CHAPTER IX

THERMOPHYSICAL PROPERTIES
9.1. Introduction

Thermophysical properties of metallic films include thermal conductivity, emissivity, diffusivity etc. Accurate measurements of these physical quantities are not easily possible due to the difficulty involved in the experimental techniques. Thermal conductivity and emissivity are closely related to each other. Despite the technological interest of thermophysical data there is a dearth of information in the literature. Even among the available data [1-15] some are not reliable. In the present work an attempt has been made to study the thermal conductivity of some metallic films as well as glass and mica substrates. The emissivity of the metallic films has also been estimated from thermal conductivity data.

9.2. Thermal Conductivity.

9.2.1. Introduction.

Knowledge of thermal conductivity of thin films is essential for an understanding of the mechanism of the heat conduction process, mean free path of heat carriers and their scattering, role of heat transfer during nucleation and growth and similar other phenomena [1]. The rapid rise in the use of thin films in cryogenic system and in vacuum insulation has stimulated considerable interest in the field of thermal conductivity. Hence
this physical quantity assumes an exceedingly important role in practical design and applications. In spite of the fundamental and technical interest, not much work has been done on thermal conductivity of thin films. Earlier investigators have developed various methods for the determination of thermal conductivity of solids in film form /2-11/. The first experimental study was only on silver films /2/. Fraiman et al /16/ have reported results of thermal conductivity for Bi films and Dua and Agarwala /13/ have evaluated theoretically for Alkali metals from resistivity data. Boiko et al /4/ determined thermal conductivity and emissivity of evaporated polycrystalline films of Al and Ag using an electron microscope. Premnath and Chopra have studied thermal conductivity of thin films of Cu and semiconducting thin films /1, 5, 6, 7/ using steady state and transient techniques. Boyce and Chung /8/ have developed a novel technique to estimate the thermal conductivity of Ag films without the knowledge of its heat capacity and density. Kelemen /9/ used pulse technique and reported results of the thermal conductivity of Cu films. But the results obtained for thermal conductivity of Al and Ag films /2, 4, 8/ are divergent. Deviations of thermal conductivity data are attributed either to the degree of purity of the sample or heat losses due to various sources. Hence an improved and modified jig has been fabricated and used to study the thermal conductivity
of metallic films and mica and glass substrates. Often Al, Ag and Cu metallic films are used as electrode materials for fabrication of thin film capacitors and mica or glass substrates. The study of thermal conductivity of Al, Ag and Cu films along with glass and mica substrates has been taken up for the present investigation.

9.2.2. Theory

(a) Heat flow through thin substrates and metallic films.

The heat flow through thin substrates may be treated as one dimensional problem since the thicknesses of the mica substrates used in the present study are of the order of 0.001 cm. Considering the flow of heat through the substrate, one end of which is heated through the heater block and the other end of which is fixed to the differential equation under steady state condition can be expressed as

\[ Q_1 = K_1 A_1 \left( \frac{d\theta}{dx} \right) S \]  \hspace{1cm} . . . 9.1.

where \( K_1 \) is the thermal conductivity of the substrate, \( A_1 \) is the cross-sectional area, \((d\theta/dx)s\) is the temperature gradient and \( Q_1 \) is the amount of heat lost per second by the sink to the surroundings.

If a film is deposited on a mica substrate of similar dimensions, equation 9.1 can be suitably modified as

\[ Q_2 = (K_1 A_1 + K_2 A_2) \left( \frac{d\theta}{dx} \right) S + F \]  \hspace{1cm} . . . 9.2.
where $K_2$ is the thermal conductivity of the film, $A_2$ is the cross-sectional area of the film, $(\text{d}T/\text{d}x)_{S+F}$ is the temperature gradient and $Q_2$ is the amount of heat lost per second by the sink to the surroundings. From equations 9.1 and 9.2,

$$K_2 = \frac{1}{A_2} \left[ \frac{Q_2}{(\text{d}T/\text{d}x)_{S+F}} - \frac{Q_1}{(\text{d}T/\text{d}x)_{S}} \right] \quad \ldots \quad 9.3.$$

The amount of heat lost per second $Q_1$ and $Q_2$ by the sinks attached to substrate and substrate with film respectively can be calculated using Stefan-Boltzmann law,

$$Q_1 = P \epsilon \sigma (\theta_1^4 - \theta_0^4)$$

$$Q = P \epsilon \sigma (\theta_1 - \theta_0) (\theta_1^3 + \theta_1^2 \theta_0 + \theta_1 \theta_0^2 + \theta_0^3) \quad \ldots \quad 9.4.$$

where $\epsilon$ is the emissivity of lead sink, $\sigma$ is the Stefan's constant, $P$ is the surface area of the sink, $\theta_0$ is the surrounding temperature (held constant) and $\theta$ is the temperature of the sink attached to substrate only.

For small temperature differences between the sink and surrounding, the above equation 9.4 can be written as

$$Q_1 = 4P \epsilon \sigma \theta_0^3 (\theta_1 - \theta_0)$$

$$Q_1 = F(\theta_1 - \theta_0) \quad \ldots \quad 9.5.$$

where $F = 4P \epsilon \sigma \theta_0^3$

Similarly the expression for heat lost $Q_2$ by the film and substrate combination with sinks of similar
dimensions can be written as
\[ Q_2 = F (\theta_2 - \theta_0) \] .. 9.6.

Here \( \theta_2 \) is the temperature of the sink fixed to the film and substrate combination.

An obvious problem associated with steady state method is the length of time required to establish the temperature equilibrium. But precise value can be obtained for thermal conductivity of thin films by making use of this method and applying the equation 9.3.

(b) **Thermal Transport by electrons and phonons.**

The total thermal conductivity of a metal is the sum of two different conductivities
\[ K = K_e + K_g \] .. 9.7.

the first one is the electronic thermal conductivity and the second is the phonon thermal conductivity /17,18,19/. In the case of pure metals \( K_g \) can be neglected since the phonon contribution to total thermal conductivity is negligibly small. In general, in the case of normal pure metals, electrons carry almost all the heat current. But in very impure metals, the phonon contribution may be nearly equal to the electron contribution since the collision between electrons and phonons becomes prominent. Detailed theories of thermal transport by pure metals have been discussed by Ziman in 'Electrons and phonons' /19/.
No precise relationship is available in the literature to express the temperature dependence of the thermal conductivity. However an empirical relation has been suggested by Chopra and Freimanth /5/ in the form

\[ K^{-1} = \alpha T^n + \beta / T \]  

which can describe the observed temperature dependence of thin metallic films. Here \( \beta \) and \( \alpha \) are constants, \( K \) is the electronic thermal conductivity and the parameter \( n \) is such that \( n = 0 \) for \( T \gg \Theta \) and \( n = 2 \) for \( T \ll \Theta \). \( \Theta \) is the Debye temperature.

(c) Electrical-thermal transport analogy and size effect.

Thermal conductivity should exhibit size effects similar to those observed in electrical conduction. Hence it is possible to make use of the same formalism for calculating the effective values of the free paths to account for the size effects. Further Klose /20/ has shown theoretically the equivalence of size effects in thermal and electrical conductivity. But it was stressed by Wyder /21/ that, in using this electrical thermal transport analogy, a clear distinction must be made between the free paths of electrons for the electrical conductivity process and those for the thermal conductivity.

According to the above electrical-thermal transport analogy, the thermal conductivity of thin metallic film can be written as

\[ \frac{K_B}{K_F} = \phi \left( \frac{t}{1_K} , P \right) \]  

\[ \ldots \ldots 9.9. \]
where $K_F$ and $K_B$ represent the thermal conductivity of the film and bulk respectively, $l_K$ is the electronic mean free path for thermal conductivity and $P$ is the specularity parameter, $P=0$ for diffuse scattering and $P=1$ for specular scattering. The function $\phi$ in the above equation 9.9. has been obtained theoretically by Fuchs /22/. The limiting form of this function for large $t/l_k$, which is generally considered valid for $t/l_k >> 1$, is reasonably accurate down to $t/l_k \approx 1$ and is given by

$$\frac{K_B}{K_F} = 1 + 0.4 \left(1 - P\right) \frac{t}{l_k} \quad t/l_k > 1 \ldots 9.10.$$  

the thickness-dependent thermal conductivity of thin films can be determined using the above formulation.

9.3. Fabrication of Thermal Conductivity Jig.

Methods like steady state and transient techniques have been applied in the measurement of thermal conductivity of thin films at different temperatures. In the present investigation, steady state technique has been used for measurements of thermal conductivity above room temperature. This method has been chosen mainly because of its simple procedure and accuracy in the measurements. Unlike other steady state methods, it measures directly the thermal conductivity and does not require any other calibration. This method requires no guard heaters. Finally, the method yields the value of thermal conductivity for a number of samples simultaneously.
The general lay out of the apparatus designed and fabricated for thin films is illustrated in Figs. 9.1, 9.2 a, b, and 9.3 a, b, ... The apparatus can accommodate 12 samples simultaneously. The jig essentially consists of a U-shaped copper block of wall thickness 1 cm, which forms the heater block. Heating element consists of a 'Kanthal' wire which gives a constant temperature and the constancy is better than ± 1K. Stabilized power supply has been used for heating. Substrates and film specimen can be fixed on the top of the heater block. A thin layer of silicone grease is applied to establish a good thermal contact between samples and heating block.

Stainless steel radiation shields are fixed to copper block to prevent the heat from reaching the sinks /23/. Lead sheets have been used to prepare sinks. The free end of the substrate is wrapped and pressed with sink and silicone grease is applied to ensure a good thermal contact between the sample and sink. Copper-constantan thermocouples are used to measure temperatures at different points as shown in Fig. 9.4. Care has been taken to ensure a perfect thermal contact, with regard to the thermocouple junctions and their terminals. The temperature measurements are made with the specimen in steady state condition (temperature independent of time) with the help of a Philips D.C. Microvoltmeter.
Fig. 9.1. Schematic arrangement of the thermal conductivity jig for thin films.

1. U-shaped Cu block
2. Kanthal heating element
3. Mica sheets
4. Steel plate
5. Radiation shields
6. Bakelite sheet
7. Thermocouple
8. Sink

(A-L) - Samples.
Fig. 9.2. (a) Top view of the Jig.

Fig. 9.2. (b) Front view of the Jig.
Fig. 9.3. Experimental set up for the steady state technique with fabricated jig (a) with bell jar.
Fig. 9.3. Experimental set up for the steady state technique with fabricated jig (b) without bell jar.
Fig. 9.4. Location of various thermocouples junctions for temperature measurement within the vacuum system.

H - Thermocouples for measuring temperature of heater block at six points.
A - Thermocouples for ambient temperature measurements at four points
S - Thermocouples for measuring temperatures of sinks attached to substrates.
F - Thermocouples for measuring temperature of sink attached to film sample.
The entire arrangement is mounted on a wooden platform (Fig.9.3b) lined with aluminium, asbestos cloth and neoprene sheets and covered with a 12" metallic bell jar (Fig.9.3a) with provision for water circulation to maintain a constant ambient temperature inside the vacuum chamber. The various connections such as thermocouple wires, power supply leads and suction tube are taken out of the vacuum system through a teflon feed-through to a front panel of terminals. A glass T-tube is connected vacuum tight to a rotary pump with provision for suction and air inlet. The current through the heater block is varied with the help of a dimmerstat.

9.3.1. Measurements.

Well cleaned mica substrates and film samples were fixed in position. The required voltage was applied to heater and vacuum of $10^{-2}$ Torr was maintained. After heating for 4 to 5 hours, the steady state was reached whence the temperature measurements were carried out using a precalibrated D.C. Microvoltmeter. Care has been taken to keep the surrounding temperature ($\theta_0$) a constant by suitably adjusting the rate of water flow. The thermal conductivity of substrate ($K_1$) and film ($K_2$) at different temperatures was calculated using the equation 9.1 and 9.3 respectively.
9.4. Thermal Conductivity of Substrate.

9.4.1. Introduction

Thermal conductivity and its variation with temperature of substrate are becoming increasingly important as new methods of fabricating thin film electronic, thermal and optical components are developed.

An ideal substrate, should provide only mechanical support for thin films formed on it, but not to interact with the film. However in practice, the substrate exerts considerable influence on the thin film characteristics. Knowledge of thermal conductivity variation with temperature is a pre-requisite for the design of thin film circuits because it is often relied upon to dissipate the heat of thin film circuit elements and thereby to limit the temperature increase. At times the substrate may be affected by excessive heating and consequently the film material also may be affected. In certain requirements, the desirability of high thermal conductivity to minimize temperature gradient is obvious. In thermal conductivity studies of metallic films, temperature independent behaviour of thermal conductivity of the substrates is preferred so that the thermal conductivity variation with temperature of the substrate may not have any influence on the properties of the film deposited over it. For other general thin film studies, it has been found qualitatively, upon investigation, that glass has got better qualities compared to other substrate materials /24,25,26,27/. It is
well known that large areas of mica are atomically smooth and that under suitably controlled conditions films with atomically smooth surfaces may be grown /17,28/. The variations of thermal conductivity of amorphous glass of known composition and crystalline mica substrates with temperature have been studied and the results compared.

9.4.2. Experimental.

9.4.2.1. Glass substrates.

The thermal conductivity of glass substrates has been studied by earlier investigators /29-35/ using the transverse flow of heat. In the present study the thermal conductivity of glass substrates (two samples of different compositions) has been determined employing the longitudinal flow of heat in the steady state technique in the temperature range 315K to 420K and making use of the modified thermal conductivity jig. Before making measurements the cleaned samples were annealed for two hours at 150°C. The compositions of the samples have been analysed using a mass spectrometer (Table 9.1). Measurements have been made as described earlier and thermal conductivity has been estimated using equation (9.1).

9.4.2.2. Mica substrate.

The thermal conductivity of mica (Mica Trading Corporation of India) along the direction parallel to the cleavage plane has been reported in the low temperature range /36/ and high temperature data corresponding to
Table - 9.1.

Physical properties of glass substrates and their compositions

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Density (g/cm³)</th>
<th>Browster angle (°)</th>
<th>Dielectric constant (ε)</th>
<th>Surface roughness (Talysurf)</th>
<th>Chemical composition of oxides</th>
<th>Chemical thermal conductivity (cal sec⁻¹ cm⁻¹ K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.25</td>
<td>SiO₂ 65</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>56°38'</td>
<td>7.59</td>
<td></td>
<td>Na₂O 20</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.5185</td>
<td>0.011</td>
<td></td>
<td>CaO 8</td>
<td></td>
</tr>
<tr>
<td>Glass-1</td>
<td>2.50</td>
<td></td>
<td></td>
<td></td>
<td>Al₂O₃ 1.5</td>
<td>0.00225</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Fe₂O₃</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>56°30'</td>
<td>5.05</td>
<td></td>
<td>Ta₂O₃ 2.5</td>
<td></td>
</tr>
<tr>
<td>Glass-2</td>
<td>2.49</td>
<td></td>
<td></td>
<td>0.7</td>
<td>SiO₂ 65</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.5108</td>
<td>0.0096</td>
<td></td>
<td>Na₂O 24</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>CaO 9.3</td>
<td>0.00209</td>
</tr>
<tr>
<td></td>
<td></td>
<td>56°30'</td>
<td>5.05</td>
<td></td>
<td>Al₂O₃ 1.2</td>
<td></td>
</tr>
</tbody>
</table>
the direction perpendicular to the cleavage planes are limited. In the present study, the change of thermal conductivity with temperature of muscovite mica \( [\text{KH}_2 \text{Al}_3(\text{SiO}_4)_3] \) along the direction parallel to the cleavage plane has been carried out in the temperature range (330K-500K) using the longitudinal flow of heat in the steady state technique with the modified jig fabricated. The physical properties of thin (\(<0.02\text{ cm.}\)) muscovite mica used for the study are presented in table 9.2. The contamination produced on mica substrates while handling and cutting and other impurities are removed by cleaning them with hydrogen peroxide (5%) for an hour, rinsed with distilled water and methanol.

Before making measurements on mica, they were dried at 75°C for 30 minutes. As described earlier, measurements have been made and thermal conductivity has been determined.

9.4.3. Results and discussion.

9.4.3.1. Glass substrates.

The mass spectral analysis of the two samples of glass substrates yielded the data presented in table 9.1 along with other properties. X-ray diffractograms (Fig.9.5 1 and 2) establish the amorphous nature of the glass substrates, which is inconformity with earlier observations.

The variations of thermal conductivities of glass substrates with temperature have been found to be linear as represented in Fig.9.6a. The \( Y \) intercepts in the above
Table - 9.2.
Physical properties of Muscovite Mica.

<table>
<thead>
<tr>
<th>Sample and its crystal system</th>
<th>Density (g/cm³)</th>
<th>Specific heat at 25°C (cal/g/°C)</th>
<th>Dielectric constant at room temperature (MHz)</th>
<th>Thermal conductivity (⊥r to cleavage plane) (cals/cm/sec/°C)</th>
<th>Hardness (Mohs)</th>
<th>Thermal expansion (⊥r to cleavage)</th>
<th>Thermal expansion (⊥l to cleavage)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Muscovite Mica</td>
<td>2.81</td>
<td>0.207</td>
<td>7.2</td>
<td>0.0016</td>
<td>2.9</td>
<td>20 x 10⁻⁶</td>
<td>8.5 x 10⁻⁶</td>
</tr>
</tbody>
</table>
Fig. 9.5. X-ray diffractograms for glass samples
No. 1 and 2.
Fig. 9.6. (a) Variation of thermal conductivity of glass substrates with temperature.
figure viz. 0.0021 and 0.00199 represent the thermal conductivity of the two samples. Sharpe's formula /35/ with factors based on weight percentages of constituent oxides has been employed to estimate thermal conductivity and the values are found to be 0.0021 and 0.00199 for the above samples respectively.

The thermal conductivity of the glass substrates has been observed to increase with increase of temperature. Similar observations have been made by earlier investigators /29-35/ using the transverse flow of heat through glasses. The rates of increase in thermal conductivity with temperature have been found to be 15\% and 10.3\% per 100°C for the two samples studied. This is also in conformity with the results reported earlier /37/.

The variation in thermal conductivity of glass substrates with temperature, can be satisfactorily explained on the basis of phonon conduction which is considered to be the primary mechanism of heat transfer in glasses. The thermal conductivity is given by $K = \frac{1}{3} cvl$, where $c$ is the heat capacity per unit volume, $v$ is the average sound velocity and $l$ is the mean free path of phonons. The random structure limits the mean free path of phonons and hence $l$ may be assumed to be fixed. The phonon velocity does not change much with increase of temperature and consequently the phonon conductivity may be considered to vary directly with the specific heat. The specific heat in turn varies linearly with temperature.
Thus the observed dependence of thermal conductivity with temperature can be accounted for. Similar observations have been made by earlier investigators for different glasses by using other methods /19,32,38,39/.

9.4.3.2. Mica substrate.

Fig. 9.6b shows the variation of thermal conductivity of mica with temperature. Thermal conductivity of mica initially decreases considerably with increase of temperature in the range 330K-385K and decreases very slowly with further increase of temperature in the range 385K-495K. The initial decrease in thermal conductivity may be attributed to the removal of air and moisture content already incorporated while cleaning. Negligibly small decrease in thermal conductivity in the temperature range 385K-495K is an obvious characteristic behaviour of a crystalline material in contrast to that exhibited by the glassy or amorphous material. The observations made by Powel et al /40/ on the variation of thermal conductivity of mica with temperature using transverse flow of heat also lend support to the present investigation on muscovite mica using longitudinal flow of heat. However the average value of thermal conductivity of muscovite mica at room temperature has been found to be 0.00117 (parallel to cleavage plane). This has been found to be less than the values reported for muscovite mica 0.0016 by earlier investigators /36,40,41/. The essential difference
Fig. 9.6. (b) Variation of thermal conductivity with temperature for mica (thickness 0.015 cm)
between a glass and a crystal lies in the fact that although
the same local order exists in each, the glass lacks the
regularly repeating long range order of the crystal.

9.5. Thermal Conductivity of Metallic films.

9.5.1. Experimental.

Copper, Aluminium and Silver films have been
formed using a 30 cm Hind High Vac. coating unit under
a vacuum of about $10^{-5}$ Torr, on to well cleaned muscovite
mica substrates. High pure materials (99.999% Balzers)
have been used for evaporation by resistive heating. Care
has been taken to obtain films of uniform thickness. The
thickness of film has been determined by multiple beam
interferometer (Fizeau fringes). The thermal conduc-
tivity of Aluminium and Silver films has been studied
in the ranges (375-485K) and (300-500K) respectively. Though
the thermal conductivity studies on Cu films have been made
by Chopra and Premnath /1,5/ here it has been carried out with
a modified jig and results have been compared.

9.5.2. Results and Discussion.

9.5.2.1. Thickness dependence.

Figs.9.7 and 9.8 show variations of thermal
conductivity of Al, Ag and Cu films with thickness at
different temperatures. The values of coefficients of
thermal conductivity of these films are considerably less
than their respective bulk values. This has been attri-
buted to the scattering of electrons at the grain boundaries.
Fig. 9.7. Variation $K$ with thickness for Al and Ag films.
Fig. 9.3. Variation of $K$ with thickness for Cu Films.
and the geometrical surfaces. Beyond certain thickness of films (Al-3760 Å, Ag-2600 Å and Cu-5000 Å) thermal conductivity becomes independent of thickness or in other-words approaches gradually the bulk value. Various authors during their studies on electrical properties of metallic films have concluded that the frozen-in imperfections depend on the deposition conditions and the thickness of the polycrystalline films deposited on mica and these imperfections are contributing to the residual electrical resistivity (temperature independent) of metallic films /17,42-44/.

Thus it has been shown that the contribution due to these imperfections increases with decrease of film thickness, as thinner films have more concentration of imperfections and inturn have greater resistivity /45/. Also the increase of film thickness may enhance the grain size and reduce the concentration of structural defects /46/. The above conclusions can be extended to the present study of the thermal conductivity of metallic films. Thus the observed thickness dependence of thermal conductivity may be due to geometrical, structural factors, lattice impurities and frozen-in structural defects. The results of the present investigations are in accordance with those obtained by earlier workers by making use of other methods /3,4,5,8,9/.

Figs.9.9 and 9.10 represent the plot of $K_t$ versus $t$ (thickness) for Al, Ag, and Cu films. According to Fuchs theory, the nature of the plot should be a straight line.
Fig. 9.9. Plot of $K_t$ vs. $t$ (thickness) for Al and Ag films.

The thermal conductivity $\kappa$ is given by $\kappa = \frac{1}{\rho c_v T}$, where $\rho$ is the density, $c_v$ is the specific heat capacity, and $T$ is the temperature.
Fig. 9.10. Plot of $K_t$ vs. $t$ for Cu Films.
The slight deviations observed in the lower thickness region in the present investigation may be attributed to the contributions from various scattering processes like scattering by grain boundaries, defects etc. in addition to the surface scattering.

9.5.2.2. Temperature dependence.

The coefficients of thermal conductivity of thin films of Al, Ag and Cu are found to decrease with increase of temperature for well annealed samples and are compared with those of bulk materials. (Figs.9.11 and 9.12). As in the case of electrical conductivity of films, the thermal conductivity by means of electrons may be due to the twin processes of scattering. The electrons are scattered by impurities, lattice imperfections and by lattice vibrations. The thermal resistance due to scattering from the boundaries is not independent of temperature. The static defects in metals (viz. impurity atoms, point and line defects etc) give rise to a thermal resistance similar to the residual electrical resistivity. These defects introduce a mean free path which is independent of temperature. As explained already, when thermal conductivity is limited by defects, assuming a constant value for ν, the specific heat of electrons will be proportional to temperature. On the basis of free electron approximation for electronic thermal conductivity, T/k versus T plots should be straight lines for T>θ, where θ is Debye tempe-
Fig. 9.11. Variation of $\kappa$ with $T$ for Al and Ag films.
**Fig. 9.12.** Variation of $K$ with $T$ for Cu films.
rature and should satisfy the equation of the form

\[ K^{-1} = \alpha T^n + \beta/T \]

where \( \alpha \) and \( \beta \) are constants. The parameter \( n \) is zero for \( T>0 \). The linear nature of \( T/K \) versus \( T \) plots for thin films of Al, Ag and Cu and for the respective bulks reveals (Figs. 9.13 and 9.14) that the value of \( n \) is very close to zero in the temperature region studied. It is also to be noted that the grain size of film increases with increase of temperature.

9.5.2.3. Effect of annealing

The effect of annealing (100°C for one hour) on thermal conductivity has been studied for Al, Ag and Cu films. This has also been represented in Figs. 9.11 and 9.12. The broken lines indicating the thermal conductivity of unannealed film follow the same trend as that of annealed film. It has been established that annealing minimizes the structural defects causing a reduction in electrical resistivity /47/. Extending the analogy to thermal conductivity we can say that, the increase in thermal conductivity of annealed films may be due to the reduction in thermal resistivity.


9.6.1. Introduction.

Emissivity of material is a surface property which is related to its thermal conductivity. Emissivity
Fig. 9.13. Plot of $T/K$ vs. $T$ for Al and Ag films.
Fig. 9.14. Plot of $T/K$ vs. $T$ for Cu films.
of thin film coating is an essential parameter in device applications, in solar energy and in space technology. Emissivity characteristics of film surfaces are useful in connection with studies of cryopumping, simulation of the solar space environment and vacuum insulation. Thin film technology makes it possible to obtain surfaces with wide spectrum of thermal emittance which finds their applications in satellite programme /43/. There is always a need for emissivity data and various workers have studied emissivity characteristics of surfaces of bulk /49, 50/, foil /51/ and thin films /48, 52-54/. Recently Boiko et al /4/ and Cunnington et al /55/ have developed techniques and determined the emissivity of metallic film surfaces. In the present study the emissivity of Cu, Al and Ag films has been determined from the thermal conductivity data using Atallah's expression /50/.

9.6.2. Theory.

Emissivity is nothing but the radiation from a surface of a skin of a metal /56/ and it is reasonable to use Atallah's equation /50/ to estimate the values of emissivity of metallic films either from the thermal conductivity or electrical resistivity data. Emissivity is the ratio of the power emitted by a surface to the power emitted by a black body under identical conditions. The emissivity will depend on the surface characteristics of a material such as degree of polish, oxide formed on the surface etc.
According to Jakoob /57/ the relation connecting normal emissivity and electrical resistivity is given by the equation
\[ \epsilon = \frac{T (r_{e273})^{1/2}}{28.5} \ldots 9.11. \]
where \( \epsilon \) is the normal emissivity of smooth and polished metallic surface, \( T \) is the absolute temperature and \( r_{e273} \) is the electrical resistivity in ohm-cm at 273 K. The relation connecting the electrical and thermal conductivity viz Wiedemann-Franz Law is given by
\[ L = \frac{K}{K_0 T} = \frac{K}{\sigma T} \ldots 9.12. \]
where \( K \) is thermal conductivity and \( \sigma = K_0 = 1/r_e \) is electrical conductivity at temperature \( T \). \( \sigma_0 \) is the Lorentz number which is a constant for pure metals and equal to \( 2.45 \times 10^{-8} \) Watt-ohm/deg\(^2\) at room temperature /53-61/. Based on experimental observations and using the above equations 9.11 and 9.12, Atallah has proposed a semi-theoretical equation relating emissivity (\( \epsilon \)) and thermal conductivity (\( K \)) of metallic surfaces,
\[ \epsilon = 1 \times 10^{-4} T K^{-1/2} \ldots 9.13. \]
where \( T \) is in absolute temperature.

The pioneering theoretical work on the radiation properties of thin metallic films was entirely based upon the Drude single (or free) electron (DSE) theory of optical constants /62/. Later anomalous skin effect theory (ASE) /63/ was used for low temperature range. It has been established that when the film thickness becomes smaller
than the electron mean free path, the electrical and thermal properties of the film will differ from those of the bulk metal /15,22,64/. To incorporate the size effect into the skin effect, Dingle /65/ established the theoretical basis for evaluating the radiative properties of thin metallic films on the basis of the ASE theory. Analysis of size and skin effect at low temperature has been made by Armaly and Tien /66/.

9.6.3. Results and discussion.

9.6.3.1. Thickness effect.

The emissivity of Al, Ag and Cu films for different thicknesses are represented in Figs.9.15 and 9.16. As the thickness increases, the emissivity first decreases gradually, and then remains constant. Similar variation has been reported for Al and Au films on Mylar, Kapton and Copper substrates /55,67/. Thinner films have higher emissivity than the thicker films. Increase of thickness beyond a certain limit (Cu-4000 Å, Al-3500 Å, Ag-2500 Å) seems to have no influence on emissivity. It may be due to the effect of inner layers and substrate being completely screened by the upper layers. Thinner films have greater thermal resistance and thus have higher emissivity. Further decrease in thermal conductivity gives less scope for conduction and much scope for emission. Thus the emissivity increases as the thickness decreases.
Fig. 9.15. Variation of emissivity with thickness for Al and Ag films.
Variation of emissivity with thickness for Cu films.

Fig. 9.16.
Fig. 9.17. Plot of $\varepsilon \times t$ vs. $t$ for Al and Ag films.
Fig. 9.13. Plot of $\varepsilon \xi t \times 10^6$ Vs. $t$ for Cu films.
Fig. 9.10. Variation of $\frac{F_i}{F}$ with $T$ for Al and Ag films.
Fig. 9.20. Variation of ε with T for Cu films.
9.6.3.2. Scattering process.

The structural defects, imperfections and surfaces are acting as centres for scattering of the heat carriers (electrons). Fuch's theory based on thickness dependence, arises out of limitation of the mean free path of the electrons by geometrical boundaries of the film /5/ and consequently predicts a straight line for $\epsilon t$ versus $t$ (thickness) curves. The slight deviations observed in the present investigation (Figs. 9.17 and 9.18) indicate that there exists other scattering processes in addition to the surface scattering.

9.6.3.3. Temperature effect

Figs. 9.19 and 9.20 show the variations of emissivity of Al, Ag and Cu films with temperature. Emissivity increases linearly as the temperature increases for the above films for various thicknesses. This is in accordance with the theory. The observations made by earlier investigators /4, 55/ on Al, Ag and Au films lend support to the present investigation. The trend of increase of emissivity with temperature for films is similar to that observed for the bulk. But the values of emissivity for thin films are slightly higher than those of the bulk materials /4, 55, 68/. This may be due to the change in surface characteristics as a result of oxide formation and the higher resistivity exhibited by the material when it is in thin film form.
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