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Synchronously Improved Voltage Gradient and Mechanical Properties of ZnO Based Varistor by Doping Ga₂O₃

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Abstract: ZnO based varistors with high voltage gradient and excellent mechanical and thermal properties were fabricated by Ga₂O₃ doping and using nanoparticles. The compositions and microstructure of the varistors, as well as their electrical, mechanical and thermal properties were investigated by XRD, XPS, SEM, E-J, C-V, mechanical and thermal expansion measurements. Also, the mechanism of Ga₂O₃ addition on electrical and mechanical properties of the varistors was discussed detailedly. Results showed that the added Ga₂O₃ preferentially occupied the lattice position of ZnO crystal through the formation of a substitutional solid solution (Donor doping), they then occupied the void position through the formation of an interstitial solid solution (Acceptor doping), in which residual Ga₂O₃ existed in the grain boundary and served as inversion boundaries. The formation of the substitutional and interstitial solid solutions helped to improve the electrical properties, when the Ga₂O₃ content was 0.40 mol%, E_{1mA} , α and K were 1235.00 V·mm⁻¹, 46.0 and 1.37, respectively, being due to the small particle size and the relative content of donor, acceptor and grain boundary in ZnO grain; The increased content of inversion boundaries stimulated the abnormal growth of ZnO grain, and the formed plate-like grain helped to improve the mechanical properties and thermal expansion coefficient of the varistors, values of σ_f , E_f , and K_{IC} reached 147.43 MPa, 213.61 GPa and 2.05 MPa·m^{1/2}, showing improvements of 25.29%, 47.67%, and 38.51%, respectively, compared with those of ZnO varistors without Ga₂O₃.

Key words: ZnO-based varistors; doping Ga₂O₃; high voltage gradient; abnormal grain growth; mechanical properties

1. Introduction

ZnO varistors are a typical polycrystalline ceramic obtained by sintering ZnO powder with minor primary additives, such as Bi_2O_3 , Pr_6O_{11} and V_2O_5 [1-3], and secondary additives such as Sb_2O_3 , SiO_2 , Co_2O_3 , MnO_2 , Al_2O_3 , Cr_2O_3 , Ni_2O_3 , Ga_2O_3 , and In_2O_3 [4, 5], it mainly works as a surge-protection device and is extensively applied in electronic and electrical systems to limit overvoltage [6, 7]. Therefore, voltage gradient of ZnO varistors is an important parameter for evaluating the performance of ZnO varistors, which can be improved through sintering modification [1, 8, 9], particle-size choice [6], and composition design [3-5, 10, 11]. For these three protocols, improving the electrical properties via composition design possesses the advantages of easy operation, wide adjustment of electrical properties, and excellent comprehensive properties of the obtained varistors, among others. Accordingly, many researchers focus on this field [12-14].

Multiple donor such as Al^{3+} , Ga^{3+} , In^{3+} , or Y^{3+} trivalent ion metallic oxide have been alternatively employed to enhance the comprehensive performance of ZnO varistor for their special electronic donor structure as well as similar ion radius between these ions and Zn^{2+} [4, 5, 15], while the multiple dopants may result in a lower voltage gradient, $517 \text{ V}\cdot\text{mm}^{-1}$ [4], $479 \text{ V}\cdot\text{mm}^{-1}$ [15] and $475 \text{ V}\cdot\text{mm}^{-1}$ [16], although other electrical properties of the obtained ZnO varistor are excellent, such as lower residual voltage(1.60) and leakage current($0.96 \mu\text{A}\cdot\text{cm}^{-2}$) as well as the higher nonlinear coefficient(87) [4], it still hinders the application of these ZnO varistor in high voltage field. Several researchers focus on the effect of single Ga_2O_3 addition on the varistor characteristics of ZnO varistor [17, 18], and the associated mechanism has been reported [4], while the disadvantage of lower voltage gradient has not been solved. Liu [6] and Vukovic [19] report that the voltage gradient of ZnO varistors can be improved by using nanoparticles as main raw materials. In addition, according to Danzer's opinion, the reason for mechanical and electrical failure of ZnO varistors is correlated. Therefore, a high strength of varistor material are both beneficial for its electrical strength and reliability [20, 21]; on the other hand, Raidl thinks that the electrical barriers at the grain boundaries of ZnO varistors are altered by mechanical stresses, which is derived from the externally applied stress as well as micro stresses that evolve naturally during fabrication of materials with anisotropic thermal expansion coefficients [22], namely, the coefficient of thermal expansion (CTE) could also affect the electrical strength and reliability of ZnO varistors.

In summary, the electrical properties of the trivalent ion metallic oxide doped ZnO varistors have been extensively studied [23, 24], but it still exists some deficiencies(such as lower voltage gradient), also the effect of dopants on the mechanical and thermal properties of ZnO varistors is rarely reported. In this work, we introduced various Ga additives into a ZnO based varistor and selected nano-ZnO particles as the main raw materials to try to

improve the voltage gradient and mechanical properties, modify the thermal properties of ZnO based varistors at same time. Furthermore, the mechanism of improving the electrical, thermal and mechanical properties of ZnO based varistors was studied system and some interesting results were obtained.

2. Experimental procedure

2.1 Raw materials

All oxides used were 99.9% pure and commercially obtained from Aladdin company. Nano-ZnO powders with particle sizes of 30 ± 10 nm were used as the main materials. Other oxides such as Bi_2O_3 , Sb_2O_3 , Co_2O_3 , SiO_2 , MnO_2 , Cr_2O_3 , and Ga_2O_3 with particle sizes of 1.0 ± 0.5 μm served as additives.

2.2 Preparation of the Ga_2O_3 doped ZnO based varistors

The composition design of the Ga_2O_3 doped ZnO based varistors followed Ref. [4] with a minor adjustments: (95.0– x) mol% ZnO, 1.0 mol% Bi_2O_3 , 1.0 mol% Sb_2O_3 , 1.0 mol% Co_2O_3 , 1.0 mol% SiO_2 , 0.5 mol% MnO_2 , 0.5 mol% Cr_2O_3 , and x mol% Ga_2O_3 ($x = 0, 0.20, 0.40, 0.60, 0.80$).

Oxides at appropriate ratios were mixed until homogenization by using a planetary mill, where alcohol was used as the medium and ZrO_2 ball was the abrasive. The homogenized mixture was dried at 80 °C to remove alcohol, and then a small amount of PVA binder solution was added into the dried mixture. After subjecting to an aging process, the mixture was pressed at 100 MPa into disks with 30 mm diameter and 3.0 mm thickness. These disks were sintered at different temperatures and holding time at a heating rate of 4 °C·min⁻¹ and a cooling rate of 2 °C·min⁻¹ in air. After sintering, the upper and lower surfaces of ZnO varistor samples were polished and then covered with silver paste, and then these samples were heated at 600 °C for 10 min in air to form electrodes [1].

The corresponding ZnO based varistors were labeled as GaX- T - t , where index GaX represented the amount of Ga_2O_3 , T was the sintered temperature in degrees Celsius, and t was the holding time at the sintered temperature.

2.3 Characterization of the Ga_2O_3 doped ZnO based varistors

Bulk density of ZnO based varistors were measured using Archimedes method [25] .

The phase constitution of ZnO based varistor was analyzed via an in-situ X-ray diffraction analysis (XRD, Smartlab, Rigaku, Japan) when $\text{Cu } K_\alpha$ worked as radiation and surface of the varistor was pre-polished. 2θ ranged between 10° and 70° and the scan speed was 1°·min⁻¹.

Microstructure of ZnO based varistor was examined via scanning electron microscopy (SEM, Regulus 8100, Hitachi, Japan) when the surface of specimen was pre-polished and glass phase was removed via etching method [1].

The electric field-current density (E - J) characteristic of ZnO based varistor was obtained via a source measurement unit (Keithley 2410, USA). The voltage gradient (E_{1mA}) is the breakdown voltage at a unit height, and the leakage current (J_L) is determined at $0.75 U_{1mA}$, the nonlinear coefficient (α) is defined by Eq(1)^[1]:

$$\alpha = \frac{\log(J_2 / J_1)}{\log(E_2 / E_1)} \quad (1)$$

Where E_2 is the corresponding electric field at $J_2 = 1 \text{ mA} \cdot \text{cm}^{-2}$ and E_1 is the corresponding electric field at $J_1 = 0.1 \text{ mA} \cdot \text{cm}^{-2}$. The residual voltage ratio K is calculated according to Eq(2):

$$K = U_n / U_{1mA} \quad (2)$$

Where U_n is the voltage under a current density of $63.7 \text{ A} \cdot \text{cm}^{-2}$, which is the standard requirement for the surge arresters applied in ultrahigh voltage (1000 kV AC) system^[23].

The capacitance-voltage (C - V) measurement of ZnO based varistor was determined under DC bias voltages using a broadband dielectric device (Novocontrol Concept 80, Germany). The most important parameters related to the Schottky barrier, including barrier height (ϕ_b), donor density (N_d) and interface state density (N_s), these values can be calculated according to Eq(3)^[4]:

$$\left(\frac{1}{C} - \frac{1}{2C_0} \right)^2 = \frac{2(\phi_b + V_{gb})}{q \cdot \varepsilon_s \cdot N_d} \quad (3)$$

In which C is the capacitance at a unit area for a single grain boundary when biased voltage for a single grain boundary is V_{gb} , C_0 is the capacitance when $V_{gb} = 0$, q is the electronic charge, and ε_s is the permittivity of ZnO grain. ϕ_b and N_d are calculated via the intercept and the slope of the curve of $\left(\frac{1}{C} - \frac{1}{2C_0} \right)^2$ versus V_{gb} , respectively. Besides, after getting ϕ_b and N_d , N_s is obtained by equations (4)^[4]:

$$N_s = \sqrt{\frac{2 \cdot \varepsilon_s \cdot N_d \cdot \phi_b}{q}} \quad (4)$$

An Instron 3382 universal electronic experimental machine was conducted the mechanical properties measurement of ZnO based varistor. All specimens were grind and the tensile surfaces were polished better than $1 \mu\text{m}$ in advance, the edge of specimen was beveled to avoid stress concentration during testing. The size of the specimen were 3 mm (height) $\times$ 2 mm (width) $\times$ 30 mm (length), a batch of five specimens was tested and the obtained values were averaged. Three - point flexural strength (σ_f) of the varistor was measured in a span of 20 mm and a loading rate of 0.5 mm min^{-1} , the slope of stress-strain curve can be used to calculate the modulus of elasticity (E_f). The fracture toughness (K_{IC}) of the specimen was measured via the single-edge-notched- beam method

(SENB), with a span of 20 mm and a loading velocity of 0.5 mm min⁻¹, notches were incised in the middle of the specimen along the height with a width of 0.3 mm to the depth of about 0.2 mm^[26].

The coefficient of thermal expansion (CTE) of ZnO based varistor was measured via a high-temperature dilatometer (Model DIL 402E, Netzsch, Selb, Germany) under an air atmosphere with a heating rate of 10 °C min⁻¹.

3 Results and discussion

3.1 Influences of sintering process on the composition and microstructure of ZnO based varistors

3.1.1 Volume density and linear shrinkage of ZnO based varistors

Bulk density plays an important role in the electrical properties of ZnO varistors^[25]. Figure 1 (a) shows the measured bulk density (ρ) of ZnO varistors sintered at different temperatures for 2 h. Clearly, with increased sintered temperatures, value of ρ initially increased and then decreased. All reached the maximum at 1100 °C due to particle growth and densification behavior^[8]; Moreover, with increased Ga₂O₃ addition, ρ initially increased and then decreased, and when the addition of Ga₂O₃ was 0.4 mol% and the sintering temperature was 1100 °C, ρ reached the maximum (5.59 g·cm⁻³). According to Wang opinion, when the addition of Ga₂O₃ was lower, Ga³⁺ preferentially occupied the lattice position of ZnO crystal via the formation of a substitutional solid solution, further increased Ga₂O₃ addition resulted in a partially occupied void position and partially occupied lattice position of ZnO crystal because of the smaller ion radii (0.062 nm for Ga³⁺ and 0.075 nm for Zn²⁺)^[27]. The formation of a Ga³⁺ solid solution in ZnO crystal could reduce the lattice energy^[28], and the small particle size of raw ZnO (30 nm) could reduce the sintering activation energy^[6], both factors helped improve the densification of ZnO varistors^[6]. When the addition of Ga₂O₃ exceeded 0.04 mol%, some additives may existed in the grain boundary of ZnO crystal to inhibit ZnO grain growth and reduce the density of the ZnO varistors^[4].

Figure 1 (b) shows the ρ value of the ZnO varistors for different holding times at 1100 °C. Similar trends can be observed, as shown in Fig. 1. When the holding time was 2 h, all values reached maximum. Thus, more detailed research should focus on ZnO varistors sintered at 1100 °C for 2 h.

Please insert Figure 1 here

Please insert Figure 2 here

3.1.2 Phase identification of ZnO based varistors

The surface of ZnO based varistors was polished to analyze their composition with a slow scan speed of $1^\circ \cdot \text{min}^{-1}$, and results are shown in Figure 2. As shown in Fig.2-a, the main composition of 6H-ZnO phase (JCPDS no.79-2205), a small amount of spinel phase $\text{Zn}_7\text{Sb}_2\text{O}_{12}$ (JCPDS no.36-1445), Zn_2SiO_4 phase (JCPDS no.70-1235), $\beta\text{-Bi}_2\text{O}_3$ (JCPDS no.78-1793), and $\gamma\text{-Bi}_2\text{O}_3$ (JCPDS no.76-2478) were detected in ZnO varistors regardless of Ga_2O_3 amount, similar to the findings of Fu [1] and Zhao [4]. The Ga_2O_3 phase was not observed in the specimens, which can be attributed to the small amount [4].

An interesting appearance can be observed in Fig.2-b that with increased Ga_2O_3 addition, diffraction peak of ZnO firstly moved toward a higher degree and then moved back, as we know that the ion radius of Ga^{3+} is slightly smaller than that of Zn^{2+} , so when the amount of Ga^{3+} added was small (e.g., $x = 0.2$, Ga0.2-1100-2h), it prioritized occupying the lattice position of ZnO in the form of a substitutional solid solution, causing the lattice constant of ZnO crystal to decrease and the diffraction peak to move toward a higher degree; When the addition of Ga_2O_3 was further increased, most Ga^{3+} ions still occupied the lattice position, whereas some Ga^{3+} ions began to occupy the pores of ZnO crystal, which could cause the lattice constant to increase and the diffraction peak to move toward a lower degree, similar to the findings of Qiu [29], and the residual Ga_2O_3 could exist in the grain boundary but did not affect the lattice constant of ZnO crystal (e.g., $x \geq 0.4$). Thus, the shift of the ZnO diffraction peak resulted from the interaction of these two effects, as shown in Figure 2 (b).

Please insert Figure 2 here

To increase understanding of the composition and chemical states, XPS spectra of Zn_{2p} , Bi_{4f} , and Ga_{2p} of ZnO varistors with different Ga_2O_3 contents were obtained and were displayed in Figure 3. The collected spectra were analyzed with XPSPEAK software, and a Shirley type background subtraction was used to fit the curve [30]. The binding energy (B.E.) and relative ratio (R.R. calculated from the relative area) under deconvoluted XPS peaks are listed in Table 1.

In the survey spectrum (Fig. 3(a)), peaks associated with Zn_{2p} , Bi_{4f} , and Ga_{2p} were detected. In the high-resolution spectra obtained for the Zn_{2p} region (Fig. 3 (b)), two peaks corresponding to $\text{Zn } 2p_{1/2}$ and $\text{Zn } 2p_{3/2}$ at B.E. values of ~ 1021.40 and ~ 1044.50 eV were located and attributed to the existence of ZnO [31]. Fig. 3(c) depicted the high-resolution spectra obtained for Bi_{4f} region. The B.E.s at ~ 164.41 and ~ 158.90 eV were ascribed to $\text{Bi } 4f_{5/2}$ and $\text{Bi } 4f_{7/2}$, respectively. The separation between $\text{Bi } 4f_{7/2}$ and $\text{Bi } 4f_{5/2}$ was about 5.5 eV, which was

characteristic of Bi^{3+} in $\beta\text{-Bi}_2\text{O}_3$ according to a previous report^[32]. Moreover, the B.E.s at ~ 165.02 and ~ 159.50 eV were ascribed to $\text{Bi } 4f_{5/2}$ and $\text{Bi } 4f_{7/2}$ of Bi^{3+} in $\gamma\text{-Bi}_2\text{O}_3$, respectively^[33]. Interestingly, with increased Ga_2O_3 content, the ratio of $\gamma\text{-Bi}_2\text{O}_3$ to $\beta\text{-Bi}_2\text{O}_3$ slightly moved to 1:1, as listed in Table 1.

As shown in Fig. 3(d), the B.E. peaks of Ga_{2p} spectra were at 1116.22, 1116.60, and 1117.02 eV, corresponding to the substitutional solid solution, interstitial solid solution, and boundary phase of Ga_2O_3 in ZnO crystal, respectively^[27, 34, 35]. It can be seen that with the increase of Ga_2O_3 content, the abundance ratio of $a/b/c$ calculated from the area under the peaks exhibited that Ga^{3+} preferentially formed a substitutional solid solution in ZnO crystal (as $a/b/c = 0.63:0.18:0.19$ in Ga0.20-1100-2h); with increased Ga^{3+} content, the amounts of Ga^{3+} for the formation of substitutional solid solution was still higher than that for the formation of interstitial solid solution, while the amount of Ga_2O_3 in the grain boundary increased quickly, and acted as the main phase when content of Ga_2O_3 equaled to 0.8 (as $a/b/c = 0.32 : 0.20 : 0.48$ in Ga0.80-1100-2h), similar to Wang's result^[27]. High content of Ga_2O_3 in the grain boundary might affect the grain growth behavior of ZnO varistors.

Please insert Figure 3 here

Please insert Table 1 here

Figure 4 shows the absolute amount of Ga^{3+} for different distribution positions with the increased Ga_2O_3 content. It can be seen that with the increase of Ga_2O_3 content, the amount of Ga^{3+} in three forms monotonically increased, and that of substitutional solid solution was always higher than the interstitial solid solution, the amount of grain boundary phase increased steeply, it exceeded the amount of substitutional solid solution when content of Ga_2O_3 exceeded 0.60 mol%; the difference between the amount of substitutional solid solution and interstitial solid solution reached maximum when content of Ga_2O_3 equaled to 0.40 mol%.

Please insert Figure 4 here

3.1.3 Microstructure characteristics of ZnO based varistors

The SEM images of ZnO based varistors with various Ga_2O_3 contents are presented in Figures 5 (a)- (e). The average grain size (d) and maximum and minimum aspect ratios of these specimens determined by the lineal intercept method are exhibited in Figure 5 (f). Interestingly, with increased Ga_2O_3 content, the particle shape of

ZnO varistors transformed from ellipse into plate-like, similar to Daneu's report [36], for examples, particle shapes of Ga0.00-1100-2h exhibited typical ellipse, while that of Ga0.20-1100-2h displayed obviously plate-like, a further increased Ga₂O₃ content resulted in an increased aspect ratios of plate-like particles for ZnO varistors, as shown in Figure 5 (f). According to Zhao's report, no plate-like grain was observed even after adding 1.44 mol% Ga₂O₃ and calcination at 1200 °C for 2 h in ZnO-Bi₂O₃ based varistors, owing to the high sintering activity of ZnO nanoparticles (~30 nm) [37]. In addition, the average grain size slightly decreased with increased Ga₂O₃ content, suggesting that the dopant concentration minimally influenced the ZnO grain size [37].

As shown in Figure 5(f), it can be seen clearly that with increased Ga₂O₃ content, the maximum and minimum aspect ratios initially increased slowly and then rapidly due to the content of inversion boundaries (IBs; where Ga₂O₃ existed in the grain boundary in ZnO grain) initially increasing slowly and then rapidly [36], being consist with XPS result (as shown in Figure 4). According to Nina's opinion [36], IBs are a major factor influencing ZnO grain growth. Under the influence of IB-forming dopants (such as SnO₂, TiO₂, and Sb₂O₃), IB nucleation occurred in ZnO grains, and these grains grew dramatically and anisotropically in the direction of the inherent IB, causing plate-like development of the grains. Given the smaller ionic radius of Ga³⁺ than that of Sb³⁺ (0.076 nm) [24, 38] and its larger electronegativity (1.579) than that of Sb³⁺ (1.476) [39], when Ga₂O₃ existed in the grain boundary, Ga³⁺ could work as an IB-forming dopant and affect the growth behavior of ZnO grain more efficiently. When combined with the XPS results in Figure 4, we can see that with increased Ga₂O₃ in ZnO varistors, more Ga₂O₃ existed in the grain boundary, consequently, the maximum and minimum aspect ratios of ZnO grain initially increased slowly and then rapidly.

Please insert Figure 5 here

3.2 Influence of Ga₂O₃ content on the electrical properties of ZnO based varistors

Figure 6 shows the electrical field-current density (E - J) and capacitance-voltage (C - V) plots of ZnO based varistors with various Ga₂O₃ amounts and sintered at 1100 °C for 2 h. The electrical parameters of the specimen deduced from these are summarized in Table 2, where E_{1mA} , J_L , α , and K represent the voltage gradient, leakage current, nonlinear coefficient, and residual voltage ratio, respectively. From Table 2, it can be seen clearly that with increased Ga₂O₃, values of E_{1mA} , J_L , and α initially increased and then decreased. Conversely, K exhibited the opposite trend, E_{1mA} and α had the maximum values of 1235 V·mm⁻¹, and 46.0, while K possessed the lowest value of 1.37 when Ga₂O₃ was doped at 0.40 mol%.

Please insert Figure 6 here

Through the C - V curves, the parameters related to the Schottky barrier including donor density (N_d), barrier height (ϕ_b), and interface state density (N_s) were calculated, and results were also shown in Table 2.

It can be seen clearly that with increased Ga_2O_3 content, the value of donor density N_d monotonously increased, and Ga0.80-1100-2h had the highest value of $2.42 \times 10^{23} \text{ m}^{-3}$, being due to the highest absolute content of Ga^{3+} formed substitutional solid solution, as listed in Figure 4; According to Fu's opinion, the Schottky barrier height (ϕ_b) formation was attributed to the defect structures at the grain boundary, where the intrinsic acceptor defects were located at the interface and the donor defects were located at the depletion layer [1]. In this paper, Ga^{3+} existed in substitutional solid solution worked as donor and existed in interstitial solid solution worked as acceptor, the former provided an electron to the conduction band and the latter generated a vacancy in the valence band, the higher amount of the difference between these two states, the higher the value of ϕ_b [18, 40]. As shown in Figure 4, when content of Ga^{3+} equaled to 0.40 mol%, specimen had the highest value of 2.24 eV. Calculated from Eq. (4), value of N_s reached maximum ($2.38 \times 10^{16} \text{ m}^{-3}$) when content of Ga^{3+} equaled to 0.40 mol%.

Thus, the lower barrier height of samples indicated that although the lower content of IBs (with Ga_2O_3 existing in the grain boundary) and sintering process offered sufficient energy to maintain grain-boundary-diffusion activity while suppressing grain-boundary migration, the energy from these factors were insufficient to form a large barrier height. Increased content of IBs benefited grain growth and also led to increased barrier height at single grain boundary. In particular, with increased Ga_2O_3 content from 0.20 mol% to 0.40 mol%, the value of ϕ_b increased from 1.24 eV to 2.25 eV. Another factor worth considering was the influence of bulk density on the electrical properties of ZnO varistors [41]. These two factors determined that the highest value of E_{ImA} was reached when the content of Ga_2O_3 was 0.40 mol%.

Please insert Table 2 here

3.3 Influence of Ga_2O_3 content on the mechanical and thermal properties of ZnO based varistors

The experimental flexural stress-strain curves and thermal expansion curves of ZnO varistors are shown in Figures 7a and 7b, respectively. Fig. 7-a reveals that all curves displayed approximately linear behavior, regardless

of Ga₂O₃ content, indicating brittle fracture^[42]. As shown in Table 3, with increased Ga₂O₃ content, σ_f , E_f and K_{IC} initially increased and then decreased, and all reached their maximum values when the content of Ga₂O₃ was 0.4 mol%, these values indicated improvements of 25.29 %, 47.67 %, and 38.51 % compared with those of ZnO varistors without Ga₂O₃, respectively. Moreover, the improvements were 44.54 %, 90.72 %, and 61.41% compared with the results of Yoshimura^[43] due to the toughness of the small grain size and plate-like shape^[44, 45].

Regarding the CTE, it increased with increased measured temperature, similar to Ni's report^[46]. At a fixed temperature, with increased Ga₂O₃ content, CTE values initially increased and then decreased, and all reached the maximum value when Ga₂O₃ content was 0.40 mol%. The CTE of ZnO is reportedly anisotropic, i.e., $6.0 \times 10^{-6} \text{ } ^\circ \text{C}^{-1}$ perpendicular to the *c* axis and $5.0 \times 10^{-6} \text{ } ^\circ \text{C}^{-1}$ parallel to the *c*-axis^[40]. Plate-like grains formed because the growth of the *c*-axis was limited in the (0001) face of ZnO crystal^[29], which helped to improve the CTE of the ZnO varistors. The bulk density of ZnO varistors also positively influenced the CTE of the materials^[40]. These two factors worked together to result in an initial increase followed by a decrease in CTE with increased Ga₂O₃ content, and value of CTE was $6.65 \times 10^{-6} \text{ } ^\circ \text{C}^{-1}$ for Ga0.40-1100-2h at 800 °C.

Please insert Figure 7 here

Please insert Table 3 here

4 Mechanism of Ga₂O₃ addition on electrical and mechanical properties of ZnO based Varistors

Figure 8 shows a schematic model of Ga₂O₃ addition on Electrical and mechanical properties of ZnO based varistors. As reported that the doping of Ga³⁺ ions in ZnO varistors possessed three functions^[18]:

First, Ga³⁺ ions replaced Zn²⁺ in ZnO lattice to form a substitutional solid solution, in this condition, Ga³⁺ acted as a donor to release an electron to the conduction band of ZnO crystal, which would reduce the resistance of ZnO grains (as shown in Fig.8-a), and the defect reaction equation was as follows^[4, 16]:

Second, when Ga³⁺ filled in the vacancy of ZnO lattice, it existed a ‘position competition’ between Ga³⁺ and Zn²⁺, which could produce a vacancy in valence band of ZnO crystal and acted as acceptor to improve the resistance of ZnO grains (Fig. 8-b), the defect reaction equation was as follows^[18]:

Third, when Ga^{3+} accumulated in the grain boundary of ZnO, the negative free charge at the boundary of ZnO grain was increased, resulted in an increased of the barrier height and a decreased of the leakage current of ZnO varistors [15, 18]. In addition, Ga_2O_3 gathered at the grain boundary of ZnO can be used as an IB-forming dopant to affect the growth behavior of ZnO grain(Fig. 8-c). Therefore, the addition of Ga^{3+} and its location play important roles on the electrical and mechanical properties of ZnO varistors, the change of electrical properties is the result of three factors.

Please insert Figure 8 here

Combined the result shown in Figure 4 and 8, it can be seen that with the increase of Ga_2O_3 content, the content of substitutional solid solution increased flatly, resulted in a monotonously increase of the donor density N_d ; When content of Ga^{3+} was 0.60 mol%, amount of substitutional solid solution was approximately equaled to that of grain boundary phase, resulted in a maximum leakage current value of ZnO varisotrs ($4.34 \mu\text{A}\cdot\text{cm}^{-2}$); Also, the rapid increase of grain boundary phase content and a decreased Schottky barrier height (ϕ_b) resulted in a clearly development of plate-like ZnO grains as shown in Figure 5s-c, d and e, and the plate-like grain could help to improve the mechanical and properties of ZnO based varisotrs.

5 Conclusions

We investigated the mechanism of Ga_2O_3 addition on electrical and mechanical properties of ZnO based varistors with nanoparticles serving as the main raw materials. The following interesting results were obtained:

1 The added Ga_2O_3 preferentially occupied the lattice position of ZnO crystal via the formation of a substitutional solid solution, which worked as donor to provide an electron to the conduction band; it subsequently occupied the void position via the formation of an interstitial solid solution and worked as acceptor to generate a vacancy in the valence band; Residual Ga_2O_3 existed in the grain boundary and mainly served as IBs to stimulate the abnormal growth of ZnO grain;

2 The formation of substitutional and interstitial solid solutions helped improve the electrical properties, when the Ga_2O_3 content was 0.40 mol%, E_{ImA} , α and K were $1235.00 \text{ V}\cdot\text{mm}^{-1}$, 46.0 and 1.37, respectively, being due to the small particle size and the relative content of donor, acceptor and grain boundary;

3 The increased content of IBs stimulated the abnormal growth of ZnO grains, the formed plate-like grain helped improve the mechanical and thermal properties, with the values of σ_f , E_f , and K_{IC} reaching 147.43 MPa, 213.61 GPa, and $2.05 \text{ MPa}\cdot\text{m}^{1/2}$, indicated improvements of 25.29%, 47.67%, and 38.51% compared with those of ZnO varistors without Ga_2O_3 .

4 The anisotropy of the thermal-expansion coefficient of ZnO and the limited growth along the c-axis of ZnO crystal (the growth of plate-like grains meant limited growth of (1000) faces in ZnO) led to an initial increase in the CET of ZnO resistor followed by a decrease with increased Ga_2O_3 content. The value of CTE was $6.65 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ for Ga0.40-1100-2h at 800 °C.

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Conflict of interest

There is no interest conflict with others.

Reference

- [1] Zhiyao Fu, Junjia He, Jiazheng Lu, Zhen Fang, Bowen Wang. Investigation of dielectric relaxation and degradation behavior of two-step sintered ZnO varistors[J]. *Ceramics International*,45 (2019) 21900-21909.
- [2] Wenbin Cao, Xin Xie, Youqing Wang, Minge Chen, Yinan Qiao, Pan Wang, Yunxia Zhang, Jianke Liu. Effect of Pr_6O_{11} doping on the microstructure and electrical properties of ZnO varistors[J]. *Ceramics International*,45 (2019) 24777-24783.
- [3] Roy, Samarpita, Roy, Tapatee Kundu, Das, Debdulal. Grain growth kinetics of Er_2O_3 doped ZnO- V_2O_5 based varistor ceramics[J]. *Ceramics International*,45 (2019) 24835-24850.
- [4] Hongfeng Zhao, Jun Hu, Shuiming Chen, Qingyun Xie, Jinliang He. High Nonlinearity and High Voltage Gradient ZnO Varistor Ceramics Tailored by Combining Ga_2O_3 , Al_2O_3 , and Y_2O_3 Dopants[J]. *Journal of American Ceramics Society*, 99 (3) (2016) 769-772.
- [5] Pengfei Meng, Jun Hu, Hongfeng Zhao, Jinliang He. High voltage gradient and low residual-voltage ZnO varistor ceramics tailored by doping with In_2O_3 and Al_2O_3 [J]. *Ceramics International*,42 (2016) 19446-19449.
- [6] Wenfeng Liu , Lei Zhang, Fanyi Kong, Kangning Wu, Shengtao Li, Jianying Li. Enhanced voltage gradient and energy absorption capability in ZnO varistor ceramics by using nano-sized ZnO powders[J]. *Journal of Alloys and Compounds*, 828 (2020) 154252-1-7.
- [7] Pengfei Meng, Xiaolei Zhao, Xiao Yang, Jinbo Wu, Qingyun Xie, Jimou He, Jun Hu, Jinliang He. Breakdown phenomenon of ZnO varistors caused by non-uniform distribution of internal pores[J]. *Journal of the European Ceramic Society*, 39 (2019) 4824-4830.
- [8] Rodolfo F.K. Gunnewiek, Claudia P.F. Perdomo, Igor C. Cancellieri, André L.F. Cardoso, Ruth H.G.A. Kiminami. Microwave sintering of a nanostructured low-level additive ZnO-based varistor [J]. *Ceramics International*, 46 (2020) 15044-15053.

- [9] Jie Liang, Xuotong Zhao, Jianjie Sun, Lulu Ren, Ruijin Liao, Lijun Yang, Weiwei Li. Enhanced electrical properties of ZnO varistor ceramics by spark plasma sintering: Role of annealing[J]. *Ceramics International*, 46 (2020) 15076-15083.
- [10] Jinlou Shen , Yujing Zhang, Mingyu Li, Runxi Bao, Meng Shen, Chi Huang, Guangzu Zhang, Yabing Ke, Honglang Li, Shenglin Jiang. Effects of Fe and Al co-doping on the leakage current density and clamp voltage ratio of ZnO varistor[J]. *Journal of Alloys and Compounds*, 747 (2018) 1018-1026.
- [11] Shuaijun Yang, Dachuan Zhu. Effect of co-doping Y_2O_3 - La_2O_3 on microstructure and electrical properties of ZnO-based varistor ceramics prepared from nanosize ZnO powder[J]. *Journal of Materials Science: Materials in Electronics* (2018) 29:3104–3109.
- [12] Xuanzhong Cheng, Zhenya Lu, Xingyue Liu, Wenbin Yi, Zhiwu Chen, Xin Wang. Improvement of surge current performances of ZnO varistor ceramics via C_3N_4 -doping[J]. *Journal of the European Ceramic Society*, 40 (2020) 2390-2395.
- [13] Xuejun Ruan, Xin Ren, Wenting Zhou, Xi Xu, Xin Wang, Manyu Wang, Ying Yan, Zheng Yao, Wen Shi, Wenqi Yu. Effects of SiO_2/Cr_2O_3 ratios on microstructures and electrical properties of high voltage gradient ZnO varistors[J]. *Journal of Materials Science: Materials in Electronics*, 30 (2019)12113-12121.
- [14] Bing Cui, Jingpeng Niu, Pai Peng, Liyi Shi, Sanming Du, Juan Liu, Dong Xu. Flash sintering preparation and electrical properties of ZnO- Bi_2O_3 -M (M = Cr_2O_3 , MnO_2 or Co_2O_3) varistor ceramics[J]. *Ceramics International*, 46 (2020) 14913-14918.
- [15] Meng Peng-fei, Hu Jun, Wu Jin-bo, He Jin-liang. Comprehensive Performances of ZnO Varistors Tailored by Multi-elements Doping[J]. *High Voltage Engineering*, 44(1)(2018) 241-247.
- [16] Hongfeng Zhao , Jinliang He, Jun Hu, Shuiming Chen, Qingyun Xie. High nonlinearity and low residual- voltage ZnO varistor ceramics by synchronously doping Ga_2O_3 and Al_2O_3 [J]. *Materials Letters* 164 (2016) 80-83.
- [17] Choon-W. Nahm. Effect of gadolinia addition on varistor characteristics of vanadium oxide-doped zinc oxide ceramics[J]. *J Mater Sci: Mater Electron*, (2013) 24:4839–4846.
- [18] Meng Pengfei, Hu Jun, Wu Jinbo, He Jinliang.High Impulse Current Discharge Capability of ZnO Varistors by Doping Gallium Ions. *Proceedings of the CSEE*, 37 (24)(2017)7377-7383.
- [19] M. Vukovic', G. Brankovic', Z. Marinkovic' Stanojevic, D. Poleti b, Z. Brankovic. Ultra-high breakdown field varistors prepared from individually synthesized nanoprecursors[J]. *Journal of the European Ceramic Society*, 35 (2015) 1807–1814.
- [20] Yuwei He , Student Member, Bengang Wei, Zhengcai Fu , Member, Mingqiu Dai, Jian Liu. MOV Failure Modes and Microstructural Characteristics Under Operating Duty Tests With Multiwaveform Multipulse Currents[J]. *IEEE Transactions on Power Delivery*, 33(5)(2018)2274-2283.
- [21] R. Danzer, B. Kaufmann, P. Supancic. Failure of high power varistor ceramic components[J]. *Journal of the European Ceramic Society*, 40 (2020) 3766–3770.

- [22] Nadine Raidl, Michael Hofstaetter and Peter Supancic. Piezotronic Effect on Electrical Characteristics of Bulk ZnO Varistors[J]. *Advanced Engineering Materials*, 19(4)(2017)1600677-1-5.
- [23] Pengkang Xie, Jianping Hu. Influence of Sintering Temperature and ZrO₂ Dopants on the Microstructure and Electrical Properties of Zinc Oxide Varistors[J]. *IEEE*, 7 (2019) 140126-140333.
- [24] K. Sandhya, N.S. Chitra Priya, Deepthi N. Rajendran, Praveen Thappily. Structural and Electrical Properties of Cerium Oxides Doped by Sb³⁺ and Bi³⁺ Cations[J]. *Journal of Electronic Materials*, s11664- 020- 08220-9.
- [25] Qianlong Dai, Ruzhong Zuo, Yudong Xu, Liangguo He. A novel temperature-stable Ba_{2-x}CaxMgTi₅O₁₃ microwave dielectric ceramic[J]. *Journal of the European Ceramic Society*, 40 (2020) 376–380.
- [26] Peng-zhao Gao, Mo-yu Xu, Zheng Yuan, Lei Cheng, Jian-jun Liang, Han-ning Xiao, Rui-he Chen. Temperature dependence of the mechanical and thermal expansion behaviors of MoSi₂-RSiC composites with a three-dimensionally (3D) interpenetrated network structure[J]. *Journal of Alloys and Compounds*, 731 (2018) 1103-1111.
- [27] Wang Xinchao, Zhou Bingqing, Yao Ruoqing, Chen Kaiwei, Zhang Haiwen, Zhang Hong. Electrical conductivity and NTC thermal sensitive characteristics of Ga-doped ZnO ceramics[J]. *Materials Science and Engineering of Powder Metallurgy*, 22(3)(2017) 378-383.
- [28] Xiao-Qiang Song, Wen-Zhong Lu, Yi-Hui Lou, Tao Chen, Shi-Wo Ta, Zhen-Xiao Fu, Wen Lei. Synthesis, lattice energy and microwave dielectric properties of BaCu_{2-x}CoxSi₂O₇ ceramics[J]. *Journal of the European Ceramic Society* 40 (2020) 3035–3041
- [29] Qiu Yu, Wang Li-ming, Xu Li-hui, Shen Yong, Wang Li-ying, Liu Ya-dong Preparation Al-Y co-doped ZnO nanosheets and its photocatalytic degradation performance [J]. *Functional Materials*, 12(50) (2019) 12097-12102, 12107.
- [30] Peng-zhao Gao, Zhi-bo Huang, Hang-bo Zheng, Xiao-pan Liu, Jin Wen, Evgeny V. Rebrov. Temperature dependence of the magnetic properties of monodispersed Co_{0.5}Zn_{0.5}Fe₂O₄ microtubes derived from different templates[J]. *Journal of Materials Science: Materials in Electronics* (2019) 30:2809–2820.
- [31] Shouli Bai, Xi Sun, Ning Han, Xin Shu, Junli Pan, Haipeng Guo, Shuanghe Liu, Yongjun Feng, Ruixian Luo, Dianqing Li, Aifan Chen. rGO modified nanoplate-assembled ZnO/CdO junction for detection of NO₂[J]. *Journal of Hazardous Materials*, 394 (2020) 121832-1-9.
- [32] Guihua Ren, Xuanyu Ren, Wentao Ju, Yinshan Jiang, Minglei Han. Zhiqiang Dong, Xiaodong Yang, Kuizhou Dou, Bing Xue, Fangfei Li. Controlled vertical growing of Bi₂O₃ nano sheets on diatomite disks and its high visible-light photocatalytic performance[J]. *Journal of Photochemistry & Photobiology A: Chemistry*, 392 (2020) 112367-1-11.
- [33] K. Gurunathan. Photocatalytic hydrogen production using transition metal ions-doped γ -Bi₂O₃ semiconductor particles[J]. *International Journal of Hydrogen Energy*, 29 (2004) 933-940.

- [34] Pralay Paul, A.K. Rajarajan, A.K. Debnath, Rekha Rao, T.V. Chandrasekhar Rao. Valence fluctuation and magnetic frustration in Ga substituted YMnO₃[J]. Journal of Magnetism and Magnetic Materials, 503 (2020) 166617-1-6.
- [35] Shravan K. Appani, Ashok Kumar Yadav, D.S. Sutar, S.N. Jha, D. Bhattacharyya, S.S. Major. X-ray absorption spectroscopy study of Ga-doping in reactively sputtered ZnO films[J]. Thin Solid Films, 701 (2020) 137966-1-9.
- [36] Nina Daneu, Aleksander ReWnik, Slavko Bernik. Grain-Growth Phenomena in ZnO Ceramics in the Presence of Inversion Boundaries[J]. Journal of American Ceramics Society, 94(5) (2011) 1619-1626.
- [37] K. Hembram, T.N. Rao, R.S. Srinivasa, A.R. Kulkarni. High performance varistors prepared from doped ZnO nanopowders made by pilot-scale flame spray pyrolyzer: Sintering, microstructure and properties[J]. Journal of the European Ceramic Society, 35 (2015) 3535-3544.
- [38] Danyang Liu, Li Yang, Zanyu Chen, Guoqiang Zou, Hongshuai Hou, Jiugang Hu, Xiaobo Ji. Ultra-stable Sb confined into N-doped carbon fibers anodes for high-performance potassium-ion batteries[J]. Science Bulletin, 65 (2020) 1003-1012.
- [39] Keyan Li, Dongfeng Xue. Estimation of Electronegativity Values of Elements in Different Valence States [J]. Journal of Physical Chemistry A 2006, 110, 11332-11337.
- [40] Hua Fu, Guang-lei Zhang . Material Properties of Materials[M]. Peking University Press, 2010.09.
- [41] Y. Al-Hadeethi, M.I. Sayyed, Y.S. Rammah. Investigations of the physical, structural, optical and gamma-rays shielding features of B₂O₃-Bi₂O₃-ZnO-CaO glasses[J]. Ceramics International, 45 (2019) 20724–20732.
- [42] Peng-zhao Gao, Lei Cheng, Zheng Yuan, Xiao-pan Liu, Han-ning Xiao. High temperature mechanical retention characteristics and oxidation behaviors of the MoSi₂(Cr₅Si₃)-RSiC composites prepared via a PIP-AAMI combined process[J]. Journal of Advanced Ceramics, 2019, 8(2): 196–208.
- [43] H.N. Yoshimura, A.L. Molisani¹, N.E. Narita¹, J.L.A. Manholetti¹, J.M. Cavenaghi. Mechanical Properties and Microstructure of Zinc Oxide Varistor Ceramics[J]. Materials Science Forum, 530-531 (2006)408-413.
- [44] Yu Zhu, Dujun Luo, Zongjia Li, Yangwei Wang, Huanwu Cheng, Fuchi Wang, Tao Chen. Effect of sintering temperature on the mechanical properties and microstructures of pressureless -sintered B₄C/SiC ceramic composite with carbon additive[J]. Journal of Alloys and Compounds, 820 (2020) 153153-1-10.
- [45] Taha, Mohammed A.; Zawrah, Mahmoud F. Fabrication of Al₂O₃-ZrO₂-Ni composites with improved toughness using nano powders prepared by mechanical alloying [J]. Ceramics International 46 (2020) 19519- 19529.
- [46] Yu-feng Ni. First principle calculation of physical properties of ZnO at high temperature and high pressure[D]. Sichuan Normal University, Master's thesis, 2011.02

Table Captions

Table 1 Binding energy (BE) and relative ratio (R.R.) of Zn_{2p}, Bi_{4f} and Ga_{2p} photoelectron peaks for ZnO based varistor

Table 2 *E-J* and *C-V* Characteristic Parameters of ZnO based varistors with various Ga₂O₃ and sintered at 1100 °C for 2h

Table 3 Mechanical and thermal properties of ZnO based varistors with different content of Ga₂O₃

Figure Captions

Figure 1 ρ values of ZnO based varistors with different amounts of Ga₂O₃ added

(a) sintered at different temperatures for 2 h; (b) sintered at 1100 °C for different holding times

Figure 2 In-situ XRD patterns of ZnO based varistors with different amounts of Ga₂O₃ added: (a) full and (b) amplified patterns

Figure 3 XPS spectra of ZnO based varistors with different amounts of Ga₂O₃ added

(a) survey scan; (b) deconvolution of Zn_{2p} spectra; (c) deconvolution of Bi_{4f} spectra; (d) deconvolution of Ga_{2p} spectra

Figure 4 Absolute amount of Ga³⁺ for different distribution locations versus the increased Ga₂O₃ content in ZnO based varistors

Figure 5 SEM images of polished and etched fracture surfaces of ZnO based varistors (a-e) and Average particle size, maximum and minimum aspect ratios of ZnO varistors (f)

(a) Ga0.00–1100-2 h; (b) Ga0.20–1100-2 h; (c) Ga0.40–1100-2 h; (d) Ga0.60–1100-2 h; (e) Ga0.80–1100-2 h

Figure 6 (a) E – J and (b) C – V plots of ZnO based varistors with various Ga₂O₃ contents and sintered at 1100 °C for 2 h

Figure 7 Stress–strain (a) and thermal expansion coefficient (b) curves of ZnO based varistors with different Ga₂O₃ contents

Figure 8 Schematic model of Ga₂O₃ addition on electrical and mechanical properties of ZnO based varistors

Figures

Figure 1

pvalues of ZnObased varistors with different amounts of Ga2O3 added (a) sintered at different temperatures for 2h; (b) sintered at1100°C for different holding times

Figure 2

In-situ XRD patterns of ZnObased varistors with different amounts of Ga2O3 added: (a) full and (b) amplified patterns

Figure 3

XPS spectra of ZnO-based varistors with different amounts of Ga₂O₃ added (a) survey scan; (b) deconvolution of Zn 2p spectra; (c) deconvolution of Bi 4f spectra; (d) deconvolution of Ga 2p spectra

Figure 4

Absolute amount of Ga³⁺ for different distribution locations versus the increased Ga₂O₃ content in ZnO based varistors

Figure 5

SEM images of polished and etched fracture surfaces of ZnO based varistors (a-e) and Average particle size, maximum and minimum aspect ratios of ZnO varistors (f) (a) Ga_{0.00}-1100-2h; (b) Ga_{0.20}-1100-2h; (c) Ga_{0.40}-1100-2h; (d) Ga_{0.60}-1100-2h; (e) Ga_{0.80}-1100-2h

Figure 6

(a) E-J and (b) C-V plots of ZnO based varistors with various Ga₂O₃ contents and sintered at 1100°C for 2 h

Figure 7

Stress-strain (a) and thermal expansion coefficient (b) curves of ZnO based varistors with different Ga₂O₃ contents

Figure 8

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