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Application of Direct Current and Temperature Stresses of Low-Voltage ZnO Based Varistor Ceramics

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Abstract: Problem statement: The stresses to humidity, DC and AC bias, multiple impulse voltages and high temperatures are known to affect the varistor performance and it is also interesting to know the effect of both DC bias and temperature stresses at the same time. **Approach:** Here, the simultaneous DC and temperature stresses degradation was investigated to see the changes of nonlinear coefficient (α) in Zn-Bi-Ti oxide low-voltage varistor ceramics sintered at various sintering temperatures (1140-1260°C) and two sintering duration times of 45 and 90 min. The current-voltage characteristics of the varistor ceramics were evaluated. **Results:** The α of ceramic was observed to be decreased with increasing sintering temperature. After loaded with DC and temperature stresses of $0.75V_{1mA}$/80°C/12 h, the α of ceramics for 90 min sintering time decreases with sintering temperature, however that sintered for 45 min sintering time increase with sintering time. **Conclusion:** The application of DC and temperature stresses in Zn-Bi-Ti oxide ceramics sintered at very long time cause the α to decrease as evidence from higher leakage current.

Key words: ZnO, low-voltage varistor, degradation

INTRODUCTION

Zinc oxide varistors is polycrystalline ceramics that consist of ZnO with minor additives and is formed through the sintering process. The resultant product, with a unique grain boundary feature, is responsible for nonlinear I-V characteristics of the device[1,2]. Such varistors are used to protect electrical equipment against voltage surges and can be used several times without being damaged. Nowadays with the development of micro-electronic technology and large scale integrated circuit, ever-increasing number of varistors is being used for low-voltage applications, such as in automobile electronics and semiconductor electronics. ZnO based varistors are widely used because of their extreme nonlinearity in their I-V characteristic that protects power and signal level in electrical circuits against dangerous voltage surges. ZnO based varistor is formed with other metal oxides of small amounts such as Bi_2O_3, TiO_2, CoO, MnO and Sb_2O_3[3-8]. These additives are the main tools that are use to improve the nonlinear response and the stability of ZnO varistor[5]. Therefore, the stability of ZnO based varistors against constant voltage biases, alternating and Direct Current (DC), or voltage surge is recognized as one of the crucial subjects to be investigated[9].

The degradation process usually leads to the reduction in the potential barrier height and causes defects near grain boundaries[10,11]. One of major challenges in the continuing development of varistor has been to reduce the degradation because this sudden degradation may increase energy loss in the varistors and results faults to the circuits[12]. It is reported[13] that DC bias can lead to a substantial increase of leakage current and decreasing breakdown voltage in ZnO based varistors. In this study the influence of simultaneously the DC and temperature stresses on the Zn-Bi-Ti oxide varistor ceramic is presented.

MATERIALS AND METHODS

Sample preparation: Oxide precursors of 99.9 % purity were used. Samples were prepared by solid state route ceramic processing. Their composition consisted

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of 99.0 mol % ZnO + 0.5 mol % Bi_2O_3 + 0.5 mol % TiO_2 powder and they were mixed in specific proportions. The mixtures were milled with zirconium balls and deionised water for 24 h. After that, the mixture was being dried at 150°C for 24 h and pre-sintered at 800°C for 2 h. The pre-sintered mixture was pulverized using an agate mortar/pestle and after 1.75 wt.% Polyvinyl Alcohol (PVA) binder addition, the granulated powder was sieved by using a 75 µm mesh screen to produce starting powder. Finally the discs of 10 mm in diameter and 1 mm in thickness approximately at a pressure 2 tons were pressed and sintered at various sintering temperatures (1140-1260°C) and two sintering duration time of 45 and 90 min with heating and cooling rate 2.66°C min^{-1}. Silver paste was coated on both faces 5 mm in diameter of the sample and was heating at 550°C for 10 min. The samples were labeled with A = 1140°C; B = 1170°C, C = 1200°C; D = 1230°C and E = 1260°C for 45 and 90 min sintering duration; respectively.

Phase, density and microstructure measurement: The crystalline phases were identified by an XRD (PANalytical (Philips) X'Pert Pro PW3040/60) with CuKα radiation and the data were analyzed by using X'Pert High Score software. The density of varistor ceramics was measured by the geometrical method[14]. One of the surfaces of samples was lapped and ground with SiC paper and polished with 1 µm diamond suspension to a mirror-like surface. The polished samples were thermally etched at 1100°C for 10, 20 and 30 min; respectively. The surface microstructure was examined by JEOL SEM, JSM-6400. The average grain size (d) was determined by lineal intercept method[13], given by:

$$d = 1.56L/MN$$

Where:
L = The random line length on the micrograph
M = The magnification of the micrograph
N = The number of the grain boundaries intercepted by lines

The compositional analysis of the selected areas was determined by an attached with Oxford Inca Energy 200 EDAX system.

Electrical measurement and DC stress: The I-V characteristic of the varistor ceramics were evaluates using a source measure unit (Keithley 236). The varistor voltage (V_{1mA}) was measured at a current of 1.0 mA and the leakage current (I_L) was measured at 0.80 V_{1mA}. In addition, the nonlinear coefficient, α, was determined from the following equation:

$$\alpha = \frac{\log I_2 - \log I_1}{\log V_2 - \log V_1} \qquad (1)$$

Where:
I_1 = 1 mA
I_2 = 10 mA
V_1 and V_2 = The voltages corresponding to I_1 and I_2, respectively

The DC and temperature stresses test was performed under one state, $0.75V_{1\,mA}$/80°C/12 h. After applying the stresses, I-V characteristics were taken at room temperature.

RESULTS

Phase, density and microstructure: The XRD analysis, Fig. 1, reveals diffraction peaks which belong to two phases, i.e., ZnO (ICSD code: 067454) and intergranular layers in the varistor ceramics. The intergranular layers are composed of Ti_6O_{11} and appeared as a very small peak in the XRD pattern for the sample sintered at 1140°C for 45 min sintering time only. Many secondary phases with small peaks were detected in the ceramics at all sintering temperatures, namely, $Bi_4Ti_3O_{12}$ (ICSD code: 024735) and $Zn_2Ti_3O_8$ (ICSD code: 022381).

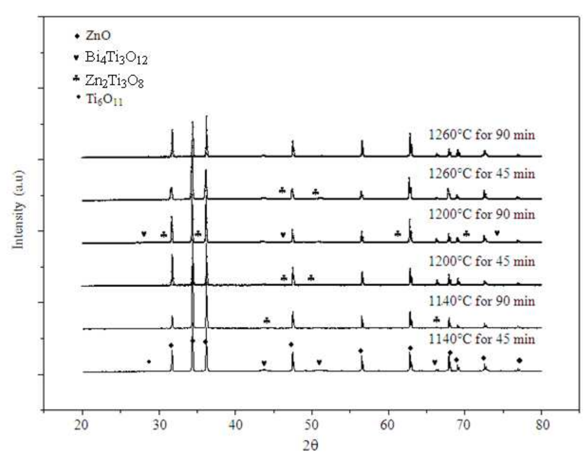

Fig. 1: XRD patterns of varistor ceramics at various sintering temperatures

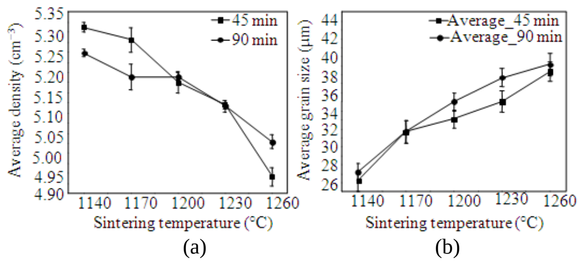

Fig. 2: (a): Average density at different sintering temperature; (b): Average grain size at different sintering temperature

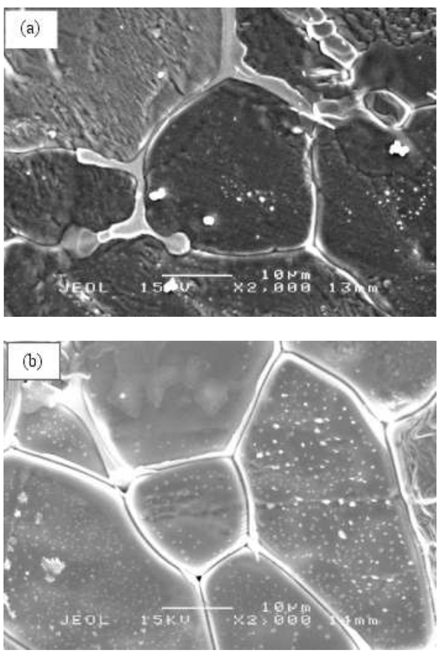

Fig. 3: SEM micrographs of sintered varistor ceramics (a): 1140°C at 45 min sintering time; (b): 1140°C at 90 min sintering time

The density of sintered ceramics decreases from 5.31-4.94 and 5.24-5.03 g cm^{-3} with the increase of sintering temperature for 45 and 90 min sintering time, respectively, Fig. 2a. For both sintering time, the grain size increases with sintering temperature, Fig. 2b and the large as well as small grains coexists as evident from SEM micrograph, Fig. 3. From EDAX analysis, the Bi and Ti were found at the grains boundaries, Fig. 4.

DC and temperature stresses: From the I-V characteristics of the ceramic, Fig. 5, it can be seen that the varistor voltage decreases and leakage current increases after DC and temperature stresses. The characteristic parameters, such as varistor voltage (V_{1mA}),

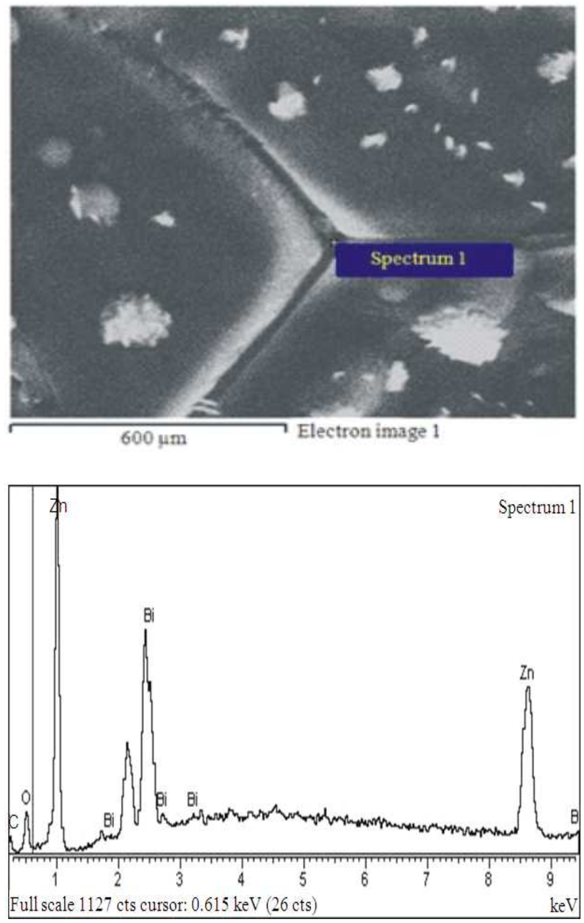

Fig. 4: EDAX micrograph of varistor ceramics at grain boundary

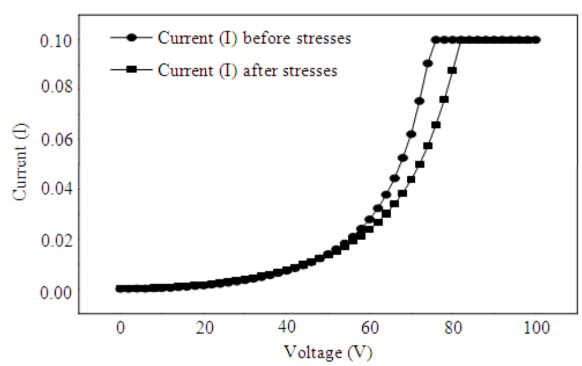

Fig. 5: I-V characteristics of the low-voltage ZnO varistor before and after DC and temperature stresses

nonlinear exponent (α) and leakage current (I_L) obtained from the Fig. 5 are summarized in Table 1.

Table 1: Variation of I-V characteristic parameters of varistor ceramics before and after DC and temperature stresses

Sample	Sintering temperature (°C)	Before stresses $V_{1\,mA}$ (V)	Before stresses I_L (μA)	Before stresses α	After stresses $V_{1\,mA}$ (V)	After stresses I_L (μA)	After stresses α
A45	1140	17.470	617.12	2.21	15.75	651.51	2.21
B45	1170	7.740	651.59	1.91	7.690	694.76	2.17
C45	1200	5.970	720.55	1.68	4.610	662.32	1.98
D45	1230	1.730	755.02	1.51	2.950	802.89	1.58
E45	1260	0.470	823.97	1.37	0.450	819.12	0.99
A90	1140	7.970	792.08	2.01	4.980	797.49	1.32
B90	1170	3.910	813.71	1.84	3.540	813.71	1.42
C90	1200	2.110	975.91	1.72	1.570	781.27	1.12
D90	1230	2.530	806.73	1.35	1.990	807.89	1.14
E90	1260	0.760	858.44	1.25	-	-	-

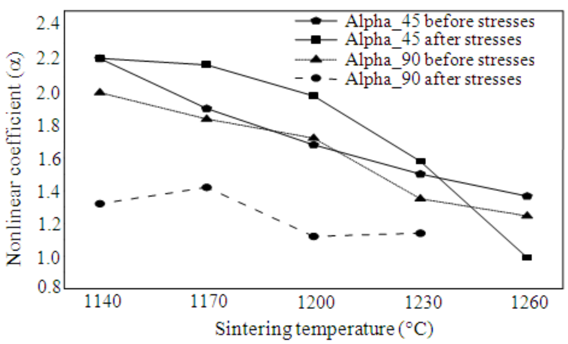

Fig. 6: The variation of average nonlinear coefficient (α) against sintering temperature for 45 and 90 min before and after DC and temperature stresses

As the sintering temperature increases the V_{1mA} value is greatly decreased from 17.47-0.47 V. In Fig. 6, all the nonlinear coefficient values, α, of samples are highest at the low sintering temperature 1140°C but later decrease with the increase of sintering temperature, with sample sintered at low sintering time (45 min) has slightly higher α compared to that of high sintering time (90 min). After applying DC and temperature stresses, the α value increases for samples sintered at 45 min but decreases for that of sintered at 90 min.

DISCUSSION

Phase, density and microstructure: The addition of a small amount of TiO_2 enhances the grain growth mechanism. This can be seen the highest density obtained at low sintering temperature, 1140°C, the grain size in the ceramics is small. This means the sample has less pores, while at high sintering temperature, the larger grain size indicates that the pores are developed in the ceramics. From EDAX analysis, the Bi and Ti were found at the grains boundaries, Fig. 4. This indicates the grain boundary is composed of ZnO and small amount of Bi which is segregated at the grain boundaries. The presence Ti indicates the Ti ions are substituted in the Zn lattice as the ionic radii of Ti ion is smaller than that of Zn radii in the grain boundaries.

DC and temperature stresses: As the sintering temperature increased the V_{1mA} value greatly decreased. This is attributed to the decrease of the number of grain boundaries due to the increase of the average grain size. The grain size directly affects the voltage in I-V characteristics where at small grain size, highest density or low porosity gives high nonlinear coefficient value. Therefore, it can be seen that for this sample the application of low sintering temperature, 1140°C, is enough to produce maximum α value. Similarly, the application of longer sintering time will produce more pores and thus lower α as can be seen for 45 and 90 min sintering time.

For the 45 min sintering time, α value increases after applying DC and temperature stresses. This is probably due to Joule's heating effect resulting from temperature stress that has similar effect as that of annealing[15]. This heating effect causes the change in microstructure of the ceramic samples at this sintered time, except sample sintered at 1260°C, rearranging itself which lead to improvement in nonlinearity. However, α decrease for the samples sintered at 90 min, or longer sintering time, after the stresses. This is assumed due to the degradation of the varistors that associated with the lowering of potential barrier at the grain boundaries. It is related to the annihilation of interface defect states after DC and temperature stressing caused by ion migration mechanism[10]. The similar α lowering effect is also observed for the ceramic sample sintered at shorter sintering time, 45 min, at the 1260°C. The sample sintered at shorter time and at 1140°C is the best because, apart of having large grain size and most dense, it's α value is the highest and does not change with DC and temperature stresses.

CONCLUSION

The Zn-Bi-Ti oxide varistor ceramic sintered sample at 1140°C for 45 min was found to have the highest density up to 5.31 g cm^{-3} and the highest nonlinear coefficient, 2.21. The application of DC and temperature stresses in Zn-Bi-Ti oxide ceramics cause the nonlinear coefficient decreases for that of sintered at 90 min but increases for that sintered at 45 min sintering time.

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