CHAPTER 5

THE ac AND dc CONDUCTION MECHANISM IN ZnO NANORODS AND NANOTUBES

5.1 Introduction

Determination of the electrical properties of one dimensional semiconductor nanostructures is important for material and growth process development as well as for further nanodevice design [1]. The increase in surface area and the quantum confinement effects have made nanostructured materials quite distinct from their bulk form in electrical properties [2]. ZnO 1D nanostructures, including nanorods and nanotubes, have been used in many electronic device applications. For example, transparent conducting ZnO thin films have been widely used as window electrodes for flat panel displays, touch panels and solar cells, because of their excellent optical transparency and controllable electrical conductivity [3-5]. It has also been widely used in piezoelectric transducers for surface acoustic wave (SAW) devices, varistor, gas sensor and optical waveguides [5-6]. Conventional ZnO thin films have been studied as semiconducting channels in thin-film transistors for electronic circuit applications [7]. For the nanodevice applications, precise control of conductivity is required [8]. A unique feature of 1D nanostructure is the large surface to volume ratio available in these systems. It consists of grains, grain boundaries and grain interfaces which play important roles in the determination of the electrical properties [9-11]. The grain boundaries having high density of defects like dangling bonds, vacancies, micropores etc. can control the transport properties of the material in a decisive manner.
Measurement of the ac conductivity of semiconductors has been extensively used to understand the conduction process and it is also a powerful tool for obtaining information about the defect states present in the system. AC measurements provide information about the interior of the materials in the region of relatively low conductivity and it is important means for studying the dynamic properties such as conductance (G), capacitance(C) and dielectric loss tangent (tanδ) of the semiconductors. This measurement also helps to distinguish between localized and free band conduction (dc conduction). In localized conduction, the ac conductivity increases with frequency, while in the free band conduction the conductivity decreases with frequency.

Various models such as the Quantum Mechanical Tunnelling (QMT) [12], Hoping Over a Barrier [13], Correlated Barrier Hopping (CBH) etc. [13] have been proposed to explain the ac conduction mechanisms in amorphous semiconductors. The study of the ac conductivity of ZnO nanorods and nanotubes reveals that Correlated Barrier Hopping is the dominant conduction mechanism in these systems. In this model it is assumed that the charge carriers hop between defect centers over the potential barrier (W) separating them. According to this model [13], the conduction occurs via a bipolaron hopping process wherein two electrons simultaneously hop over the potential barrier between two charged defect states (D⁺ and D⁻) and the barrier height is correlated with the intersite separation via a Coulombic interaction. Shimakawa [14] suggested further that, at higher temperatures, D⁰ states are produced by thermal excitation of D⁺ and D⁻ states and single polaron hopping (i.e., one electron hopping between D⁰ and D⁺ and a hole between D⁰ and D⁻) becomes a dominant process. Generally, CBH model is applicable only for the amorphous materials and it is valid at least for temperatures above
100K [15]. Nevertheless the surface defects are assumed to be responsible for the correlated barrier hopping type of conduction mechanism in ZnO nanorods and nanotubes. Quite a few researchers have studied the ac conductivity of ZnO [9-11], although a systematic study of the ac conduction mechanism of ZnO nanorods and nanotubes in a wide temperature range is still lacking. This chapter describes the frequency and temperature dependence of ac conductivity of ZnO nanorods and nanotubes over the frequency range 100 Hz-1 MHz and temperature range 303K-543K. The frequency and the temperature dependence of ac conductivity is well described in the CBH model and the experimental results are well interpreted in terms of bipolaron and single polaron hopping. This chapter also discusses the variation in the dc conductivity of consolidated ZnO nanorods and nanotubes with different temperatures.

The measurement of ac conductivity was carried out using Hioki 3532–50 Hi-Tester in the frequency range of 100 Hz-1 MHz and at various temperatures between 303K and 543K. DC electrical measurement was carried out using a Keithley Model 617 electrometer. DC electrical resistance was measured by applying a voltage of 5V across the samples from a constant-voltage source using the Keithley electrometer. The resistance of the samples was measured at different temperatures between 313 and 423K keeping each temperature constant within ±1 K.

5.2 Theoretical models

The measured total conductivity $\sigma_{\text{total}}$ at angular frequency $\omega$ and temperature can be written as [16]

$$\sigma_{\text{total}} = \sigma(\omega) + \sigma_{\text{dc}}$$

(1)
Where \( \sigma_{dc} \) and \( \sigma(\omega) \) are the dc and frequency-dependent ac conductivities, respectively and it is assumed that ac and dc conductivities are due to completely different processes. However, the dc conductivity represents the ac conductivity in the limit \( \omega \to 0 \); the separation given by equation (1) is no longer useful.

The \( \sigma_{ac} \) was calculated using the relation [17],

\[
\sigma_{ac} = \varepsilon' \varepsilon_0 \tan \delta \tag{2}
\]

Where \( \varepsilon' \) is the real part of dielectric constant of the material, \( \varepsilon_0 \) is the dielectric constant of free space and \( \tan \delta \) is the dielectric loss tangent.

In many amorphous semiconductors and insulators, the ac conductivity invariably has the form [15]

\[
\sigma(\omega) = A\omega^s \tag{3}
\]

where \( A \) is a constant dependent on temperature and \( s \) is a frequency exponent, generally less than or equal to 1.

Many different theories for ac conduction in amorphous semiconductors [15] have been proposed to account for the frequency and temperature dependence of the ac conductivity and its frequency exponent \( s \). It is commonly assumed that the pair approximation holds, in which the motion of carriers leading to relaxation is contained within a pair of sites. Therefore the dielectric loss occurs because the carrier motion is considered to be localized within pairs of sites. In essence, two distinct processes have been proposed for the relaxation mechanism, namely quantum mechanical tunneling through the barrier separating two equilibrium positions and classical hopping of a carrier over the barrier or some combination or variant of the two, and it is variously assumed that electrons or polarons or atoms are the carriers responsible. QMT model refers to the
carrier motion that occurs through tunneling between two localized states near the Fermi level. In CBH model, the charge carriers hop over the potential barrier between two charged defect states [13].

5.2.1 Quantum-mechanical tunneling (QMT) models

In the QMT process [12, 15], three types of carriers are distinguished, namely electrons, small polarons and large polarons. Within the pair approximation, the ac conductivity for single-electron motion undergoing QMT and obtained the following expression:

$$\sigma(\omega) = C e^2 K_B T \alpha^{-4} \left[ N(E_F) \right]^2 \omega R_{\omega}^{-4}$$

(4)

Where C is a numerical constant, taken as $\pi^2/24$. $N(E_F)$ is the density of states at the Fermi level, assumed to be constant, and $R_\omega$ is the hopping distance at a particular frequency $\omega$, given by

$$R_\omega = \frac{1}{2\alpha} \ln \left( \frac{1}{\omega \tau_0} \right)$$

(5)

The frequency dependence of $\sigma(\omega)$ in the form of equation (3) can be deduced using the relation

$$s = \frac{d \ln \sigma(\omega)}{d \ln \omega}$$

(6)

And for the QMT model, s gives

$$s = 1 - \frac{4}{\ln(1/\omega \tau_0)}$$

(7)

The above results are obtained in a wide-band case, i.e., for $\Delta_0 >> K_B T$, where $\Delta_0$ is the band width. Thus for QMT of electrons, the frequency exponent, s, is temperature-independent but frequency-dependent and the ac conductivity is linearly dependent on temperature.
5.2.1.1 Small polaron tunneling

A temperature-dependent frequency exponent can be obtained within the framework of the Quantum Molecular Transport (QMT) in the pair approximation by assuming that the carriers form non-overlapping small polarons [15]. Transport of an electron between degenerate sites having a random distribution of separations will, therefore, generally involve an activation energy, the polaron hopping energy $W_H = W_p/2$. In this case, the frequency exponent becomes

$$s = 1 - \frac{4}{\ln(1/\omega\tau_0) - W_H / k_B T}$$ \hspace{1cm} (8)

Now it is noted that $s$ is temperature dependent, increasing with increasing temperature.

In the case of small-polaron QMT, the expression for the conductivity remains the same as for electron QMT [equation (4)], with a modification in the tunneling length

$$R_\omega = \frac{1}{2\alpha} \left[ \ln \left( \frac{1}{\omega\tau_0} \right) - W_H / k_B T \right]$$ \hspace{1cm} (9)

The behaviour of this model is that $s$ can apparently become infinity at sufficiently high frequency and at low temperatures due to the hopping length $R_\omega$ tending to zero, when the term in the square bracket of the expression in equation (9) tends to zero. That means the contribution to the overall conductivity due to the small-polaron tunneling would tend to zero at higher frequencies and lower temperatures where the value of $R_\omega$ is minimum.

5.2.1.2 Large polaron tunneling

Long et al. [18] discussed the ac conductivity expected from a model in which tunneling of polarons is still the dominant mechanism, but where an appreciable overlap of the polaron distortion clouds occurs. Long considered the case of large polarons, i.e. those for which the spatial extent of the polaron is large compared with the inter atomic
spacing, characteristic of ionic lattices. For such polarons, overlap of the potential wells of neighbouring sites is possible because of the long-range nature of the dominant Coulombic interaction, with the result that the polaron hopping energy is reduced

\[ W_H = W_{H0} (1 - r_p / R) \]

Where \( r_p \) is the polaron radius and \( W_{H0} \) is given by

\[ W_{H0} = \frac{e^2}{4\varepsilon_p r_p} \]

Where \( \varepsilon_p \) is the effective dielectric constant. It is assumed that \( W_{H0} \) is constant for all sites, whereas the intersite separation \( R \) is a random variable. The ac conductivity for the overlapping-large-polaron tunneling (OLPT) \([15, 18]\) model is given by

\[ \sigma(\omega) = \frac{\pi^4}{12} e^2 \left( K_B T \right)^2 \left[ N(E_F) \right]^2 \frac{\omega R_\omega^4}{2\alpha K_B T + W_{H0} r_p / R_\omega^2} \]

Where \( R_\omega \) is given by

\[ R_\omega = \frac{1}{2\alpha} \left[ \ln \left( \frac{1}{\omega \tau_0} \right) - \frac{W_{H0}}{K_B T} \right] + \frac{1}{2\alpha} \left[ \ln \left( \frac{1}{\omega \tau_0} \right) - \frac{W_{H0}}{K_B T} \right]^2 + \frac{8\alpha r_p W_{H0}}{K_B T} \]

The frequency exponent \( s \) in this model can be evaluated as

\[ s = 1 - \frac{8\alpha R_\omega + 6W_{H0} r_p / R_\omega K_B T}{\left( 2\alpha R_\omega + W_{H0} r_p / R_\omega K_B T \right)^2} \]

Thus the OLPT model predicts that \( s \) should be both temperature and frequency dependent. The frequency exponent \( s \) decreases from unity with increasing temperature. For large values of \( 2\alpha r_p \), \( s \) continues to decrease, eventually tending to the value of \( s \) predicted by the QMT model of nonpolaron forming carriers, whereas for small values of
2αp, s exhibits the minimum at a certain temperature and subsequently increases with increasing temperature in a similar fashion to the case of small-polaron QMT.

5.2.2 Classical Hopping models

5.2.2.1 Hopping over a barrier (HOB)

The process which has been proposed for the relaxation mechanism is classical hopping over a barrier [13, 15], where the random variable is \( \zeta = \frac{W}{K_B T} \). For the case of atomic motion, the following expression is obtained

\[
\sigma(\omega) = \frac{3}{\pi} \eta \frac{N p^2 K T}{W_0 \Delta_0} \tanh \left( \frac{\Delta_0}{2 K T} \right) \omega \quad \text{(15)}
\]

Where \( \eta \) is a mean-field correction term, \( N \) is the number of pair states per unit volume, \( p \) is the dipole moment associated with the transition, and it is assumed that the energy difference between sites, \( \Delta \), is randomly distributed in the range \( 0 < \Delta < \Delta_0 \) and the barrier height is also randomly distributed in the range \( 0 < W < W_0 \). In the case of simple HOB where the barrier height is not dependent on the intersite separation, the frequency exponent of \( \sigma(\omega) \) is predicted to be unity and to be independent of temperature and frequency. In the case of atomic tunneling, an expression of \( \sigma(\omega) \) is obtained similar to equation (16), with \( s = 1 \), if the dipole moment is uncorrelated with the tunneling distance.

5.2.2.2 Correlated Barrier Hopping (CBH)

In CBH, the relaxation also occurs by HOB but the barrier height \( W \) is correlated with the intersite separation as a result of the coulombic interaction between the charge-carrier and the charged-defect centers. But in HOB, the relaxation variable is independent of the intersite separation \( R \), and hence the hopping distance is independent of frequency. This restriction was lifted by Pike [19], who proposed a model of electron transfer by
thermal activation over the barrier between two sites, each having a coulombic potential well associated with it. This model considers hopping of charge carriers between two defect sites (D⁺ and D⁻) over a barrier separating them, rather than tunneling through the barrier. The hopping process may be considered such that the carriers are ejected from a D⁻ site into one of the excited levels. Assuming a two-electron localized wavefunction can exist within the potential spanning both centers, the carriers may transfer to the neighbouring site without recourse to tunneling. The carriers ejected from the initial D⁻ center drop into the D⁺ center and converting it to a D⁻ center. The energy $W_M$ is the energy that would be required to take two electrons from the D⁻ state to the continuum (the conduction band) in the absence of a nearby D⁺ center. The potential barrier ($W$) over which carriers must hop is the random variable in the problem; variations in $W$ arise from variations in the distance $R$ separating the two centers. The coulombic interaction between two neighbouring sites lowers the binding energy $W_M$, and the barrier height $W$ is then related to $R$ via the equation

$$W_M - W = \frac{4ne^2}{\pi \varepsilon \varepsilon_0 R}$$

(16)

Where $W_M$ is maximum barrier height, $n$ is the number of electrons involved in the hopping process, $n=1$ for single polaron hopping and $n=2$ for bipolaron hopping, $e$ is an electronic charge, $\varepsilon$ and $\varepsilon_0$ are the dielectric constants of material and free space, respectively.

The ac conductivity can be evaluated for this mechanism as

$$\sigma_{ac}(\omega) = \frac{n\pi^3}{24} N^2 \varepsilon \varepsilon_0 \omega R^6$$

(17)
Where N is the concentration of pair states and the hopping distance $R_\omega$ at a frequency $\omega$ is given by

$$R_\omega = \frac{ne^2}{\pi \varepsilon \varepsilon_0 [W_M - KT \ln(1/\omega \tau_0)]}$$  \hspace{1cm} (18)$$

The frequency exponent for this model can be evaluated as

$$s = 1 - \frac{6KT}{W_M - KT \ln(1/\omega \tau_0)}$$  \hspace{1cm} (19)$$

In this model the frequency exponent $s$ increases towards unity as $T$ tends to 0 K.

**5.3 Frequency dependence of ac conductivity of ZnO nanorods and nanotubes**

Figure 5.1 and 5.2 shows the frequency dependence of ac conductivity ($\sigma_{ac}$) of ZnO nanorods and nanotubes, respectively at different temperatures. It is clear from these figures that the ac conductivity increases with increasing frequency and temperature.

The frequency exponent $s$ is obtained by the fit of the experimental data using equation (3) and plotted as a function of temperature in figure 5.3 and 5.4. The exponent $s$ decreases smoothly with increasing temperature and is independent of frequency in the investigated frequency range. A similar behaviour of the ac conductivity with frequency ($\sigma_{ac} \propto \omega^s$) has also been observed in Zinc Oxide nanocrystals [11].
Fig. 5.1 Variation of $\sigma_{ac}$ with frequency at different temperatures

Fig. 5.2 Variation of $\sigma_{ac}$ with frequency at different temperatures
Fig. 5.3 Temperature dependence of the frequency exponent $s$ of ZnO nanorods

Fig. 5.4 Temperature dependence of the frequency exponent $s$ of ZnO nanotubes
Figure 5.3 and 5.4 shows that the frequency exponent $s$ decreases with increasing temperature. The frequency exponent $s$ decreases with increasing temperature in contrast with the QMT model, which predicts a temperature-independent $s$ of a value of 0.81[15]. Small-polaron QMT model [15] is also not a suitable mechanism for explaining the results of ZnO nanorods and nanotubes because it predicts an increase in $s$ with increase in temperature, in sharp contrast with the experimental observation shown in figure 5.3 and 5.4. Large-polaron QMT [18] model is also not applicable for the present system, since this model predicts that, $s$ exhibits a minimum at a certain temperature and subsequently increases in a fashion similar to small polaron QMT, which is not observed in figure 5.3 and 5.4. In the case of simple HOB model barrier heights is not dependent on the intersite separation, the value of frequency exponent, $s$, is predicted to be unity and this rules out the applicability of this model to the ZnO nanorods and nanotubes.

In CBH model [15], the value of $s$ decreases with increase of temperature. Hence, it is the most suitable mechanism for explaining the behaviour of investigated data of ZnO nanorods and nanotubes. This model fits to the experimental values of $s$ of ZnO nanorods and nanotubes as a function of temperature, made with use of equation (19) as shown in figure 5.3 and 5.4. The values of $W_M$ and $\tau_0$ of ZnO nanorods are obtained by the fitting procedure at the temperature region 303-463K is 0.92 eV and $7.65 \times 10^{-10}$ s$^{-1}$, respectively and the same at the region 463-543K is 0.45 eV and $1.83 \times 10^{-7}$ s$^{-1}$, respectively. The values of $W_M$ and $\tau_0$ of ZnO nanotubes obtained by fitting procedure at the temperature region 303-463K is 1.25eV and $2.16 \times 10^{-12}$ s$^{-1}$, respectively and the same at the region 463-543K is 0.76eV and $1.78 \times 10^{-9}$ s$^{-1}$, respectively. In the fitting procedure, a fixed frequency ($\omega=10^4$ s$^{-1}$) has been assumed. The value of $W_M$ is expected to be much
smaller for the case of single polaron CBH than for bipolaron CBH [20]. It is observed from figure 5.3 and 5.4 that the fit appears to be reasonable over a considerable temperature range. In the temperature region, 303-463K, the CBH mechanism involving bipolaron transport gives a satisfactory description of the experimental data. In ZnO nanorods and nanotubes, hopping of electrons/holes between positive and negative surface defect centers (e.g. V_o, V_zn) may constitute the bipolaron hopping mechanism. The best fitted values of W_M and τ_0 are used to calculate the density of pair states for bipolaron hopping and these values of both ZnO nanorods and tubes at different temperatures are shown in table 5.1 and 5.2.

The departure from the bipolaron hopping behaviour at higher temperatures can be explained well by the single polaron hopping (i.e., one electron hopping between D^o and D^+ and a hole between D^o and D^-). According to Shimakawa [14] at higher temperatures, D^o states are produced by the thermal excitation of D^+ and D^- states and the single polaron hopping becomes a dominant process. W_M for single polaron hopping is the maximum energy required to transfer an electron between D^o and the appropriate band, whether D^- and D^+. The experimental results are in good agreement with the theory hence the thermally activated single polaron hopping is the dominant conduction mechanism in ZnO nanorods and nanotubes at higher temperatures. As the temperature increases, the bipolaron hopping centers (D^+ and D^-) are converted into single polaron centers (D^o) and the density of bipolaron hopping centers decreases with increasing temperatures.
Table 5.1 Physical parameters obtained by fitting the experimental data to CBH model for ZnO nanorods (bipolaron hopping).

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>( R_\omega ) (( A^0 ))</th>
<th>( N ) (m(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>303K</td>
<td>12.332</td>
<td>8.59\times10^{25}</td>
</tr>
<tr>
<td>363K</td>
<td>12.751</td>
<td>7.65\times10^{25}</td>
</tr>
<tr>
<td>403K</td>
<td>12.840</td>
<td>7.11\times10^{25}</td>
</tr>
<tr>
<td>463K</td>
<td>12.999</td>
<td>6.99\times10^{25}</td>
</tr>
</tbody>
</table>

Table 5.2 Physical parameters obtained by fitting the experimental data to CBH model for ZnO nanotubes (bipolaron hopping).

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>( R_\omega ) (( A^0 ))</th>
<th>( N ) (m(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>303K</td>
<td>10.128</td>
<td>1.01\times10^{26}</td>
</tr>
<tr>
<td>363K</td>
<td>10.730</td>
<td>9.22 \times10^{25}</td>
</tr>
<tr>
<td>403K</td>
<td>11.366</td>
<td>8.37\times10^{25}</td>
</tr>
<tr>
<td>463K</td>
<td>11.659</td>
<td>8.02 \times10^{26}</td>
</tr>
</tbody>
</table>

5.4 Temperature dependence of ac conductivity of ZnO nanorods and nanotubes

The ac conductivity versus temperature of ZnO nanorods and nanotubes is shown in figure 5.5 and 5.6. By increasing the temperature, the ac conductivity shows strong temperature dependence and all curves converge at high temperature. This may be due to the thermally activated hopping of charge carriers between different localized states.
According to CBH model, the temperature dependence of $\sigma_{ac}$ is expressed in the power law form as

$$\sigma_{ac} \propto T^n$$  

(20)

where $n = (1 - s) \ln(1/\omega \tau_0)$ for the narrow band limit, which is effective above room temperature and $n \leq 2$ for the wide band limit [15]. It is clearly indicated in figure 5.5 and 5.6 that $n$ does not tend to have a constant value, but increases with increase in temperature and decreases with increase in frequency.

Fig. 5.5 Temperature dependence of ac conductivity in ZnO nanorods at various frequencies
The values of n calculated from the experimental data of nanorods and nanotubes at different frequencies and temperatures are shown in table 5.3 and 5.4. The experimental values of n obey the theoretical prediction as obtained in the narrow band limit. It can also be noted from figure 5.5 and 5.6 that the temperature dependence of ac conductivity exhibits different activation energies. The activation energy for low-temperature regime (303-463K) is $\Delta E_1$ and that for high-temperature regime (463-543K) is $\Delta E_2$, which are calculated from the least square fitting to the Arrhenius relation and listed in table 5.5 and 5.6 for ZnO nanorods and nanotubes, respectively.
The activation energy is found to increase with increasing temperature. $\Delta E_1$ arises due to correlated forward and backward hopping of charge carriers that occurs between the localized states. $\Delta E_2$ is the activation energy of carriers that hop across the gap into extended states due to thermal agitation. The observed behaviour of these activation
energies with frequency and temperature is consistent with bipolaron and single polaron hopping in CBH model.

Table 5.5 Activation energies of ZnO nanorods at various frequencies and temperatures

<table>
<thead>
<tr>
<th>Frequency</th>
<th>$\Delta E_1$ (eV)</th>
<th>$\Delta E_2$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 Hz</td>
<td>0.099</td>
<td>1.47</td>
</tr>
<tr>
<td>1 KHz</td>
<td>0.086</td>
<td>1.34</td>
</tr>
<tr>
<td>10 KHz</td>
<td>0.080</td>
<td>1.23</td>
</tr>
<tr>
<td>100 KHz</td>
<td>0.071</td>
<td>0.9</td>
</tr>
<tr>
<td>1 MHz</td>
<td>0.063</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Table 5.6 Activation energies of ZnO nanotubes at various frequencies and temperatures

<table>
<thead>
<tr>
<th>Frequency</th>
<th>$\Delta E_1$ (eV)</th>
<th>$\Delta E_2$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 Hz</td>
<td>0.27</td>
<td>1.71</td>
</tr>
<tr>
<td>1 KHz</td>
<td>0.23</td>
<td>1.57</td>
</tr>
<tr>
<td>10 KHz</td>
<td>0.19</td>
<td>1.44</td>
</tr>
<tr>
<td>100 KHz</td>
<td>0.15</td>
<td>1.29</td>
</tr>
<tr>
<td>1 MHz</td>
<td>0.10</td>
<td>0.92</td>
</tr>
</tbody>
</table>

Due to high surface to volume ratio of nanotubes, large numbers of surface defects are present in the ZnO nanotubes compared to that of nanorods. Hence, the ac conductivity of ZnO nanotubes is found to be little more compared to nanorods. The high
defect density and small hopping distance of ZnO nanotubes also give strong evidence of this enhanced ac conductivity.

5.5 dc Conductivity

The dc electric field conductivity values as a function of reciprocal temperature obtained in the present study are shown in figure 5.7.

![Arrhenius plot for the dc conductivity of ZnO nanorods and nanotubes](image)

**Fig. 5.7 Arrhenius plot for the dc conductivity of ZnO nanorods and nanotubes**

For ZnO nanorods and nanotubes, dc conductivity is found to increase with increasing temperature, which is attributed to the increased thermally activated drift mobility of the charge carriers in accordance with hopping conduction model. DC conductivity of the samples exhibits weak temperature dependence at low temperatures. The calculated activation energies of ZnO nanorods and nanotubes are shown in table 5.7 consistent with the hopping theory [21].
Table 5.7 Numerical values of $\sigma_{dc}$ and $E_a$ with different temperature

<table>
<thead>
<tr>
<th>ZnO</th>
<th>$\sigma_{dc}$ ((\Omega m))$^{-1}$</th>
<th>$E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>303 K</td>
<td>503 K</td>
</tr>
<tr>
<td>Nanorods</td>
<td>8.75 E-09</td>
<td>8.70 E-06</td>
</tr>
<tr>
<td>Nanotubes</td>
<td>1.46 E-08</td>
<td>1.27 E-05</td>
</tr>
</tbody>
</table>

The interwell hopping [22] (the hopping of charge carriers from ions located in one attractive defect potential well to an adjacent defect potential well) associated with zinc interstitials and oxygen vacancies may be the dominant conduction mechanism observed in ZnO nanostructures subjected to a dc electric field at high temperature, while intrawell [22] (the hopping of charge carriers between ions within an attractive defect potential well) hopping at low temperature. The numerical values of dc conductivity of ZnO nanotubes are slightly higher than the nanorods only at low temperatures that may be due to its high defect density. But coming to high temperature region, the dc conductivity of both nanorods and nanotubes are merging to one. The observed dc conductivity of the samples is less few orders in magnitude than their ac conductivity in the low temperature region. This is expected because dc conductivity is determined by the most different transition in complete percolation paths between the electrodes, while ac conductivity is determined by the easiest local movement of charges. The absolute value of these two ac and dc conductivity may not be closely related, it is evident that their temperature dependence is completely different.
5.6 Conclusions

Analysis of the ac data in the light of various theoretical models show that Correlated Barrier Hopping is the most appropriate model for explaining the ac conduction mechanism in both the ZnO nanorods and the nanotubes, in which the bipolaron transport dominates at lower temperatures and the single polaron transport dominates at higher temperatures. The experimental value of temperature exponent n is seen obeying the theoretical prediction as obtained in the narrow band limit. The calculated values of activation energies with frequency and temperature are consistent with the CBH model. The variation of dc electrical conductivity of ZnO nanorods and nanotubes with temperature are also studied. The calculated activation energy values were indicative of conduction predominantly due to hopping of charge carriers. The activation energies of the ZnO nanorods and nanotubes calculated from the Arrhenius plots are consistent with the hopping conduction mechanism. This chapter also concludes that ZnO nanotubes have higher ac and dc conductivity in comparison with ZnO nanorods due to its high surface defect density.

5.7 References


