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THE AMMONIA VAPORS INFLUENCE ON THE ELECTRICAL CHARACTERISTICS OF NANOSIZED TIN DIOXIDE FILMS OBTAINED USING A POLYMER

In the presented paper the effect of ammonia vapors on the electrical properties of nanosized tin dioxide films obtained using polymers was investigated to assess the possibility of their use as an ammonia sensor's sensitive element at room temperature. Ammonia vapor leads to a decrease in the conductivity of the studied SnO_2 films. This is due to the fact that the adsorbed ammonia molecules increase the height of the intergranular potential barriers, and the surface shut-off bend of the energy bands. The main role in this is played by the processes of physical adsorption of ammonia molecules. The sensitivity of the films to ammonia vapor is in the range of 0.35-0.63 and reaches a maximum at a voltage of 300 V. The processes of adsorption and desorption take place in two stages and are reversible, as evidenced by the calculated time constants of adsorption and desorption.

Introduction

Among gas-sensitive materials, tin dioxide occupies a leading position due to its physico-chemical properties [1,2]. The main of these properties is stability in active chemical media and the ability to change their physical parameters, in particular, conductivity and optical properties, depending on the composition of the environment [3]. Such properties make it possible to use tin dioxide for other purposes, such as transparent electrodes, catalysts of chemical reactions, and the like. [4.5]. The need in just such materials is due to the needs in environmental monitoring in all potentially dangerous cases: in chemical, food, medical industries, energy enterprises, heavy industry, agriculture, everyday life, etc. [6]. Like many other chemicals harmful to health and the environment, ammonia is tightly controlled [7]. Ammonia sensors are created using various technological methods based on many materials [8-10], among them nanomaterials and nanocomposites occupy the main place [11, 12]. The main sensitive parameter for monitoring ammonia vapors is an electrical conductivity (or electrical resistance), which changes in response to environmental changes [13]. The reason for such change is the surface reactions of the detected molecules or ions with physically or, most often, chemically adsorbed oxygen molecules (ions) [14]. This leads to a change in the concentration of electrons in the conduction band of the sensitive material. Typically, such reactions of chemical adsorption with the separation of oxygen atoms into ions associated with a surface, takes place at an elevated temperature. As a rule, sensors to monitor any composition are kept for several hours or even days switched on at an operating temperature (from 160 to 350 C). The use of nanomaterials leads to a reduction in such forming time and to a decrease in the operating temperature of the sensor.

In the presented work the effect of ammonia vapors on the electrical properties of nanosized tin dioxide films obtained using polymers was investigated to assess the possibility of their use as an ammonia sensor's sensitive element at room temperature.

Samples and research methods

Samples of tin dioxide films were obtained by the sol-gel method using polymers for nanoscale structuring of the film. The prepared solutions of bis(acetylacetonato)-dichlorotin(IV) and polyvinyl acetate in acetone were mixed and applied to glass substrates. Sample blanks dried in a drying oven were annealed in a muffle furnace with a gradual temperature increase and holding them for an hour at a temperature of 500 °C, and gradual subsequent cooling to room temperature. The resulting films are smooth, transparent, and the presence of a nanoscale structure is confirmed by AFM studies.

At a research procedure by standard methods, current-voltage characteristics, temperature dependences of dark current, kinetic dependences of current were measured. All characteristics were measured in dry air and in air with ammonia vapor.

Results and discussion

Fig. 1 shows the current-voltage characteristics (CVC) of a tin dioxide film measured in an atmosphere of dry air and ammonia vapor at room temperature.

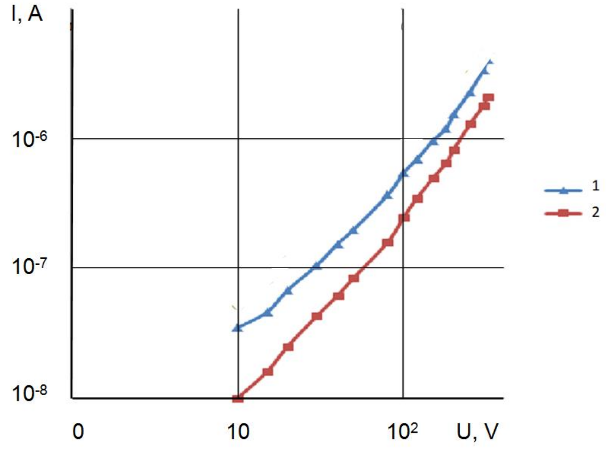

Fig. 1. Current-voltage characteristics of the SnO_2 film, measured in dry air (1), and in ammonia vapor (2), T = 292K.

It may be noted that the I - V characteristic measured in a dry air atmosphere (curve 1, Fig. 1) is superlinear and has a weak tendency to exponential current-voltage dependence. This dependence is typical for the barrier mechanisms of current flow. The latter suggests that, in the studied SnO_2 films, intercrystalline potential barriers are definitely present and noticeably affect the current flow.

In ammonia vapor, the resistance of the film is greater compared with the resistance in air; the superlinearity of its I–V characteristic also increases (Fig. 1, curve 2). It may be concluded, that the adsorption of ammonia molecules contributes to an increase of intercrystalline potential barriers heights and to an increase in the surface shut-off of energy bands bending. This usually occurs due to the interaction with chemisorbed oxygen ions on the surface of tin dioxide [15]. At the same time the chemisorption of oxygen on tin dioxide begins at a temperature of about 160-200 °C [14]. The nanosize of particles promotes reducing the temperature of chemisorption, so, that some of the oxygen can be chemisorbed at room temperature. As it is shown in [16], these can be only O^{2-} ions. The chemical reaction between oxygen adsorbed on the surface of a tin dioxide film and ammonia is possible if the temperature rises to 800 °C [17]. Tin dioxide is a catalyst for such reactions, it helps to lower the reaction temperature, but not to room temperature. In addition, the result of such a reaction should be a decrease in the resistance of the film and an increase in its conductivity. We have the opposite result - a decrease in the conductivity of the film when ammonia is injected. This fact indicates that the process of conductivity changing (decreasing) in our case has a different mechanism. The ammonia decomposition in VITRO is possible at an even higher temperature (1200-1300 °C), but in a catalyst presence - at 600 °C, although the process begins at 300 °C. But even during this process, which is similar to the dissociation of water molecules on the surface of the film, the conductivity should increase.

A number of chemical reactions on the surface of a tin dioxide film with a decrease of conductivity are described in [18]. However, as shown below, when calculating the adsorption and desorption constants, the processes occurring on the surface take place in two stages and are reversible. The reactions presented in [18], have the only one of reversible type.

To explain the resulting decrease in conductivity upon tin dioxide film contact with ammonia, it is advisable to consider the processes of physical adsorption of oxygen and ammonia, as well as the creation of ammonia complexes with surface atoms of tin or its oxides using Van-der-Waals interaction. These processes can take place at room temperature. There is no exchange of carriers (charges) between the adsorbate and the adsorbent at physical adsorption. However, the current flow may be influenced by the barriers growth due to physical adsorption and, as a consequence, to a decrease in the carrier's mobility in the near-surface region, which also leads to a decrease in conductivity.

In Fig. 2 shows the temperature dependences of the dark current in the SnO2 film measured in dry air and in ammonia vapor at a constant voltage of U = 150 V.

It can be noted that both during heating and during cooling in ammonia vapor and in air, the current changes with temperature according to an exponential law. Conductivity has an activation character, and the conduction activation energy is approximately the same in all areas, regardless of the medium and temperature and is (0.39 - 0.46 eV).

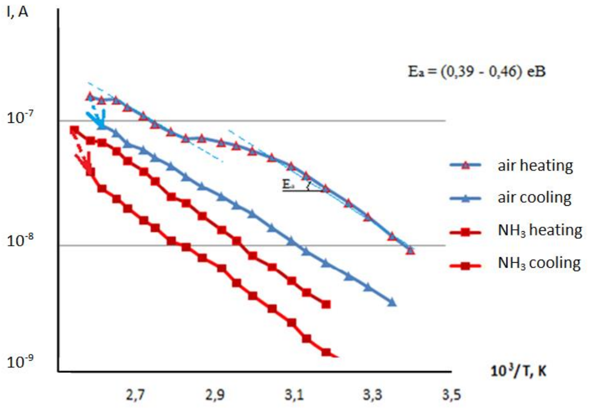

Fig. 2. Temperature dependences of the dark current measured in dry air and in ammonia vapor. (U = 150 V)

The obtained values of the activation energy can be explained on the basis of the model of an inhomogeneous semiconductor with large-scale potential fluctuations. In such a semiconductor, under the action of charged impurities potential (first of all, those adsorbed at intercrystalline boundaries), the energy bands are curved with the formation of a random potential relief [19]. The electrons' motion in a curved zone is possible if their energy exceeds a certain critical value E_{cr}, which is called the level of flow for electrons. The energy position of the percolation level is defined by the nature of the potential relief. An electron, which energy exceeds the level of percolation, can pass over the maximums of the potential relief or bypass them [20]. Therefore, the activation energy E_a = (0.39 - 0.46) eV determined from the temperature dependence is the activation energy of electrons from the Fermi level to the percolation level.

Study of nanostructured SnO_2 films' sensitivity to ammonia

In order to clarify the sensitivity of nanostructured films to ammonia vapors, the film was placed in a chamber where ammonia vapors and dry air were periodically admitted. The admission time of ammonia vapor or dry air was 90 seconds. The relaxation curve of the current flow in this case is shown in Fig. 3.

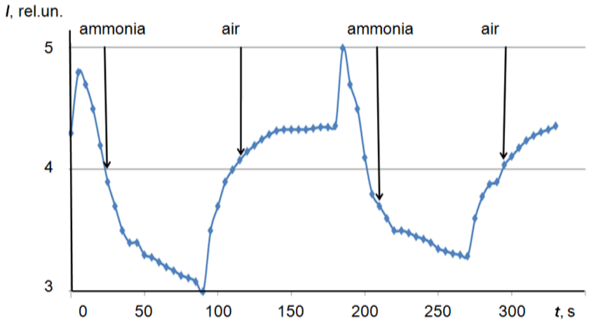

Fig. 3. Kinetics of the current changes in the film with periodic letting of ammonia vapors and dry air into the chamber (V = 300V).

It can be seen from Fig. 3 that when ammonia vapor is let into the chamber, the current rapidly decreases in about 30 s. For another 60 s., the current continues to decrease, but more slowly. Thus, adsorption of ammonia molecules on the surface of SnO_2 films leads to its electrical conductivity decrease. When the chamber is blown off by dry air, the conductivity of the SnO_2 film is restored to its original values. The shape of the current relaxation curve also indicates that the process of adsorption of ammonia is more inertial than the process of their desorption from the surface of the SnO_2 film. In addition, adsorption occurs in two stages: the first is fast (up to 30 s) and the second, which is much slower.

The current relaxation was measured in the range of applied voltages from 150 V to 320 V. For each voltage, the sensitivity S of the film to ammonia vapor was calculated using the formula:

$$S = \frac{I_0 - I}{I_0} \qquad (1)$$

where is I_0 - the current in the film in dry air; I is the current in the film in an atmosphere of ammonia vapor.

The calculation results are presented in Table 3.

Table 3.
Dependence of the SnO_2 film sensitivity on the applied voltage

***V*, Volt**	**150**	**200**	**250**	**300**	**320**
S, rel.un.	0,34	0,39	0,55	0,63	0,57

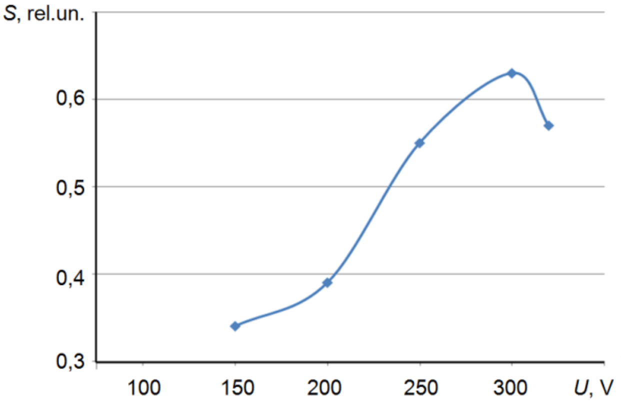

Fig. 4. The ammonia vapor sensitivity-voltage dependence of the SnO_2 film.

The dependence of the sensitivity of the SnO_2 film on the applied voltage is shown in Fig. 4; it can be seen that the sensitivity increases with an increase in the applied voltage and reaches a maximum value of 0.63 relative units at a voltage of 300 V.

The shape of the current relaxation curves (Fig. 3) suggests that the rise and fall of the current value with time occurs according to an exponential law. In particular, the current's decay (ammonia adsorption):

$$\mathbf{I = I_0 e^{-\frac{t}{\tau_a}}}. \qquad (2)$$

Current's rise (ammonia desorption):

$$\mathbf{I = I_0 \left(1 - e^{t/\tau_d}\right)}. \qquad (3)$$

Here τ_a and τ_d are some constants characterizing the inertia of adsorption and desorption processes.

To confirm these assumptions, the current decay and rise curves were plotted in the relevant coordinates:

$$ln\left(\frac{I_0}{I}\right) \div t \quad \text{and} \quad ln\left(\frac{1}{1 - I/I_0}\right) \div t$$

(Fig. 5 and Fig. 6). Their satisfactory straightening in the above coordinates made it possible to calculate the time constants of adsorption and desorption. As can be seen from the given dependences, the processes of adsorption and desorption have two parts: a relatively fast adsorption with a time constant of 13.4 s and a relatively slow one with a time constant of 21.8 s. The values of desorption time constants are also close to these values. They are: 19.5 s for slow desorption and 13.2 s for fast desorption. The presence of two sections in the given dependences may indicate that the adsorption and desorption of ammonia occur in two stages. For adsorption, the first step is a fast one, but for desorption it is a slow step.

The processes of physical adsorption of both oxygen and ammonia in condition of the established dynamic equilibrium can proceed in parallel. That is, ammonia molecules are physically adsorbed on the film surface centers which are free at the moment of adsorption. Moreover, the presence of two time constants for adsorption and desorption also indicates a two-stage mechanism of this process. Usually, ammonia molecules easily join to metal atoms due to the unbalanced charge of the nitrogen atom. In some studies of tin dioxide films, the presence of under-oxidized forms of tin: Sn, SnO was shown [21]. As a rule, they are adsorption centers. Upon contact with ammonia, even without chemical interaction, a shift in the electron density of the surface tin atom (most likely associated with an oxygen vacancy) can occur. This leads to a change in the surface potential and, as a consequence, to a decrease in the mobility of charge carriers.

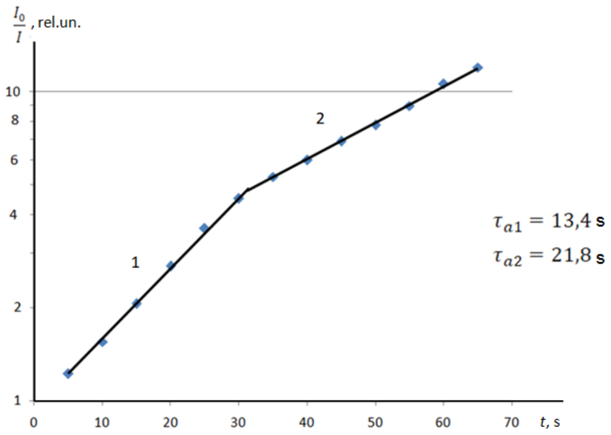

Fig. 5. Current relaxation when ammonia vapor is injected into the chamber (V = 300V).

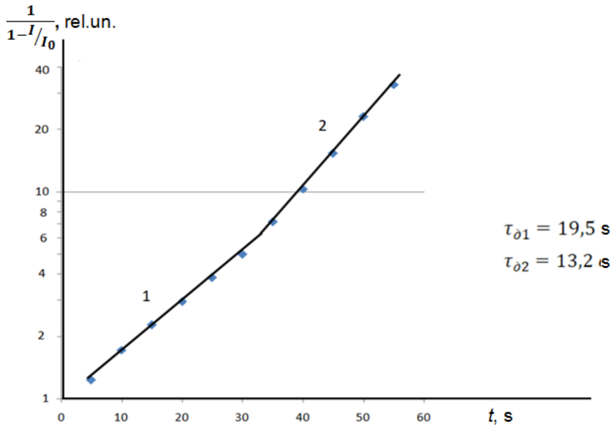

Fig. 6. Relaxation of the current at admitting dry air into the chamber. (V = 300V).

Two time constants of adsorption show that adsorption centers associated with atoms of metallic tin can be filled at first (fast adsorption with a time constant of 13.4, and then of tin oxide on the film surface – slow adsorption with a time constant of 21.8. Desorption is in the opposite direction Thus, the proximity of the values of adsorption and desorption constants and their behavior confirm the assumption about the role of physical adsorption processes in the sensitivity of the studied tin dioxide films at room temperature.

Conclusions

The studied nanostructured films of tin dioxide can be used as an elementary basis for gas sensors detecting the composition of the atmosphere and operating at room temperature.

Ammonia vapor leads to a decrease in the conductivity of the studied SnO_2 films. This is due to the fact that the adsorbed ammonia molecules increase the height of the intergranular potential barriers, and the surface shut-off bend of the energy bands. The main role in this is played by the processes of physical adsorption of ammonia molecules.

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Summary

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Key words: tin dioxide, thin films, ammonia adsorption**.**

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Чебаненко А.П., Филевская Л.М., Гриневич В.С., Сминтина В.А., Негруца О.С.

ВПЛИВ ПАРІВ АМІАКУ НА ЕЛЕКТРИЧНІ ХАРАКТЕРИСТИКИ НАНОРОЗМІРНИХ ПЛІВОК ДІОКСИДУ ОЛОВА, ОТРИМАНИХ З ВИКОРИСТАННЯМ ПОЛІМЕРУ

Резюме

У представленій роботі досліджено вплив аміаку на електричні властивості нанорозмірних плівок діоксиду олова, отриманих із використанням полімерів, з метою оцінки їх можливості використання в якості чутливого елемента датчика аміаку при кімнатній температурі. Пари аміаку призводять до зменшення провідності плівок SnO_2. Це пов'язано з тим, що адсорбовані молекули аміаку збільшують висоту міжзеренних потенційних бар’єрів та поверхневий вигин енергетичних зон. Основну роль у цьому відтворюють процеси фізичної адсорбції молекули аміаку. Чутливість плівок до пари аміаку знаходиться в діапазоні 0,35-0,63 і досягає максимуму при напрузі 300 В. Процеси адсорбції та десорбції протікають у дві стадії і є зворотними, про що свідчать розраховані сталі часу адсорбції та десорбції.

Ключові слова: діоксид олова, тонкі плівки, адсорбція аміаку.

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Чебаненко А.П., Филевская Л.Н., Гриневич В.С., Смынтына В.А., Негруца О.С.

ВЛИЯНИЕ ПАРОВ АММИАКА НА ЭЛЕКТРИЧЕСКИЕ ХАРАКТЕРИСТИКИ НАНОРАЗМЕРНЫХ ПЛЕНОК ДИОКСИДА ОЛОВА, ПОЛУЧЕННЫХ С ИСПОЛЬЗОВАНИЕМ ПОЛИМЕРА

Резюме

В представленной работе исследовано влияние паров аммиака на электрические свойства наноразмерных пленок диоксида олова, полученных с использованием полимеров, с целью оценки возможности их использования в качестве чувствительного элемента датчика аммиака при комнатной температуре. Пары аммиака приводят к снижению проводимости исследованных пленок SnO_2. Это связано с тем, что адсорбированные молекулы аммиака увеличивают высоту межзеренных потенциальных барьеров и поверхностный запирающий изгиб энергетических зон. Основную роль в этом играют процессы физической адсорбции молекул аммиака. Чувствительность пленок к парам аммиака находится в диапазоне 0,35-0,63 и достигает максимума при напряжении 300 В. Процессы адсорбции и десорбции протекают в две стадии и являются обратимыми, о чем свидетельствуют рассчитанные постоянные времени адсорбции и десорбции.

Ключевые слова: диоксид олова, тонкие пленки, адсорбция аммиака.

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