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THE ELECTRICAL CHARACTERISTICS OF NANOSCALE SnO2 FILMS, STRUCTURED BY POLYMERS

The electrical characteristics of nanoscale tin dioxide layer were studied. They showed the significant differences in the conductivity values of films in vacuum and in air, which indicates a visible influence of adsorption interaction with oxygen in the air. The dark current temperature dependence activation character was established due to different donors type centers contribution to the conductivity which are “shallow” at low temperatures and are more "deep" at high temperatures. The values of the energy depth of these levels were calculated. The films’ conductivity changes at their heating at vacuum and at the subsequent cooling at vacuum till the initial temperature are reversible and repeatable many times, which testifies the stability of the electrical characteristics of the SnO2 films and is perspective for use of the layers as adsorptive-sensitive elements of gas sensors.

1. Introduction

A good combination of physical properties of tin dioxide (conductivity, its sensitivity to the external environment changes and electromagnetic radiation), stability of characteristics and low-cost production makes it to be one of the most popular and promising material for sensor [1, 2].

Tin dioxide plays its important role as a material for solid-state gas sensors whose operation is based on changing the conductivity of a sensitive layer at gas adsorption. Various kinds of nanostructured SnO_2 exhibit better properties compared to their bulk types both for gas analysis and for a wide range of other applications. Chemical and electrical properties of tin dioxide in nanocrystalline state depend strongly on particles’ size [1, 2]. The grain size decreasing influences both the defects role in surface layers on electronic processes in them and increases the contribution of grain boundaries to the transport processes of charge carriers.

Tin dioxide is a degenerative semiconductor with electronic conductivity due to a wide range of donor levels in the bandgap with activation energies of 0,21, 0,33, 0,52, 0,6, 0,72 eV [3, 4]. The SnO_2 film samples have donor levels which are typically shallow. Their activation energies are in thin interval of 0,15 eV and they decrease with the increase in charge carriers quantity.

Semiconductor metal oxides’ conductivity exists due to their composition deviation from stoichiometry. Defects (anion and cation) vacancies also play an important role in their conductivity. In the oxide semiconductor films deviations from stoichiometry, and hence the electrical properties, change reversible at their interaction with the gas environment. Their conductivity significantly depends on the structure of the layers, grain size and barrier effects on the grain boundaries, adsorption processes on surfaces, effect of temperature and external electric field. All these factors must be taken into account at the analysis of experimental results.

Since the main physical parameters (grain size, considerable surface area, the grains’ structure features etc.) are determined by technological peculiarities, then electrophysical properties also depend on technological factors. [5]

The present work is devoted to the investigation of current-voltage characteristics (I-V) and the dark current temperature dependences (DCTD) of nanoscale SnO_2, structured by poly-

mers, aiming the study their electrical conductivity mechanisms and the influence of adsorption processes on their electrical properties.

2. Sample preparation and experimental techniques

Nanostructured tin dioxide thin films were obtained using polymer materials by the sol-gel method [6]. Bis(acetylacetonato)dichlorotin (BADCT) was used as a tin dioxide precursor [7]. The polyvinyl acetate (PVA) was used as a polymer material for structured of nanofilms.

Experimental technique for SnO_2 nanofilms' electro-physical characteristics measurements was based on a standard method of current-voltage and current-temperature dependence registration.

The SnO_2 films were supplied with contacts of Indium thermally deposited in a high vacuum on the surface of the films shaped as two parallel strips. The distance between the electrodes was 2 mm.

3. Results and discussion

Fig. 1 shows current-voltage characteristics of SnO_2 films with different content of the precursor, measured on air at room temperature. They were independent on the polarity of the applied voltage and linear, which indicates the Ohmic type of indium contacts conductivity and negligible barrier effects influence.

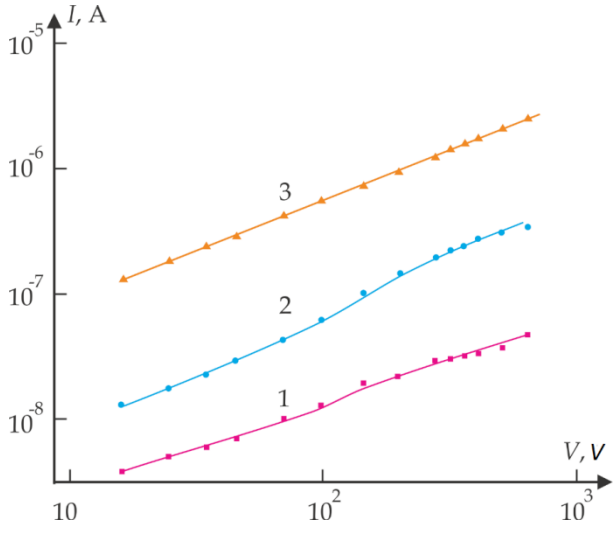

Fig. 1. I-V characteristics of SnO_2 with the content of precursor 1% (1), 5% (2) and 10% (3), measured in air (T = 290 K).

It may be seen the correlation between the precursor's concentration increasing in the initial solution and the films' resistance reduction. This may be connected with precursor's concentration increasing which resulted in the film's thickness growth, with the subsequent growth of charge carriers concentration and number of defects which contribute to the film conductivity increase too. Besides that, it is known that carrier mobility increases with film thickness increasing what also influences the conductivity.

Current–voltage characteristics of one of the samples measured in air (curve 1), and then in vacuum (curve 2) are shown in Fig.2. As it can be seen, the electrical conductivity of the films in vacuum increases significantly. The latter supposes that the value of the electrical conductivity of the investigated films greatly affect the processes of adsorption (desorption) of oxygen on their surface [8].

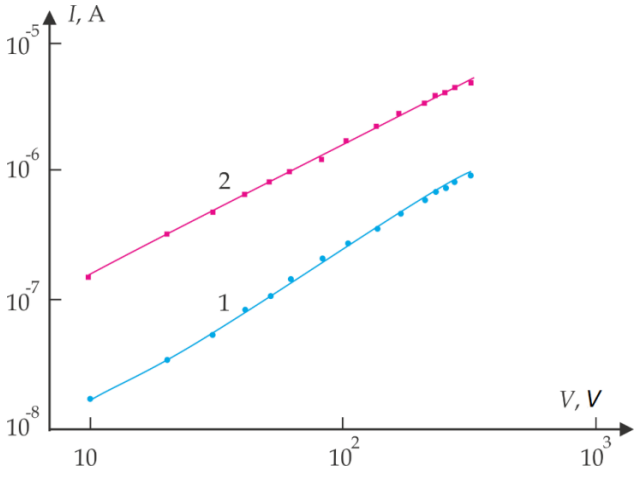

Fig. 2. I-V characteristics of sample with precursor content of 5% in air (1) and in vacuum (2). (T = 290 K).

The oxygen influence on the conductivity of the films is also confirmed by the results presented in Fig.3. Curve 1 (Fig.3) depicts the current–voltage characteristic of one of SnO_2 films measured in air at 290 K. Then, air was evacuated from the measuring chamber (to a pressure of about 10^{-3} mm Hg). The film was heated in vacuum to a temperature of 410 K and then again cooled to a room temperature. After that measuring of I-V curves (at 290 K) in vacuum was repeated (Fig. 3, curve

2). The significant increase in conductivity of the film (more than two orders of magnitude) is associated with desorption of oxygen and the formation of oxygen vacancies acting as donors [8] on the films' surfaces.

Curve 3 (Fig.3) was measured in 15 min after the atmospheric air was let into the chamber. It may be noticed a decrease in the electrical conductivity of the film due to atmospheric oxygen adsorption.

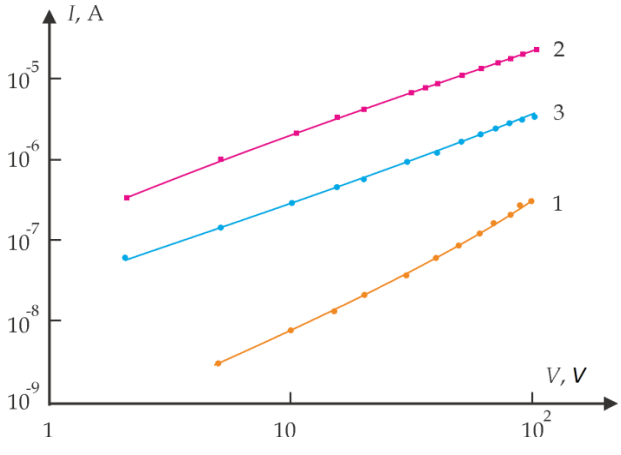

Fig. 3. I-V curves of the SnO_2 film with the precursor content of 10%(T = 290 K) (commentary in the text).

The decreasing current relaxation (Fig. 4) was observed in the process of air inlet into the chamber.

Straightening of the initial section of the current-time dependence in the coordinates $ln I \div t$ shows that in the initial time interval (0 to 30 seconds), the current decreases with time according to exponential law $I \sim exp\left(-\frac{t}{\tau}\right) I \sim exp\left(-\frac{t}{\tau}\right)$. Calculated from the graph the value for the relaxation time constant, τ was approximately 18 seconds. In later periods the rate of relaxation decreases monotonously. Thus, the processes of oxygen adsorption on the film surface at room temperature are characterized by definite inertia.

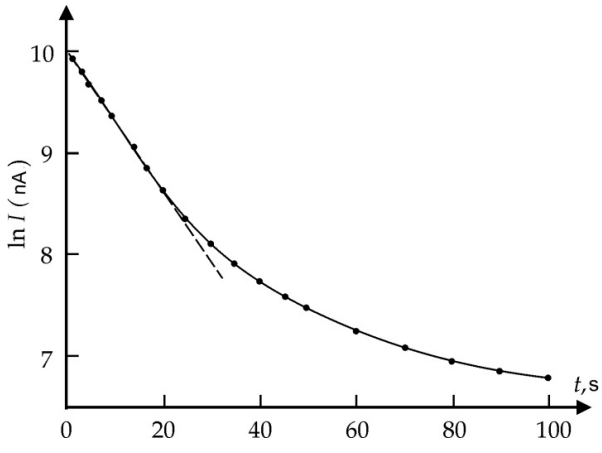

Fig. 4. Relaxation of current in the sample at letting air in the measurement chamber (V = 60 V).

The decreasing relaxation of current is associated with interaction of the film surface with oxygen at the inlet of atmospheric air. The initial section of the graph is associated both with a relatively rapid filling of the surface centers by oxygen ions, thus capturing electrons of conductivity and the disappearance of oxygen vacancies. In the future, the process of current relaxation slows down, because the near-surface layers of adsorbed oxygen limit the access to the surface for air oxygen.

The temperature dependences of dark current were fulfilled for the studied SnO_2 films. The results of these calculations for films with content of the precursor 1%, 5% and 10% are presented in Fig.5.

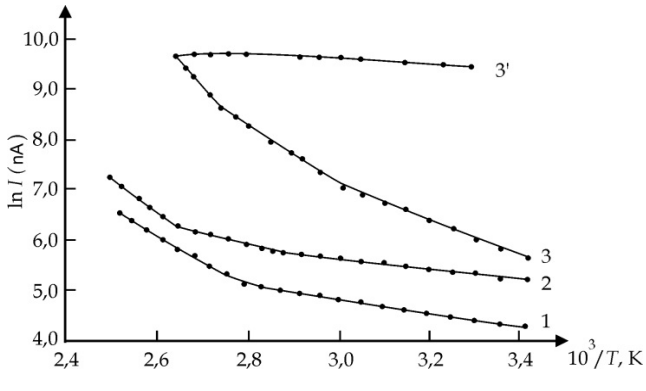

Fig. 5. The temperature dependence of dark current measured at U = 60 V for SnO_2 with the content of the precursor 1% (1), 5% (2) and 10% (3). Curve (3) measured at the sample cooling (U = 80 V).

The DCTD curves have the activation character at heating. The conductivity is contributed by different types of donor centers, "shallow" at low temperatures and "deeper" at high temperatures.

Depth values of the energy levels calculated from the slopes of the straight sections DCTD curves for different series of specimens are shown in the table.

Table

The content of precursor (%)	1	5	10
The ionization energy of donors (eV)	0,19 0.27	0,13 0,21 0,34	0,23 0,31 0,53

Obtained energies' values of 0.19 eV and 0.13 eV are close to literature value of donor level at 0.15 eV associated with double ionized oxygen vacancies formation [9]. The nature of donor centers, associated with other energy values in the table, remains unclear.

A large set of obtained values of the activation energy can be related to the fact that in the test films due to their nano structure the energy of known levels may change, for example, for those, which corresponds to oxygen vacancies. The additional levels associated with peculiarities of the films production and their storage may appear. There may be levels due to the presence in the films of tin monoxide SnO, etc.

Curve 3' (Fig.6) depicts DCTD of the samples measured at cooling. As can be seen, the current decreases at cooling enough slowly.

The conductivity of the film after its cooling to room temperature remains much higher than prior to the procedure of heating the film. This may be due to discharging of donor oxygen levels at high temperatures when the surface curve of energy bands decreases (the thickness of the surface potential barrier decreases correspondingly), thus resulting in the films conductivity increasing. It worth to note, that the above described features of DCTD behavior, measured at cooling, were observed for all series of the samples.

The process influencing the conductivity magnitude changes of the films by heating and subsequent cooling at vacuum till initial temperature is reversible and repeatable many times. For example, if at the end of the measurement the curve 3' (Fig. 6) the measuring chamber is filled with air, then after a certain period of time the current is reduced to levels (at the same temperature) corresponding the curve 3 (Fig.6).

The latter supposes that the electrical characteristics of the SnO_2 films is quite stable, which allows using them as adsorptive-sensitive elements for gas sensors.

4. Conclusions

The studies of electrical properties of nanolayers of tin dioxide revealed the following features:

The conductivity of the investigated films in vacuum and in air differs more than an order of magnitude, which indicates the considerable influence of adsorption interaction with oxygen in air.

Curves DCTD taken at heating the samples are of activation type due to different types of donor centers contribution to conductivity. Obtained values of the energies of 0.19 eV and 0.13 eV are close to the known from literature value of the ionization energy of the donor level at 0.15 eV associated with the formation of double ionized oxygen vacancies.

The change in conductivity of the films during heating and subsequent cooling at vacuum till the initial temperature is reversible and repeatable many times, which shows the stability of the electrical characteristics of the SnO_2 films and allows using them as adsorptive-sensitive elements for gas sensors.

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Abstract

The electrical characteristics of nanoscale tin dioxide layer were studied. They showed the significant differences in the conductivity values of films in vacuum and in air, which indicates a visible influence of adsorption interaction with oxygen in the air. The dark current temperature dependence activation character was established due to different donors type centers contribution to the conductivity which are “shallow” at low temperatures and are more “deep” at high temperatures. The values of the energy depth of these levels were calculated. The films’ conductivity changes at their heating at vacuum and at the subsequent cooling at vacuum till the initial temperature are reversible and repeatable many times, which testifies the stability of the electrical characteristics of the SnO_2 films and is perspective for use of the layers as adsorptive-sensitive elements of gas sensors**.**

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ЕЛЕКТРИЧНІ ХАРАКТЕРИСТИКИ НАНОРОЗМІРНИХ ПЛІВОК SNO_2, СТРУКТУРОВАНИХ З ВИКОРИСТАННЯМ ПОЛІМЕРІВ

Резюме

Проведені в роботі дослідження електричних характеристик нанорозмірних шарів діоксиду олова дозволили виявити істотні відмінності в значеннях провідності плівок у вакуумі й на повітрі, що свідчить про помітний вплив адсорбційної взаємодії з киснем повітря. Встановлено активаційний характер кривих ТЗТТ зразків, що обумовлено внеском у провідність різних типів донорних центрів - більше «дрібних» при низьких температурах і більше «глибоких» при високих температурах. Розраховано значення глибини залягання цих енергетичних рівнів. Зміна величини провідності плівок при прогріві у вакуумі й наступному охолодженні у вакуумі до вихідної температури є оборотним і багаторазово відтворюваним, що свідчить про стабільність електричних характеристик досліджуваних плівок SnO_2 і перспективно для використання шарів в якості адсорбційно-чутливих елементів газових сенсорів.

Ключові слова: діоксид олова, нанорозмірні шари, електричні характеристики

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Л. Н. Филевская, А. П. Чебаненко, В. С. Гриневич, Н. С. Симанович

ЭЛЕКТРИЧЕСКИЕ ХАРАКТЕРИСТИКИ НАНОРАЗМЕРНЫХ ПЛЕНОК SNO_2, СТРУКТУРИРОВАННЫХ С ИСПОЛЬЗОВАНИЕМ ПОЛИМЕРОВ

Резюме

Проведенные в работе исследования электрических характеристик наноразмерных слоев диоксида олова позволили выявить существенные отличия в значениях проводимости пленок в вакууме и на воздухе, что свидетельствует о заметном влиянии адсорбционного взаимодействия с кислородом воздуха. Установлен активационный характер кривых ТЗТТ образцов, что обусловлено вкладом в проводимость различных типов донорных центров – более «мелких» при низких температурах и более «глубоких» при высоких температурах. Рассчитаны значения глубины залегания этих энергетических уровней. Изменение величины проводимости пленок при прогреве в вакууме и последующем охлаждении в вакууме до исходной температуры является обратимым и многократно воспроизводимым, что свидетельствует о стабильности электрических характеристик исследуемых пленок SnO_2 и перспективно для использования слоев в качестве адсорбционно-чувствительных элементов газовых сенсоров.

Ключевые слова: диоксид олова, наноразмерные слои, электрические характеристики