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Electrical measurements of dielectric properties of molybdenum-doped zinc oxide thin films

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ABSTRACT

Effects of molybdenum element content on electrical conductivity of ZnO sprayed thin films were investigated using the impedance spectroscopy method in the frequency ranging from 5 Hz to 13 MHz for temperature lying in 300–475 °C domain. It is observed that AC conductivity is a power law. The values of dielectric constants ε_1 and ε_2 were found to decrease with frequency and increase with temperature. The activation energy determined from the plot of both DC conductivity and the hopping frequency with 1000/*T* shows that the hopping conduction is the dominant mechanism. Also, experimental data of DC conductivity were analyzed using the small polaron hopping model. The impedance analysis of undoped ZnO and Mo-doped ZnO (1% and 2%) shows only one semicircle implying the response originated from a single capacitive element corresponding to the bulk grains. However, the same analysis for ZnO:Mo (3%) shows two semicircles which proves the existence of grain boundaries. Finally, analyses of polaron hopping mechanism and Urbach tailing allow some explanations of these transport phenomena. This study shows an effective variation of electrical measurements of Mo-doped ZnO films in terms of temperature leading to possible use of such films as gas sensors.

1. Introduction

Recently, there has been a considerable interest in the investigations of metallic oxide thin films. This is due to the fact that the deposited oxides have a wide variety of applications. In fact, zinc oxide belonging to this family is a wide band gap which can be applied in several devices [1]. It is a promising candidate for many applications such as solar cells, gas sensors, acoustic devices and electrode cells [2–5].

To improve the optical as well as the electrical properties of ZnO thin films, various elements such as Al, Co, Mn, and Ni have been tested [6–8] as doping agents. Moreover, AC conductivity and dielectric properties provide a fundamental method to understand the nature of conduction and defect centers which are presented in crystalline and non-crystalline thin films [9–11]. In this context, electrical conductivity of M-doped ZnO (M=Y, Fe, Mn etc.) was widely studied [12–14].

The main feature of the electrical conductivity in the transition metal-doped ZnO can occur by a hopping mechanism [15–17]. Thus, polaron hopping theory was originally used to explain electrical transport in semiconductors where the conduction can take place by transfer of electrons between localized states [18]. Indeed, doping creates distortion in the crystal lattice of the pure zinc oxide which is related to the urbach energy [19]. Around these defects, the charge carriers are localized on some sites creating a small polaron [20–22]. As it is reported in the literature, the presence of more than one valance states on transition metal ions suggests that electrical conduction is attributed to a hopping mechanism of electrons from low valence state to high valance one [23–25].

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In the present work, which is an additional physical investigation to both structural and optical ones of Mo doped ZnO sprayed thin films [19], frequency and temperature dependences of the electrical and dielectric properties have been conducted by investigation of the complex impedance spectroscopy with their real and imaginary parts. These results have been discussed in terms of doping level and Urbach tailing, which may explain the observed temperature dependence.

2. Experiment

2.1. ZnO thin films preparation

Zinc oxides thin films have been prepared on glass substrates by spray pyrolysis of Zinc acetate dihydrate ($Zn(CH_3COOH)_2 \cdot 2H_2O$) and ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$) which was used as a source of molybdenum with a Mo-to-zinc molar ratios (Mo/Zn) was 0–3% according to the protocol summarized previously [19].

2.2. Experimental set up

In order to perform a detailed experimental study of the electrical conductivity of ZnO and Mo-doped ZnO films in the frequency range (5 Hz–13 MHz) at various temperatures 300–475 °C, we used the impedance meter (Hewlett-Packard 4192 analyzer) to measure the real and imaginary components of impedance parameters (Z' and Z''). The configuration for electrical measurements is performed using two electrodes as described by Ouni et al. [26]. This electrical measurement was carried out using two electrodes painted on the two extremities of the sample using silver paste. The AC conductivity was calculated from the following equation: $\sigma_{AC}=L/Z'A$, where L is the distance between electrodes and A is the cross-sectional area. The thickness of films is in 0.6–0.7 μm domain. Finally, the DC conductivity was obtained by extrapolation at zero frequency from AC measurements.

3. Impedance analysis

3.1. Complex impedances analysis

Complex impedances spectrum of polycrystalline films can be interpreted using the equivalent circuit model that provides a representation of the electrical properties of the frequency regions. Therefore, each region is represented by a semicircle [27]. In addition, depressed arc is typical for a dipolar system involving multirelaxation processes [28–30].

Fig. 1 shows the complex impedance spectra (Z'' vs Z') obtained by plotting the imaginary part with corresponding real part for ZnO and Mo-doped ZnO (1–3%) at different temperatures. The analysis data show only one semi-circle for all samples except for ZnO:Mo 3% sample

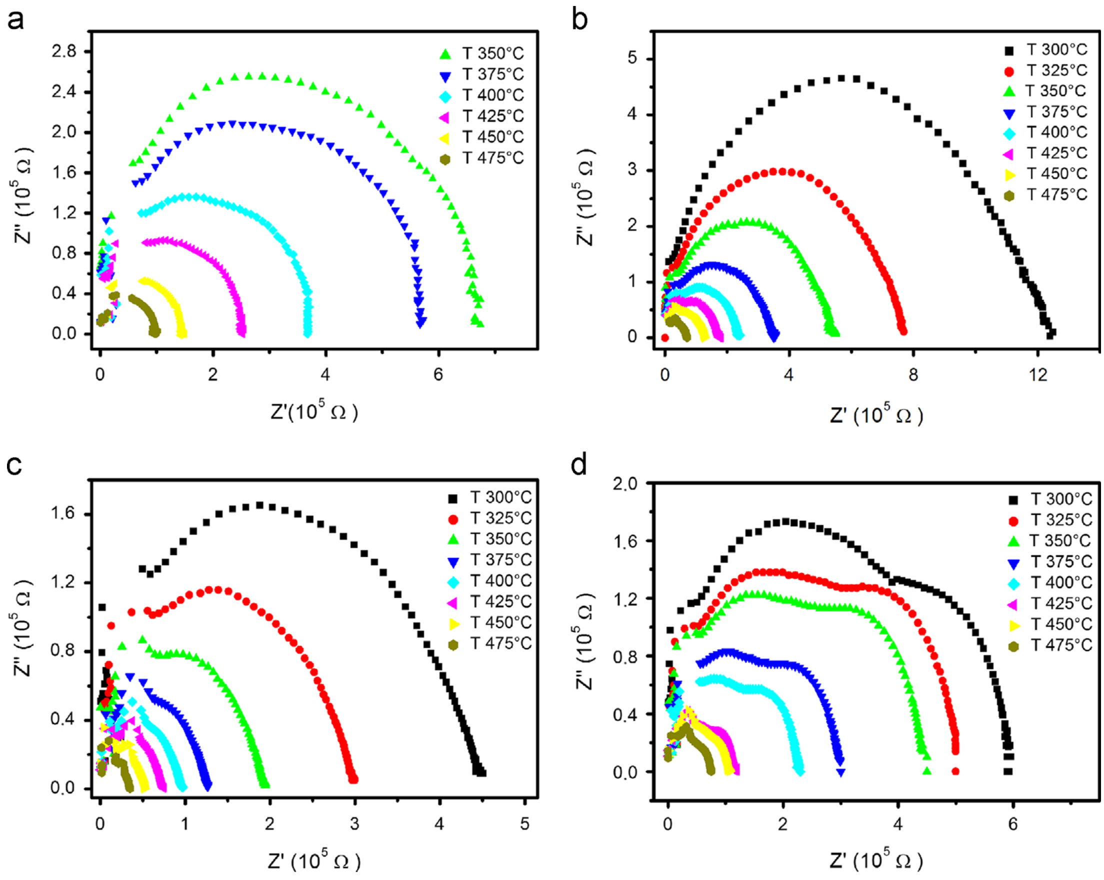

Fig. 1. Complex impedance plots (Z'' vs Z') at different temperatures for (a) ZnO, (b) ZnO:Mo 1%, (c) ZnO:Mo 2% and (d) ZnO:Mo 3%.