Impedance Spectroscopy of Nano-Grain ZnO Thin Films

Sumati Pati
N. C. (Auto) college, Jajpur
Jajpur, India
E-mail: sumatipati.11@gmail.com

Abstract:- ZnO thin films of various thicknesses were prepared by metal organic chemical vapor deposition technique. The structural and micro structural characteristics of the grown films are studied using XRD and FESEM respectively. The film thickness is estimated from the cross sectional micrographs and is also verified using filmetrics studies. The electrical response of all the nano-grain ZnO thin films was studied using impedance spectroscopic technique. The circuit parameters were determined using an equivalent circuit model presuming both the grain and grain boundary contributions to the conductivity. The variation in conductivity of thin films with their thicknesses was attributed to the microstructure of the thin films and traping of oxygen vacancies on the surface of the film.

Key words*: Thin film; MOCVD; Film thickness; Impedance spectroscopy.*

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1. Introduction

Semiconducting metal oxides such as ZnO in thin film form are of great technological interests for applications in various sectors which includes semiconductor devices [1-2], transparent conductors [3], solar cell [4], varistors [5], liquid-crystal displays [6], spintronic applications [7], gas sensors [8], etc. Zinc oxide is an n-type semiconductor and is an important material due its wide range of applications as cited above. Zinc oxide in the nanocrystalline form is of more interest owing to its peculiar properties compared to its bulk counterpart [9-11]. In the nano-grain ZnO the grain boundaries play an important role in their electrical conduction. Impedance spectroscopy is a useful technique to study these electrical properties of the materials [11-15]. The origin of resistance or capacitance, and the role of defects such as oxygen vacancies within the material can be efficiently interpreted using this impedance spectroscopy [11]. The electrical properties and various application of zinc oxide are investigated by several authors [16, 14]. Dachum Zhao et al. [16] reported conductivity and activation energy for conduction in ZnO thin film deposited by DC gas discharge activated reactive deposition. Lee et al. [14] reported the impedance spectroscopy of ZnO having a grain size of 60 nm produced by gas condensation method. In the present work the impedance spectroscopy of nano-grain ZnO thin films grown by MOCVD growth technique is studied. The measurements are carried out for all the grown thin films of various thicknesses at different temperatures ranging from room temperature up to 200^{o}C. The effects of film thickness and temperature on the impedance behavior are analyzed and a possible model is proposed.

2. Experimental procedure

In the present study the ZnO thin films were grown on the fused quartz substrates using the MOCVD growth technique. Diethyl-zinc and tert butanol were used as the zinc and oxygen precursors respectively. N_2 gas was used as carrier gas. The required amount of precursor materials was maintained by controlling their flow rates using mass flow controllers (MFCs). The flow rates of the Diethyl-zinc and tert-butanol were maintained at 20 and 60 sccm, respectively. The chamber was kept at atmospheric pressure and the growth temperature was maintained at 450 ^{o}C. The details of the MOCVD growth procedure was illustrated elsewhere [8]. The complex impedance measurement of all the grown thin films was carried out using an impedance analyzer in the frequency range of 100 Hz–1 MHz by varying the temperature from RT to 200 ^{o}C. The analyzer

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was connected to a PC through a GPIB interface, and for data acquisition Lab View v8.5 software was used. The details of this measurement procedure can be found elsewhere [17]. The Nyquist plots of these films were also analyzed from these data.

3. Results and Discussion

Impedance spectroscopy is a useful technique to identify the contribution of grain, grain boundary, and electrode to the overall dielectric characteristics of the material. Nyquist diagram or Cole-Cole plot is a convenient tool to determine the resistance of the material. In this work, we have measured the complex impedance spectra of all the grown ZnO thin films of various thicknesses at different temperatures.

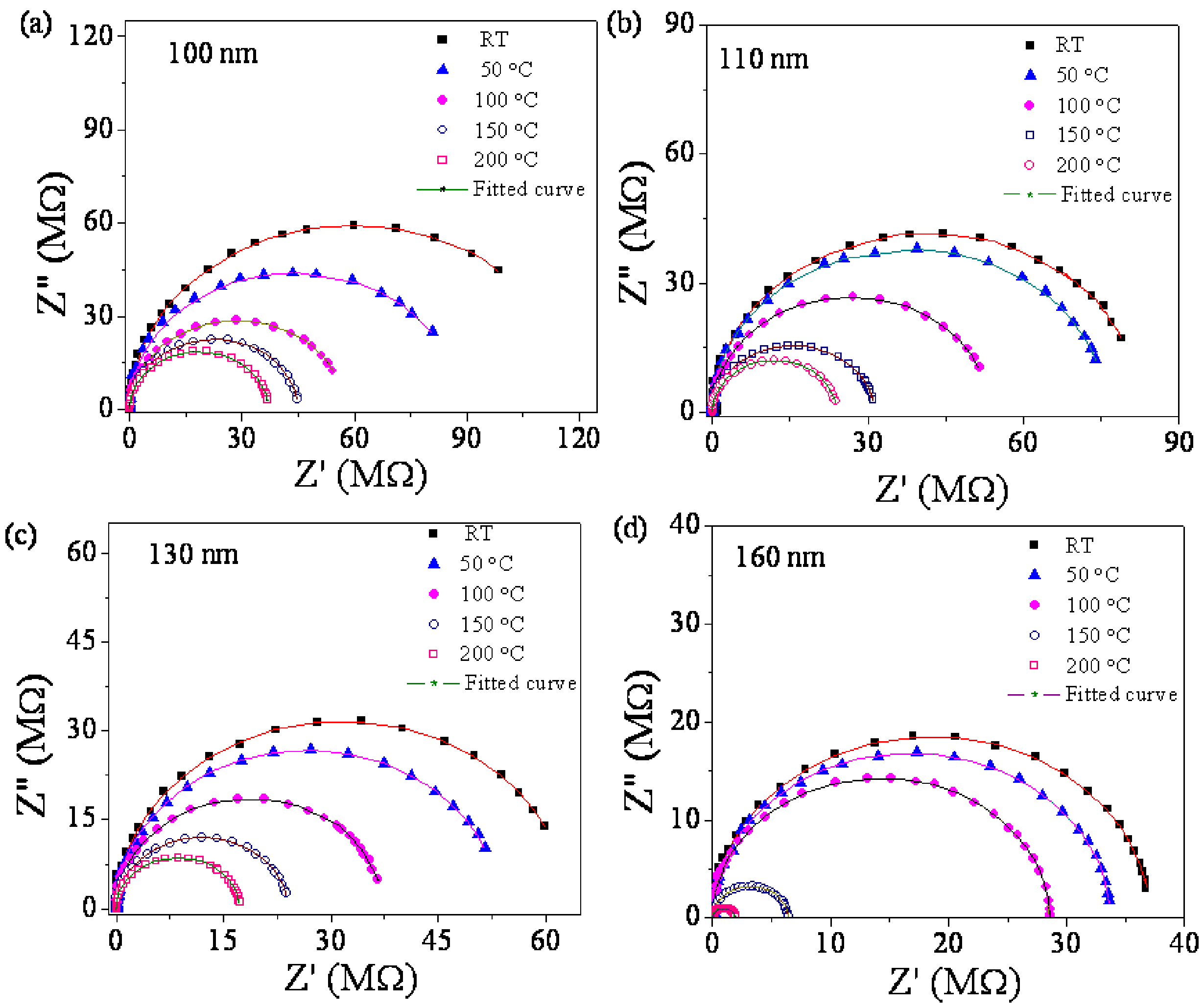

Fig. 1: The Cole-Cole plots (in log-log scale) of complex impedance spectra of ZnO thin films of (a) 100 nm, (b) 110 nm, (c) 130 nm, and (d) 160 nm thickness at various temperatures in the range RT to 200 °C

The measured complex impedance (Z*) of the sample can be expressed as [12]:

$$Z^* (\omega) = Z' (\omega) - Z'' (\omega) \quad (1)$$

Where Z' (ω) and Z'' (ω) are the real and imaginary impedance components as a function of frequency.

Fig. 1 shows the plot of the imaginary (Z″(ω)) versus real (Z′(ω)) part of the complex impedance (Cole-Cole plot) of ZnO thin films of various thicknesses (a) 100 nm, (b) 110 nm, (c)130 nm, and (d) 160 nm, measured at different temperatures ranging from RT to 200 °C.

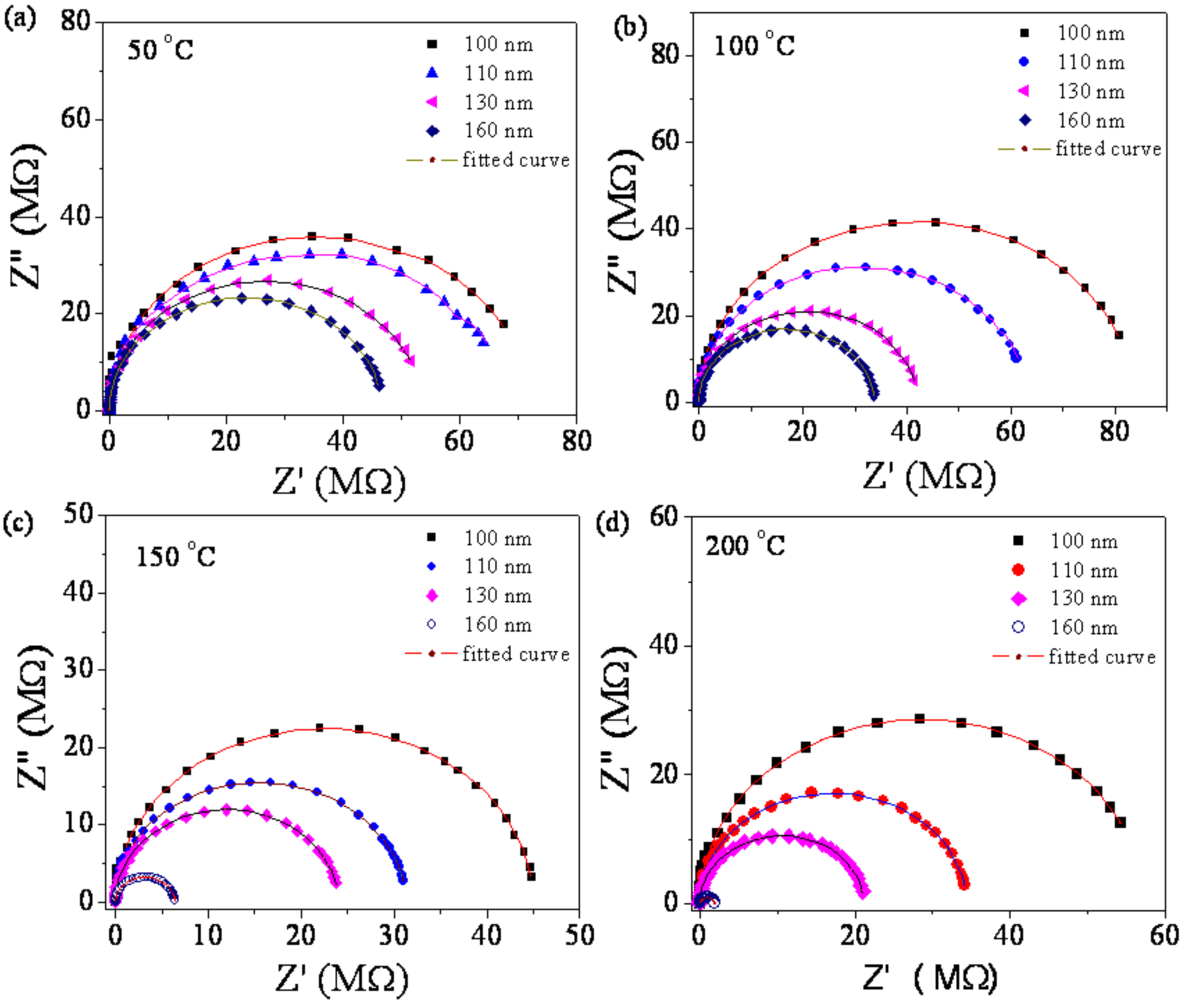

Fig. 2: The Cole-Cole plots (in log-log scale) of complex impedance spectra of ZnO thin films of various thicknesses as function of temperature (a) 50 °C, (b) 100 °C, (c) 150 °C, and (d) 200 °C

As envisaged from the figure, the impedance spectra of all these films are characterized by single semicircular arcs and the diameter of the imaginary circles (the intersection of this Cole-Cole plot on the real axis) are systematically reduced with the increase in temperature. As the intersection of this Cole-Cole plot on the real axis represents the conductivity of the sample [11], it indicates the increase in conductivity with temperature irrespective of the film thickness. This feature indicates the systematic enhancement of the dc conductivities of each film with the increase in temperature.

To further clarify this feature, the data measured for various thin films is plotted for individual temperatures as shown in Fig. 2 (a-d). From the figure single semicircles of reducing diameter are observed with the increasing film thickness. This indicates the systematic improvement of conductivities with increasing film thickness at each measured temperatures. This increase in conductivity with film thickness was also confirmed from the micro structural studies of the thin films reported in our previous work [8].

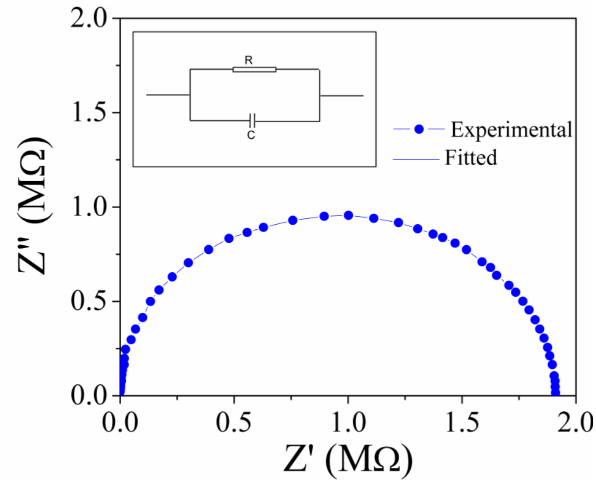

Fig. 3: A typical impedance spectrum of ZnO thin film with fitted curve showing its semicircular (depressed) nature. Inset shows the proposed equivalent circuit for the experimental data

Fig. 3 shows one typical impedance spectrum. Presence of only one semicircle in the Cole-Cole plot in each film at all temperatures represents the Debye type of relaxation [12]. For this type of response each component of the material (grain, grain boundary, and electrode) has some contribution to the semicircle with different mean relaxation time (τ = RC, where R is the resistance and C is the capacitance). The grains contribute at high frequencies, the grain boundaries at intermediate frequencies and electrodes at low frequencies [17]. However, presence of a single semicircle indicates that the relaxation time associated with each component is identical [12], that is

$$\tau = R_g\, C_g = R_{gb}\, C_{gb} = R_c\, C_c \qquad (2)$$

To identify the contributions to the impedance spectra the impedance curves are fitted by an equivalent circuit composed of a resistance and a capacitance in parallel as sketched in the inset of Fig. 3.

The grain resistances R at each temperature for all the films are estimated from the intersection of the semicircular arc with the real axis (diameter of the arc, R = 2Z') [12]. The relaxation frequency ω_{max} (the frequency at the top of the semicircle), is noted from the figure. Subsequently, the value of C is estimated using the relation $\omega_{max}RC = 1$. These values are tabulated as in Table 1.

As indicated in the table the value of resistance reduces systematically with increase in temperature for all films and with the increase in thickness of the film at each temperature.

Table 1- The fitting values of the impedance spectra of ZnO thin films of various thicknesses at different temperatures

	100 nm		110 nm		130 nm		160 nm	
T (^{o}C)	R (MΩ)	C (pF)	R (MΩ)	C (pF)	R (MΩ)	C (pF)	R (MΩ)	C (pF)
RT	197.06	80.55	157.6	153.07	109.98	286.42	73.44	733.01
50 ^{o}C	161.12	141.00	148.18	177.38	103.00	361.31	67.02	883.83
100 ^{o}C	108.88	321.12	102.72	363.87	73.12	736.27	57.20	1220.35
150 ^{o}C	89.68	496.22	62.30	1030.21	47.44	1760.09	12.68	24800.00
200 ^{o}C	73.92	729.13	47.46	1760.85	34.42	3300.00	3.60	283000.31

The temperature dependence of the resistance (as estimated from Fig. 1) can be described by the following equation [17]:

$$\sigma = \sigma_o \exp(-E_a/k_B T) \quad (3)$$

Where σ_0 is the pre-exponential factor, E_a is the activation energy of dc charge carriers, and k_B is the Boltzmann constant.

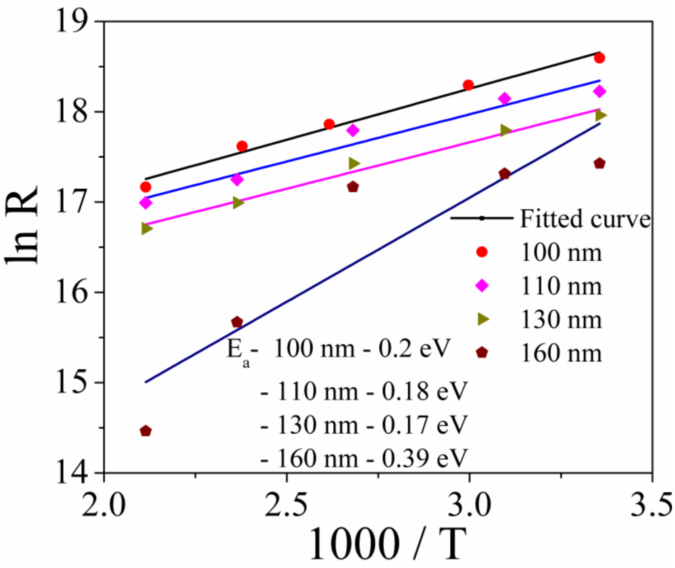

Fig. 4: Arrhenius plots (ln (R) *vs* 1000/T) for the ZnO thin films of various thicknesses

From the linear best fit of the plot between ln (R) vs 1000/T the activation energy (slope) is estimated according to Eqn. 3. Fig. 4 show the ln (R) vs 1000/T variation and their linear best fit for all the thin films. The estimated activation energies are noted in the inset of the figure. As shown in Fig.4, the activation energies for dc conduction decreases up to 130 nm film thickness and with further increase of thickness the activation energy is increased. The decrease in the activation energy with film thickness is expected owing to the higher conductivity of thicker films. However, the increase in the activation energy (for 160 nm, thickest film) is probably due to the trapping of mobile charge carriers (electrons).

4. Conclusions

Nano-grain ZnO thin films of various thicknesses were grown using MOCVD growth technique. The dielectric characteristics of the grown films were studied using complex impedance spectroscopy measurement. The resistance of the material was estimated from the Nyquist diagram, or Cole-Cole plot. The contribution of grain, grain boundary, and electrode to the overall dielectric characteristics of the material is identified and an equivalent circuit model is proposed. The variation in conductivity of the grown thin films with thickness is attributed to the microstructure of the thin films and traping of oxygen vacancies on the surface of the film.

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