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SnO_2 AND ZnO FILMS STRUCTURED USING POLYMERS FOR AMMONIA DETECTION

The electrophysical properties in air and in the atmosphere with ammonia vapor content of nanosized films of ZnO and SnO_2 structured in the process of production using polymers were studied. The investigated electrophysical properties of those films in air and in an atmosphere containing ammonia vapors showed the presence of significant changes in the conductivity of both types of films. The nature of these changes is somewhat different. In ammonia vapors, the current in a zinc oxide film is many times greater than in air. And the tin oxide film in ammonia vapor becomes more high-resistant in comparison with its resistance in air. It was found that the conductivity of both types of films is controlled by intercrystalline potential barriers. However, upon contact with ammonia vapors, these barriers decrease in the zinc oxide films, while the opposite process is observed in the tin dioxide film. The reversible nature of the processes of ammonia molecules interaction with oxide films is observed in both cases. Both for ZnO and for SnO_2 the sensitivity to ammonia is recorded already at room temperature. It was also established that the initial characteristics of both types of films were quickly restored without additional measures. These facts make the studied nanostructured films of ZnO and SnO_2 using polymers to be promising material for sensitive elements for ammonia gas sensors.

Introduction

Nanosized oxide materials, in particular tin and zinc oxides are actively used as ones for gas analysis [1-3]. Due to their electronic characteristics (large band gap), chemical resistance in the active medium, as well as a large active surface area, they provide a significant response in their conductivity and long-term operation. To increase the efficiency of these materials as sensitive elements of gas sensors, various technological methods are used to increase their active surface, for the main physical and chemical processes responsible for this parameter occur mainly at the interface, being the surface of the sensitive element. Among the production technologies are both physical (atomic layer-by-layer deposition, magnetron sputtering, etc.) [4] and chemical (vapor-phase deposition on a heated substrate, methods of decomposition of organometallic compounds, sol-gel methods [5,6], hydrothermal method [7]). The latter are the most popular due to their relative simplicity and low cost. By such methods with various modifications it is possible to receive various nanostructures - from film to micellar-like [8].

The ammonia content control, like of many other pollutants, is essential to ensure the safety of the environment. This applies to public places, ambient air and the air of production areas. This makes the need for constant monitoring of the gaseous environment composition and the improvement of devices for it as a priority for environmental protection. Therefore, the creation of efficient, high-speed and renewable gas sensors elements sensitive to ammonia becomes a necessary solution to this problem. Oxide nanomaterials, namely, tin and zinc oxides, exhibit high sensitivity to ammonia vapors and are used as materials for sensitive elements of ammonia sensors. [9]. For the operation of sensors based on them, as a rule, additional heating and a sufficiently long recovery time of the active element after interaction with the detected gas are required. Therefore, lowering the operating temperature and rapid recovery after interaction with the detected gas is necessary to save energy and materials when creating and operating sensors.

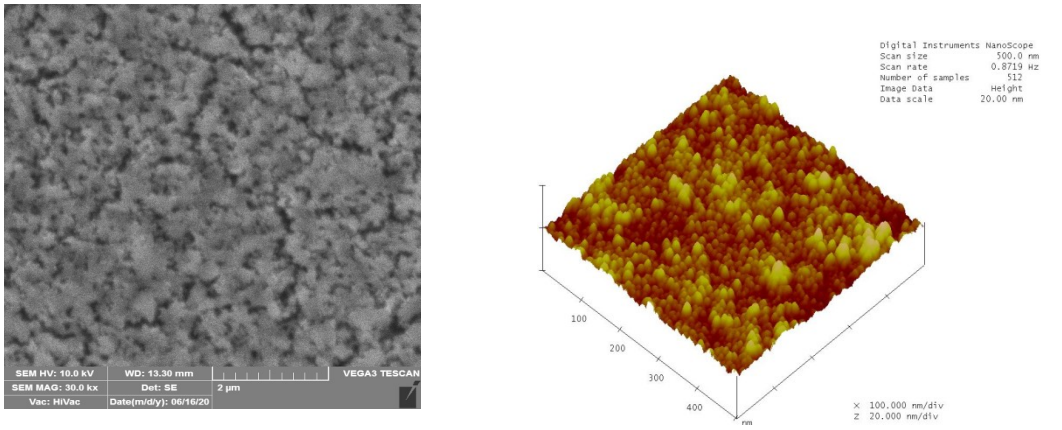
In the work, the electrophysical properties in air and in the atmosphere with ammonia va-

por content of nanosized films of zinc and tin oxides structured in the process of production using polymers were studied in order to evaluate their application as effective and renewable sensitive elements for ammonia sensors.

Methods for films production and research

The precursor's solutions (organometallic compounds of zinc and tin) were mixed with polymer solutions during their preparation and applied by drop coating method onto prepared glass substrates. Zinc acetate was used as a precursor for zinc oxide, and bis(acetylacetonato)dichlorotin(IV) was used for tin oxide. The latter was obtained by the technology described in [10]. The workpieces dried in a drying oven were annealed in air in a muffle furnace. After the removal of the products of polymer thermal decomposition during annealing, the transparent nanostructured metal oxides remain on the substrate. Figure 1 shows an electronic microscope image of the obtained zinc oxide films (a), as well as a three-dimensional AFM image of the surface of tin oxide films. The images confirm the presence of nanostructuring in the films under study.

The study of the electrophysical properties in air and their changes in the presence of ammonia vapors were carried out according to standard methods in the equipment described in [11].



a) b)

Fig. 1. SEM image of the studied zinc oxide film (a) and three dimensional tin dioxide film's surface view (b).

Results and discussion

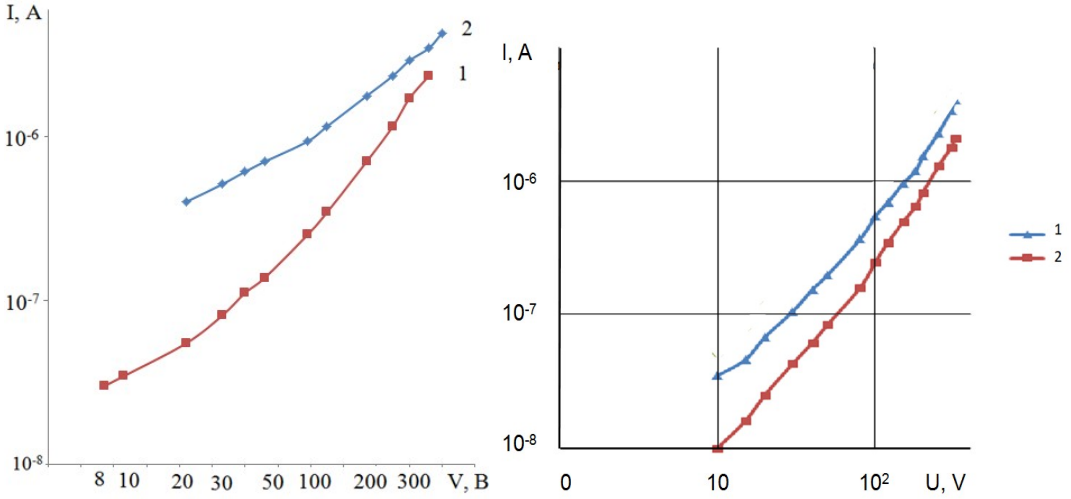
The band gap of the obtained oxide films established from its optical density vs energy study was from 2.9 to 3.15 eV for both types of films. The resistance of both types of oxide films calculated from the current-voltage characteristics was (0.2-3) x10^9 Ohm, what is expected for wide gap materials.

The electrical conductivity of polymer-structured nanosized zinc and tin oxide films was found to be sensitive to the ammonia content in the surrounding atmosphere. It is interesting that the character of the conductivity change of the films is not similar.

Figure 2 shows the current-voltage characteristics of the studied films of zinc oxide (a) and tin dioxide (b) in air (curves 1 in both figures) and in an atmosphere with an ammonia vapor content (curves 2). It can be seen in both figures that current-voltage characteristics measured in the atmosphere with an ammonia vapor content, differs from I–V characteristics measured in air .

Curve 1 in Figure 2a shows the current-voltage characteristic of the ZnO film measured in air. The exponential nature of the dependence of the current on the applied voltage is confirmed by the straightining of the CVC in lnI-V ^ coordinates (1/4). This means that the current flow in the ZnO film in air at room temperature is conditioned by over-barrier Schottky emission over thin intercrystalline barriers [12]. The presence of these barriers is

also confirmed by the nanocrystalline grain sizes of the film in SEM images.



a) b)

Fig. 2. CVC of ZnO film (a) and SnO_2 film (b) in air (curves 1 in both figures) and with ammonia vapor (curves 2 in both figures) at 290 K.

The CV characteristic of SnO2 films in a dry air atmosphere (curve 1, Fig. 2b) is superlinear and shows a weak an exponential dependency of the current on the applied voltage. This dependence is also due to the barrier mechanisms of current flow. Thus, the intercrystalline potential barriers in the tin dioxide film, as in the zinc oxide film, noticeably influence the current flow.

Curve 2 in Fig. 2a shows the I-V characteristic of the ZnO film in an atmosphere with ammonia vapor. It is noteworthy that in ammonia vapor, the current in the film (especially in the region of low voltages) is several times higher than in air. As shown in [13], during the adsorption of ammonia on the surface of ZnO, the nitrogen atom (N) is mainly bound with the surface zinc atom (Zn). This configuration is stable when NH3 is adsorbed on the zinc oxide surface. NH3 molecules are molecular chemisorbed on the ZnO surface and become charged donors. With this character of adsorption, the equilibrius surface energy bands bending decreases, which leads to the conductivity growth of thin zinc oxide films under the influence of NH3 vapors. This is the nature of the current flow change in zinc oxide films in an atmosphere with ammonia vapor in Fig. 2a.

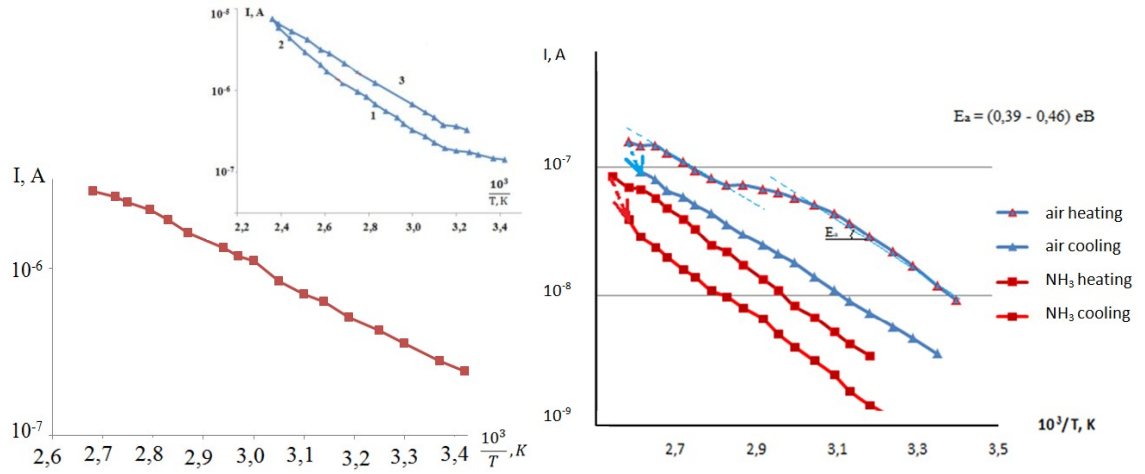
In ammonia vapor, the studied SnO2 film, unlike to the ZnO film, on the contrary, becomes more resistive than that in air. The superlinearity of its CV characteristic also increases (Fig. 2b, curve 2). Thus, it may be supposed, that the adsorption of ammonia molecules promotes the intercrystalline potential barriers growth in the tin dioxide film and an increase of the blocking bend of the surface energy bands. It is known [14] that ammonia molecules can form complexes SnO_2 [NH3] on the surface of tin dioxide. The formation of such complexes on intergranular barriers increases the surface bending of the zones. The consequence of this is a decrease in the conductivity of the film.

The conductivity decrease upon contact of a tin dioxide film with ammonia is possible in the processes of physical adsorption of oxygen and ammonia, besides the creation of ammonia complexes with surface atoms of tin or its oxides. These processes can take place at room temperature. But in the case of physical adsorption, there is no exchange of carriers (charges) between the adsorbate and the adsorbent. However, the nanostructuring of the film grains leads to a slight decrease of the chemisorption reactions temperature. In addition, it is also possible to influence the current

transfer due to a decrease in the carrier mobility of the near-surface region and an increase in barriers to current flow due to physical adsorption, which can also lead to a decrease in conductivity.

Figure 3 shows the current temperature dependences in the ZnO (a) and SnO2 (b) films.

The zinc oxide film current temperature dependence measured in air and in ammonia vapor has an activation character. The activation energy of conductivity in ammonia vapor calculated from its slope is Ea≈0.32 eV. The obtained value of Ea is close to the activation energies obtained with the CTD of the ZnO film in an air atmosphere (0.35-0.37) eV (in the inset in Fig. 3a). The established values indicate that the electrical conductivity is controlled by intercrystalline potential barriers and the current flow mechanism in both cases can be described by a semiconductor model with large-scale fluctuations of the potential relief [15].



a) b)

Fig.3.The current temperature dependence in ZnO film in dry air and in ammonia vapor (V = 100 B) (a) and SnO_2 film in dry air and in ammonia vapor (U = 150 V) (b).

The same picture is observed in the current temperature dependence of tin dioxide films (Fig. 3b). The only difference is in a decrease in conductivity in ammonia vapors. The slope of all curves is almost the same and corresponds to the activation energy Ea = 0.39-0.45 eV. This slope shows that the conductivity is also controlled by defects and the activation energy approaching the depth of the levels corresponding most likely to ionized molecularly adsorbed oxygen [16]. A decrease in the conductivity in this case is possible due to the surface oxygen molecules influence in the presence of ammonia molecules when complexes are formed on the SNO2 [NH3] surface. The curves' slope retention may indicate both the localization of ammonia molecules on the same surface defects where oxygen has already been preliminarily adsorbed, and binding with oxygen itself.

The current kinetic changes during periodic inflow of ammonia vapors or dry air into the measuring chamber are shown in Figure 4a. It can be seen that the presence of ammonia leads to an almost double current growth in the ZnO film. The response time (the time of reaching 90% of the steady-state current value) is about 48 s, which indicates to low inertia of the ammonia absorption process. The current strength decrease to its initial value (that is, the process of ammonia desorption) after admitting dry air into the chamber is more inertial than the adsorption process. The recovery time (the time necessary to reach 90% of the current from its stationary value) is about 180 s. It can be seen that the decrease in the first seconds is quite sharp. This behavior indicates to a weak bond of the most of the adsorbed molecules with the zinc oxide surface.

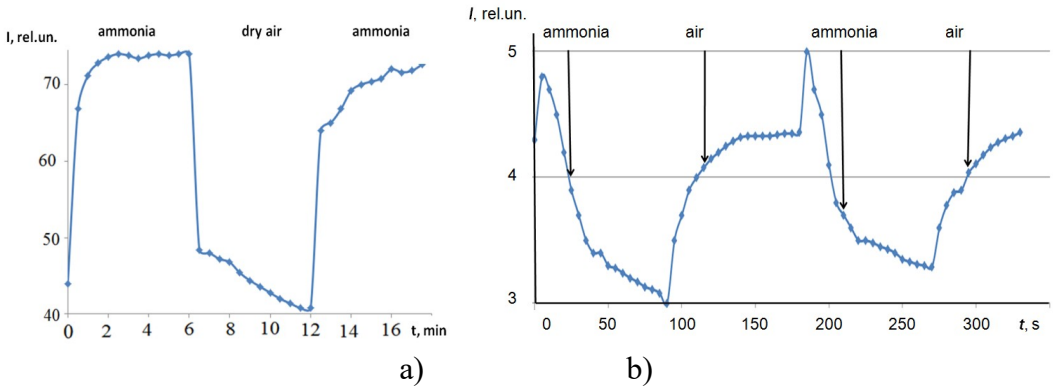


Fig. 4. Kinetics of the current in the ZnO film measured at periodic inflow of ammonia vapor or dry air into the chamber (V = 175 B) at T = 293 K(a) and for the SnO2 film (V = 300 V) (b).

A slightly different picture of nanosized SnO_2 films sensitivity to ammonia is shown in Fig. 4b. The current strength decreases when ammonia is let into the test chamber. The response time in this case is slightly higher and amounts to about 70-75 s. The recovery time is close to the response time. The short desorption time shows a weak bond of adsorbed molecules with the surface of the tin dioxide film, which can be supposed at room temperature. The said also confirms the physical nature of the adsorption of ammonia on tin dioxide films at room temperature. Desorption of chemisorbed molecules even on nanosized crystallites would require more energy, which means that during desorption (with the admission of dry air) such a sharp change in conductivity would not be registered.

Despite all the differences in the mechanisms of sensitivity of zinc oxide and tin dioxide, their behavior when interacting with ammonia has common features. Both types of films show a fairly rapid recovery of the original characteristics without additional actions - an increase in temperature or field action. Besides that, the observed processes of both oxides films' interaction with ammonia occur at room temperature. These properties are extremely important in gas analysis applications as sensitive elements.

Conclusions

The investigated electrophysical properties of nanosized films of zinc and tin oxides, structured using polymers in the process of production, in air and in an atmosphere containing ammonia vapors showed the presence of significant changes in the conductivity of both types of films. The nature of these changes is somewhat different.

In particular, in ammonia vapors, the current in a zinc oxide film (especially in the region of low voltages) is many times greater than in air. And the tin oxide film in ammonia vapor becomes more high-resistant in comparison with its resistance in air, that is, its electrical conductivity decreases. These facts indicate to different mechanisms of chemisorption processes on different oxides, since ammonia acts as a donor for zinc oxide, and exhibits acceptor properties for tin dioxide.

It was found that the conductivity of both types of films is controlled by intercrystalline potential barriers. However, upon contact with ammonia vapors, these barriers decrease in the zinc oxide films, while the opposite process is observed in the tin dioxide film.

The reversible nature of the processes of ammonia molecules interaction with oxide films is observed in both cases. At the same time, both for zinc oxide and for tin oxide, the sensitivity to ammonia is recorded already at room temperature. It was also established that the initial characteristics of both types of films were quickly restored without additional measures. These facts make the studied nanostructured films of tin and zinc oxides using polymers to be promising material for sensitive elements for ammonia gas sensors.

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Summary The electrophysical properties in air and in the atmosphere with ammonia vapor content of nanosized films of ZnO and SnO_2 structured in the process of production using poly-

mers were studied. The investigated electrophysical properties of those films in air and in an atmosphere with ammonia vapors showed the presence of significant changes in the conductivity of both types of films. The nature of these changes is somewhat different. In ammonia vapors, the current in a zinc oxide film is many times greater than in air. And the tin oxide film in ammonia vapor becomes more high-resistant in comparison with its resistance in air. It was found that the conductivity of both types of films is controlled by intercrystalline potential barriers. However, upon contact with ammonia vapors, these barriers decrease in the zinc oxide films, while the opposite process is observed in the tin dioxide film. The reversible nature of the processes of ammonia molecules interaction with oxide films is observed in both cases. Both for ZnO and for SnO_2 the sensitivity to ammonia is recorded already at room temperature. It was also established that the initial characteristics of both types of films were quickly restored without additional measures. These facts make the studied nanostructured films of ZnO and SnO_2 using polymers to be promising material for sensitive elements for ammonia gas sensors.
Key word: tin oxide, zinc oxide, nanosized thin films, sensitivity, ammonia detection.

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ПЛЕНКИ SnO_2 И ZnO, СТРУКТУРИРОВАННЫЕ С ИСПОЛЬЗОВАНИЕМ ПОЛИМЕРОВ ДЛЯ ОБНАРУЖЕНИЯ АММИАКА

Резюме

Изучены электрофизические свойства на воздухе и в атмосфере с содержанием паров аммиака наноразмерных пленок ZnO и SnO_2, структурированных в процессе получения с использованием полимеров. Исследованные электрофизические свойства этих пленок на воздухе и в атмосфере с парами аммиака показали наличие значительных изменений проводимости обоих типов пленок. Природа этих изменений различна. В парах аммиака ток в пленке оксида цинка во много раз больше, чем в воздухе. А пленка оксида олова в парах аммиака становится более высокоомной по сравнению с ее сопротивлением на воздухе. Было обнаружено, что проводимость обоих типов пленок контролируется межкристаллическими потенциальными барьерами. Однако при контакте с парами аммиака эти барьеры уменьшаются в пленках оксида цинка, тогда как в пленке диоксида олова наблюдается обратный процесс. В обоих случаях наблюдается обратимый характер процессов взаимодействия молекул аммиака с оксидными пленками. И для ZnO, и для SnO2 чувствительность к аммиаку регистрируется уже при комнатной температуре. Также было установлено, что исходные характеристики обоих типов пленок быстро восстанавливались без дополнительных мер. Эти факты делают исследованные наноструктурированные с использованием полимеров пленки ZnO и SnO_2 перспективным материалом для чувствительных элементов газовых сенсоров аммиака.

Ключевые слова: оксид цинк, диоксид олова, наноразмерные тонкие пленки, чувствительность, детектирование аммиака.

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ПЛІВКИ SnO_2 І ZnO, СТРУКТУРОВАНІ З ВИКОРИСТАННЯМ ПОЛІМЕРІВ, ДЛЯ ВИЯВЛЕННЯ АМІАКУ

Резюме

Вивчено електрофізичні властивості на повітрі та в атмосфері з вмістом парів аміаку нанорозмірних плівок ZnO та SnO_2, структурованих у процесі одержання з використанням полімерів. Досліджені електрофізичні властивості цих плівок на повітрі та в атмосфері з парами аміаку показали наявність значних змін провідності обох типів плівок. Природа цих змін різна. У парах аміаку струм у плівці оксиду цинку в багато разів більший, ніж у повітрі. А плівка оксиду олова в парах аміаку стає більш високоомною порівняно з її опором на повітрі. Виявлено, що провідність обох типів плівок контролюється міжкристалічними потенційними бар'єрами. Однак при контакті з парами аміаку ці бар'єри зменшуються в плівках оксиду цинку, тоді як плівці діоксиду олова спостерігається зворотний процес. В обох випадках спостерігається оборотний характер взаємодії молекул аміаку з оксидними плівками. І для ZnO, і для SnO2 чутливість до аміаку реєструється вже за кімнатної температури. Також було встановлено, що вихідні характеристики обох типів плівок швидко відновлювалися без додаткових заходів. Ці факти роблять досліджені наноструктуровані з використанням полімерів плівки ZnO та SnO2 перспективним матеріалом для чутливих елементів газових сенсорів аміаку.

Ключові слова: оксид цинку, діоксид олова, нанорозмірні тонкі плівки, чутливість, детектування аміаку.

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