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Meyer-Neldel Rule in Ac Conductivity of Cu Doped ZnO Thin Films

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ABSTRACT

Ac charge transport mechanisms have been comparatively investigated in ZnO thin films having different Cu dopant. A comparative study of the applicability of quantum mechanical tunelling and correlated barrier hopping model to obtained ac electrical conductivity results has been performed. Comparing the temperature dependence of the frequency exponent shows that the correlated barrier hopping model best describes the experimental data on the ac conductivity in ZnO:Cu thin films. In order to gain an understanding of the applicability of Meyer-Neldel rule, the dependence of the thermal activation energy on Cu doping concentration in these films has also been studied. The obtained experimental results indicated that Meyer-Neldel rule can be succesfully applied ac conductivity data for highly Cu doped films but not others which has been explained on the basis of distribution variations in density of states.

Keywords: Meyer-Neldel rule, ac charge transport mechanism, ZnO, thin film

1. INTRODUCTION

As an alternative to widely used indium tin oxide (ITO) film, zinc oxide (ZnO) films have attracted considerable interest as a transparent conducting electrode [1]. Because of its direct band gap of 3.37 eV [2] and large exciton binding energy of 6 meV [3], ZnO thin film has a great potential in various area including gas sensor [4], light emitting diodes and UV lasers [5] and surface acoustic wave devices [6]. Many recent investigations have indicated that the electrical properties of the ZnO films may be modified by doping with Al, In and Ga [7-10]. In spite of a large amount of work having been done on the effect of various impurities on the structural and morphological properties of ZnO films [11, 12], the spread of activation energy in metal-oxide semiconductor is not fully understood. In general, the observed low temperature behaviour of the conductivity is attributed to the hopping of charge carrier over the barrier. However, no previous work has been performed on the applicability of Meyer-Neldel (MN) rule to the temperature dependence of ac conduction in ZnO thin film. It is well known that Cu doping leads to creation of donor states below the conduction band and the electrical behaviour of ZnO films dominated by the Cu doped dopant concentration. Hence, a study of ac conductivity and the applicability of MN rule in Cu doped ZnO thin film would be interesting. In the present work, the ac conduction properties of spray pyrolysed ZnO film with different Cu dopant concentration has been investigated in the frequency range 100 – 13×10^6 Hz. The obtained

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conductivity data has been analyzed in the light of MN rule.

2. EXPERIMENTAL

Indium tin oxide (ITO) coated glasses were used as substrates to deposit Cu doped and pure zinc oxide films. Film deposition were carried out by spray pyrolysis technique from zinc acetate precursor. For the deposition of ZnO films, 0.5 g zinc acetate dihydrate was dissolved in appropriate amount of isopropyl alcohol containing monoethanolamine under stirring for 2 h at 60 ºC. Copper chloride ($CuCl_2$) was used as dopant source. The concentration of the dopand was varied systematically between 0% and 6%. The resulting solution was sprayed onto the pre-heated ITO coated glass substrates at a constant temperature of 460 °C. A K type thermocouple was used to monitor the temperature of the substrate. Compressed nitrogen was used as the carrier gas. The structure of the ZnO:Cu films was investigated by X-ray diffraction (XRD) pattern. The XRD analysis was performed on a Rigaku XRD diffractometer using CuKα radiation (1.54059Å) as X-ray source. Impedance spectra of the samples were measured as function of temperature between 300 and 450 K and in the frequency range of 100 – 13×10^6 Hz by using a HP 4192 A impedance analyser. In order to avoid from ambient effect, impedance measurements were performed under 10^{-3} mbar. A schematic represantation of the impedance measurement system is shown in Figure 1.

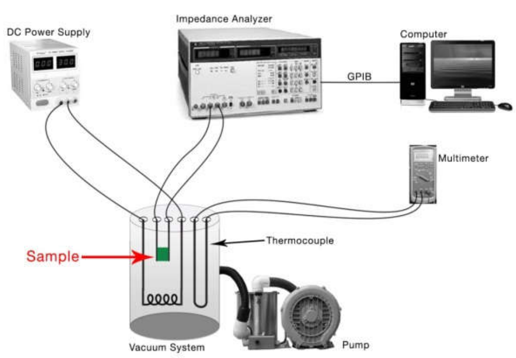

Figure 1. Schematic represantation of the experimental set-up

3. RESULTS AND DISCUSSION

3.1. Structural analysis

In order to investigate the crystal structure and the phase composition the XRD pattern of ZnO and ZnO:Cu samples was recorded by using CuKα radiation as X-ray source. The recorded XRD patterns of pure zinc oxide and doped films with different copper concentrations is presented in Figure 2. The obtained XRD spectrum indicated the formation of hexagonal structure of ZnO. XRD analysis also showed that the (002) preferential orientation of all films is along crystal plane. The other peaks observed at 31.76º, 36.16º, 47.55º, and 56.61º are associated with (100), (101), (110), and (102) planes.

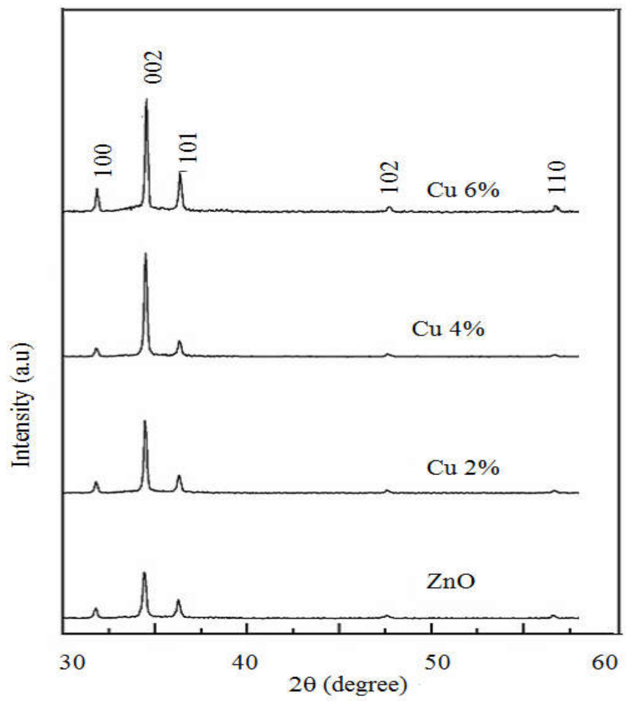

Figure 2. XRD patterns of spray pyrolysis deposited ZnO and Cu doped ZnO thin films

3.2. Ac conductivity studies

Figure 3 shows the room temperature ac conductivity variations with frequency for undoped and Cu doped ZnO films. Figure 3 shows that the room temperature conductivity of the ZnO films increase with the increase in Cu dopant concentration. The increase in conductivity with Cu dopant concentration can be attributed to the increase in carrier concentration in the doped ZnO films. A strong frequency dependence for all films investigated is clear. A rewiev of the present literature suggests that for a large variety of materials, the expression for the ac conductivity can be written as

$$\sigma_{ac} = A\omega^{m} \quad (1)$$

where A is a constant, ω is the angular frequency of applied signals, m is an exponent. Although there is no unique interpretation for the observed frequency dependence of conductivity, it is known that this type of behaviour is characteristic of many metal-oxide semiconductors and molecular materials [13-16]. Quantum mechanical tunnelling (QMT) and correlated barrier hopping (CBH) models are widely used for evaluating the frequency dependence of the conductivity. In QMT model, a charge carrier motion between localized states near the Fermi level is assumed. According to the QMT model, the frequency dependence of the conductivity should obey Eq. (2).

$$\sigma_{ac}(\omega) = \frac{\pi}{3} q^2 kT (N_F)^2 \beta^{-5} \omega \left(\ln\left(\frac{\nu_0}{\omega}\right)\right)^4 \quad (2)$$

where q is the electronic charge, ω is the angular frequency, N_F is the density of localized states at Fermi level, β is the inverse localization length of wave function and ν_0 is the characteristic phonon frequency. According to QMT model the exponent m should be temperature independent with a constant value around 0.8.

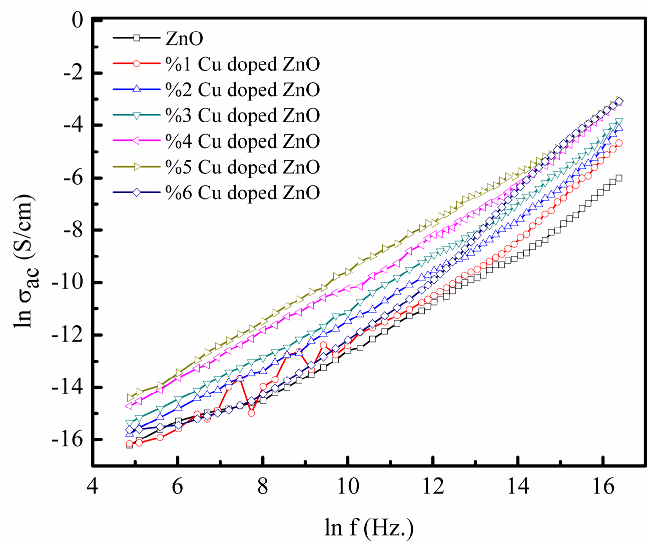

Figure 3. Variation of the conductivity with frequency for pure and Cu doped ZnO films

On the other hand, CBH model assumes that the charge transport take places via polaron hopping process over the potential barrier separating hoping centers. In CBH model, the frequency dependent is given by,

$$\sigma_{ac}(\omega) = \frac{\pi^2 N^2 \varepsilon}{24} \left(\frac{8q^2}{\varepsilon E_o}\right)^6 \frac{\omega^m}{\tau_0^\beta} \quad (3)$$

where E_0 is the optical band gap and ε is the dielectric constant of the material. CBH model predicts a temperature dependent exponent m which is given by,

$$m = 1 - \frac{6kT}{E_0 + kT\ln(\omega\tau_0)} \quad (4)$$

In order to decide which mechanism is more appropriate for the observed frequency dependency, the values of the exponent m were derived from the slope of the curves showed in Figure 3. The variation of the m with temperature for all films investigated is depicted in Figure 4. As can be seen from the Figure 4, the exponent m decreases with increasing temperature. In the light of this finding it can be concluded that the QMT model is not appropriate to model ac conduction in pure and Cu doped ZnO films. The decreasing trend in exponent with increase in temperature confirms that ac conductivity in investigated films obeys the CBH model.

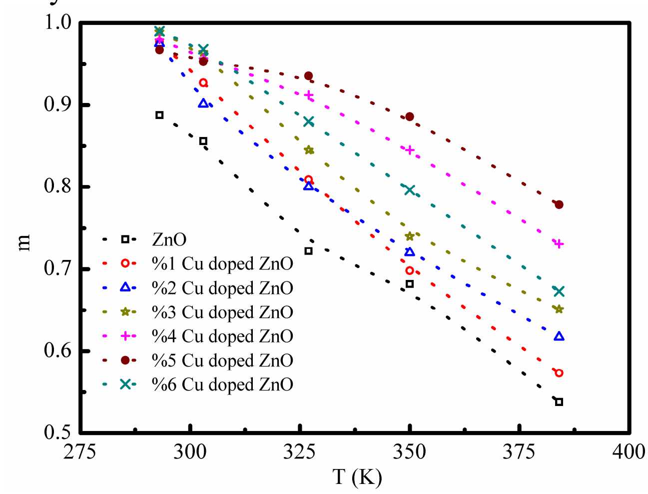

Figure 4. Temperature dependence of the exponent m for all films

3.3. Meyer-Neldel rule

In thermally activated processes, the dependence of electrical conductivity, σ(T), on the temperature is given by

$$\sigma(T) = \sigma_0 \exp\left(-\frac{E_A}{kT}\right) \quad (5)$$

where σ_0 is pre-exponential factor, E_A is the thermal activation energy. In 1937, Meyer and Neldel [17] have discovered that thermal activation energy varies and it can be correlated to pre-exponential factor σ_0 as,

$$\sigma_0 = \sigma_{00} \exp\left(\frac{E_A}{kT_{MN}}\right) \quad (6)$$

where σ_{00} is a constant and T_{MN} is the characteristic Meyer-Neldel temperature. This type of relation has been observed in many thermally activated processes [18, 19] and known as Meyer-Neldel relation. A combination of Eq. (5) and (6) gives,

$$\sigma(T) = \sigma_{00} \exp\left(\frac{E_A}{kT_{MN}}\right)\exp\left(-\frac{E_A}{kT}\right) \qquad (7)$$

The applicability of the Meyer-Neldel rule to the measured ac conductivity data were checked by extracting the thermal activation energy. For this purpose, ac conductivity variations at various fixed frequencies were plotted in the Arrhenius form. As a represantative result, the Arrhenius plots for the 4% Cu doped ZnO film at indicated fixed frequencies is presented in Figure 5. The variation of the ac conductivity with inverse temperature reveals that the charge transport occurs through an activated process which has single activation energy in the operating temperature range. The obtained results suggests that Eq.(5) can be used to represent the temperature dependence of the ac conductivity for samples investigated.

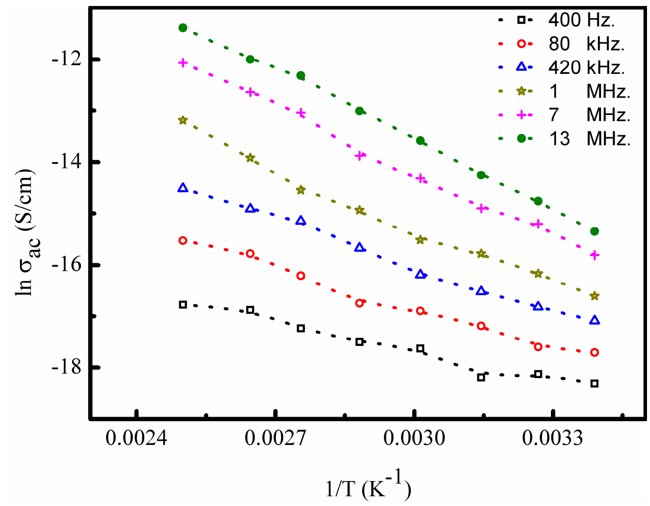

Figure 5. The temperature dependences of the measured ac conductivity at various frequencies for 4% Cu doped ZnO thin film

With the aid of Eq. (5), the value of the activation energy and pre-exponential factor derived from the slope and intercept of the ln σ_{ac} *vs* 1/T graphs. The variation of derived values of pre-exponential factor with thermal activation energy of the conductivity is shown in Figure 6. The linear relationship between the pre-exponential factor and ac thermal activation energy for the samples of 4%, 5% and 6% Cu doped ZnO films is clear. Deviation from linearity for other films is also clear.

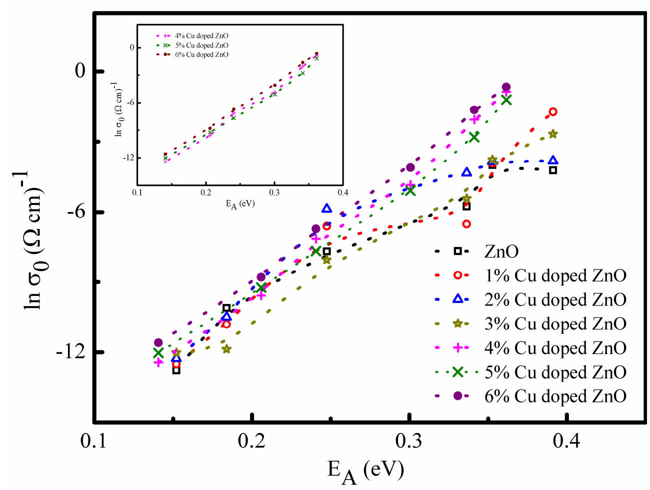

Figure 6. Variation of the pre-exponential factor with activation energy

A detailed literature survey indicates that various models have been investigated to explain Meyer-Neldel rule. A model which is developed by Fang [20], describes that the annealing time parameter obeys the Meyer-Neldel rule. Recently, Koga and Sestak [21] have discussed that a change of activation energy is thus compensated by the same change the logarithm of the pre-exponential factor due to the kinetic compensation effect. According to Roberts [22] and Cohen et al.[23] the origin of Meyer-Neldel rule in polycrystalline or amorphous semiconductors is due to long-range electrostatic random potential or exponential tailing of the majority band states. Another model which is proposed by Kemeny and Rosenberg [24] assumes that electrons and polarons tunnel through interatomic barriers from activation energy states. It should be mentioned here that the major drawback of the above mentioned models is that these models could not provide a universal explanation of MNR in any materials. These literature survey show definitely that a single general MNR equation for all material systems are not applicable to explain the observed MNR.

It can be concluded that the ac charge transport in ZnO films take place through thermally excited electrons. The applicability of MNR to the experimental ac conductivity data for highly Cu doped samples can be atrributed to the exponential energy distribution of traps. The presence of any defects such as O vacancies and native defects with exponential energy distribution, which acts as trap centers for the charge carriers, may be responsible for the observed behaviour of ac conductivity in highly doped samples. It is also well known that, the distribution of the density of states may not be symmetrical with respect to the center of the band because of tailing of localized states at the band edges and the presence of defect states in the gap. Therefore, the main contribution to the experimentally obtained pre-exponential factor comes from the shift of Fermi level and temperature dependent shift of conduction and valance band edges [25]. When the Fermi level lies in conduction band tail or close to the minimum of density of states, a linear variation of pre-exponential factor with activation energy can be observed. On the other hand, if the Fermi level approaches the boundaries and the density of states spectrum is flat near the edge the linear relation between the pre-exponential factor and the thermal activation energy diminishes [26]. According to Kikuchi [27] another reason for the deviation from linearity in ln σ_0 vs. E_A plots is the reduction in the minimum of density of state. In heavily doped samples, potential barrier formation does not occours because of the large number of defect states. In this case, the Fermi level lies in the gap where the density of states does not vary much and charge transport is governed by the band tail transport. In weakly doped films, low values of free electron concentrations is expected. Because of low value of doping concentration an improvement in film microstructure is also expected which leads to delocalization of the tail states causing the Fermi level shift towards the band edge. Lower density of available free carriers and low value of defect density may cause a large increase in dangling bond density. In this case, the Fermi level lies in the plateau region of the density of states and this cause the observed deviation from linearity in ln σ_0 vs. E_A plots.

4. CONCLUSION

The ac conduction mechanism Cu doped ZnO thin films were studied in a temperature range of 300 and 450 K and in the frequency range of 100 – 13×10^6 Hz. The measured ac conductivity data were discussed in terms of quantum mechanical tunelling and correlated barrier hoping models. Analysis of the temperature dependence of the frequency exponent showed that, the ac conductivity data in pure and Cu doped ZnO films agrees fairly well with the predictions of the correlated barrier hopping model. A linear relation between the pre-exponential factor and thermally activation energy reveals that the Meyer-Neldel rule can be applied to highly Cu doped ZnO.

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