VOL. 11, NO. 1, JANUARY 2016 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences

www.arpnjournals.com

ELECTROPHYSICAL AND PHYSICAL-MECHANICAL PROPERTIES OF THE COMPOSITE SnO_2-Ag (SEMICONDUCTOR-METAL) CERAMIC MATERIAL

Kirko Vladimir I.[1, 2], Dobrosmyslov Sergey S.[1], Nagibin Gennadij E.[1], Koptseva Natalia P.[1]
[1]Siberian Federal University, Krasnoyarsk, Russia
[2]Krasnoyarsk State Pedagogical University named after Victor Astafijev, Krasnoyarsk, Russia
E-Mail: decanka@mail.ru

ABSTRACT

We investigated the physical and electrical properties of ceramics based on SnO2-Sb2O3-AgO. Electrical properties were investigated in the temperature range 20-1000 0K. It is shown that in the temperature range 200-450 0K dependence of the electrical resistivity ceramics with temperature shifts from an exponential curve to another, characterized by a high electrical resistivity. This is explained by the closure of the mesh silver percolation channels formed in the synthesis of ceramics.

Keywords: ceramics based on tin, high electrical conductivity, percolation channels silver.

INTRODUCTION

The SnO_2-based ceramics is being widely used in many industries (Nistro, 2003). Tin dioxide is semiconductor with the forbidden band energy 3.54 eV (Knunyats, *et al.,* 1988) having unique properties - in the first place high electrical conductivity and chemical resistance.

Chemically resistant ceramics of a high electrical conductivity is of great interest as electrode material (Jinhuai, *et al.,* 2003) operating at high temperatures, for instance in aluminium electrolysis and glass production (Kirko, *et al.,* 2010).

Without additives SnO_2 has a low sinterability and electrical conductivity (Bueno and Varela, 2006). The poor sinterability is caused by the domination of evaporation-condensation processes over diffusion. The intensive evaporation starts at 1100 ºC (Haarber, *et al.,* 2010). To improve sinterability there are used additives such as ZnO (Bureno, *et al.,* 2008), CuO (Kirko, *et al*., 2012), MnO_2 (Yatao, *et al.,* 2010; Zuca, *et al.,* 1991), CoO (Cerri, *et al.,* 1996), Fe_2O_3 (Zuca, *et al.,* 1991). And electrical properties are improved with V_2O_5 (Mahipal and Mastikhi, 1992) and Sb_2O_3 (Ciorcero, *et al.,* 2011).

In spite of the substantial improvement of the material's electrophysical properties at high temperatures (above 600 ºC), its electrical conductivity remains low at the room temperature, that makes it difficult for the material to be used and requires additional conditions (Dobrosmislov, *et al.,* 2010). The reduction of the material's electrical resistance at low temperatures will allow widening the field of its application (Figure-1).

In semiconductors the total electric current is a sum of partial currents, provided by p- and n-type conductivities (Zeeger, 1981). In case of a contact of a p-type semiconductor with a metal there appears a space charge region of ionized donors and the blocking contact, or Schottky barrier, forms (Parker, 1994).

This means that the addition of Ag superdispersed particles into td.1) he ceramics structure will allow an additional number of charge carriers to appear in the semiconductor-metal contact zone that will increase the electrical conductivity (Lakishev, 1996).

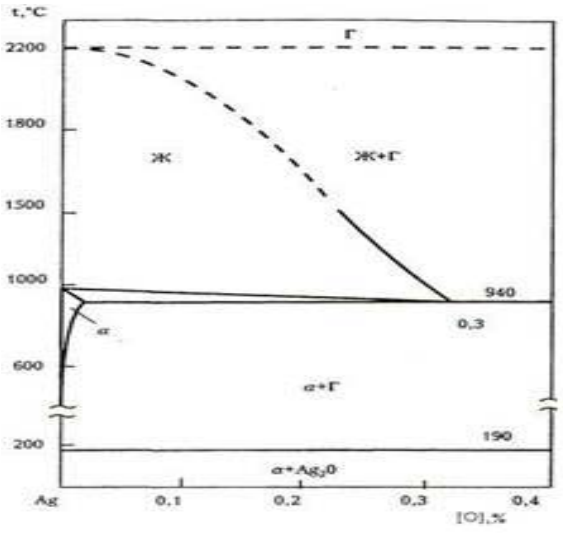


Figure-1. Phase diagram Ag-O.

It can be seen from the phase diagram Ag-O in Figure-1 that in the range 850 - 900 ºC there takes place

the reduction of silver from its oxide. Accordingly, the addition of the silver oxide into the initial furnace charge allows making a ceramic material with silver particle additives.

THE EXPERIMENTAL TECHNIQUE

The synthesis technique: The material was synthesized according to the following technique: the furnace charge preparation→ pressing the powder with 5% polyvinylalcohol (PVA) → sintering at 1300 and 1400ºC.

For physical-mechanical tests the ceramic specimens were made in the form of cylinders 15 mm in diameter and of 10 mm height. For electrophysical measurements the specimens had the rectangular shape 5×4×50 mm.

The research of physical-mechanical properties of the specimens was carried out according to the State Standards 24468-80, 530-95, 20419-83. The resistivity within the temperature range 20-1000 °C was measured with the four-point probe method (Dharmasema and Wadley, 2002). To measure mechanical characteristics there was used the instrument Instron 3369. The material structure was identified by the X-ray phase analyzer XRD 6000 and electron microscope JEOL JSM-6490 LV.

To increase the electrical conductivity at high temperatures antimony oxide additives were used. When sintering at high temperatures the dissolution of antimony atoms in the SnO_2 crystal lattice occurs (Galahov, *et al.,* 1987) that provides the p-type conductivity of the material and substantial reduction of the band-gap energy (Ciorcero, *et al.,* 2011). To improve the conductivity at low temperatures there are used superdispersed metallic silver particles that increase the charge carrier's concentration in the semiconductor-metal contact zone.

The physical-mechanical properties of the composite SnO_2-Ag (semiconductor-metal) material are presented in Table-1.

Table-1. The physical-mechanical properties of the composite material.

No.	Charge composition, %			Sintering temp., °C	Density, kg/m^3	Open porosity, %	Strength, MPa
	SnO_2	Sb_2O_3	AgO				
1	2	3	4	5	6	7	8
1	96	2	2	1300	4366	34.3	48.8
2	92	2	6	1300	4552	29.6	70.6
3	90	2	8	1300	4619	31.7	67.3
4	96	2	2	1400	3760	43.1	37.1
5	92	2	6	1400	3798	43.1	37.0
6	90	2	8	1400	4377	52.4	31.1

The conducted research of physical-mechanical properties of the SnO_2-Ag composite material showed that the ceramics is badly sintered and has as a consequence a high porosity and low strength. This is caused by the following. It is well known that to intensify sintering it is necessary that the material should be well wetted by a liquid phase (Savitskiy, 1991). However, the limiting wetting angle for SnO_2 at the porosity 0.01 % and within the temperature range 950-1020 °C is (72.4 ± 4.3) degrees (Denisova, 2009). Silver reduced from its oxide inhibits the SnO_2 diffusion. The degradation of basic physical-mechanical properties of the material, when increasing the sintering temperature from 1300 to 1400 ºC, supports the fact that silver inhibits sintering.

The X-ray phase analysis (Figure-2) of the material confirmed the presence of a metallic silver phase in the ceramics structure.

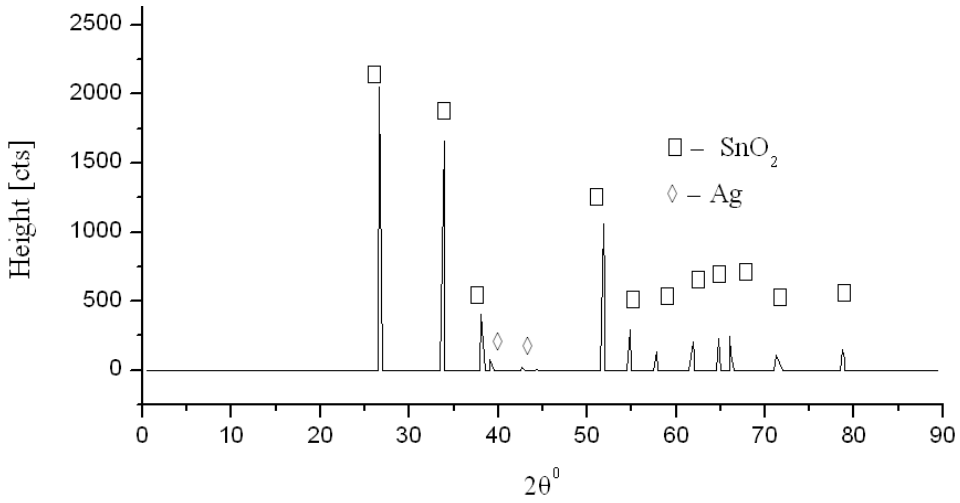
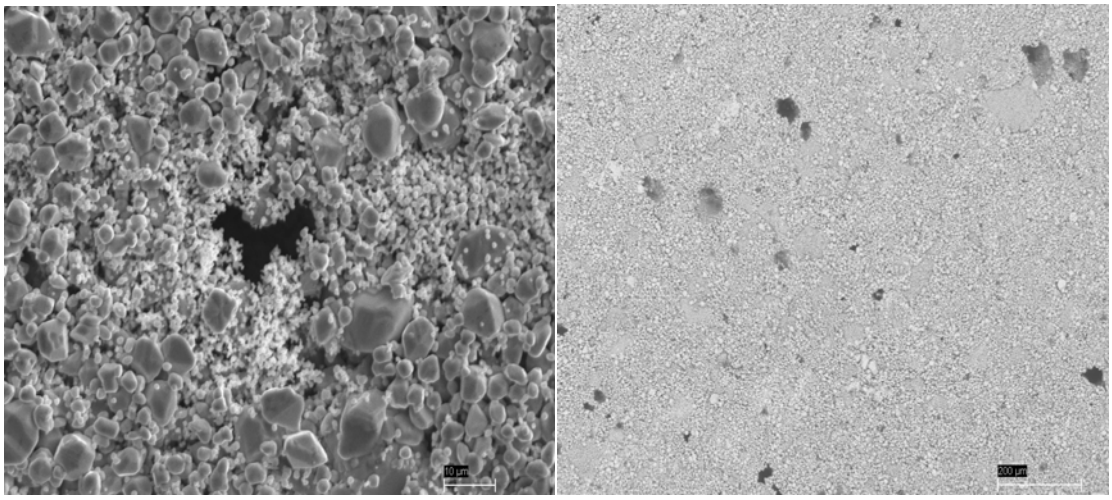


Figure-2. The X-ray diffraction pattern of a specimen with the initial furnace charge composition 90%SnO_2-2%Sb_2O_3-8% AgO.

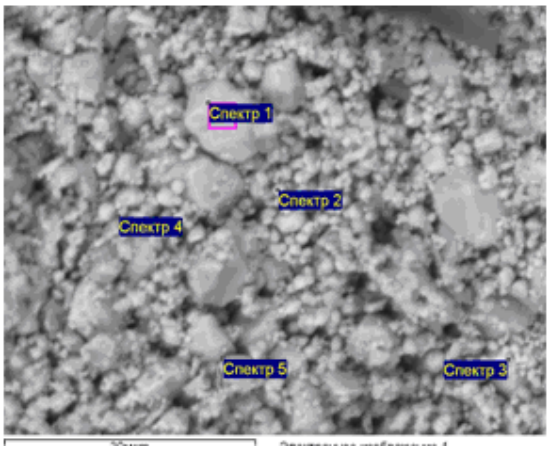
The raster electron microscopy showed (Figure-3) that silver segregates in the form of superdispersed particles. And there are pores of a significant size in the material that supports poor sintering and low physical-mechanical properties.



a) b)

Figure-3. The raster electron microscope photography of the specimen with the initial furnace charge composition 90%SnO_2-2%Sb_2O_3-8%AgO a) – x2000; (b) – x100.

The micro X-ray spectroscopic analysis results (Figure-4) showed that silver is dispersed quite uniformly, but its concentration is not high that may be associated with its partial dissolution in the tin dioxide structure.



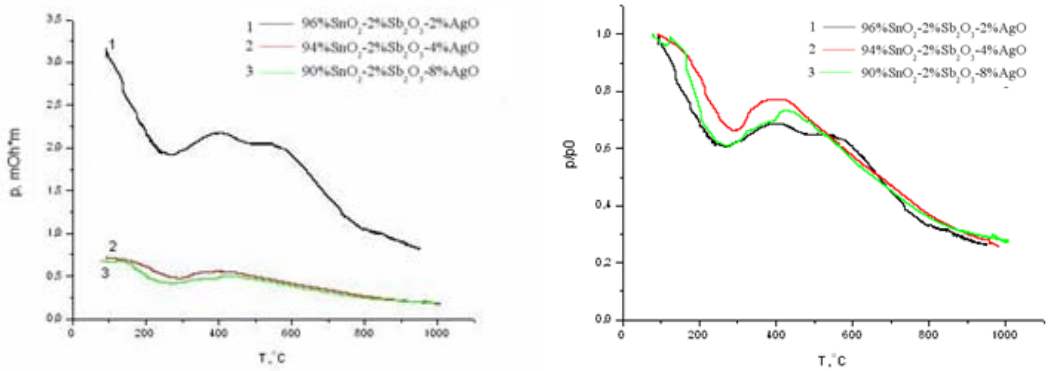
Spectrum	O	Ag	Sn	total
Spectrum1	23.23	0.38	76.39	100.00
Spectrum2	36.48	0.58	62.94	100.00
Spectrum3	32.74	0.50	66.76	100.00
Spectrum4	28.88	0.39	70.74	100.00
Spectrum5	29.74	0.46	69.80	100.00
Average val.	30.21	0.46	69.32	100.00
standard deviation	4.91	0.08	4.99	
max	36.48	0.58	76.39	
min	23.23	0.38	62.94	

Figure-4. The photography and micro X-ray spectroscopic analysis of the specimen 96%SnO_2-2%Sb_2O_3-2% AgO.

ELECTROPHYSICAL PROPERTIES OF THE CERAMICS

In Figure-5 there are presented the resistivity measurement results of the SnO_2-Ag composite material sintered at 1300 °C.

As follows from the research carried out the superdispersed silver particles affect significantly the electrical conductivity of the material. Firstly, a significant drop of the temperature of the percolation beginning is observed. Secondly, the shape of the curve in Figure-5 suggests that there is a possibility of the electron passage from the metallic particles into the tin dioxide conduction band. It can also be noted that when the silver portion increases, there takes place saturation of the conduction band by charge carriers, and the resistivity doesn't depend on the silver concentration any more.

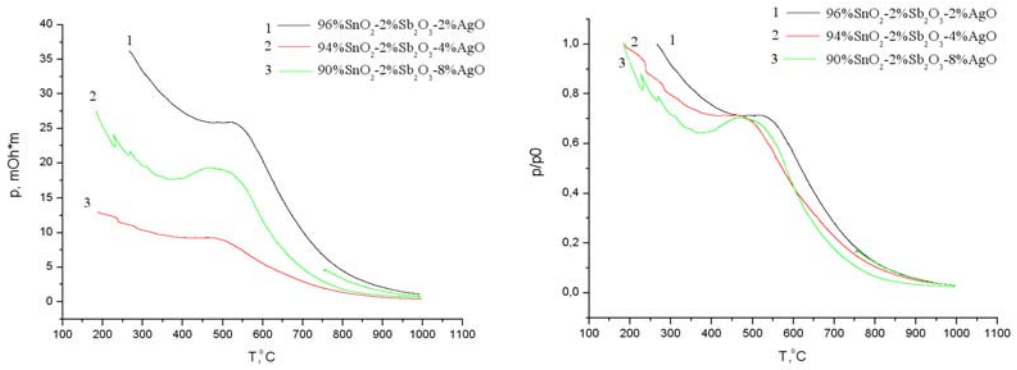


a) b)

Figure-5. The resistivity (a) and comparative resistivity (b) of the SnO_2-Ag composite material sintered at 1300 °C vs. temperature.

In Figure-6 there are presented the resistivity measurement results of the SnO_2-Ag composite material sintered at 1400 °C.

The increased sintering temperature leads to increased resistivity in the low temperature range. In the range above 900 °C the resistivity is almost independent of the silver concentration. An influence of the additional space charge on the material conductivity at high temperatures is almost absent. This effect can be explained by the fact that the potential barrier value on the semiconductor-metal boundary doesn't depend on temperature.



a) b)

Figure-6. The resistivity (a) and comparative resistivity (b) of the SnO_2-Ag composite material sintered at 1400 °C vs. temperature

CONCLUSIONS

The usage of the silver oxide additives when making SnO_2-based ceramics allows decreasing significantly the composite material resistivity, especially at low temperatures, which is associated with silver reduction from its oxide. This effect is associated with the formation of the space charge region in the semiconductor-metal contact zone.

Temperature dependencies of the resistivity for the materials with 4 and 8 weight % of silver and sintered at 1300 ºC are practically the same.

For the ceramics sintered at 1400 ºC there is observed an obvious dependence of the resistivity on the concentration. The percolation beginning temperature increases by 150 ºC compared to that of the material sintered at 1300 ºC. The sintering temperature increase may lead to silver particles being distributed more uniformly along the grains' boundaries.

ACKNOWLEDGMENT

The work was carried out under the support of the organization "Scientific and scientific-pedagogical staff of innovative Russia" - the state contracts № 14.740.11.1293 and № 14.B37.21.0131.

The work was carried out within the Russian Foundation for Basic Research project № 12-03-31323 (RFBR project № 12-03-31323).

REFERENCES

Nisiro D., Fabbri G., Celotti G. C. and Bellosi, A. 2003. Influence of the additives and processing conditions on the characteristics of dense SnO2-based ceramics. Journal of materials science. 38(12): 2727-2742.

Knunyats I.L. 1988. Himicheskaya entsiklopediya. T. 3, Moskva.

Jinhuai Liu, Xingjiu Huang, Gang Ye, Wei Lui, Zheng Jiao, Wanglian Chao, Zhongbai and Zhou Zengliang Yu. 2003. H_2S Detection sensing characteristic of CuO/SnO_2. Sensor. 3: 110-118.

Kirko V.I., Dobrosmislov S.S., Nagibin G.E., Stepanov E.I. and Rezinkina O.A. 2010. Issledovanie fisiko-mehanicheskih i electrofisicheskih svoystv electroprovodyashih ogneupornih keramik na osnove SnO-Sb_2O_3-CuO. Ogneupori i tehnicheskaya keramika. 6, 7-10.

Bueno P. R. and Varela J. A. 2006. Electronic Ceramics Based on Polycrystalline SnO_2, TiO_2 and (Sn_xTi_{1-x}) O_2 Solid Solution. Materials Research. 3 (9): 293-300.

Haarber G.M., Kvalheim E., Patvik A.P., Xiao S,J., Mokkelbost Y. 2010. Depolarised gas anodes for aluminium electrowinning. Trans. Nonferrous Met. Soc. China. 20: 2152-2154.

Bueno P.R.B., Varela, J.A., and Longo E. 2008. SnO2, ZnO and related polycrystalline compound semiconductors: An overview and review on the voltage-dependent resistance (non-ohmic) feature. Journal of the European Ceramic Society. 28: 505-529.

Kirko V.I., Dobrosmislov S.S., Nagibin G.E., Stepanov E.I. and Rezinkina O.A. 2012. Osobennosti fisiko-mehanicheskih i visokotemperaturnih elektrofisicheskih svoystv keramicheskih poluprovodnikovih materialov na osnove SnO_2 s dobavkami MnO_2 i CuO. Vestnik SibGAU, 1 (41): 118-122.

Yatao Chen, Ping He, Ping Huang, Li Wang, Xiaofang, Yi and Faqin, Dong. 2010. SnO_2-modified MnO_2 Electrode Materials for Electrochemical Capacitor. ECS Transactions. 28(8): 107-115.

Zuca St., Terzi M., Zaharescu M. and Matiasovski K. 1991. Contribution to the study of SnO2-based ceramics: Part II. Efect of various oxide additives on the sintering capacity and electrical conductivity of SnO2. J. Mat. Sci. 26, 1673-1676.

Cerri J.A., Leite E.R., Gouvea D. and Longo E. 1996. Effect of Cobalt (II) Oxide and Manganese (IV) Oxide on Sintering of Tin (IV) Oxide. 1996. Journal of the American Ceramic Society. 79(3): 799-804.

Mahipal B. & Mastikhi V.M. 1992. Study of tin dioxide and antimony tetroxide supported vanadium oxide catalysts by solid-state 51V and 'H NMR technique. Solid State Nuclear Magnetic Resonance. l: 245-249.

Ciorcero J. R., Pianaro S.A., Bacci G., Zara A.J., Tebcherani S.M., Long E. 2011. Influence of the concentration of Sb2O3 on the electrical properties of SnO2. J Mater Sci: Mater Electron. 22: 679-68.

Dobrosmislov S. S., Kirko V.I., Nagibin G.E., Stepanov E.I. and Rezinkina O.A. 2010. Investigation of Physical-mechanical and Electric Properties of Conducting SnO2-based Ceramics. Journal of Siberian Federal University. Engineering and Technologies. 3(3): 316-321.

Zeeger K. 1977. Fisika poluprovodnikov. Moskva, Izdatelstvo "Mir".

Parker G. 1994. Introductory semiconductor device physics. Prentice Hall.

Lakishev N.P. (ed.). 1996. Diagrammi sostoyaniya dvoynih metallicheskih. Moskva, Mashinostroenie.

Dharmasena K. P. and Wadley H. N. G. 2002. Electrical conductivity of open-cell metal foams. Journal of materials research. 17(03): 625-631.

Galahov F.Y. and Shervinskaya A.K. 1987. Diagrammi sostoyaniya system tugoplavkih oksidov. Leningrad, Institut himii silikatov, Nauka.

Savitskiy P. 1991. Zidkofaznoe spekanie system s vzaimodeystvuyshimi komponentami. Novosibirsk, Nauka, Sibirskoe otdelenie.

Denisova L.T., Biront V.S., Zeer G.M., Denisov V.M., Osipovich T.B. and Kirik S.D. 2009. O katastroficheskom okislenii rasplavov Ag-Sn Journal of Siberian Federal University. Engineering and Technologies. 3 (2): 283-293.