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Electrical Properties of Mechanically Activated Zinc Oxide

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Abstract:

Microstructural properties of a commercial zinc oxide powder were modified by mechanical activation in a high-energy vibro-mill. The obtained powders were dry pressed and sintered at 1100°C for 2 h. The electrical properties of grain boundaries of obtained ZnO ceramics were studied using an ac impedance analyzer. For that purpose, the ac electrical response was measured in the temperature range from 23 to 240°C in order to determine the resistance and capacitance of grain boundaries. The activation energies of conduction were obtained using an Arrhenius equation. Donor densities were calculated from Mott-Schottky measurements. The influence of microstructure, types and concentrations of defects on electrical properties was discussed.

Keywords: *Zinc oxide, Ceramics, Mechanical activation, Electrical properties.*

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1. Introduction

Zinc oxide is an important wide-band gap semiconductor (E_g = 3.36 eV at room temperature and 3.437 eV at 2 K) with exceptional physical, chemical and mechanical characteristics. Due to its specific properties it can be used for different applications in optoelectronics, field emission display, photovoltaic solar cells, gas sensors, varistors or ultrasonic transducers [1-6]. It belongs to materials with a highly marked tendency to a non-stoichiometric composition, type $M_{1+x}O$, due to the existence of various native defects. Besides, the effects of dopants are very important. Zinc oxide exhibits strong n-type conductivity with the electrons moving in the conduction band as charge carriers. In spite of extensive investigations, the source of such conductivity is still in debate. For many years n-type conductivity has traditionally been attributed to native defects [7]. There are several types of defects in zinc oxide, but two species of intrinsic donorlike defects: zinc interstitials Zn_i, and oxygen vacancies V_O are of special interest. Intrinsic defects in zinc oxide acting as electron acceptors are zinc vacancies V_{Zn}, interstitial oxygen O_i, and antisite oxygen O_{Zn}. Great fluctuation of zinc oxide resistivity, in the range of $10\text{-}10^{10}$ Ωm [8], first of all is the consequence of the types and number of intrinsic and eventually extrinsic defects depending on ZnO forms and preparation condition. Thus, it is very important to understand the electrical activities of relevant impurities and defects.

The grain boundaries of polycrystalline materials play a significant role in their electrical properties [9, 10]. A double Schottky barrier could be formed at the grain

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[*)] Corresponding author: katarina@ibiss.bg.ac.yu boundaries. Fig. 1. shows the energy band diagram of a double Schottky barrier, where E_V is the valence band, E_C is the conduction band, E_F is the Fermi level and Φ_B is the barrier height. The ionized shallow donor (density N_0, energy $E_0(x)$) provides the presence of free electrons. The interface density of states is $N_S(E)$ and the neutral states are represented by open circles. The height and width of the Schottky barrier depends on the concentration of interface states and donor states. On the other hand material resistivity depends on the height and width of the potential barrier, concentration of donor states as well as on grain size.

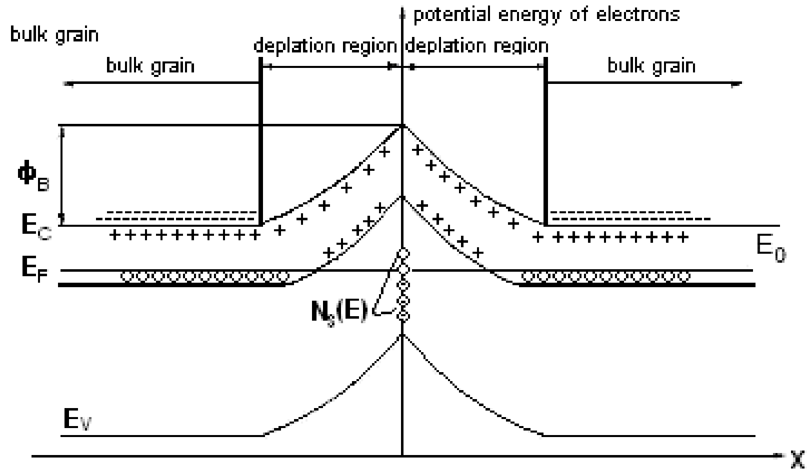


Fig. 1. Schematic energy band diagram of a double Schottky barrier.

The electrical properties of grains and grains boundaries can be characterized separately by impedance spectroscopy measurements [11-13]. In general, the results of these measurements can be presented by several semicircles in the Z' - Z'' plane. Each semicircle represents the contribution of a particular process (electrodes and contact, grain boundaries, grain interior) to the total impedance of the sample.

Mott-Schottky measurements are the common method for studying the capacitive behavior of a double Schottky barrier. Using these results it is possible to obtain information about average donor density, based on the following equation:

$$\left(\frac{1}{C}-\frac{1}{2C_0}\right)^2=\frac{2}{q\varepsilon_s N_d}(\phi+V), \tag{1}$$

where C is the capacitance per unit area of a grain boundary, q is the electron charge, ε_s is the dielectric constant of zinc oxide, N_d is the donor density, Φ is the barrier height, and V is the applied voltage per grain boundary.

One of the methods widely used for the modification of physico-chemical properties of a powder is mechanical activation in high-energy mills. In the process of mechanical activation of zinc oxide powder it is possible to decrease the grain and crystallite size, but also to change the localization and concentration of both native defects and impurities incorporated in the crystal lattice, by suitable selection of milling parameters. Also, suitable selection of sintering parameters during thermal treatment, such as the sintering temperature, heating and cooling rate, atmosphere, can influence zinc oxide defect states.

This report presents the results of a study of the grain boundary properties of mechanically activated and sintered zinc oxide specimens using impedance spectroscopy in a wide frequency range. Also, Mott-Schottky measurements were done and the influence of microstructure on the electrical properties obtained was discussed.

2. Experimental procedure

The samples prepared for this study were formed from commercial zinc oxide powder (Kemika, p. a. 99,96%). The zinc oxide powder was submitted to mechanical treatment in air by milling in a high-energy vibro mill with steel rings (CUP Mill Type MN 954/3 KHD Humboldt Wedag AG) in a continual regime. The activation time was 30 and 300 minutes. Samples were denoted as Z1, Z2 and Z3 for the time of activation of 0, 30 and 300 min, respectively.

All powders were compacted by an uniaxial double action pressing technique at a pressure of 49 MPa to form cylindrical compacts with a green density of pellets in the range of 50 to 60% ρ_T.

The obtained compacts were sintered at 1100˚C for 2 h at the heating rate of 15˚C/min. The densities of sintered samples were in the range of 94% to 96% ρ_T. For electrical measurements the sintered samples were polished and coated with a silver paste on both sides.

Impedance measurements were carried out using a Gamry EIS300 Impedance analyzer in the frequency region of 1 Hz to 300 kHz, and in the temperature interval 23-240˚C. The obtained experimental results were fitted in the ZView program. Mott-Schottky measurements were done in the temperature range from 23 to 240˚C at a frequency of 100 kHz.

The microstructure of the fractured surface of sintered zinc oxide samples was analyzed by scanning electron microscopy using a JSM 5300-JEOL device. The obtained micrographs were used for assessment of the mean grain size using a SemAfore digital slow scan image recording system (JEOL version 4.01).

3. Results and discussion

Changes of the particle size and structure during mechanical activation of the ceramic parent material cause the morphological and structural metastability of the starting powders and affect the sintering process, either positively or negatively.

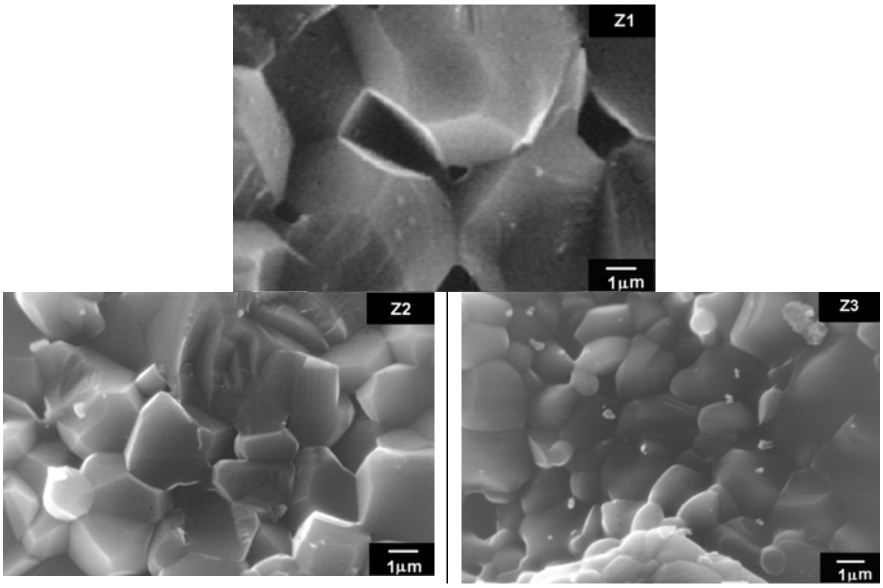
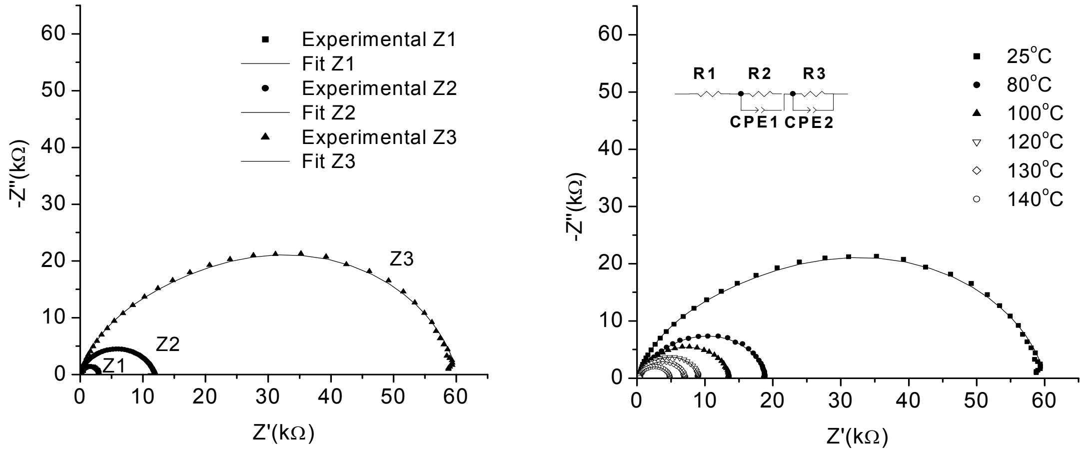


Fig. 2. Micrographs of sintered samples Z1, Z2, and Z3.

The SEM micrographs of the sintered samples are shown in Fig. 2. As can be seen from micrographs mechanical activation greatly influences the grain size of sintered zinc oxide. The mean grain size of sintered ZnO is 8.6, 2.7 and 1.8 μm for samples Z1, Z2 and Z3, respectively. As it can be expected, the bigest grains are in the non-activated ZnO, and the grain size decreases with increasing activation time. Having in mind that the grain size and porosity has a major effect on electrical properties in polycrystalline materials it can be expected that the noticed difference in the morphology of differently activated ZnO samples in a certain way will influence electrical properties of activated zinc oxide.



a) b)

Fig. 3. Nyquist plots of sintered sample: a) Z1, Z2 and Z3 at RT, b) Z3 at various temperatures.

The impedance spectra of sintered samples Z1, Z2 and Z3 at various temperatures are shown in Fig. 3. Although all three samples apparently exhibit one semicircle, only the spectra of Z1 and Z2 could be analyzed in this way. A detailed analyses of experimental data showed that the results could be interpreted in terms of an equivalent circuit involving grain boundary resistance R_{gb} and a constant phase element, CPE, only for samples Z1 and Z2, but for sample Z3 two serially connected R-CPE'S should be involved. A constant phase element was used instead of a capacitor as the impedance spectra of all samples can be described as depressed semicircles, i.e. non-Debye processes occurred in them. The impedance function of a CPE is:

$$Z_{CPE} = A^{-1}(j\omega)^{-n} \tag{2}$$

where A and n are the parameters, while the angular frequency is $\omega = 2\pi f$. Real values of capacity can be calculated from equation:

$$C = \left(AR^{-(n-1)}\right)^{\frac{1}{n}} \tag{3}$$

where C is the capacity and R is the resistance.

Fitting was performed in the ZView program using model I (Fig. 4a) for Z1 and Z2 samples and model II (Fig. 4b) for the Z3 sample.

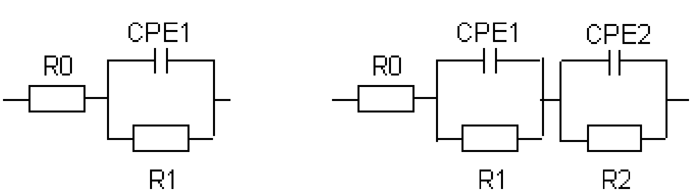


Fig. 4. Equivalent electric circuit for: a) model I and b) model II.

Model I presents an equivalent circuit where a resistor (R_o) and one R_1-CPE_1 element are serially connected. The total impedance, Z, can be presented by the formula:

$$Z = Z' + jZ'' = R_0 + \frac{R_1}{1 + R_1 A_1 (j\omega)^{n_1}} \tag{4}$$

where R_1 is the grain boundary resistance; parameters A_1, n_1 and ω have the same meaning as was given for eq. 2.

After some transformations the formulas for the real and imaginary part of impedance can be obtained:

$$Z' = R_0 + \frac{R_1\left(1 + R_1 A_1 \omega^{n_1} \cos\left(\frac{n_1\pi}{2}\right)\right)}{1 + 2R_1 A_1 \omega^{n_1} \cos\left(\frac{n_1\pi}{2}\right) + \left(R_1 A_1 \omega^{n_1}\right)} \tag{5}$$

$$-Z'' = \frac{R_1^{\,2} A_1 \omega^{n_1} \sin\left(\frac{n_1\pi}{2}\right)}{1 + 2R_1 A_1 \omega^{n_1} \cos\left(\frac{n_1\pi}{2}\right) + \left(R_1 A_1 \omega^{n_1}\right)^2} \tag{6}$$

Model II presents an equivalent circuit consisting of a serially connected resistor R_o and two elements, R_1-CPE$_1$ and R_2-CPE$_2$. In this case the total impedance of the equivalent circuit can be presented by the formula:

$$Z = Z' + jZ'' = R_0 + \frac{R_1}{1 + R_1 A_1 (j\omega)^{n_1}} + \frac{R_2}{1 + R_2 A_2 (j\omega)^{n_2}} \tag{7}$$

where R_1 and R_2 are the resistances for two different processes on the grain boundary.

The real and imaginary part of impedance can be presented as:

$$Z' = R_0 + \frac{R_1\left(1 + R_1 A_1 \omega^{n_1} \cos\left(\frac{n_1\pi}{2}\right)\right)}{1 + 2R_1 A_1 \omega^{n_1} \cos\left(\frac{n_1\pi}{2}\right) + \left(R_1 A_1 \omega^{n_1}\right)} + \frac{R_2\left(1 + R_2 A_2 \omega^{n_2} \cos\left(\frac{n_2\pi}{2}\right)\right)}{1 + 2R_2 A_2 \omega^{n_2} \cos\left(\frac{n_2\pi}{2}\right) + \left(R_2 A_2 \omega^{n_2}\right)} \tag{8}$$

$$-Z'' = \frac{R_1^{\,2} A_1 \omega^{n_1} \sin\left(\frac{n_1\pi}{2}\right)}{1 + 2R_1 A_1 \omega^{n_1} \cos\left(\frac{n_1\pi}{2}\right) + \left(R_1 A_1 \omega^{n_1}\right)^2} + \frac{R_2^{\,2} A_2 \omega^{n_2} \sin\left(\frac{n_2\pi}{2}\right)}{1 + 2R_2 A_2 \omega^{n_2} \cos\left(\frac{n_2\pi}{2}\right) + \left(R_2 A_2 \omega^{n_2}\right)^2} \tag{9}$$

In the impedance spectrum of the sample Z3 (Fig 3b) two relaxation processes exist, but with similar values of the time constant, resulting in their overlapping and the appearance of only one deformed semicircle on the Nyquist plot. The order of magnitude of capacitance (from 10^{-10} to 10^{-12} F), obtained by fitting experimental results using model II, suggests that the semicircles are due to grain boundaries. Similar values of resistance and capacitance were obtained by other authors for nanophase ZnO [14].

The values of resistance of grain boundary region, R_{gb}, also obtained by fitting, were used for calculation of apparent activation energies for charge transport through the grain boundaries, E_a. These energies were calculated from the slope of the Arrhenius plot according to equation:

$$\ln R = \ln A_0 + \frac{E_a}{k} \cdot \frac{1}{T}, \tag{10}$$

where R is resistance of the grain boundary region, A_0 is the pre-exponential constant, E_a is the apparent activation energy, k is the Boltzman constant, and T is temperature. The results relating these energies and resistivities are shown in Tab. I. Apparent activation energies in the range of 0.10 to 0.43 eV indicate high conductivity of samples. It can be noticed that the electrical resistivity increase with increase of the activation time (at room temperature), and these values are in accordance with literature data for polycrystalline ZnO in the range of 10 to 10^{10} Ωm [8].

Tab. I Resistivity and apparent activation energies for conduction

Sample	ρ (kΩcm)	E_a (eV)
Z1	14.8	0.10
Z2	20.5	0.11
Z3	53.7	0.43

Because of the low resistivity of ZnO samples spectro-chemical analysis of zinc oxide powders was done (Tab. II).

Tab. II Spectro-chemical analysis of ZnO powder

Sample	Fe (wt%)	Si (wt%)	Mg (wt%)	Sn (wt%)
Z1	traces	10^{-2}	10^{-3}	10^{-3}
Z2	0.02	10^{-2}	10^{-3}	10^{-3}
Z3	0.05-0.1	10^{-2}	10^{-3}	10^{-3}

These results indicate the presence of an iron admixture. As their concentrations increase with the increase of activation time it could be concluded that this originates from the vibro mill vessel and rings. Also, its influence on electrical properties of sintered ZnO samples can be expected because Fe ions can be incorporated in the crystal lattice acting as electron donors [15].

A Mott-Schottky measurement was used in order to study the capacitive behavior of the double Schottky barrier. Donor density, N_d can be obtaining from these measurements, using the Mott-Schottky equation (Eq. 1). By Plotting $\left(\frac{1}{C}-\frac{1}{2C_0}\right)^2$ versus the applied voltage according to eq. 1, it is possible to calculate N_d from the slope of the line. The results obtained for sample Z2 at various temperatures are shown in Fig. 5.

The obtained values of donor concentration at different temperatures were used to determine the energy of donor levels, E_d, from the slope of the curve $\ln N_d$ versus T^{-1} (Fig. 6.) with utilization of equation:

$$N_d = N_0 \cdot \exp(-E_d / 2kT), \tag{11}$$

The energies of donor levels are 1.52, 0.83 and 0.86 eV for samples Z1, Z2 and Z3 respectively. According data in [16] our obtained value of 1.52 eV suggests that oxygen vacancies have a dominant role in the conduction process in sample Z1. Mechanically activated samples showed significantly higher concentrations of donors. The iron, incorporated in Zn^{2+} sites in valence states higher than 2, introduces new defect levels and acts as an electron donor.

This investigation confirmed a strong influence of mechanical activation in high-energy mills on electrical properties of ZnO. First of all, mechanical activation leads to powder grinding and increase of the number of potential barriers per length unit, which consequently results in a higher resistance of sintered samples. On the other hand, increase in the concentration of zinc oxide native defects and formation of new energy levels, due to incorporation of Fe ions, results in an increase of the N_d concentration. The measured values of resistance of the samples are a sum of all the above mentioned influences.

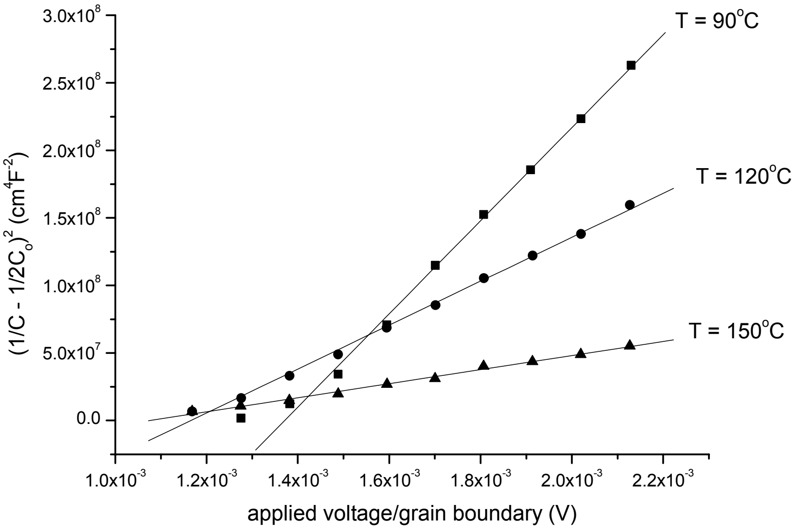


Fig. 5. Plot $(1/C - 1/2C_0)^2$ vs V for sample Z2 at different temperatures.

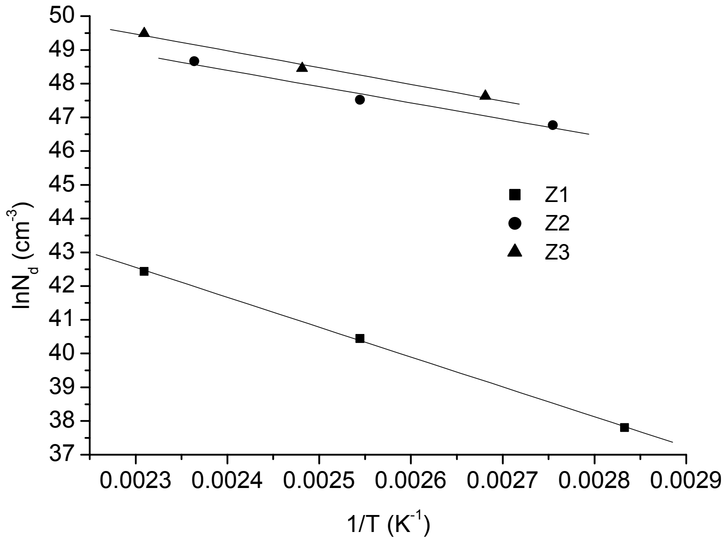


Fig. 6. Plot $\ln N_d$ vs $1/T$ for all samples.

This study showed that the influence of admixtures, which can be introduced to a powder during mechanical activation should be seriously considered, especially when milled ZnO powders should be further processed for electronic use.

4. Conclusions

The results of impedance spectroscopy analyses depict low resistivity of all samples, but also increase of resistivity with an increase in the milling time. Several processes take place during milling: powder grinding, grain size decrease, increase in defect concentration and introduction of new defects due to admixture incorporation. All these processes strongly influence the electrical properties. Our investigation confirmed incorporation of Fe ions, as electron donors, in the ZnO crystal lattice. It was found that oxygen vacancies with $E_d = 1.52$ eV are the dominant type of defect in non-activated ZnO, but in activated samples a strong influence of Fe ion incorporation resulting in an energy level of 0.85 eV is noted.

Acknowledgements

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Садржај: *Микроструктурна својства комерцијалног цинк-оксидног праха модификована су механичком активацијом у високоенергетском вибромлину. Добијени прахови компактирани су и синтеровани на 1100^{o}C у трајању од 2 h. Електрична својства границе зрна добијене цинк-оксидне керамике проучавана су импедансном спектроскопијом. Мерења су вршена у температурном интервалу од 23 до 240^{o}C. Привидне енергије активације провођења одређене су на основи Аренијусове зависности. Мот-Шоткијев модел коришћен је за израчунавање концентрације донора. Разматран је утицај микроструктуре, као и утицај типа и концентрације дефеката на електрична својства.*

Кључне речи: *цинк-оксид, керамике, механичка активација, електрична својства.*