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Statistical evaluation of grain boundaries of varistors with modified bismuth oxide

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Oxide varistors are made of inhomogeneous material whose properties are determined by active grain boundaries. It is essential that in the microstructure of a varistor only active grain boundaries are present as only such boundaries are involved in the process of conduction. Commercial varistors are characterized by a microstructure with a large amount of electrically inactive areas which include zinc-antimony spinel, bismuth oxide, and pores. Studies on elimination of inactive grain boundaries, which are the intergranular areas rich in reaction products of varistor components and pores, lead to an improvement in the microstructure, thereby improving the electrical properties of the varistor. The results were evaluated using statistical methods, defining the percentage of active grain boundaries in the varistor. Statistical analysis showed that the best results were obtained for a bismuth oxide varistor doped with antimony oxide, containing nearly 100 % conductive grain boundaries in its body.

Keywords: *ZnO varistors; modified microstructure; nonlinear properties; semiconductor materials*

1. Introduction

Varistors are ceramic elements used for protection of electrical grids and powered electronics against voltage surge. They possess an ability to absorb considerable energy even from lightning discharge.

Currently, the primary component of oxide varistors is zinc oxide doped with metal oxides that ensure the non-linear current-voltage characteristics of the varistor [1].

The varistor microstructure, besides grains of zinc oxide surrounded by a layer of bismuth oxide [2], is composed of the products of reaction between the varistor components located in intergranular areas of the varistor. These areas are not involved in the process of current conduction and therefore their presence in the varistor microstructure is undesirable. Because the operating voltage of a varistor is dependent on the number of ZnO grain boundaries, it is very important to eliminate the electrically inactive areas. It can be achieved in two ways: by modifying the bismuth oxide in such way as creating a thin layer that surrounds the grains of zinc oxide and by minimizing the amount of additions that form electrically inactive areas in varistor [3–5].

It has been proven that modification of bismuth oxide with small quantities of other metal oxides results in significant change in the varistor structure. Bismuth oxide, when pre-bound with another metal oxide, changes the mechanism of varistor sintering process and modifies its microstructure. In varistors containing modified bismuth oxide, a uniform distribution of the intergranular phase was achieved whereas standard varistors, containing non-modified bismuth oxide, comprise large unwanted agglomerates of intergranular phases that are excluded from the current conduction mechanism [6, 7].

These oxides were added in an amount of 15 mol%. After mixing with bismuth oxide they were sintered, then grinded and sieved.

Modified bismuth oxide was added to the varistor bulk in a quantity of 0.3 mol%. The samples were made using typical ceramics methods in the form of pellets, and sintered at high temperature.

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It is important to quantify the type of grain boundaries and electrical properties of the varistor, as reported by Boggs et al. [8] in their work assuming a constant size and amount of grains in a hypothetical varistor.

If the ZnO element thickness is T and the average grain thickness is S then the minimum average number of grain boundaries between the electrodes L = T/S. If the probability of a grain boundary being nonconducting is P and we think of the grains as being cubes with the sides of the length L, then in a first approximation, the mean number of active grain boundaries through which the current passes between electrodes is:

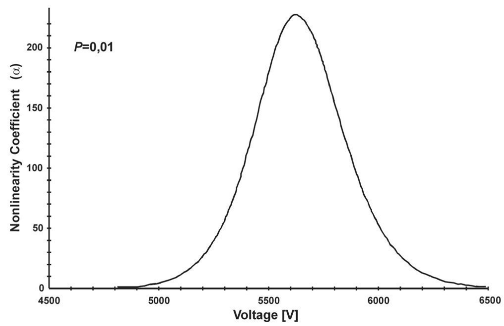
$$B = L \times \left(1 + \frac{P}{1-P}\right) \tag{1}$$

Increasing the number of non-conducting grain boundaries increases the current density at the grain boundaries resulting in a local temperature rise, when active grain boundaries are close to the pores.

In a particular case, each path may be considered theoretically as being independent of the other, which does not actually occur. If two paths of greatly differing lengths pass near each other, the current is likely to flow from one path to the other as a result of a potential difference between them. This effect is not likely to be large for small probabilities P, as the distribution of path lengths is narrow. At larger probabilities P, the number of non-conducting grain boundaries would reduce the likelihood of interconnection of the paths. In addition, the grading across the disk must be roughly uniform, so that even if two paths of different lengths are near each other, the probability of their having substantially differing potentials is not great [8].

Fig. 1 shows the voltage dependence of nonlinearity coefficient α due to the likelihood of inactive grain boundaries at the assumption of a constant grain size.

In case when a varistor has only active grain boundaries (P = 0) and all the path lengths are the same, the shape of characteristics V-α is symmetrical, and can be compared to a Gaussian curve.



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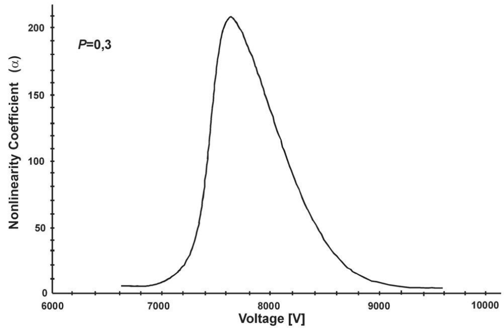

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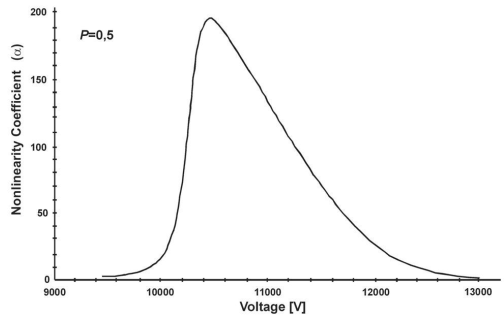

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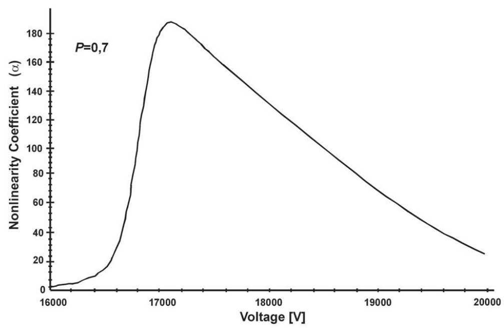


(d)

Fig. 1. α-V characteristics of a hypothetical varistor with a constant grain size: (a) 100 % active grain boundaries, (b) 30 % of inactive grain boundaries, (c) 50 % of inactive grain boundaries, (d) 70 % of inactive grain boundaries [8].

However when the probability P of inactive grain boundaries increases, the graph V-α becomes more asymmetrical.

It seems most likely in the case when a varistor has 30 % to 50 % of inactive grain boundaries (P = 0.3 to 0.5) [8].

2. Experimental

As materials for samples preparation, chemically pure chemicals were used. The oxides Sb_2O_3, SnO_2, PbO and SiO_2 in the amount of 15 mol% were added and mixed with bismuth oxide. So prepared samples were sintered at 810 °C (rising temperature at a rate of 3 °/min), then grinded and sieved.

Modified bismuth oxide was added to the varistor bulk in a quantity of 0.3 mol%. The samples were made using typical ceramics methods in the form of pellets and sintered at 1250 °C. The prepared varistors were 10 mm in diameter and 2 mm thick.

The current-voltage characteristics of the modified varistors were measured using a current generator SPEB-1, in the range of 10 mA to 100 A. The influence of dopants on the electrical properties of the varistor was also studied.

To observe the effects of doping and to assess possible mechanisms of interaction of additives, a TESCAN (VEGA II SBH) scanning electron microscope with EDS microanalyzer of chemical composition (Oxford Instruments) was used. The crystalline phases were studied using a powder diffractometer DRON II with high-temperature X-ray attachment. The study confirmed the incorporation of dopants into the structure of bismuth oxide and enabled the identification of crystalline phases.

3. Results and discussion

In the investigated varistors, decreasing amount of additives and various modifications of bismuth oxide were studied. Bismuth oxide was modified by oxides of metals such as Sb, Sn, Pb and with Si. The varistors were characterized by a uniform microstructure and a small amount of inactive areas in the matrix rich with bismuth oxide and spinel phase as well as good electrical parameters. The characteristics of nonlinearity coefficient α versus voltage V measured on the fabricated modified varistors and α-V characteristics calculated using statistical methods by Boggs et al. [8] were compared and normalized with height and position. This allowed us to determine an approximate amount of inactive grain boundaries P in the studied varistors and thus to select the varistor with the best microstructure. The comparison is shown in Fig. 2.

From the comparison of α-V characteristics of the tested varistors it follows that the modifiers introduced to bismuth oxide effectively influence the mechanism of conductivity of the varistors. The best compatibility with the function describing 100 % conduction of grains is manifested in the varistor where oxide bismuth was modified by antimony. Varistors with unmodified bismuth oxide, varistors with bismuth oxide modified by Pb, and commercial varistor demonstrate compliance with the features characterizing 50 % to 70 % of inactive grain boundaries. However, although varistors with bismuth oxide modified by Si and Sn have symmetrical characteristics (similar to 100 % conductive grain bounderies) but due to the smaller width, they do not fit to any proposed statistical characteristics. It is possibly related to another conductivity mechanism of the grain boundaries.

A comparison of the microstructure of a commercial varistor and a varistor with 100 % conductivity of grain bounderies modified by Sb was carried out using morphological studies on Tescan SEM microscope (Fig. 3).

The presented images of morphology show that the microstructure of the varistor modified by antimony is characterized mainly by grains of zinc oxide (dark grey), a small amount of pores (black) and zinc antimony spinel (light grey). The amount of bismuth oxide is so small that it is barely distinguished (white). Inactive areas in this case amount to 6.54 %. The structure is completely different from the microstructure of commercial varistor,

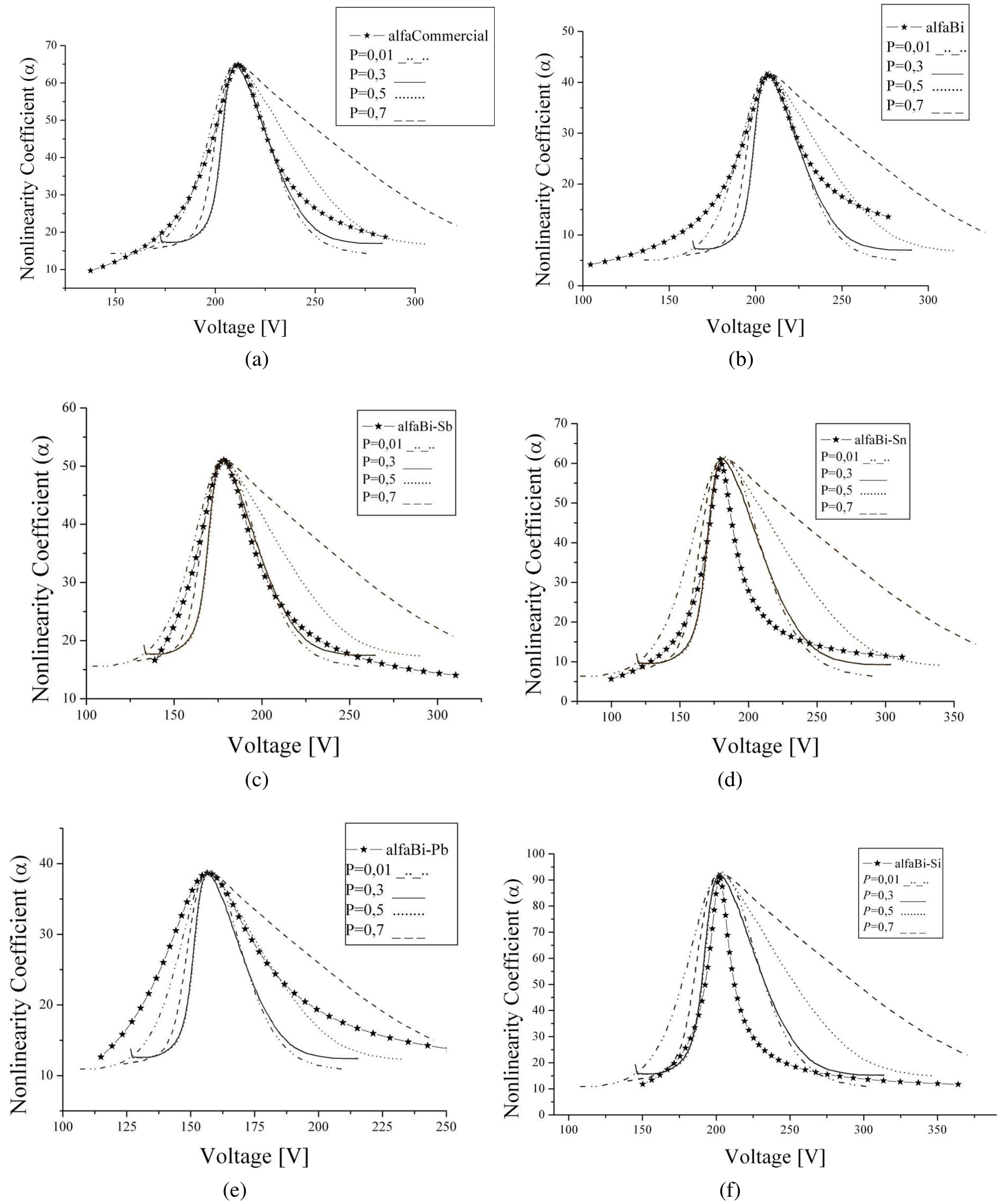


Fig. 2. Comparison of the α-V characteristics of varistors (a) commercial, (b) unmodified and modified by (c) Sb, (d) Sn, (e) Pb, (f) Si with statistically calculated characteristics [8] for the hypothetical varistors (P-0.01 – _.._, P-0.3 – ____, P-0.5 – ....., P-0.7 – _ _ _).

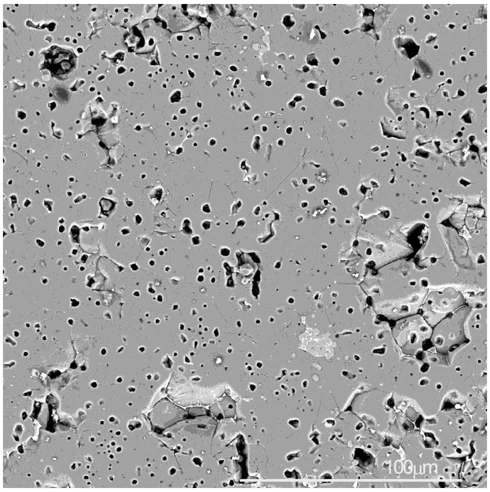
where inactive areas are 29.1 %. The pores in both cases represent more than 6 % of area. Percentages of various phases are shown in Table 1.

As can be seen from the X-ray analysis (Fig. 4), the base of the varistors doped with 0.3 mol% modified bismuth oxide is crystalline ZnO (x), antimony zinc spinel $Zn_{2.33}$ $Sb_{.67}O_4$ (+) and crystalline bismuth oxide βBi_2O_3 (*). This confirms the incorporation of dopants into the structure of bismuth oxide.

Additionally, α-V curves of the modified and commercial varistors were approximated with

Table 1. Morphological analysis of varistor phases; comparison of varistors commercial and modified by Sb.

Sample of varistor	Dark grey – zinc phase [%]	Light grey – spinel phase [%]	White – bismuth phase [%]	Black – pores [%]
Bi-Sb	93.46	0.4	0.02	6.12
Commercial	70.9	14.86	7.36	6.88



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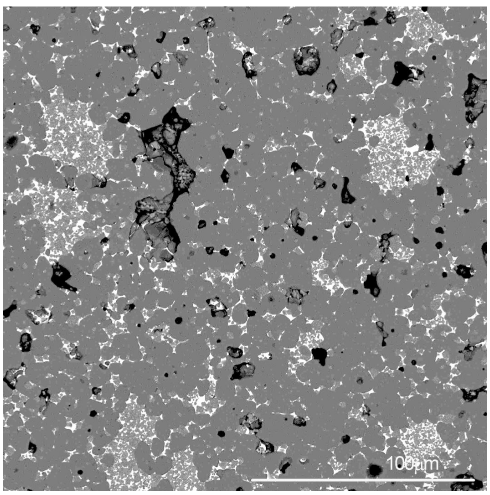


(b)

Fig. 3. SEM images (Tescan) of microstructure of varistors: (a) doped by bismuth oxide modified by Sb, (b) commercial varistor.

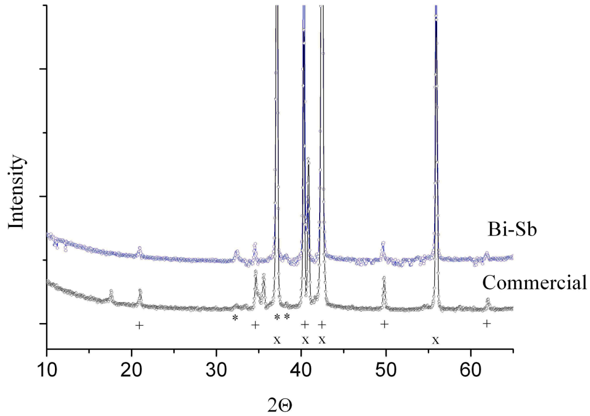


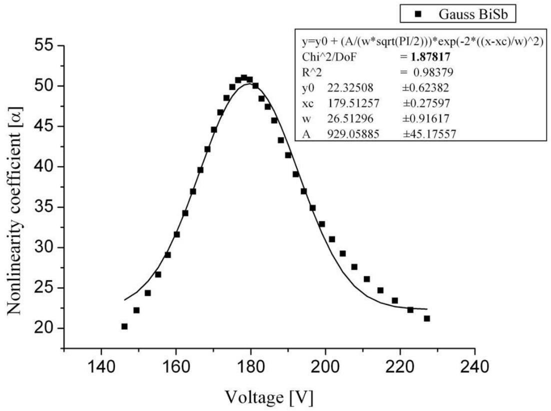
Fig. 4. X-ray diffraction patterns of varistors: commercial and modified by bismuth oxide.

Gaussian curve and collected using the same starting point, the area under the graph and the same width at half maximum point and its severity (Fig. 5).

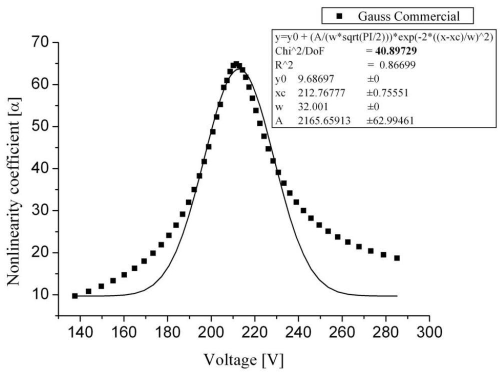
The analysis shows that the curve deviation from the Gaussian function for the varistor doped with bismuth oxide modified by Sb is 1.87, whereas for the commercial varistor it is 40.89. The results determined from the Gaussian function confirm the approximation of the graph of the varistor modified by antimony oxide. The other additives have not given such positive effects.

4. Conclusions

In currently used varistors, characterized by a microstructure which consists mainly of zinc oxide, intergranular phase: $Zn_7Sb_2O_{12}$ spinel, bismuth oxide and pores, the intergranular phase and pores occupy about 30 % of varistor volume and do not participate in the conduction of electricity. The conduction current in the varistor is determined by the number of grain boundaries of zinc oxide, and the nonlinearity of α-V characteristics determines the properties of the grain boundaries. Modification of bismuth oxide by doping other metal oxides appears to be a good direction of research aiming at developing methods of even distribution of dopants



(a)



(b)

Fig. 5. Approximation of α-V characteristics of varistors by a Gaussian function (a) varistor doped with bismuth oxide modified by Sb, (b) commercial varistor.

in the varistor structure. Analyzing the waveform of measured and approximated characteristics, one can find that the best compliance with the model proposed by the authors [8], describing 100 % conductive grain boundaries was obtained for the varistor doped with bismuth oxide modified by Sb.

Acknowledgements

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