The Nonlinear Characteristics of Different Additives added V2O5-ZnO Varistor

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Keywords: varistor, V2O5, CoOx, MnOx

Abstract. Most commercial ZnO varistors containing Bi₂O₃ exhibit excellent varistor properties, but they have a few drawbacks due to Bi₂O₃ having high volatility and reactivity and higher sintering temperature. In this study, V₂O₅ is added as the varistor forming oxide to lower down the sintering temperature of ZnO varistors for the further developing the chip Varistor array by using the Ag as the inner electrode. It is found that the sintering temperature of V₂O₅-added ZnO will be lower down to about 600°C. But the addition of V₂O₅ has no improvement in the electrical characteristics, and they need many additives to obtain the high performance. For that, the nonlinear properties in these Varistors can be improved by incorporation of some oxide additives. Different MnOₓ oxides (MnO, MnO₂, and Mn₃O₄) and CoOₓ oxides (CoO and Co₃O₄) are used as the minor oxide additives. The influences of different MnOₓ and CoOₓ oxides on the nonlinear voltage–current density (V-I) characteristics and the nonlinear exponent (α) of V₂O₅-ZnO varistor will be well developed.

Introduction

ZnO varistors are one kind of semiconductor ceramic manufactured by sintering ZnO powder mixed with minor other oxide additives. The ZnO varistors are a polycrystalline structured material consisting of semiconductor zinc oxide grains. The minor oxide additives will form second phase and locate at the grain boundaries, and that will lead to the nonlinear voltage-current density (V-I) characteristics. The ZnO varistors exhibit highly nonlinear V–I characteristics, which is expressed by I =kV^α, where k is a constant and α is nonlinear exponent as an index or figure of merit for indicating the effectiveness of a varistor. In the past, ZnO varistors are greatly divided into Bi₂O₃- [1] and Pr₆O₁₁-based [2] with varistor forming oxide (VFO). In this study, V₂O₅ is added as the varistor forming oxide to lower down the sintering temperature of ZnO varistors for the further developing the chip Varistor array by using the Ag as the inner electrode [3-5]. It is found that the sintering temperature of V₂O₅-added ZnO will be lower down to about 600°C. But the addition of V₂O₅ has no improvement in the electrical characteristics, and they need many additives to obtain the high performance, i.e., the nonlinear properties in these Varistors can be improved by incorporation of some oxide additives. Different MnOₓ oxides (MnO, MnO₂, and Mn₃O₄) [5-7] and CoOₓ oxides (CoO and Co₃O₄) [8-9] are used as the minor oxide additives. It is found that the addition of different CoOₓ oxides and MnOₓ oxides in ZnO ceramics will reveal different electrical characteristics. And it is also found that the valence of the added oxides will influence the nonlinear characteristics of ZnO varistors.
Experimental Procedure

The ceramic materials (99.5-x) mol% ZnO + 0.5 mol% V$_2$O$_5$ + x mol% MO were prepared by
the mixed oxide method, where x=0.05, 0.1, 0.3, 0.5, 0.75, and 1.0 and MO were MnO, Mn$_3$O$_4$,
MnO$_2$, CoO, and Co$_3$O$_4$, respectively. Reagent-grade raw materials of ZnO, V$_2$O$_5$, MnO, Mn$_3$O$_4$,
MnO$_2$, CoO, and Co$_3$O$_4$ with higher than 99.5% purity were used as starting materials, mixed
according to the composition (99.5-x) mol% ZnO + 0.5 mol% V$_2$O$_5$ + x mol% MO, and
ball-milled for 5h with deionized water. After drying and grinding, the (99.5-x) mol% ZnO + 0.5
mol% V$_2$O$_5$ + x mol% MO mixtures were pressed into pellets. The pellets were then sintered in an
atmosphere of ambient air for 2h at 900°C, and cooling rates of 5°C C/min. For electrical
measurements, the as-sintered specimens were lapped on both surfaces to ensure flat and parallel
surfaces. The ZnO varistors were coated with conductive silver paint on both surfaces, then the
varistors were cured to provide ohmic contacts. The $I-V$ characteristics were determined at room
temperature by using a variable dc power supply.

Results and Discussion

Fig. 1 shows the voltage-current density (V–I) characteristics of varistor ceramics with the
different contents of different MnO, Mn$_3$O$_4$, and MnO$_2$. For MO= MnO (Fig.1(a)) and using the
voltage revealing at 0.1mA as the reference values of breakdown voltage, the breakdown voltage
first increases as the content of MnO increases from 0.05 mol% to 0.5mol%, reaches a maximum
value at 0.5 mol%-MnO- added ZnO varistor, and then decreases critically by further increase the
content of MnO to 0.75 mol% and 1.0 mol%; When MO= Mn$_3$O$_4$ (Fig.1(b)) is used as the additive,
the breakdown voltage linearly decreases as the content of Mn$_3$O$_4$ increases from 0.05mol% to
1.0mol%; When the MO= MnO$_2$ (Fig.1(c)) is used as the additive, at first, the breakdown voltage
critically decreases as the content of Mn$_3$O$_4$ increases from 0.05mol% to 0.3 mol%, and then the
breakdown voltage saturates as more 0.3mol% MnO$_2$ is added. These results suggest that the same
metal oxides but with different valence will influence the nonlinear V-I characteristics of ZnO
varistors.

Figure 1: The voltage-current density (V–I) characteristics of different MO-added ZnO varistors (a)
MO=MnO, (b) MO=MnO$_2$, and (c) MO=Mn$_3$O$_4$. 
The nonlinear exponent (α) of varistor specimens with different contents of MnO, Mn₃O₄, and MnO₂ are presented in Fig. 2(a). The relationship between the electric field E and the current density J is commonly shown as a curve with an empirical relation \( J = KE^\alpha \), where K is a proportion factor and the nonlinear coefficient (α) is determined by

\[
\alpha = \frac{\log J_2 - \log J_1}{\log E_2 - \log E_1},
\]

where \( J_1 = 1.0 \text{ mA/cm}^2 \), \( J_2 = 10.0 \text{ mA/cm}^2 \), and \( E_1 \) and \( E_2 \) are the electric fields corresponding to \( J_1 \) and \( J_2 \), respectively. For \( MO = \text{MnO and Mn}_3\text{O}_4 \) (Fig. 2(a)), except 1 mol%-\( \text{Mn}_3\text{O}_4 \) is added, the \( \alpha \) values are lower than 20; For \( MO = \text{MnO}_2 \), the \( \alpha \) values are lower than 20 as the content of \( \text{MnO}_2 \) is less than 0.15mol% and the \( \alpha \) values increase apparently from 20 to 30 as the content of \( \text{MnO}_2 \) increases from 0.3mol% to 1mol%. The leakage currents of \( \text{MnO-}, \text{Mn}_3\text{O}_4-, \) and \( \text{MnO}_2\)-added varistors are also shown in Fig. 2. The most varistors have the low leakage current of lower than 100 μA except as the contents of \( \text{MnO}, \text{Mn}_3\text{O}_4, \) and \( \text{MnO}_2 \) are less than 0.15mol%.

![Fig. 2](image1)

Fig. 2 The (a) nonlinear exponent \( \alpha \) values and (b) leakage current of varistor as a function of different contents of MnO, Mn₃O₄, and MnO₂.

Fig. 3 shows the current density–electric field (\( J–E \)) characteristics of the varistor ceramics with the different contents of CoO and Co₃O₄ oxides. For \( MO = \text{CoO} \) (Fig. 3(a)), the breakdown voltage first decreases as the content of CoO increases from 0.05 mol% to 0.5mol%, reaches a minimum value at 0.5 mol%-CoO-added ZnO varistor, and then increases apparently by further increase the content of CoO to 0.75 mol% and 1.0 mol%; When the Co₃O₄ (Fig. 3(b)) is used as the additive, the breakdown voltage linearly decreases as the content of Co₃O₄ increases from 0.05mol% to 1.0mol%. These results suggest again that the same metal oxides but with different valence will influence the electrical characteristics of ZnO varistors.

![Fig. 3](image2)

Figure 3: The voltage-current density (\( V–I \)) characteristics of different MO-added ZnO varistors (a) \( MO = \text{CoO} \) (b) \( MO = \text{Co}_3\text{O}_4 \).

The nonlinear exponent (α) of varistor specimens with different contents of CoO and Co₃O₄ are presented in Fig. 4(a). For all \( MO = \text{CoO and Co}_3\text{O}_4 \), the \( \alpha \) values of all fabricated ZnO varistors are lower than 5 (Fig. 4(a)). The leakage currents of CoO- and Co₃O₄-added varistors are also shown in Fig. 4 and the most varistors have the high leakage current. For \( MO = \text{CoO} \), the leakage current are in the range of 200 μA ~ 400 μA; For \( MO = \text{Co}_3\text{O}_4 \), the leakage current are in the range
of 200 μA ~ 500 μA. And that will be the reason to lead the low $\alpha$ values in the CoO- and Co$_3$O$_4$-added varistors.

Fig. 4 The (a) nonlinear exponent $\alpha$ values and (b) leakage current of varistor as a function of MO and contents of CoO and Co$_3$O$_4$.

**Conclusions**

1. (99.5-x) mol% ZnO + 0.5 mol% V$_2$O$_5$ + x mol% MO varistors have a low sintering temperature of 900°C.
2. The $\alpha$ values increase apparently from 20 to 30 as the content of MnO$_2$ increases from 0.3 mol% to 1 mol%.
3. The most MnO-, Mn$_3$O$_4$-, and MnO$_2$-added varistors have a small leakage current of lower than 100 μA except as the content of MnO$_2$ are less than 0.15 mol%.
4. For all MO= CoO and Co$_3$O$_4$, the $\alpha$ values are lower than 5.
5. For MO= CoO, the leakage current are in the range of 200 μA ~ 400 μA; For MO= Co$_3$O$_4$, the leakage current are in the range of 200 μA ~ 500 μA.
6. The valence of added oxides has larger influence on the $\alpha$ values and the leakage current of fabricated varistors.

**Acknowledgments:** The authors will acknowledge to the financial support of the National Science Council of the Republic of China by the contract NSC 95-2221-E-390-009.

**References**