CHAPTER IV
DIELECTRIC PROPERTIES

4.1 Introduction

In recent years a great deal of interest has developed in finding out the use of high quality dielectric films for various device applications. The rapid development of electronic industries has increased the demands for new dielectric materials, particularly those with low temperature coefficient of capacitance over a wide range of temperatures. From the analysis of the properties of several thin film insulators, it becomes evident that a large number of dielectric materials are available for the fabrication of thin film capacitors. But only those films which are thermally, chemically and electrically stable are actually used in the fabrication of capacitors. Since the above mentioned qualities are found in rare earth compounds, especially in oxides and fluorides, these compounds seem promising materials for several practical applications[1-5]. Many researchers have reported studies on rare earth compounds[6-14] in thin film form and in pressed pellet form. Neodymium oxide and fluoride are some of the promising representatives of the wide group of rare earth compounds and considerable work has been carried out on these materials[15-30].

Kadzhayan and Egian[21] have studied the properties of Nd$_2$O$_3$ films prepared by sputtering as well as by the oxidation of Nd
metal films. Illins and Ushchabovskii[25] have investigated the 
dielectric properties of some of the rare earth oxide (Nd$_2$O$_3$, 
Tb$_2$O$_3$, and Dy$_2$O$_3$) films with f.c.c. structures. Likewise, 
Bertulis and Tolutis[28] have studied the dielectric properties of 
NdF$_3$, PrF$_3$ and CeF$_3$ thin films. Among the various 
electrodes (Ag, Au, In and Al) tried, only Al electrodes gave 
satisfactory results. Recently Dharmadhikari and Goswami have 
studied dielectric properties of vacuum deposited neodymium oxide 
and fluoride thin films[15,30].

Even though study of dielectric properties is more important, 
because these studies help to understand certain fundamental 
physical properties of the system, like structure, localised 
charges, defects, internal field and electrical conduction in 
solids, from the above survey it is obvious that only very little 
work has been carried out on the dielectric properties of 
neodymium oxide and fluoride thin films. With these in mind, an 
elaborate study has been carried out on the dielectric properties 
of thermally deposited neodymium oxide and fluoride thin films. A 
brief theory is given in the first part followed by experimental 
details and concludes with a discussion on the results.

4.2 Theory of dielectrics

4.2.1 Coulomb's Law

In conformity with the basic law of electrostatics-Coulomb's 
law-the force of attraction or repulsion acting between two 
charges, $q_1$ and $q_2$, separated by a distance 'd' in a medium of
permittivity $\varepsilon$' is

$$F = \frac{q_1 q_2}{4\pi \varepsilon_0 \varepsilon d^2} \hat{d}_0$$

.......... (4.1)

where $\hat{d}_0$ is a unit vector directed along a straight line connecting the two charges, $\varepsilon_0$ the electric constant or permittivity of free space ($8.854 \times 10^{-12}$ F/m) and the product $\varepsilon \varepsilon_0$ is called the absolute dielectric constant (or capacitivity) of a dielectric.

4.2.2 Gauss Law

Another most important theorem to be remembered is that of Gauss. It states that the total electric flux, $\phi$, emanating from a closed surface is equal to the total charge enclosed by that surface. Denoting the charges enclosed by the surface by $q_1, q_2, \ldots, q_i, \ldots, q_n$, where the $q$'s may be positive or negative, this theorem may be expressed mathematically by means of a surface integral as follows:

$$\phi = \int \int \vec{D}.d\vec{s} = \sum_{i=1}^{n} q_i$$

.......... (4.2)

where $\vec{D}$ represents the flux density (in C/m$^2$) at the centre of the surface element represented by the outwardly directed vector $d\vec{s}$; the integration extends over the entire closed surface.

4.2.3 Relative permittivity or dielectric constant ($\varepsilon'$)

The electric potential at the surface of a sphere of radius $R$...
having a charge $q$ surrounded by vacuum is

$$V = \frac{q}{4\pi \varepsilon_0 R} \quad \ldots \ldots \quad (4.3)$$

If the sphere is surrounded by a dielectric, we have instead, replacing $\varepsilon_0$ by $\varepsilon$

$$V = \frac{q}{4\pi \varepsilon R} \quad \ldots \ldots \quad (4.4)$$

The relation $q/V$ for the sphere is then $4\pi \varepsilon R$, a constant quantity, independent of the charge $q$. The electric capacity of an isolated conductor is defined as the ratio of its charge to its potential, $C = q/V = 4\pi \varepsilon R$. If the sphere is surrounded by vacuum instead of a dielectric, we have for its capacity $C = 4\pi \varepsilon_0 R$. Therefore surrounding a sphere, and in general any conductor, by a dielectric increases its electric capacity by a factor $\varepsilon/\varepsilon_0$. This is due to the screening effect of the opposite charges induced on the surface of the dielectric adjacent to the conductor. These charges reduce the effective charge of the conductor and decrease the potential of the conductor by the same factor.

The concept of electric capacity can be extended to a system of conductors. Let us consider the case of two conductors having charges $+q$ and $-q$. If $V_1$ and $V_2$ are their respective potentials, so that $V = V_1 - V_2$ is their potential difference the capacity of the system is defined as
This arrangement constitutes what is called a capacitor. A typical capacitor is formed by two parallel plane conductors separated by a distance \( d \), with the space between them filled by a dielectric. The electric field in the space between the conductors is uniform and is given by, \( \xi = (V_1 - V_2)/d \). But if \( \sigma \) is the surface charge density, the intensity of the electric field in the space between the conductors or plates is \( \xi = \sigma/\varepsilon \).

Therefore \( V_1 - V_2 = \xi d = (\sigma/\varepsilon)d \).

On the other hand, if \( A \) is the area of the metal plates, we must have \( q = \sigma A \). Therefore by making the substitutions in equation (4.5), we obtain the capacity of the system as

\[
C = \frac{\varepsilon A}{d} \quad \text{(4.6)}
\]

This suggests a practical means for measuring the permittivity or the dielectric constant of the material between the plates, resulting in

\[
C_o = \frac{\varepsilon_o A}{d} \quad \text{(4.7)}
\]

Then the capacity of a capacitor after filling the space between the plates with the material being investigated is equation (4.6). Then we have
This ratio of the two capacitors gives the relative permittivity or the dielectric constant of the material placed between the plates. The dielectric constant of a dielectric substance is entirely an intrinsic property of the constituted ions and is accordingly more amenable to analysis than loss, which is usually extrinsic near room temperature. In the absence of the electrode effects, the dielectric constant comprises of four components arising out of

(i) extrinsic nature of the material ($\varepsilon_{e_x}$)
(ii) electronic polarisability ($\varepsilon_e$)
(iii) ionic polarisability caused by the vibration of the nuclei($\varepsilon_n$) and
(iv) deformation of the ions ($\varepsilon_d$)

4.2.4 Complex dielectric constant ($\varepsilon^*$) and dielectric loss (tanδ)

The electrical energy expended by an electric field in a material is known as dielectric loss (power loss). Generally the total polarisability of a system is the sum of the individual polarisabilities i.e., electronic, ionic and orientational contributions to the polarisation. Since these are additive, a material may be characterized by a complex dielectric constant. Let us consider a parallel plate capacitor filled with a dielectric which is characterized by $\varepsilon^*$. The functions $\varepsilon'(w)$ and $\varepsilon''(w)$ are assumed to be given. Let the applied alternating field

\[
\frac{C}{C_0} = \frac{\varepsilon}{\varepsilon_0} = \varepsilon_r
\]

\[\text{(4.8)}\]
produce a field

\[ E = E_0 \cos \omega t \] ............ (4.9)

where \( E_0 \) is independent of time and \( \omega/2\pi \) is the frequency in cycles per second.

Let us suppose that a dielectric is subjected to an alternating field \( E = E_0 \cos \omega t \). The induced current in the dielectric will not change immediately, i.e., the current and voltage are maximum and minimum at different times. If a field of this type has persisted for a sufficient length of time \( D \) too must be periodic in time. In general, however, \( D \) will not necessarily be in phase with \( E \), but will show a phase shift \( \delta \), i.e.

\[ D = D_0 \cos(\omega t - \delta) \]

\[ = D_0 \cos \omega t \cos \delta + D_\epsilon \sin \omega t \sin \delta \]

\[ = D_1 \cos \omega t + D_2 \sin \omega t \] ............ (4.10)

where \( D_1 = D_0 \cos \delta \), \( D_2 = D_0 \sin \delta \) and \( \delta \) is the phase angle.

From the equations connecting \( E \) and \( D \) (\( D=\varepsilon E \)) it can be seen that \( D_0 \) is proportional to \( E_0 \) and the ratio \( D_0/E_0 \) usually depends on frequency. Therefore we introduce two frequency dependent dielectric constant \( \varepsilon' \) and \( \varepsilon'' \) which are given by

\[ \varepsilon' = \frac{D_1}{E_0} = \frac{D_0}{E_0} \cos \delta \] ............ (4.11)
\[ \varepsilon'' = \frac{D_2}{E_0} = \frac{D_0}{E_0} \sin \delta \]  \hspace{1cm} \ldots \ldots (4.12) \\

and these two can be expressed by a single complex dielectric constant,

\[ \varepsilon^* = \varepsilon' - j\varepsilon'' \]

where \( \varepsilon' \) is the relative permittivity and \( j\varepsilon'' \) is a component associated with the resistive vector. The factor \( \sin \delta \) is a measure of the energy absorbed by a dielectric. From equations (4.11) and (4.12)

\[ \tan \delta = \frac{\varepsilon''}{\varepsilon'} \]  \hspace{1cm} \ldots \ldots (4.13) \\

The loss factor can also be expressed as follows. When an alternating e.m.f. (V) is applied across a condenser, the current \( i \) through it can be expressed as

\[ i = j\omega \varepsilon \varepsilon_0 V \]  \hspace{1cm} \ldots \ldots (4.14) \\

provided that the dielectric is a perfect one. Generally, an in-phase component of current will appear corresponding to a resistive current between the condenser plates. It is usual to refer to the resistance of a loss current in addition to a charging current by the introduction of a complex permittivity. Then

\[ i = \omega \varepsilon_0 V(\varepsilon'' + j\varepsilon') \]  \hspace{1cm} \ldots \ldots (4.15)
The magnitude of $\varepsilon''$ will be defined by the magnitude of in-phase, or 'loss' component of the current. The performance of a condenser is described in terms of its loss angle $\delta$ which is the phase angle between the total current $i$ and the purely quadrature component $i_L$. If the in-phase component is $i_C$, then

$$|i| = (|i_L|^2 + |i_C|^2)^{1/2} \quad \text{(4.16)}$$

and

$$\tan\delta = \frac{i_L}{i_C} = \frac{\varepsilon''}{\varepsilon'} \quad \text{(4.17)}$$

4.2.5 Polarization

A dielectric increases the storage capacity of a capacitor by neutralising some of the charges at the electrode surfaces which otherwise would contribute to the external field. This is due to the alignment of the electrostatic dipoles in the medium under the influence of the applied field. This process of producing relative displacement of bound charges in a dielectric by an external electric field is known as the polarization. Thus the polarization $P$ which is defined as dipole moment per unit volume is related to the displacement $D$ and the field $E$ in vacuum by the relation

$$\vec{D} = \varepsilon_0\vec{E} + \vec{P} \quad \text{(for vacuum)}$$

or

$$\vec{P} = \vec{D} - \varepsilon_0\vec{E} \quad \text{(4.18)}$$

When a dielectric material of permittivity $\varepsilon'$ is inserted this reduces to
\[ \tilde{P} = \varepsilon_0 (\varepsilon' - 1) \tilde{E} \] ............... (4.19)

Also \( \tilde{P} \) is equal to the electric dipole moment per unit volume induced in the substance by the applied field and is given as

\[ \tilde{P} = N \tilde{u} \] ............... (4.20)

where \( N \) is the number of dipoles and \( \tilde{u} \) is the average dipole moment due to the charged particles. Further \( \tilde{u} \) is assumed to be proportional to a local electric field inside the dielectric. If this is denoted by \( \tilde{E}_i \), being the value of the field acting on the dipole, we define

\[ \tilde{u} = \alpha \tilde{E}_i \] ............... (4.21)

where the proportionality factor \( \alpha \) is called the polarizability of the dipole, i.e., the average dipole moment per unit field strength.

From equations (4.19 to 4.21)

\[ \tilde{P} = \varepsilon_0 (\varepsilon' - 1) \tilde{E}_i = Na\tilde{E}_i \] ............... (4.22)

which, links the macroscopically measured permittivity to the three molecular parameters namely \( N \), \( \alpha \) and \( \tilde{E}_i \), is the well known Classius equation.

Since \( \alpha \) is defined in terms of dipole moment, its magnitude will be a measure of the extent to which electric dipoles are formed by the atoms or molecules. The formation of dipoles may arise due to various mechanisms, any or all equations which
contribute to the value of $\alpha$. In general there are four such mechanisms.

The electronic polarizability ($\alpha_e$) arises from the displacement of the electron cloud in an atom relative to the positively charged nucleus, i.e., from the deformation of the electron shell about the nucleus. This usually occurs at optical frequencies (high frequencies) and so is also called the optical polarizability. Dielectrics having the same type of atoms exhibit such a type of polarizability.

Atomic or ionic polarizability occurs due to displacement and/or deformation of charged atoms/ions with respect to other oppositely charged atoms/ions. Solids containing more than one type of atoms, but having no permanent dipoles, exhibit this type of polarization.

The asymmetric charge distribution between the unlike partners of a molecule gives rise, in addition, to permanent dipole moments which exist also in the absence of an electric field. Such moments experience a torque in an applied field that tends to orient them in the field direction, thus giving rise to orientational or dipolar polarizability ($\alpha_d$).

These three mechanisms of polarization are due to charges that are locally bound in atoms, in molecules, or in the structures of solids and liquids. The deviation of the fourth one, i.e., the interfacial or space charge polarizability ($\alpha_i$), from these mechanisms is explained below. In thin films, there are number of defects such as lattice vacancies, impurity centres,
dislocations, interstitials etc. When an electric field is applied free charge carriers, migrating through the crystal, impeded in their motion, either because they become trapped in the material or on interfaces, or because they cannot be freely discharged or replaced at the electrodes, space charges and a macroscopic field distortion results. This may in turn induce its image charge on the electrode and thus gives rise to a dipole moment. In real crystals and more so in thin films [31-33] this mechanism is often observed partly because thin film generally has a density of carrier trapping defects particularly those in their surface region and hence the electrode/insulator interface dominates.

Thus the total polarizability of the system is the sum of the individual polarisabilities,

\[ \alpha = \alpha_e + \alpha_a + \alpha_d + \alpha_i \quad \ldots \ldots \quad (4.23) \]

4.2.6 Relaxations

Relaxation is a process, which applies to linear systems where a response and a stimulus are proportional to one another in equilibrium. Relaxation is a delayed response to a changing stimulus in such a system. The stimulus is mainly an electric field and the response is a polarization. The lag between field and polarization implies an irreversible degradation of free energy to heat.

The dielectric flux density \( D \) resulting from an applied
alternating field $E$ would differ in phase from $E$. This is due to the inertia of the polarisation which, when the frequency becomes high enough, cannot follow the field variation giving rise to a 'relaxation' of the measured permittivity. This behaviour may be stated by an equation of the type

$$\varepsilon_r(w) = \varepsilon_\infty + \int \alpha(t) \exp(jwt) \, dt \quad \ldots \ldots \quad (4.24)$$

in which $\varepsilon_\infty$ is the value of permittivity at infinite frequency which is a constant and $\alpha(t)$ is a sort of decay factor accounting for the lagging of polarisation behind the applied field. Most of the relaxations can be described by means of Debye equations.

4.2.6.1 The Debye equations

Debye proposed an exponential form for the decay factor

$$\alpha(t) = \alpha(o) e^{-t/\tau} \quad \ldots \ldots \quad (4.25)$$

where $\tau$ is a relaxation time characteristic of the dielectric, which may be a function of the temperature but not of time.

Substituting this in the above equation,

$$\varepsilon_r(w) = \varepsilon_\infty + \int \alpha(o) \exp\left(jw-1/\tau\right) t \, dt \quad \ldots \ldots \quad (4.26)$$

which, on integration, yields

$$\varepsilon_r(w) = \varepsilon_\infty + \frac{\alpha(o)}{(1/\tau) - jw} \quad \ldots \ldots \quad (4.27)$$
At \( w=0, \) \( \varepsilon_r(w) = \varepsilon_s \) and this gives

\[
\varepsilon_s = \varepsilon_\infty + \tau \alpha(0) \quad \text{............ (4.28)}
\]

Substituting this in equation 4.25,

\[
\alpha(t) = \frac{\varepsilon_s - \varepsilon_\infty}{\tau} \exp\left(-\frac{t}{\tau}\right) \quad \text{............ (4.29)}
\]

Using equation (4.29) in (4.24) we have

\[
\varepsilon_r(w) = \varepsilon_\infty + \int \frac{\varepsilon_s - \varepsilon_\infty}{\tau} \left[\exp\left(-\frac{t}{\tau}\right)\right] \left[\exp(jw t)\right] dt
\]

Therefore,

\[
\varepsilon_r(w) = \varepsilon' - j\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1-jw t} \quad \text{............ (4.30)}
\]

Equating real and imaginary parts,

\[
\varepsilon' = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + w^2 \tau^2} \quad \text{............ (4.31)}
\]

\[
\varepsilon'' = \frac{(\varepsilon_s - \varepsilon_\infty) \omega \tau}{1 + w^2 \tau^2} \quad \text{............ (4.32)}
\]

and

\[
\tan\delta = \frac{\varepsilon''}{\varepsilon'} = \frac{(\varepsilon_s - \varepsilon_\infty) \omega \tau}{\varepsilon_s + \varepsilon_\infty w^2 \tau^2} \quad \text{............ (4.33)}
\]

Equations (4.31) to (4.33) are known as the Debye equations and \( \tau \) is the relaxation time.

Application of the Debye equations to the given relaxations
requires a microscopic analysis of the dipole in question to give a relation between \((\varepsilon_s - \varepsilon_\infty)\) and the number of the dipoles etc. It may be expected that \((\varepsilon_s - \varepsilon_\infty)\) and hence the peak height of the tan\(\delta\) is usually proportional to the number of the dipoles. The movement of the position of the maximum in tan\(\delta\) or \(\varepsilon''\) with temperature or frequency is a measure of the activation energy of the process since \(\tau_{\text{max}}\) usually obeys an Arrhenius relation

\[
\tau = \tau_0 \exp(-Q/kT)
\]

where \(Q\) is the activation energy.

### 4.2.6.2 Cole - Cole diagrams

In a solid, a dipole finds itself in a regular electrostatic field due to all the other dipoles. It may have a number of equilibrium positions in this field, separated from each other by potential barriers. In the simplest case of equilibrium positions, Debye type of relaxation should occur. In dipolar solids, generally the molecular dipoles have more than two equilibrium positions. This shows that the frequency spectrum of permittivity is broader and flatter than predicted by the simple Debye formulae. The relaxation time obtained by such a curve, then represents an average of a number of different relaxation times, which corresponds to transitions between the different equilibrium positions.

Cole and Cole\([34]\) showed that the feature of relaxation behaviour, in accordance with the Debye equations, is that a graph
of \( \varepsilon'' \) against \( \varepsilon' \) over the entire frequency range will always be a semicircle. This may be seen by suitable rearrangement of equations (4.31) and (4.32) to give

\[
(\varepsilon' - \varepsilon_\infty)^2 + (\varepsilon'')^2 = \frac{(\varepsilon_S - \varepsilon_\infty)^2}{(1 + \omega^2 \tau^2)} \quad \ldots \ldots (4.34)
\]

substituting from equation (4.31) gives

\[
(\varepsilon' - \varepsilon_\infty)^2 + (\varepsilon'')^2 = (\varepsilon_S - \varepsilon_\infty) (\varepsilon' - \varepsilon_\infty) \quad \ldots \ldots (4.35)
\]

i.e. \((\varepsilon')^2 - \varepsilon' (\varepsilon_S + \varepsilon_\infty) + \varepsilon_S \varepsilon_\infty + (\varepsilon'')^2 = 0 \quad \ldots \ldots (4.36)\)

At \( \omega = 0 \) and \( \omega = \infty \) we know that \( \varepsilon'' = 0 \), and that \( \varepsilon' = \varepsilon_S \) and \( \varepsilon_\infty \) respectively. In addition at \( \omega \tau = 1 \), \( \varepsilon'' \) has its maximum value of \( \frac{\varepsilon_S - \varepsilon_\infty}{2} \) and \( \varepsilon' = \frac{\varepsilon_S + \varepsilon_\infty}{2} \). If we take axes of \( x = \varepsilon' \) and \( y = \varepsilon'' \), then the above conditions yield the points \((\varepsilon_S, 0), (\varepsilon_\infty, 0)\) and \( \frac{\varepsilon_S + \varepsilon_\infty}{2}, \frac{\varepsilon_S - \varepsilon_\infty}{2} \). These points found to lie on circle given by

\[
[x - \frac{\varepsilon_S + \varepsilon_\infty}{2}]^2 + y^2 = \left[ \frac{\varepsilon_S - \varepsilon_\infty}{2} \right]^2 \quad \ldots \ldots (4.37)
\]

which is the equation of a circle whose centre is at the point \( \left[ \frac{\varepsilon_S + \varepsilon_\infty}{2}, 0 \right] \) and has a radius \( \frac{\varepsilon_S - \varepsilon_\infty}{2} \). This is illustrated in Fig.4.1. On simplifying equation (4.37)
Fig. 4.1. Cole-Cole plot for single relaxation time.
\[(\varepsilon')^2 - \varepsilon'(\varepsilon_S + \varepsilon_\infty) + \varepsilon_S \varepsilon_\infty + (\varepsilon'')^2 = 0\]

which is the same equation as (4.36) showing that, for a Debye relaxation, the locus of \(\varepsilon_R = \varepsilon' - j \varepsilon''\), plotted on an Argand diagram, will always be a circle.

Experimentally it is often difficult to extend the frequency of an a.c. bridge measurement sufficiently high to obtain \(\varepsilon_\infty\). If the experimental points are plotted as a Cole diagram and a semicircle drawn through them, \(\varepsilon_\infty\) is obtained from the intercept with the x axis. Equations (4.31) and (4.32) can be rearranged to give

\[
\varepsilon' = \varepsilon_\infty + \frac{\varepsilon''}{\omega \tau} \quad \ldots \ldots \quad (4.38)
\]

and

\[
\varepsilon' = \varepsilon_S - \omega \tau \varepsilon'' \quad \ldots \ldots \quad (4.39)
\]

Thus the relaxation time may be obtained from the slopes of a straight line drawn from the origin to a point on the circle for which \(\omega\) is known. Knowing the values of \(\varepsilon_S\) and \(\varepsilon_\infty\), the value of the dipole strength \(A = Np^2 / (3\varepsilon_0k)\), where \(N\) is the dipole concentration, \(p\) the dipole moment, \(k\) the Boltzmann constant and \(\varepsilon_0\) the permittivity of free space, can be obtained from the equation \(\varepsilon_0 - \varepsilon_\infty = A/T\), where \(T\) is the temperature in K.

When the material has a spread of relaxation times, Cole and Cole showed that equation 4.26 should be replaced by the more general expression

\[
\varepsilon' - j\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_S - \varepsilon_\infty}{1 - (j\omega \tau_a)(1-\beta)} \quad \ldots \ldots \quad (4.40)
\]
where \( \tau_a \) is the mean relaxation time and \( \beta \) is a constant of value between 0 and 1. If the results are plotted in an Argand diagram, the points still lie on a circle, but its centre is depressed below the \( \varepsilon' \) axis. If the radius of the circle is drawn to the points \((\varepsilon_s, 0)\), the angle between the radius and the \( \varepsilon' \) axis is equal to \( \beta(\tau_2) \). \( \beta \) may be expressed as a spreading factor of the actual relaxation times about the mean value \( \tau_a \). There is no molecular interpretation for this factor, but it is useful in analysing a complicated relaxation spectrum.

4.2.7 Temperature coefficients of capacitance and permittivity
(TCC and TCP)

The temperature coefficient of permittivity, a factor used to estimate changes in the permittivity of a material with changes in its temperature, defined as

\[
TCP = \frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_1 (T_2 - T_1)}
\]

is an important practical figure for assessing the expected behaviour of thin film circuits. In the above equation \( \varepsilon_1 \) and \( \varepsilon_2 \) are the permittivities of specimen at temperatures \( T_1 \) and \( T_2 \) respectively.

Since the capacitance of a capacitor is proportional to the permittivity of the dielectric between the two plates, it is possible to relate TCP to the mean TC of capacitance (TCC). The
formula for the latter is

\[ TCC = \frac{C_2 - C_1}{C_1(T_2 - T_1)} \] ........ (4.42)

where \( C_1, C_2 \) are capacitances of the specimen at temperatures \( T_1 \) and \( T_2 \) respectively. The relation between TCC and TCP has the form

\[ TCC = TCP + \alpha \]

where \( \alpha \) is the linear expansion coefficient. Neglecting changes in the linear dimensions of a specimen with temperature changes, the TCP and TCC of the specimen may be assumed equal in magnitude.

The growing interest in the choice of material for application as capacitors suggests that the temperature coefficient of capacitance of dielectrics is to be investigated thoroughly. The value of TCC up to about 650 ppm/K is comparable to dielectric films investigated so far as thin film capacitor (TFC) elements[35]. A value around this range implies further investigations into the material for suitability of application as thin film capacitor.

4.2.8 Frequency dependent behaviour of dielectric constant and dielectric loss in thin films

The dielectric constant \( \varepsilon' \) and the power factor \( \tan\delta \) are not absolute constants for an actual dielectric, both quantities depending on many factors, viz., on the temperature, the frequency
and the magnitude of the alternating voltage, the humidity of air etc. The frequency dependence of tanδ in thin films is a very important factor and has been subject matter of various investigators. Most dielectrics have loss invariant with frequency at room temperature. Usually the dielectric constant decreases with increasing frequency at very low frequencies the dipoles are oriented by the electric field without time lag, (ε' having its maximum value ε₀). In this case the orientation of the dipoles is not accompanied by any loss of energy, tanδ consequently being low. At very high frequencies the dipoles are not able to follow the variations of the field, whereas the normal thermal agitation is still present. In this case the dielectric constant is defined by the deformation polarization alone, which takes place without time lag (i.e. to say towards the optical frequencies); at the same time tanδ, which is proportional to the loss of energy per period, also a small value. At intermediate frequencies ;the dielectric constant decreases from ε₀ to ε∞, while the frequency defined by wτ = 1 the orientation has its maximum phase difference with respect to the electric field tanδ having its maximum value.

The loss factor of thin film capacitors shows a general behaviour of increasing loss at very low or very high frequencies with a wide minimum in the intermediate range, as a result of superposition of various loss mechanisms. Losses in a bulk capacitor arise due to : (1) the dielectric not being a perfect insulator, i.e., the loss due to the leakage resistance Rp of the
capacitor, which is placed in parallel with C (this d.c. contribution to the dissipation factor is given by \( \frac{1}{\omega R_p C} \), where \( \omega \) is the angular frequency and is dominant at low frequencies): (2) a.c. dielectric loss consisting of a frequency-independent contribution (at room temperature) present at all levels of loss superimposed by ac relaxation peaks. In thin dielectric films, where the majority of the current is carried by defects, the frequency-independent loss is thought to be due to a wide range of distribution of relaxation processes in the film. However, in ideal materials, such as single crystals and amorphous films, it has been suggested that the most likely mechanism is impurity conduction and ionic conduction. The a.c. relaxation peaks, which generally occur below 1Hz and very rarely between 100 Hz and 1MHz, can be due to a variety of causes such as interfacial polarisation effects consisting of relaxations of charge build up at the metal-dielectric interface, or the structural vibrations of the lattice itself.

In all these cases, if the temperature is raised, these peaks shift to higher frequencies and their behaviour is well described by the Debye equation[36]. Besides the leakage losses and the dielectric losses, there is yet another source of loss which is very dominant in thin film capacitors. This arises from the resistance \( R_s \) of the electrodes, which is placed in series with the capacitance \( C \). The loss due to the electrode resistance is given by \( \omega CR_s \) and is significant at high frequencies. Within
certain limits, the high-frequency characteristics of thin film capacitors can be improved by using thicker and highly conductive electrodes.

Frequency independent behaviour of loss has been found in SiO films[37]. However loss peaks in loss factor have been found for SiO films[33] and other alkali halides[38] at frequencies in the range 0.01 Hz and these have been attributed to the interfacial polarisation. It is a rare phenomenon to observe loss peaks in dielectrics in the frequency range 100 Hz to 1 MHz. When such peaks are found in this region they have been ascribed to the relaxation of pairs of point defects. At higher frequencies peaks are caused due to the structural vibrations and are observed in polymer films[39].

The loss invariance with the frequency is explained as follows. Initially, such a loss in dielectric was assumed to arise due to the presence of pinholes in the deposited films. But Harrop and Campbell[40] rejected this assumption on the ground that tanδ generally shows some correlation with forbidden energy gap of the dielectric. Thus regarding the factors dominating the loss in a given film mathematical models of a spread of relaxation frequencies have proved invaluable in calculating the relative invariance of loss with temperature near room temperature[41]. The model proposed by Young [42] suggested that the observed dielectric loss was due to an exponential variation of conductivity through the thickness of the film. However, the slight deviation from the exponential law caused the model to
breakdown. Mention can be made in particular of tanδ_{min} also observed by Maddocks and Thun [43] for ZnS films. The observed features cannot possibly be due to the natural relaxation effect of a capacitor or due to interfacial polarisation, since the frequency region for such effects to be observable is too large (>10^9 Hz) for the former and too small (10^{-3} to 1.0 Hz) for the latter. Further the presence of such processes would give a tanδ_{max} and not tanδ_{min} as observed here. The model proposed by Simmons et al. [44] have been able to explain both qualitatively and quantitatively the a.c. behaviour of vacuum deposited highly doped MoO_3 films by assuming the presence of an added series capacitance due to Schottky barriers at the electrode-dielectric interface.

Studies on the dielectric behaviour of thin film capacitors of oxides[2,8,10,43,45-51], halides[38,52], sulphides[33,34,53,54] etc., showed pronounced loss peak maxima or minima in the frequency dependent loss factor curves. Recently Goswami and Goswami [35] proposed a model which accounts for the a.c. conduction behaviour of vacuum deposited thin film capacitors. This model specially accounts for the tan δ_{min} in the frequency spectra. In this model, a thin film capacitor system comprises of (i) an inherent capacity element C unaffected by frequency and temperature (ii) a discrete resistance element due to the dielectric film in parallel with C and (iii) a small series resistance r due to electrodes, leads etc. Thus the series
capacitance and $\tan \delta$ are given by

$$C_s = \frac{1 + \frac{1}{w^2 R^2 C^2}}{\frac{1}{w^2 R^2 C}} \quad \ldots \quad (4.43)$$

$$\tan \delta = \frac{1}{wRC} + \frac{r}{wR^2C} + wrC \quad \ldots \quad (4.44)$$

$\tan \delta_{\text{min}}$ will be observed at a frequency given by

$$w_{\text{min}} = \left[ \frac{1}{wRC^2} \right]^{\frac{1}{2}} \quad \ldots \quad (4.45)$$

The increase of $\tan \delta$ at higher frequencies is due to lead resistance. The temperature dependence of resistance is given by

$$R = R_0 \exp \left[ \frac{\Delta E}{kT} \right] \quad \ldots \quad (4.46)$$

According to this equation $R$ will increase with decreasing temperature and $w_{\text{min}}$, therefore, will be lowered at lower temperatures. Thus $w_{\text{min}}$ will shift to lower frequencies at lower temperatures and vice versa.

In view of Simmons et al[44] it is possible to evaluate activation energy from the capacitance vs frequency curves at different temperatures, since they have exactly the same functional form. Hence

$$C_s = \text{function of } (wR) = \text{function of } [wR_0 \exp(\Delta E/kT)] \quad \ldots \quad (4.47)$$
For any constant capacitance,
\[ \omega R = A \] \hspace{1cm} (4.48)

where \( A \) is a constant whose magnitude depends on the particular value of the capacitance. Equating equations (4.46) and (4.48) we have

\[ \omega = A R_0^{-1} \exp \left( \frac{-\Delta E}{kT} \right) \] \hspace{1cm} (4.49)

Hence a plot of \( \log \omega \) or \( \log f \) (\( f = 2\pi f \)) with inverse absolute temperature for any constant capacitance will result in a linear plot with slope \( -\Delta E/k \). Thus \( \Delta E \) can be evaluated.

4.3 Measurements

The measurements of the two important parameters, the capacitance and the dielectric loss involved in the study of dielectrics, were made (\( f = 1-30 \text{ kHz} \)) directly using a 0.1% Radart Universal Bridge (Eastern Electronics, India). The apparatus is same as the Wheatstone's bridge but for presence of two capacitance components of a capacitor as a series as well as a parallel network. The equivalent parallel (\( C_p \)) and series (\( C_s \)) capacitance are connected by the relations.

\[ C_p = \frac{C_s}{1 + D^2} \quad \text{and} \quad C_s = C_p \left( \frac{1 + Q^2}{Q^2} \right) \]

where \( D \) is the loss factor and \( Q \) is the quality factor. Throughout the study the equivalent series capacitance \( C_s \) (D-
position) has been measured. The loss factor is given by
\[
\tan \delta = \tan \delta_f \times \frac{f}{1000}
\]
where \( \tan \delta_f \) is the loss measured at any arbitrary frequency \( f(\text{Hz}) \).

The r.m.s. voltage applied across the thin film capacitor throughout the study is 50 mV. Both the capacitance and \( \tan \delta \) were measured in a vacuum of 1.33 Pa with the Universal bridge coupled with an external audio oscillator. The copper-constantan thermocouple was used for measuring the temperatures of the sample during the study. The dielectric constant has been calculated from these measured values with the knowledge of the capacitor area and the dielectric film thickness.

Since the as deposited films contain many defects such as voids, grain boundaries, pinholes, etc., they were subjected to annealing treatment at about 383K in a vacuum of 1.33 Pa for repeated one hour cycles. Unannealed capacitors were used for aging studies and the variation of dielectric parameters with time have noted at regular intervals. The annealing treatment was repeated until the capacitors attain stability.

The dielectric and other related physical properties of neodymium oxide and fluoride thin films were studied on well stabilised capacitors. The dielectric parameters were measured at low and high frequencies (100 Hz to 100 kHz, 10kHz to 10MHz) with Hewlett Packard digital LCR bridge (Model 4274 A and 4275 multi frequency LCR meter) at various temperatures.
4.4 Results and Discussion

4.4.1 Aging and Annealing

Freshly prepared films were subjected to aging studies. The variation of capacitance and tanδ with aging is shown in Figs. 4.2 and 4.3, respectively. It has been observed that the capacitance and the loss factor decrease showed a continuous with the increase of time and eventually became more or less constant. During aging or self-annealing structural changes and a redistribution of atoms take place. The drastic changes in the interior of the capacitor with the removal of defects may be responsible for the large reduction of capacitance during the initial period of aging. It is seen that the capacitance becomes constant after about 40 days and 45 days for neodymium oxide and fluoride films respectively.

The stabilization of these capacitors would also be achieved by repeated annealing cycles at about 383 K in a vacuum of 1.33 Pa. Even after about forty days of aging some of the defects such as neodymium interstitials are not reduced. This can be recovered by the annealing process in vacuum. It has been found from Figs. 4.4 and 4.5 that the decrease of capacitance with increasing number of cycles is attributed to the reduction or removal of defects which may relieve the stress in the film. The stress relief is probably associated with the local structural rearrangements and also with reduction of the number of weak paths through the film. This reduction may lower the concentration of charge carriers and thereby enhances the resistivity of the film. This in turn reduces the capacitance. The physical expansion of
Fig. 4.2 Variation of capacitance with time.
Fig. 4.3 Variation of $\tan \delta$ with time.
Fig. 4.4  Change of capacitance with frequency at different annealing cycles ($\text{Nd}_2\text{O}_3$; d=260 nm and $T=383 \text{ K}$)
Fig. 4.5 Change of capacitance with frequency at different annealing cycles of a NdF₃ film capacitor.
the dielectric material also reduces the capacitance.

From Fig. 4.6 it is clear that the tanδ_min shifts towards the lower frequency region as the number of annealing cycles increased. Both the annealing processes decrease the defects to the maximum possible level and hence the resistance of the films increases. The shifting of tan δ_min towards the lower frequency region can be explained by assuming that the capacitor system comprises (i) an inherent capacity element (C), (ii) a discrete resistance element parallel to C, and (iii) a series resistance (r) due to leads[35]. According to this

\[ C_S = \frac{1}{w^2 R^2 C} + C \]  \hspace{1cm} (4.50)

\[ \tan \delta_{\text{min}} = \frac{1}{(wRC^2)^{1/2}} \] \hspace{1cm} (4.51)

and \[ w_{\text{min}} = \frac{1}{rRC^2} \] \hspace{1cm} (4.52)

Equation (4.50) reveals that the series capacitance (C_s) decreases as R increases and from the equation (4.51) it is clear that the tanδ_min decreases as R increases. Similarly equation (4.52) shows that w_min decreases as R increases. These results clearly indicate the shifting of tanδ_min towards the lower frequency region as the number of annealing cycles increases. After three or four annealing cycles there is no appreciable
Fig. 4.6 Change of $\tan \delta$ with frequency at different annealing cycles ($Nd_2O_3$; $d=265$ nm; $t=60$ min. and $T=383$ K).
variation of these parameters with frequency. Thus the dielectric properties of these capacitors assume constant values by heat treatment. Annealing effect on the loss factor of NdF$_3$ films is shown in Fig.4.7.

According to Siddal[45] the reduction in the capacitance values noted for certain high loss capacitors during annealing may be either due to the decrease in permittivity or to the increase in effective film thickness. This lends support to our findings. The decrease in magnitude of $\tan\delta_{\text{min}}$ may be attributed to the reduction of number of dipoles resulting due to annealing. Similar aging and annealing effect has been reported for many dielectric films by various workers[10,48,55-58].

4.4.2 Effect of thickness

The dielectric constant of a solid is a property which depends on the atoms and molecules present and their arrangements. Hence it is a bulk property. However, practically in the case of thin films it depends on the thickness of the films[2,59].

The dielectric constant is an important parameter in the selection of materials for device applications. As the thickness of the films is also an equally significant parameter a systematic study on the thickness dependence of the dielectric parameters has been made in the present investigation[Figs.4.8(a) and 4.8(b)]. Thickness dependence of thin films has been well established by various workers[2,59]. The variations of dielectric constant with the film thickness are shown in Fig.4.8(b) for both neodymium
Fig. 4.7 Change of $\tan \delta$ with frequency at different annealing cycles of a NdF$_3$ film capacitor.
Fig. 4.8(a) Variation of $C$ and $\tan \delta$ with film thickness.
Fig. 4.8(b) Variation of dielectric constant with film thickness.
oxide and fluoride films. It has been observed that in both the Nd$_2$O$_3$ and NdF$_3$ films, the dielectric constant increases with thickness initially and attain saturation after about 150 nm.

The thickness dependence of dielectric constant is thought to arise due to the presence of voids in the thinnest films. As the films become thicker the density of voids decreases resulting in a higher value of dielectric constant and when the films become sufficiently thick for the voids to disappear, the dielectric constant becomes thickness independent.

This is mainly because vacuum deposited films usually contains agglomerations and hence voids, dislocations etc. in the deposits. In these types of films, the dielectric constant can be considered to consist of two types of dielectric media namely (i) the material and (ii) air or vacuum in the void and discontinuity region. Therefore the effective dielectric constant will depend on the amount of voids and discontinuities in the films. With the increase of the thickness, the density of defects decreases and the films tend to become continuous when they are sufficiently thick. Once the films are continuous and thick enough then the dielectric constant becomes characteristics of the material and hence independent of the film thickness. Similar results were observed for Eu$_2$O$_3$ films by Jayaraj and Vallabhan[11], ZnS films by Goswami and Goswami[35] and MoO$_3$ films by Simmons et al[60,61].

4.4.3 Effect of frequency and temperature on dielectric parameters

The variations of capacitance, tanδ and the dielectric
constant with frequency (1-30 kHz) at various temperatures for both neodymium oxide and neodymium fluoride film capacitors formed by vacuum deposition method are shown in Fig.4.9 to 4.14. At all temperatures above 363 K capacitance is found to decrease with frequency but this variation is less pronounced as the temperature decreased. At room temperature and below, however the capacitance was highly frequency independent. In the case of fluoride films at high temperatures and low frequencies capacitance can be seen to saturate at a level which appears virtually to be independent of film thickness. Similar dispersion characteristics have also been observed for all the films studied with different thicknesses. However at higher frequencies it shows less temperatures dependance.

In the case of Nd$_2$O$_3$ the loss factor decreased with frequency at all temperatures and a striking loss minimum was observed. The very small increase or hump in loss in the low temperature region may be ascribed to the relaxation of pairs of point defects. It is seen that the portion of tan$\delta_{\text{min}}$ shifted to the high frequency region with increase of temperature. It is interesting to note that the magnitude of tan$\delta$ also increases with increase of temperature. These features are in good agreement with the results reported for other dielectric materials[2,5,10].

The increase of both capacitance and tan$\delta$ towards the low frequency region may be attributed to interfacial polarization in that region. The charge carriers existing in the dielectric film can migrate for some distance under the influence of an applied
Fig. 4.9 Variation of capacitance with frequency at different temperatures (Nd$_2$O$_3$ : d=260 nm).
Fig. 4.10 Variation of capacitance with frequency at different temperatures (NdF₃).
Fig. 4.11 Variation of $\tan \delta$ with frequency at different temperatures ($\text{Nd}_2\text{O}_3$:d=260 nm).
Fig. 4.12 Variation of $\tan \delta$ with frequency at different temperatures ($\text{NdF}_3; d=70 \text{ nm}$).
Fig. 4.13 Variation of dielectric constant versus frequency (Nd$_2$O$_3$; d=200 nm).
Fig. 4.14 Variation of dielectric constant versus frequency (NdF$_3$; $d=70$ nm)
field. When such carriers are blocked at the electrodes a space charge region results. The resulting space charge region leads to a substantial increase in capacitance towards low frequencies in both the films. Similar observations have been reported by Mahalingam et al. [8] and Birey [56] for La$_2$O$_3$ and MoO$_3$ films respectively.

Unlike Nd$_2$O$_3$ films, tanδ of NdF$_3$ capacitors showed a different behaviour. The tanδ increased with frequency attained a maximum, tanδ$_{max}$, and then decreased with frequency. This reveals a relaxation effect in these films, which can be reasonably attributed to the dielectric relaxation phenomenon arising from the dipolar orientation. It is found that the loss peak shifts towards higher frequency region with increase of temperature. Similar loss peaks have been reported by earlier investigators during their studies on other insulating films [33, 48, 55, 61, 63].

The relative variation in the capacitance ($\Delta C/C\%$) normalized at 10kHz for Nd$_2$O$_3$ films varied from 1.93 to -0.41\% in the frequency region studied while that for NdF$_3$ varied from 3.94 to -1.91\%.

4.4.4 High frequency performances

High frequency studies of dielectric properties have been independently performed and the experimental results are shown in figures 4.15 to 4.18. The capacitance is found to remain constant at and below room temperature in all the films in the frequency range from 1 kHz to 10 MHz. This characteristic, hence display a frequency
Fig. 4.15 Variation of $C$ versus $f$ (Ni$_2$O$_3$).
Fig. 4.16 Variation of $C$ versus $f$ ($\text{NdF}_3$).

d = 295 nm
$A = 493 \times 10^{-6} \text{m}^2$
Fig. 4.17 Variation of $\tan \delta$ versus $f$ ($\text{Nd}_2\text{O}_3$)
Fig. 4.18 Variation of tanδ versus f \( (\text{NiF}_3) \).
independence in this region, referring on the intrinsic details of the dielectric material. The behaviour of $\tan\delta$ is also similar in all cases and has a tendency to decrease with the increase in frequency. In the case of neodymium fluoride, $\tan\delta$ increases with increase in temperature and attains a maximum and then decreases. The $\tan\delta_{\text{max}}$ and its shift towards higher frequency region is very prominent.

4.4.5 Cole-Cole plots

Figs. 4.19(a) and 4.19(b) show the plots of $\varepsilon''$ against $\varepsilon'$ for NdF$_3$ film of thickness 295 nm at different temperatures. The skewed arc indicates, according to Cole – Davidson[64], the presence of more than a single type of dipoles. Figs. 4.20 and 4.21 shows the plots of $\varepsilon'$ versus $\varepsilon''/\omega$ and $\varepsilon'$ versus $\varepsilon''/\omega$. It is clear that each of these plots gives two different sections of straight lines showing the absorptions (relaxation process) overlapping on the frequency scale studied. The two types of dipoles present, can also be inferred from the fact that the Cole – Davidson arc (Figs. 4.19(a) and 4.19(b)) can be resolved into two simple Debye semicircles (overlapping partly). In evaporated solid films, the arrangement of nearest neighbour atoms is not exactly same for all the dipoles. Hence the dipoles cannot be characterized by a single relaxation time as in the simple Debye model. The slopes of the individual section gives the relaxation times of the two dipoles. The relaxation times for the two types of dipole relaxations, at 423K, are (1) $3.987 \times 10^{-8}$ sec and (2)
Fig. 4.13(a) Cole-Cole plots of a NdF₃ film of thickness 295 nm at 383 and 403 K.
Fig. 4.20 Plot of dielectric constant against Log(ε''w)
Fig. 4.21 Plot of dielectric constant against $\log(e''/w)$.
7.24 x 10^{-6} \text{ sec respectively. Fig.4.22 shows the dependence of } \\
\alpha = (\varepsilon' - 1)/(\varepsilon' + 2) \text{ with inverse absolute temperature at different } \\
frequencies. The dipole moment (p), dipole strength (A) and the 
dipole concentration (N) have been estimated as 1.071 x 10^{-27} \text{ Cm}, \\
2.34 x 10^4 \text{ and } 3.01 x 10^{27} \text{ m}^{-3} \text{ respectively. It has been observed } \\
that the centres of the semicircles are lying below the \varepsilon' - \text{axis.}

If the radius is extrapolated to the points (\varepsilon_\infty, 0) and (\varepsilon_s, 0), 
the angle between the radius and the \varepsilon' - \text{axis is equal to } \beta n/2.

The spreading factor \beta has been calculated and it is found to be 
temperature dependent, its value tending to zero at higher 
temperatures. Similar observations have been reported by earlier 
investigators on various dielectric materials [33, 50, 65, 66].

Knowing \beta, \tau_a can be determined using the relation 
\nu/u = (\omega \tau_a)^{1-\beta}, 
where \nu and \nu are the distances from the experimental point to \varepsilon_s 
and \varepsilon_\infty respectively and \nu is the angular frequency. The values of 
\beta and \tau_a along with the values of \varepsilon_s and \varepsilon_\infty obtained from the 
above diagrams are presented in table 4.1.

4.4.6. Thermal dipole activation energy

The activation energy for the electrical conduction process 
has been determined using the relation

\[ f_{\text{relax}} = f_0 \exp\left(-E/kT\right) \]

by plotting the frequency (at which tan\delta is minimum and maximum for 
Nd_2O_3 and NdF_3 films respectively) against the inverse absolute 
temperature (Figs.4.23 and 4.24). It is clearly seen from the
Fig. 4.22 Plot of $\alpha$ against the inverse absolute temperature.
**Table 4.1**

Dielectric parameters derived from Cole-Cole plots

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>Parameters</th>
<th>( \varepsilon_\infty )</th>
<th>( \varepsilon_S )</th>
<th>( \beta )</th>
<th>( \tau_a (\text{sec}) \times 10^{-5} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>383</td>
<td>8.00</td>
<td>63.5</td>
<td>0.378</td>
<td>0.289</td>
<td>13.3</td>
</tr>
<tr>
<td>403</td>
<td>10.25</td>
<td>80.0</td>
<td>0.211</td>
<td>0.278</td>
<td>1.48</td>
</tr>
<tr>
<td>423</td>
<td>10.75</td>
<td>92.5</td>
<td>0.011</td>
<td>0.220</td>
<td>0.90</td>
</tr>
</tbody>
</table>

**Table 4.2**

Activation energies determined by various methods.

<table>
<thead>
<tr>
<th>Activation energy (eV)</th>
<th>( \text{Nd}_2\text{O}_3 )</th>
<th>( \text{NdF}_3 )</th>
<th>( \text{Log } f_{m,n} ) vs 1/T</th>
<th>1</th>
<th>2</th>
<th>1</th>
<th>2</th>
<th>Type A</th>
<th>Type B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Log ( f_{m,n} ) vs 1/T</td>
<td>0.037</td>
<td>0.245</td>
<td>0.273</td>
<td>1.24</td>
<td>0.63</td>
<td>1.17</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1. Low temperature region.
2. High temperature region.
Fig 4.23 Plot of log \( f_{\text{min}} \) against inverse absolute temperature (\( \text{Nd}_2\text{O}_3; d = 295\text{nm} \))
Fig.4.24 Plot of $\log [f_{\text{max}}]$ against inverse absolute temperature (NdF$_3$; $d = 70$nm)
figures that, in each case, there are two temperature regions with different activation energies. The activation energy has also been determined from the measured values of the relaxation times (Figs. 4.25 and 4.26) and are shown in table 4.2.

4.4.7 Temperature coefficients of capacitance and permittivity (TCC and TCP)

The temperature dependance of the capacitance for various constant frequencies is shown in Figs. 4.27 and 4.28 for Nd$_2$O$_3$ and NdF$_3$ films respectively. The experimental curve (Fig. 4.27) exhibits a gradual rise in the capacitance with temperature upto certain value after which a steep increase is seen in the capacitance. The large increase of capacitance beyond certain temperature in all the films may be attributed to ionic motion in the form of dipolar reorientation. TCC of the capacitors has been found to be 646 ppm/K at 1 kHz and at room temperature and increased gradually with temperature and attains a maximum of 2183 ppm/K at 463 K. The temperature coefficient of permittivity (TCP) has also been determined [Figs. 4.29 and 4.30]. Its value was found to be 623 ppm/K at 1 kHz and at room temperature. The linear expansion coefficient ($\alpha$) observed from the difference between TCC and TCP is 23 ppm/K. TCC has also been calculated using Gever's eqn.[41]

$$\text{TCC} = A \tan\delta - \alpha \varepsilon$$

and is found to be 475 ppm/K at 1 kHz and at room temperature. This value has been compared with the measured one. The difference
Fig 4.25 Mean relaxation time against inverse absolute temperature, (NdF₃; d = 295nm).
Fig. 4.26 Plot of \( \ln(w) \) versus \( 1/T \) for (A) 0.45 ev (B) 1.17 ev.
Fig 4.27 Capacitance versus temperature at different frequencies (Nd$_2$O$_3$: $d = 260$ nm).
Fig. 4.28 Capacitance versus temperature at different frequencies (NdF₃: d = 295 nm).
Fig. 4.29 Dielectric constant versus temperature at different frequencies (Ni$_2$O$_3$; $d = 260$ nm).
Fig. 4.30 Dielectric constant versus temperature at different frequencies (NdF₃: d = 295 nm).
between these two values of TCC is due to the approximation in the constant $A(=0.05 \pm 0.01/K)$. The intrinsic TCC of the material has also been determined as 380 ppm/K.

The temperature coefficients of capacitance and permittivity of NdF$_3$ film capacitors, at 1 kHz and at room temperature, have been found to be 1625 and 1569 ppm/K, respectively. The linear expansion coefficient ($\alpha$) observed for NdF$_3$ film capacitor is 56 ppm/K.

Table 4.3 summarizes the observed dielectric parameters of vacuum deposited neodymium oxide and fluoride films.
Table 4.3

Dielectric parameters estimated in the present investigation.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nd$_2$O$_3$</td>
</tr>
<tr>
<td></td>
<td>d=260 nm</td>
</tr>
<tr>
<td>C (nF)</td>
<td>0.984</td>
</tr>
<tr>
<td>$\varepsilon'$</td>
<td>5.660</td>
</tr>
<tr>
<td>tan$\delta$</td>
<td>0.0136</td>
</tr>
<tr>
<td>TCC (ppm/K)</td>
<td>646</td>
</tr>
<tr>
<td>TCP (ppm/K)</td>
<td>623</td>
</tr>
<tr>
<td>$\alpha$ (ppm/K)</td>
<td>23</td>
</tr>
<tr>
<td>$\Delta C/C$ (%)</td>
<td>1.93 to 3.94</td>
</tr>
<tr>
<td>(at 10 kHz)</td>
<td>-0.41%</td>
</tr>
<tr>
<td>Activation</td>
<td>0.245</td>
</tr>
<tr>
<td>energy (eV)</td>
<td></td>
</tr>
</tbody>
</table>
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