue modification.

When Sb is evaporated on a substrate cooled to 195°K to 90°K, semiconducting film is obtained (68) that changes irreversibly to the metallic form near 273°K; the activation energy is found to be 0.07 ev at high and 0.11 ev at low temperatures. The crystallites each having a size around 1,00,000 A.U. are composed of mosaic whose individual element measures about 30,000 A.U. across. Such crystalline film is bluish by transmitted light (69) showing spherical structure, the region around each nucleus having roughly trigonal symmetry. Besides these amorphous and crystalline forms a heterogeneous form is also known to be possessed by Sb films; Ruedl (70) has studied the crystallization mechanism in heterogeneous films.

Infra-red optical constants of Sb are obtained by Beattie and Conn (71) with a fair degree of accuracy; they are also obtained (72) in the temperature range 290°K to
Moss (73) has given an excellent explanation of the electrical and optical properties of Sb together with many other elements. Infra-red transmission of Bi and Sb films (74) imply that these filters being opaque in visible region, have a short wavelength cut-off varying from 10,000 A.U. to 30,000 A.U.; reflection filters have also been prepared for 1,00,000 to 4,00,000 A.U. wavelengths. Rustgi et al (75) investigated in detail the optical properties of Sb in the vacuum ultra-violet where the frequency at which the film changes from reflecting to transmitting medium is compared with the plasma frequency and also with electron energy characteristic losses. On the other hand, a relation is established between surface density and transmission for wavelengths 4500 A.U., 5380 A.U. and 6650 A.U.. Cardona and Greenaway (76) plotted the reflection curves for Bi and Sb; application of Kramers - Kroning relation enabled a detailed comparison of the optical constants obtained from reflection and transmission measurements. For the bulk polycrystalline samples of these semimetals, Potapov (77) calculated the optical constants in the wavelength range 10,000 A.U. to 1,40,000 A.U. at 2.5° K.

Bowling et al (78) have discussed the reflecting power of thin Sb films while Ruedy (79) studied the crystal structure and surface flow in such films. Sennet and Scott (80) have also thrown light on structural and optical behaviour of Sb films. Baum (81) reported that the transition
from the first to the second modification was very rapid on a glass substrate at room temperature. Highly uniform thin films of Sb were used for transmission measurements in the visible part of electromagnetic spectrum by Condas (82).

1.5 SCOPE FOR PRESENT STUDY

It appears from the reviews of work done on Bi and Sb films in the preceding pages that the interest of workers is directed, in general, to the study of the structural and other physical properties of these films. The optical properties of thin films of these semimetals have been investigated mainly for wavelengths in the ultra-violet and in the infra-red regions. Moreover, Bi and Sb have not been studied on account of the lack of data in the major part of the spectral regions.

It is with this view in mind that thin films of Bi and Sb are selected for the present investigations. Their optical constants are determined in the visible region. All dimensions of the film, except its thickness, are kept identical during the entire study and the optical constants are calculated for the following wavelengths: $\lambda = 4348$ A.U., 4790 A.U., 5085 A.U., 5461 A.U., 5790 A.U. and 5893 A.U. Murmann - Försterling's theory is used for calculating these constants and a comparative study of this theory with Vašlček's theory is also presented.