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INFLUENCE OF Sb_2O_3 ADDITION ON ELECTRIC PARAMETERS AND STABILITY OF ZnO VARISTORS

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Abstract: Zinc oxide ceramics containing Bi_2O_3 and other metal oxides as additives exhibit a highly nonohmic property in current - voltage characteristics and is widely used for absorption of transient surges in electronic circuits. The nonlinearity effect is produced by potenial Schottky´s barriers which are partly caused by oxygen ions adsorbed on the ZnO grain surfaces. The passage of current during the varistor operation causes, among others, the desorption of oxygen ions from ZnO surfaces and its lost to the ambient. Oxygen ion desorption contributes to varistor degradation by creation in an intergranular layer a δ-Bi_2O_3 phase characterised by great number of oxygen vacancies and high ionic conductivity. Decrease of Bi_2O_3 ionic conductivity, being the main component of intergranular layer, is equivalent to decrease of degradation coefficient. It can be achieved by addition of varistor ceramics with Sb_2O_3. Antimony oxide can dissolve in δ-Bi_2O_3 or react with ZnO and O phases forming $Zn_7Sb_2O_{12}$ spinel and amorphic Bi_2O_3. What more it was found that Sb_2O_3 doping modifies δ-Bi_2O_3 phase in less conductive form. The compositions originally added with 0.3 and mol1%. modified δ-Bi_2O_3 crystal lattice at the greatest rate. More antimony oxide caused that the amount of Sb_2O_3 dissolved in δ-Bi_2O_3 decreased and more spinel particles appeared.

Vpliv dodatka Sb_2O_3 na električne parametre in stabilnost ZnO varistorjev

Ključne besede: keramika, ZnO varistorji cink oksidni, parametri elektricni, stabilnost, Sb_2O_3 oksidi antimona, dodatki

Izvleček: Cink oksidna keramika, ki vsebuje Bi_2O_3 in druge kovinske okside z dodatki ima skrajno nelinearno tokovno-napetostno karakteristiko in se uporablja za izdelavo elementov, ki ščitijo elektronske sestave pred prehodnimi napetostno-tokovnimi preobremenitvami. Nelinearnost karakteristike je posledica potencialnih Schottky zapor, ki jih deloma povzročajo kisikovi ioni adsorbirani na površino ZnO zrn. Električni tok, ki teče med delovanjem varistorja, povzroča med drugim desorbcijo kisikovih ionov s površine ZnO zrn v okolje. Desorbcija kisikovih ionov pomeni degradacijo varistorja, saj povzroča tvorbo faze δ-Bi_2O_3 v prostorih med zrni, ki jo karakterizira prisotnost velikega števila kisikovih vakanc in visoka ionska prevodnost. Zmanjšanje ionske prevodnosti Bi_2O_3, ki je glavna komponenta plasti med zrni, je ekvivalentno zmanjšanju koeficienta degradacije. Omenjeno lahko dosežemo z dodatkom Sb_2O_3. Antimonov oksid se lahko raztopi v δ-Bi_2O_3 ali pa reagira z ZnO in O fazo ter tvori $Zn_7Sb_2O_{12}$ spinel in amorfni Bi_2O_3. Dodatno je bilo ugotovljeno, da Sb_2O_3 zmanjša prevodnost δ-Bi_2O_3 faze. Dodatki s sestavo 0.3 in mol1% so v največji meri spremenili kristalno strukturo δ-Bi_2O_3. Večje količine antimonovega oksida so povzročile manjšo topnost Sb_2O_3 v δ-Bi_2O_3 in povečanje števila spinelnih delcev.

INTRODUCTION

ZnO varistor ceramics consists of ZnO grains separated from each other by an intergranular layer formed by products of additives reactions between each other and with ZnO. The reactions in the process of varistor fabrication are well known /1,2/. Fundamental compo-sition of varistor ceramics constitute ZnO, spinel type and Bi-rich phases. The presence of Bi-rich phase is essential for non - ohmic property in varistor voltage - current characteristics.

During the sintering the starting low temperature α-Bi_2O_3 type phase by interstep $Bi_2(Zn_{4/3}Sb_{2/3})O_6$ pyrochlore phase converts in spinel phase and Bi-liquid which, during cooling, crystallises in high temperature δ-Bi_2O_3 phase.

$$Bi_2(Zn_{4/3}Sb_{2/3})O_6 + ZnO \rightarrow \underset{\text{spinel}}{Zn(Zn_{4/3}Sb_{2/3})O_4} + \underset{\text{liquid}}{Bi_2O_3}$$

Nonlinerity is related to potential barriers on ZnO grains boundaries. The height of these barriers depend on the kind and amount of additives and oxygen ions. Oxygen ions adsorb on ZnO grains during cooling to the room temperature in the following sequence:

$$O_2 \rightarrow O_2^- \rightarrow 2O^- \rightarrow 2O^{2-}$$
$$\text{temperature}\rightarrow$$

It is said /3/ that 10% of potential barriers is caused by adsorbed oxygen ions. The oxygen participation in formation of potential barriers is, in all probability, much greater because ZnO ceramics sintered in nitrogen atmosphere does not show varistor behaviour.

Oxygen ion adsorption benefits by oxygen vacancies of intergranular δ-Bi_2O_3 phase. Due to oxygen vacancies δ-Bi_2O_3 facilities oxygen transition from the air to ZnO grain borders. Anyway the high -temperature δ-Bi_2O_3 -phase exhibit an extremely high ionic conductivity which causes the desorption of oxygen ions and increase of leakage currents.

It is known /4,5/ that Bi_2O_3 ionic conductivity can be decreased by doping varistor ceramics with pentoxides. Pentoxides M_2O_5 dissolved in δ-Bi_2O_3 phase modify Bi_2O_3 lattice constants and reduce the oxygen vacancies according to the following expression:

$$Bi_{4(1-x)}\,M_{4x}O_{6+4x}\square_{2-4x}$$

where $\square$ states for oxygen vacancy.

Since, in varistor ceramics, Sb_2O_3 converts into Sb_2O_5 the above is valid for antimony oxide as well. Dissolving in δ-Bi_2O_3 phase Sb_2O_3 modifies δ-Bi_2O_3 lattice constants and probably decreases δ-Bi_2O_3 ionic conductivity. Reduction of oxygen vacancies in δ-Bi_2O_3 phase in the vicinity of Sb_2O_3 hinders the oxygen desorption from ZnO grains and in this way retards the varistor degradation.

EXPERIMENTAL PROCEDURE

For preparation of varistor samples the different: 0.3, 0.5, 1, 1.5, 2, and 3 mol % amount of Sb_2O_3 were added to a reagent grade ZnO powder. The other additives were kept at a stable ratio: 1mol% Bi_2O_3, 0.8 mol% NiO, 0.5 mol% MnO, 0.4 mol% Cr_2O_3, 0.5 mol% Co_2O_3.

Varistor samples were prepared by conventional wet-mixed-oxide ceramic technology. All mixtures were wet milling for 24 hours and dried. After addition of an organic binder and the pressing of the granulate to 15 mm disc, the green samples were sintered in an atmosphere of ambient air at 1250°C for 1 hour and then furnace cooled.

As -sintered samples have been electrically charaterised for identifications of breakdown voltages $V_{1mA/mm}$, α coefficients and varistor degradation. To make electric contacts a thin layers of silver were evaporated onto the both surfaces of discs.

The crystal phases in sintered bodies were identified by X-ray powder diffractometer using CoK_α Fe filtered radiation. Chemical composition of samples and microstructure SEM observations were carried out using Electron Probe X-ray Jeol JXA 5a Microanalyzer.

RESULTS

The basic I-V characteristics of varistors were measured by dc current in range from 10 μA up to 10 mA at room temperature.

The influence of Sb_2O_3 addition on non-linearity coefficients for three ranges of currents is presented in Fig.1. As can be seen the addition of Sb_2O_3 improves varistors non-linearity coefficients α. The mean non-linear exponents reached a steady - state value 50 but when 3% of Sb_2O_3 was added they significantly decreased. The suitable, from the point of view of non linearity property, is the addition of 0.3 - 1.5 mol% Sb_2O_3.

The correlation between the breakdown voltage and Sb_2O_3 is shown in Fig. 2. The breakdown voltage of varistor without antimony oxide was 80 $V_{1mA/1mm}$ and grew up to 470V for samples with 0.3 mol% Sb_2O_3 and did not change distinctively with further Sb_2O_3 addition.

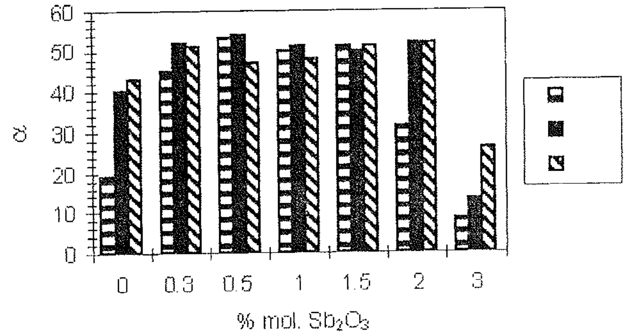

Fig.1: The influence of Sb_2O_3 addition on non-linearity coefficients α_1 -(0.01-0.1mA), α_2 -(0.1-1mA), α_3 -(1-10mA)

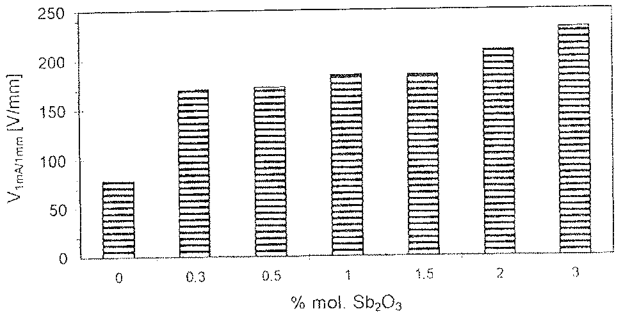

Fig. 2: Dependence of breakdown voltage $V_{1mA/1mm}$ on Sb_2O_3 addition.

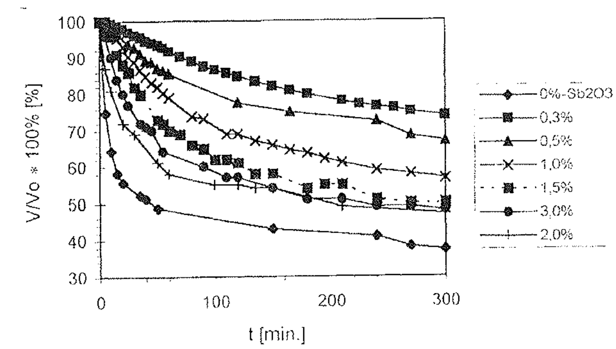

Fig. 3: Varistors degradation characteristics after electrical degradation in 50μA DC electric field at 115°C for 5 hours.

Varistors degradation characteristics after electrical degradation in 50 μA DC electric field at 115°C for 5 hours are presented in Fig. 3. As can be seen even small addition of Sb_2O_3 (0.3mol%) improved significantly varistor stability.

After 24 hours from disconnecting the degrading electrical field the ageing samples were measured electrically. The nonlinerity coefficient changes after ageing are shown in Fig. 4. As can be seen nonlinerity coefficients were polarity dependent and the changes of α

were asymmetrical. The electrical field mostly affected the pre-breakdown regions (α_1 and α_2). At higher currents the polarity effect partly disappeared and samples with 0.3-2 mol% Sb_2O_3 had sufficiently good α coefficients before and after degradation.

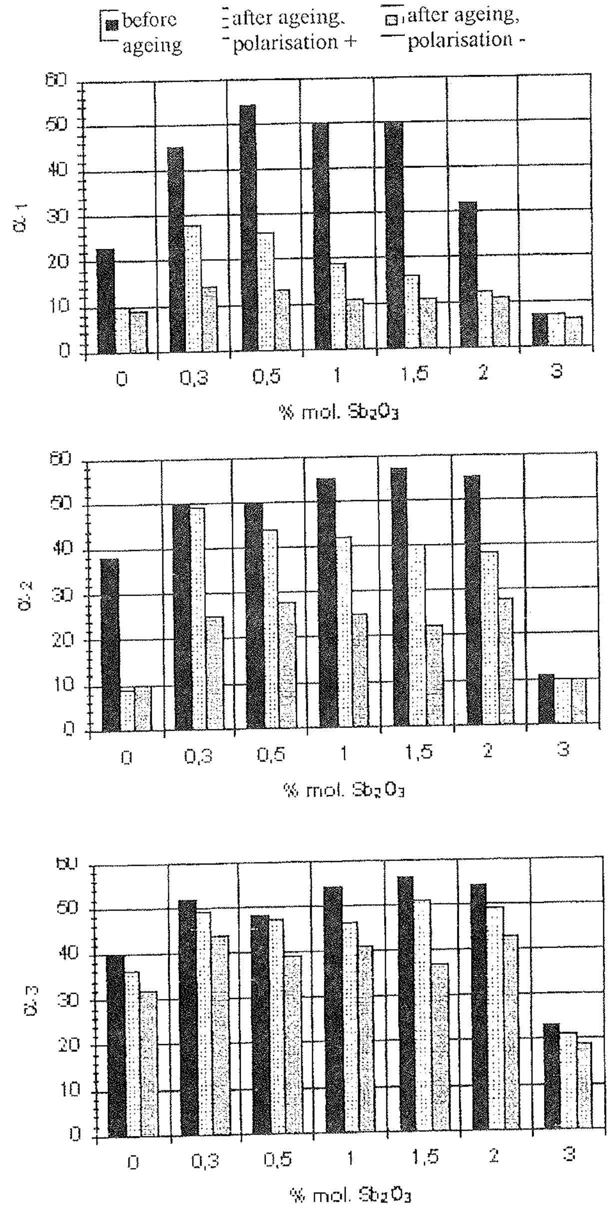

Fig. 4: *Dependence of nonlinerality coefficient α on Sb_2O_3 addition before and after ageing.*

From the results of X-ray powder diffraction measurements the following crystal phases in varistor ceramics were identified: ZnO, δ Bi_2O_3 or mixture of δ-Bi_2O_3 and β Bi_2O_3 (β - X-ray diffraction peaks overlap on those of δ -phase) and $Zn_7Sb_2O_{12}$ i.e $Zn(Zn_{4/3}Sb_{2/3})O_4$ spinel phase. As it was expected, the varistor compositions originally added with more antimony oxide had more spinel particles but unexpectedly X-ray intensities of δ Bi_2O_3 characteristic peaks decreased. Although it is possible that Bi_2O_3 volatization to the ambient increased in Sb_2O_3 presence we put it on conversion of Bi_2O_3 crystal phases into glass amorphic one.

As can be seen from Fig. 5 the vicinity of Sb_2O_3 changed the positions of Bi_2O_3 characteristic peak what gives the evidence that Sb_2O_3 penetrates into δ Bi_2O_3 structure and modifies its crystal lattice constants. Addition of 0.3 mol% Sb_2O_3 modified δ Bi_2O_3 lattice constants at the greatest rate.

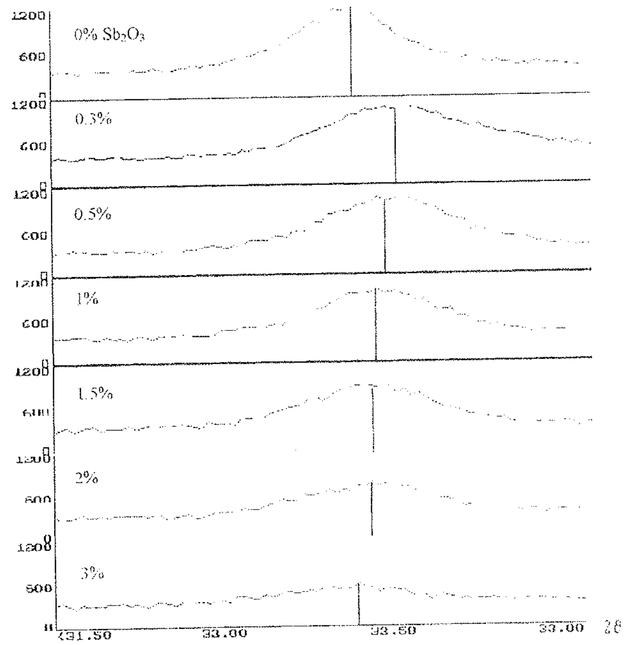

Fig. 5: *Position of the strongest δ Bi_2O_3 diffraction peak in varistor samples doped with different amount of Sb_2O_3.*

The quantity SEM measurements presented in Table 1 proved that only Sb dissolved in δ-Bi_2O_3 is able to modify δ-Bi_2O_3 lattice constants. The Sb dissolved in δ-Bi_2O_3 phase amounted to 0.6 wt.% in samples originally doped with 0.3 and 0.1mol% Sb_2O_3. These were also the samples in which Sb modified δ-Bi_2O_3 lattice constants. The further addition of Sb_2O_3 caused the Bi_2O_3 phase self - purification and the Sb amount dissolved in δ-Bi_2O_3 dropped to 0.1wt.%. It can be inferred that at higher concentration Sb_2O_3 more readily comes into reactions with ZnO and forms spinel phase then dissolves in δ-Bi_2O_3.

Table1: *The quantity SEM measurements of the spinel and Sb contents in varistor samples.*

mol %Sb_2O_3 in varistor composition	0.0	0.3	0.5	1.0	1.5	2.0	3.0
wt% Sb dissolved in δ-Bi_2O_3	0.0	0.6	0.6	0.4	0.1	0.0	0.0
spinel wt% in varistor after sintering	0.0	2.2	2.6	2.8	3.5	3.4	3.6

Elsewhere presented measurements /6/ gave the evidence that modified δ-Bi_2O_3 phase had a desirable smaller ionic conductivity.

CONCLUSION

Carried out investigations fully proved the ability of modification of varistor electrical properties and stability by doping varistor ceramics with appropriate amount of Sb_2O_3. It was found that addition of Sb_2O_3 modifies δ-Bi_2O_3 phase in less conductive form. The compositions originally added with 0.3 and mol1%. modified δ-Bi_2O_3 crystal lattice at the greatest rate.

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