INVESTIGACIÓN Revista Mexicana de Física **58** (2012) 313–316 AGOSTO 2012

Current saturation in In_2O_3-SrO ceramics: a role of oxidizing atmosphere

A. Bondarchuk[a], O. Shpotyuk[b], A. Glot[a], and H. Klym[c]
[a]*Universidad Tecnológica de la Mixteca,*
Huajuapan de León, Oaxaca, 69000, México.
[b]*Lviv Scientific Research Institute of Materials, Lviv, Ukraine, 79031.*
[c]*Lviv Polytechnic National University, Lviv, Ukraine, 79013.*

Recibido el 25 de julio de 2011; aceptado el 10 de abril de 2012

Current-voltage dependence in In_2O_3-SrO ceramics contains a region where the current is increased weaker than the voltage. Such behavior is observed in oxygen atmosphere and is not registered in an inert one. Nonlinear current-voltage dependence is explained in terms of a relation between electronic processes at the grain boundaries and adsorption of oxygen in electric field. The role of adsorption processes is discussed on the basis of obtained data (current-voltage dependences, pore size distribution, secondary electron microscopy, and humidity sensitivity of conductance).

Keywords: Current limiting; indium oxide ceramics; adsorption processes.

La dependencia de la corriente contra el voltaje de la cerámica In_2O_3-SrO contiene una región en la cual la corriente aumenta en una menor proporción que el voltaje. Este comportamiento de corriente se observa en un ambiente de oxidación y no se registra en el argón. La dependencia no lineal entre el voltaje y la corriente se explica considerando la relación entre los procesos electrónicos y los procesos de adsorción en los bordes de grano en el campo eléctrico. El rol del proceso de adsorción se analiza tomando en cuenta los datos recibidos (las dependencias de las corrientes contra el voltaje, distribución de tamaño de poros, la microscopía de los electrones secundarios, y la sensibilidad de la conductancia a la humedad).

Descriptores: Limitación de corriente eléctrica; cerámica a base de óxido de indio; procesos de adsorción.

PACS: 72.20.-i; 73.30.+y; 73.20.-r

1. Introduction

The wide-band-gap oxide semiconductor In_2O_3 is widely used for the preparation of transparent electrodes for opto-electronic devices [1] and as a material for the preparation of film [2] and ceramic [3] sensors. Additionally, In_2O_3-based ceramics can exhibit non-Ohmic current-voltage behavior [4].

Nonlinear current-voltage dependence (I(U)) in oxide ceramics is described empirically in terms of a power-law function $I=BU^{\alpha}$ where α is the nonlinearity coefficient, α=(U/I)/(dI/dU), and B is the constant [5]. In low electric fields Ohm's law takes place and α=1. In higher fields, deviations from Ohm's law can be observed. Two cases are possible: superlinear, exploited in varistors [5], where the current rises more strongly than voltage (in this case $\alpha > 1$); or sublinear where current rises more weakly than voltage ($\alpha < 1$).

The sublinear I-U behavior has been found in In_2O_3-SrO ceramics sintered at 1100°C [6-9]. Such behavior can be explained in terms of a modified barrier model proposed in [6]. In this model I-U behavior is related to additional oxygen adsorption which appears after voltage application. Thus, the In_2O_3-SrO ceramics is of interest as this material has nonlinear I-U behavior and sensitivity to a gaseous environment [6].

The oxygen adsorption at the grain boundary (GB) in the bulk of a sample is possible only if this material exhibits open porosity. Therefore, it would be interesting to study the pore structure in In_2O_3–SrO ceramics and its relationship with electrical properties of material. In this paper, current-voltage dependences in different gas environments and pore size distribution in In_2O_3-SrO ceramics were studied and discussed.

2. Experimental details

Indium oxide based ceramics (mol.%) $90In_2O_3$–10SrO were prepared by the conventional mixed oxides method with sintering at a temperature of 1370 K [6]. The sintered samples were cylindrical tablets with a diameter of 1 cm and a thickness of 0.07–0.2 cm. Ag-electrodes fired in air at 1070 K were used.

Current–voltage dependences in air and in a flux of dry argon were studied at room temperature, utilizing a Keithley-2400 unit. Voltage was increased consecutively by steps ΔU=0.2 V with the duration of each step Δt = 3.0 s. Current was measured at the beginning and at the end of each step as time dependence of current in In_2O_3-SrO ceramics at fixed voltage was observed [8]: current at low voltages increases with time, and at high voltages it decreases with time for about 5–10 min. After this period, current is practically unchangeable.

Before recording I(U) dependences, the sample was heat treated in a flux of dry argon at 1070 K and then was cooled to room temperature in Ar. After this, the sample was stored in a flux of argon at room temperature for two hours before recording I(U) characteristic in Ar. Then the sample was placed in air and stored there for 2 hours before registration of I(U) dependence in air. After that, the sample again was placed in the flow of dry argon and stored there for 2 hours before recording I(U) characteristic in Ar.

For measurements in air with different relative humidity (10% and 50%) the sample was placed in a closed chamber above the surface of the saturated water solution of proper salt. Before these measurements the sample was stored for 48 hours in the atmosphere with the humidity of 50%. The measurements of electrical current were performed at a fixed voltage of 1V.

Pore size distribution in In_2O_3-SrO ceramics was defined using Porosimeter 4000, Carlo Erba Strumentazione, and software MILES 200. To fill macro- and mesopores ($>$ 50 nm) by Hg, the porosimeter PASCAL 140 was used. After measuring with porosimeter PASCAL 140, the Hg-dilatometer with the sample was placed into Porosimeter 4000 working at a wide range of pressure (from atmospheric to 4000 bar). Pore size distribution was studied in the region from 2 nm to 900 nm.

3. Results and Discussion

To find out a role of oxidizing atmosphere in I-U behavior in In_2O_3-SrO ceramics, current-voltage dependences in different gaseous environments were studied. Figure 1 shows curves which were recorded in argon (curves 1,2), then in air (curves 3,4), and again in argon (curves 5,6). Obtained data show that the sublinear region ($\alpha < 1$) of current-voltage dependence is observed only in air (curves 3,4 in Fig.1). The I(U) dependences in argon before and after measurement in air do not contain the sublinear region and they are practically linear (curves 1,2 and 5,6 in Fig. 1). These results show that the presence of sufficient oxygen in gaseous environments is a necessary condition for the appearance of the sublinear I-U behavior in In_2O_3-SrO ceramics.

Discussed nonlinearity of I-U curve is observed in air at both polarities of voltage [7] in the samples with different electrodes [4,6-9]. The sublinear region of I-U curve is observed at the steady state and at the nonsteady state [8]. At the non-steady state the fixed voltage is applied for a short time and current is still varied with time. At the steady state the fixed voltage is applied for a long time and current is not varied with time. Thus, the sublinear region of I-U curve is observed to be independent of the duration of voltage step.

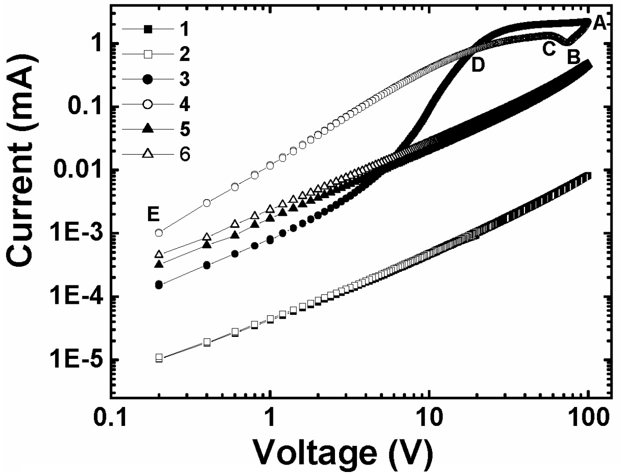

FIGURE 1. Current versus voltage for In_2O_3-SrO sample recorded in argon (curves 1,2), air (curves 3,4), and again in argon (curves 5, 6). Data were obtained at increase (1, 3, 5) and decrease (2, 4, 6) of voltage.

The current-voltage dependence in In_2O_3-SrO ceramics can be explained in terms of a modified barrier model [6]. In this model grain-boundary states which are occupied by electron (filled grain-boundary states) are associated with adsorbed oxygen in charged form. Grain-boundary states which are not occupied by electron (empty grain-boundary states) are associated with adsorbed oxygen in neutral form. The density of empty and filled grain-boundary states is assumed to be equal to the density of adsorbed oxygen in neutral and charged forms, respectively. The capture of electrons at the grain-boundary states leads to the transition of adsorbed oxygen from neutral to charged form. The adsorption equilibrium at the grain surface is maintained at the expense of adsorption and desorption oxygen only in the neutral form [6]. Therefore, if the amount of adsorbed oxygen in neutral form is decreased (as a result of capture of electrons at the grain-boundary states), the adsorption-desorption equilibrium at the grain boundary is broken and additional oxygen adsorption starts.

In the equilibrium state at GB (when voltage bias is zero), the capture of electrons at the grain-boundary states is balanced by their emission and the barrier height is not changed. However, under applied voltage the barrier height is decreased and the capture of electrons at the grain-boundary states is increased. This results in the transition of adsorbed oxygen from neutral to charged form, and the adsorption-desorption equilibrium at the grain boundary is broken. Additional oxygen adsorption appears and leads to a rise in the number of empty states at GB. Therefore, under applied voltage the capture of electrons dominates over their emission until adsorption equilibrium is reached. Thus, the barrier height is increased and as a result of this, the sublinear I-U behavior takes place (Fig. 1, curve 3).

The current-voltage characteristics in argon are sufficiently reproduced at increase and decrease of voltage (Fig. 1, curves 1,2 and 5,6). However the I(U) dependence in air exhibits hysteresis: curves recorded at increase and decrease of voltage do not coincide and intersect (Fig. 1, curves 3, 4). This hysteresis can be also explained in terms of the proposed model [6]. When the voltage just starts to decrease (point A on curve 4 in Fig. 1), the adsorption-desorption equilibrium at GB is not yet reached [6]. There is some deficit of adsorbed oxygen in the neutral form at the grain boundaries. Therefore, in spite of the voltage decrease, the additional oxygen adsorption continues for some time yet and it supports the capture of electrons at the grain-boundary states. Respectively the barrier height and resistance are increased (the region from point A to point B on curve 4 in Fig. 1). However, voltage decrease leads to a lowering of the electron capture and the emission starts to dominate [13]. The emission of

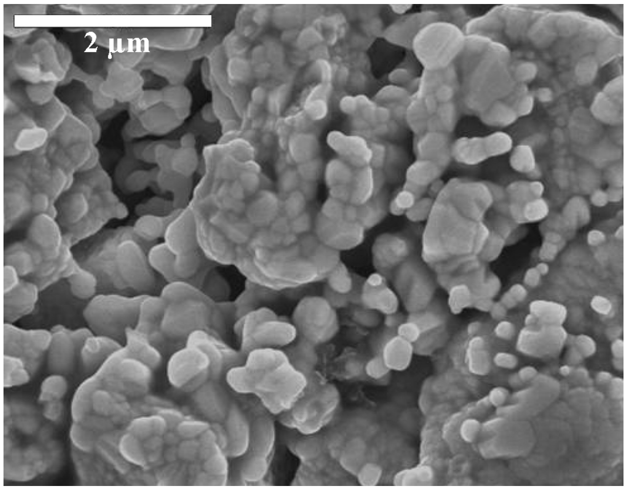

FIGURE 2. SEM micrographs of the surface of In_2O_3-SrO ceramics.

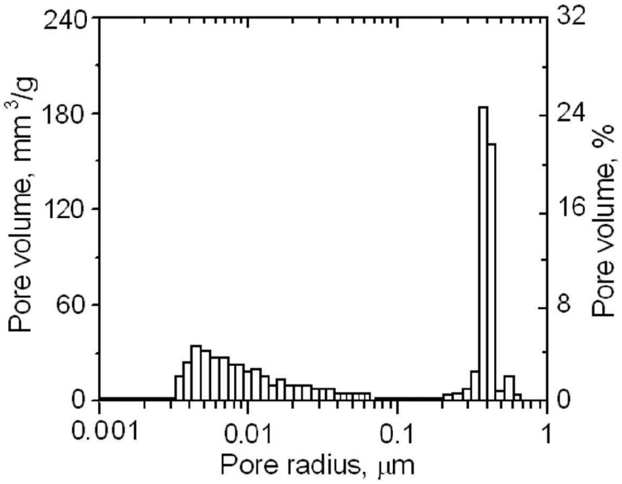

FIGURE 3. Pore size distribution in In_2O_3-SrO ceramics.

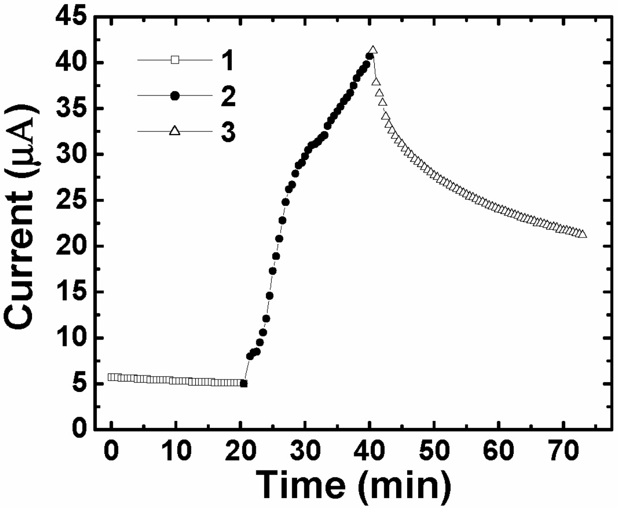

FIGURE 4. Time dependence of current (at 1 V) for In_2O_3-SrO sample in air with relative humidity 10% (curves 1, 3) and 50% (curve 2).

electrons accumulated on GB leads to the current being slightly increased at the decrease in voltage (the region BC on curve 4 in Fig. 1). This emission of electrons can explain the fact that the current in the region DE (on curve 4 in Fig. 1) is higher at voltage decrease than at the increase of voltage (curve 3, Fig. 1).

The mentioned adsorption processes at GB in the bulk of a sample are possible only if the material has a developed structure of open pores. It is known that open porosity can determinate the humidity sensitivity of ceramics [14]. To verify whether studied material exhibits open pores, the porosity in In_2O_3–SrO ceramics was examined using scanning electronic microscopy (Fig. 2) and the Hg-porosimetry (Fig. 3).

SEM micrographs of the surface show the high porosity in In_2O_3-SrO ceramics (Fig. 2). It was found that this material exhibits bimodal distribution of pores composed of open meso- and macropores (Fig. 3). The mesopores as sociated with the first peak in pore-size distribution in the range of 0.003-0.1μm (Fig. 3) are responsible for capillary condensation of moisture (as in humidity-sensitive $MgAl_2O_4$ ceramics [15]). The macropores related to the second peak (0.2-0.7 μm) are favorable for moisture absorption from environment into the bulk of ceramics [15]. It was shown that the ramified porous structure of ceramics with transport pores (open macro- and mesopores from nm to hundreds nm) is the necessary condition for effective development of humidity-sorption processes [15]. Such pores are necessary to pass humidity from outside to fine inner mesopores. However, in In_2O_3-SrO ceramics such transport pores in the range of 0.1-0.2 μm are not registered (Fig. 3). The bimodal pore distribution observed in In_2O_3-SrO ceramics suggests rather weak humidity sensitivity in this material.

To verify this supposition, the sensitivity of In_2O_3-SrO ceramics to variations in the relative humidity of air was studied (Fig. 4). It was found that the resistance is decreased with time if the ceramic sample was placed in air with higher humidity. Observed changes in the resistance of In_2O_3-SrO ceramics are less than one decade (Fig. 4). This indicates that In_2O_3-SrO ceramics exhibit rather weak sensitivity to humidity. This is in accordance to the results of Hg-porosimetry (Fig. 3). The observed decrease in resistance of In_2O_3-SrO ceramics in humid air can be explained by the lowering of the barrier height at GB [16]. Probably this lowering of the barriers in humid air can be expressed more strongly in the outer part of a sample than in the central part as it was observed in SnO_2 varistor ceramics in humid air [16]. Also some contribution of surface leakage in humid air cannot be excluded completely for In_2O_3-SrO ceramics.

It is reasonable to suppose that water adsorption can be responsible for the change of resistance at low voltage after the change of gaseous environment (Fig. 1, curves 1-6). The resistance decreases after the change from dry argon to air (Fig. 1, curves 2 and 3). But the resistance is increased if air is substituted by argon (Fig. 1, curves 4 and 5). In the last case, the change of resistance is weaker because the adsorbed water cannot get out from a sample quickly at room temperature.

4. Conclusion

It was shown that for the appearance of sublinear I-U behavior in In_2O_3-SrO ceramics it is necessary to have enough oxygen in a gaseous environment. Nonlinear current-voltage dependence can be explained taking into account a relationship between electronic and adsorption processes at the grain boundary under applied voltage. The high porosity of In_2O_3-SrO ceramics is favorable for adsorption processes of oxygen at the grain surfaces in the bulk of ceramic sample. However, only low sensitivity of electrical resistance to the variation in relative humidity is registered. This fact can be due to the absence of open pores with sizes of 0.1-0.2 μm which are optimal for the transport of moisture from the surface to the bulk of a sample.

Acknowledgments

The electrical measurements were conducted with the support of the National Science and Technology Council of Mexico (CONACYT) under the project “Convocatoria Ciencia Básica 2010”.

---

1. H. L. Hartnagel, A. K. J. Dawar, and C. Jagadish, *Semiconducting Transparent Thin Films* (Institute of Physics, Bristol, 1995) p.358.
2. K. Arshak and K. Twomey, *Sensors* **2** (2002) 205.
3. G. Korotcenkov *et al.*, *Sensors and Actuators B* **103** (2004) 13.
4. A. Glot, G. Behr, and J. Werner, *Key Eng. Mater.* **206–213** (2002) 1441.
5. D.R. Clarke, *J. Am. Ceram. Soc.* **82** (1999) 485.
6. A. Bondarchuk, A. Glot, G. Behr, and J. Werner, *Eur. Phys. J.: Appl. Phys.* **39** (2007) 211.
7. A. Bondarchuk, A. Glot, G. Behr, and J. Werner, *Journal of Physical Studies* **7** (2003) 313.
8. A.B. Glot, A.N. Bondarchuk, and S.V. Mazurik, *Photoelectronics* **9** (2000) 110.
9. A.B. Glot, S.V. Mazurik, B.J. Jones, A.N. Bondarchuk, R. Bulpett, and N. Verma, *Journal of the European Ceramic Society* **30** (2010) 539.
10. T.R.N. Kutty and V. Ravi, *Mater. Sci. Eng. B* **25** (1994) 119.
11. J. Chen, J.Y. Chen, and J.Y.M. Lee, *Appl. Phys. Lett.* **69** (1996) 4011.
12. E.R. Leite, E.J. Lee, C. Ribeiro, and E. Longo, *J. Am. Ceram. Soc.* **89** (2006) 2016.
13. A. Bondarchuk, *CURRENT LIMITING IN OXIDE CERAMIC STRUCTURES In: Applied Physics in the 21st Century* (Horizons in World Physics, Volume 266, 2009); Ed.: Raymond P. Valencia, (Nova Science Publishers, Inc., New York, ISBN: 978-1-60876-074-9).
14. E. Traversa, *Sensors and Actuators* **23** (1995) 135.
15. I.B. Vynnyk, I.V. Hadzaman, H.I. Klym, O.Ya. Mrooz, and O.I. Shpotyuk, *Technology and Design in Electronics* (in Rus.) **2** (2006) 60.
16. A.V. Gaponov, A.B. Glot, A.I. Ivon, A.M. Chack, and G. Jimenez-Santana, *Mater. Sci. Eng. B* **145** (2007) 76.