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## **Non-ohmic conduction in tin dioxide based ceramics with copper addition**

**A.V. Gaponov<sup>1</sup>, A.B. Glot<sup>2</sup>**

<sup>1</sup>*Dnipropetrovsk National University, 72, Gagarin Ave., 49010 Dnipropetrovsk, Ukraine*

*E-mail: alexei\_gaponov@ukr.net*

<sup>2</sup>*Universidad Tecnológica de la Mixteca, Carretera a Acatlima km.*

*2.5, Huajuapán de León, Oaxaca, 69000, México*

*E-mail: alexglot@mixteco.utm.mx*

**Abstract.** The current-voltage characteristics and temperature dependences of electrical conductivity in SnO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub>-Nb<sub>2</sub>O<sub>5</sub>-Cr<sub>2</sub>O<sub>3</sub>-CuO semiconductor ceramics are studied, and possible mechanism of non-ohmic conduction in these materials is discussed. Due to addition of CuO up to 0.5 mol.%, the nonlinearity coefficient is increased up to 75, and the electric field is decreased down to 3900 V·cm<sup>-1</sup> (at 1 mA·cm<sup>-2</sup>). It makes CuO addition useful for the preparation of SnO<sub>2</sub>-based varistors. It is concluded that the electrical conduction is controlled by grain-boundary barriers. The activation energy of electrical conduction  $E_{\sigma}$  (the barrier height  $\phi$ ) is decreased with an increase in the electric field  $E$ . The higher slope of the  $E_{\sigma}(E)$  dependence at high fields can be related to a participation of minority carriers (holes). The addition of more than 0.5 mol.% CuO leads to degradation of the varistor effect due to percolation via quite conductive CuO-based intergranular phase.

**Keywords:** non-ohmic conduction, grain boundary, varistor, barrier height, tin dioxide ceramics.

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### **1. Introduction**

Zinc oxide (ZnO) ceramics with certain additives exhibits strong non-ohmic conduction and, therefore, these materials are used for fabrication of varistors – transient voltage suppression devices [1, 2]. Quite high non-ohmic conduction was also observed in tin dioxide (SnO<sub>2</sub>) based ceramics [3, 4]. This observation means that ZnO ceramics are not unique materials with highly nonlinear current-voltage characteristics. ZnO varistors exhibit some disadvantages (for example, electrical and thermal degradation) [2, 5, 6]. Therefore, there is a hope that varistors based on tin dioxide could possess better properties [5, 6]. It was realized that basic electrical behaviour of SnO<sub>2</sub> and ZnO varistors are quite similar, because electrical conduction in these ceramics is controlled by the grain-boundary barriers [3-6].

In recent years, SnO<sub>2</sub> ceramics with the varistor effect were rather intensively studied [7-10] mainly from

the materials science view-point. However, the mechanism of non-ohmic conduction in SnO<sub>2</sub> varistor ceramics is still unclear. It was shown that addition of oxides with a low melting point (Bi<sub>2</sub>O<sub>3</sub>, V<sub>2</sub>O<sub>5</sub>, CuO) gives certain improvements in the density and electrical parameters of SnO<sub>2</sub> varistor ceramics [11-15]. Probably, addition of copper oxide to SnO<sub>2</sub>-CoO-Nb<sub>2</sub>O<sub>5</sub>-Cr<sub>2</sub>O<sub>3</sub> looks quite useful for the achievement of desired parameters of SnO<sub>2</sub> varistors [14, 15]. Thus, in this paper we have studied SnO<sub>2</sub>-CoO-Nb<sub>2</sub>O<sub>5</sub>-Cr<sub>2</sub>O<sub>3</sub> ceramics with various amounts of CuO addition. But there is no information about the conduction mechanism in these materials. Therefore, it would be interesting to study the high-field conduction at various temperatures in recently developed SnO<sub>2</sub>-CoO-Nb<sub>2</sub>O<sub>5</sub>-Cr<sub>2</sub>O<sub>3</sub>-CuO varistor ceramics.

Usually, the current-voltage characteristics of oxide varistors are approximated within the narrow range of current densities by the empiric expression  $j = BE^{\beta}$ ,

where  $j$  is the current density and  $E$  is the electric field,  $\beta$  is a dimensionless constant (nonlinearity coefficient) and  $B$  is a constant with dimension giving the current density  $j$  in  $\text{A} \cdot \text{cm}^{-2}$ , if the electric field  $E$  is expressed in  $\text{V} \cdot \text{cm}^{-1}$ . The nonlinearity coefficient is defined by the expression  $\beta = (E/j) (dj/dE)$ . Usually the nonlinearity coefficient is estimated at a fixed current density (for example, at  $1 \text{ mA} \cdot \text{cm}^{-2}$ ). In this case, it can be denoted as  $\beta_1$ . For the indication of the electric field range where the nonlinearity of  $j(E)$  characteristic takes place, the value of the electric field at  $1 \text{ mA} \cdot \text{cm}^{-2}$  ( $E_1$ ) is introduced. The values  $\beta_1$  and  $E_1$  are used frequently as the main empiric parameters of a varistor.

However, the empiric  $j(E)$  expression and empiric parameter  $\beta_1$  cannot enable in understanding the mechanism of non-ohmic conduction. Therefore, starting from the assumption that non-ohmic conduction in ZnO and SnO<sub>2</sub> varistor ceramics is attributed to the decrease of the barrier height with electric field, the expression for the current-voltage characteristic was obtained [12, 16, 17]:

$$j(E) = \sigma_0 E \exp(\alpha E), \quad (1)$$

where  $\sigma_0$  is the conductivity of material at low electric fields,  $\alpha$  is the nonlinearity factor. In the case of thermionic emission across the barrier, the parameter  $\alpha$  is proportional to the rate of change in the barrier height  $\phi$  with the electric field  $E$  [12, 16, 17]:

$$\alpha = \frac{1}{kT} \left( - \frac{d\phi}{dE} \right), \quad (2)$$

where  $k$  is the Boltzmann constant,  $T$  is the absolute temperature.

Therefore, in this paper electrical properties of SnO<sub>2</sub>-CoO-Nb<sub>2</sub>O<sub>5</sub>-Cr<sub>2</sub>O<sub>3</sub> ceramics with various amounts of CuO addition were studied, then current-voltage characteristics of some SnO<sub>2</sub>-CoO-Nb<sub>2</sub>O<sub>5</sub>-Cr<sub>2</sub>O<sub>3</sub>-CuO ceramics at different temperatures were obtained, and the dependences of the activation energy of electrical conduction on the electric field were found from them.

## 2. Experimental details

Ceramics were prepared by the conventional oxide mixture method using distilled water. The compositions were (mol.%) (99.4 -  $x$ ) SnO<sub>2</sub>, 0.5 Co<sub>3</sub>O<sub>4</sub>, 0.05 Nb<sub>2</sub>O<sub>5</sub>, 0.05 Cr<sub>2</sub>O<sub>3</sub>,  $x$  CuO,  $x = 0; 0.1; 0.5; 2; 8$  (Table). After wet milling and drying, obtained powder was pressed in tablets 12 mm in diameter and about 0.7 mm in thickness under the axial pressure 45 MPa. Pressed disks were sintered at 1520 K in air. The details of preparation are described in [14, 15]. To determine the grain size, scanning electron microscopy (SEM) was used. The shrinkage  $\gamma$  was calculated according to the expression  $\gamma = (D_0 - D) D_0^{-1}$ , where  $D_0$  and  $D$  are diameters of a sample before and after sintering, respectively.

Electrical measurements were performed using In-Ga eutectic electrodes prepared at room temperature (for the study of current-voltage characteristics of the samples with various CuO amounts at 300 K) and Ag-electrodes obtained at 1070 K (for the measurements at different temperatures). It was found that such a heat treatment at 1070 K leads to a decrease in nonlinearity of current-voltage characteristics.

Current-voltage characteristics were recorded in air within the temperature range 300–423 K. The relative humidity of ambient air was about 50 % at 300 K. The results were obtained avoiding a self-heating of the samples. The nonlinearity coefficient  $\beta_1$  and electric field  $E_1$  were estimated at the current density  $10^{-3} \text{ A} \cdot \text{cm}^{-2}$ .

Temperature dependence of dc electrical conductivity  $\sigma(T)$  was obtained in the range 300–473 K at heating and cooling the samples in air with a rate close to 1 K/min. Below about 350 K, conductivity was decreased at heating due to desorption of water molecules [11, 18]. The activation energy of electrical conduction  $E_\sigma(0)$  at low electric fields (in ohmic region) was estimated from the high-temperature (350–473 K) part of  $\sigma_0(T)$  dependence using the equation:

$$\sigma_0 = \sigma_{00} \exp(-E_\sigma(0)/kT), \quad (3)$$

where  $\sigma_{00}$  is a constant.

**Table. Some parameters of SnO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub>-Nb<sub>2</sub>O<sub>5</sub>-Cr<sub>2</sub>O<sub>3</sub>-CuO ceramics (electrical parameters were obtained for the samples with In-Ga electrodes).**

CuO (mol.%)	0	0.1	0.5	2	8
Linear shrinkage $\gamma$ (%)	9.0	9.2	11.7	11.4	9.3
Average grain size $l_g$ ( $\mu\text{m}$ )	4	5	8	8	8
Electrical conductivity $\sigma$ ( $\text{Ohm}^{-1} \cdot \text{cm}^{-1}$ )	$1.2 \cdot 10^{-12}$	$3.2 \cdot 10^{-12}$	$4.8 \cdot 10^{-12}$	$1.4 \cdot 10^{-10}$	$5.7 \cdot 10^{-9}$
Activation energy of electrical conduction $E_\sigma$ (eV)	1.2	1.0	0.94	0.65	0.34
Nonlinearity coefficient $\beta_1$	54	61	75	7.6	3.1
Electric field $E_1$ ( $\text{V} \cdot \text{cm}^{-1}$ )	6280	4870	3900	8540	14740
Normalized nonlinearity coefficient $\beta_E = \beta_1/E_1$ ( $\text{cm} \cdot \text{V}^{-1}$ )	$8.6 \cdot 10^{-3}$	$1.25 \cdot 10^{-3}$	$1.9 \cdot 10^{-3}$	$8.9 \cdot 10^{-4}$	$2.1 \cdot 10^{-4}$
Relative dielectric permittivity $\epsilon$ (1 kHz)	114	397	865	130	60

The capacitance was measured at the frequency 1 kHz using LCRG meter Tesla BM 591.

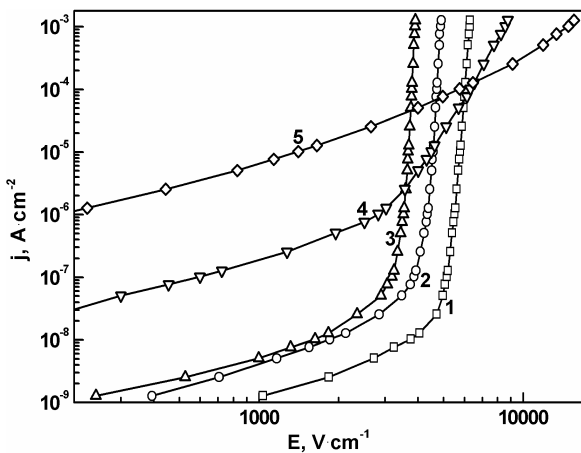
### 3. Results and discussion

The current-voltage characteristics of  $\text{SnO}_2\text{-Co}_3\text{O}_4\text{-Nb}_2\text{O}_5\text{-Cr}_2\text{O}_3\text{-CuO}$  ceramics with various CuO amounts are shown in Fig. 1. Rather strong variation in the low-field conductivity  $\sigma$ , nonlinearity coefficient  $\beta_1$  and electric field  $E_1$  for the samples with different CuO additions have been found (Table).

The addition of CuO in the range 0–0.5 mol.% gives some increase in the nonlinearity coefficient (Fig. 1, curves 1 to 3). The highest value  $\beta = 75$  was found for the sample with 0.5 mol.% CuO (Table). This value is higher than that observed by us earlier [14] due to the absence of heat treatment at 1070 K (due to use of In-Ga eutectic electrodes). Higher amounts of CuO addition (more than 0.5 mol.%) cause a strong decrease in the nonlinearity and a rise of the low-field conductivity (Fig. 1, curves 4 to 5).

The reason for an increase in the nonlinearity coefficient on CuO addition in the range 0–0.5 mol.% (Fig. 1 and Table) can be due to the formation of higher amount of liquid CuO-phase and related more homogeneous distribution of  $\text{Co}_3\text{O}_4$  and  $\text{Cr}_2\text{O}_3$  impurities throughout a sample. These additives play an important role in the obtaining of  $\text{SnO}_2$  ceramics with highly nonlinear current-voltage characteristics [3, 6].

Within the range 0 to 0.5 mol.% CuO, the electric field  $E_1$  (at current density  $10^{-3} \text{ A}\cdot\text{cm}^{-2}$ ) is decreased (Fig. 1, curves 1 to 3). It is explained by the grain size growth with the copper oxide content (Table). Observed slight increase in the low-field conductivity in the range 0–0.5 mol.% CuO (Fig. 1, curves 1 to 3) is rather due to the grain growth. Such a change is typical for a transition from high-voltage to low-voltage ZnO varistors.



**Fig. 1.** Current density vs. electric field in  $\text{SnO}_2\text{-Co}_3\text{O}_4\text{-Nb}_2\text{O}_5\text{-Cr}_2\text{O}_3$  varistor ceramics with various amounts of CuO addition, mol.%: 0 (1), 0.1 (2), 0.5 (3), 2 (4), 8 (5).

Subsequent decrease in the nonlinearity coefficient with CuO addition in the range 2–8 mol.% (Fig. 1 and Table) can be due to percolation across the fairly conductive intergranular CuO phase covering  $\text{SnO}_2$  grains and acting as an electrical shunt to the grain boundaries. Similar situation was recently observed in  $\text{SnO}_2\text{-Co}_3\text{O}_4\text{-Nb}_2\text{O}_5\text{-Cr}_2\text{O}_3\text{-V}_2\text{O}_5$  varistor ceramics with variation in  $\text{V}_2\text{O}_5$  addition [13].

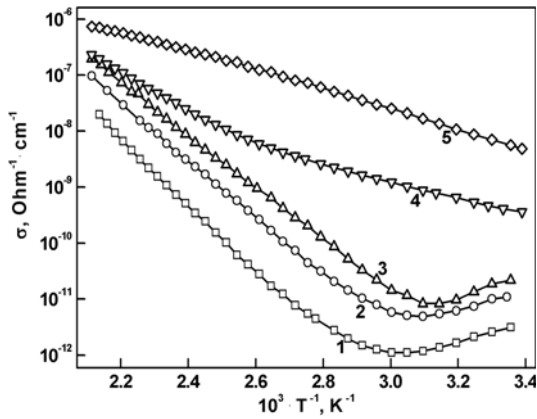
Temperature dependences of dc electrical conductivity  $\sigma(T)$  for the samples with different CuO amount have been shown in Fig. 2. With a rise in CuO addition, the electrical conductivity at a fixed temperature is increased, and the activation energy of electrical conduction  $E_\sigma$  becomes lower (Table). Below about 350 K, conductivity of ceramics with CuO addition in the range 0–0.5 mol.% (curves 1-3 in Fig. 2) was affected by humid air (see [11, 13, 18]). In the case of low CuO amounts, humid air can penetrate inside the sample and reach grain-boundary areas. Though at higher values of CuO additives,  $\sigma(T)$  curves are not distorted in the low-temperature part (curves 4 and 5 in Fig. 2) probably because CuO-phase covers  $\text{SnO}_2$  grains [14] and prevents penetration of humid air to the grain-boundary regions.

Electrical conduction in  $\text{SnO}_2$  ceramics is controlled by the grain-boundary potential barriers [3-16]. The activation energy of electrical conduction  $E_\sigma$  is a measure of the barrier height  $\phi$  ( $\phi \cong E_\sigma$ ), because using the literature data for single crystals [19] it can be assumed that the Fermi level in the doped  $\text{SnO}_2$  grain bulk is situated quite close to the conduction band edge. Oxygen vacancies and Nb impurities can serve as shallow donors in  $\text{SnO}_2$  [19]. The observed decrease in the low-field barrier height with CuO addition can be explained by the presence of CuO-phase in the samples [15].

The relative dielectric permittivity  $\epsilon = 114$  of  $\text{SnO}_2\text{-Co}_3\text{O}_4\text{-Nb}_2\text{O}_5\text{-Cr}_2\text{O}_3$  ceramics (Table) is quite high due to the existence of thin depletion grain-boundary regions. In the range 0–0.5 mol.% CuO, the grain size  $l_g$  is increased, and therefore,  $\epsilon$  of ceramics becomes higher (Table). However,  $\text{SnO}_2\text{-Co}_3\text{O}_4\text{-Nb}_2\text{O}_5\text{-Cr}_2\text{O}_3\text{-CuO}$  ceramics with 2–8 mol.% CuO exhibits lower  $\epsilon$  values (Table) due to the influence of copper oxide phase with not high relative dielectric permittivity about 10.

As far as the electrical conduction in  $\text{SnO}_2$  ceramics near room temperature is thermally-activated process with a rather high activation energy [11-14], the thermionic emission across the barrier is the most probable conduction mechanism near 300 K. In this case, the temperature dependence of conductivity  $\sigma(T, E) = j(T, E)/E$  in electric field can be written in the form similar to Eq. (3) where  $E_\sigma(0)$  should be replaced for the activation energy at any electric field  $E_\sigma(E)$ . Then, using Eqs (1) and (2) we have:

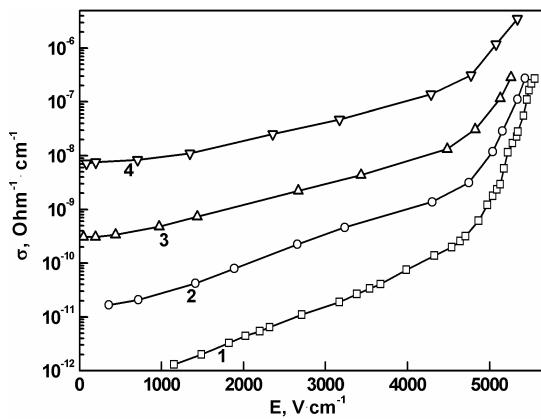
$$E_\sigma(E) = E_\sigma(0) - \left( -\frac{d\phi}{dE} \right) E. \quad (4)$$



**Fig. 2.** Temperature dependence of dc low-field electrical conductivity in air (heating) for SnO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub>-Nb<sub>2</sub>O<sub>5</sub>-Cr<sub>2</sub>O<sub>3</sub>-CuO varistor ceramics with various amounts of CuO addition, mol.%: 0 (1), 0.1 (2), 0.5 (3), 2 (4), 8 (5).

The activation energy is linearly decreased with electric field, if the rate of change of the barrier height with electric field is constant. This can be experimentally verified.

In Fig. 3, current-voltage characteristics of studied ceramic material have been presented in the scale  $\log(j/E) - E$ . Two regions with different non-zero slopes are seen. They are related to the nonlinearity factors  $\alpha = \alpha_1$  (for mean fields) and  $\alpha = \alpha_2 > \alpha_1$  (for the high ones), respectively. The ohmic region with  $\alpha = 0$  at lowest fields is not revealed. The value  $\alpha_1$  is related to the increase in conductivity at electric fields that are lower than in the highly nonlinear region. The value  $\alpha_2$  is related to the highly nonlinear region of current-voltage characteristic which is empirically described by the nonlinearity coefficient  $\beta_1$  estimated at  $1 \text{ mA} \cdot \text{cm}^{-2}$ .

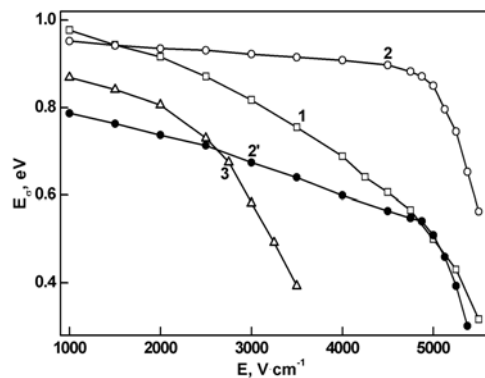


**Fig. 3.** Dependence of electrical conductivity on electric field for SnO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub>-Nb<sub>2</sub>O<sub>5</sub>-Cr<sub>2</sub>O<sub>3</sub>-CuO varistor ceramics (with 0.1 mol.% CuO addition) at various temperatures: 304 (1), 343 (2), 383 (3) and 423 K (4).

From the family of current-voltage characteristics at various temperatures, the dependences of conductivity  $\sigma(T, E) = j(T, E)/E$  at fixed electric fields on temperature were plotted. The activation energy of electrical conduction  $E_\sigma(E)$  was estimated from the high-temperature part of  $\sigma(T)$  dependence (at about 400 K) because at this region thermionic conduction mechanism is more probable. The obtained dependence of the activation energy on electric field is presented in Fig. 4 (curve 2). Rather high values of  $E_\sigma$  in Fig. 4 are in accordance with assumed thermally activated transition of electrons. The slight decrease of the slope inherent to the experimental dependence in the scale  $\log \sigma - T^{-1}$  at lower temperatures (in the vicinity of 320 K) gives respective displacement of the  $E_\sigma(E)$  curve to lower values (curve 2' in Fig. 4). Lower values of the activation energy can be related to the gradual changeover from thermionic emission to thermally-assisted tunnelling. At thermally-assisted tunnelling, electrons cross the barrier at different energies with a maximum at certain energy. This energy probably reflects the activation energy at thermally-assisted tunnelling. Such situation also takes place in ZnO varistors below about 300 K [5].

The  $j(E)$  characteristics at various temperatures were also obtained for the samples with different amounts of CuO additives, and the same treatment of experimental data was performed. It is seen that for all the studied samples of SnO<sub>2</sub> varistors the barrier height is decreased with electric field (Fig. 4). Earlier, similar behaviour was found for SnO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub>-Nb<sub>2</sub>O<sub>5</sub>-Cr<sub>2</sub>O<sub>3</sub>-Bi<sub>2</sub>O<sub>3</sub> varistor [12].

It is clearly seen that for the sample with the high nonlinearity coefficient ( $\beta_1 = 61$ ),  $E_\sigma(E)$  dependence exhibits a low-field part with low slope and a high-field part with higher slope (Fig. 4, curve 2). Relatively weak decrease of  $E_\sigma$  at low electric fields in comparison with



**Fig. 4.** Field dependence of the activation energy of electrical conduction in SnO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub>-Nb<sub>2</sub>O<sub>5</sub>-Cr<sub>2</sub>O<sub>3</sub> ceramics (curve 1; nonlinearity coefficient  $\beta_1 = 54$ ), in SnO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub>-Nb<sub>2</sub>O<sub>5</sub>-Cr<sub>2</sub>O<sub>3</sub> ceramics with 0.1 mol.% CuO (curves 2 and 2'; nonlinearity coefficient  $\beta_1 = 61$ ) and with 0.5 mol.% CuO (curve 3; nonlinearity coefficient  $\beta_1 = 21$ ). The activation energy was estimated at temperatures near 400 K (curves 1-3) and near 320 K (curve 2').

the model of grain boundary with fixed interface charge [20] is due to the capture of electrons at the interface. The experimental confirmation of this effect was obtained recently from the isothermal capacitance decay at a voltage bias and subsequent increment of capacitance at zero bias [14].

At high electric fields where high nonlinearity is observed, the activation energy of electrical conduction and the barrier height in SnO<sub>2</sub> varistors (0.3–0.5 eV) are still quite high (Fig. 4). This fact means that the conduction process is thermally activated not only at low but also at high electric fields. This makes possible fairly simple explanation of conduction in SnO<sub>2</sub> varistors as thermionic emission across the barrier with the barrier height dependent on electric field.

The experimental dependence of the barrier height on the electric field  $\varphi(E)$  in SnO<sub>2</sub> based varistors consists of two parts: the first one gives a slight decrease in the barrier height at low electric fields, and the second gives a stronger decrease at higher fields. It is necessary to mention that according to the developed approach [12, 16, 17], the obtained dependence  $\varphi(E)$  (Fig. 4, curve 2) reflects a shape of the  $\log \sigma$  dependence on the electric field (Fig. 3, curve 1).

It is interesting to note that  $\alpha$ -values in Fig. 3 are temperature-dependent, because the slopes of curves are gradually decreased with temperature. This fact is related to the thermionic emission of electrons across the grain-boundary barrier (see Eq. (2)).

Probably, a higher slope of the  $\varphi(E)$  dependence at high fields in SnO<sub>2</sub> varistors is related to a decrease of the negative interface charge on absolute value as a result of impact ionization in reverse biased depletion region or Zener tunnelling from valence to conduction band. It can lead to appearance of minority carriers (holes) in n-SnO<sub>2</sub>. As a possible confirmation of hole generation at high fields in ZnO varistors, the observation of electroluminescence [21, 22] and negative capacitance [23] are considered. Earlier the negative capacitance was observed in SnO<sub>2</sub> varistors with low nonlinearity [4], and recently we have observed the negative capacitance in SnO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub>-Nb<sub>2</sub>O<sub>5</sub>-Cr<sub>2</sub>O<sub>3</sub>-CuO ceramics with high nonlinearity [24].

#### 4. Conclusions

Electrical properties of tin dioxide based SnO<sub>2</sub>-Co<sub>3</sub>O<sub>4</sub>-Nb<sub>2</sub>O<sub>5</sub>-Cr<sub>2</sub>O<sub>3</sub> ceramics with CuO addition in the range 0–8 mol.% are studied. The nonlinearity coefficient is increased from 54 to 75 in the range 0–0.5 mol.% CuO, and further it is decreased to 3–7 in the range 2–8 mol.% CuO. The conduction mechanism in ceramics with 0–0.5 mol.% CuO is grain-boundary controlled. The decrease in the barrier height with the voltage is responsible for non-ohmic behaviour. The activation energy of electrical conduction  $E_{\sigma}$  in SnO<sub>2</sub> varistors as a function of electric field  $E$  is obtained experimentally. For the samples with a high nonlinearity coefficient,

$E_{\sigma}(E)$  dependence exhibits the low-field part with low slope and high-field part with higher slope. The highly nonlinear rise of the current density with electric field (the varistor effect) is related to the strong decrease in the activation energy  $E_{\sigma}(E)$  (the barrier height). As far as the activation energy is quite high (about 0.3–0.5 eV) at high electric fields, the conduction process is thermally activated not only at low but also at high electric fields. The higher slope of  $E_{\sigma}(E)$  dependence at high fields can be related to a contribution of minority carriers (holes).

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