CHAPTER II
THEORETICAL ASPECTS

In this chapter the theoretical models proposed to account for the electrical and dielectric/ optical behaviour of cermet-type films, are briefly outlined. These theoretical approximations were applied to different cermet systems [1-6].

2.1 Electrical conduction

It is considered that all the cermet films fall in one of the two categories of either at high
metal concentrations or high insulator concentrations. The high metal concentrations consist of continuous metal matrix in which the insulating phase is dispersed. Here, the conduction behaviour is metallic. The resistivity values will be 2 to 3 orders of magnitude higher than that of the bulk metal and the temperature coefficient of resistivity is positive. The high insulator concentrations consist of continuous insulator matrix in which the metal particles are dispersed and the conduction behaviour of such films is nonmetallic. The resistivity values range in the order of $10^{-2} - 10^{10}$ ohm-cm and the temperature coefficient of resistance will be normally negative. Though a transition region exists between these two categories, it is very small and does not cover more than two orders of magnitude of resistivity approximately.

C A Neugebauer et al [7-8], studied the activation energy for conduction for Cr-SiO, Au-SiO and Au-SiO$_2$ cermet films. The linear behaviour of log p vs reciprocal of temperature for the compositions in the range 30 to 70 vol%, suggested an activated conduction mechanism. The activation energy increased rapidly with increasing insulator concentrations. Moreover, it
was found to be influenced by the nature of the metal in the cermet system, the deposition conditions, the substrate material and the annealing temperatures.

After a systematic investigation on the Cr-SiO cermet system, a simple model for electrical conduction mechanism for thin cermet films was developed by Joze Gasperic et al [9] in this model, it is assumed that a thin cermet film consists of many cubic metal grains separated by insulating layers of the same thickness If 'C' is the thickness of the insulating layer between the metal grains and 'a' is the cube edge of the metal grain, $V_m$ and $V_i$ are the volume percentages of metal and insulator grains, then the value of $c/a$ will be

$$\frac{c}{a} = \frac{1 - V_m}{V_m^{\frac{1}{3}}} \quad \ldots \quad (1)$$

The elementary cube of the metal and the insulator layer are treated as two resistors coupled in series and the resistivity of such a film is

$$\rho = V_m \rho_m + V_i \rho_i \quad \ldots \quad (2)$$

where, $\rho_m$ and $\rho_i$ are the resistivities of metal and
insulator films respectively. As \( \rho_m \ll \rho_i \) the resistivity \( \rho \) can be written as

\[
\rho \propto V_i \rho_i
\]

(3)

From the equation of current density in an insulating film between two metal grains, during tunnelling, the equation for resistivity of the dielectric phase \( \rho_i \) will be

\[
\rho_i = \frac{22 \beta \exp (A \phi_{\omega}) \sin (\pi BKT)}{C} \frac{1}{T}
\]

(4)

where, \( A = 1 \) 025C \( m^* \gamma_i \) in \( \text{eV}^{-1} \), \( B = 0.5125 \) C \( m^* \phi_{\omega} \gamma_i \) in \( \text{eV}^{-1} \), \( C \) in \( A \), '\( \phi_{\omega} \)' is the average height of the potential barrier, 'K' is the Boltzmann constant, 'T' is the absolute temperature, \( m^* \) is the effective mass of the electrons in the insulator. The value of 'B' was found from the experimental data of Arrhenius diagram as \( R = f(1/T) \), where, 'R' is the resistance during tunnelling, which depends on the temperature as

\[
R \propto \frac{\sin (\pi BKT)}{\pi BKT}
\]

(5)

The equation (4) can be written as
\[
\rho_v = \frac{22.8 \exp \left( 1.025 \left( m^* / q_m \right) \right) \sin \left( 0.5125 \frac{\pi}{T} \left( m^* / q_m \right) \right)}{C}
\]

The TCR, \( \alpha \), deduced from equation (4) can be written as

\[
\alpha = \frac{-1}{T \left( 1 - \frac{\pi}{T} \frac{BKT}{\tan \left( \frac{\pi}{BKT} \right)} \right)} / ^\circ C
\]

The experimental results obtained were very close to those theoretical values calculated with this model for Cr-SiO films in the metal concentrations from 5 to 30 vol%.

R.M. Hill et al. [10-18] presented an analytical method for determining the energy dependence of the electrical conduction in poorly conducting materials and applied to understand the results on Nb-Al₂O₃ cermets films.

The approach developed is based on the magnitude of conductivity and its variation with temperature. The small temperature dependence of the electrical conductivity which is observed in cermets over a wide temperature range suggested that the transport occurs in an energy region very close to the Fermi level. Moreover, the small magnitude of the conductivity indicates
that the states through which the carriers move are not completely delocalised. Since, the conductivity is an increasing function with temperature, the activation energy for conduction is

\[ \Delta \left[ E_c(T) \right] = -\frac{d \left( \ln \tau \right)}{d \left( 1/\sqrt{KT} \right)} \]  \hspace{1cm} (6)

Here, \( \Delta(E_c(T)) \) is a function of temperature. As mentioned earlier, it was considered that the charge transport occurs through a set of states, whose energies are close to the Fermi energy. These states will have a density \( N(E) \) in energy space and can be further characterised by a carrier mobility which may or may not be energy dependent. Hence, to characterise the transport properties in terms of energy dependent conductivity, \( \sigma\left( E \right) \), the measured conductivity is given by the Kubo-Greenwood relationship

\[ \sigma = -\int \sigma\left( E \right) \frac{df}{dE} \, dE \]  \hspace{1cm} (7)

In the above equation, the term \( \sigma\left( E \right) \), varies slowly with \( E \), in comparison with the sharply peaked derivative of the Fermi function with respect to energy. At any temperature \( T \), there is a certain energy which
gives the maximum contribution to the conductivity integral. With this assumption the integral in equation (7) can be evaluated, that has a maximum at \( E = E_m \). By expanding in a Taylor series near \( E_m \), the final result is

\[
\Delta [\log E_\sigma(T)] = E_m \tanh \left( \frac{E_m}{2KT} \right) - \frac{3-2p}{2KT} \left( \frac{p}{2-2p} \right) \quad (8)
\]

and

\[
\sigma(E_m) = 2\pi \frac{v_L}{\eta} \cos h \left( \frac{E_m}{2KT} \right) \left( 1-p \right) \quad (9)
\]

where,

\[
2 \left( \frac{2}{KT} \right) \cos h \left( \frac{E_m}{2KT} \right) \left( \frac{2}{2KT} \right) \frac{\partial^2}{\partial E^2} \log (\sigma(E)) \quad (10)
\]

and closely related to the second derivative of the Kubo- Green Wood integral

An iterative method for determining the required function of \( \sigma(E) \) at any temperature can be obtained from the equations (8)-(10). By assuming a starting value \( p \) and knowing the magnitude of \( \Delta(E_\sigma) \) from the experimental results at any temperature, it is
possible to determine the energy value $E_m$ from equation (8) and thus the form of $\varphi(E)$ from equation (9) and the cycle can be repeated until $P$ does not change significantly from one iteration to the next.

2.2 Optical properties

Numerous investigations [19, 20] were done on the optical properties of thin metal films of gold and silver dispersed in a dielectric medium. The optical properties of these films were explained by Maxwell-Garnett on the basis of structural discontinuities in the films. All the experimental results were interpreted in terms of the theory of Maxwell-Garnett [21-26], which takes into account the modification of the applied electric field at any point within the medium by the dipole fields of the surrounding metal particles. This theory assumes that the metal particles are spherical and small compared to the wavelength of light. The Maxwell-Garnett theory is derived from the Clausius-Mossotti equation applied to a collection of metal particles. This expresses the relationship between the dielectric constant of ensemble of particles $\varepsilon(w)$, the volume density 'n' and the polarisability $\alpha(w)$ of the
metal particles as
\[
\varepsilon(w) - 1 \quad \frac{4}{3} \pi n \alpha(w) \quad (11)
\]

This is applicable where the metal particles are dispersed in vacuum. A slight modification of this equation applicable to metal particles dispersed in an insulating medium rather than vacuum is
\[
\frac{\varepsilon(w) - \varepsilon_i(w)}{\varepsilon(w) + 2\varepsilon_i(w)} = \frac{4}{3} \pi n \varepsilon_i(w) \quad (12)
\]

where, $\varepsilon_i(w)$ is the dielectric constant of insulator.

Since the metal particles are spherical and are immersed in a medium of dielectric constant $\varepsilon_m(w)$, by substituting $\varepsilon_i(w)$ for the polarisability $\alpha(w)$, the above equation leads to Maxwell-Garnett result
\[
\frac{\varepsilon(w) - \varepsilon_i(w)}{\varepsilon(w) + 2\varepsilon_i(w)} = (1-x) \quad \frac{\varepsilon_m(w) - \varepsilon_i(w)}{\varepsilon_m(w) + 2\varepsilon_i(w)} \quad (13)
\]

In this equation, $'\varepsilon_m(w)'$ is the dielectric constant of the metal, $'\varepsilon_i(w)'$ is the dielectric constant of the insulator and 'x' is the volume fraction of insulator. If the dielectric constants of metal,
insulator and their relative concentrations are known, the dielectric behaviour of granular metal can be estimated very easily from the above relation.

R W Cohen et al (23) studied the optical properties of granular gold and silver. In the analysis of the experimental results, various particle shapes were considered by introducing a depolarisation factor \[ L_m \text{'} \], for insulator rich films, \( L_m \text{'} \), for metal rich films in the Maxwell-Garnett approximation.

A more generalised approximation for insulator rich films in which the metal particles are distributed in the continuous insulator matrix is given by

\[
\frac{\varepsilon(\omega) - \varepsilon_i(\omega)}{L_m \varepsilon(\omega) + (1-L_m) \varepsilon_i(\omega)} = (1-x) \frac{\varepsilon_m(\omega) - \varepsilon_i(\omega)}{L_m \varepsilon_m(\omega) + (1-L_m) \varepsilon_i(\omega)} \tag{14}
\]

This equation is valid for insulator rich films and inconsistencies arise for larger concentration of metal particles. In the metal rich region the neighbouring metal particles touch and form a metal continuum and the particles depart from sphericity. The value of \( L_m \text{'} \) varies in the range \( 0 \leq L_m \text{'} \leq 1 \). By substituting \( L_m \text{'} = 0 \) in the above equation, the equation for \( \varepsilon(\omega) \) is,
\( \varepsilon(w) = x \varepsilon_1(w) + (1-x) \varepsilon_m(w) \quad (15) \)

This equation represents the case for flat metallic plates whose normals are perpendicular. Similarly, by substituting \( L_m = 1 \) in equation (14), the equation for \( \varepsilon(w) \) will be:

\( \varepsilon^{-1}(w) = x \varepsilon_1^{-1}(w) + (1-x) \varepsilon_m^{-1}(w) \quad (16) \)

This represents the case for flat metallic plates whose normals are parallel. The substitution of \( L_m = 1/3 \) in equation (14) agrees with the results that are obtained from equation (13) of Maxwell-Garnett for spherical approximation.

Similarly, the approximation for metal rich compositions can be obtained by performing the transformations \( \varepsilon_m \rightarrow \varepsilon'_n, \varepsilon_m \rightarrow \varepsilon_m, \ (1-x) \rightarrow x \) and \( L_m \rightarrow L'_n \) in equation (14) and is written as

\[
\begin{align*}
\varepsilon(w) - \varepsilon_m(w) & = x \\
(1-x) \varepsilon(w) & = L' \varepsilon'_n(w) + (1-L') \varepsilon_m(w)
\end{align*}
\]

where, \( L'_n \) is the effective depolarisation factor of insulating inclusions. The above equation is valid for metal rich compositions. Here it is considered that the
Insulating particles are dispersed in a continuous matrix, rather than metal particles dispersed in a continuous insulating matrix.
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