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LETTER

A simple approach to oxide varistor materials

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Non-Ohmic conduction is observed in many oxide ceramic semiconductor materials on the basis of ZnO [1], TiO_2 [2] and SnO_2 [3, 4]. These ceramics are used as varistors—semiconductor devices with nonlinear symmetric current-voltage characteristic (CVC). Varistor ceramics consist of highly conductive grains with grain-boundary potential barriers formed during sintering [1–5]. Non-Ohmic conduction in ZnO varistors is explained by thermionic emission enhanced by barrier lowering at low fields with a combination of other mechanisms at high fields [5–8].

However, in spite of a deep understanding of varistor action [5–10], there is no simple analytical expression of CVC related to the mechanism of non-Ohmic conduction. Instead of that the empirical power-law relation

$$j = BE^{\beta}, \tag{1}$$

is used (j is the current density, E is the electric field). The values of the nonlinearity coefficient β and electric field E_1 (measured at fixed current density $j = 1$ mA cm^{-2}) are empirical parameters of a varistor. It is difficult to explain why β values for high-voltage varistors (fine-grained ceramics) [11, 12] are usually much higher than for low-voltage devices (large-grained ceramics) [13, 14]. Therefore, it is not clear how to compare the nonlinearity of varistor materials with different electric field E_1. From a materials science view-point it would be desirable to get a formula for CVC with natural nonlinearity parameter which could reflect the main aspects of the non-Ohmic conduction in varistor ceramics. In this letter such simple approach is developed.

Assume that conduction mechanism in ZnO varistor at temperature $T \geq 300$ K is thermionic emission enhanced by barrier lowering at low and high fields and the barrier height $\phi(U)$ is decreased slightly at low fields and sharply at high fields (the high-field barrier height decrease is related to tunneling from interface states or impact ionization in the depletion region). Strong decrease of $\phi(U)$ at high fields ensures high values of the nonlinearity coefficient (60–70). Small temperature shift of highly-nonlinear $j(E)$ characteristic to lower fields can be explained as temperature increase of thermionic current across fairly low barrier at high fields (using $\nu = (1/E_1)(dE_1/dT)$, $\beta = (E/j)(dj/dE)$ and differentiating $j(U,T)$ on temperature one can have $\phi(U) \cong -\nu\beta \mathrm{kT}^2 \cong 0.19$ eV for $\nu \cong -5 \cdot 10^{-4}$ K^{-1}, $\beta = 50$, $T = 300$ K, what is close to the experimentally observed barrier height at high fields [6]). At low temperatures $T \leq 300$ K thermally activated tunneling or tunneling at Fermi level takes place. For simplicity consider here only high temperature ($T \geq 300$ K) region.

Within the thermionic emission model in a diode approximation the current density emitted over a barrier at the voltage U is the difference between two currents flowing in the opposite directions: $j = AT^2 \exp(-\phi(U)+\eta)/kT)(1 - \exp(-qU/kT))$, where A is the Richardson's constant, T is the absolute temperature, η is the distance between the conduction band edge and the Fermi level inside the grain, k is the Boltzmanńs constant, q is the elementary charge. At low voltages $U << kT/q$ $J(U)$ characteristic is linear. At high voltages $U \gg kT/q$ it becomes strongly nonlinear due to the decrease of $\phi(U)$. Then the current density increment is:

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$$dj = -\frac{1}{kT} j(U) \frac{d\varphi}{dU} dU. \quad (2)$$

In a grain-boundary controlled non-Ohmic material the current density increment contains two parts. One is due to the increment of electric field at constant conductivity: $\sigma(E)dE = \frac{j}{E}dE$. Other reflects the conductivity increase due to the barrier height lowering. It can be proportional to the current density and to the increment of electric field (see Eq. 2). Then the current density increment in non-Ohmic material can be written as:

$$dj = \frac{j}{E} dE + \alpha j dE. \quad (3)$$

Integration of Eq. 3 gives CVC of varistor material:

$$j(E) = \sigma_0 E \exp(\alpha E), \quad (4)$$

where the constant of an integration σ_0 is the conductivity of a material at low fields, the nonlinearity factor

$$\alpha = \frac{L}{kT}\left(-\frac{d\varphi}{dU}\right)$$

is proportional to the rate of the barrier height with voltage, L is the average distance between barriers ($U \cong LE$). At low fields ($\alpha E \ll 1$) Ohm's law $j = \sigma_0 E$ takes place. At high fields $\sigma(E) = j(E)/E$ is increased with electric field exponentially: $\sigma(E) = \sigma_0 \exp(\alpha E)$.

The nonlinearity factor $\alpha = d(\ln \sigma(E))/dE$ is numerically equal to the increment of $\ln \sigma(E)$ at $\Delta E = 1$ V cm^{-1}. The nonlinearity coefficient $\beta = (E/j)(dj/dE) = 1 + \alpha E$ (see Eqs. 1 and 4). If $\beta \gg 1$, then a variation of the electric field in a highly nonlinear region is small ($E \cong E_1$) and

$$\alpha \approx \beta/E_1 = \beta_E \quad (5)$$

where β_E is the normalized nonlinearity coefficient. It can be estimated using usually available parameters β and E_1.

CVC of two samples are shown in Fig. 1 in double logarithmic scale lg j–lg E. Curve 1 is for ZnO–Bi_2O_3–Co_3O_4–MnO_2–NiO–TiO_2 low-voltage varistor with large grain size and curve 2 is for ZnO–Bi_2O_3–Co_3O_4–MnO_2–Sb_2O_3 high-voltage varistor with small grain size. Details of the preparation procedure are in [15] and [11], respectively. In Fig. 2 the same data are presented in log σ–E scale according to Eq. 4. CVC of low-voltage varistor can be approximated by Eq. 4 at least for four decades of σ (Fig. 2, curve 1). For CVC of high-voltage varistor two values of α can be distinguished, α_1 and $\alpha_2 > \alpha_1$ (Fig. 2, curve 2). In Table 1 some electrical parameters of these samples are shown. The nonlinearity coefficient of high-voltage varistor is greater (Table 1) and the slope of

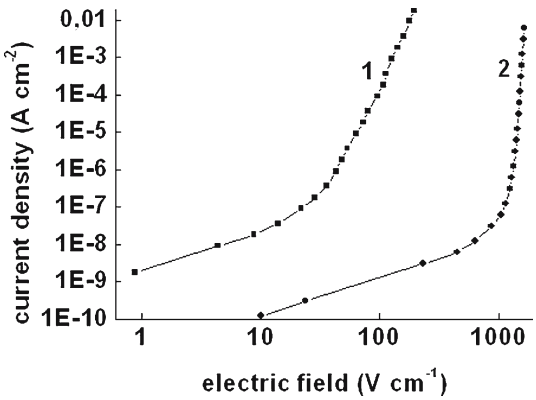

Fig. 1 Current density versus applied field for ZnO–Bi_2O_3–Co_3O_4–MnO_2–NiO–TiO_2 low-voltage (curve 1) and ZnO–Bi_2O_3–Co_3O_4–MnO_2–Sb_2O_3 high-voltage (curve 2) ceramic varistors

curve 2 in Fig. 1 is higher. However, the slope of curve 2 in Fig. 2 in high-field region is lower than the slope of curve 1. Respectively, the nonlinearity factor α_2 for high-voltage varistor is lower than α for low-voltage varistor (Table 1). The values of the normalized nonlinearity coefficient β_E and the nonlinearity factor α are approximately equal (Table 1) according to Eq. 5. It is found as well that similar situation takes place for other low-voltage [13, 14] and high-voltage [11, 12] varistors.

Therefore, the conductivity of low-voltage varistor is increased with electric field even stronger (or at least not weaker) than the conductivity of high-voltage varistor in spite of high-voltage varistor is usually characterized by much higher empirical nonlinearity coefficient β. Observations of high empirical nonlinearity coefficient β for materials with high electric field E_1 mean that $\beta P E_1$ (see Eq. 5).

Quite strong increase of $\sigma(E)$ in low-voltage varistors at low fields is due to a relatively small number of key barriers connected in series along the percolation path. In that case even low voltage applied to a sample can effec-

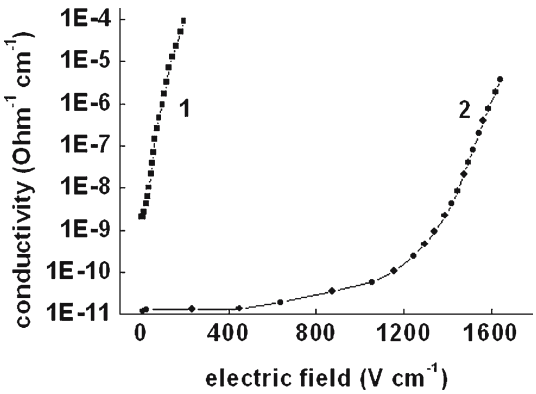

Fig. 2 Plot of conductivity against electric field for ZnO–Bi_2O_3–Co_3O_4–MnO_2–NiO–TiO_2 low-voltage (curve 1) and ZnO–Bi_2O_3–Co_3O_4–MnO_2–Sb_2O_3 high-voltage (curve 2) ceramic varistors

Table 1 Electrical parameters of ZnO varistor ceramics with large and small grains

Material	E_1,V cm^{-1}	β	β_E, cm V^{-1}	α, cm V^{-1}
ZnO–Bi_2O_3–Co_3O_4–MnO_2–NiO–TiO_2	130	7	5.38×10^{-2}	6.32×10^{-2}
ZnO–Bi_2O_3–Co_3O_4–MnO_2–Sb_2O_3	1585	50	3.15×10^{-2}	3.16×10^{-2}*

*High-field value α_2 is shown

tively decrease the barrier height of key barriers and cause strong growth of the conductivity.

Suggested simple phenomenological approach can be useful to compare properties of new materials. For example, SnO_2 based varistor SnO_2–Co_3O_4–Nb_2O_5–Cr_2O_3–La_2O_3 has very high $\beta = 142$ and $E_1 = 11525$ V cm^{-1} [16]. In this case $\beta_E = 1.23 \cdot 10^{-2}$ cm V^{-1} (see Eq. 5). However, for SnO_2–Bi_2O_3–Co_3O_4–Nb_2O_5–Cr_2O_3 varistor with $\beta = 53$ and $E_1 = 3400$ V cm^{-1} [17] higher value-$\beta_E = 1.56 \cdot 10^{-2}$ cm V^{-1} is found. It means that the conductivity of varistor with high nonlinearity coefficient β and high electric field E_1 is increased with electric field not too strongly.

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