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EFFECT OF DC AND TEMPERATURE STRESSES ON NONLINEAR COEFFICIENT OF ZnO CERAMIC VARISTORS

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ABSTRACT

DC and temperature stresses deterioration were investigated to see the changes of nonlinear coefficient in Zn-Bi-Ti oxide low-voltage ceramics varistors that were sintered at various sintering temperatures from 1140°C to 1230°C and two sintering duration time of 45 and 90 minutes. The sintered ceramic was characterized with XRD, observed with VPSEM for surface morphology, analysed with EDAX for elemental analysis at particular sample area. The sintered ceramics density were observed to decrease with increasing sintering temperature and the Zn-Bi-Ti oxide ceramic sintered at 1140 °C for 45 minutes was found to have the maximum nonlinear coefficient. After applying DC and temperature stresses of $0.75V_{1mA}$/ 80°C/ 12 h, the nonlinear coefficient value in 90 minutes sintering time decreased with sintering temperature.

INTRODUCTION

Polycrystalline Zinc Oxide ceramic varistors which consists of ZnO with several additives is formed through a sintering process. It's unique grain boundary feature is responsible for nonlinear current-voltage (*I-V*) characteristics of the device [1, 2] and thus is used to protect electrical equipment. Currently ZnO based varistors are being used for low-voltage applications such as in automobile electronics and semiconductor electronics. It is widely used because of it's extreme nonlinearity in it's *I-V* characteristic that protect power and signal level of electrical circuits against dangerous voltage surges. Hence, the stability of ZnO based varistors under subjugation to constant voltage biases, AC and DC, or voltage surge is accepted as one of the important subjects to be investigated [3].

The defects near grain boundaries and the reduction in potential barrier height normally contribute to the deteriorating process [4, 5]. One of major challenges in the continuing development of varistor is to reduce their deterioration. Sudden deterioration during operation may increase energy loss by the varistors and causes faults to the circuits in some cases [6]. It is reported [7] that DC bias can lead to a substantial increase of leakage current and decreasing breakdown voltage in ZnO based varistors. In this paper the influence of the effect of the DC and temperature stresses on the Zn-Bi-Ti oxide varistor ceramic for a particular duration is presented.

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EXPERIMENTAL PROCEDURES

Sample preparation

Oxide precursors of 99.9 % purity were used. Samples were prepared by solid state route ceramic processing. Their composition consisted of 99.0 mol % ZnO +0.5 mol % Bi_2O_3+0.5 mol % TiO_2 powder were mixed in specific proportions. The mixtures were milled with zirconium balls and deionised water for 24 h. After 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 binder addition, the granulated powder was sieved by using a 75 µm mesh screen to produce a starting powder. Finally discs of 10 mm in diameter and approximately 1 mm in thickness were pressed at a pressure 2 tons and sintered at various sintering temperatures (1140°C to 1230°C) and two sintering duration time of 45 and 90 minutes with heating and cooling rate 2.66 °C min^{-1}. Silver paste was coated on both surfaces 5 mm of the diameter sample and was heated at 550 °C for 10 minutes.

Phase, density and microstructure measurement

The crystalline phases were identified by an X-ray diffractometry (PANalytical (Philips) X'Pert Pro PW3040/60) with CuKα radiation and the data were analyzed by using X'Pert High Score software. The density (ρ) of ceramic varistors was measured by the geometrical method [8]. Either surface of the 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 20 minutes. The surface microstructure was examined by Scanning Electron Microscope (JEOL JSM-6400). The average grain size (d) was determined by linear intercept method [7], given by $d = 1.56L/MN$, where L is the random line length on the micrograph, M is the magnification of the micrograph, and N is the number of the grain boundaries intercepted by the lines. The compositional analysis of the selected areas was determined by an attached energy dispersion X-ray microanalysis (EDAX) system.

Electrical measurement and DC stress

The direct current (DC) and temperature stresses test were performed under one state, $0.75V_{1\ mA}$/80 °C/12 h. Before and after applying these stresses, the *I-V* characteristics of the varistor ceramics were evaluated using a source measure unit (Keithley 236) at room temperature. From the *I-V* characteristic 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, and V_1 and V_2 are the voltages corresponding to I_1 and I_2, respectively.

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RESULTS AND DISCUSSIONS

Phase, density and microstructure

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

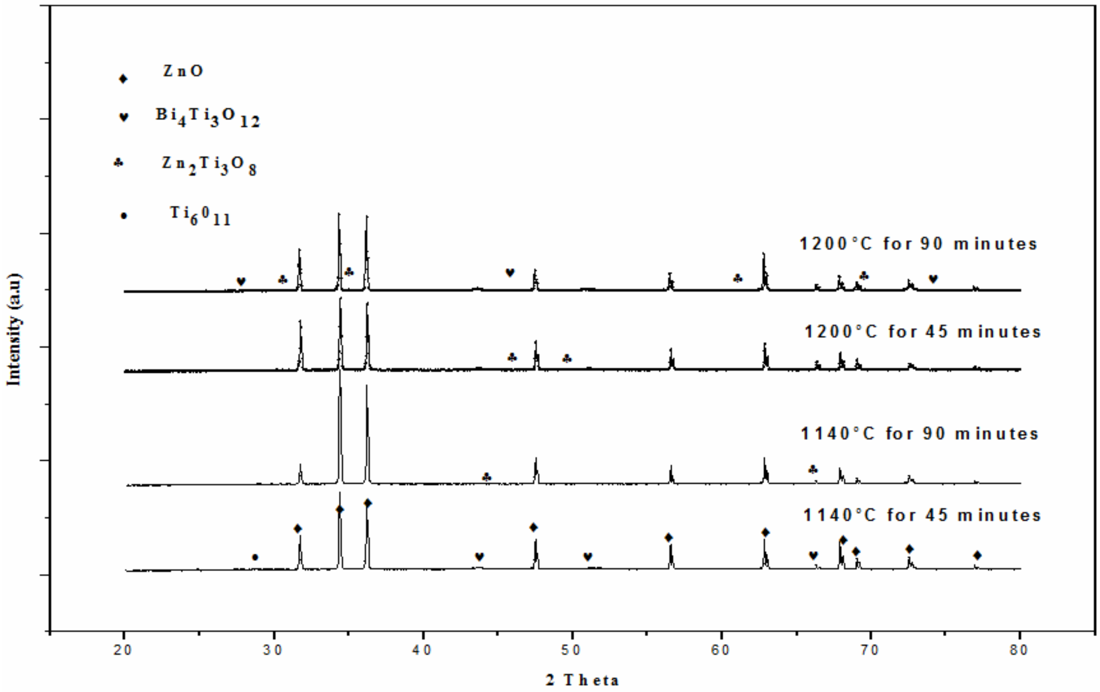

Figure 1: XRD patterns of varistor ceramics at 1140 and 1200°C

The density of sintered ceramics decreases with increasing sintering temperature from 5.31 to 4.94 gcm^{-3}, and 5.24 to 5.03gcm^{-3} for both sintering time 45 and 90 minutes, respectively (Figure 2(a)) but the grain size increase with sintering temperature (Figure 2(b)). The addition of a small amount of TiO_2 enhances the grain growth therefore with increase of sintering temperature this also creates pore in between the grain. More pores are created in longer sintering time duration. Large and small grains coexist together as shown in Figure 3. From EDAX analysis, the Bi and Ti were found at the grains boundaries as in Figure 4. This indicates that the grain boundary is composed of ZnO and small amount of Bi which is segregated at the grain boundaries. The presence of Ti indicates that the Ti ions are substituted in the Zn lattice as the ionic radii of Ti ion are smaller than that of the Zn radii in the grain boundaries.

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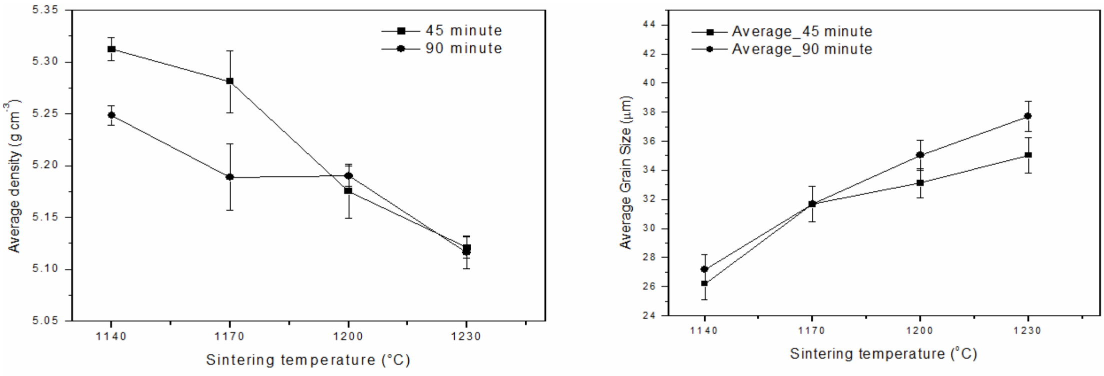

(a) (b)

Figure 2: (a) Average density against sintering temperature, and (b) Average grain size against sintering temperature.

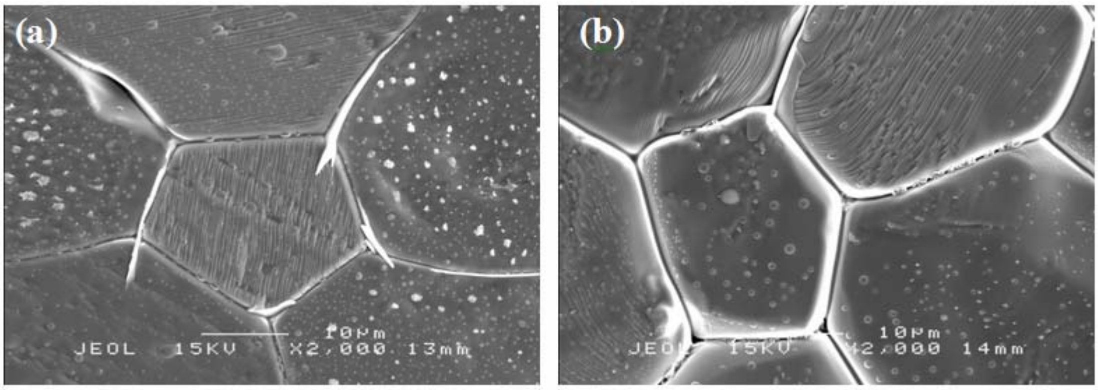

Figure 3: SEM micrographs of ceramic varistor sintered at 1230°C at sintering time of (a) 45 minutes, and (b) 90 minutes.

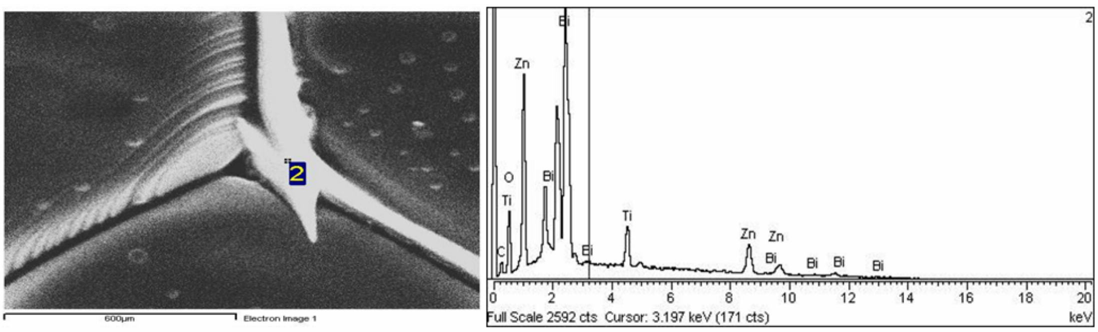

Figure 4: EDAX micrograph of ceramic varistor at the grain boundary

DC and temperature stresses

From the *I-V* characteristics of the ceramic in Figure 5, it can be seen that the varistor voltage decreases and leakage current increases after DC and temperature stresses. The

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characteristic parameters, such as varistor voltage (V_{1mA}), nonlinear coefficient (α), and leakage current (I_L) obtained from Figure 5 are summarized in Table 1. As the sintering temperature increased, the V_{1mA} value greatly decreased from 17.47 to 1.73 V. This is attributed to the decrease of the number of grain boundaries due to the increase of the average grain size. In general, the smaller the grain size, the higher the varistor voltage. α at 1140 °C, has a maximum value 2.21, but further increase of sintering temperature to 1230 °C causes α to decrease as in Figure 6. The grain size directly affects voltage in *I*-*V* characteristics where at small grain size and highest density gives high α value. Therefore, it can be seen that for this sample, the incorporation of low sintering temperature, 1140 °C, is enough to obtain maximum α value. For the 45 minutes sintering time, α 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 [9]. The Joule's heating effect causes the change in microstructure of the ceramic samples sintered at 45 minutes, rearranging itself which lead to improvement in nonlinearity. α decreases for the samples sintered at 90 minutes after the DC and temperature stresses. This is probably due to the deterioration of the varistors that are associated with the lowering of the potential barrier at the grain boundaries. It is related to the annihilation of interface defect states after DC and temperature stressing. The most probable accepted mechanism is the ion migration [4]. α decreases due to the mechanism when the ZnO varistors is under DC and temperature stresses.

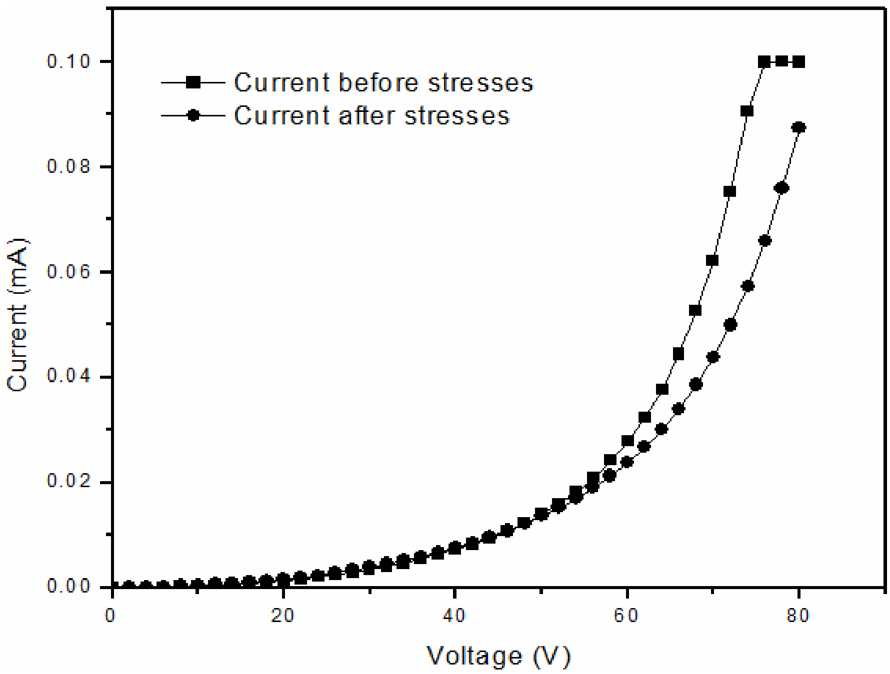

Figure 5: *I*-*V* characteristics of the low voltage ZnO varistor before and after DC and temperature stresses.

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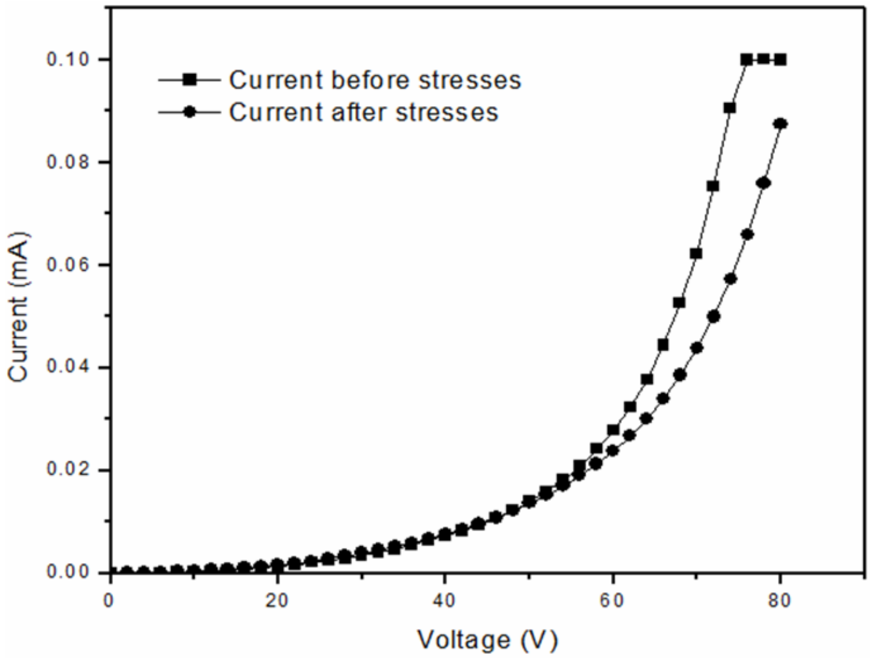

Figure 6: The variation of average nonlinear coefficient (α) against sintering temperature for 45 and 90 minutes before and after DC and temperature stresses.

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

Sintering temperature (^oC)	**Before stresses**			**After stresses**		
	$V_{1 mA}$ (V)	I_L (μA)	α	$V_{1 mA}$ (V)	I_L (μA)	α
1140	17.47	617.12	2.21	15.75	651.51	2.21
1170	7.74	651.59	1.91	7.69	694.76	2.17
1200	5.97	720.55	1.68	4.61	662.32	1.98
1230	1.73	755.02	1.51	2.95	802.89	1.58
1140	7.97	792.08	2.01	4.98	797.49	1.32
1170	3.91	813.71	1.84	3.54	813.71	1.42
1200	2.11	975.91	1.72	1.57	781.27	1.12
1230	2.53	806.73	1.35	1.99	807.89	1.14

CONCLUSIONS

The Zn-Bi-Ti Oxide ceramic varistor sample sintered at low sintering temperature (1140 °C) and in short time duration (45 minute) was found to have the highest density and highest nonlinear coefficient. The treatment of DC and temperature stresses on Zn-Bi-Ti oxide ceramics caused the nonlinear coefficient to increase for the sample sintered at 45 minutes but decreased for the sample sintered at 90 minutes.

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