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Comparison of electrical properties of zinc oxide varistors manufactured from micro and nano ZnO powder

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Zinc oxide varistors are semiconductor ceramics, which their excellent nonlinear electrical characteristics which are induced from their grain boundaries and depend on their microstructures. Based on a theoretical aspect, finer primary particles with a narrow size distributions offer better electrical properties. Then these properties are related to the size and morphology of ZnO grains. In this research, zinc oxide micro and nano powders were synthesized by a sol-gel method and the effect of the ZnO particle size on the electrical properties of zinc oxide varistors was investigated. The results showed that if ZnO nano powder is used instead of micro powder for fabrication of varistors, the sintering time and temperature were decreased; also, the electrical properties such as the nonlinear coefficient and breakdown voltage were increased up to 43 and 4750 V/cm versus 34.8 and 2920 V/cm respectively.

Key words: Varistor, ZnO, Electrical property, Nano powder, Nonlinear coefficient, Break down voltage.

Introduction

Varistors are made from semiconducting ceramics such as ZnO and other metal oxides (Bi_2O_3, Sb_2O_3, Co_2O_3, Cr_2O_3 and SiO_2, etc.). Due to their excellent nonlinear coefficient and low leakage current, they have been used in electrical and electronic systems such as surge protection devices for many years [1]. In operation, a varistor is connected between the power source and ground. When the electric field exceeds the switching field, the surge is carried away through the varistor, thus protecting the circuit or the power utility. It is, therefore, desirable to control varistor characteristics in order to optimize specific protection needs and device size requirements

The resistance and fracture voltage of these varistors depend intensively on the microstructural conditions and so, grain size, and microstructural homogeneity are the most important parameters in varistor manufacturing. One of the ways to reach these goals is to use homogeneous zinc oxide nano powder for varistor production. Homogeneous zinc oxide powders are necessary for the manufacture of high performance ZnO varistors, because this increases the homogeneity of the microstructure which is vital for an improvement of the electrical and electronic characteristic of these ceramics [1-4]. Numerous investigators have studied the effects of processing and microstructure on electrical conduction in ZnO varistors [2-6]. It has been reported that varistors with inhomogeneous microstructures often suffer from a large deviation of the current/voltage characteristics due to high local currents and overloads caused by single large grains, which give rise to rapid degradation of the varistor in electrical operation. Hence, careful control of the microstructure of ZnO material is needed to obtain the values necessary for the breakdown voltage and nonlinearity exponent [7].

Nano-scale particles possess different physical and chemical properties compared to bulk materials. Better sinterability, higher homogeneity and other unusual properties may be expected because of their nano-sized crystallites, large surface areas and different surface properties [5]. Therefore, the synthesis of varistors with ZnO nano powder should improve their properties drastically [6, 7].

In this research, the effect of ZnO nano powder size on the electrical properties of ZnO varistors was investigated. For this purpose a sol-gel method was applied for the fabrication of zinc oxide powders with nano sizes and some varistors were fabricated from these powders with some additives. The morphology and particle size of the fabricated ZnO powders were studied by SEM, TEM and a zetasizer and their electrical parameters were investigated by conventional methods also. This study intends to explore a technique which is suitable for industrial application.

Experimental Procedures

The starting materials for the synthesis of ZnO nano powder were zinc nitrate ($Zn(NO_3)_2 \cdot 6H_2O$), and citric acid ($C_6H_8O_7 \cdot H_2O$). Also zinc oxide micro powders (Merck company product No. 1088461000, CAS No. 1314-13-2) were used for fabrication of a conventional varistor when

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its properties was measured for comparison. The raw materials for manufacturing zinc oxide varistors were ZnO as a body and Bi_2O_3, Sb_2O_3, CoO, Cr_2O_3, and MnO powders as additives. All of the materials which have been used in this study were analytical grade purity.

Fig. 1 shows the flow chart of the synthesis ZnO powder by a sol-gel method. For the synthesis of zinc oxide nano powders by a sol-gel method, 5 g. of hydrated zinc nitrate was dissolved in Di-ionized water then one mole of citric acid was added (stoichiometric ratios was selected for the reaction). In order to forming a homogenous sol, the solution was heated at 70 °C by a magnetic heater-stirrer. After that, the solution was cooled and its pH was adjusted with ammonia. After adjusting the pH, the sample was heated again up to 100 °C and heated until excess water was evaporated and the sol became viscose. Then the viscose sol temperature was increased up to 150 °C and was stirred until gelation occurred. Zinc oxide gels were dried at 100 °C, calcinated at 400 °C, and then their morphology and particle size were studied by a scanning electron microscope (Philips XL30), a transmission electron microscope (Philips CM200 FEG) and zeta sizer (Malvern 3000 HAS).

Zinc oxide varistor samples were fabricated by a mixing, pressing and sintering method. In this method, zinc oxide powder with other additives and deionized water, were ball-milled in a polyethylene jar with ZrO_2 balls for 18 hours. The mixed powders were dried and pressed into 10 mm diameter and 2 mm height discs by 70 MPa pressure. The samples were sintered at 1100 °C for 1 h. The discs were sintered at 1200 °C for 2 h.Two types of zinc oxide varistor samples were manufactured, one type using the nano sized zinc oxide powder and the another type from micro sized zinc oxide powder (commercial powder from Merck Company). The final density and porosity of varistor samples were measured to ASTM-C20-48 standard; also the hardness of the samples was measured by a Shimadzu HMV-200. The electrical properties (nonlinear coefficient and breakdown voltage) of fabricated samples were investigated by traditional methods (I-V curves). Data for the electrical properties were obtained from standard DC resistivity measurements over the range of current densities from 10^{-6} to 10^{-3} A/cm^2. For both sample types, silver paste was applied to the two faces of the discs to provide electrodes for electrical properties measurements. The nonlinear coefficient (α) was determined from 1 :

$$\alpha = \frac{\log I_2 - \log I_1}{\log V_2 - \log V_1} \qquad (1)$$

where $I_1 = 0.1$ mA/cm^2, $I_2 = 1.0$ mA/cm^2, and V_1 and V_2 are the electrical voltages corresponding to I_1 and I_2 respectively. The breakdown voltages were calculated from the slope change of the I-V curves (from nonlinear to linear behavior).

Results and Discussion

The microstructures of the synthesized zinc oxide nano powders are shown in Fig. 2 and their particle size distribution have been measured and are plotted in Fig. 3. Based on Figs. 2 and 3, the zinc oxide powders which have been synthesized by a sol-gel method are nano sized. Also, although some agglomeration is revealed in Fig. 2(b) but most of the agglomerated particles still has diameters less than 100 nm (Fig. 3 curve). On the other hand, the average particle size of synthesized powders was 50 nm and the powder shapes were almost uniform.

The density (green and sintered), porosity and hardness of two varistor samples were studied and are shown in Table 1. An increase of the sintered density by increasing the green density is related to the packing ability of the powders during compaction. The high green density suggests that most of the agglomerates present in these nano powders were relatively soft and thus easily disrupted mechanically during pressing. Therefore, the higher

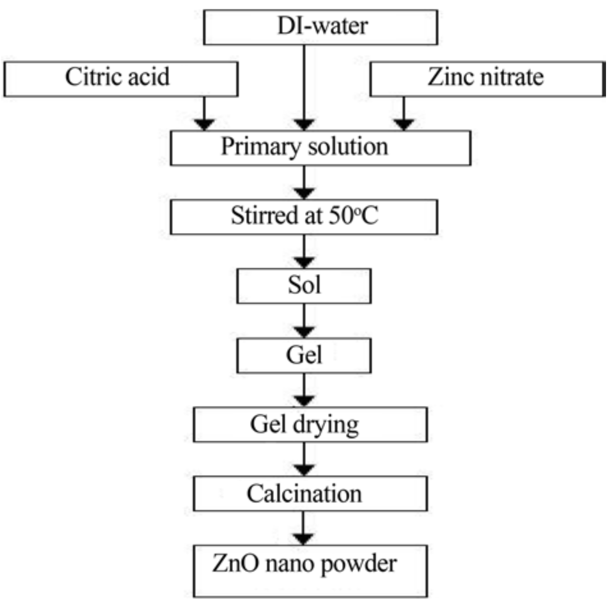

Fig. 1. Flow chart for synthesis of ZnO nano powder by a sol-gel method.

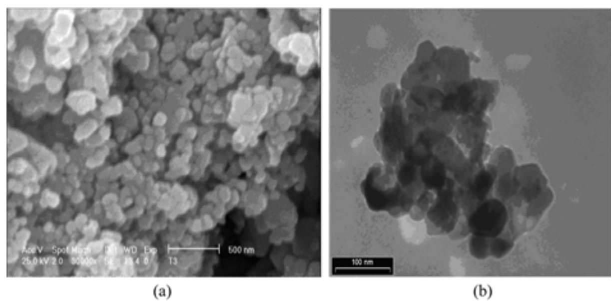

Fig. 2. Morphology of ZnO nano powders synthesized by a sol-gel method (a) SEM image (b) TEM image.

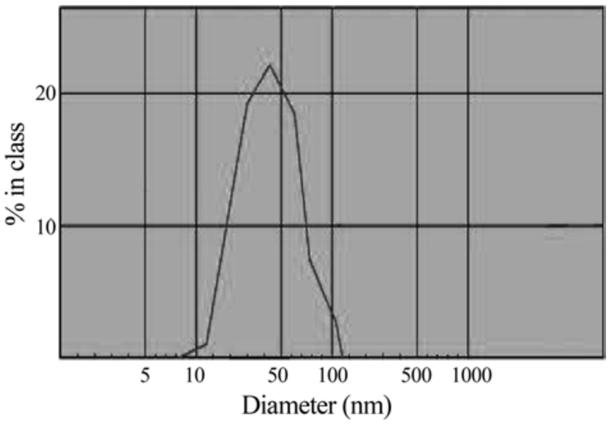

Fig. 3. Particle size distribution of ZnO nano powder synthesized by a sol-gel method.

Table 1. Density, porosity and hardness of two varistors samples

Properties	Fabricated from micron ZnO powder	Fabricated from nano ZnO powder
Green density (g/cm^3)	3.07	3.43
Sintered density (g/cm^3)	5.44	5.57
Porosity (%)	0.136	0.005
Hardness (Vickers)	125	251

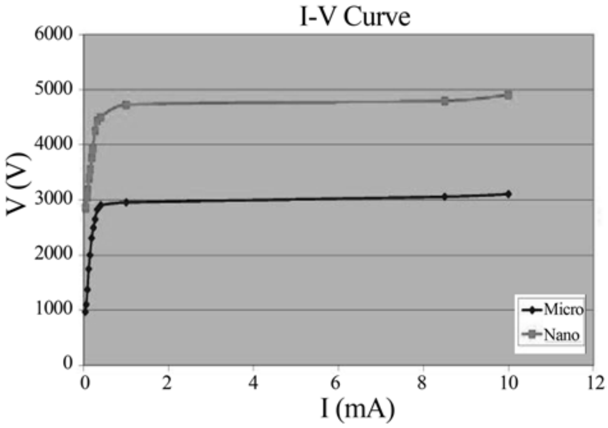

Fig. 4. I-V curve of varistors samples fabricated from nano and micro sized zinc oxide powders.

Table 2. Nonlinear coefficient and breakdown voltage of varistors made from nano and micro sized zinc oxide powders

Properties	Micro zinc oxide varistor sample	Nano zinc oxide varistor sample
Nonlinear coefficient (α)	34.8	43
Breakdown voltage (V/cm)	2920	4750

compressibility of ZnO green powders gives an uniform grain morphology and as a result, a finer and more uniform microstructure in ZnO varistors will be formed. Also, based on Table 1, the sintered density of varistor samples have been increased when they are manufactured from nano sized powders. This may be related to the high surface area of zinc oxide nano powders. By decreasing the powder size, sintering would be completed faster and at a lower temperature and a high density will be achieved. Also, the porosity of varistor samples manufactured from nano powders, were decreased because of a complete sintering process and isolation of the porosity. On the other hand, the hardness of varistors made from nano powders was improved greatly.

I-V curve of varistor samples fabricated from nano and micro sized zinc oxide powders are plotted in Fig. 4. Also the non-ohmic parameter a, and the breakdown voltage $V_{1mA}/_{cm}$ of samples were calculated and are shown in Table 2. This figure and this table reveal that by using zinc oxide nano powders for the fabrication of varistors, the nonlinear coefficient has been increased to 43 which is about 25% more than varistors which are fabricated from ZnO micron powders. On the other hand, the breakdown voltage, which was measured under a current density J = 1 mA/cm^2, has been increased about 63% by decreasing the ZnO powder size from micro to nano. Increasing the nonlinear coefficient may be related to the decrease in porosity because as shown in Table 1, nano powders decrease the porosity greatly. Also by decreasing the particle size, the grain size of varistors made from nano powders were decreased substantially. This phenomena increases the grain boundary area and this structure will increase the breakdown voltage.

This study revealed that the electrical properties of the varistors prepared from nano sized powders were superior to those of varistors prepared from micro sized powders. Since the homogeneity of the microstructure plays an important role in determining the electrical properties of ZnO varistors [7-9], it was expected that the differences of the electrical properties between the 2 samples (fabricated from micron and nano powders) resulted from a difference in the homogeneity and defects in the microstructure. The homogeneity of the microstructure has the ability to affect the grain boundary properties, which control the electrical properties of the ZnO varistors [7-9].

Conclusions

In this study, the following results were obtained :

1. Nano powder zinc oxide with 50 nm average grain size was synthesized by a sol-gel method.
2. Fabrication of varistors using ZnO nano powders increased the density and hardness up to 5.57 g/cm^3 and 251 Vickers respectively, on the other decreased the porosity up to 27 times.
3. By using nano powder, the nonlinear coefficient (a) was improved up to 23%.
4. The breakdown voltage was increased from 2920 to 4750 V/cm when nano sized powders were used to manufacture varistors instead of micron sized ones.
5. The physical, mechanical and electrical properties

of varistors fabricated from ZnO nano powders prove that this material is the best candidate for fabrication of these varistors.

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