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LETTER

# Microstructure and varistor properties of $ZnO–V_2O_5–MnO_2$-based ceramics

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Recent developments in electronic design have tended toward smaller and higher density packaging of circuitry. This results in a greater susceptibility to surges. Once attacked by surge, electronic circuits can be destroyed in as short as 0.1 μs. ZnO doped with several different metal oxides are semiconducting ceramics possessing varistor behaviors, which exhibit abruptly increasing current in accordance with increasing voltage. This non-ohmicity of current–voltage properties is due to the presence of a double Schottky barrier (DSB) formed at active grain boundaries containing many trap states. Owing to highly non-ohmicity, these ceramic devices are widely used in the field of overvoltage protection systems [1, 2]. ZnO ceramics cannot exhibit a varistor behavior without adding heavy elements with large ionic radii such as Bi, Pr, Ba, etc. Commercial $Bi_2O_3$- and $Pr_6O_{11}$-based ZnO varistor ceramics cannot be co-fired with a silver inner-electrode (m.p. 961 °C) in multilayered chip components because of the relatively high sintering temperature above 1000 °C [3, 4]. Therefore, new varistor ceramics are required in order to use a silver inner-electrode. Among the various ceramics, one candidate is the binary $ZnO–V_2O_5$ system [5–9]. This system can be sintered at relatively low temperature in the vicinity of about 900 °C. This is important for multilayer chip component applications, because it can be co-sintered with a silver inner-electrode without using expensive palladium or platinum metals.

To develop varistor ceramics of high performance, it is very important to comprehend the influences of additives on varistor properties. $MnO_2$ is often added to $Bi_2O_3$-doped ZnO varistors to improve the varistor properties [10, 11]. In this report, the influence of $MnO_2$ on the microstructure and varistor properties of ternary $ZnO–V_2O_5–MnO_2$ (ZVM)-based ceramics was examined.

Reagent-grade raw materials were prepared for ZnO non-ohmic ceramics with a ternary composition, such as (99.5–$x$) mol% ZnO + 0.5 mol% $V_2O_5$ + $x$ mol% $MnO_2$ ($x$ = 0.0, 0.25, 0.5, 1.0, 2.0). Raw materials were mixed by ball-milling with zirconia balls and acetone in a polypropylene bottle for 24 h. The powder was pressed into discs 10 mm diameter and 2 mm thickness at a pressure of 80 MPa. The discs were sintered at 900 °C for 3 h. The final samples were 8 mm in diameter and 1.0 mm in thickness. Silver paste was coated on both faces of the samples and the electrode was formed by heating at 600 °C for 10 min. The area of electrodes was approximately 0.196 $cm^2$.

The surface microstructure was examined by scanning electron microscopy (SEM, Model S2400, Hitachi, Japan). The average grain size (d) was determined by the linear intercept method [12]. The crystalline phases were identified by powder X-ray diffraction (XRD, Model D/max 2100, Rigaku, Japan) with $CuK_\alpha$ radiation. The sintered density ($\rho$) was measured by the Archimedes method. The voltage–current (V–I) characteristics were measured using an I–V source (Keithley 237). The breakdown voltage ($V_B$) was measured at 1.0 $mA/cm^2$ and the leakage current ($I_L$) was measured at 80–% of the breakdown voltage. In addition, the non-ohmic coefficient ($\alpha$) is defined by the empirical law, $J = K \cdot E^\alpha$, where J is the current density, E is the applied electric field, and K is a constant. $\alpha$ was determined in the current density range of 1.0 $mA/cm^2$ to 10 $mA/cm^2$, where $\alpha = 1/(\log E_2 – \log E_1)$, and $E_1$ and $E_2$ are the electric field corresponding to 1.0 $mA/cm^2$ and 10 $mA/cm^2$, respectively. Five samples for non-ohmic resistors (sintered at the same

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time) were used for all electrical measurements and their average value is presented.

Figure 1 shows SEM micrographs of the ZVM-based ceramics containing different amounts of $MnO_2$. The grain structure is very heterogeneously distributed throughout the samples. The undoped samples showed abnormal grain growth of ZnO. The non-uniformity of grain size was significantly reduced with an increase of $MnO_2$ dopant levels. With increasing $MnO_2$ dopant levels, the average grain size decreased from 16.2 to 5.2 μm. Therefore, the incorporation of $MnO_2$ effectively reduced abnormal grain growth. At the same time, doping with $MnO_2$ did not significantly modify the densification process. The sintered density was in the range of 94.6% to 95.7% of the theoretical density (TD) (pure ZnO, TD = 5.78 g/cm$^3$). The XRD patterns of the ZVM-based ceramics are shown in Fig. 2. These patterns revealed the presence of $Zn_3(VO_4)_2$ as a secondary phase, in addition to primary phase of hexagonal ZnO. No secondary phase related to $MnO_2$ was detected. The detailed microstructure parameters are summarized in Table 1.

Figure 3 shows the electric field–current density (E–J) characteristics of the ZVM-based ceramics for different amounts of $MnO_2$. The varistor properties are characterized by non-ohmicity in the E–J characteristics. The curves show the conduction characteristics divide into two regions: an ohmic region before breakdown and a non-ohmic region after breakdown. The sharper the knee of the

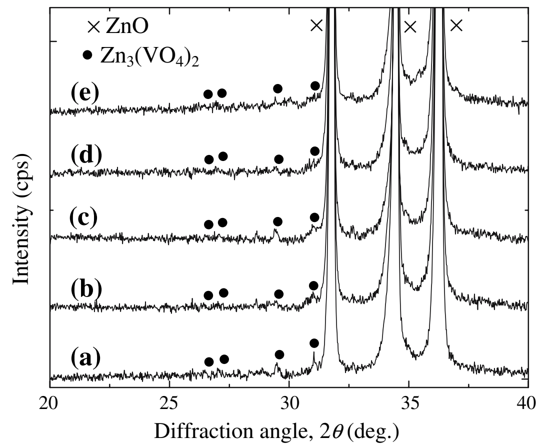


**Fig. 2** XRD patterns of the ZVM-based ceramics for different amounts of $MnO_2$; (**a**) 0.0 mol%, (**b**) 0.25 mol%, (**c**) 0.5 mol%, (**d**) 1.0 mol%, and (**e**) 2.0 mol%

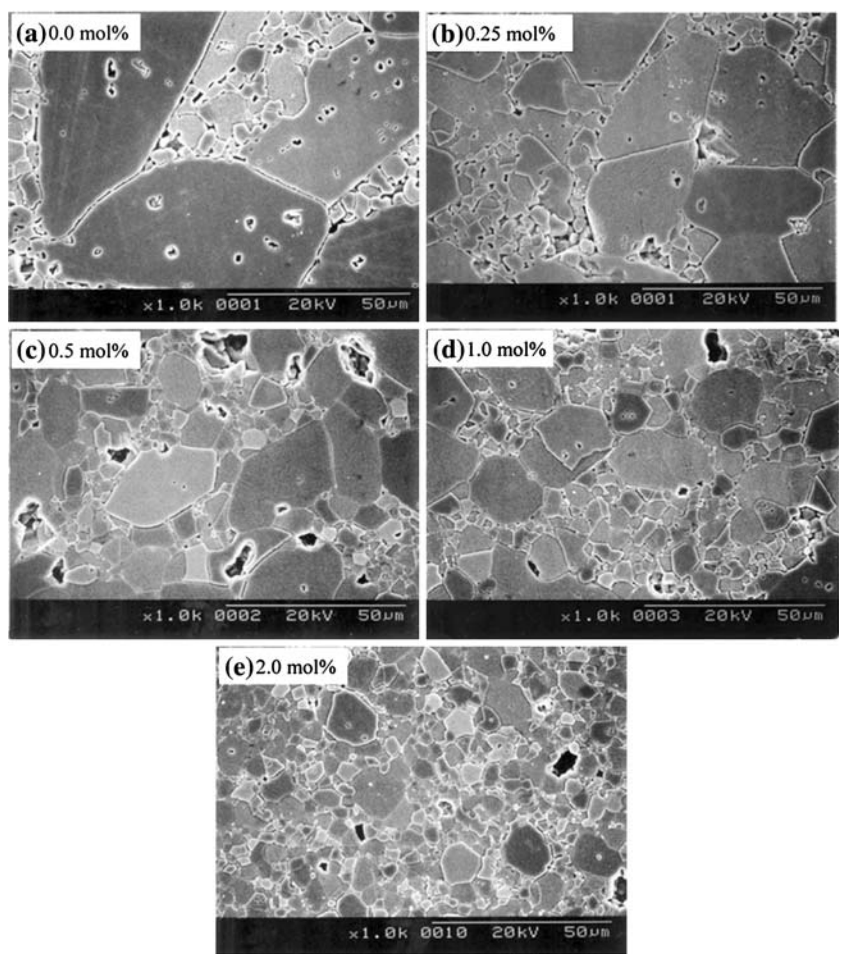


**Fig. 1** SEM micrographs of the ZVM-based ceramics for different amounts of $MnO_2$

**Table 1** Microstructure and V–I characteristic parameters of the ZVM-based ceramics for different amounts of $MnO_2$

| $MnO_2$ amount (mol%) | d (μm) | $\rho$ (g/cm$^3$) | $V_B$ (V/mm) | $V_b$ (V) | α | $I_L$ (μA) |
|---|---|---|---|---|---|---|
| 0.0 | 16.1 | 5.53 | 17.5 | 0.28 | 2.2 | 0.16 mA |
| 0.25 | 12.2 | 5.50 | 53.5 | 0.65 | 11.4 | 0.17 mA |
| 0.5 | 8.4 | 5.47 | 69.9 | 0.58 | 16.8 | 0.13 mA |
| 1.0 | 7.9 | 5.48 | 78.1 | 0.62 | 24.9 | 89.4 |
| 2.0 | 5.2 | 5.51 | 99.2 | 0.52 | 27.2 | 32.9 |

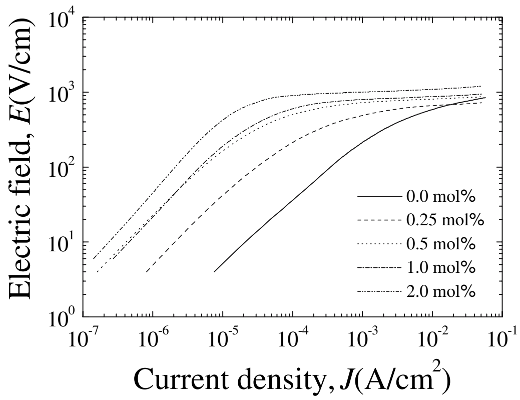


**Fig. 3** E–J characteristics of the ZVM-based ceramics for different amounts of $MnO_2$

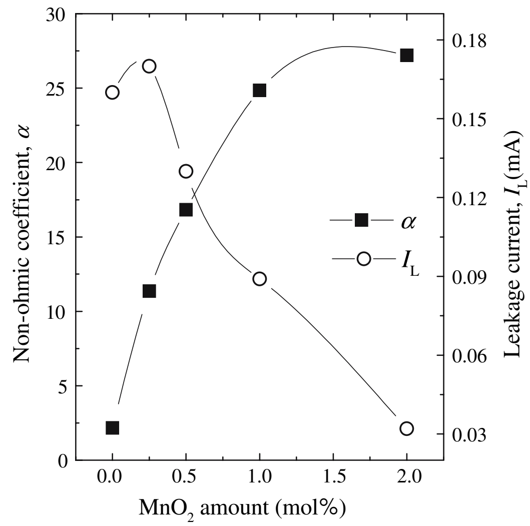


**Fig. 4** Non-ohmic coefficient and leakage current of the ZVM-based ceramics as a function of $MnO_2$ concentration

curves between the two regions, the better the non-ohmic properties. The undoped samples showed very poor non-ohmic properties. On adding more $MnO_2$, the knee gradually becomes more pronounced and the varistor properties are enhanced. Therefore, the incorporation of $MnO_2$ seems to remarkably enhance varistor properties. The breakdown voltage ($V_B$) increased from 17.5 to 99.2 V/mm with increase in $MnO_2$ concentration. The increase of $V_B$ with increasing $MnO_2$ concentration can be explained by the increase in the number of grain boundaries owing to the reduction in the average ZnO grain size. The breakdown voltage per grain boundary ($V_b$) for the ZVM-based ceramics was in the range of 0.5–0.6 V, which exhibited a much lower $V_b$ value than the general value of 2–3 V for $Bi_2O_3$ and $Pr_6O_{11}$-based ZnO varistors. This suggests that the ZVM-based ceramics can be used in the manufacture of low-voltage varistors.

Figure 4 shows the variation of the non-ohmic coefficient (α) and the leakage current ($I_L$) of the ZVM-based ceramics as a function of $MnO_2$ concentration. The α and $I_L$ values are derived from the E–J curves shown in Fig. 3. The α-value of undoped samples was only 2.2, whereas the α value of $MnO_2$-doped samples significantly increased from 11.4 to 27.2. In particular, when the $MnO_2$ level is more than 1.0 mol%, the samples exhibited relatively good varistor properties. The maximum non-ohmic coefficient was 27.2, which was obtained from the addition of 2.0 mol% $MnO_2$. The $I_L$ value was not affected much by MnO2 concentration less than 0.5 mol%. However, the $I_L$ value decreased to 32.9 μA with the addition of 2.0 mol% $MnO_2$. It resulted in the conclusion that doping the binary $ZnO–V_2O_5$-based ceramics with $MnO_2$ remarkably improves the non-ohmic properties, resulting in a higher non-ohmic coefficient and a smaller leakage current. The detailed V–I characteristic parameters are summarized in Table 1.

In summary, for all samples, the microstructure of the $ZnO–V_2O_5–MnO_2$-based ceramics consisted of ZnO grains and $Zn_3(VO_4)_2$ as a secondary phase. The addition of $MnO_2$ to the $ZnO–V_2O_5$-based ceramics was found to reduce abnormal grain growth of ZnO. The varistor properties were improved with the increase of $MnO_2$ concentration and a maximum non-ohmic coefficient ($\alpha = 27.2$) was obtained for the samples containing 2.0 mol% $MnO_2$. Thus the $ZnO–V_2O_5–MnO_2$-based ceramics is a potential candidate for chip varistors with a silver inner-electrode.

## References

1. Levinson LM, Pilipp HR (1986) Am Ceram Soc Bull 65:639
2. Gupta TK (1990) J Am Ceram Soc 73:1817

3. Nahm C-W (2001) Mater Lett 47:182
4. Nahm C-W (2002) J Mater Sci Lett 21:201
5. Tsai J-K, Wu T-B (1994) J Appl Phys 76:4817
6. Tsai J-K, Wu T-B (1996) Mater Lett 26:199
7. Kuo CT, Chen CS Lin I-N (1998) J Am Ceram Soc 81:2942
8. Hng H-H, Knowles KM (1999) J Eur Ceram Soc 19:721
9. Hng H-H, Halim L (2003) Mater Lett 57:1411
10. Pike GS, Kurtz SR, Gourley PL, Philipp HR, Levinson LM (1985) J Appl Phys 57:5512
11. Greuter F, latter G, Rossineli M, Stucki F (1989) Am Ceram Soc Westerville OH 3:31
12. Wurst JC, Nelson JA (1972) J Am Ceram Soc 55:109