Influence of Fine Crystal Percentage on the Electrical Properties of ZnO Ceramic-Based Varistors

Abdullah Aljaafari 1,* and Ahmed Sedky 2

1 Department of Physics, College of Science, King Faisal University P.O. Box 400, Al-Ahsa 31982, Saudi Arabia
2 Physics Department, Faculty of Science, Assiut University, Assiut 71511, Egypt; sedky1960@yahoo.com
* Correspondence: aaljaafari@kfup.edu.sa

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Abstract: Herein, the effect of nanocrystal percentage in bulk-ZnO varistors was studied. The structure of ZnO nanocrystals was examined using X-ray diffraction (XRD) and field-emission scanning electron microscopy (FE-SEM). The XRD studies showed that the nanocrystals were indexed with the hexagonal wurtzite structure of ZnO nanostructures. The average crystallite size deduced from XRD analysis ranged between 135 and 273 nm, eight-fold lower than that of the nanoparticles observed in FE-SEM micrographs (1151–2214 nm). The percentage of nanocrystals added into the ZnO varistor was increased from 0 to 100%. Electrical measurements (I–V profiles) showed that the non-linear region, breakdown field, and activation energy were found to decrease with the addition of ZnO fine crystals up to 10% and then increased upon a further increase in fine crystals. However, the electrical conductivity measured at room temperature was improved, and the highest value of 2.11 × 10⁻⁵ was observed for 10% fine crystals and then decreased upon a further increase in the fine crystal concentration in bulk ZnO. The breakdown field decreased with the increase in the percentage of ZnO nanostructures in the varistor up to 10% and then increased upon the further addition of ZnO nanostructures. The nonlinear coefficient (α) was decreased from 18.6 for bulk ZnO and remained close to unity for the samples that contained fine crystals. The electrical conductivity was generally improved with the increase in the concentration of the ZnO fine crystals. The activation energy was found to be 128, 374, and 815 meV for the bulk samples and 164, 369, and 811 meV for the samples that contained 100% fine crystals for the three temperature regions of 300–420, 420–580, and 580–620 K, respectively. These results will provide a pathway toward the determination of a correlation between the electrical and microstructural properties of ZnO-based varistors for future device applications.

Keywords: ZnO nanocrystals; ZnO varistor; breakdown field; nonlinear I–V; activation energy

1. Introduction

Over the past decades, ZnO has been used in various applications including varistors, transparent electrodes, gas sensors, and photocatalysis [1–8]. ZnO polycrystalline nanostructures show nonlinear I–V characteristics due to the potential barriers formed at the inter-grain boundaries [9–11]. The formation of the nonlinearity, in parallel with high current densities and breakdown fields, is the most significant property of varistors. The increase in current is more rapid than that in voltage; the I–V curve shows an upturn region at current densities beyond 10³ A/cm² and breakdown fields (≤5000 V/cm). This upturn region indicates that the voltage drops at the grains and controls ZnO for varistor applications. Generally, the nonlinearity phase depends on the density, chemical composition of the compound, and nanostructure development [12–15].

Nanotechnology is of increasing importance in many research branches due to the interesting properties associated with the sizes of small particles [16–18]. Although the bulk ZnO material is well known for having a wurtzite hexagonal structure, ZnO nanocrystals have different crystalline
structures depending on how they are prepared [19]. It has been reported that the ZnO distributed nanoparticles have an enhanced luminous intensity compared to the ZnO bulk [20]. Moreover, cubic ZnO nanoparticles can be formed by flash evaporation [21]. In addition, it is accepted that fine nanoparticles of face-centered-cubic structure of a few hundred nanometers in size can form multiple nanoparticles with a diamond structure [22–27]. In the last few years, extensive studies on the synthesis, characterization, and physical properties of nanomaterials have been conducted. Enormous research has been focused on metal oxide nanoparticles owing to their unusual properties upon entering the nanoscale regime [28,29].

The electrical characteristics of ZnO ceramic varistors are dependent on their microstructural features as follows: (i) the grain boundaries between the ZnO grains, which have nonlinear current–voltage characteristics with an optimum breakdown voltage, can be low—or the grain boundary may not exhibit varistor behavior at all, possess ohmic characteristics, and define the characteristics of the varistor in the pre-break-down region, and (ii) the ZnO grains and their sizes—which define the number of grain boundaries between the electrodes and thus the breakdown voltage of the varistor—and their conductivity define the performance of the varistor at high currents in the upturn region of the current–voltage characteristics [30]. Previous studies showed that some dopants have a significant effect on the pre-break-down and the upturn current–voltage characteristics of varistors even with minute amounts of additives. For example, in very small amounts, aluminum is a potential dopant for increasing the conductivity of the ZnO grains and enhancing the varistor’s performance at high currents [31–34]. Various physicochemical properties of ZnO nanostructures can be strongly affected by the presence of deep and shallow defect-related in-gap states, which depend on the material’s growth conditions in a way that is still far from being understood. Thus, a relationship or the effect of the dopant on the electrical properties of ZnO varistors needs to be studied.

However, to the best of our knowledge, the effect of nanocrystals on the characteristics of bulk ZnO varistors and their correlation have not been reported. Therefore, in this work, we studied the effect of increasing the fine crystal amount in the bulk-ZnO varistor on the electrical properties. The variation in the breakdown field (EB) versus fine crystal content is well studied. The electrical conductivity of the bulk and mixed phase ZnO was investigated. The activation energy versus ZnO fine crystal amount was determined. The structure and morphology were characterized by using XRD and FE-SEM techniques.

2. Experimental Details

2.1. Preparation

The experiment was started with raw ZnO (Sigma-Aldrich ZnO powder, <5 µm particle size, 99.9%) with an average crystallite size of 273 nm and particle size of 2214 nm. In advance, ZnO powder was milled (using RETSCH-Planetary Ball milling PM400) for several hours to obtain fine crystals with a size of 144 nm. Then, the samples were prepared by mixing the raw powders with these fine crystals in determined percentages of 0.0, 5, 10, 30, 50, 75, and 100%, using the conventional solid-state reaction method. The obtained mixture was then calcined for 900 °C in air for 12 h. The as-obtained powder was then pressed into a disk (diameter, 1.0 cm, and thickness, 0.3 cm). These disks were sintered for 10 h at 1000 °C in air. The disks were then cooled down to room temperature. The densities of the bulk samples were measured in terms of volume and weight.

2.2. Characterizations

Microstructure analysis of the obtained products was performed using an X-ray diffractometer (XRD-Philips Type PW 1710, Amsterdam, The Netherlands) with CuKα radiation of 1.5406 Å. The surface morphologies were studied using FE-SEM (FE-SEM-Model JEOL JMS-7000, Peabody, MA, USA). The I–V characteristics were measured with a Keithley meter (Model 6517, Beaverton, OR, USA), DC power supply of 5.0 kV, and digital multimeter. The products were polished well and
inserted into copper electrodes. The current was measured relative to the applied voltage at room temperature. For the electrical contacts, high-quality silver paste was used on the sample surfaces. Then, electrical resistivity ($\rho = (R\ell/A)$) as a function of the temperature measurements was determined in the range of 300–620 K, and the electrical conductivity was calculated ($\sigma = (1/\rho)$). The values of electrical conductivity were used to calculate the activation energy of the considered samples.

3. Results and Discussion

3.1. Structural Analysis of ZnO Nanomaterials

The XRD patterns (Figure 1a–f) show that all the samples exhibited a hexagonal wurtzite crystal structure; no other impurity lines can be observed, implying that the ZnO fine crystal content was 100%. The standard peaks of ZnO (100), (002), (111), (102), (110), (103), (200), and (112) are observed [35–37]. To further confirm whether the ZnO fine crystals were localized for ZnO in the cell, the lattice parameters of the samples were calculated using $c = 2d_{(002)}$, $a = d((100))/(\cos 30)$ and are listed in Table 1. However, we could not find any significant changes in the lattice parameters $a$ and $c$ with the addition of ZnO fine crystals. The values ranging from 3.20 to 3.22 Å for the lattice parameter $a$ and 5.145 and 5.17 Å for the $c$ parameter are in agreement with the previous data based on ZnO ceramics [36,38]. Additionally, the average crystallite size $D_{hkl}$ was calculated using Scherer’s equation [28]:

$$D_{hkl} = \frac{k\lambda}{\Delta\theta \cos\theta}$$  \hspace{1cm} (1)

where $\lambda$ is the X-ray wavelength ($\lambda = 1.5418\text{Å}$), $\Delta\theta$ is the half maximum line width, $\theta$ is the Bragg angle, and $k$ is a constant ($k = 0.9$ for this type of ceramic). The average crystallite size ($D_{(111)}$) against the percentage of fine crystal content for all the samples is listed in Table 1. It is clear that $D_{(111)}$ was reduced with the addition of fine crystals into the bulk up to 100% with 10% fluctuation. The values of average crystallite size range from 143 to 273 nm for fully raw powder (0.0% sample).

Figure 1. XRD patterns of mixed powder; (a) 0.0, (b) 5, (c) 10, (d) 50, (e) 75, and (f) 100% of fine crystals.
Table 1. Lattice parameters, and average crystallite and particle sizes for ZnO mixed samples.

| Fine Crystal Percent | Lattice Parameters | Crystallite Size (nm) | Particle Size (nm) |
|----------------------|-------------------|-----------------------|-------------------|
|                      | A (Å)             | C (Å)                 |                   |
| 0                    | 3.203             | 5.145                 | 273               |
| 5                    | 3.214             | 5.149                 | 163               |
| 10                   | 3.223             | 5.163                 | 143               |
| 30                   | 3.226             | 5.170                 | 153               |
| 50                   | 3.222             | 5.159                 | 154               |
| 75                   | 3.222             | 5.166                 | 173               |
| 100                  | 3.224             | 5.171                 | 174               |

FE-SEM images for the mixed powder are shown in Figure 2a–f. In the raw powder product, the shape of the grains was quite dissimilar, and there was a precipitation of grains on the main grains. With the incorporation of fine crystals, the shape and average size of the grains changed but they were still uniformly distributed on the original particles. With the further increase in the fine crystal content, the original particles appeared with a larger size and were connected to each other. These fine crystals may be responsible for a good link between the grains and the homogenous distribution within the matrix. Generally, the particles appeared with two different sizes: micro- and nano-size. The micro-sized particles belong to the bulk ZnO phase, while the nano-sized ones belong to the fine crystal phase.

![FE-SEM images of samples](image_url)

*Figure 2. FE-SEM images of samples; (a) bulk-ZnO, (b) 10%, (c) 30%, (d) 50%, (e) 75%, and (f) 100% of fine crystals.*

The average particle size (D) can be determined from the lineal intercept method using the equation \( D = (1.56 L)/MN \), where \( L \) is the random line length, \( M \) is the magnification, and \( N \) is the number of grain boundaries intercepted by the lines on the micrograph [34]. The average particle size, listed in Table 1, ranged from 1277 to 2214 nm, which is eight times higher than the crystallite size obtained from XRD analysis. This variation can be explained by the FE-SEM images showing the plates containing multiple crystallites. The average crystallite and particle sizes are shown in Figure 3.
3.2. I–V Characteristics

Figure 4 shows the I–V curves of the samples containing various concentrations of fine crystals. It is obvious from the I–V curves of the bulk ZnO that there are three regions: the first region and third one exhibit ohmic behavior, while the second region clearly shows nonlinear performance (upturn region). Additionally, this second region (nonlinear region) disappears for samples with ZnO fine crystals. This indicates that the potential barrier was completely deformed upon the addition of ZnO fine crystals even at very low doping contents (5%). The electric current densities generally shifted to higher values compared to those in the bulk sample. The breakdown field $E_B$ is defined by the field applied when the current through the varistor is 1 mA/cm$^2$ \cite{39,40}. The variation in $E_B$ versus the fine crystal content is shown in Figure 5. The value of $E_B$ decreased with the addition of ZnO fine crystals up to a content of 10%, followed by an increase with a content of 100%, but its value was generally lower than that for bulk-ZnO. This is, of course, logical and consistent with the absence of nonlinearity in the I–V curves for all the mixed phases.

The I–V relationship of a varistor is described by the following \cite{38,39}:

$$J = (E/C)^\alpha$$  \hspace{1cm} (2)

where $J$ is the density of current, $E$ is the electric field, $C$ is a proportionality constant corresponding to the resistance of the ohmic resistor (nonlinear resistance), and $\alpha$ is the nonlinear coefficient ($\alpha = \log V / \log I$).

The value of $\alpha$ was calculated from the slope of the I–V curves plotted on a log scale, as described in \cite{6}. Figure 6 shows the variation of $\alpha$ with doping percentage in three regions.
The value of $\alpha$ was calculated from the slope of the $I$–$V$ curves plotted on a log scale, as described in [6]. Figure 6 shows the variation of $\alpha$ with doping percentage in three regions.

Table 2 depicts a similar result. Apparently, the values of $\alpha$ decreased from 18.6 for the bulk phase and remained close to 1.5 for the samples with fine crystal percentages in the second region, which was also the same in the first and third regions. If one looks at the above results, one can see a good correlation between the crystallite size and nonlinear coefficient. Evidently, a non-ohmic feature of the bulk-ZnO varistor was suppressed upon adding ZnO fine crystals, shifting the breakdown fields to lower values.

| Fine Crystal Content (%) | $E_b$ (V/cm) | $\alpha_1$ | $\alpha_2$ | $\alpha_3$ |
|--------------------------|--------------|------------|------------|------------|
| 0                        | 1580         | 0.53       | 18.6       | 1.36       |
| 5                        | 62           | 1.00       | 1.39       | 2.06       |
| 10                       | 51           | 1.08       | 1.32       | 1.88       |
| 30                       | 170          | 1.11       | 1.16       | 1.93       |
| 50                       | 173          | 1.07       | 1.13       | 2.60       |
| 75                       | 113          | 0.83       | 0.99       | 1.76       |
| 100                      | 410          | 0.35       | 2.75       | 1.62       |
3.3. Electrical Conductivity

The electrical conductivity of the bulk and mixed phase ZnO was controlled by defects generated at high temperatures and the presence of doping, whether they were specifically added to the materials or not. During the cooling, defects may have migrated to the grain boundaries and disappeared (intrinsic defects) or accumulated if the solubility limit (extrinsic defects) was reached.

This process of migration is slow and thermally activated, indicating that defects near grain boundaries are efficiently eliminated at temperatures not much lower than the sintering temperature. Additionally, the electrical conductivity ($\sigma$) across the first ohmic region at room temperature was calculated using the relation $J = \sigma E$. The electrical conductivity for the ZnO varistors doped with ZnO fine crystals is shown in Figure 7 and in Table 3. Except for the 10% sample, it can be seen that $\sigma$ is improved by fine crystal addition, in good agreement with the $I$–$V$ measurements.

![Figure 7. Electrical conductivity at room temperature for ZnO samples.](image)

**Table 3. Electrical conductivity and activation energy of ZnO samples.**

| Fine Crystal Content (%) | $\sigma$ (S/cm) | $E_a$ (meV) | $E_a$ (meV) | $E_a$ (meV) |
|--------------------------|-----------------|-------------|-------------|-------------|
|                           |                 | (300–420 K) | (420–580 K) | (580–620 K) |
| 0                        | $2.20 \times 10^{-7}$ | 128         | 374         | 815         |
| 5                        | $1.02 \times 10^{-6}$ | 81          | 232         | 614         |
| 10                       | $2.11 \times 10^{-5}$ | 33          | 38          | 398         |
| 30                       | $8.00 \times 10^{-6}$ | 53          | 210         | 265         |
| 50                       | $2.06 \times 10^{-6}$ | 17          | 228         | 447         |
| 75                       | $4.31 \times 10^{-6}$ | 55          | 242         | 534         |
| 100                      | $2.47 \times 10^{-7}$ | 164         | 369         | 811         |

The resistivity-versus-temperature measurements were performed at high-temperature ranges (300–620 K). From the values of resistivity, the electrical conductivities were calculated and are shown in Figure 8; the conductivity–temperature dependence was found to obey Athenian’s relation:

$$\Sigma = \sigma_0 \exp(-E_a)/(K_BT)$$  \hspace{1cm} (3)

$$\ln\sigma = \ln\sigma_0 - 11.594E_a(eV)(1000/T)$$  \hspace{1cm} (4)
where $\sigma$ and $\sigma_0$ are the electrical conductivities at temperatures $T$ and $T_0$, respectively, and $E_a$ is the activation energy. Evidently, $\sigma$ increases with temperature for all samples. Through the temperature range chosen for the conductivity measurement, it was possible to differentiate the regions corresponding to various activation energies. The profile was separated into three regions according to the following temperature intervals: $(300 \text{ K} \leq T \leq 420 \text{ K})$, $(420 \text{ K} \leq T \leq 580 \text{ K})$, and $(580 \text{ K} \leq T \leq 620 \text{ K})$. The values of $E_a$ were calculated from the slope of each plot by using the above logarithmic relation. Figure 9 shows the activation energy versus the ZnO nanoparticle doping content across the above three regions. Similar values are listed in Table 3. It is clear that $E_a$ generally decreased with the addition of fine crystals up to 5%, followed by an increase upon increasing the fine crystal content to 100%. However, the values of $E_a$ remain lower than those of the bulk ZnO sample.

![Figure 8](image)

**Figure 8.** Plot of $\ln \sigma$ versus $1000/T$ for ZnO samples.

![Figure 9](image)

**Figure 9.** Activation energy for ZnO samples.

Decreasing the activation energy will decrease both the potential barrier and band gap. The interesting point here is that the values of $E_a$ for the bulk-ZnO sample, in the second and third regions, are consistent with those obtained for the 100% fine crystal sample ($E_a = 128, 374, \text{and} 815 \text{ meV for the bulk sample, and 164, 369, and 811 meV for the 100% sample}$).

As compared to numerous previous investigations [41,42] based on microphase ZnO varistors, $E_a$ varied between 500 and 1300 meV at high temperatures ($T > 673 \text{ K}$) and was less than 100 meV at low temperatures ($T > 373 \text{ K}$). These values are comparable to the data obtained for ZnO nanocrystalline compounds ($E_a = 570 \text{ meV}$) [41,42]. Furthermore, the behavior of $E_a$ with the addition of ZnO fine crystals is similar to that of the grain size (Figure 2b).
Based on the above results, the probability of the ZnO fine crystals moving into the grain boundaries is considered to be very high at the sintering temperature. The nanosized crystals are able to localize at the edge of the grain and help in creating some other sensitive inter-grain conduction paths. The conduction paths can work in parallel [1,43] over the grain boundary and entirely deform the potential barrier that builds up between the grains. This is in good agreement with the $I$–$V$ characteristics, where the linear behavior for the ZnO varistor is established. By contrast, a good correlation between the behaviors of the grain size, nonlinear coefficient, breakdown field, and activation energy with ZnO fine crystal addition can be reported.

Generally, the variations in the nature of the grain boundary and arrangement are well expected. In previous work, by measuring large numbers of individual grain boundaries, Einzinger et al. [44] reported that there can be considerable variation in the breakdown voltage from one boundary to another. They also showed that some boundaries were ohmic and some were nonlinear, while others were insulating. These results indicated above revealed that varistor properties closely depend on the microstructure features.

3.4. Discussion

Various efforts have made to present the fact that physiochemical properties of ZnO nanostructures can be strongly affected by the presence of deep and shallow defect-related in-gap states, which depend on the material’s growth conditions. However, controlling the conductivity in ZnO has remained a major concern [45,46]. Even relatively small concentrations of native point defects and impurities (down to $10^{-14}$ cm$^{-3}$ or 0.01 ppm) can significantly affect the electrical and optical properties of semiconductors [47–50]. Therefore, understanding the role of native point defects (i.e., vacancies, interstitials, and antisites) and the incorporation of impurities is key for controlling the conductivity in ZnO. For a long time, it has been postulated that the unintentional n-type conductivity in ZnO is caused by the presence of oxygen vacancies or zinc interstitials [51–53]. However, recent state-of-the-art density functional calculations corroborated by optically detected electron paramagnetic resonance measurements on high quality ZnO crystals have demonstrated that this attribution to native defects cannot be correct [54–60]. It has been shown that oxygen vacancies are actually deep donors and cannot contribute to n-type conductivity [56,59,60]. In addition, it was found that the other point defects (e.g., Zn interstitials and Zn antisites) are also unlikely causes of the observed n-type conductivity in as-grown ZnO crystals [57,58]. Instead, the cause would be related to the unintentional incorporation of impurities that act as shallow donors, such as hydrogen, which is present in almost all growth and processing environments [61,62].

4. Conclusions

In summary, the structure, $I$–$V$ characteristics, and electrical conductivity dependence temperature of a bulk ZnO varistor modified with nanosized crystals of less than 200 nm are well studied, and their relationship has been established. It was observed that only average crystallite and particle sizes were affected by the addition of ZnO fine crystals; however, the hexagonal wurtzite structure of bulk ZnO ceramics remained unchanged. Different varistors were prepared with the bulk ZnO and bulk-mixed fine crystals of ZnO, and the electrical measurements of the varistors were performed under different conditions. As seen in the $I$–$V$ characteristics, a linear behavior for mixed ZnO was observed. The non-linear region, breakdown field, and activation energy were found to decrease with the addition of ZnO fine crystals up to 10%, and then increased upon a further increase in fine crystals. However, the electrical conductivity measured at room temperature was improved and exhibited values higher than that of bulk ZnO. The values of the nonlinear coefficient decreased from 18.6 to 1.5 for the samples mixed with the fine crystals. Activation energy values of 128, 374, and 815 meV for the bulk sample and 164, 369, and 811 meV for the samples that contained 100% fine crystals for the three temperature regions of 300–420, 420–580, and 580–620 K, respectively, were obtained. Thus, nanosized crystals at grain boundaries of ZnO ceramics can fully deform the potential barriers of ZnO
varistors. The results obtained in this work might be helpful in elucidating the role of dopants in the nanoregime and establish the relationship between electrical and microstructural properties, which is a key requirement for a ZnO varistor.

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