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Degradation of oxide varistor ceramics in air atmosphere containing NO_2 at elevated temperatures

Alexander Glot[a], Elisabetta Di Bartolomeo[b], Aleksei Gaponov[c], Riccardo Polini[b,*], Enrico Traversa[b]

[a]Instituto de Electronica y Computacion, Universidad Tecnologica de la Mixteca, Huajuapan de Leon, Oaxaca 69000, Mexico
[b]Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma "Tor Vergata", Via della Ricerca Scientifica, 00133 Rome Italy
[c]Department of Radioelectronics, Dniepropetrovsk National University, Dniepropetrovsk 49050, Ukraine

Abstract

The heat treatment of commercial zinc oxide based varistor ceramics at temperatures of 200–300 °C in air with 1000 ppm of NO_2 causes strong shift of voltage-current characteristic (VCC) to low voltages. Subsequent exposure to pure air leads to partial restoration of VCC. Scanning electron microscopy analysis showed microstructural changes of samples after heat treatment in air with 1000 ppm of NO_2. Chemical reactions between NO_2 molecules and oxygen chemisorbed or Bi-rich oxide phases at grain boundaries followed by the lowering of grain boundary potential barriers can be the reason of observed degradation.

Keywords: Grain boundary; NO_2; Sensors; Varistors; ZnO

1. Introduction

Zinc oxide based ceramic varistors are widely used for overvoltage protection of electronic and electrical equipment. Degradation of voltage-current characteristics (VCC) of zinc oxide varistor ceramics with electric and thermal stresses is related to the reduction of oxygen content at the grain boundaries mainly at the outer portions of the materials.[1]

Recently, some zinc oxide based as well as tin dioxide based ceramics with nonlinear VCC were used as gas sensors.[2–4] The NO_2 gas sensitivity of so-called varistor-type gas sensors was studied in the range of relatively low concentrations (0–100 ppm) of nitrogen dioxide.[2–4] To the best of our knowledge, the electrical properties of ZnO based varistor ceramics were not studied at higher concentrations of NO_2.

However, the information about the behavior of ZnO varistor ceramics in polluted air such as in combustion process products, could be very important for certain varistor applications.

In this work, the severe degradation of VCC of ZnO-based varistor ceramics in air with the addition of 1000 ppm of NO_2 at temperatures in the 200–300 °C range is reported.

2. Experimental procedure

The degradation phenomenon was observed for zinc oxide based varistor ceramics with different additives as well as for tin dioxide based varistor ceramics. For the sake of clarity, results are presented only for commercially available zinc oxide based varistor ceramics in the system $ZnO–Bi_2O_3–Sb_2O_3–Co_3O_4–MnO_2$ with some additives. Ceramic bodies were prepared by a conventional solid state reaction method. Pressed pellets were sintered in air by heating at a rate 300 °C/h up to 1250 °C, holding this temperature for 1 h, and subsequent cooling to room temperature at the same rate. Silver electrodes were deposited on planar surfaces of cylindrical shaped samples by additional firing of Ag paste (maximum temperature 800 °C). Ceramics were characterized by nonlinearity coefficient $\beta = 50–60$ and electric field E_1 (at highly nonlinear part of VCC) of about 1500 V/cm. The thickness of the samples was 0.08 cm and their diameter was 1.5 cm. For electrical

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* Corresponding author. Tel.: +39-06-7259-4414; fax: +39-06-7259-4328.
E-mail address: polini@uniroma2.it (R. Polini).

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measurements, portions of a whole cylindrical sample with cross section of about 0.3 cm^2 were used.

To study VCC in a whole range of dc current up to 2 mA using a 50 V source, besides samples with silver electrodes on both the opposite parallel planes (“sandwich type electrodes”), samples with both electrodes on the same plane side (“planar type electrodes”) were used too. Thin gold wires were attached to Ag electrodes as current collectors, using gold paste fired at 800 °C. The obtained samples were connected to the measurement circuit in a sample holder with controlled atmosphere. Atmospheres of pure air, air with addition of 100 or 1000 ppm of NO_2, and air with addition of 1000 ppm of CO were obtained by connecting the measurement chamber to a gas flow controller providing a gas flow rate of 100 cm^3/min.

Voltage-current characteristics were recorded using a KEITHLEY 487 picoammeter/voltage source (with maximum voltage 50 V) controlled by a computer. Voltage was increased stepwise from zero up to given values and then decreased to zero with the same rate, recording the current at each voltage value. All measurements were carried out at fixed temperature in the range of 20–300 °C under the flow of gas.

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were used to characterize the changes of physical-chemical properties of ceramics as a result of degradation.

3. Results and discussion

VCC of ZnO ceramics in air at 300 °C was stable. No change in VCC was observed exposing the sample with sandwich type electrodes to air at 300 °C even for very long time. Otherwise, dramatical changes of VCC were observed after sufficiently long (more than 36 min) heat treatment of ZnO ceramics at 300 °C in air with 1000 ppm of NO_2. In Fig. 1 VCCs of ZnO based varistor with sandwich type electrodes after exposure to air with 1000 ppm of NO_2 at 300 °C for different times are reported. Initially VCC did not change (Fig. 1a) but after several minutes some changes in VCC were observed. In Fig. 1(curves b–e), the shift of VCCs to lower voltages with increasing NO_2 exposure time is reported.

For the sample with planar type electrodes, the changes of VCC were observed for shorter NO_2 exposition times due to current flow in the vicinity of the surface (Fig. 2). In samples with both types of electrodes (Figs. 1 and 2) a sharp jump in current at certain threshold voltages was observed.

After the atmosphere was changed to pure air, the conductance of samples gradually decreased due to possible oxidation in air at 300 °C (Fig. 3a and b). The difference in electrodes geometry for the samples might explain the observed different variation of VCC shape (Fig. 3a and b) and the sublinear behavior of VCC ($\beta < 1$) at low voltages for the sample with planar electrodes (Fig. 3b).

Fig. 4a shows the initial VCC of ZnO ceramics with planar type electrodes recorded in air at 20 °C. VCC of the same sample after heat treatment of 25 min at 300 °C in air with 1000 ppm of NO_2 was shifted to low voltages (Fig. 4b). After keeping the same sample in air at 20 °C for 4 months, the VCC did not fully return to its initial position (Fig. 4c). VCC was fully restored after heating the sample at 300 °C in air. Therefore, the observed shift of VCC was mainly irreversible.

In air with 1000 ppm of CO (which is a reducing gas) or even in air with 100 ppm of NO_2 the mentioned degradation was not observed. It seems to point out

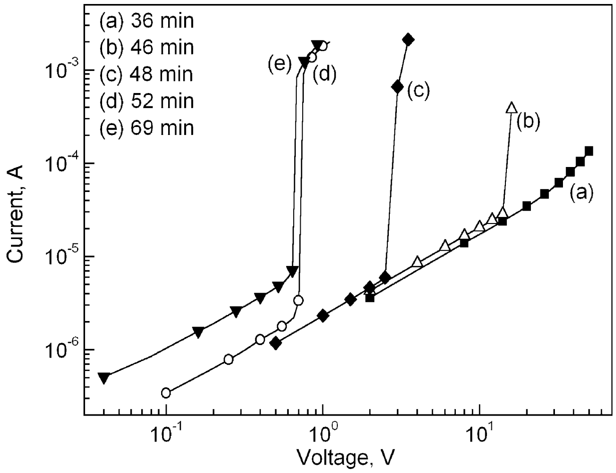


Fig. 1. Voltage-current characteristics of ZnO based varistor ceramics with sandwich type electrodes after exposure in air with 1000 ppm of NO_2 at 300 °C for different times.

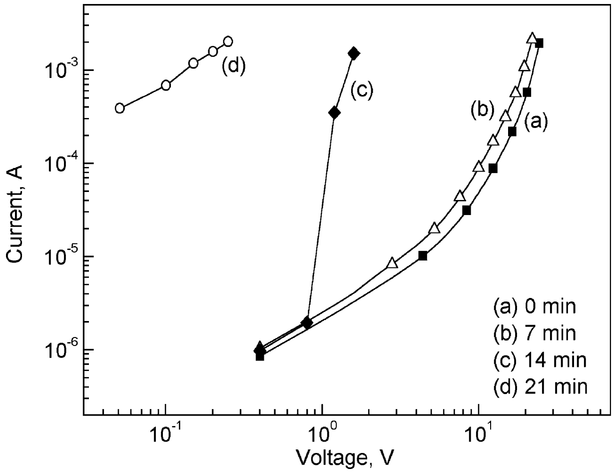


Fig. 2. Voltage-current characteristics of ZnO based varistor ceramics with planar type electrodes after exposure in air with 1000 ppm of NO_2 at 300 °C at different times.

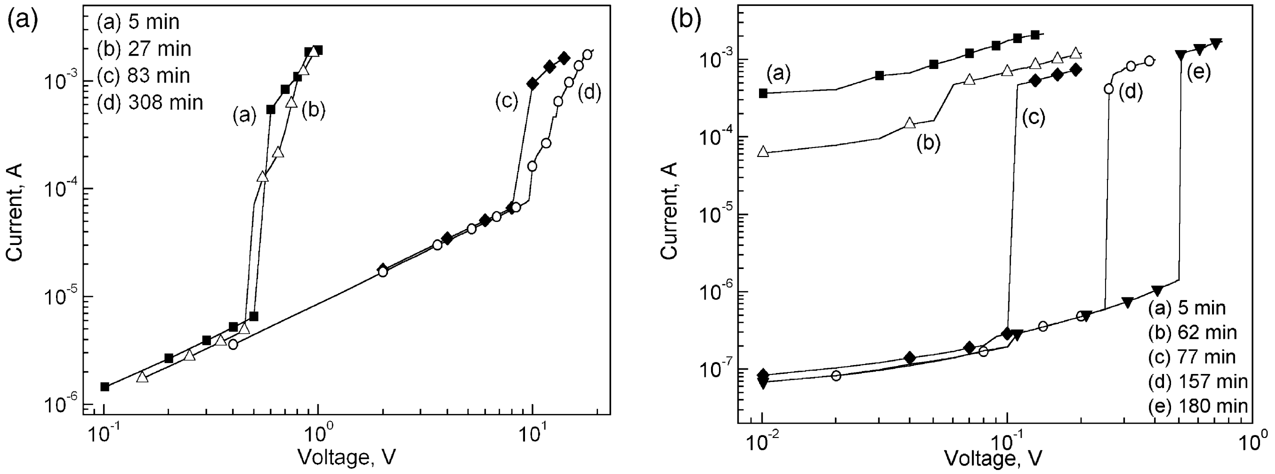


Fig. 3. Voltage-current characteristics of ZnO based varistor ceramics with sandwich (a) and planar type (b) electrodes after exposure in air at different times at 300 °C after exposure in 1000 ppm of NO_2 in air at 300 °C at different times as shown in Figs. 1 and 2, respectively.

that some chemical reactions occur in air with 1000 ppm of NO_2, which cause the decrease of the heights of grain boundary (GB) potential barriers followed by the increase in conductance.

SEM micrographs of the fracture surface of an as-prepared sample (Fig. 5a) and of a sample exposed for 80 min to 1000 ppm of NO_2 in air at 300 °C (Fig. 5b) are very different: after interaction with NO_2, the surface of grains was covered by small particles with pyramidal shape (Fig. 5b). Spot EDS analysis on such particles showed very high intensity of Bi signal with respect to Zn. However, when the electron beam was positioned on the varistor grains, the signal of Bi was very small with respect to the Zn signal. Therefore, after the heat treatment in air with 1000 ppm of NO_2 at 300 °C some changes of bismuth oxide based phase can take place due to chemical reactions, leading to a decrease in the oxygen content at grain boundaries and causing the decrease in GB potential barrier heights.

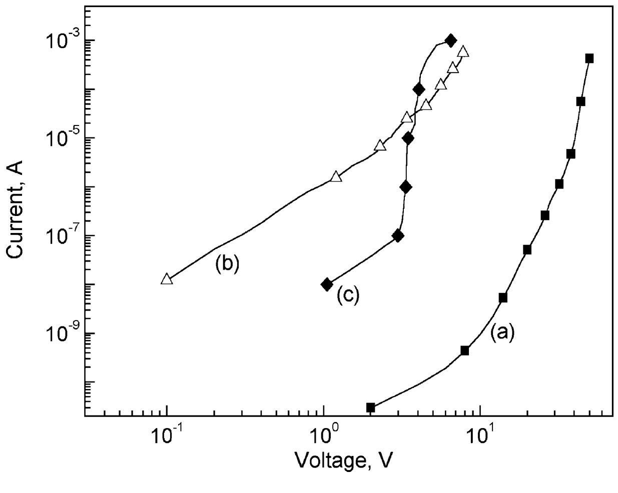
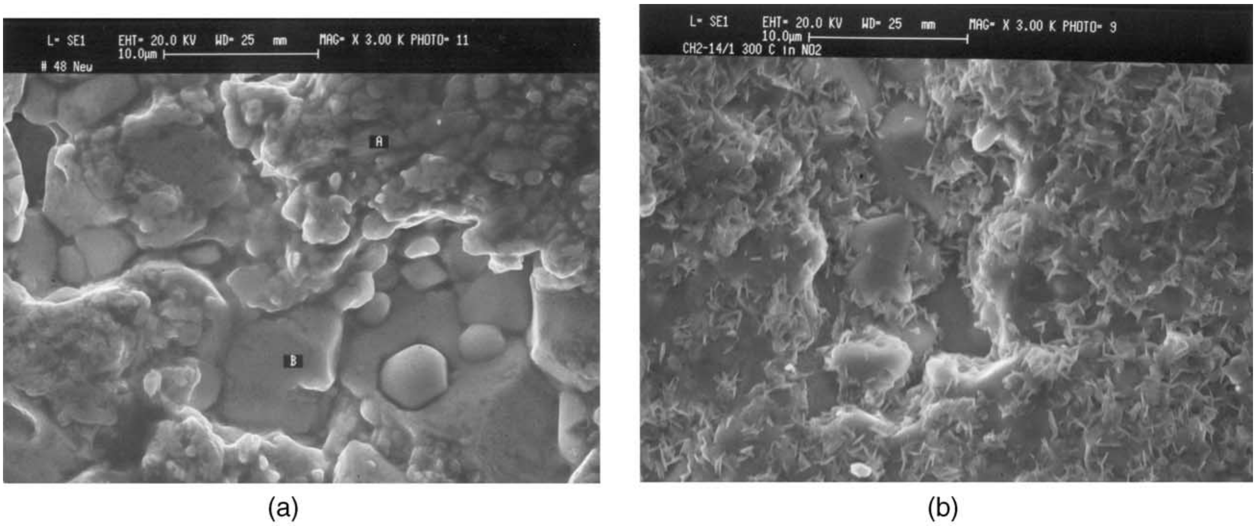


Fig. 4. Voltage-current characteristics of ZnO based varistor ceramics with planar type electrodes recorded in air at 20 °C (a), after 25 min of exposure in air with 1000 ppm NO_2 at 300 °C (b), and after 4 months in air at 20 °C (c).

The mentioned changes in the ceramic surface could be detected after a long enough heat treatment in air with a quite high concentration of NO_2. However, electrical properties of ceramics are sensitive to NO_2 even at the earlier stages of degradation.

The details of chemical changes at the surface of zinc oxide based varistor ceramics are not obvious and two options may be possible. (i) Direct chemical reduction of ceramic surface due to the interaction of NO_2 with chemisorbed oxygen according to the reaction $NO_2 + O \rightarrow NO + O_2$. Such a reaction can be considered as possible.[5] As a consequence, the amount of chemisorbed oxygen at GB is decreased and the heights of potential barriers are lowered leading to nonlinear VCC at low voltages. However, this reaction would not explain the formation of the observed Bi-rich phase. (ii) The reaction of NO_2 with the surface of ceramics gives some new surface phase with high electrical conductivity. The leakage is increased and VCC is shifted to low voltages.

Quite high nonlinearity of VCC in air with NO_2 addition (Figs. 1 and 2) may be a consequence of not only non-ohmic processes but also of two additional factors. On one hand, VCC in Figs. 1 and 2 are recorded during continuous chemical reaction and some chemical changes of ceramics are possible between the beginning and the end of the VCC recording process. On the other hand, some additional influence of local Joule heating is possible due to larger current density near the surface. Non-ohmic behavior of ceramics in gas environment (air with NO_2) is observed several times, however, threshold voltage is decreased over time



(a) (b)

Fig. 5. SEM micrographs of the fracture surface of ZnO based varistor ceramics prior (a) and after (b) an 80 min heat treatment at 300 °C in air with 1000 ppm of NO_2.

(Figs. 1 and 2). In such conditions the shape of non-linear VCC does not reflect the electronic processes but reflect rather degradation of grain boundary potential barriers under the influence of chemical reaction and additional local Joule heating.

4. Conclusions

It is observed that in air with 1000 ppm of NO_2 at 200–300 °C voltage-current characteristics of ZnO based varistor ceramics is shifted to lower voltages and after that in pure air slight reverse shift of it to higher voltages takes place, though the observed degradation is irreversible. The scanning electron microscopy and energy dispersive X-ray spectroscopy confirm the change of ceramics surface after exposure of ceramics in air with NO_2.

The observed degradation was related to chemical reactions between NO_2 and grain boundary oxygen or grain boundary bismuth oxide based phase causing the decrease in the height of grain boundary potential barriers and subsequent shift of voltage-current characteristics to lower voltages.

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