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Improved non-linear behaviour of ZnO-based varistor thick films prepared by tape casting and screen printing

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Abstract

Thick films of ZnO-based varistors have been prepared by screen printing and tape casting techniques. The manufacture of varistor thick films by screen printing shows two critical problems; the excessive volatilization of Bi_2O_3 during the sintering step, due to the exaggerated area–volume ratio of these devices and the lack of density of the green compacts, problem inherent to screen printing technology. Tape casting improves compact density and it is also possible to include an additional press step before sintering. An electrical and microstructure comparison between thick films prepared by both technologies has been carried out for a wide range of sintering temperatures. Although far from the electrical response of bulk ceramics, the results obtained show good varistor behavior when sintering the films at low temperatures.

Keywords: ZnO; Varistors; Tape casting; Thick films

1. Introduction

Ceramic materials based in Bi_2O_3 doped ZnO showing highly non-linear current–voltage response find applications as varistor devices.[1,2] Recently, potential of thick films for low voltage electrical circuits have attracted attention, and those manufactured by tape casting and screen printing techniques are the most promising ones. Both technologies have been developed in the field of microelectronics and among its many advantages, the low cost, the possibility of miniaturization and the design versatility can be enumerated. However some critical technological problems also remain unsolved.[3,4] Particularly in the case of varistor thick films a lack of reliability in the electrical response is still obtained, regardless of the technique employed for producing the films. The origin of such inconvenience should be found on the relatively low green density of the films as well as on an excessive bismuth loss by vaporization. A high level of porosity is unavoidable when preparing the films by screen printing technology. However recent studies have partially overcome this restriction either by applying a mechanical pressure onto the calcined films,[3] or by using a proper processing strategy that improves the densification of the ceramic body.[5] On the other hand when preparing the thick films by tape casting technology, the film is joined to the substrate during a pressing step that gives place to an improved compact density.

But as mentioned, an excessive bismuth loss by vaporization is also behind the lack of reliability of varistor thick films. Bi_2O_3 volatilization takes place from the Bi-rich liquid phase formed during sintering to promote proper densification. Furthermore this dopant is also involved in the formation of active grain boundaries at ZnO/ZnO homojunctions that lead to the characteristic non-linear behaviour.[6] In this way volatilization of bismuth has dramatic consequences on the varistor microstructure as well as in its electrical response. Unfortunately in the case of thick films we have to face another inconvenience. Previous works with bulk varistor samples showed that volatilization of bismuth increases noticeably with the sintering temperature,[7] but also with the area–volume ratio of the ceramic compact.[8] Obviously such effect is more accentuated in the thick film geometry, where the area–volume ratio is about two orders higher than in bulk samples. In principle this constrains the attainment of good varistor properties in thick film

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devices which, at the present time, can not be compared to the excellent results obtained in bulk samples.[9] However these differences could be reduced by acting once again over the processing strategy.[10] In a typical varistor composition based on the ZnO–Bi_2O_3–Sb_2O_3 ternary system, the liquid phase is formed together with a spinel type phase around 950 °C, after decomposition of an intermediate pyrochlore compound.[11] Incorporating the spinel phase in the starting formulation avoids such reactions and the bismuth liquid phase is then released at temperatures as low as 740 °C (eutectic reaction in the ZnO–Bi_2O_3 binary system).[12,13] As a result dense varistor films can be obtained at lower sintering temperatures, so minimizing the bismuth loss by vaporization and allowing the achievement of a high degree of non-linearity. In the present contribution this strategy is applied to produce varistor thick films by screen printing and tape casting techniques.

2. Experimental

A standard varistor composition in which the antimony oxide was substituted by the equivalent amount of previously synthesized $Zn_7Sb_2O_{12}$ spinel type phase was used as precursor of the pastes.[10] The precursor powder was obtained by means of a classical mixed-oxide route including ball milling for 2 h in ethanol. The pastes were prepared by mixing the varistor powder (60 wt.%) in a planetary mill with an organic vehicle (40 wt.%) that provides flexibility as well as good homogeneity. Different organic vehicles were used in each case: α-terpineol, ethylcellulose and [2-(2-butoxy-ethoxy-ethyl)]acetate for the screen printing ink, and ethanol, ethylmethylketone, polyvinylbuthyral, polyethylenglycol and benzylbuthylphtalate for the tape casting paste.[14]

Subsequently the obtained pastes were deposited on dense alumina substrates that were previously covered with a platinum electrode; the Pt electrode is attached to the alumina surface by screen printing and the assembly is fired together at 850 °C for 30 min. Deposition of the pastes followed different steps for each technology: thick films prepared by screen printing consist of six layers of varistor slurry that were dried in oven (150 °C) after each deposited layer. The organic vehicle was removed according to DTA results[5] at 425 °C for 0 h, with heating and cooling rates of 0.5 °C/min and with several soaking times of 30 min at 195, 270 and 385 °C. After calcination the green thickness of the films is always in the range between 60 and 70 μm. In the case of tape casting the slurry is cast over a polymer sheet which is easily removed after drying the film at room temperature. The height (aperture) between the blades and the supporting table determines now the thickness of the film. After drying, the film is subjected to a press step at 80 °C/0.6 bar for 10 min and the organic vehicle is now removed by calcination at 500 °C for 2 h, with a heating rate of 0.2 °C/min and a cooling rate of 1 °C/min. This calcination gives place to green thickness of 80–100 μm.

Finally both types of films were sintered in air at temperatures ranging between 900 and 1150 °C for 1h. In the case of screen printed films an average thickness of 30–40 μm was obtained, while those prepared by tape casting yielded an average thickness of 40–50 μm after sintering. In all the cases values of >90% of the theoretical density were achieved. In addition, pellets with the same composition were prepared with the objective of carry out an electrical and microstructural comparison between thick films and bulk varistors.

Phase characterization of the starting varistor powder was performed by X-ray diffraction (XRD) in a D5000 Siemens Diffractometer using Cu $K\alpha_1$ radiation. The average particle size of this powder was determined by using a Laser Coulter of Malvern Instruments. The porosity was measured by means of mercury intrusion on calcined samples with a Pore Master 33 equipment of Quantachrome Instruments. Sintered thick films were characterized by a cold field emission scanning electron microscope (FE-SEM Hitachi S-4700) equipped with EDS. For electrical characterization, gold electrodes were deposited by sputtering on the top of the film and *V–I* measurements were carried out using a DC power multimeter (Keitley 2410). The value of the *non-linear coefficient α* was evaluated from the current density interval between 1 and 10 mA/cm^2.

3. Results and discussion

XRD pattern of the starting powder used to prepare varistor thick films by screen printing and tape casting techniques is depicted in Fig. 1. As observed together with the peaks of the major ZnO phase, peaks of Bi_2O_3 and spinel $Zn_7Sb_2O_{12}$ phases are also detected according to the selected processing strategy. Average particle size of this mixture was determined to be around 0.8 μm.

Thick films were then prepared as mentioned in the previous section and the first differences come to appear when measuring the porosity of both types of films. As it is illustrated in Table 1, after calcination the average pore size in both films is almost the same however the total pore volume per mass unit is clearly higher in the film prepared by screen printing. This fact was expected, since the problem of high porosity is inherent to the technique itself, even although processing strategies that provide a higher densification are employed.[3,5] On the other hand, the volume of porosity in the film prepared by tape casting is at the same level of the pressed pellet. This should be attributed to the pressing stage included after casting the slurry.

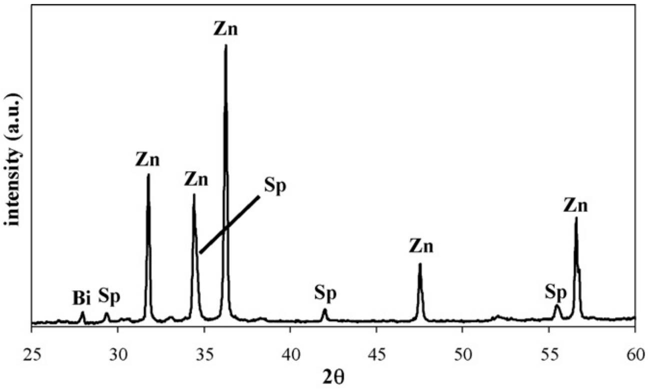

Fig. 1. XRD pattern of the starting powder previous to sintering Zn = ZnO (JCPDS 36-1451), Bi = Bi_2O_3 (JCPDS 71-0465, Sp = $Zn_7Sb_2O_{12}$ (JCPDS 36-1445).

Table 1
Average pore size and total pore volume per mass for thick film prepared by screen printing and tape casting and for a bulk varistor, calcined at 500 °C for 2 h

Calcined sample	Average pore size (μm)	Total pore volume per mass (cm^3/g)
Thick film screen printing	0.28	0.90
Thick film tape casting	0.26	0.66
Bulk varistor	0.15	0.65

SEM micrographs in Fig. 2 show the microstructure of the films prepared by screen printing and tape casting after sintering at 950 °C for 1 h. Both images show evidence of the presence of a liquid phase as well as relatively small grains, with an average size clearly below the micron (similar to the particles sizes of the starting materials). These pictures also show those differences observed in the green films, that is, a higher level of porosity in the screen printed sample (Fig. 2A). Such differences should be reflected in the electrical properties of these two systems. In this way Table 2 depicts the values of the non-linear coefficient α for both types of films sintered between 900 and 1150 °C. In all cases, soaking time is 1 h, since higher soaking times increase the Bi_2O_3 lost considerably and consequence of this the electrical

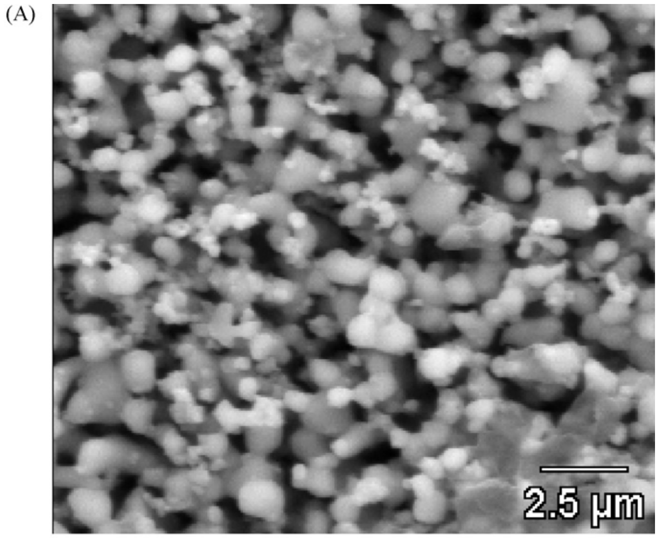

Fig. 2. SEM micrographs of the as-sintered surface for thick films prepared by screen printing (A) and tape casting (B) sintered at 950 °C, 1 h.

Table 2
Evolution of non-linear coefficient α with sintering temperature for thick films prepared by screen printing and tape casting

Sintering temperature (°C)	Screen printing	Tape casting
900	20	16
950	15	18
1000	10	18
1050	9	11
1100	7	6
1150	5	4

Soaking time = 1 h.

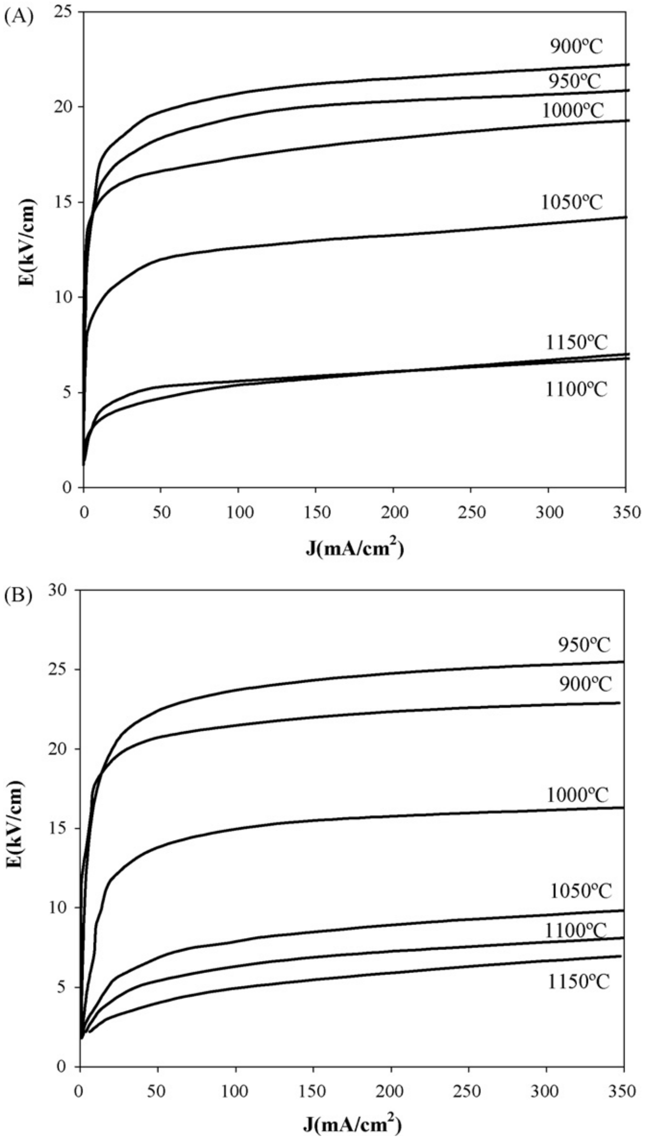

Fig. 3. *I–V* curves for thick films prepared by screen printing (A) and for tape casting (B) sintered at different temperatures. Soaking time 1 h.

response is degraded.[8] Results presented in Table 2 demonstrate that is possible obtain thick films by both technologies with a good varistor behaviour referring to the non-linear coefficient although in all the cases, the samples show higher leakage currents than bulk samples (1–1.5 mA/cm^2). The values obtained for the breakdown voltage for the samples sintered at lower temperatures which show the higher value of α are comprised between 15 and 25 kV/cm. Fig. 3 shows the I versus V curves for thick films prepared by screen printing and tape casting sintered at different temperatures. Nevertheless, thick films prepared by tape casting technology show a good electrical response in a wider sintering temperature range (900–1000 °C) due to a higher density than those prepared by screen printing. This major density hinders the excessive volatilization of Bi_2O_3 until high temperatures are reached. As consequence of this higher density, thick films prepared by tape casting lead to obtain a major reproducibility in the electrical response than those prepared by screen printing for all the sintering temperatures.

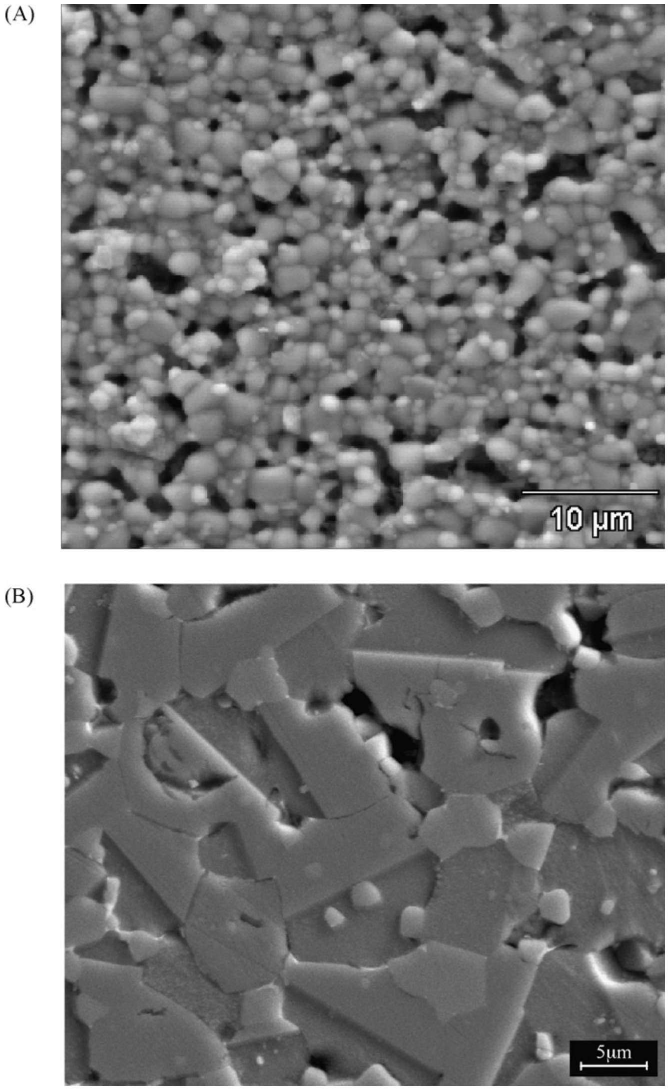

Fig. 4. SEM micrographs of the as-sintered of a thick film prepared by tape casting (A) and polished and chemically etched bulk varistor surface (B), sintered at 1180 °C, 2 h.

However, although it has been possible obtain good electrical response for ZnO-based varistors prepared as thick films, this behaviour is inferior to the behaviour obtained for bulk varistors ($\alpha \sim 50$) in pellets sintered at suitable conditions for bulk varistor (1180 °C, 2 h).

If any microstructure of the thick films prepared by both technologies, independently of the sintering temperature is compared with the microstructure of a sintered bulk varistor is easy understand the different varistor behaviour obtained in each case. As example, Fig. 4 shows the microstructure of a bulk varistor sintered at 1180 °C, 2 h (standard conditions for bulk ZnO-based varistor with this composition) and a thick film prepared by tape casting, sintered in the same conditions. Bulk varistor shows an excellent varistor behaviour ($\alpha = 50$) whereas sample prepared as thick film does not present good varistor behaviour ($\alpha = 3$). Thick film microstructure shows high porosity, consequence of the excessive Bi_2O_3 volatilization during sintering. Due to this volatilization, at the end of the sintering process grain growth takes place in absence of liquid phase and therefore the mater transport is limited. As consequence of this, the development of the characteristic microstructure does not occur homogeneously in thick films and the excessive Bi_2O_3 volatilization prevent the formation of a substantial quantity of potential barriers, responsible of the varistor behaviour. Therefore the electrical response is different between ZnO-based varistors prepared as thick films or like bulk. Thick films sintered at lower temperatures do not densify sufficiently, and the development of the characteristic microstructure is not uniform although the presence of Bi_2O_3 allows obtaining good varistor behaviour in certain areas of the sample.

4. Conclusions

Tape casting technology allows manufacturing thick films with more homogeneous microstructures than screen printing, which lead to a more reproducible electrical response in all the samples. Thick films of ZnO-based varistors have been prepared by screen printing and tape casting technologies, obtaining α values as high as 20 for sintering temperatures ranging between 900 and 1000 °C. Electrical response obtained for ZnO-based varistors as thick films is not as good as for bulk varistors. Such a different behaviour is originated in the microstructural features. Even if bulk samples and thick films are sintered in the same conditions, grain growth is completely different because of the Bi_2O_3 volatilization in thick films.

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