Fig. 6.1 Illustration of the fabricated Al/MgO:Li\(^+\)/p-Si capacitor structure used for electrical measurements
Fig. 6.2 Experimental arrangement of measuring electrical parameters of Al/MgO:Li\textsuperscript{+}/p-Si structure
Fig. 6.3 I-V Characteristics of Li$^+$ implanted MgO thin films
Fig. 6.4 Variation of ideality factor and barrier height as a function of Li\(^+\) dose in MgO.
Fig. 6.5 Variation of normalized current and series resistance as a function of radiation dose under an applied voltage of 10 V.
Fig. 6.6 Nyquist plot of impedance at 30°C for Al/MgO:Li+/p-Si capacitor
Fig. 6.7 $Z'$ as a function of temperature and frequency
Fig. 6.8 \( Z'' \) as a function of frequency and temperature

Al/MgO-Li\(^+\)/p-Si MIS capacitor
Fig. 6.9 Nyquist plot of MgO-Li⁺ thin films at room temperature
Fig. 6.10 Real part of impedance at different temperature
Fig. 6.11 Impedance Z” variation with frequency of MgO-Li+
Fig. 6.12 Complex impedance and tanδ variation with frequency at 30 ºC
Fig. 6.13 Frequency dependence of $M'$ of MgO-Li$^+$ thin films at different temperatures.
Fig. 6.14 Frequency dependence of $M''$ MgO-Li$^+$ thin films at different temperatures
Fig. 6.15 Master curve of $M''(\omega)$ spectra for Li$^+$ implanted MgO thin film
Fig. 6.16 Frequency dependence of normalized parameters ($Z''/Z''_{\text{max}}$) and ($M''/M''_{\text{max}}$) at (a) 30 °C (b) 90 °C
Fig. 6.17 AC conductivity in Li⁺ implanted MgO films as a function of frequency at different temperatures
CHAPTER – VI

ELECTRONIC AND DIELECTRIC PROPERTIES OF Al/MgO:Li+/p-Si STRUCTURE Li+ IMPLANTED MgO THIN FILMS

6.1 INTRODUCTION

The influence of crystalline nature of dielectric films on their electrical characteristics are presented in this chapter with the experimental results obtained for the Li+ ion implanted MgO thin films. The Poole-Frenkel and Schottky mechanisms and the associated electronic hopping are discussed in detail. The main objective is to study the various mechanisms of electronic and ionic currents through the Li+ implanted magnesium oxide thin films. In the present study conductivity is mainly concerned with sandwich structures in which the dielectric medium is placed between a metal and a semiconductor electrode.

In oxide dielectric films, electronic conduction is associated with the motion of electrons in the conduction band and holes in the valence band or hopping of bound carrier (here electrons) between localized sites in the dielectric thin film. Such type of electronic conduction requires high energy to excite a carrier, which can be supplied thermally by the applied electric field that leads avalanche process. While in hopping process, less energy is required and is only favored in the case of highly disordered thin films. Further, dielectric films differ in their electric properties according to the different preparation conditions.

The Al/MgO:Li+/p-Si (MIS) structures used in this study were fabricated using boron-doped single crystals silicon wafer with (100) surface orientation having thickness of 1.2 mm and 2-5 Ωcm resistivity using the spray pyrolysis technique. Even though there is difficulty in fabrication of hetero-structures with good interface quality, some researches have been reported about the feasibility of making MgO/Si structure with out inter-diffusion [1-5]. For the fabrication process, Si wafer was degreased in organic solvent of CHClCCl2, CH3COCH3 and CH3OH consecutively. Preceding each cleaning step, the wafer was rinsed thoroughly in de-ionized water of resistivity of 18 MΩcm. Later they were etched in hydrofluoric acid in order to remove the residual oxide. After drying, the wafers were transferred to the substrate holder for MgO thin film deposition. The substrate holder was placed over a heater
and the distance between the substrate and nozzle was adjusted for uniform coating (30 cm). Magnesium acetate in ethanol was used as the precursor of MgO with an acid catalyst and tri ethylene glycol (TEG) to facilitate high temperature processing. The precursor was sprayed into fine droplets from the atomizer and was carried to the substrate by a compressed carrier gas (0.4 kg/cm²). The sprayed solution of magnesium acetate was thermally decomposed into oxide layer on the silicon substrate. Magnesium oxide (MgO) films were implanted with 1.5 MeV Li⁺ ion to various fluences in the range 10¹³-10¹⁵ ions/cm².

After identifying the crystalline quality, high purity Al metal (99.999%) with a thickness of 0.2 µm was thermally evaporated over Li⁺ implanted MgO coatings to a predefined area (3.14 mm²). Aluminium was chosen as electrode material because of its small grain size in comparison with film thickness [6]. Resulted Al/MgO/p-Si MIS structure (Fig. 6.1) was then engaged for electrical conductivity measurement using a single power supply and two sensitive detectors, one for current and the other for voltage measurements. In the present study, the circuit used for measuring current and voltage of MgO specimens that offer high electrical resistance is shown in Fig. 6.2. The impedance measurements were carried out in the frequency range 40 Hz to 100 kHz using HP 4192 A LF impedance analyzer at the test signal of 40 mVrms in the temperature range 30-90 °C.

6.2 I-V MEASUREMENTS ON Li⁺ IMPLANTED MgO FILMS

The MgO thin films used in this study were deposited on p-Si substrates using the spray pyrolysis technique. Deposited MgO films were implanted with 1.5 MeV Li⁺ ion to various fluences in the range 10¹³-10¹⁵ ions/cm². Electrodes were made by evaporating aluminium onto the lateral surfaces. The electrical response is usually independent of the contact electrode material. For I-V measurements, voltage is applied to the film with a voltage source and the current is measured with an electrometer (Oriel). Typical current-voltage (I-V) characteristics of the MIS Schottky diode with MgO as the insulator layer before and Li⁺ implantation for various fluences are shown in Fig. 6.3.

It is clear from the I-V characteristics that when a dc voltage is applied at 30 °C to a MgO thin film implanted with Li⁺, semiconducting characteristics is observed. The characteristic is similar to that of a diode in the forward direction with
a series resistance ‘$R_s$’. The resistance ‘$R_s$’ is the bulk resistance of the sample. For a forward biased diode in series with a resistance ‘$R_s$’, the current-voltage relation fit the equation [7],

$$V = \frac{n k T}{q} \ln \left( \frac{1}{I_s} + 1 \right) + IR_s$$

(6.1)

Where ‘$n$’ is the ideality factor of the junction and ‘$I_s$’ is the saturation current.

Above equation manifests that for larger bias voltage in excess of $\frac{kT}{q}$, the current density is proportional to $\exp \left( \frac{qV}{kT} \right)$. This ideal behavior is never observed practically and the current varies proportional to $\exp \left( \frac{qV}{nkT} \right)$. We can get a best fit for higher values of ‘$n$’ greater than 1. A larger value of ‘$n$’ implies the existence of an interfacial layer and in addition explains the recombination of electrons and holes in the depletion region. By careful examination of the I-V characteristic curve, three of the parameters can be obtained, the linearity factor ‘$n$’, bulk resistance ‘$R_s$’, and the barrier height ‘$\phi_b$’. Also, it is evident from the figure that at intermediate and high voltage regions, the ohmic behavior of electrical conduction is apparent for the MIS structure fabricated with Li$^+$ implanted MgO to a fluence of $10^{15}$ ions/cm$^2$. The linearity of the curve indicates the quadratic dependence of current versus voltage and therefore the space-charge limited conduction is completely disappeared at these regions [8].

Moreover, large enhancement in conductivity has been observed when MgO thin films are implanted with Li$^+$ ions. This enhancement has been attributed to both doping and structural changes caused by defects [9-13]. The enhancement in electrical conductivity with Li$^+$ implantation is similar to the result previously reported for the MgO single crystals implanted with either Fe or Li ions [9, 12]. These results indicates that the performance and reliability of MIS Schottky structure depends mainly on the formation of insulator layer between metal and semiconductor interface, the interface states distribution between semiconductor and insulator layer, series resistance and an inhomogeneous Schottky contacts. Many studies have been put forwarded [14-16] to inspect the presence of an interfacial insulator layer on the behavior of Schottky diodes.
Deviations from the ideal electrical behavior may be caused due to the quality of the insulator layer between the metal and semiconductor, series resistance and the formation of barrier height. When the insulator layer thickness is in the order of few hundred nanometers, the interface states are not in equilibrium with semiconductor [17]. Due to this reason, the potential drop across the device is less than the applied bias. This change is reflected in the ideality factor that changes the slope of the I-V curve.

In order to reveal the changes in the ideality factor, the thermionic equation connecting the forward bias and current is considered.

\[
I = A* A^* T^2 \exp \left( -\frac{q\phi_b}{nkT} \right) \left[ \exp \left( \frac{qV}{kT} \right) - 1 \right]
\]

(6.2)

where, \( AA^* \exp \left( -\frac{q\phi_b}{nkT} \right) \) is reverse saturation current \((I_o)\), ‘A’ is the diode area, \( A^* \) is the effective Richardson constant, ‘\( \phi_b \)’ is the barrier height and ‘\( V \)’ is the applied voltage.

The ideality factor ‘\( n \)’ can be found experimentally from the slope of

\[
\ln \left( \frac{I}{1 - \exp \frac{qV}{kT}} \right)
\]

vs. \( V \) in the forward bias region. The zero-bias barrier height can be obtained from the reverse saturation current \((I_o)\).

\[
q\phi_b = kT \ln \left( \frac{A* A^* T^2}{I_o} \right)
\]

(6.3)

where, \( A=3.14 \text{ mm}^2 \), the diode area and \( A^* = 32 \text{ A/cm}^2\text{K}^2 \) for p type Si.

Fig. 6.4 shows the variation in the ideality factor ‘\( n \)’ and the zero bias barrier height \((\phi_b)\) as a function of \( Li^+ \) fluence of the Schottky diode. As can be seen the values of ‘\( n \)’ is found to increase while the value of ‘\( \phi_b \)’ decrease with increasing radiation dose. The results accounts for a net increase in carrier density in the depletion region. The hole trap centers are responsible for the electrical current enhancement [18-22].

The variation in the series resistance \( R_s \) with \( Li^+ \) implantation can be observed by noting the ideality factor ‘\( n \)’ for a specified applied voltage ‘\( V \)’. The value of \( R_s \) is calculated using the formula [23],
\[ R_s = \frac{V - \left[ n \frac{kT \ln (I/I_o)}{q} \right]}{I} \]  

(6.4)

where, ‘I’ and ‘n’ are the respective values for the applied potential V.

Fig. 6.5 shows the variation of normalized current \((I-I_0)/I_o\) and series resistance \(R_s\) on radiation dose under the applied voltage of 10V for the MIS Schottky diode. The values of the normalized current are observed to increase with increasing radiation dose. As can be seen form figure, there is less increase in the value of currents monitored with the increase of implantation fluence around \(10^{13}\) ions/cm\(^2\). Then it gradually increases and between the fluence of \(10^{14}\) and \(10^{15}\) ions/cm\(^2\), a very fast increase in the value of current is observed. This kind of variation in current is observed for many of the MIS structures [24, 25].

The current variation is attributed to the changes in the series resistance ‘\(R_s\)’ due to implantation of \(\text{Li}^+\) ions. At the biased voltage of 10V, the series resistance value varies from 3.3 to 8.44 k\(\Omega\) as the fluence varies from 0 to \(10^{15}\) ions/cm\(^2\). It is evident from the I-V plot that at the bias of 10V, ohmic behavior is dominating and this may be due to the decrease in the value of ‘\(R_s\)’. Therefore, the space charge limited conduction is completely vanished at higher bias voltages.

6.3 A.C IMPEDANCE AND MODULUS SPECTROSCOPY STUDIES ON Li+ IMPLANTED MgO THIN FILMS

6.3.1 Complex Impedance Spectroscopy Studies

Impedance analysis has been widely used to study the dielectric behavior of polycrystalline ceramic material. In general, the dielectric properties of materials arise due to intra-grain, inter-grain and other electrode effects. In dielectrics, the motion of charge could take place by charge displacement, dipole reorientation, space charge formation etc. [26, 27]. In order to understand the electric properties of a sample, grain, grain boundary and electrode combinations must be separated out. To achieve this, appropriate equivalent circuit representation has been formulated in terms of impedance.

In the present study, the impedance, dielectric and modulus analysis are carried out by forming metal-insulator-semiconductor (MIS) structure. Magnesium oxide thin films acts as the insulating layer between the silicon and aluminium.
electrodes. The effect of implantation on MgO film surface with Li$^+$ ions and their
dependence in impedance and dielectric properties have been analyzed. Obtained
results are summarized in the coming sections.

6.3.2 Impedance Analysis

Nyquist plot analysis is used to characterize bulk grain, grain boundary and
electrode interface contribution from the successive semicircles of impedance
exhibiting in the complex plane. This enables one to study the grain or bulk resistance
($R_g$) and grain boundary resistance ($R_{gb}$), which are useful in understanding the charge
transfer phenomena.

Fig. 6.6 shows the Nyquist plot of the fabricated capacitor with MgO thin
films as a dielectric layer between electrodes recorded at room temperature. The
impedance plot exhibits semicircle of impedance in the real and imaginary planes.
Semicircles can be used to characterize bulk grain, grain boundary and electrode
interface configurations. Usually high frequency semicircle originates from the bulk
conduction and dielectric processes. Low frequency semicircle is due to ion and
electron transfer at the surface containing the electrode. Intermediate frequency
semicircle provides information on the grain boundary and/or impurity phase
impedance.

For the present MIS structure, only one semicircle in the intermediate
frequency region is seen which is ascribed to the grain boundary contribution. This
type of impedance variation can be represented as an equivalent circuit, which
consists of a resistive element in parallel with a capacitor. This is the most common
interpretation for polycrystalline materials like MgO, having a contribution of grain
boundary. The frequency at the semicircle maxima $\omega_{\text{max}}$ for each RC element is given
by,

$$\omega_{\text{max}} = 2\pi f_{\text{max}} = (RC)^{-1} = \tau^{-1}$$

(6.5)

where, $\tau = RC$ is the relaxation time for the respective regions. Usually, the
capacitance of the grain boundaries is larger than that of the bulk grain. Therefore, the
relaxation time

$$\tau = RC = \rho \varepsilon_r \varepsilon_o$$

(6.6)

is larger for the grain boundaries. The grain boundary resistance of the sample is
extracted from the Nyquist plot, which is of the order of megohm (28.19 M$\Omega$). The
capacitance value for the grain boundaries is calculated by noting the frequencies at the Debye peak maxima and is found to be in the order of picofarad (14 pF). This result is in agreement with the reported values for the TiO$_2$ thin film capacitors [28]. The relaxation time of the process is about $3.95 \times 10^{-4}$ sec, which is due to the rotational fluctuations of molecular dipoles. If the frequency of the applied electric field corresponds to reorientation time ($\tau$) of molecular dipoles, the imaginary part of impedance shows a characteristic pattern. In addition, the semicircular arc starts at the origin; hence, no series electrode resistance is included in the equivalent circuit representation.

The a.c. impedance behavior of Li$^+$ ions implanted MgO thin films have been studied by forming thin film capacitor. The Li$^+$ implanted MgO thin films to a fluence of $10^{15}$ ions/cm$^2$ were sandwiched between aluminum electrode and the substrate (p-Si). The area of the top electrode is 3.14 mm$^2$ and the ion implanted MgO layer thickness is 0.497 $\mu$m. The impedance studies were performed in the frequency range 40 Hz – 100 kHz at temperatures between 30 °C and 90 °C using an impedance/gain phase analyzer.

In order to study the poly-dispersive nature of the dielectric relaxation in MgO films implanted with ions, impedance analysis is formulated in the temperature range of 30 °C - 90 °C. Fig. 6.7 and Fig. 6.8 show the real and imaginary part of the impedance as a function of frequency at different temperatures. Both $Z'$ and $Z''$ are frequency dependent. $Z'$ decreases with frequency whereas $Z''$ increases to a maximum (Debye peak) and then decreases. The $Z''$ peak is not symmetrical and the amplitude of the peak not remains constant. It varies with temperature and the peak shift to the high frequency side with temperature. Also, a single relaxation mechanism is seen in the entire frequency range. Noting the peak values of $Z'$ and $f_{max}$ from the Argand plot, the relaxation time of the dielectric process is estimated. The grain boundary impedance ($R_{gb}$) grain boundary capacitance ($C_{gb}$) and the grain boundary relaxation time ($\tau_{gb}$) are listed in Table 6.1, which are determined at different temperatures.
Table 6.1

Impedance parameter of the fabricated MIS structure

<table>
<thead>
<tr>
<th>Impedance parameter</th>
<th>30</th>
<th>50</th>
<th>70</th>
<th>90</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain boundary resistance ((R_{gb})) (MΩ)</td>
<td>5.16</td>
<td>0.306</td>
<td>0.260</td>
<td>0.21</td>
</tr>
<tr>
<td>Grain boundary capacitance ((C_{gb})) pF</td>
<td>15.42</td>
<td>17.34</td>
<td>15.31</td>
<td>15.16</td>
</tr>
<tr>
<td>Grain boundary relaxation time ((\tau)) x 10^{-5} sec</td>
<td>7.95</td>
<td>0.53</td>
<td>0.40</td>
<td>0.32</td>
</tr>
<tr>
<td>Bode plot slope (capacitive behavior) (30 °C)</td>
<td>-0.87</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Barrier layer capacitance at 1kHz (30 °C) (pF)</td>
<td>298</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The a.c response on MgO thin films implanted with Li\(^+\) ions to a fluence of 10^{15} ions/cm\(^2\) have been analyzed to study the different electric contributions of defective states localized at the grain boundary or at the grain surface. The charge transport in an insulating material may be due to charge displacement, dipole reorientation and space charge formation. Charge transport process causes a number of different polarization mechanisms that results frequency dispersion or dielectric relaxation in the material under an applied a.c electric field [27]. For electrical characterization, aluminium electrode is made above the MgO thin films implanted with Li\(^+\) ions. The substrate silicon is served as the bottom electrode. Experiments are performed in the temperature range 30-90 °C.

Fig. 6.9 shows the complex impedance spectrum of MgO-Li\(^+\) thin films at room temperature. A single semicircular arc due to the consequence of the grain boundary conduction is observed in the intermediate frequency region. Similar spectra recorded at higher temperature ensure a distinct effect on the spectra. This feature is almost similar at different temperatures with a difference in radii of curvature of arc. The radius of the arc reduces with rise in temperature and is a representative of the
The electrical process taking place in the material. The intercepts of the semicircle arc in the Z’ axis is used to calculate the grain boundary resistance while the corresponding frequency value evaluated from the apex of the semicircles arc are used to calculate the grain boundary capacitance. As temperature increases, the grain boundary resistance is found to decrease, due to the shift in radius of the semicircular arcs. At room temperature, the grain boundary resistance is 5.160 MΩ and it is decreased to 210 kΩ at 90 °C. The values of relaxation time determined in the region of measuring temperature is found to decrease linearly on increasing value of the temperature suggesting the typical semiconductor behavior.

The real part of impedance versus frequency and temperature is reported in Fig. 6.10. After an initial constant value, impedance starts to decrease and the onset of the impedance decrease moves to higher frequencies as temperature increases. This nature indicates the presence of high frequency dispersion. The frequency independent contribution at low frequencies shows the presence of a conductive channel within the material. The curves also display an increase in AC conductivity with the increase in temperature. This result may be related to the release of space charge because of reduction in the barrier properties. Also, the decrease of Z’ with rise in temperature show negative temperature co-efficient of resistance type behavior of the material.

Fig. 6.11 shows the variation of the imaginary part of impedance with frequency at different temperatures. The spectra are characterized by some of the features in the pattern:

(i) The values of $Z''_{\text{max}}$ decreases and shifts to higher frequencies with the increasing temperature

(ii) The asymmetric peak broadening of peaks suggests that there is a spread of relaxation times [29]. The spreading is indicated by the width of the curves. The merge of $Z''$ values in the high frequency region may possibly an indication of the accumulation of space changes in the material.

The complex impedance variation with frequency is shown in Fig. 6.12. Slope of the plot gives information about the nature of the capacitor. Obtained value of the slope 0.87 is deviated from the value for the true capacitor. This indicates the degrading nature of the dielectric MgO layer after implanted with lithium ions. In the implanted layer, conduction path may be induced, which degrades the dielectric
quality of the magnesium oxide. This behavior is again reflected in the dissipation factor (tan\(\delta\)). Very high values of tan\(\delta\) in the low frequency region indicate the DC conducting behavior of the material.

### 6.3.3 Modulus Analysis

The complex dielectric function \(\varepsilon^*\) and its dependence on external electric field frequency and temperature originates from different processes like microscopic fluctuations of molecular dipoles, propagation of mobile charge carriers, polarization due to separation of charges at the interface etc. Contribution of polarization of charges at the interface to the dielectric loss can be orders of magnitude larger than the dielectric response due to molecular fluctuations. The microscopic and macroscopic processes have frequency and temperature dependence of the real and imaginary part of the complex dielectric function. The methods, to quantify the contributions to the dielectric spectra are discussed in this section.

Relaxation process are characterized by a peak in the imaginary part \(\varepsilon''\) and a step like decrease of the real part \(\varepsilon'\) of the complex dielectric function \(\varepsilon^* = \varepsilon' - j \varepsilon''\) with increasing frequency. In contrast, conduction phenomena show an increase of the imaginary part of the dielectric function with decreasing frequency. For pure ohmic conduction, the real part of \(\varepsilon^*\) is independent of frequency and for non-ohmic conduction, the real part of \(\varepsilon^*\) increases with decreasing frequency.

Further, the investigation of relaxation process that is related to the rotational fluctuation of molecular dipoles can be analyzed with the complex dielectric function \(\varepsilon^*\). If the frequency of the applied electric field equals the reorientation time \(\tau\) of the molecular dipoles, \(\varepsilon'\) decreases with frequency and \(\varepsilon''\) exhibits a maximum. The frequency corresponds to \(\varepsilon''\) maximum is the relaxation frequency of the fluctuating dipoles. The dipole strength \(\Delta\varepsilon\) of a relaxation process can be determined from the loss peak \(\varepsilon''\) or from the step in \(\varepsilon'\).

In order to allow accurate assessment of the impedance data, complex electric modulus formalism have been discussed for various dielectric materials [30, 31]. In modulus formalism, the electric modulus \(M^*\) is defined in terms of the reciprocal of the complex relative permittivity \(\varepsilon^*\).

\[
M^* = \frac{1}{\varepsilon} = M' + jM''
\]  \hspace{1cm} (6.9)
where,

\[ \varepsilon^* = \frac{1}{j\omega C_0 Z} \quad (6.10) \]

\[ M' = \frac{\varepsilon'}{\varepsilon'^2 + \varepsilon''^2} \quad (6.11) \]

\[ M'' = \frac{\varepsilon''}{\varepsilon'^2 + \varepsilon''^2} \quad (6.12) \]

'\( C_0 \)' is the vacuum capacitance of the sample holder.

The modulus data expressed in the complex modulus formalism enables to understand the phenomenon of conductivity relaxation in terms of variation of \( M' \) and \( M'' \) as a function of frequency and temperature. The complex modulus plane analysis is based on the plot of imaginary part of \( M'' \) against real part of \( M' \) over a wide range of frequencies (40 Hz to 100 kHz in the present study). The plot is a single or a series of semicircular arcs. Each semicircular arc represents the parallel combination of resistance and capacitance of grain/grain boundary/electrode interface contribution in the conduction process. The semicircular arc in the low frequency region represents grain boundary/electrode interface contribution and an arc in the high frequency region represents the dominance of bulk grains. Magnesium oxide, the material considered in the present study exhibits a single semicircular arc in the low frequency region representing the dominance of grain boundary impedance. The impedance element representing the film/electrode interface is negligible because of the lower value of contact resistance. Extracting the values of \( R_{gb} \), the grain boundary resistance; \( C_{gb} \), grain boundary capacitance and \( \tau \), the relaxation time are discussed in detail in the previous section. In this section, importance is given to the electric modulus response with frequency at different temperatures. The real and imaginary component of dielectric constant of the material is determined initially to find out the electric modulus \( M^* \).

To study the relaxation mechanism in MgO thin films implanted with Li\(^+\) ions to a fluence of \( 10^{15} \) ions/cm\(^2\), the same modulus formalism has been adopted. In modulus formation, \( M' \) and \( M'' \) are plotted as a function of frequency. The peak observed in these plots corresponds to a relaxation process. The peak height in impedance plot is proportional to the resistance of that process, while the peak height in \( M \) against frequency plot is inversely proportional to the capacitance. The peak
position corresponds to the frequency ‘f_{\text{max}}’ is related to the relaxation time ‘\tau’ as
\[ 2\pi f_{\text{max}} \tau = 1. \]

Fig. 6.13 and Fig. 6.14 shows respectively the frequency dependence of M’ and M” for the MgO thin films implanted with Li^+ ions at various temperatures. As in hydrogen ion implanted MgO specimen, the position of the peak in M” shifts to higher frequencies with increasing temperature and a strong dispersion of M” exists.

The step like response of M’ shows the two distinct conduction mechanisms. In low frequency region, charge carriers are mobile to a large distance and in high frequency region; carriers are confined to a small region. Moreover, the broad nature of the peaks indicates the non-Debye nature of the material.

In order to confirm the dynamical processes occurring at different temperatures, the spectra for M”(\omega) of MgO-Li^+ is scaled by M”_{\text{max}}. The frequency axis is scaled by the relaxation frequencies. The modulus master curve is shown in Fig. 6.15 that enables an insight into the dielectric processes occurring in the material as a function of temperature. It could be observed that the spectra for M”(\omega) for different temperatures merge on a single master curve. This process indicates that the conducting processes occurring at different temperatures are independent of temperature. Moreover, the value of the parameter \beta, determined from full width at half height (FWHH) for all temperatures are the same which is wider than the Debye peak (1.14 decades). From the FWHH, the average value of \beta is found to be 0.395. This value of \beta clearly indicates that the relaxation is non-exponential. The variation of normalized parameters Z”/Z”_{\text{max}} and M”/M”_{\text{max}} as a function of frequency for the Li^+ implanted MgO thin films at 30 °C is shown in Fig. 6.16. As can be seen, there is no frequency shifts at any frequency regions. The perfect match between both parameters implied no changes in the polarization [32]. The distinct curves of Z’/Z”_{\text{max}} and M”/M”_{\text{max}} indicates that the polarization is due to localized conduction of carriers that have single relaxation process in the material even at high temperature also.

6.4. AC CONDUCTIVITY

Measurement of AC conductivity in insulating materials has been extensively used to understand the conduction process in these materials. The generally accepted view is that the AC conductivity is dominated by localized states within the energy
Measurement of AC conductivity is therefore a powerful experimental method to obtain information about the localized states. Many workers [33-35] have carried out such measurements on a variety of materials.

In the present study, complex impedance spectroscopy (CIS) has been carried out for describing the electrical processes occurring in a system on applying an AC signal across the sample sandwiched between the electrodes. The output response of such an experimental measurement, when depicted in a complex plane plot, appears in the form of a succession of semicircles representing the contribution to the electrical properties due to the bulk material, grain boundary effect and interfacial polarization. CIS technique is therefore useful to separate the effects arising from each component in a polycrystalline sample very easily. Impedance measurements on a material provide data having both resistive (real part) and reactive (imaginary part) components. It can be displayed in a complex plane plot in terms of any of the formalism like complex impedance, complex admittance, complex permittivity, and complex modules.

Moreover, the peak of the semicircular arc in the complex impedance spectrum provides the relaxation frequency of the material and their respective resistance and capacitances. The bulk conductivity (σ_{dc}) of a material is a thermally activated process obeying Arrhenius behavior, which can be estimated in terms of the bulk resistance (R_b) evaluated from complex impedance spectrum. The bulk conductivity can be calculated in accordance with the relation,

\[ \sigma_{dc} = \frac{1}{R_b} \frac{d}{A} \]  

(6.13)

where, ‘d’ is the thickness and ‘A’ is the area of the sample.

The AC conductivity of the material describing the frequency dependent behavior of the conduction process can be evaluated in accordance with the relation.

\[ \sigma_{AC} = \omega \varepsilon' \varepsilon_o \tan \delta \]

(6.14)

where, tan δ is the dielectric loss, ε’ the permittivity and ‘ε_o’ the permittivity in vacuum.

### 6.4.1 Experimental Details

Thin films of magnesium oxide were obtained by conventional spray pyrolysis technique. Ion implantation with 1.5 MeV Li^+ ions to a fluence of 10^{15} ions/cm^2 have
been carried out in a 3 MV peleton accelerator. The film thickness ranged in μm and was measured using stylus profiler. For AC measurements, films were sandwiched between two electrodes. Top aluminium electrode is thermally evaporated on to the MgO film surface to a pre-defined area and the silicon substrate served as the bottom electrode. A programmable LCZ bridge was used to measure the impedance $Z$, the capacitance $C$ and the phase $\phi$ directly. The total conductivity was calculated from the equation.

$$\sigma_{\text{tot}}(\omega) = \frac{d}{ZA} \quad (6.15)$$

where, ‘$d$’ is the thickness of the film and ‘$A$’ is the area of cross section of the sample. The dielectric constant ($\varepsilon'$) was calculated from the equation,

$$\varepsilon' = \frac{Cd}{A\varepsilon_o} \quad (6.16)$$

where, ‘$\varepsilon_o$’ is the permittivity of free space.

The dielectric loss $\varepsilon''$ was calculated from the equation,

$$\varepsilon'' = \varepsilon' \tan\delta \quad (6.17)$$

where, $\delta = 90 - \phi$ and ‘$\phi$’ is the phase angle.

The AC conductivity of Li$^+$ implanted MgO films were measured in the frequency and temperature ranges 40-100,000 Hz and 30-90 °C respectively.

### 6.4.2 AC Conductivity in Li$^+$ Implanted MgO Thin Films

AC conductivity measurements have been carried out in MgO thin films implanted with lithium ions to a fluence of $10^{15}$ ions/cm$^2$. Fig. 6.17 shows the variation of ac electrical conductivity variation at different temperatures as a function of frequencies.

As seen from figure, conductivity increases with temperature drastically as the sample is heated from 30 °C to 40 °C. After that, there are no remarkable changes in conductivity with temperature. In addition, it is observed that at low frequency region, there is dispersion in conductivity. This may be due to the changes in the dielectric constant of the film at that region. The real part of the dielectric constant decreases strongly with increasing frequency and this decrease depend on the contribution of polarizability. The increase in frequency leads to a decrease in orientational polarization and this takes more time than electronic and ionic polarization. This trend reduces the value of the dielectric constant value at higher frequencies. Due to these
variations, the conductivity dispersions are observed at low frequency region [36]. Further, the orientational polarization is connected with the thermal motion of molecules. The dipoles cannot orient themselves at low temperatures [37] and when the temperature is increased, the orientation of dipoles is possible. Due to the increase in orientational polarization, the conductivity increases. At the intermediate and high frequency regions, the ac conductivity is independent of frequency. On comparing the conductivity variations with implantation, the MgO thin films implanted with Li$^+$ ions are more conductive than the H$^+$ implanted films. At 100 Hz, lithium implanted films have conductivity of about $1.07 \times 10^7$ S/m, whereas H$^+$ implanted films have only $4.11 \times 10^{-8}$ S/m.

6.5 CONCLUSIONS

MgO thin films were deposited on single crystalline Si (111) wafers and then implanted with Li$^+$ for the fabrication of MIS structures. Aluminium electrode was deposited as the metal top electrode. I-V measurements have been studied in the range of $20 - 20 \times 10^4$ V/cm. Ohmic region has been observed in low fields, space charge effects in moderate fields and Poole Frenkel conduction in high electric fields. Current is found increasing with increase in the radiation dose of Li$^+$ ions. The current transport mechanism in ion-implanted samples consists of trap assisted tunneling as well as thermionic emission. Zero bias potential barrier height decreases with implantation fluence.

From the slope of the Bode plot, the purity of the capacitor and the barrier layer capacitance were determined. The effect of ion implantation on impedance parameters have been studied by both the impedance and electric modulus analysis. All the capacitors exhibited non-Debye type relaxation, showing distinct curves of $Z''/Z''_{\text{max}}$ and $M''/M''_{\text{max}}$ and the dipole polarization was observed because of conduction of localized carriers. The AC conductivity of Li$^+$ implanted MgO films have been investigated in the frequency range $0.04 - 100$ kHz at different temperatures 30-90 °C. The AC conductivity of MgO:Li$^+$ thin films was found to obey the power law $\omega^s$. The temperature dependence of both AC conductivity and exponent ‘s’ were interpreted by the correlated barrier hopping model. The AC conductivity was increasing with temperature and frequency. Further, the conductivity increased with temperature, but the conductivity variation with frequency was not observed.
REFERENCES


