Chapter IV

Electrical Properties of Pure, Mn and Ni Doped Zinc Oxide Nano particles at various pH Levels

4.1 Introduction

The various Electrical studies on DC conductivity, AC Conductivity and Dielectric properties have been studied in this chapter. The detailed studies are carried out based on pure; Mn and Ni doped Zinc Oxide for different pH values. The four probe method and Precision impedance analyzer (LCR –Z) method are used to measure and study the electrical behavior of material with different samples.

Four Probe Method

The four probe method is the familiar one which is widely used for the measurement of electrical conductivity of the material. The Schematic view of this method is shown in the Figure 4.1. The four probe technique was developed by Wenner in 1916 to measure the earth’s resistivity [1].

![Four Probe Method](image)

**Figure 4.1 Schematic view of Four Probe Method**
Four Probe Arrangements

It has four individually spring loaded probes which are equally spaced and mounted on a Teflon bush. It will offer good electrical insulation between the probes. A Teflon spacer near the tips is also provided to keep the probes at equal distance. The whole arrangement is mounted on a suitable stand and leads are provided for the voltage measurement. In this arrangement, well prepared polished pellets and electrodes have been used.

The four probe set-up contains three units as follows

(i) Multi range Digital Voltmeter:

It has A/D Converter ICL 7107 as primary unit. It has good accuracy for the range below 10μV and has input bias current of 10pA max. The external reference is preferable rather than internal reference due to degradation in performance and internal heating.

(ii) Constant Current Generator:

It is also called as regulated current generator which is able to produce constant output as we required for various temperatures. The feedback is used here to limit the load current of the supply and also the load current can be varied with the help of potentiometer. The supply is a highly regulated and practically ripple free d.c. source. The digital panel meter is used here to display the resultant output.

(iii) Oven / Heater Power Supply:

This power supply is used to drive the entire product. The voltage rating of the above said power supply is determined by the step down transformer.

4.2 DC Conductivity studies of Pure, Mn and Ni Doped Zinc Oxide

Semiconductor which is doped stoichiometrically doped with suitable dopants will provide appreciable electrical properties. Extrinsically doped such semiconductors obey the fundamental physical laws and statistics that govern the electrical properties of these materials. How the dopant occupies the positions available in the host matrices, it contributes its electrical conductivity Brown, I. G.et al [2] and enhances or suppress the electrical properties are analyzed. The dopability of a semiconductor is usually limited by the dopant solubility. The dopant solubility depends on the formation energy of the defect it forms, which is determined by the chemical potentials of the dopant and elements forming the lattice Wagner, R. S et al [3]. A low solubility may result from the formation
of a secondary phase at high doping levels, segregation, precipitation or substitution at the wrong lattice site. Doping methods such as co-doping and cluster-doping have emerged in the last few years to address the issue of low acceptor dopant solubility in ZnO. Briefly, the intentional introduction of donors and acceptors in a specific ratio can enhance the acceptor solubility by minimizing the ionic potentials and lowering the Madelung energy (electrostatic energy of an ionic crystal given by the sum of pairwise interactions between ions treated as point charges). These methods predict that the issue of low acceptor solubility in ZnO can be overcome by introducing donors, which will lower both the lattice energy and the acceptor defect formation energy.

In fact, the doping limit rule can be viewed as an extension to wide band gap semiconductors of the vacuum pinning rule, which was originally established by Walukiewicz for transition-metal-doped semiconductors. In the present work, Mn and Ni ions were used as the dopants and incorporated into the experimental stage of preparation ZnO. Both the dopants are having less ionic radii than the Zn which will easily get into the ZnO matrices. Moreover the dopant concentration is well within the prescription limit given Vegard’s law.

![Figure 4.2 DC Conductivity of Pure ZnO](image.png)
Figure 4.3 DC Conductivity of Mn doped ZnO

Figure 4.4 DC Conductivity of Ni doped ZnO
From the DC analysis it is understood that as synthesized undoped ZnO possess n-type conduction which is due to the availability of high dense oxygen vacancies in the matrices. The typical current voltage characteristic plots for pelletized pristine ZnO shows appreciable I/V behaviour. The change current linearly with the varying voltage shows its good electrical nature of the nanoparticles. When the pH of the growth medium raised from 9.0 to 10.0 the electrical behaviour of the sample appreciably enhanced and it gives good current conduction values which are understood as the number of vacancies in the ZnO is reduced so the more number of charge carriers participated in the electrical conduction. Further raise in the pH value of medium enhances the particle aggregation leads to raise in the particle sizes. So exposure to the electrical potential is limited so that the electrical conductivity is lowered down. This is shown in the Figure 4.3.

In contrast, the I-V curve for Mn and Ni-doped ZnO nanoparticles are shown in the Figures 4.4 and 4.5 shows a steep increase in conductance, indicating a great enhancement in conductivity by doping. The current of the doped nanoparticles changed from about 15 -22 mA and 16-30 mA for Mn doped and Ni doped ZnO respectively as the voltage V was varied from 2 to 4.5 V. For thin films, doping of cations of higher valence state than Zn (Zn$^{2+}$) into ZnO, such as In, Ga, Mn and Ni, leads to an increase in the electrical conductivity. Referred to the pure undoped ZnO nanoparticles, the doped Ni enhances the conductivity Monteiro et al [4], probably due to the presence of trivalent Ni$^{3+}$ cations. A Ni$^{3+}$ cation would contribute a hole carrier, and the oxygen vacancies are likely to be eliminated by annealing in air at high temperature; therefore, the possible carriers are p-type.

**LCR Meter**

An LCR meter is a type of electronic test equipment used to measure the inductance (L), capacitance (C), and resistance (R) of an electronic component. In the simpler versions of this instrument the impedance was measured internally and converted for display to the corresponding capacitance or inductance value. Readings should be reasonably accurate if the capacitor or inductor device under test does not have a significant resistive component of impedance. More advanced designs measure true inductance or capacitance, as well as the equivalent series resistance of capacitors and the Q factor of inductive components. Most LCR meters use AC signals to measure the impedance of components. The schematic view of this instrument is shown in the Figure 4.5.
Operation

Usually the device under test (DUT) is subjected to an AC voltage source. The meter measures the voltage across and the current through the DUT. From the ratio of these the meter can determine the magnitude of the impedance. The phase angle between the voltage and current is also measured in more advanced instruments; in combination with the impedance, the equivalent capacitance or inductance, and resistance, of the DUT can be calculated and displayed. The meter must assume either a parallel or a series model for these two elements. The most useful assumption, and the one usually adopted, is that LR measurements have the elements in series (as would be encountered in an inductor coil) and that CR measurements have the elements in parallel (as would be encountered in measuring a capacitor with a leaky dielectric).

Handheld LCR meters typically have selectable test frequencies of 100 Hz, 120 Hz, 1 kHz, 10 kHz, and 100 kHz for top end meters. The display resolution and measurement range capability will typically change with test frequency. Bench top LCR meters typically have selectable test frequencies of more than 100 kHz. They often include options to superimpose a DC voltage or current on the AC measuring signal. Lower end meters offer the possibility to externally supply these DC voltages or currents while higher end devices can supply them internally.

4.3 AC Conductivity studies of Pure, Mn and Ni Doped Zinc Oxide

The variation of ac conductivity for doped ZnO nanoparticles at room temperature has been analyzed. This is shown in the Figure 4.6. It is clear from the graphs that the conductivity increases as the frequency of applied ac field increases. The ac conductivity of a dielectric sample can be calculated using the relation:

\[ \sigma_{ac} = \varepsilon'' \varepsilon_0 \omega \tan \delta \]  

\[ (4.1) \]
Where, $\omega$ is the angular frequency. It is also evident from Figure 4.6 that the ac conductivity decreases as the pH value of the medium increases from 9.0 to 11.0 in the ZnO precursor. It can be attributed to the fact the presence of Mn and Ni $^{2+}$ hole doping induced by Zn$^{2+}$ vacancies that enhances the defects created by the donor which leads to the dilution of the system. Hence, n-type conductivity of the host ZnO matrix decreases as pH increases. The ac conductivity of dielectric materials is temperature and frequency dependent, and obeys the empirical formula of frequency dependence and is governed by the ac power law, A.M. Abo El Ata et al [5]:

$$\sigma_{ac}(\omega) = B \omega^n$$ \hspace{1cm} (4.2)

Where, ‘B’ and ‘n’ are constants that depend upon both the temperature and composition; B has the units of conductivity and n is dimensionless. The value of n starts from 0 and ends at 1. When n = 0, the electrical conduction is frequency independent or dc conduction and for n$^{-1}$, the conduction is frequency dependent or ac conduction, M.A. El-Hiti et al [6]. The exponent parameter n has been calculated for each composition by plotting ln s versus ln v according to the above equation 4.2 , which represents straight lines with slope equal to the exponent parameter n and intercept parts equal to ln B on vertical axis at ln v = 0. The values of the exponent ‘n’ have been found to vary between 0.0735 and 0.1057, which suggests that the conduction phenomenon in the studied samples is due to the hopping of charges.

It is understood that power law dependence of $\sigma_{ac}$ corresponds to short range mechanism belongs to the hopping via different length and heights of energy barriers associated with the trap sites. It is observed that in all the cases, $\sigma_{ac}$ remains constant up to 105 Hz. The $\sigma$ (f) is almost constant over the low frequency range from 100 Hz to critical frequency. The measured value of $r$ (f = 10 kHz) is of the order of 10$^{-1}$ S/cm$^{-1}$ such high value is attributed to the high level of protonation and crystallinity of the sample. It is well known that $r$/depends, apart from frequency f and temperature, on the degree of protonation percent and crystallinity of the composites, Aashish Roy et al [7]. The dependence of $r$ (/) on composite is shown in the inset which gives the plot of $r$ (/ = 10 kHz) as a function of 10 wt % of ZnO of the composites. The maximum value of 0.1 S/cm$^{-1}$ conductivity is observed for pH 10.0 at 5.0 9 106 Hz. It is noticed that $r$ (/) increases steeply with an increase in 10 wt % of Mn and Ni ions ZnO nanoparticles in grown at pH 9.0, 10.0 and 11.0. This behavior is attributed to the addition of NH$_3$ molecules to the
growth medium which plays two types of roles namely chelating agent which aggregates the nanoparticles and structure determining parameter of prepared ZnO nanoparticles because the nano sized particles provide high surface-to-volume ratio and this results in high quantity of surface atoms of nanoparticles, which can lead to the insufficiency of surface atomic coordination and high surface energy. Therefore, the surfaces are highly active, which promote the flow of charge particles through particle matrix. The above 40–50 wt% conductivity decrease may be due to increase in the disorderliness of the doped semiconductor with increasing amount of hydrogen ions in the ZnO nanoparticles. The ZnO nanoparticles could possibly induce conformational changes in Mn and Ni doping leading to a reduction in the order and a consequent reduction in delocalization length, which is reflected by a decrease in conductivity. This is shown in the Figures 4.7 and 4.8.

![Graph showing AC conductivity of Pure ZnO](image)

**Figure 4.6 AC conductivity of Pure ZnO**
Figure 4.7 AC conductivity of Mn doped ZnO

Figure 4.8 AC conductivity of Ni doped ZnO
4.4 Dielectric studies of Pure, Mn and Ni Doped Zinc Oxide

The dielectric properties of a material can be discussed with the applied field frequency, surrounding thermal state, structure of the materials and so on. The dielectric behavior of solid material is described by expressing the relative dielectric constant as a complex quantity made up of a real component and an imaginary component, i.e.,

\[ \varepsilon^* = \varepsilon' + j\varepsilon'' \]  \hspace{1cm} (4.3)

where \( \varepsilon' \) is the real part of the dielectric and \( \varepsilon'' \) is the imaginary part of dielectric constant, representing the energy storage capacity of the dielectric material as the function of polarization and the energy loss respectively. When the electric field is applied to a material, it will give response to the applied field in the above parameters. To understand this, following aspects should also be considered namely the intergranular potential barrier on the electrical properties of ceramic, the microstructure, composition and, the frequency dependent real dielectric constant can be calculated using the relation:

\[ \varepsilon = \frac{C_p t}{\Lambda \varepsilon_0} \]  \hspace{1cm} (4.4)

Where, \( C_p \) is the capacitance of the specimen in Farad (F), \( t \) is thickness of pellet, \( \varepsilon_0 \) is the permittivity of free space (\( 8.854 \times 10^{-12} \) F/m) and \( \Lambda \) is the cross sectional area of the flat surface of the pellet. The complex or imaginary dielectric constant for all the samples was calculated using the relation: \( \varepsilon_0 + \varepsilon' = \tan \delta \); where \( \tan \delta \) is the dielectric loss tangent which is proportional to the loss of energy from the applied field into the sample (this energy is dissipated as heat) and therefore denoted as dielectric loss.

**Dielectric Studies on pure ZnO grown at pH 9.0, 10.0 and 11.0**

The Variation of the dielectric constant with frequency at room temperature for ZnO prepared at different pH values are shown in Figure 4.9. The Non linearity relation between the frequency and dielectric constant was witnessed from the analysis. From this study it is understood that the dielectric constant decreases with increasing frequency which is typical dielectric behavior of oxide nano systems.
Figure. 4.9 Variation of Dielectric constant with frequency for Pure ZnO nanoparticles at room temperature.

The higher magnitude of dielectric constant is the resultant of all the contributions drawn from electronic, atomic ionic and interfacial polarization. As frequency increases the contribution from the space charge and orientational polarisation reduces and so dielectric constant decreases. At higher frequency the dielectric constant completely ceases. This is shown in the table 4.1.
Table 4.1 pH values Vs Dielectric constant

<table>
<thead>
<tr>
<th>S.No</th>
<th>composition</th>
<th>1KHz</th>
<th>10KHz</th>
<th>100KHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pure ZnO pH 9.0</td>
<td>140</td>
<td>121</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>Pure ZnO pH 11.0</td>
<td>349</td>
<td>285</td>
<td>224</td>
</tr>
<tr>
<td>3</td>
<td>Pure ZnO pH 10.0</td>
<td>374</td>
<td>314</td>
<td>278</td>
</tr>
</tbody>
</table>

Dielectric constant is increased after the addition of NH₃ to the growth medium. Addition of pH 10.0 grown ZnO sample shows high dielectric constant than other compositions. Compared to the pH 9.0 and 11.0 grown samples, pH 10.0 grown samples shows high dielectric values due to the optimum concentration of electron and hole contribution in the sample. Also the study reveals that the pH 10.0 is the optimum growth pH value for ZnO nanosystems. This is shown in Figure 4.10.

Figure 4.10 Variation of the dielectric constant with respect to the pH values

Dielectric Studies on Mn doped ZnO prepared at pH 9.0, 10.0 and 11.0

The dielectric studies on Mn doped ZnO prepared at pH 9.0, 10.0 and 11.0 is shown in the Figure 4.11. The variation of real part of dielectric constant with respect to the frequency of applied electric field between the ranges of 1Hz and 1000 Hz for all the
samples. It is observed that the dielectric constant decreases as pH of the growth medium increases with constant dopant concentration. The decrease in dielectric constant indicates the formation of microstructure with semiconducting ZnO grains surrounded by insulating grain boundaries and also suggest the existence of interface states in the grain boundaries. It is also evident that all the samples are shown the dielectric dispersion.

![Graph showing dielectric properties of Mn doped ZnO nanoparticles](image)

**Figure 4.11 Dielectric Properties of Mn Doped ZnO Nanoparticles**

**Dielectric Studies on Ni doped ZnO prepared at pH 9.0, 10.0 and 11.0**

The dielectric studies on Ni doped ZnO prepared at pH 9.0, 10.0 and 11.0 is shown in the Figure 4.12. The dispersion is rapid at lower frequencies but it is slow and approaches to almost frequency independent behavior at high frequencies (microwave frequency). The observed dielectric behavior can be explained in the light of Maxwell–Wagner interfacial type of polarization , J. Maxwell [8], K.W. Wanger [9] and Koops phenomenological theory , C.G. Koops [10]. According to this model, a dielectric medium is assumed to be made of well conducting grains which are separated by poorly conducting (or resistive) grain boundaries. The grain boundaries are found to be more effective at lower frequencies, while grains are effective at higher frequencies. The grain boundaries are formed during the sintering process due to the superficial reduction or oxidation of crystallites in a porous material as a result of their direct contact with the firing atmosphere, M.A. El Hiti [11], P. Reddy [12]. The frequency independent behavior of all
the samples at higher frequency of applied electrical field is just because of the charge carriers which are responsible for different mechanisms of polarization which lag behind the applied alternating field. As a result they cannot follow the changes in the applied field over a certain frequency limit, as the frequency increases.

![Dielectric Properties of Ni Doped ZnO Nanoparticles](image)

**Figure 4.12 Dielectric Properties of Ni Doped ZnO Nanoparticles**

Dielectric loss (tan δ) is represented as dissipated energy in a dielectric system. It is considered to be caused by domain wall resonance. At higher frequency the losses are found to be low since domain wall motion is inhibited and magnetization is forced to change rotation. According to Eq. 4.1 tan δ is proportional to the imaginary part of dielectric constant, M. Mehedi Hassan et al [13]. The dielectric loss decreases with the increase in frequency for all the samples which exhibit dispersion behavior similar to the dielectric constant. The value of tan δ is large at lower frequencies, while it becomes lower at higher frequencies. Plot of tan δ for Mn doped and Ni doped ZnO displays small humps at the frequency if lower region which may represent the relaxation peaks. Such peaks happen when jumping frequency of localized electric charge carrier becomes approximately equal to that of the externally applied ac electric field, A.M. Abdeen et al [14]. It is evident that the overall values of tan δ are found to decrease with the increasing concentration of Mn and Ni $^{2+}$ ions for all the samples.
4.5 Conclusion

The electrical properties of pure and metal transition doped ZnO nano particles are studied in this chapter for different pH values. DC and AC Electrical measurements are made by four probe method and LCR bridge method and their results are accounted. The pH plays an important role on the electrical properties of the semiconductor Nano particles which are witnessed through this. The DC measurements proved that pH 10.0 grown Ni doped ZnO particles shows appreciable electrical behaviour which is shown by V-I curve. The AC measurements are made for pelletized ZnO nanoparticles for various frequency ranges. From this it is understood that the doping process done at different pH values allow the doping ions at different levels, which shows the pH alters the carrier concentration in the ZnO matrices. The curves are plotted for various frequencies versus dielectric through which the conductivity and its results are accounted. From this the study reveals that Ni doped ZnO shows good Ac conductivity behaviour than the pure and Mn doped samples. The appreciable conductivity is witnessed because of the successful substitution of Ni $^{3+}$ ion in ion $^{2+}$ places and hole conduction. Dielectric constant is varied with different frequencies are observed and recorded. The result proves that pure ZnO with pH 10.0 has good dielectric constant. It has also been as to how the dielectric constant decreases with the increasing of frequencies in doped material at different pH values.
References


