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Effects of MgO doping in ZnO–0.5 mol% V_2O_5 varistors

H.H. Hng *, K.Y. Tse

School of Materials Science & Engineering, Division of Materials Science, Nanyang Technological University, Nanyang Ave, Singapore 639798, Singapore

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Abstract

The effects of MgO (0–40 mol%) on the microstructure and the electrical properties have been studied in a binary ZnO–0.5 mol% V_2O_5 system. The microstructure of the samples consists mainly of ZnO grains with MgO and γ-$Zn_3(VO_4)_2$ as the minority secondary phases. MgO is found to be effective as a grain growth inhibitor in controlling the ZnO grain growth, and a more uniform microstructure can be obtained. The non-linear coefficient α value is found to increase with the amount of MgO, and a highest value of 8.7 is obtained for the sample doped with 10 mol% MgO. Further addition of $\geq$20 mol% MgO decreases the α value.

Keywords: B. Microstructure-final; D. ZnO; D. MgO; E. Varistors; V_2O_5

1. Introduction

ZnO varistors derive their non-linear current–voltage behaviour from the addition of small amounts of other metal oxides, such as Bi_2O_3, Pr_6O_{11}, MnO_2 and Co_3O_4 [1,2]. It is generally believed that effective varistor forming ingredients are heavy elements with large ionic radii, such as Bi and Pr, which segregate to grain boundaries and form intergranular phases [3,4]. However, studies have shown that relatively light element vanadium is also a potential varistor former, since ZnO–V_2O_5 system exhibits varistor behaviour, similar to that of ZnO–Bi_2O_3 system [5–8]. The ZnO–V_2O_5 system is of interest because the ceramic can be sintered at a relatively low temperature of about 900 °C.

ZnO varistors exhibit non-linear current–voltage (*I–V*) characteristics and other electrical properties that are directly related to their microstructure, specifically the ZnO grain size that affects the varistor breakdown voltage per unit thickness [1–4]. To achieve a given breakdown voltage, one can change either the varistor thickness or the grain size by using grain growth inhibitors. Sb_2O_3 is a commonly used grain growth inhibitor for Bi_2O_3-doped ZnO varistors [2]. However, it has been shown that the use of Sb_2O_3 in V_2O_5-doped ZnO varistor requires a high sintering temperature of 1200 °C in order for the pellet to be sintered [8]. MgO is another oxide which has been reported to control grain growth in Bi_2O_3-doped ZnO varistors [9]. Hence, in this work, the feasibility of using MgO to control grain growth in V_2O_5-doped ZnO varistors will be studied. In addition, its effects on the final microstructure and current–voltage behaviour of the varistor will also be investigated.

2. Experimental procedure

High purity oxide powder starting materials were used for the preparation of the ZnO varistor samples. MgO, in the range of 0–40 mol%, was mixed with a mixture of ZnO–0.5 mol% V_2O_5 powder by ball milling with alumina balls and deionised water for 24 h. The mixtures were then dried, pressed into pellets, and sintered in an atmosphere of ambient air for 4 h at 1000 °C and cooled at 5 °C/min.

For electrical measurements, the as-sintered specimens were lapped on both surfaces to ensure flat and parallel surfaces. They were coated with conductive silver paint on both surfaces, then heat cured to provide ohmic contacts. The current–voltage (*I–V*) characteristics were determined at room temperature using a variable dc power supply (Kikusui Withstanding Voltage Tester, TOS 5051). X-ray diffraction analysis of the sintered samples was carried out using Cu Kα radiation on a Shimadzu Lab X-ray diffractometer. Microstructures were

* Corresponding author. Tel.: +65 67904140; fax: +65 67909081.
E-mail address: ashhhng@ntu.edu.sg (H.H. Hng).

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examined by SEM (JEOL JSM 5310) equipped with energy dispersive X-ray analysis (EDX).

3. Results and discussion

3.1. X-ray diffraction (XRD)

Typical XRD traces for undoped and doped MgO samples are shown in Fig. 1. In all the samples, ZnO was the main phase and only very small quantities of secondary phases were detected. In agreement with previous work on V_2O_5-doped ZnO ceramics [5–8], these secondary phases were found to be zinc vanadates. Brown and Hummel [10] identified three zinc orthovanadates, $Zn_3(VO_4)_2$, which they designated as α, β and γ. However, later studies [11,12] have queried the existence of polymorphism in $Zn_3(VO_4)_2$, and it was confirmed that neither β- nor γ-$Zn_3(VO_4)_2$ phases exist. In fact, it was deduced that the β-phase is actually $Zn_4V_2O_9$ (JCPDS 77-1757) phase, and the γ-phase (JCPDS 19-1470) could be an oxide compound composed of zinc, vanadium and manganese or it can be a mixture of zinc vanadates. $Zn_4V_2O_9$ was detected in the binary ZnO–V_2O_5 sample that is not doped with MgO, which agrees with our previous work [8]. However, for samples containing MgO, the γ-$Zn_3(VO_4)_2$ was formed instead. The γ-phase was identified in our samples using the JCPDS file card data, although it should be noted that the identification of the γ-polymorph on this basis is not definitive (see the discussion in the paper by Hng et al. [11]).

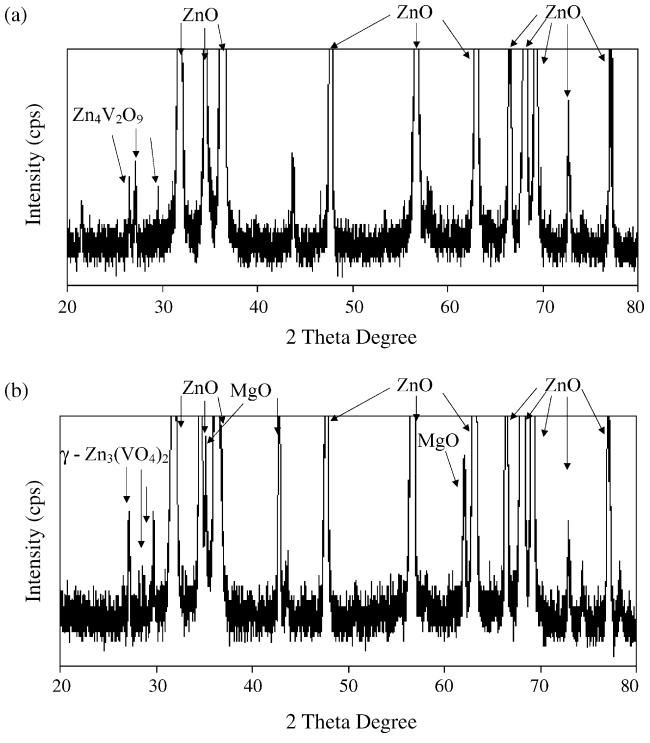

Fig. 1. Typical XRD traces (Cu Kα) for: (a) ZnO–0.5 mol% V_2O_5 (0 mol% MgO) and (b) ZnO–0.5 mol% V_2O_5–MgO (10 mol% MgO) samples.

For all the samples containing MgO, additional peaks corresponding to the MgO phase was also observed. MgO exhibits limited solubility in the ZnO as evidenced from previous works [13,14], where a maximum of 4 mol% of MgO can dissolve in the ZnO phase at 1573 K at atmospheric pressure.

3.2. Microstructural observations

Low magnification SEM images revealing the typical microstructure of V_2O_5-doped ZnO varistors are shown in Fig. 2. The binary system (ZV) showed exaggerated ZnO grain growth which previous studies have also reported [5–7]. However, the addition of sufficient amount of MgO yields a small-grained ceramic. The addition of MgO has also reduced the abnormal grain growth that is often observed in ZnO–V_2O_5 systems.

The average ZnO grain sizes shown in Table 1 were obtained from the SEM micrographs by multiplying the average linear intercept length of the grains by 1.56 [15]. The initial addition of MgO to ZnO–0.5 mol% V_2O_5 ceramics brought about a significant decrease in grain size. Subsequent increase in MgO content from 10 to 40 mol% showed a gradual decrease in grain size to about 4 μm. MgO is a well-known densification aid and grain growth inhibitor for the sintering of Al_2O_3 [16], and it has also been used successfully as a grain size inhibitor in ZnO–Bi_2O_3 varistor systems [9].

3.3. Current–voltage characteristics

The effect of MgO addition on the electrical properties of the V_2O_5-based ZnO materials were characterised by their electric field–current density (*E–J*) properties. Typical *E–J* curves are shown in Fig. 3. The corresponding parameters obtained from these curves are summarised in Table 1, where the point at which non-linearity begins is given by the onset electric field $E_{1\,mA/cm^2}$ and leakage current density J_{leak}.

The effects of MgO content on the various electrical parameters are presented graphically in Fig. 4 together with the effect on the average ZnO grain size. The leakage current density J_{leak} is not affected much by the addition of MgO. However, the onset electric field $E_{1\,mA/cm^2}$ and the non-linear coefficient α are greatly affected by the MgO content. As the amount of MgO is increased, the $E_{1\,mA/cm^2}$ values increase. This is consistent with the observed decrease in average ZnO grain size as MgO content increases. MgO addition slows down the grain growth, and this increases the number of barriers per unit thickness, and hence increases the $E_{1\,mA/cm^2}$ values. The non-linear coefficient α, on the other hand, exhibits a different trend. Initial addition of 2 mol% MgO does not have much effect on the α value. When MgO is increased to 10 mol% MgO, a significant increase in the α value is observed. However, subsequent addition of MgO cause a decrease in the α value. The existence of an optimum MgO content to obtain a high α value was also reported by Smith et al. [9] in their work on the effects of MgO on

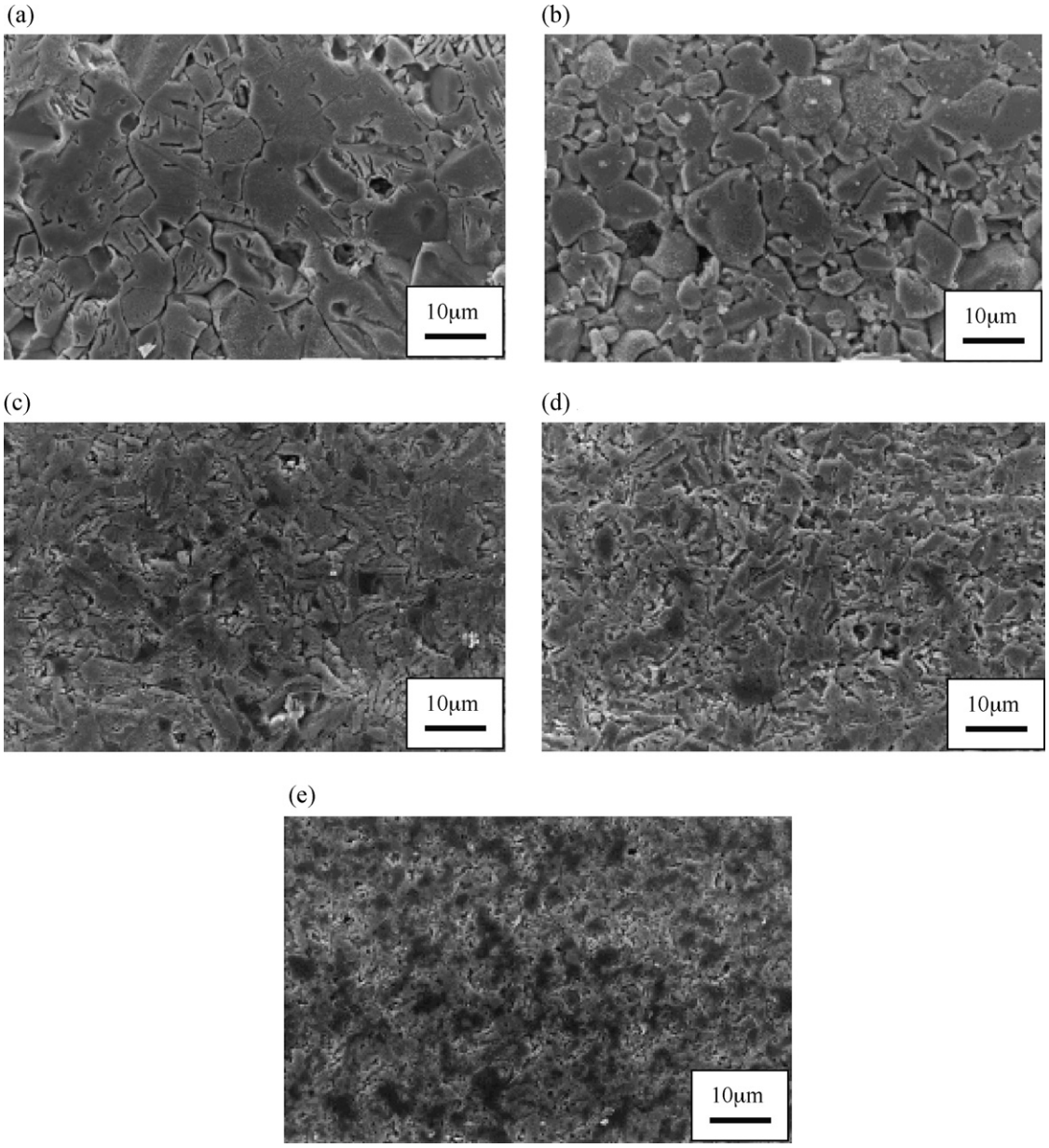

Fig. 2. SEM micrographs of V_2O_5-doped ZnO varistors containing various amounts of MgO: (a) 0 mol%; (b) 2 mol%; (c) 10 mol%; (d) 20 mol%; (e) 40 mol%.

Table 1
Summary of sample composition, average ZnO grain size and electrical results for the different ZnO–V_2O_5–MgO varistor ceramics

Sample	Composition	Average ZnO grain size (μm)	$E_{1\,mA/cm^2}$ (V/cm)[a]	J_{leak} ($\times 10^{-4}$ A/cm^2)[b]	Non-linear coefficient, α[c]
ZVM0	ZnO–0.5 mol% V_2O_5	17.5	240	6.3	4.3
ZVM2	ZnO–0.5 mol% V_2O_5–2 mol% MgO	9.8	450	6.9	4.1
ZVM10	ZnO–0.5 mol% V_2O_5–10 mol% MgO	6.0	850	7.7	8.7
ZVM20	ZnO–0.5 mol% V_2O_5–20 mol% MgO	5.2	850	7.5	4.3
ZVM40	ZnO–0.5 mol% V_2O_5–40 mol% MgO	4.0	1200	5.9	2.9

[a] Electric field at 1 mA/cm^2.
[b] Current density at $0.8E_{1\,mA/cm^2}$.
[c] $\alpha = \log(J_2/J_1)/\log(E_2/E_1)$ where $J_1 = 1$ mA/cm^2 and $J_2 = 10$ mA/cm^2.

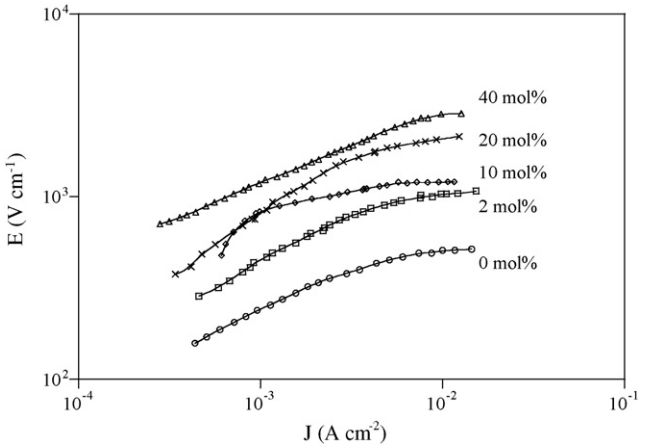

Fig. 3. The electric field–current density (E–J) curves for the various ZnO–V_2O_5–MgO samples.

ZnO–Bi_2O_3 system. They observed a decrease in the α value when 1 mol% of MgO was added, and a maximum α value of 17 was obtained at 13.2 mol% of MgO, which decreased eventually as MgO content increased.

It should be noted that the maximum α value obtained in the current study for the V_2O_5-doped ZnO varistors is far below that of commercially available Bi_2O_3-doped multi-component ZnO varistors. However, from the current study, we have managed to control the abnormal ZnO grain growth in the V_2O_5-doped ZnO system, which allows the use of a much lower sintering temperature of 900 °C as compared to the Bi_2O_3-doped ZnO varistor system. Hence, further work can now be done to enhance the varistor performance by composition optimisation with the addition of transition metal oxides to produce multi-component V_2O_5-doped ZnO varistor system.

4. Conclusion

MgO was found to be effective as a densifying aid and grain growth inhibitor in ZnO–V_2O_5. Addition of MgO to the binary ZnO–0.5 mol% V_2O_5 system controlled the abnormal ZnO grain growth, and the average ZnO grain size reduced significantly to about 4 μm when 40 mol% of MgO was added. The electrical properties deteriorated when more than 10 mol% MgO was added. A maximum non-linear coefficient of 8.7 was obtained for the sample containing 10 mol% MgO in 0.5 mol% V_2O_5-doped ZnO varistor. Hence, it can be concluded that in order to achieve optimum electrical properties and at the same time control the ZnO grain growth in V_2O_5-doped ZnO varistors, only up to 10 mol% MgO can be added. Based on the current results, further work can now be done to enhance the varistor performance through the addition of transition metal oxides to produce multi-component V_2O_5-doped ZnO varistor system.

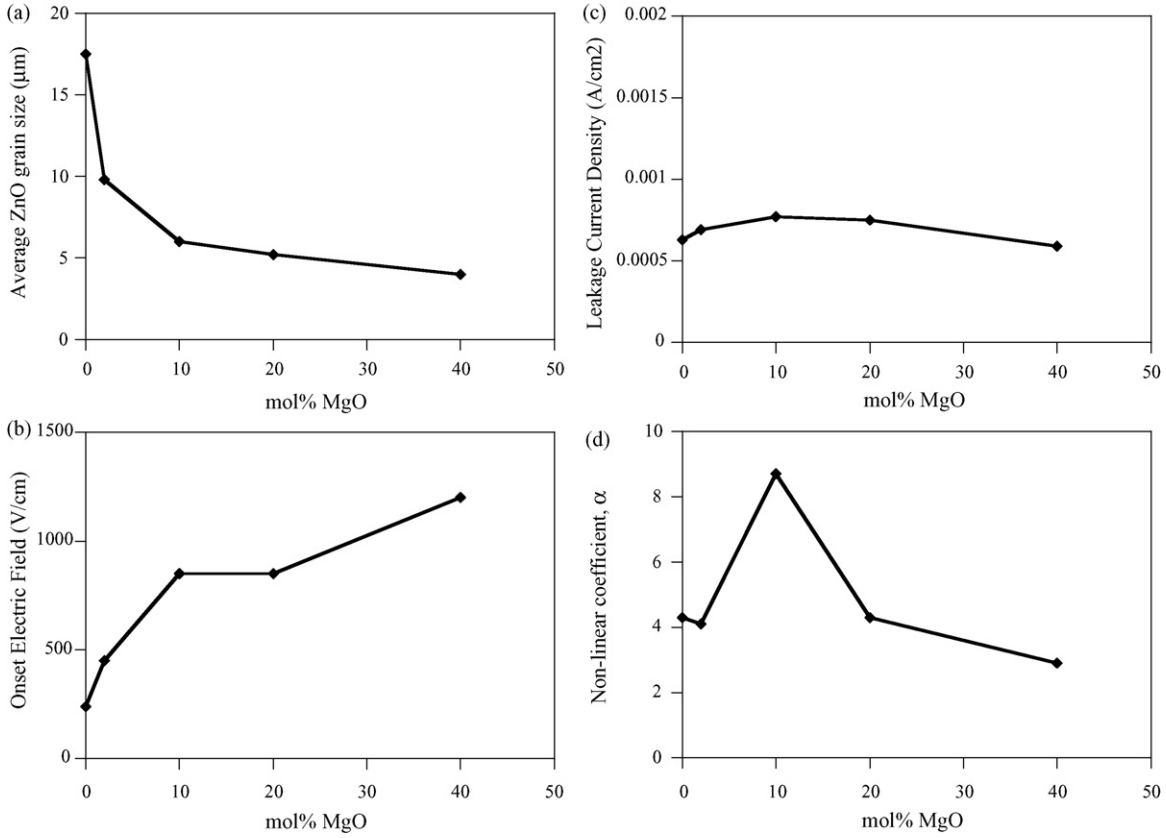

Fig. 4. Effects of MgO content on: (a) average ZnO grain size; (b) onset electric field, $E_{1\,mA/cm^2}$; (c) leakage current density, J_{leak}; (d) non-linear coefficient, α.

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