Electrical properties of varistors based on tin oxide.

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Abstract. Tin oxide varistors may be an alternative for zinc based ones. The comparative analysis of both materials showed that, after adding suitable dopants, SnO\textsubscript{2} has similar semiconducting properties as ZnO. SnO\textsubscript{2} varistors were made in two versions: low- and high-added. The distinction lied in the added barium-bismuth compound in an amount of 0.3% and 0.8% respectively. Other metal oxides commonly used in varistors were added as well. Varistors were created using conventional ceramic technology applying sintering temperature 1250 °C.

1. Introduction
Some semiconductor oxides exhibit non-linear nature of the current-voltage relationship. This property has found practical application in varistors which in electrical circuits are elements serving to protect equipment against surges. ZnO varistors, due to their high coefficient of nonlinearity (approx. 50), high energy absorption, low leakage current and quick response to changes in voltage, are widely used as fuses in electrical appliances and as a surge arresters in the distribution and transmission power lines. SnO\textsubscript{2}, due to its high electrical stability and less complex microstructure may be competitive to ZnO [1].

The properties that predispose ZnO for use in electrical engineering result from the fact that in its crystal lattice are interstitial atoms of zinc which cause that junctions of single crystals exhibit nonlinear electrical properties and their electrical properties can be easily modified using dopants. Not without significance is that zinc oxide elements can be easily prepared by conventional ceramic technology. The only disadvantage in the application of zinc oxide in varistors is a high conductivity of oxygen ions and low electrical stability at high currents.

When it comes to tin oxide it is characterized by a low degree of compaction during sintering, which predisposes it to be used in gas sensors [2] rather then in varistors. The poor compaction at low temperatures results from a low coefficient of diffusion of SnO\textsubscript{2} [3]. At higher temperatures (over 1273K) the process of sintering is worsened by the formation of the intermediate phases, a high partial pressure of SnO\textsubscript{2} vapors [4, 5] and the predominance of surface diffusion mechanisms over the evaporation – condensation ones. The evaporation - condensation (at high temperatures) processes cause only grain growth while tin oxide grains as such are not sintered. Sintering tin oxide can only be achieved through dopants, which are able to modify the crystal lattice of the SnO\textsubscript{2} grains [6].

The varistor effect in ZnO varistors, as well as in those based on SnO\textsubscript{2} ceramics is due to the transport of the majority carriers (electrons) by the potential barrier formed at the grain boundaries.

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during sintering in an oxidizing atmosphere [7]. Varistors based on SnO₂ as compared to the ZnO varistors are more resistant to degradation.

The phenomena of degradation of both SnO₂ and ZnO varistors were examined by [8], using two different approaches: The first method consisted of applying a DC voltage at elevated temperature and degrading with impulse 8/20 current (type lightning). The surface charge accumulated on the grain boundaries was analyzed before and after degradation using electrostatic force microscopy (EFM). As it appeared, prior to the process of degradation, in SnO₂ varistors the 85% of barriers were active, while the ZnO varistors contained only 30% of barriers that effectively participated in conduction by creating the semiconductor voltage barriers causing a drop of approx. 3V at 1mA. As a result of the degradation with pulses, the changes occurred in both cases. In the case of ZnO varistors, the current-voltage characteristics were essentially ohmic, due to the destruction of potential barriers (about 99% of interphase junctions were conductive). However, the SnO₂ system after the degradation with pulse currents continued to show no-ohmic behavior, although with a significant reduction in the amount of effective barriers (from 85% to 5%). In the case of aging with DC current, the SnO₂ system showed minimal differences in an amount the effective barriers before and after aging, whereas in the ZnO one, their number reduced from 30% to 5%. This result demonstrates that to the destruction of potential barriers and annihilation of defects much more energy is needed in the SnO₂ system than in ZnO one. Results obtained by [8] indicates that the SnO₂ varistors are suitable for high voltage applications and to that extent are potentially promising substitute for ZnO varistors.

2. Preparation of samples.
As materials for samples preparation the chemically pure (CP) chemicals were used. The samples compositions are given in Table 1.

| Symbol of sample | BaBiO₂ₓSb₂O₃ | Cr₂O₃ | NiO | Co₂O₃ | MnO | SnO₂ | ZnO |
|------------------|-------------|-------|-----|-------|-----|------|-----|
| WSn00            | 0,2         | 0,2   | 0   | 1     | 0,5 | 0,05 | 0   |
| WSn05            | 0,2         | 0,05  | 0,6 | 1     | 0,5 | 0,15 | 0,5 |
| WSn02            | 0,2         | 0,05  | 0   | 1     | 0,5 | 0,3  | 0,2 |
| WSn98            | 0,3         | 0,05  | 0,05| 1     | 0,5 | 0,15 | 97,83|
| WSn90            | 0,8         | 0,1   | 0,1 | 0,2   | 1   | 0,2  | 90,00|

The mixtures of powders were then fabricated in varistors by forming in discs and sintering at 1250°C. The WSn00, WSn05 and WSn02 are the ZnO varistors with a small addition of SnO₂ while the WSn98 and WSn90 are the SnO₂ varistors, respectively low- and high-added with Ba-Bi compound. The samples were then subjected to microscopic and electrical examinations.

3. Experimental results
3.1. Microscopic characterization of samples
As can be seen in Figs 1 and 2, in the WSn00 sample there were no separate Bi or Ba phases while in the WSn05 sample there were some numbers of micron grains, which are BaCr₂O₄ grains in all probability.
SEM observations of microstructures of WSn98 and WSn90 (Figs 3 and 4) varistor samples show homogeneous microstructures with evenly distributed bright spots, which are liquid phase of bismuth oxide. Due to it, in varistor body there are not areas excluded from work. The darker spots seen in the pictures are pores that were formed during polishing of the samples, whereby the tin oxide grains were washed out.

3.2. Electrical characterization of samples

The current-voltage characteristics were performed applying current in the range of 20 μA - 5 mA DC and a pulse current of 100 mS length, repeated every 1s. The I-V curves of both, ZnO varistors with small addition of SnO$_2$ and SnO$_2$ varistors are shown in Figs 5 and 6.

Varistor voltages of ZnO varistors with small addition of SnO$_2$ were 270 V/mm and 300 V/mm and nonlinearity coefficients $\alpha$ were about 50. Varistor voltages of WSn90 and WSn98 SnO$_2$ varistors were 270 V/mm and 320 V/mm respectively, while corresponding nonlinearity coefficients $\alpha$ were 6.4 and 4.4 respectively.
Figure 5. I-V curves of ZnO varistors with small addition of SnO₂

Figure 6. I-V curves of both low- and high-doped SnO₂ varistors.

4. Summary
Zinc oxide based varistors with small additions of tin oxide exhibited high (about 50) nonlinearity coefficients $\alpha$ and varistor voltages 270 and 300 V/mm. Similar varistor voltages have been exhibited by varistors made of tin oxide, but despite similar content of dopants, their $\alpha$ coefficients were significantly lower, 4.4 and 6.4. However, the microstructure of both types of varistors do not differ in a fundamental way. Added dopants were homogeneously distributed in bodies of both ZnO and SnO₂ varistors. The differences in I-V characteristics can be attributed to the different features of grain boundaries.

5. References
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