Microhardness, microstructure and electrical properties of ZVM ceramics

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Abstract: The effect of Mn₃O₄ addition on microhardness, microstructure and electrical properties of vanadium oxide doped zinc oxide varistor ceramics is systematically investigated. The Vicker's microhardness H_V has decreased with increasing the amount of Mn₃O₄. Also, the average grain size has decreased from 27.51 μm to 19.55 μm with increasing the amount of Mn₃O₄ up to 0.50 mol%, whereas an increase in Mn₃O₄ up to 0.75 mol% has caused the average grain size to increase and then it decreases with increasing Mn₃O₄ from 0.75 mol% to 1.00 mol%. The sintered density has decreased from 5.38 g/cm³ to 5.31 g/cm³ with increasing the amount of Mn₃O₄. The varistor ceramic modified with 0.50 mol% Mn₃O₄ has exhibited excellent nonlinear properties, with 16.29 for the nonlinear coefficient and 441.9 $\mu\text{A}/\text{cm}^2$ for the leakage current density. Furthermore, the sample doped with 0.50 mol% Mn₃O₄ has been found to possess donor density as $0.77 \times 10^{18} \text{ cm}^{-3}$ and 0.916 eV barrier height.

Keywords: ceramics; electrical properties; microstructure; varistor; Mn₃O₄ doped ZnO–V₂O₅ varistor

1 Introduction

ZnO based varistors are semiconducting ceramic devices exhibiting nonlinear symmetrical current–voltage (I – V) or current density–electric field (J – E) characteristics for both voltage polarities [1]. This is due to the presence of inter-granular layers with high resistance between ZnO grains having low resistance and Schottky barrier arising due to the surface states caused by the dopants. Such behaviors enable them to absorb large amount of energy. Consequently, they

have been extensively used for protecting electronic circuits, against voltage surges and for the voltage stabilization of electrical power lines.

The I – V characteristic relation is expressed as [1]:

$$I = KV^\alpha$$

where K is a constant and α is the nonlinear coefficient related to the material's microstructure. Besides the above coefficient, there are two other parameters, the breakdown voltage V_B and the leakage current I_L . The breakdown voltage is calculated by the simple equation [2,3]:

$$V_B = N_{gb} \times V_{gb} = (t/D)V_{gb}$$

where N_{gb} is the number of grain boundaries across the varistor's thickness t ; D is the average grain size; and

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V_{gb} is the average voltage per grain boundary (≈ 3 V).

Also, in terms of the current density J and the applied electric field E , the above I – V relation is rewritten as

$$J = (E/C)^a$$

where C is a constant. Then the breakdown field $E_B = V_{gb}/D$ [3] is usually taken as the field applied when the current flowing through the varistor is 1 mA [4]. Since the grain boundary barriers in the ZnO based varistors are of Schottky type, the current density J in the first ohmic region of varistor characteristics is related to the electric field E at a given absolute temperature T by the equation [5,6]:

$$J = AT^2 \exp[(\beta E^{1/2} - \phi_B)/(kT)]$$

where $A = 4\pi e m k^2 / h^3$ is the Richardson's constant; ρ is the varistor density; e is the electron charge; m is the electron mass; k is the Boltzmann constant; h is the Plank's constant; β is a constant related to the grain number per unit length and the barrier width ω ; and ϕ_B is the Schottky barrier height formed on the grain surfaces and arises due to the surface states caused by the dopants. Therefore, the electrical conductivity σ of ZnO varistors could be calculated from the slopes of the J – E curves in the first and third ohmic regions, while in the second nonlinear region where the current strongly increases due to the decrease of ϕ_B , the conductivity is given by [7]:

$$\sigma_2 = \sigma_1 \exp[(\alpha - 1)(E_2 - E_1)/E_2]$$

where σ_1 is the conductivity corresponding to the first ohmic region; σ_2 is the conductivity of the second region; and E_1 and E_2 are two values on the linear part of the breakdown region.

The effects of doping ZnO based ceramics with few mole percentages of different oxides of some metals, e.g., Bi, Sb, Co, Mn, Ni, Cr, Al and Fe, have been investigated by several authors [8–16]. Reported results of those studies show that the important physical properties mentioned above are closely related to the compositions and microstructures, i.e., they are dependent on density, grain size, morphology, distribution of any secondary phases and porosity. Therefore, by controlling these parameters, the nonlinear coefficient and breakdown field values could be improved in order to obtain the required electrical performance. Also, each of the above dopants plays a distinctive role in the subtle tuning of the final nonlinear characteristics of the varistor ceramics, while the overall electrical characteristics are resulted from the collective effect of all the microstructural features.

Multilayer chip ceramic products require that the

inner-electrode materials should have their melting points (MP) relatively higher than the sintering temperature of their components [17–19]. Therefore, new ceramics are developed where a silver inner-electrode (MP = 961 °C) can be used for making multilayer components which have their sintering temperatures around 900 °C. Among those products, the binary system ZnO–V₂O₅ has become a good candidate [17,20–24], since it can be sintered at a temperature in the vicinity of about 900 °C which is important for multilayer chip applications due to its ease of co-firing (sintering) with silver inner-electrode without using expensive palladium or platinum metals as electrode materials. However, effects of adding some different metal oxides and rare earths to the binary system ZnO–V₂O₅ on the electrical properties have been investigated by several authors, e.g., Mn ions [25], Mn₃O₄ and Nb₂O₅ [26], Mn₃O₄ and Er₂O₃ [27], MnO₂–Er₂O₃ and Nb₂O₅ [28,29], MnO₂–Nb₂O₅ and Bi₂O₃ [30], and MnO₂ [31,32]. The reported results of these works are dealt with the effects of different doping or the effects of sintering temperature on the microstructure, nonlinear and conduction behaviors of tested ceramics.

The present work is aimed to investigate and throw more lights on the microstructure and electrical properties of $x\text{Mn}_3\text{O}_4$ –0.5V₂O₅–(99.5– x)ZnO (ZVM) ceramics, where $x=0, 0.15, 0.30, 0.50, 0.75$ and 1.00 mol%, as prepared by the conventional ceramic method and sintered at 900 °C for 5 h. Besides, X-ray diffraction, scanning electron microscopy and energy dispersive X-ray analyses have been used to characterize the prepared ceramics.

2 Experimental

Reagent-grade raw materials of ZnO, V₂O₅ and Mn₃O₄ were used for preparing ZnO based ceramics by solid state reaction technique according to the formula $x\text{Mn}_3\text{O}_4$ –0.5V₂O₅–(99.5– x)ZnO, where $x=0, 0.15, 0.30, 0.50, 0.75$ and 1.00 mol%. Weighed raw materials were mixed by ball-milling in exist of acetone for 28 h. The mixture was dried at 120 °C for 12 h. The dried mixture was milled using an agate mortar and after 0.8 wt% polyvinyl alcohol binder addition for 3 h. The powder was uniaxially pressed into discs of 12 mm in diameter and 1.5 mm in thickness at a pressure of 9500 psi. The discs were put

in porcelain crucible and sintered at 900 °C in air for 5 h, and then the furnace was cooled to room temperature. The sintered samples were lapped and polished to 1.0 mm thickness. Silver paste was coated on both surfaces of the samples, and the ohmic contacts were formed by heating at 300 °C for 5 min.

At first, both the sintered density and the Vicker's microhardness H_V were measured at room temperature 27 °C. The density ρ was determined by the Archimedes method with toluene as immersing liquid, while H_V was found by using a microhardness tester (HMV-2, Ver. 1.28, Shimatzu, Japan) where each sample was loaded at force equal to 4.902 N for 30 s and then H_V was estimated according to the relation $H_V = 0.1891P/d^2$, where P is the load applied and d is the diagonal length of indenter impression.

The current density–electric field (J – E) characteristics of the samples were recorded at room temperature. An electric circuit composed from a 500 V DC Gelman power supply (Model: 38207 ANN ARBOR, MICH., USA 48106), a digital multi-meter (GW Digital Multimeter Model: GDM-8034) and an auto ranging microvolt (Model: 197A DMM-Keithley) was used to measure the current passing through and voltage across the sample. The breakdown field (E_B) was measured at a current density of 1.0 mA/cm², and the leakage current density (J_L) was measured at $0.80E_B$. In addition, the non-ohmic coefficient (α) was determined from the current–voltage curve plotted on a log–log scale, from which the slope of the curve gives the value α [8].

Also, for doing microstructure investigations, both surfaces of the samples were lapped and ground with SiC paper and polished with 0.3 μ m Al₂O₃ powder to mirror-like surfaces. The polished samples were chemically etched using 1HCl:1000H₂O for 40 s and then coated with gold. The surface microstructure was then examined by a scanning electron microscope (SEM, JEOL, JSM5410, Japan). The average grain size (D) was determined by the linear intercept method using the expression $D = 1.56L/(MN)$ [33], where L is the random line length on the micrograph; M is the magnification of the micrograph; and N is the number of the grain boundaries intercepted by lines. The compositional elemental analysis of the selected areas on micrographs was determined by an attached energy dispersive X-ray analysis (EDX) system. The crystalline phases were identified by powder X-ray diffraction (XRD, X'pert-PRO MPD, Analytical,

Almelo, the Netherlands) with Cu K α radiation.

3 Results and discussion

3.1 Microstructure investigations

3.1.1 Density and microhardness

Figure 1 shows the compositional dependences of both the sintered density ρ and the Vicker's microhardness H_V of $x\text{Mn}_3\text{O}_4\text{--}0.5\text{V}_2\text{O}_5\text{--}(99.5\text{--}x)\text{ZnO}$ ceramics sintered at 900 °C for 5 h, where x changes from 0 to 1.00 mol%. This figure reveals that ρ and H_V are rapidly decreased with increasing the Mn₃O₄ content up to 0.15 mol%. Then, the density continues its decreasing up to 0.50 mol% of Mn₃O₄, while beyond this content it decreases slowly with the gradual increase of Mn₃O₄ up to 1.00 mol%. H_V has also slowly decreased as x increases from 0.15 mol% to 1.00 mol%, the end of tested range. Typical average results for both ρ and H_V are listed in Table 1. The obtained values for ρ in Table 1 are comparable with those reported for the same materials [17]. The above dependences of both ρ and H_V on the mole percentage of Mn₃O₄ content can be interpreted as follows. Although gradual replacement of ZnO (molecular weight 81.369) by the same amount of Mn₃O₄ (molecular weight 228.812) in the ZnO based varistor matrix is supposed to increase the molecular weight of prepared samples, the bulk density is decreased all over the tested range as seen in Fig. 1. Also, it is

Fig. 1 Compositional dependences of the sintered density ρ and the Vicker's microhardness H_V of $x\text{Mn}_3\text{O}_4\text{--}0.5\text{V}_2\text{O}_5\text{--}(99.5\text{--}x)\text{ZnO}$ ceramics sintered at 900 °C for 5 h, where x changes from 0 to 1.00 mol%.

Table 1 Average calculated values of density ρ , Vicker's microhardness H_V , molar volume V and grain size D as found from both XRD and SEM results

x (mol%)	ρ (g/cm ³)	H_V (MPa)	Molar volume V (cm ³ /mol)	Average grain size (XRD) D (nm)	Average grain size (SEM) D (μ m)
0.00	5.379	17.726	15.224	34.502	27.513
0.15	5.359	13.209	15.324	31.110	21.303
0.30	5.347	12.456	15.399	29.002	20.458
0.50	5.329	11.212	15.506	27.211	19.545
0.75	5.316	10.440	15.613	34.129	24.982
1.00	5.310	9.799	15.700	30.510	23.670

known that the density equals the molecular weight divided by the molar volume. This volume which increases due to the weak connectivity of the ceramic structure results in a decrease in microhardness of the varistor ceramics with increasing the Mn_3O_4 content (Table 1) in addition to the formation of some pores in the ZnO polycrystalline grains of varistor matrix by sintering at high temperature 900 °C (as will be seen in the SEM micrographs in Fig. 3). Thus, the observed decrease in density could be attributed analogously to an increase in the molar volume and the obtained decrease in microhardness due to the weakness of the structural connectivity and coupling between the ZnO grains [13]. On the other hand, it has been assumed that the decrease of sintered density is attributed to the volatility of V species for V_2O_5 with low melting point 690 °C [28].

3.1.2 XRD analysis

Figure 2 shows the dependence of XRD patterns of tested varistors on the mole percentage of Mn_3O_4 content. As indicated in Fig. 2, the observed diffraction graphs for all tested samples confirm the presence of the wurtzite hexagonal structure of the main ZnO primary phase. All diffraction peaks corresponding to this phase are indexed according to their reflection planes of polycrystalline Miller orientations (100), (002) and (101) [7,13,34] as indicated in Fig. 2 with (101) index having the high-intensity major peak. Besides, there are some secondary phases, such as $\text{Zn}_3(\text{VO}_4)_2$ appeared as a result of the presence of ZnO– V_2O_5 which acts as a liquid phase sintering aid for the formation of it [17,27–30] and Mn-rich Mn_3O_4 (for samples with $x=0.75$ mol% and $x=1.00$ mol%) [25,30]. The average crystallite size D is calculated in terms of X-ray line broadening at full width half maximum (FWHM) by using Scherer's equation [7,13,24] for all tested samples and the average values are summarized in Table 1.

Fig. 2 Dependence of XRD patterns of tested ceramic varistors on the mole percentage of Mn_3O_4 content.

3.1.3 SEM and EDX analyses

Figure 3 shows the SEM micrographs of the samples with different amounts of Mn_3O_4 (x from 0 to 1.00 mol%). Inspection of this figure reveals the occurrence of ZnO major phase of large grains, and other different minor phases with small grains disperse randomly in the former major one such as $\text{Zn}_3(\text{VO}_4)_2$ and Mn-rich Mn_3O_4 in addition to some pores (black regions), in agreement with Refs. [17,20] and the above XRD results (Fig. 2). Observed grains are of different sizes and are randomly distributed throughout the samples. The average value of grain size D of observed grains was calculated for all specimens according to the equation [33], and the typical average values are listed in Table 1. This table indicates that the values of D , even found from either XRD or SEM, have similarly changed with the gradual doping of Mn_3O_4 , in which D values decrease from 34.502 nm to 27.211 nm (XRD) and from 27.513 μ m to 19.545 μ m (SEM) with increasing the content of Mn_3O_4 from 0 up to 0.50 mol%. Then they increase up to 34.129 nm (XRD) and 24.982 μ m (SEM) upon increasing the Mn_3O_4 content to 0.75 mol%, and finally a slight decrease is observed in both D values to 30.510 nm (XRD) and 23.670 μ m (SEM) with increasing the content of Mn_3O_4 to 1.00 mol%, the end of tested range.

Figure 4 shows the EDX analyses for the ceramic varistors with $x = 0.15$, 0.50 and 1.00 mol% of Mn_3O_4 at the interior of ZnO grain as well as on the grain boundary. Within EDX detection limit, all figures show the existence of elements V, Mn and Zn both at the interior of ZnO grain and on the grain boundary, which indicates that both V and Mn species are dissolved in ZnO grains and reside on their boundaries as well. This will prove their effects on the electrical parameters as will be seen in the Section 3.2.2.

Fig. 3 SEM micrographs of $x\text{Mn}_3\text{O}_4-0.5\text{V}_2\text{O}_5-(99.5-x)\text{ZnO}$ samples: (a) $x=0.00$ mol%, (b) $x=0.15$ mol%, (c) $x=0.30$ mol%, (d) $x=0.50$ mol%, (e) $x=0.75$ mol% and (f) $x=1.00$ mol%.

Fig. 4 EDX analyses for the ceramic varistors with $x=0.15$, 0.50 and 1.00 mol% of Mn_3O_4 at the interior of ZnO grain ((a), (c) and (e)) and on the grain boundary ((b), (d) and (f)).

It is worth mentioning that the comparison of the compositional dependences of the grain size between EDX results observed here and those reported [17] for the same composition samples, indicates that the grain size is only consistent with those reported results in the x range from 0 to 0.50 mol% of Mn_3O_4 and differs beyond this content, where the previous reported results show that D is nearly constant in the range from 0.5 mol% to 2 mol% of Mn_3O_4 [17]. On the other hand, EDX results of this work show the existence of both V and Mn elements on the boundaries as well as in the ZnO grain (Fig. 4), while it was reported that no V spiece was found in the ZnO grains [17]. The above differences in both results may be because the preparation of specimens (grinding methods) and sintering times in the two works are different (5 h here and 3 h there), and only one specimen with $x=2$ mol% of Mn_3O_4 was presented there [17] for EDX analysis while specimens with lower contents $x=0.15$, 0.50 and 1.00 mol% of Mn_3O_4 are investigated in the present work.

3.2 Electrical characterization

3.2.1 Current density–electric field (J – E) characteristics

Figure 5 shows the compositional dependence of the current density–electric field (J – E) characteristics of $x\text{Mn}_3\text{O}_4$ – $0.5\text{V}_2\text{O}_5$ – $(99.5-x)\text{ZnO}$ ceramics prepared by solid state reaction technique and sintered at 900 °C for 5 h, where $x=0, 0.15, 0.30, 0.50, 0.75$ and 1.00 mol%. Inspection of Fig. 5 reveals that the varistor properties are basically characterized by non-ohmicity in all obtained J – E plots and each plot is divided into two regions, an ohmic region before the breakdown and a non-ohmic one after the breakdown with some overlap between them. However, the sharper the knee of the curves between the two regions is, the better the nonlinear properties are. Also, it can be noted from Fig. 5 that the plot corresponding to the un-doped sample

($x=0$ mol% of Mn_3O_4) shows very poor non-ohmic properties, but with increasing the Mn_3O_4 content, in other tested samples up to 0.50 mol%, the knee gradually becomes more pronounced and the non-ohmic properties are enhanced where the breakdown electric field E_B increases, and after the above content of Mn_3O_4 , the J – E characteristics show an overlap with more doping up to 1.00 mol%, which again results in a decrease in the breakdown field as seen in Fig. 5.

Using the J – E characteristics of Fig. 5, the breakdown electric field E_B , nonlinear coefficient α , leakage current density J_L , barrier height ϕ_B , donor concentration N_d , density of states N_s , barrier width ω and non-ohmic conductivity σ are calculated and their typical average values are summarized in Table 2.

3.2.2 Breakdown field and grain size

The compositional dependences of both the breakdown field E_B and average grain size D are shown in Fig. 6. From this figure, converse behaviors of changes are observed for the two parameters, as functions of the mole percentage of Mn_3O_4 content, i.e., E_B has increased and shows a peak value (1409 V/cm) at 0.50 mol% of Mn_3O_4 , whereas D decreases and has a

Fig. 5 Compositional dependence of J – E characteristics of tested varistor ceramics $x\text{Mn}_3\text{O}_4$ – $0.5\text{V}_2\text{O}_5$ – $(99.5-x)\text{ZnO}$, where $x=0, 0.15, 0.30, 0.50, 0.75$ and 1.00 mol%.

Table 2 Average calculated values of the breakdown field E_B , nonlinear coefficient α , leakage current density J_L , barrier height ϕ_B , donor concentration N_d , density of states N_s , barrier width ω and non-ohmic conductivity σ

x (mol%)	E_B (V/cm)	α	J_L (mA/cm ²)	ϕ_B (eV)	N_d (10 ¹⁸ cm ⁻³)	N_s (10 ¹² cm ⁻²)	Barrier width ω (nm)	Non-ohmic conductivity σ (10 ⁻⁴ (Ω ·m) ⁻¹)
0.00	118.30	5.33	0.6611	0.837	1.13	2.98	26.40	89.30
0.15	229.10	5.63	0.7713	0.856	0.88	2.71	30.66	5.33
0.30	493	11.36	0.6026	0.879	0.83	2.62	31.52	3.28
0.50	1409	16.29	0.4419	0.916	0.77	2.57	33.47	0.18
0.75	1138	7.62	0.5844	0.894	0.20	1.30	64.74	0.38
1.00	1907	14.66	0.5028	0.909	0.16	1.18	72.51	0.09

Fig. 6 Compositional dependences of both the breakdown field E_B and average grain size D of $x\text{Mn}_3\text{O}_4-0.5\text{V}_2\text{O}_5-(99.5-x)\text{ZnO}$ ceramics.

trough value (19.545 μm), and vice versa is occurred at 0.75 mol% of Mn_3O_4 . On the other hand, on increasing the mole percentage of Mn_3O_4 beyond 0.75 mol% up to 1.00 mol%, E_B increases and D decreases (Tables 1 and 2). This obtained behavior of change of E_B could be interpreted based on the changes observed in the average value of grain size D , i.e., the initial increase of E_B with the increase of Mn_3O_4 content up to 0.50 mol% is owing to the increase in the number of grain boundaries [17,26–30] which is resulted from the corresponding decrease in the average grain size and vice versa in the final part, the rest of tested range up to 1.00 mol%.

3.2.3 Nonlinear coefficient and leakage current density

Variations of the nonlinear coefficient α and the leakage current density J_L as functions of the mole percentage of Mn_3O_4 content of tested ceramics are shown in Fig. 7. Inspection of this figure reveals that α increases from 5.33 for the un-doped sample to 16.29 reaching this maximum for that which doped with 0.50 mol% of Mn_3O_4 , whereas further additions of Mn_3O_4 have led α to decrease and reach the value of 7.62 at 0.75 mol% of Mn_3O_4 and then increase again to 14.66 at 1.00 mol% of Mn_3O_4 content. On the other hand, J_L value decreases from 0.6611 mA/cm^2 with the increase of Mn_3O_4 amount from $x=0$ up to 0.50 mol% reaching a minimum value, 0.4419 mA/cm^2 at $x=0.50$ mol%, whereas further additions of Mn_3O_4 have led J_L to increase to 0.5844 mA/cm^2 at 0.75 mol% and decrease to 0.5028 mA/cm^2 at $x=1.00$ mol% of Mn_3O_4 content to show an opposite behavior to that observed for α . The behaviors of both the nonlinear coefficient α and the leakage current density J_L mentioned above are related to the variation of the density of interface states

Fig. 7 Variations of average values of the nonlinear coefficient α and the leakage current density J_L as functions of mole percentage of Mn_3O_4 content.

N_s at the grain boundaries, and subsequently they are dependent on the Schottky barrier height ϕ_B according to the variation of the concentration of electronic donor states N_d (Table 2). It is worth mentioning that the observed value of $\alpha=16.29$ for the ceramic doped with 0.50 mol% of Mn_3O_4 in this work is less than that reported for the same ceramic which was 22.4 [17]. This is perhaps due to different conditions of preparation and soaking time (5 h here and 3 h there) in spite of the two works were done at the same sintering temperature 900 $^{\circ}\text{C}$.

3.2.4 Barrier height and donor concentration

The donor concentration N_d and barrier height ϕ_B were determined by using the grain boundary defect model [5,6] defined previously in the introduction part of this work as

$$J = AT^2 \exp[(\beta E^{1/2} - \phi_B)/(kT)]$$

where by considering the measured current density–electric field values in the ohmic region for all samples (Fig. 5), keeping the temperature constant (at room temperature 27 $^{\circ}\text{C}$) and plotting $\ln J$ versus $E^{1/2}$, the values of β and ϕ_B can be derived from the obtained slopes and intersections of the extrapolated regression lines with the $\ln J$ axis, respectively. Also, since [32,34]

$$\beta = [(1/(r^* \omega))(2e^3/(4\epsilon_0 \epsilon_r))]^{1/2}$$

where r^* is the number of grains per unit length (it could be obtained from SEM micrographs (Fig. 3)); ω is the barrier width; e is the electron charge; ϵ_0 is the vacuum dielectric constant (8.85×10^{-14} F/cm); and ϵ_r is the relative dielectric constant (8.5 for ZnO), then N_d can be deduced from the equation [35]:

$$\omega^2 = (2\phi_B \epsilon_0 \epsilon_r)/(e^2 N_d)$$

and thus the density of states $N_s = N_d \cdot \omega$ [28] can also be determined and typical values for these parameters

are listed in Table 2. The variations of both the barrier height and donor density with the mole percentage of Mn_3O_4 content in tested varistors are shown in Fig. 8.

The illustrated figure (Fig. 8) indicates that ϕ_B increases from 0.837 eV to 0.916 eV by Mn_3O_4 addition up to 0.50 mol%, then decreases to 0.894 eV with the gradual doping of Mn_3O_4 up to 0.75 mol% and then increases to 0.909 eV at 1.00 mol% of Mn_3O_4 content. This behavior agrees with that one where it has been reported that the incorporation of Mn_3O_4 above 0.50 mol% causes the electronic inactivity of grain boundaries [17]. Anyhow, the nonlinear electrical conductivity σ shows an opposite behavior to that observed for the barrier height ϕ_B (Table 2). On the other hand, the donor density N_d shows a decrease from $1.13 \times 10^{18} \text{ cm}^{-3}$ to $0.12 \times 10^{18} \text{ cm}^{-3}$ with increasing of Mn_3O_4 content from 0 to 1.00 mol%.

3.2.5 General discussion

In general, the above characterizations of physical properties, density and microhardness in addition to microstructural and electrical properties of the tested $x\text{Mn}_3\text{O}_4-0.5\text{V}_2\text{O}_5-(99.5-x)\text{ZnO}$ ceramics, x changing from 0 to 1.00 mol%, reveal that all investigated properties are dependent on the ceramic composition rather than the secondary phases, i.e., on the mole percentage of Mn_3O_4 doping content, the different measurements obtained from employed techniques in this work show no monotonic behaviors of changes for investigated properties. Anyhow, the effect on the properties depends on the manner in which the Mn ions enter the ZnO major matrix of the hexagonal structure wurtzite phase. When Mn is dissolved in these ZnO grains, it can behave as a deep donor [13]

Fig. 8 Variations of the barrier height ϕ_B and the donor density N_d with the mole percentage of Mn_3O_4 content.

and depress the concentrations of the intrinsic donors (oxygen vacancies). In this way, the conductivity, mainly arising from ionization of intrinsic donors, is lowered on doping up to 0.50 mol% of Mn_3O_4 content. This helps to increase the nonlinear coefficient α and the barrier height ϕ_B , and decrease the donor density N_d and the conductivity σ (Figs. 7 and 8 and Table 2). On the other hand, with increasing Mn content through the interstitial positions, it can behave as an acceptor and has its effect to decrease the nonlinear coefficient and the height barrier ϕ_B as observed in the above mentioned figures. Also, the behavior of nonlinear coefficient α , in accordance with the incorporation of mole percentage of Mn_3O_4 , can be related to the variation of the Schottky barrier height ϕ_B according to the variation of the density of electronic states N_s , the donor concentration N_d and the barrier width ω at the grain boundaries (Table 2). The doping of Mn_3O_4 into the ceramic matrix has decreased the density of interface states N_s , donor concentration N_d and increased the barrier width ω as seen in Table 2. It is therefore believed that the decrease of donor concentration N_d with the increase of Mn_3O_4 content is associated with a decrease of partial pressure of oxygen in the materials [17]. The variation in α with further increase in Mn_3O_4 is attributed to the variation of barrier height ϕ_B as observed in Table 2.

The ceramic microstructure has also been affected by the incorporation of Mn_3O_4 into the ceramic matrix, where obtained results show that the gradual substitution of ZnO by the same amount of Mn_3O_4 up to 0.50 mol% has led to:

(1) Decreasing the ceramic density and the Vicker's microhardness due to the produced increase in the molar volume and the decrease in the connectivity of the microstructure as well as weak coupling between the ZnO grains, respectively (Fig. 1 and Table 1). These results are consistent with SEM photographs (Fig. 3) where the grains are not close together through the weak link regions, i.e., the dark region (pores) between them.

(2) Decreasing the average grain size D due to the resulted increase in the number of grain boundaries and hence the breakdown electric field E_B is increased. However, further increases in Mn_3O_4 content from 0.50 mol% to 0.75 mol% and from 0.75 mol% to 1.00 mol% has increased and decreased the average grain size, respectively, to show their reverse behaviors for the obtained breakdown electric field.

4 Conclusions

Microstructure, sintered density, Vicker's microhardness and electrical properties of varistor ceramics prepared by solid state reaction having compositional formula $x\text{Mn}_3\text{O}_4-0.5\text{V}_2\text{O}_5-(99.5-x)\text{ZnO}$, $x=0, 0.15, 0.30, 0.50, 0.75$ and 1.00 mol%, were investigated. Both the microhardness and the sintered density of varistor samples have decreased with increasing the Mn_3O_4 content. XRD and SEM investigations show the presence of the major ZnO wurtzite phase of hexagonal structure and some secondary phases, such as $\text{Zn}_3(\text{VO}_4)_2$ and Mn-rich Mn_3O_4 .

Also, the results obtained from $J-E$ show that, all electrical properties: breakdown field, nonlinear coefficient, the Schottky barrier height, barrier width, the conductivity of nonlinear region, donor concentration and density of surface states at ZnO grain boundaries of the samples tested are dependent on the microstructure, i.e., on the grain size of existed phases, mentioned above, which affect the breakdown field. It is worth mentioning that the $99\text{ZnO}-0.5\text{V}_2\text{O}_5$ ceramic which doped with 0.50 mol% Mn_3O_4 and sintered at 900°C for 5 h has exhibited optimum value for the nonlinear coefficient (16.29), the lowest leakage current density (0.4419 mA/cm^2) and the highest potential barrier height (0.916 eV). This shows that the above sample can be used in the manufacture of low-voltage varistors and multilayer components.

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References

- [1] Gupta TK. Application of zinc oxide varistors. *J Am Ceram Soc* 1990, **73**: 1817–1840.
- [2] Peiteado M, Fernández JF, Caballero AC. Processing strategies to control grain growth in ZnO based varistors. *J Eur Ceram Soc* 2005, **25**: 2999–3003.
- [3] Levinson LM, Philipp HR. Zinc oxide varistors—A review. *Am Ceram Soc Bull* 1986, **65**: 639–646.
- [4] Deshpande VV, Patil MM, Ravi V. Low voltage varistors based on CeO_2 . *Ceram Int* 2006, **32**: 85–87.
- [5] Pianaro SA, Bueno PR, Longo E, et al. A new SnO_2 -based varistor system. *J Mater Sci Lett* 1995, **14**: 692–694.
- [6] Dhage SR, Ravi V, Yang OB. Low voltage varistor ceramics based on SnO_2 . *Bull Mater Sci* 2007, **30**: 583–586.
- [7] Sedky A, Al-Sawalha A, Yassin AM. Enhancement of electrical conductivity of ZnO ceramic varistor by Al doping. *Egyptian Journal of Solids* 2008, **31**: 205–215.
- [8] Matsuoka M. Nonohmic properties of zinc oxide ceramics. *Jpn J Appl Phys* 1971, **10**: 736.
- [9] Glot AB. A model of non-ohmic conduction in ZnO varistors. *J Mater Sci: Mater El* 2006, **17**: 755–765.
- [10] Inada M. Formation mechanism of nonohmic zinc oxide ceramics. *Jpn J Appl Phys* 1980, **19**: 409.
- [11] Houabes M, Bernik S, Talhi C, et al. The effects of aluminium oxide on the residual voltage of ZnO varistors. *Ceram Int* 2005, **31**: 783–789.
- [12] Bernik S, Daneu N. Characteristics of ZnO-based varistor ceramics doped with Al_2O_3 . *J Eur Ceram Soc* 2007, **27**: 3161–3170.
- [13] Sedky A, El-Suheel E. A comparative study between the effects of magnetic and nonmagnetic dopants on the properties of ZnO varistors. *Physics Research International* 2010, **2010**: 120672.
- [14] Sedky A, Abu-Abdeen M, Almulhem AA. Nonlinear $I-V$ characteristics in doped ZnO based-ceramic varistor. *Physica B* 2007, **388**: 266–273.
- [15] Sawalha A, Abu-Abdeen M, Sedky A. Electrical conductivity study in pure and doped ZnO ceramic system. *Physica B* 2009, **404**: 1316–1320.
- [16] Gupta TK. Microstructural engineering through donor and acceptor doping in the grain and grain boundary of a polycrystalline semiconducting ceramics. *J Mater Res* 1992, **7**: 3280–3295.
- [17] Nahm CW. Improvement of electrical properties of V_2O_5 modified ZnO ceramics by Mn-doping for varistor applications. *J Mater Sci: Mater El* 2008, **19**: 1023–1029.
- [18] Nahm C-W. The nonlinear properties and stability of $\text{ZnO-Pr}_6\text{O}_{11}\text{-CoO-Cr}_2\text{O}_3\text{-Er}_2\text{O}_3$ ceramic varistors. *Mater Lett* 2001, **47**: 182–187.
- [19] Nahm C-W. $\text{ZnO-Pr}_6\text{O}_{11}\text{-CoO-Cr}_2\text{O}_3\text{-Er}_2\text{O}_3$ -based ceramic varistors with high stability of nonlinear properties. *J Mater Sci Lett* 2002, **21**: 201–204.
- [20] Tsai JK, Wu TB. Non-ohmic characteristics of $\text{ZnO-V}_2\text{O}_5$ ceramics. *J Appl Phys* 1994, **76**: 4817.
- [21] Tsai J-K, Wu T-B. Microstructure and nonohmic properties of binary $\text{ZnO-V}_2\text{O}_5$ ceramics sintered at 900°C . *Mater Lett* 1996, **26**: 199–203.
- [22] Kuo C-T, Chen C-S, Lin I-N. Microstructure and nonlinear properties of microwave-sintered $\text{ZnO-V}_2\text{O}_5$ varistors: I, Effect of V_2O_5 doping. *J Am Ceram Soc* 1998, **81**: 2942–2948.

- [23] Hng HH, Knowles KM. Characterisation of $\text{Zn}_3(\text{VO}_4)_2$ phases in V_2O_5 -doped ZnO varistors. *J Eur Ceram Soc* 1999, **19**: 721–726.
- [24] Hng HH, Halim L. Grain growth in sintered ZnO–1 mol% V_2O_5 ceramics. *Mater Lett* 2003, **57**: 1411–1416.
- [25] Nahm C-W. Effect of Mn doping on electrical properties and accelerated ageing behaviours of ternary ZVM varistors. *Bull Mater Sci* 2011, **34**: 1385–1391.
- [26] Nahm C-W. Nb_2O_5 doping effect on electrical properties of ZnO– V_2O_5 – Mn_3O_4 . *Ceram Int* 2012, **38**: 5281–5285.
- [27] Nahm C-W. Non-ohmic properties and impulse aging behavior of quaternary ZnO– V_2O_5 – Mn_3O_4 – Er_2O_3 semiconducting varistors with sintering processing. *Mat Sci Semicon Proc* 2013, **16**: 1308–1315.
- [28] Nahm C-W. Characteristics of ZnO– V_2O_5 – MnO – Nb_2O_5 – Er_2O_3 semiconducting varistors with sintering processing. *Mat Sci Semicon Proc* 2013, **16**: 778–785.
- [29] Nahm C-W. Effect of erbium on varistor characteristics of vanadium oxide-doped zinc oxide ceramics. *J Mater Sci: Mater El* 2013, **24**: 27–35.
- [30] Nahm C-W. Varistor characteristics of vanadium oxide-doped zinc oxide ceramics modified with bismuth oxide. *J Mater Sci: Mater El* 2013, **24**: 70–78.
- [31] Hng HH, Chan PL. Microstructure and current–voltage characteristics of ZnO– V_2O_5 – MnO_2 varistor system. *Ceram Int* 2004, **30**: 1647–1653.
- [32] Liu H-Y, Kong H, Ma X-M, *et al.* Microstructure and electrical properties of ZnO-based varistors prepared by high-energy ball milling. *J Mater Sci* 2007, **42**: 2637–2642.
- [33] Wurst JC, Nelson JA. Lineal intercept technique for measuring grain size in two-phase polycrystalline ceramics. *J Am Ceram Soc* 1972, **55**: 109–111.
- [34] Senthilkumaar S, Rajendran K, Banerjee S, *et al.* Influence of Mn doping on the microstructure and optical property of ZnO. *Mat Sci Semicon Proc* 2008, **11**: 6–12.
- [35] Morris WG. Physical properties of the electrical barriers in varistors. *J Vac Sci Technol* 1976, **13**: 926–931.