ХІМІЧНІ СЕНСОРИ

CHEMICAL SENSORS

HUMIDITY SENSORS BASED ON SnO_2-Co_3O_4-Nb_2O_5-Cr_2O_3 SEMICONDUCTOR VARISTOR CERAMICS

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Abstract. The varistor effect in SnO_2-Co_3O_4-Nb_2O_5-Cr_2O_3 ceramics with different additions is accompanied by a strong humidity-sensitivity effect in the low-field electrical conductivity. The low-field electrical conductivity and dielectric permittivity of ceramics are increased when air relative humidity rises from 10 to 93%. Such effects are observed both in the samples prepared by solid-phase sintering without or with CaO addition and in the samples prepared by liquid-phase sintering with CuO or V_2O_5 additions. The lowest humidity-sensitivity effect was found in the liquid-phase sintering samples due to the more solid structures and the secondary phases which are located between the SnO_2 grains. For the studied samples the values of humidity sensitivity coefficient $1.8 \cdot 10^3$-$3.2 \cdot 10^5$ at low electric fields and the nonlinearity coefficient 30-57 at high electric fields ($E_1 = 5.3$-$7 \ kV \cdot cm^{-1}$) were calculated. The properties of oxide ceramics are explained by electrical conductivity which is controlled by the grain-boundary potential barriers. The barrier height decreases with the increase both of air relative humidity at low electric fields and of voltage at high electric fields. Strong humidity sensitivity is a key factor for sensor application of SnO_2-based ceramics.

Keywords: humidity sensor, tin oxide, varistor, oxide ceramics, grain boundary, electrical conductivity

СЕНСОРИ ВОЛОГОСТІ НА ОСНОВІ НАПІВПРОВІДНИКОВОЇ ВАРИСТОРНОЇ КЕРАМІКИ SnO_2-Co_3O_4-Nb_2O_5-Cr_2O_3

О. В. Гапонов

Анотація. Варисторний ефект у SnO_2-Co_3O_4-Nb_2O_5-Cr_2O_3 кераміці з різними домішками супроводжувався сильним вологочутливим ефектом для електричної провідності у слабкому полі. Електропровідність у слабких полях і діелектрична проникність кераміки збільшувались при зростанні відносної вологості повітря з 10 до 93%. Такі ефекти спостерігались як для твердо-фазних синтезованих зразків без або з CaO домішкою, так і для рідко-фазних синтезованих зразків з CuO або V_2O_5 домішками. Найменшу вологочутливість мають рідко-фазні синтезовані зразки у зв'язку з їх більш щільною структурою й існуючими вторинними фазами, які розташовуються між зернами SnO_2. Для досліджених зразків обчислені значення коефіцієнта вологочутливості $1,8 \cdot 10^3$-$3,2 \cdot 10^5$ при слабких електричних полях і коефіцієнта нелінійності 30-57 при сильних електричних полях (E_1 = 5,3-7 кВ·см$^{-1}$). Властивості оксидної кераміки пояснюються електричною провідністю, яка контролюється потенціальними бар'єрами на межах зерен. Висота бар'єрів зменшується як зі збільшенням відносної вологості повітря при слабких електричних полях, так і напруги при сильних електричних полях. Велика вологочутливість є ключовим фактором для сенсорного використання кераміки на основі SnO_2.

Ключові слова: сенсор вологості, оксид олова, варистор, оксидна кераміка, межа зерен, електрична провідність

СЕНСОРЫ ВЛАЖНОСТИ НА ОСНОВЕ ПОЛУПРОВОДНИКОВОЙ ВАРИСТОРНОЙ КЕРАМИКИ SnO_2-Co_3O_4-Nb_2O_5-Cr_2O_3

А. В. Гапонов

Аннотация. Варисторный эффект в SnO_2-Co_3O_4-Nb_2O_5-Cr_2O_3 керамике с различными добавками сопровождался сильным влагочувствительным эффектом для электрической проводимости в слабом поле. Электропроводность в слабых полях и диэлектрическая проницаемость керамики увеличивались при повышении относительной влажности воздуха с 10 до 93%. Такие эффекты наблюдались как для твердофазных синтезированных образцов без или с CaO добавкой, так и для жидкофазных синтезированных образцов с CuO или V_2O_5 добавками. Наименьшую влагочувствительность имеют жидкофазные синтезированные образцы в связи с их более плотной структурой и существующими вторичными фазами, которые размещаются между зернами SnO_2. Для исследованных образцов вычислены значения коэффициента влагочувствительности $1,8 \cdot 10^3$-$3,2 \cdot 10^5$ при слабых электрических полях и коэффициента нелинейности 30-57 при сильных электрических полях (E_1 = 5,3-7 кВ·см$^{-1}$). Свойства оксидной керамики объясняются электрической проводимостью, которая контролируется потенциальными барьерами на границах зерен. Высота барьеров уменьшается как при повышении относительной влажности воздуха при слабых электрических полях, так и напряжения при сильных электрических полях. Большая влагочувствительность является ключевым фактором для сенсорного использования керамики на основе SnO_2.

Ключевые слова: сенсор влажности, оксид олова, варистор, оксидная керамика, граница зерен, электрическая проводимость

1. INTRODUCTION

Tin dioxide is well known as a material for the manufacture of gas sensors [1-4], humidity sensors [3-7] and varistors [8-14]. The tin oxide based ceramics has non-Ohmic electrical conductivity which is caused by the grain-boundary potential barriers [8 - 14]. It is the two Schottky barriers at the SnO_2 grain boundaries which are connected in opposite directions.

One of the important properties of SnO_2-based varistor ceramics is the sensitivity of its electrical conductivity to the air relative humidity [3-8]. The humidity-sensitive or varistor properties can prevail depending upon the additions to the ceramic samples. The combining of both properties is due to the grain-boundary nature of both effects [15-18]. Therefore the devices with combined properties of a relative-humidity sensor and a varistor can be used. For example, such ceramics were investigated earlier in SnO_2-ZnO-CoO system with SiO_2, GeO_2 or Bi_2O_3 additions [8] and in SnO_2-Co_3O_4-Nb_2O_5-Cr_2O_3 system with Bi_2O_3 [15, 16], V_2O_5 [17] or CuO [18] additions. The GeO_2, Bi_2O_3, V_2O_5 and CuO oxides have low melting temperatures which are less than burning temperatures of samples. Therefore ceramics with these additions have liquid phases in the process of sintering.

Recently we have found that CaO and BaO additions to tin oxide based ceramics can provide varistor effect [19]. Such ceramics have no liquid phases at sintering but have intergranular inclusions. The behaviour of these ceramic materials in air with different relative humidity is very important for sensor application.

In order to study the influence of different oxides on the humidity sensitivity and other electrical properties of SnO_2-based ceramics we investigated SnO_2-Co_3O_4-Nb_2O_5-Cr_2O_3 varistor system with several additions prepared by solid-phase sintering (without additions or with CaO addition) and liquid-phase sintering (with CuO or V_2O_5 additions). The electrical properties of ceramics which were sintered differently have not been thoroughly investigated before. The received results are presented in this paper below.

2. EXPERIMENTAL DETAILS

The samples (99.4-x) SnO_2 - 0.5 Co_3O_4 - 0.05 Nb_2O_5 - 0.05 Cr_2O_3 - x A (mol. %), where x = 0 or 0.5, A = $CaCO_3$, CuO or V_2O_5, were prepared by a conventional mixture method. Mixture of powders was wet-milled with distilled water, dried and pressed in tablets 12 mm in diameter and about 0.7 mm thick under axial pressure 45 MPa. Pressed tablets were sintered in air at the temperatures 1250°C during 1 hour. While heating the tablet with carbonate addition, the decomposition $CaCO_3$ with CO_2 emission took place and this compound changed into CaO [19].

The microstructure of ceramics was studied by the scanning electron microscope Zeiss Supra 35VP. The shrinkage of the samples γ was calculated by the expression

$$\gamma = \frac{D_0 - D}{D_0}, \qquad (1)$$

where D_0 and D are the diameters of the sample before and after sintering respectively.

Electrical characteristics were obtained after storage of the samples in the room conditions during four months after the sintering in order to achieve the stability of their electrical properties [17]. In-Ga-eutectic electrodes were used in tested samples. Current-voltage characteristics were recorded by applying dc voltage in air with fixed relative humidity w and measuring the steady-state current. The possible self-heating of samples during the measurement was detected as the increase of current at a fixed voltage. The results were obtained avoiding the self-heating of the samples. They are presented as the dependence of the current density j on the electric field E to compare properties of different materials.

The nonlinearity coefficient β was calculated by

$$\beta = \frac{E}{j}\frac{dj}{dE} = \frac{d(\log j)}{d(\log E)} \approx \frac{\log(j_1 / j_{0.1})}{\log(E_1 / E_{0.1})}, \qquad (2)$$

where E_1 and $E_{0.1}$ are the applied electric fields corresponding to the current densities $j_1 = 1\,\mathrm{mA \cdot cm^{-2}}$ and $j_{0.1} = 0.1\,\mathrm{mA \cdot cm^{-2}}$ respectively.

The fixed values of air relative humidity w in the 10-93% range were obtained by putting samples into a closed chamber above the surface of water solution of a proper salt for about 1 hour before starting measurements. Current-voltage characteristics were recorded at $w_1 = 10\%$ and then at higher relative humidity. Before the next increase of the relative humidity the samples were kept again at $w_1 = 10\%$ and current-voltage characteristics were recorded again. The irreversible changes of conductivity were not observed. The humidity sensitivity coefficient

$$S = \frac{\sigma_{w2} - \sigma_{w1}}{\sigma_{w1}} \qquad (3)$$

was calculated at electric field 0.5 E_1 and relative humidity $w_1 = 10\%$ and $w_2 = 93\%$.

The temperature dependence of dc electrical conductivity $\sigma(T)$ was obtained at heating of samples in air. It allows estimating the grain-boundary potential barrier height φ_0 in high-temperature part of $\sigma(T)$ dependences. The values of φ_0 is only slightly less than the activation energy of electrical conduction E_σ [20] found by formula

$$E_\sigma \approx -0.2 \frac{\Delta \log \sigma}{\Delta(1000/T)}, \qquad (4)$$

where σ is the electrical conductivity and T is the absolute temperature. Low-temperature part of $\sigma(T)$ dependences contains an anomalous area related to non-zero relative humidity [15 - 18].

The dielectric permittivity of the ceramics at different values of air relative humidity was calculated by formula

$$\varepsilon = \frac{Ch}{\varepsilon_0 S}, \qquad (5)$$

where h is the sample thickness, S is the electrode area and ε_0 is the electric constant. The capacitance C at frequency 1 kHz was measured by *LCRG* meter Tesla BM 591.

3. RESULTS AND DISCUSSION
3.1. Microstructure

The micrographs of all studied ceramic materials are shown in Fig. 1. The obtained parameters for these samples are presented in Table 1. The average grain size of SnO_2-Co_3O_4-Nb_2O_5-Cr_2O_3

sample is 3.54 μm. This material was sintered enough but its porosity is significant (Fig. 1a). For that reason this ceramics has the environmental sensitive effects. The sample with CaO addition has the less porous structure (Fig. 1b) and slightly less value of average grain size (2.58 μm) than the SnO_2-Co_3O_4-Nb_2O_5-Cr_2O_3 sample. It is probably connected with the segregation of the ion Ca^{2+} with large ion radius (104 pm) on the grain boundaries of SnO_2 (ion radius for Sn^{4+} 67 pm) [19]. This leads to the unfavorable conditions for SnO_2 grain growth and the worsening of burning. This conclusion is proved by a smaller value of linear shrinkage for the sample with addition (6.25%) as compared to that for the sample without CaO addition (8.25%). The SnO_2, Co_3O_4, Nb_2O_5, Cr_2O_3 and CaO oxides have melting temperatures which are considerably higher than the burning temperature of ceramics (1250°C). Therefore the sintering of samples with and without CaO addition is a solid-phase one.
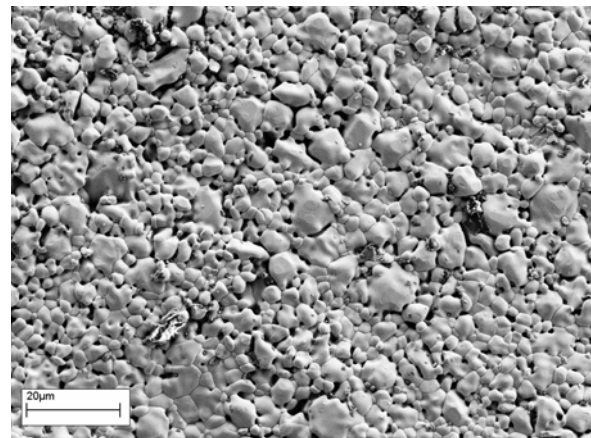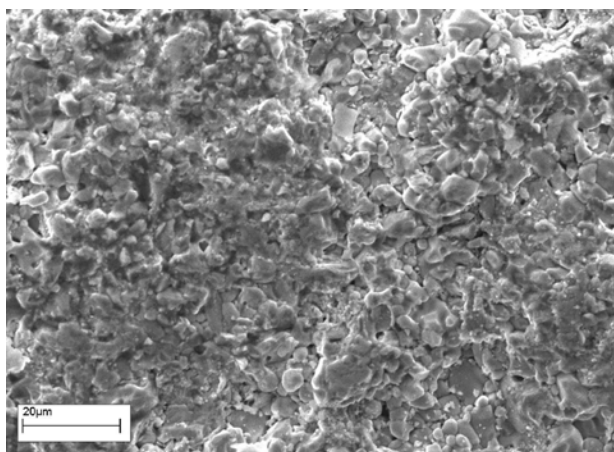

(a)
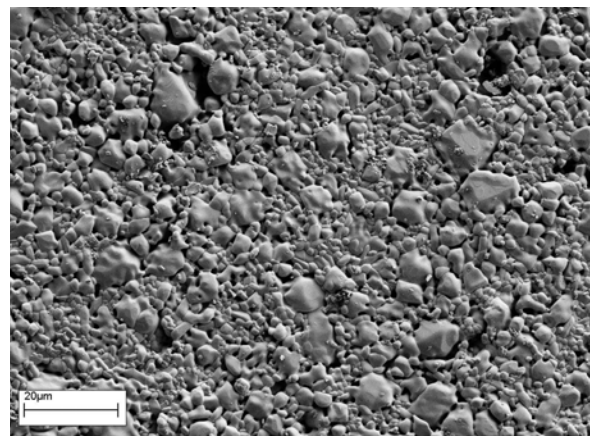
(b)
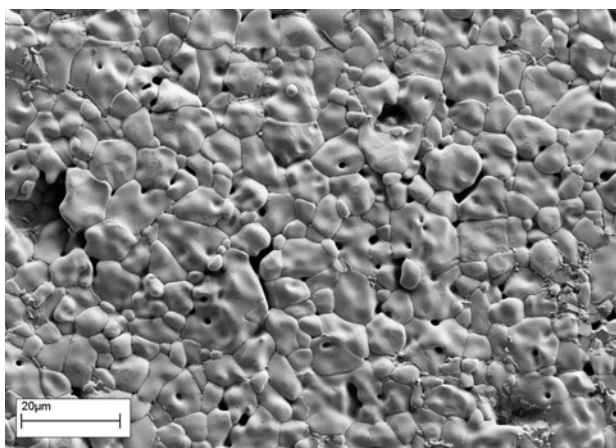
(c)

(d)

Fig. 1. Micrographs of the as-sintered surface of SnO$_2$-Co$_3$O$_4$-Nb$_2$O$_5$-Cr$_2$O$_3$ ceramics without (a) and with CaO (b), CuO (c) and V$_2$O$_5$ (d) additions.

In the micrographs of ceramics with CuO and V$_2$O$_5$ additions the tin oxide grains and the intergranular layers are seen (Figs. 1c and 1d). These layers occur rather inhomogeneously throughout such samples. They locate between the SnO$_2$ grains at CuO addition (Fig. 1c) and even covered the surface of SnO$_2$ grains at V$_2$O$_5$ addition (Fig. 1d). These are CuO-pure [18] and V$_2$O$_5$-pure [17] secondary phases which are liquid at the high burning temperature and solidify during cooling at the sintering. The CuO-rich liquid phases foster the grain growth at high temperatures in the process of burning [18]. Therefore the average grain size in such ceramics (5.8 μm) is more than that in the ceramics

without addition. The V$_2$O$_5$-rich intergranular layers are randomly distributed throughout the sample and inhibit the grain growth [17]. The SnO$_2$ grains rise only to 3.23 μm at sintering of ceramics with V$_2$O$_5$ addition. The linear shrinkage of SnO$_2$-Co$_3$O$_4$-Nb$_2$O$_5$-Cr$_2$O$_3$ samples with CuO and V$_2$O$_5$ additions is large enough (10.92 and 12.17% respectively). The great values of the linear shrinkage confirm the presence of a liquid component at burning and the formation of materials with the strong solid structure (Figs. 1c and 1d). Thus, the sintering of ceramics with CuO and V$_2$O$_5$ additions is a liquid-phase one.

The structural peculiarities of the studied samples must correlate with their electrical properties. The appearance of different intergranular inclusions and layers at the sintering can change the conditions of grain-boundary potential barrier formation. So, the electrical characteristics of examined ceramics are investigated and presented below.

3.2. Electrical characteristics

Current-voltage characteristics of SnO$_2$-based ceramics with different additions measured in air at room conditions are presented in coordinate $j(E)$ in Fig. 2. The obtained electrical parameters of this ceramics are presented in Table 1. $j(E)$ characteristic of SnCoNbCr sample is highly nonlinear (Fig. 2, curve 1) with values of nonlinearity coefficient $\beta \approx 50$ and breakdown electric field $E_1 = 5630$ V·cm^{-1}. The relative dielectric permittivity $\varepsilon = 274$ of this sample is quite high due to the formation of the sufficiently large grains (see Fig. 1a) and the existence of thin depletion layers at the grain boundaries [10, 12].

The CaO addition leads to the some increase of electric field E_1 up to 7000 V·cm^{-1} (Table 1) though the value of nonlinearity coefficient remains quite high ($\beta \approx 30$). The observed increase of the electric field E_1 in the sample with CaO addition (Fig. 2, curve 2) is due to the decrease of the average grain size (see Fig. 1b) and to the increase of the number of grain boundaries per unit length correspondingly. The relative dielectric permittivity of the sample is also correlated with average grain size [17]. Therefore the value

of dielectric permittivity of the ceramics with CaO addition $\varepsilon = 78$ is less than that for SnO_2-Co_3O_4-Nb_2O_5-Cr_2O_3 sample.
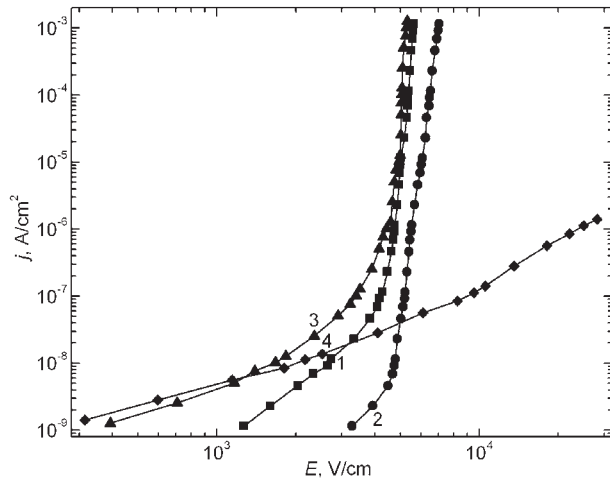
Fig. 2. j(E) characteristics of SnO_2-Co_3O_4-Nb_2O_5-Cr_2O_3 ceramics without (1) and with CaO (2), CuO (3) and V_2O_5 (4) additions at room conditions.

In ceramics with CuO addition the average grain size is larger than for the ceramics without addition. So, the electric field E_1 is less (Fig. 2, curve 3), but the dielectric permittivity is larger (Table 1) than that of SnO_2-Co_3O_4-Nb_2O_5-Cr_2O_3 ceramics. The sample with CuO addition exhibits quite large value of nonlinearity coefficient $\beta \approx 57$. Probably, the tin oxide grains are wet sufficiently by the CuO-pure liquid phases at the sintering (see Fig. 1c) and therefore the Co_3O_4 and Cr_2O_3 oxides are homogeneously distributed on the sample. These additions are responsible for the high nonlinearity of current-voltage characteristics of the ceramics [10].

The V_2O_5 addition to the SnO_2-Co_3O_4-Nb_2O_5-Cr_2O_3 ceramics causes the significant decrease of the nonlinearity coefficient and the increase of breakdown electric field (Fig. 2, curve 4). The vanadium oxide forms quite conductive phases which cover SnO_2 grains (see Fig. 1d) and working as an electric shunt to the grain boundaries [17]. Therefore the nonlinearity of current-voltage characteristics became considerable less and it became impossible to reach the breakdown electric field E_1 (at $j = 1$ mA·cm^{-2}) in our experiment. Besides, the sample with V_2O_5 addition exhibits lower value $\varepsilon \approx 14$ (Table 1) due

to the influence of vanadium oxide phase with not high relative dielectric permittivity [21, 22].

The high nonlinearity of current-voltage characteristics in SnO_2-Co_3O_4-Nb_2O_5-Cr_2O_3 ceramics and in ceramics with CaO and CuO additions ($\beta = 30 - 57$) is attributed to the grain-boundary nature of conductivity for different tin oxide based varistors [8-19]. In these samples the grains are quite conductive but grain-boundary areas are resistive due to the formation of grain-boundary potential barriers during sintering of ceramics in air atmosphere. Therefore the SnO_2-Co_3O_4-Nb_2O_5-Cr_2O_3 sample has low-field electrical conductivity $\sigma = 9.1 \cdot 10^{-13}$ Ohm^{-1}·cm^{-1}. The values of electrical conductivity became larger with the addition of CuO and V_2O_5 oxides to the ceramics (Table 1). Such samples have quite conductive intergranular phases and, consequently, the electrical conductivity of ceramics increases.

The decrease of low-field conductivity σ up to $3.5 \cdot 10^{-13}$ Ohm^{-1}·cm^{-1} is observed in the case of CaO addition (Table 1). This effect is connected with the decrease of the grain size (as a result, the significant decrease of the grain boundary cross-section and the increase of grain neck resistivity) and also to the increase of the grain-boundary potential barrier height (see later about this). The effect with lowered low-field conductivity is reproducible if air relative humidity increases. In such conditions the sample with CaO addition has the lowest electrical conductivity.
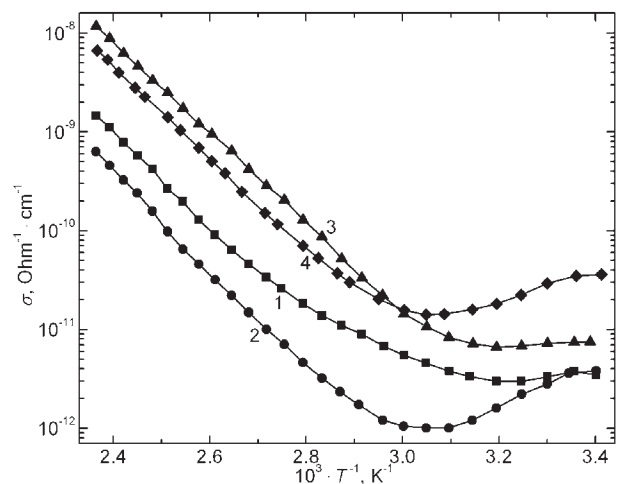

Fig. 3. Temperature dependences of electrical conductivity of SnO_2-Co_3O_4-Nb_2O_5-Cr_2O_3 ceramics without (1) and with CaO (2), CuO (3) and V_2O_5 (4) additions.

To explain the observed alteration of the low-field conductivity in the ceramics with different additions the temperature dependences of electrical conductivity were investigated (Fig. 3). The obtained values of the activation energy of electrical conduction E_σ of studied samples are presented in Table 1.

and V_2O_5 additions respectively. It causes the increase of low-field electrical conductivity in these samples (Fig. 2). With adding CaO in SnO_2-Co_3O_4-Nb_2O_5-Cr_2O_3 ceramics the activation energy of electrical conduction slightly increases up to 1.03 eV which leads to the decrease of conductivity (Fig. 2).

Table 1.

Parameters of SnO_2-Co_3O_4-Nb_2O_5-Cr_2O_3 ceramics with different additions at room conditions

Parameters	Additions			
	$-$	CaO	CuO	V_2O_5
Average grain size l_g, μm	3.54	2.58	5.80	3.23
Linear shrinkage γ, %	8.25	6.25	10.92	12.17
Electric field E_1, V·cm^{-1}	5630	7000	5280	23710*
Nonlinearity coefficient β	49.9	30.4	56.7	2.4*
Dielectric permittivity ε	274	78	489	14.4
Electrical conductivity σ, Ohm^{-1}·cm^{-1}	$9.1 \cdot 10^{-13}$	$3.5 \cdot 10^{-13}$	$3.2 \cdot 10^{-12}$	$4.5 \cdot 10^{-12}$
Activation energy of electrical conduction E_σ, eV	0.97	1.03	0.91	0.94
Humidity sensitivity coefficient S	318180	220540	1830	8920

* at $j = 10^{-6}$ A·cm^{-2}

All $\sigma(T)$ dependences are quite complicated: they cannot be approximated by a straight line in the whole studied temperature range 20 - 150°C (Fig. 3). At low temperatures in the range about 20 - 50°C the decrease of low-field conductivity at heating is caused by desorption of water molecules [15 - 18]. The humid air at room conditions can penetrate inside the ceramics and reach grain boundary areas. At heating water molecules evaporate and electrical conductivity of samples decreases (Fig. 3). Further temperature growth (50 - 150°C) gives thermally-activated increase of low-field conductivity.

The obtained value $E_\sigma = 0.97$ eV for SnO_2-Co_3O_4-Nb_2O_5-Cr_2O_3 sample gives quite correct estimation of the barrier height [20]. The addition of different oxides leads to some variation of $\sigma(T)$ dependences (Fig. 3). Commonly, the values of activation energy are quite high (Table 1). The weak decrease of E_σ up to 0.91 and 0.94 eV is found for ceramics with CuO

Thus, in the SnO_2-Co_3O_4-Nb_2O_5-Cr_2O_3 sample and in the ceramics with different additions the electrical conductivity is controlled by the grain-boundary potential barriers. The thermionic emission across the barrier is the most probable conduction mechanism near about 20 - 150°C.

3.3. Effect of humidity on the electrical properties

Low-field electrical conductivity of various tin oxide based ceramics is increased with the growth of air relative humidity [3 - 8, 15 - 18]. However, the humidity sensitivity of solid-phase sintering and liquid-phase sintering ceramic materials is studied insufficiently. Therefore we decided to study current-voltage characteristics of all obtained samples at different humidity of air.

For example, the $j(E)$ dependences of SnO_2-Co_3O_4-Nb_2O_5-Cr_2O_3-CuO ceramics measured in air with various relative humidity are shown in

Fig. 4. They are close to linear ones at low electric fields but they are highly nonlinear at higher electric fields. The rise of relative humidity from 10 to 93% causes the strong shift of low-field part of $j(E)$ characteristics to higher current but high-field part of these characteristics changes weakly (Fig. 4). This effect is reversible and reproducible. If such samples are placed in dry air (with relative humidity 10%) after humid air (with relative humidity 34 - 93%), then their characteristics return to the initial state.
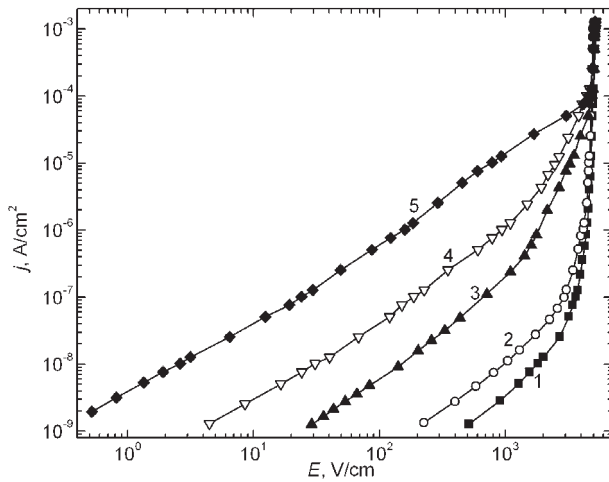

Fig. 4. j(E) characteristics of SnO$_2$-Co$_3$O$_4$-Nb$_2$O$_5$-Cr$_2$O$_3$-CuO ceramics in air with relative humidity 10 (1), 34 (2), 51 (3), 82 (4) and 93% (5).

For comparison the humidity sensitivity of tin oxide based ceramics with different additions, we presented in Fig. 5 the $j(E)$ characteristics of all investigated samples in air with relative humidity 10 and 93%. The rise of relative humidity causes the increase of low-field electrical conductivity for all ceramics. The sample with CuO addition showed the lowest increase than the other samples (Fig. 5). The intergranular layers of CuO-pure secondary phases prevent the access of the humid air into the electrical active areas of grain boundaries and diminish the role of barrier-related sensitivity mechanism.
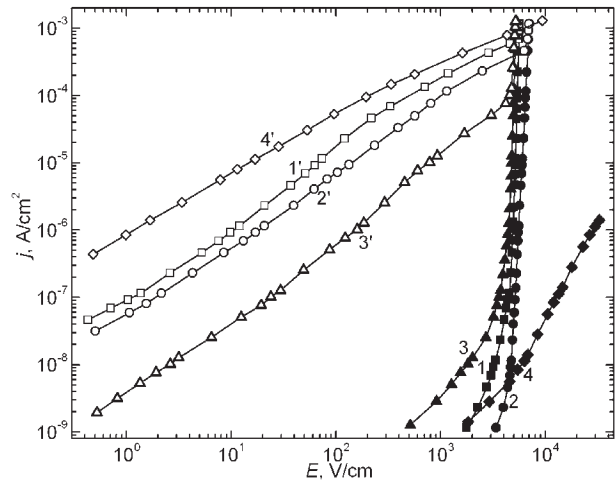

Fig. 5. j(E) characteristics of SnO$_2$-Co$_3$O$_4$-Nb$_2$O$_5$-Cr$_2$O$_3$ ceramics without (1, 1') and with CaO (2, 2'), CuO (3, 3') and V$_2$O$_5$ (4, 4') additions in air with relative humidity 10% (1, 2, 3, 4) and 93% (1', 2', 3', 4').

In order to estimate the influence of humidity on the characteristics of studied samples the values of humidity sensitivity coefficient S are presented in Table 1. For the solid-phase sintering ceramics the addition of CaO oxide causes the decrease of the value S. It can be explained by the segregation of the secondary solid phases at the grain boundaries [19] and the decrease of the environmental influence on the electrical properties of ceramics. For the liquid-phase sintering samples with CuO and V$_2$O$_5$ additions the humidity sensitivity is less (Table 1) because such ceramics are more solid and less porous. Besides, solidified at sintering the CuO and V$_2$O$_5$ secondary liquid phases located at grain boundary areas and even cover surface of SnO$_2$ grains (see Figs. 1c and 1d) and partially prevent the penetration of humid air into the grain boundaries. For that reason the electrical conductivity increases less at higher humidity. Therefore humidity sensitivity of liquid-phase sintering samples is lower than that of the solid-phase sintering ceramics.

The high humidity sensitivity of studied material is explained by the grain boundary controlled conduction mechanism [8, 15 - 18]. The observed increase of the low-field electrical conductivity with the rise of air relative humidity (Figs. 4 and 5) can be caused by the decrease of the grain-boundary barrier height. It was

shown earlier that the potential barrier height decreases only by nearly 20% if air relative humidity reaches about 80% [16]. Therefore the grain-boundary potential barriers at high humidity are still sufficiently high to be decreased at high voltages. Thus, highly-nonlinear $j(E)$ dependences are still observed at high values of relative humidity (Figs. 4 and 5).

The rise of low-field electrical conductivity at the increase of air relative humidity is connected with the adsorption of water molecules at the near-surface areas of studied ceramics. These molecules can dissociate according to the equation

$$H_2O \leftrightarrow H^+ + OH^-. \qquad (6)$$
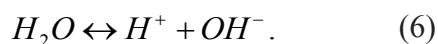
The quite mobile proton H^+ can penetrate to the grain-boundary areas and interact with oxygen which has been chemisorbed there at the sintering of ceramics in oxidizing atmosphere. For that reason the total negative charge at the near-surface grain boundary can become lower in absolute value. This leads to the decrease of potential barrier heights. Therefore in air with higher relative humidity the grain-boundary barriers are lower at the near-surface areas of sample and the low-field electrical conductivity of ceramics is larger than in air with lower relative humidity.

If the samples were placed into the dry air (with relative humidity 10%) after recording of current-voltage characteristics, desorption of water molecules began. The grain-boundary potential barrier heights are increasing and the low-field electrical conductivity of samples is decreasing. The $j(E)$ characteristics return to the initial state.

The existence of the grain-boundary potential barriers in studied ceramics is confirmed by the following observed facts: strong non-Ohmic conduction at relatively low electric fields (see Fig. 2), thermally-activated electrical conductivity (see Fig. 3) and reversible increase of dielectric permittivity with the rise of relative humidity. The last statement is related to the decrease of grain-boundary barrier height as well as the width of these barriers at higher air humidity. The less the grain-boundary barrier width is the larger dielectric permittivity of sample is. This conclusion is proved by the values of dielectric permittivity for all samples with different additions (Table 2). The dielectric permittivity of ceramics is increasing with the rise of air relative humidity.

Table 2.

Dielectric permittivity of SnO$_2$-Co$_3$O$_4$-Nb$_2$O$_5$-Cr$_2$O$_3$ ceramics without and with CaO, CuO and V$_2$O$_5$ additions at different values of air relative humidity

Relative humidity, %	Additions			
	–	CaO	CuO	V$_2$O$_5$
10	245.7	77.2	483.3	14.2
34	254.5	77.5	484.3	14.3
51	275.8	86.7	505.8	27.1
82	399.1	223.5	569.4	3759
93	885.1	265.5	677.0	876147

Thus, the discussed humidity-sensitive effect in tin oxide based ceramics leads to the increase of low-field electrical conductivity in humid air in comparison with dry air. The obtained results for SnO$_2$-based humidity-sensitive ceramics allow using it as the sensors that are the devices for measuring the air relative humidity.

4. CONCLUSIONS

The humidity-sensitive properties and varistor characteristics are observed in solid-phase and liquid-phase sintering of SnO$_2$-based ceramics with different additions. These peculiarities are explained by the decrease of the grain-boundary potential barrier height and width on relative humidity (at low electric fields) and on voltage (at high electric fields). The estimated values of barrier height of studied samples are 0.91 - 1.03 eV. Low-field electrical conductivity and dielectric permittivity of investigated ceramics are increased with the rise of air relative

humidity. The lowest humidity sensitivity coefficient $S = 1830$ and highest nonlinearity coefficient $\beta = 57$ at electric field $E_1 = 5280$ V·cm^{-1} were obtained for SnO_2-Co_3O_4-Nb_2O_5-Cr_2O_3-CuO sample. The values S is decreased with CaO addition (solid-phase sintering) and greatly decreased with CuO and V_2O_5 additions (liquid-phase sintering). The CaO addition provides the lowest value of low-field electrical conductivity for studied samples. The observed decrease of the conductivity at low field correlates with the experimentally found increase of the activation energy of electrical conduction and the decrease of the grain size. The studied ceramics are prospective materials for humidity sensors and varistor production.

ACKNOWLEDGMENTS

REFERENCES

[1]. B. M. Kulwicki. Ceramic sensors and transducers // J. Phys. Chem. Solids, 45 (10), pp. 1015-1031 (1984).

[2]. W. Gopel, K. D. Schierbaum. SnO_2 sensors: current status and future prospects // Sens. Actuat. B: Chem., 26 (1-3), pp. 1-12 (1995).

[3]. J. F. McAleer, P. T. Moseley, J. O. W. Norris, D. E. Williams. Tin dioxide gas sensors. Part 1. Aspects of the surface chemistry revealed by electrical conductance variations // J. Chem. Soc., Faraday Trans. 1, 83 (4), pp. 1323-1346 (1987).

[4]. J. F. McAleer, P. T. Moseley, J. O. W. Norris, D. E. Williams, B. C. Tofield. Tin dioxide gas sensors. Part 2. The role of surface additives // J. Chem. Soc., Faraday Trans. 1, 84 (2), pp. 441-457 (1988).

[5]. E. Traversa. Ceramic sensors for humidity detection: the state-of-the-art and future developments // Sens. Actuat. B: Chem., 23 (2-3), pp. 135-156 (1995).

[6]. Z. Chen, C. Lu. Humidity sensors: a review of materials and mechanisms // Sensor Lett., 3 (4), pp. 274-295 (2005).

[7]. S. P. Yawale, S. S. Yawale, G. T. Lamdhade. Tin oxide and zinc oxide based doped humidity sensors // Sens. Actuat. A: Phys., 135 (2), pp. 388-393 (2007).

[8]. A. B. Glot. Conductivity of SnO_2 based ceramics // Inorg. Mater., 20 (10), pp. 1522-1523 (1984).

[9]. A. B. Glot, A. P. Zlobin. Nonohmic conductivity of tin dioxide ceramics // Inorg. Mater., 25 (2), pp. 274-276 (1989).

[10]. S. A. Pianaro, P. R. Bueno, E. Longo, J. A. Varela. A new SnO_2-based varistor system // J. Mater. Sci. Lett., 14 (10), pp. 692-694 (1995).

[11]. P. N. Santosh, H. S. Potdar, S. K. Date. Chemical synthesis of a new tin dioxide based (SnO_2 : Co, Al, Nb) varistor // J. Mater. Res., 12 (2), pp. 326-328 (1997).

[12]. A. B. Glot. Non-ohmic conduction in oxide ceramics: tin dioxide and zinc oxide varistors. Chap. 10 in Ceramic Materials Research Trends, Ed. P.B. Lin, pp. 227-273, Nova Science Publishers, Inc., New York (2007).

[13]. A. B. Glot, A. V. Gaponov, A. P. Sandoval-Garcia. Electrical conduction in SnO_2 varistors // Phys. B: Condensed Matter., 405 (2), pp. 705-711 (2010).

[14]. A. V. Gaponov, A. B. Glot. Non-ohmic conduction in tin dioxide based ceramics with copper addition // Semicond. Phys., Quant. Electron. & Optoelectr., 14 (1), pp. 71-76 (2011).

[15]. I. Skuratovsky, A. Glot, E. Di Bartolomeo, E. Traversa, R. Polini. The effect of humidity on the voltage-current characteristic of SnO_2 based ceramic varistor // J. Eur. Ceram. Soc., 24 (9), pp. 2597-2604 (2004).

[16]. I. Skuratovsky, A. Glot, E. Traversa. Modelling of the humidity effect on the barrier height in SnO_2 varistors // Mater. Sci. Eng. B, 128 (1-3), pp. 130-137 (2006).

[17]. A. V. Gaponov, A. B. Glot, A. I. Ivon, A. M. Chack, G. Jimenez-Santana. Varistor and humidity-sensitive properties of SnO_2-Co_3O_4-Nb_2O_5-Cr_2O_3 ceramics with V_2O_5 addition // Mater. Sci. Eng. B, 145 (1-3), pp. 76-84 (2007).

[18]. A. B. Glot, A. P. Sandoval-Garcia, A. V. Gaponov, R. Bulpett, B. J. Jones, G. Jimenez-Santana. Electronic properties of SnO_2-based ceramics with double function of varistor and humidity sensor // Adv. in Tech. of Mat. and

Mat. Proc. J., 10 (1), pp. 21-32 (2008).

[19]. A. V. Gaponov, O. V. Vorobiov, A. M. Vasyliev. Electrical parameters of SnO$_2$ based varistor ceramics with CaO and BaO additions // Phys. Chem. Solid State, 17 (1), pp. 81-87 (2016).

[20]. M. Batzill, U. Diebold. The surface and materials science of tin oxide // Prog. Surf. Sci., 79, pp. 47-154 (2005).

[21]. A. I. Ivon, I. M. Chernenko. Dielectric polarization of vanadium pentoxide // Izv. Vyssh. Ucheb. Zaved., Fiz., 21 (1), pp. 111-113 (1978).

[22]. R. Sengodan, B. Chandar Shekar, S. Sathish. Morphology, structural and dielectric properties of vacuum evaporated V$_2$O$_5$ thin films // Phys. Proc., 49, pp. 158-165 (2013).

HUMIDITY SENSORS BASED ON SnO$_2$-Co$_3$O$_4$-Nb$_2$O$_5$-Cr$_2$O$_3$ SEMICONDUCTOR VARISTOR CERAMICS

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Summary

The aim of this article is to study the influence of different oxides on the humidity-sensitivity properties and electrical characteristics of SnO$_2$-based semiconductor ceramics. In this paper we have investigated SnO$_2$-Co$_3$O$_4$-Nb$_2$O$_5$-Cr$_2$O$_3$ varistor ceramics with three various additions prepared by solid-phase sintering (without or with CaO addition) and liquid-phase sintering (with CuO or V$_2$O$_5$ additions).

The microstructure of samples was studied by the scanning electron microscope. The current-voltage characteristics, the values of dielectric permittivity of the ceramics at air relative humidity 10 - 93% and the temperature dependences of electrical conductivity were recorded.

The low-field electrical conductivity and dielectric permittivity of ceramics are increased when air relative humidity rises from 10 to 93%. Such effects are observed both in the samples prepared by solid-phase sintering and in the samples prepared by liquid-phase sintering. The lowest humidity-sensitivity effect was found in the liquid-phase sintering samples due to the more solid structures and the secondary phases which are located between the SnO$_2$ grains. For the studied samples the values of humidity sensitivity coefficient $1.8 \cdot 10^3$-$3.2 \cdot 10^5$ at low electric fields and the nonlinearity coefficient 30-57 at high electric fields (E_1=5.3-7 kV·cm^{-1}) were calculated.

The properties of oxide ceramics are explained by electrical conductivity which is controlled by the grain-boundary potential barriers. The barrier height decreases with the increase both of air relative humidity at low electric fields and of voltage at high electric fields. Strong humidity sensitivity is a key factor for sensor application of SnO$_2$-based ceramics.

Keywords: humidity sensor, tin oxide, varistor, oxide ceramics, grain boundary, electrical conductivity

СЕНСОРИ ВОЛОГОСТІ НА ОСНОВІ НАПІВПРОВІДНИКОВОЇ ВАРИСТОРНОЇ КЕРАМІКИ SnO$_2$-Co$_3$O$_4$-Nb$_2$O$_5$-Cr$_2$O$_3$

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Реферат

Метою цієї статті є вивчення впливу різних оксидів на вологочутливі властивості й електричні характеристики напівпровідникової кераміки на основі SnO$_2$. В цій роботі ми провели дослідження варисторної кераміки SnO$_2$-Co$_3$O$_4$-Nb$_2$O$_5$-Cr$_2$O$_3$ з трьома різними домішками, виготовленої шляхом твердо-фазного синтезу (без або з CaO домішкою) і рідко-фазного синтезу (з CuO або V$_2$O$_5$ домішками).

Мікроструктура зразків досліджена в скануючому електронному мікроскопі. Були зареєстровані вольт-амперні характеристики, значення діелектричної проникності кераміки при відносній вологості повітря 10 - 93% і температурні залежності електричної провідності.

Електропровідність у слабких полях і діелектрична проникність кераміки збільшувались при зростанні відносної вологості повітря з 10 до 93%. Такі ефекти спостерігались як для твердо-фазних синтезованих зразків, так і для рідко-фазних синтезованих зразків. Найменшу вологочутливість мають рідко-фазні синтезовані зразки у зв'язку з їх більш щільною структурою й існуючими вторинними фазами, які розташовуються між зернами SnO$_2$. Для досліджених зразків обчислені значення коефіцієнта вологочутливості 1,8·10^3-3,2·10^5 при слабких електричних полях і коефіцієнта нелінійності 30 - 57 при сильних електричних полях (E_1=5,3-7 кВ·см$^{-1}$).

Властивості оксидної кераміки пояснюються електричною провідністю, яка контролюється потенціальними бар'єрами на межах зерен. Висота бар'єрів зменшується як зі збільшенням відносної вологості повітря при слабких електричних полях, так і напруги при сильних електричних полях. Велика вологочутливість є ключовим фактором для сенсорного використання кераміки на основі SnO$_2$.

Ключові слова: сенсор вологості, оксид олова, варистор, оксидна кераміка, межа зерен, електрична провідність