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Screen-printed varistors: New strategy for high non-linear coefficient

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Abstract

Screen-printed thick film varistors (TFV) based on ZnO powder were developed with the aim to protect IGBT power transistors against overvoltages. The electrical characteristic of TFV was shown to depend on the electrode composition. Furthermore, characterization of the microassembly [electrodes/ZnO/Al_2O_3 substrate] proved that in the case of ZnO layers fired at 1200 °C, the low non-linearity coefficients ($\alpha < 10$) were correlated to the bismuth oxide evaporation and/or migration to the substrate. Higher non-linear coefficients were obtained only with electrode inks containing small amounts of Bi_2O_3. The obtained values of α larger than 40 are the highest ones so far recorded for ZnO TFV and compare well to those of ceramics.

Keywords: Electrical properties; ZnO; Varistors; Thick film

1. Introduction

Zinc oxide varistors are very efficient for surge or transient voltage protection in electronic and electrical applications, thanks to their excellent non-ohmic properties.[1–4] Capability of high energy absorption of varistors is also useful to power or semiconductor industry. Although ceramic varistors are widely used, surface mount devices are suited solutions, since the reduction of leads minimizes inductive effects and allows elimination of overvoltage generated by fast rising transients.[5] In order to protect electronic components like IGBT power switches during repeated open/close operations,[6] ZnO thick film varistors (TFV) appear to be a nice alternative for the following reasons: direct integration of the screen-printed varistors (no soldering step), reduction of leads, better thermal dissipation across the substrate and easy control of the threshold voltage.

So far, ZnO TFV deposited with conventional screen-printing technology on alumina substrates exhibited rather low non-linear coefficient ($\alpha < 20$), compared to ceramics ($\alpha > 50$).[7–12] This was mainly attributed to the manufacturing process of screen-printed TFV, which induces a lack of compacity of the ZnO layers. Densification strategies implied working on the starting powder composition, temperature profile, maximum temperature firing, liquid sintering phase, pressing step, etc. Moreover, the chemical interactions of screen-printed ZnO with both substrate and additives usually present in commercial electrode inks have not been sufficiently taken into account, especially their influence on the non-linear properties.

de la Rubia Lopez et al.[11] produced a pertinent work on different processing strategies for densifying their ZnO TFV, based on the formation of a Bi_2O_3 rich liquid phase at low temperature in order to control its evaporation. They obtained encouraging results with a non-linear coefficient $\alpha \sim 20$ for a sintering temperature of 900 °C. Nevertheless, this temperature is usually considered too low for the formation of the microstructure at the origin of highest α coefficients obtained in ceramics ($\alpha > 50$). As for ceramics, high sintering temperature ($1100 < T(°C) < 1200$) as well as the control of the "Bi_2O_3 cycle" (chemical reactivity, diffusion to the alumina substrate, evaporation, ...) are obviously key parameters to reach high non-linearity in ZnO TFV.

The aim of the present work is to obtain ZnO TFV with high α values, comparable to those of ceramics. In this respect, electrical characterizations of ceramics and ZnO TFV, both prepared with the same ZnO varistor powder and sintered at 1200 °C, will be investigated. The chemical interactions which occur during firing of the microassembly [electrode/ZnOlayer/Al_2O_3] will be focussed on, with regard to Bi_2O_3.

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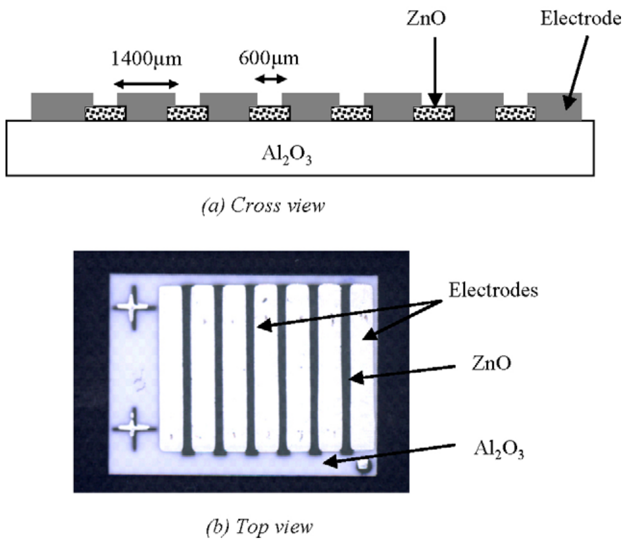

Fig. 1. Thick film configuration of TFV for high threshold voltages: (a) cross-view of the TFV design and (b) top view of screen-printed samples.

2. Experimental

Ceramics and TFV were prepared from a standard powder composition of 96.1 mol% ZnO, 1.2 mol% Sb_2O_3, 1.0 mol% Bi_2O_3, 0.5 mol% Co_3O_4, 0.4 mol% Cr_2O_3, 0.5 mol% Mn_2O_3 and 0.3 mol% NiO.

Ceramic disks of 1.4 mm thickness and 10 mm diameter were pressed 10 min at 160 MPa and sintered with an optimized 2:30 h temperature profile (25 min at 400 °C, 20 min at 820 °C, 30 min at 1200 °C and cooling back to room temperature at a rate of 20 °C min^{-1}). Two screen-printed pairs of electrodes were deposited, one on both sides of the disk (sandwich configuration) and the other on the same side (planar configuration).

ZnO screen-printing paste was prepared from an ethyl cellulose based organic vehicle mixed in a ball mill with the standard ZnO powder also used for ceramics. The amounts of mineral and organic phases were adjusted to match the rheological properties of the printing paste. In order to get a high threshold voltage ($V_{br} > 600$ V) with ∼1–3 μm ZnO grain size, the distance between electrodes had to be greater than 600 μm. With screen-printing technology, such a value was achieved easily with a planar configuration (Fig. 1). Six elements of ZnO pastes (10 mm × 1 mm) were directly deposited onto classical 96% alumina substrates. After removal of the organic solvents in an oven at 120 °C during 20 min, the samples were fired with a 2:30 h temperature profile previously optimized for the ZnO ceramics. The average thickness of the ZnO layers measured with laser equipment was about 35–40 μm after firing.

Electrodes were screen-printed on both ceramic disks and thick films with the commercial Ag ESL 9912A ink, silver being mostly used for ceramic varistor. Planar electrodes of 1.4 mm × 10.4 mm and 5–8 μm thick, screen-printed with a space of 600 μm were dried for 20 min at 120 °C in an oven and fired 10 min at 850 °C in a belt furnace (Fig. 1).

The average grain sizes of TFV and ceramics were estimated from SEM micrograph of polished surface of the samples.

I–V characteristics of the varistors were measured with a Tektronix 371A. The non-linear coefficient α was calculated from the power law $I = kV^{\alpha}$, using the relationship

$$\alpha = \frac{d(\log I)}{d(\log V)} \approx \frac{\log I_2 - \log I_1}{\log V_2 - \log V_1}$$

where V_1 and V_2 were the voltage for $I_1 = 1$ mA and $I_2 = 3$ mA, respectively. The breakdown voltage V_{br} was defined for $I = 1$ mA.

3. Results and discussion

After elaboration, starting ZnO powder was validated on the basis of *I–V* characteristics of ceramic disks. We observed that the electrical behaviour of the ceramic disks screen-printed with Ag ESL 9912A electrode, was the same whatever the configuration, planar or sandwich. High values of non-linear coefficients $\alpha \sim 63$ obtained with our ceramics were in good agreement with those of commercial ones $\alpha > 50$ (Harris Semiconductor V660LA50A). The measured switch fields $V_{br} \sim 0.4$ kV mm^{-1} for laboratory ceramic varistors and $V_{br} \sim 0.3$ kV mm^{-1} for commercial ones compare also well considering the slight difference in ZnO grain diameter (7–8 μm and ∼10 μm, respectively).

But on the other hand, a low value of $\alpha \sim 6$ was surprisingly measured for TFV samples with Ag ESL 9912A electrodes. Taking into account the volume of ZnO layer ∼275 times lower than that of ceramic disks, it is likely that the much smaller amount of bismuth phases (at the origin of non-linear properties) completely diffused into the Al_2O_3 substrate and/or evaporated during the liquid phase sintering of the ZnO layer. A SEM micrograph of ZnO/Al_2O_3 substrate showed a strong porosity of ZnO layer and a diffusion zone of 3–4 μm at the interface was observed (Fig. 2). Analysis of the samples with a CAMECA SX100 Electron Probe Micro Analyser (EPMA) confirmed that

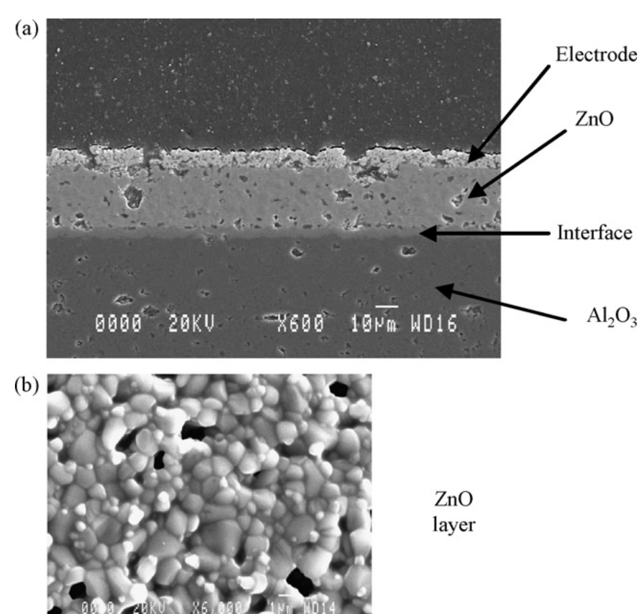

Fig. 2. SEM micrographs of (a) ZnO TFV and (b) ZnO layer after firing at 1200 °C.

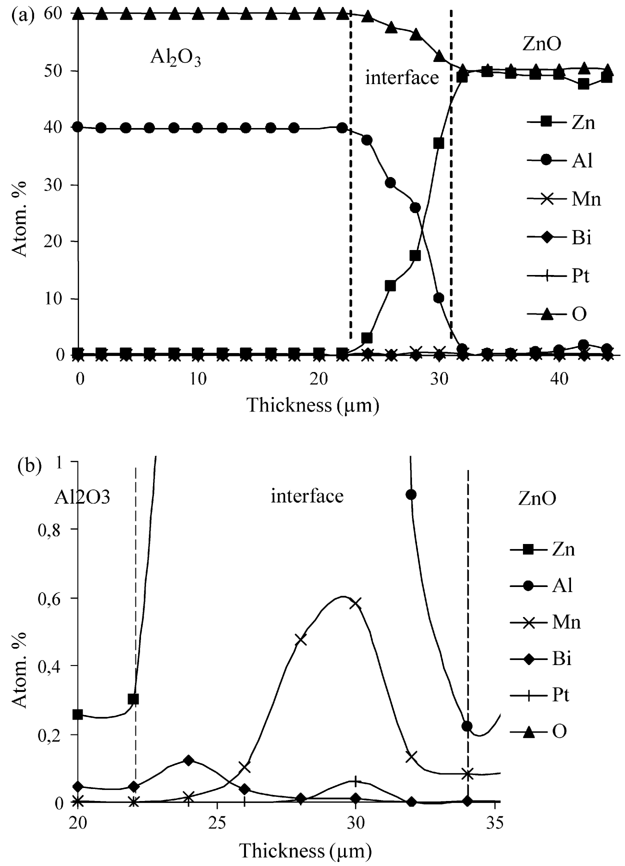

Fig. 3. Castaing Electron Probe Micro Analysis of (a) microassembly and (b) interface of ZnO layer/alumina sintered at 1200 °C.

Bi phases practically vanished from the ZnO layer and that a very small amount of Bi < 0.2 atom% was only detected at the interface ZnO/Al_2O_3 (Fig. 3(a and b)). The affinity between Al_2O_3 and Bi_2O_3 was also observed by Metz et al.[13] in an interesting work concerning the influence of the sintering process on non-ohmic properties of ceramic varistors. The authors demonstrated that, at firing temperatures higher than 1100 °C, careful sintering conditions were necessary to control Bi_2O_3 evaporation and/or diffusion to the alumina used as ceramic support in the furnace. They also suggested that a very low residual concentration of bismuth in the final varistors was sufficient to induce outstanding non-linear behaviour. Moreover, direct writing fabrication of ZnO TFV on an alumina substrate with Micropen system by Thover et al.[14] confirmed the Bi_2O_3 diffusion to the substrate and/or evaporation during the firing process. The authors observed a maximum value $\alpha \sim 30$ for a sintering temperature of 900 °C. The increase of the sintering temperature up to $T \sim 1250$ °C enhanced the chemical interactions of Bi phases with the substrate, which gradually led to the degradation of the non-linear properties of their ZnO TFV.

We thus, decided to study the influence of the bismuth-content in electrode inks on the TFV properties by selecting commercial inks on the basis of the analysis of their mineral part with the CAMECA SX100 Electron Probe Micro Analyser (EPMA). According to their Bi_2O_3 content, Pt Heraeus LPA88-11S (0%), Ag ESL 9912A (0%), Pt ESL 5545LS (~0.9 mol%) and Ag ESL 9912IXL (~0.5 mol%) pastes were chosen. The Ag ESL 9912IXL paste, manufactured specifically for us by ESL Company, contained the same silver powder as the Ag ESL 9912A paste and the same additives as the Pt ESL 5545LS one. The results showed that high non-linear coefficients $\alpha > 33$ were only obtained for TFV with Pt ESL 5545LS and Ag ESL 9912-IXL electrodes (Table 1), though the same non-linear behaviour ($\alpha > 49$) was observed for ceramics whatever the electrodes composition. The presence of 0.9 mol% Bi_2O_3 in the Pt ELS 5545LS paste and of 0.5 mol% Bi_2O_3 in the Ag ESL 9912IXL paste, may thus, explain the occurrence of the non-linear properties of the ZnO TFV (Table 1). It is also worth noticing that TFV made with identical ZnO layer (T_{firing} = 1200 °C) but metallized with sputtered Pt electrodes (containing obviously no additive), also exhibit low values $\alpha \sim 4$.

The optimum range of firing temperatures for obtaining the highest non-linear coefficient for the Pt ESL 5545LS electrodes ($\alpha \sim 35$) was determined to be 800–980 °C (Table 2). Below this temperature range, no chemical interaction between the bismuth oxide of the electrode and the zinc oxide layer occurs. Between 800 and 980 °C, the ZnO layer is assumed to recover bismuth-rich phases proceeding from the bismuth oxide originally present in the electrode. These Bi-rich phases are known to condition the occurrence of the non-linear behaviour. Above this temperature range, the mechanism described by Thover et al.[14] and which explains the low α values above 900 °C is again applicable: the bismuth phases either diffuse to the alumina substrate or evaporate.

However, the switch fields do not seem to depend only on the bismuth content in the electrode pastes. The switch fields $1.1 < V_{br}$ (kV mm^{-1}) < 1.5 measured for TFV with Pt ELS 5545LS and Ag ESL 9912IXL electrodes containing bismuth match the V_{br} values calculated for 1–3 µm ZnO

Table 1
Electrical characteristics of ZnO TFV with Bi_2O_3-content in Pt and Ag screen-printing inks and sputtered Pt

Electrode	T_{firing} (°C)	Thick film (TFV)		Initial Bi_2O_3 (mol%)
		V_{br} (kV mm^{-1})	α	
Pt ESL 5545LS	850	1.5	33	0.9
Pt Heraeus LPA88-11S	950	0.3	4	0.0
Ag ESL 9912IXL	850	1.1	43	0.5
Ag ESL 9912A	850	1.3	6	0.0
Pt sputtered	–	0.5	4	0.0

Table 2
Variation of the electrical characteristics of TFV with the firing temperature of Pt ESL 5545LS electrode

T_{firing} (°C)	V_{br} (kV mm^{-1})	α
600	0.6	4
700	1.4	12
800	1.4	33
850	1.5	35
980	1.5	35
1200	0.2	4

grain size. Conversely, a larger range of switch fields $0.3 < V_{br}$ ($kV\,mm^{-1}$) < 1.3 is observed with the other electrodes. These results may be explained on the basis of the work of Olsson and Dunlop[15] on ceramic varistors. The authors showed that the breakdown voltages did not correlate systematically with the ZnO grain size and with the Bi_2O_3 content, but might also depend on the average distance between ZnO junctions and on the relative volume fraction of multiple ZnO grain junctions formed during the sintering process. In the case of ZnO TFV, one may assume that the glass frit generally present in commercial screen-printing electrode inks plays a significant part in this type of mechanism during the firing process. Though this problem is beyond the scope of the present paper, the interaction of the glass frit with the ZnO layer has certainly to be considered when optimizing the electrical characteristics of ZnO TFV.

4. Conclusion

Up to now, lots of works have been carried out with ceramic and thick film varistors in order to improve their electrical characteristics. Most of them have dealt with Bi_2O_3-rich liquid phase for controlling the microstructure and thus, the non-linear electrical properties. Although sintering varistors at low temperature remains an interesting challenge, the non-linear coefficient of ZnO TFV in these conditions is unlikely to exceed a value of 30. It is suggested in this study that a good strategy consists in keeping the sintering process of the ZnO layer at high temperature ($T_{firing} = 1200\,°C$), as for ceramics, in order to form the required microstructure and phases at the origin of the non-linear properties. The disappearance of Bi_2O_3 from the ZnO layer into the substrate or its evaporation during this high temperature process is then compensated by the screen-printing and firing in the temperature range 800–980 °C of an electrode paste containing small amounts of Bi_2O_3. Using this strategy, the highest value $\alpha \sim 43$ ever recorded for a ZnO TFV, was obtained in this work with silver electrodes containing ∼0.5 mol% Bi_2O_3. A better control of the firing temperature of the ZnO thick film ($1100 < T(°C) < 1200$) and a better control of the Bi_2O_3 content in the electrode inks should give rise, as for ceramics, to non-linear coefficient $\alpha > 50$.

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