# Desorption thermal degradation model of zinc oxide ceramics

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## Abstract

The desorption degradation model of nonlinear zinc oxide ceramics with intercrystalline potential barriers is developed. It allows to connect the decreasing of surface electronic states concentration with desorption of oxygen at heating up of the grain boundary by electrical current in process of degradation.
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*Keywords:* $Z_nO$; Degradation; Desorption; Surface electronic states

## 1. Introduction

The study of the degradation phenomena of metal oxide varistor ceramics is one of the problems of varistor ceramics manufacture. Two principal degradation mechanisms have been proposed: (1) the electromigration of zinc interspitials in the depletion layer followed by chemical interaction with the grain-boundary defects that form the potential barrier, thereby lowering the barrier height and increasing the leakage current;[1,2] (2) the interface states are associated with the chemisorption of oxygen at the grain boundaries, and during degradation, oxygen desorption occurs.[1,3,4] A number of the observable phenomena, such as the deformation of current–voltage (*I–V*) characteristics resulting in the S-type *I–V* characteristics at significant currents, the decreasing of the classification voltage ($U_c$) and the nonlinearity factor ($\alpha$) confirm the essential role of the thermal factors in degradation processes of such objects.[5–7]

The Joule heating by electrical current which is taking place through contacts between crystallites, is one of the most probable reasons of instability of the grain boundary structures. The heating causes the change of electrical parameters of the ceramics such as the electrical conductivity, the filling degree of the local electron states, etc. on the one hand, and causes the loss of oxygen from the crystallite surface, on the other hand. That can result in degradation of nonlinear properties of oxide varistor ceramics observable at the first stage, when the symmetry of *I–V* characteristics is not yet broken.[3,4]

However, till now the role of thermal and desorption processes in the degradation of the electrical characteristics of oxide varistor ceramics has not been sufficiently investigated because it is based, mainly on qualitative representations.[3–7] More detailed theoretical investigations of the thermal degradation of oxide varistor ceramics and another polycrystalline materials with grain boundary potential barriers are necessary.

One of the most probable mechanisms of such ceramics degradation in the constant electric field can be irreversible change of the surface electron state concentration connected with the desorption of oxygen due to the Joule heating at the grain boundary.[4,5] This is the subject of the present work.

## 2. Theory

The static and pulse current–voltage and capacitance–voltage (*C–V*) characteristics and their changes in the process of degradation were the basic theoretical characteristics, which were analyzed. The double Shottky barrier model was the base for the account. This model itself is two counterly included areas of a space charge of adjacent semiconductor crystallites of zinc oxide divided by a thin dielectric layer of intercrystalline phase.[5,8]

The known equation for the account of thermal effects in the static characteristics was used[5]

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$$C\frac{dT}{dt} = JE - a(T - T_0), \qquad (1)$$

where $C$ and $a$ are specific heat and a heat conductivity of polycrystalline structure, respectively; $T$ and $dT/dt$ are average temperature in the structure and the speed of its change, respectively; $T_0$ is the temperature of the environment; $E$ and $J$ are electric field and density of the current, respectively. It was assumed that the grain boundary potential barriers are identical for the whole structure. According to existing conduction mechanisms in the polycrystalline structures, the current is controlled by thermoelectron emission between the ZnO conduction bands, the tunneling through the bulk charge area, the electron transitions with the participation of surface electronic states at the grain boundaries and the field emission from the valence band of one crystallite into the conduction band of another.[8,9]

Basing on the representations of the electronic theory of chemisorption and considering, that adsorption of oxygen at ZnO surface is described by the known Roginsky–Zeldovich equation,[10] for the analysis of adsorption–desorption processes it is possible to use the kinetic equation

$$\frac{dN_s}{dt} = A\exp(-\gamma N_s) - \nu N_s \exp\left(\frac{-\Delta E}{kT}\right), \qquad (2)$$

where the second part takes into account the desorption processes, the $N_s$ is the concentration of oxygen chemisorptional molecules; $A$, $\gamma$, $\nu$ are constants weakly dependent on temperature; $k$ is the Boltzmann constant; $\Delta E$ is the activation energy of desorption, estimated as the sum of ionization energy of the surface electronic states and physical adsorption energy of an oxygen molecule. It was assumed that the chemisorped oxygen contribution to the density of interface states is much greater than native zinc vacancies contribution and the $N_s$ was accepted equal to the surface electron states concentration.

The unknown factors were estimated to be $A$ of $8.4\,\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$ and $\gamma$ of $4.9\,\mathrm{cm}^2$, by the $dN_s/dt = A\exp(-\gamma N_s)$ dependence approximation of the experimental kinetic oxygen adsorption isotherms for ZnO, given.[11] The estimated factors were used in the proposed desorption thermal degradation model.

## 3. Results and discussion

The calculated theoretical curves according proposed model are given in Figs. 1–7.

The current–voltage characteristics of the structure with identical grain boundary potential barriers for a stationary case ($dT/dt = 0$) are submitted in Fig. 1 (curve 1). The I–V characteristics have a S-type kind. Fig. 2 shows the dependence of temperature and the surface electron state concentration $N_s$ on dc current $J_0$ which causes thermal degradation. It can be seen, that the temperature increases with increase of the $J_0$. The growth of the temperature results
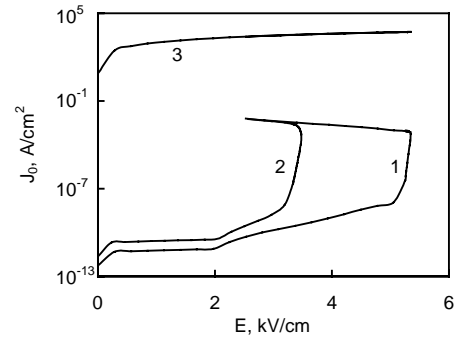


Fig. 1. A static current–voltage characteristics of the structure with identical grain boundary barrier at increasing (1) and decreasing (2) voltage and I–V characteristic at the absence of potential barriers (3).
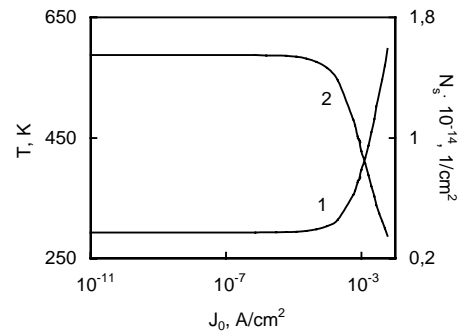


Fig. 2. Dependence of the barrier temperature (1) and the surface electron state concentration $N_s$ (2) on dc degradation current.
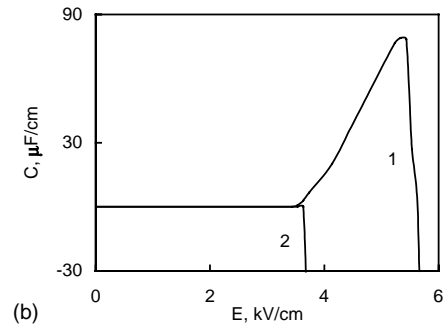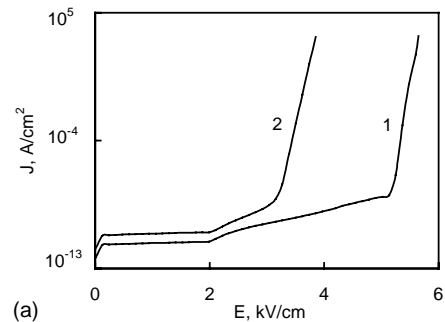


Fig. 3. A pulse current–voltage (a) and capacitance–voltage (b) characteristics of polycrystalline structure before (1) and after (2) thermal degradation.
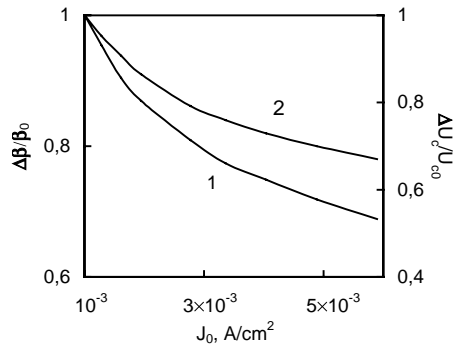
Fig. 4. Dependence of the nonlinearity factor $\beta$ (1) and the classification voltage $U_c$ (2) on the dc degradation current.
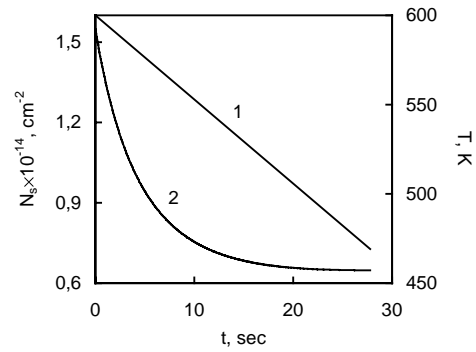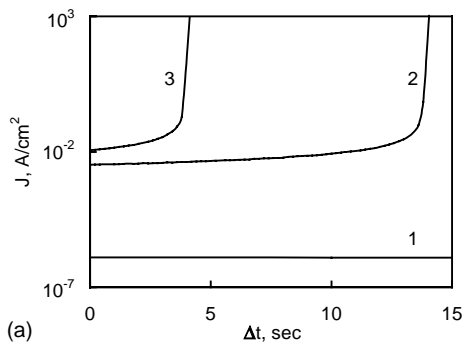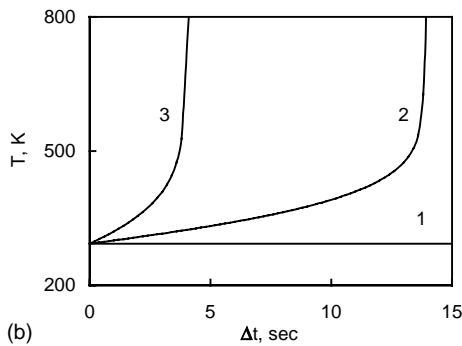


Fig. 7. Temporary dependencies of the structure temperature (1) and surface electronic states concentration (2) after voltage pulse, which had heated the polycrystalline structure up to $600\,°C$.



Fig. 5. Dependencies of a current density (a) and warming structure temperature (b) on the pulse duration at various electrical fields (kV/cm): (1) 5.27; (2) 5.39; (3) 5.4.
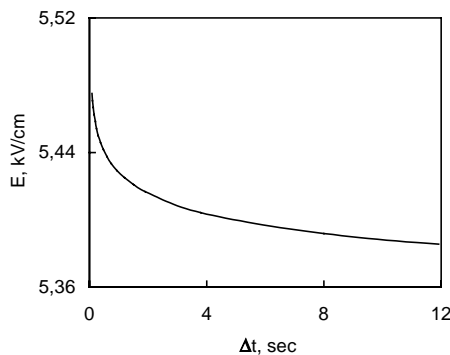


Fig. 6. The relationship between amplitude and duration of a rectangular voltage pulse, ensuring heating up to $600\,°C$.

in the displacement of adsorption–desorption balance to the oxygen desorption at the grain boundaries and decreasing of $N_s$(see Fig. 2).

Assuming, that after decreasing of the temperature $N_s$ does not change, this process can be considered as thermal degradation mechanism of zinc oxide ceramics. Such mechanism of degradation causes the deformation and displacement of initial static *I–V* characteristics to the low voltages (see Fig. 1), that corresponds to the experimentally observable hysteresis of the *I–V* characteristics.[5]

The pulse current–voltage and capacitance–voltage characteristics of the considered structures before and after degradation are shown in Fig. 3. It can be seen that the *I–V* characteristics after thermal degradation are displaced to the low voltages (Fig. 3a, curve 2). The *C–V* characteristics is most deformed at the region of capacitance increase (Fig. 3b, curve 4). In the process of degradation this region is reduced down to complete disappearance. The decrease of such technical parameters of varistor as the classification voltage $U_c$ and the nonlinearity factor of *I–V* characteristics $\alpha$ takes place during degradation, that corresponds to the experiment.[5,6] The analysis has also shows, that the amplitude of decrease of the $\alpha$ and the classification voltage increase with the growth of the initial surface electronic states concentration $N_{s0}$. This result becomes clear if to take into account, that the increase of $N_{s0}$, causes the increase of intercrystallite potential barrier height that forms nonlinear properties of varistors, and at a long heating the surface electronic states concentration approaches its certain equilibrium meaning value. The more is deviation of initial value $N_{s0}$ from equilibrium, the more is worsening of the $U_c$ and $\alpha$.

The results of the analysis of non-stationary heating of the structure by a pulse electrical current carried out according to the Eq. (1), were shown in Fig. 5. As we can see, the value of current density $J$ and temperature are independent on time at small pulse voltage $U_i$ ($(U_i/d) < E_{max}$, where $E_{max}$ is the maximal electrical field for initial *I–V* characteristics Fig. 1 and $d$ is the thickness of the polycrystalline structure). At higher $U_i$ a sharp growth $J$ and temperature was observed.

Fig. 6 shows that the duration of the rectangular pulses ensuring warming up of structure up to fixed temperature decreases with the growth of amplitude $U_i/d$, as it needs the same energy. The time changes of the structure temperature and the surface electronic states concentration at the influence of electrical pulses is submitted in Fig. 7. It is taken into account, that during the action of a short pulse of the voltage $U_i$, that is short in comparison with characteristic establishment time of adsorption–desorption processes, the change of the $N_s$ is not present. The essential reduction of the $N_s$ due to the desorption of oxygen molecules takes place only after termination of the pulse, when the structure cools down. Thus, the influence of a pulse current results in the changes of concentration surface electronic states concentration, similar to those received for thermal degradation at a dc current.

## 4. Conclusions

The desorption thermal degradation model of non-homogenuous structures with intercrystalline potential barriers has been developed. The reduction of the concentration of surface electronic states due to oxygen desorption at heating up of ceramic varistor structures by a dc electrical current results in the deformation of current–voltage and capacitance–voltage characteristics.

It was shown, that the obtained results may be applied for interpretation of degradation processes of the varistor oxide ceramics at the first stage of degradation when the symmetry of current–voltage characteristics is kept.

It has been found, that the passage of pulse currents through varistor structure results in thermal and desorptional effects, basically, similar to those considered for the dc current.

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