Structure factor of the gas sensitivity improvement of bilayer tin dioxide films

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Comparative studies of electric conductivity and gas sensitivity have been carried out for two types of tin dioxide films (single- and bilayer ones). The free surface area of the bilayer films was increased intentionally by applying the second layer as a thin nanodispersed tin dioxide layer with a developed relief. The gas sensitivity of the bilayer films has been shown to exceed by 2 to 4 times that of the single-layer ones at the same thickness. This and others features of the bilayer films have been explained by the improved adsorbing ability thereof and, consequently, by a stronger depletion of free charge carriers in the layer at oxygen adsorption.

Проведены сопоставительные исследования электропроводности и газочувствительности пленок диоксида олова двух типов: 1-слойных и 2-слойных. Площадь свободной поверхности 2-слойных пленок была преднамеренно увеличена за счет нанесения второго слоя в виде тонкого нанодисперсного слоя диоксида олова с сильно развитым рельефом. Показано, что при одинаковой толщине газочувствительность 2-слойных пленок в 2–4 раза выше, чем у 1-слойных. Это и другие отличия 2-слойных пленок объяснены их повышенной адсорбционной способностью и, соответственно, более значительным обеднением слоя свободными зарядоносителями при адсорбции кислорода.

The function of miniature adsorbing-semiconducting resistive gas sensors is based on the dependence of semiconducting film electric conductance on the chemical nature and concentration of impurity particles adsorbed on the semiconductor surface from the environment [1]. The critical role of the surface becomes apparent in this case in the fact that the highest values of gas sensitivity and fast-action are attained in the sensors containing thin polycrystal films due to their anomalously high actual free surface areas. A significant drawback of very thin films is an unsatisfactory thickness reproducibility, because it is difficult to control if the amount of substance to be condensed is too small. Therefore, the film conductivity is irreproducible, too. It is shown [2] that it is possible to eliminate that drawback by using bilayer SnO_2 films. In this case, the SnO_2 underlayer is rela-

tively thick (250 nm) and has the average grain size of about 200 nm. It is deposited at the condensation temperature of 400°C. Above that layer, a thin amorphous layer (10 to 20 nm) is deposited at the condensation temperature of 150°C and a higher oxygen content in the vacuum chamber. Due to those condensation conditions, the nanodispersed structure of the thin upper layer (the crystallite size of 2 to 5 nm) is conserved after the stabilizing annealing in air at 550°C for 2 h and the free surface relief is highly developed.

The studies of those bilayer (bidispersed) films [2] have shown that those provide a good conductance reproducibility (±30 %) as well as a higher gas sensitivity as compared to that of single-layer films of a comparable thickness. In other words, in the bilayer films, there is no dimensional effect found before [3] and consisting in the gas
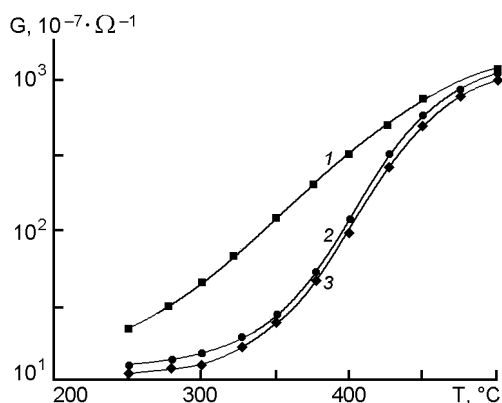
Fig. 1. Temperature dependences of conductivity for tin dioxide films of *1*, *2*, *3* series.

Fig. 2. Time change of temperature and conductivity for tin dioxide samples of the three groups under stepwise isothermal annealing (T curve) in vacuum.

sensitivity reduction of SnO_2 films as the thickness thereof increases. This is an unexpected result. In this connection, said bilayer films are of interest due to their higher gas sensitivity as well as model objects for elucidation of numerous problems concerning the physical nature of SnO_2 film gas sensitivity at different morphology and improvement of that property in the bilayer system with said different morphology of the upper and underlayer. These problems are studied in this work by comparative study of the gas sensitivity features in single-layer and bilayer films.

Three sample groups were studied. The No.1 group includes single-layer polycrystal SnO_2 films of 250 nm thickness condensed at the substrate temperature of 400°C and post-annealed in air at 500°C for several hours. The coherent scattering domain size in such films is 200 to 300 nm, thus, those can be considered to be single-grain in thickness. The group 2 consists of bilayer films wherein the first (adjacent to the substrate) layer is identical with the 1st group films while the second one deposited onto the 1st layer at 150°C is about 10 nm thick and consists of dispersed particles of 2 to 5 nm size. The samples of the group 3 differ from those of the group 2 only in that the upper layer is more thick (about 30 nm). The grain structure morphology was determined by raster electron microscopy. The film of a thickness above 200 nm were studied also by X-ray diffraction in monochromatic Cu Kα radiation.

The temperature dependence of electric conductivity was examined for the all film groups under heating in air and in vacuum as well as under ethanol vapor exposure in isothermal regime and under thermal cycling.
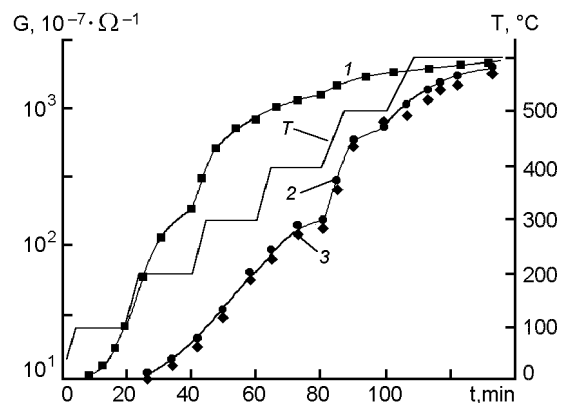
In Fig. 1, presented are the electric conductivity of single- and bilayer films being heated in air. The sample temperature was varied within 250–500°C range. The conductivity is seen to increase under heating. This is due to oxygen and moisture desorption [4]. Two facts are worth to note. First, the heating in 350–450°C effects the bilayer film conductivity to a greater extent than for the single-layer ones. Second, the conductivity variations depend only slightly on the thickness of the nanodispersed structure upper layer (plots for groups 2 and 3 are almost coincident).

Fig. 2 presents the film conductivity variation under heating in a vacuum chamber (10^{-2} Pa residual pressure). In this case, the sample heater temperature was increased up to 600°C in 100°C steps every 20 min. The temperature change duration at each step was 2 min. The conductivity variation character is qualitatively similar to that shown in Fig. 1. The additional desorptive action of vacuum becomes apparent as the fact that the temperature range where the conductivity characteristics of single- and bilayer films do not coincide is shifted towards higher temperatures. The difference in absolute conductivity values of the films is increased, too.

We have compared the gas sensitivity of single- and bilayer SnO_2 films at 450°C. To that end, the relative conductivity (G/G_0) changes were registered in time after a short-time exposure of the samples to a dosed amount of a reducing impurity (ethanol vapor) in a measuring device providing
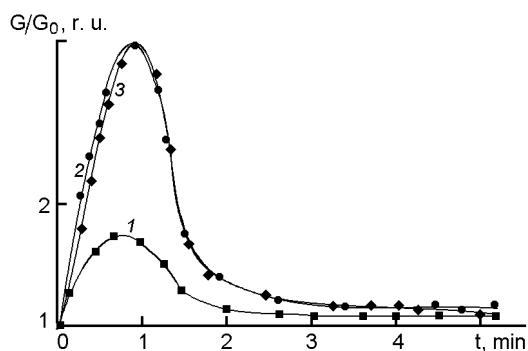
Fig. 3. Time change of relative conductivity for tin dioxide samples of the three groups at fixed temperature of 450°C.

Fig. 4. The bilayer film surface image in a scanning electron microscope.

an air stream. Here, G_0 is the sample conductivity prior to the exposure and G, thereafter. The examination results are shown in Fig. 3. The samples of the 2 and 3 groups are seen to behave identically to one another within the experimental error (±5 %). It is to note that both these groups show a higher gas sensitivity as compared to the single-layer films of a comparable thickness.

The gas sensitivity of the sample groups was compared also in the thermal cycling regime where the sample heater temperature was changed periodically from 400 to 500°C and vice versa at 10 s intervals. Note that the time pulsation of the sample conductivity after the single introduction of ethanol vapor dose was synchronous with the temperature pulsation. The examination results under thermal cycling are as follows. The time changes of the relative conductivity after the single introduction of ethanol vapor into the analyzing chamber of the measuring device are qualitatively similar for the three sample groups. In contrast to the static temperature regime (Fig. 2), not only the relaxation duration but also the time to attain the maximum G/G_0 value are the same for the three sample groups in the thermal cycling regime. Moreover, the change amplitude of G/G_0 is increased by about 1.5 times in the presence of of ethanol vapor for all the three sample groups. The total response duration to the single introduction of the impurity vapor is reduced, too. The distinctions between the 2 and 3 sample groups are insignificant as before.

The examinations have shown that all the samples behave qualitatively similarly under different temperature regimes and in different media. Thus, the processes defin-
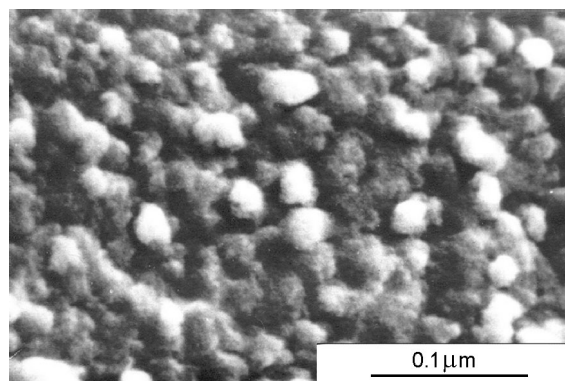
ing the gas sensitivity thereof are of the same physical nature. The results obtained agree well with one of the models considered in [4]. The main attention is paid to the charge transfer process in the depleted layer formed due to the presence of localized states at the surface where oxygen ions are adsorbed. The oxygen adsorbed on the free surface extracts the conductivity electrons from the volume of the SnO_2 film, thus converting it into a more high resistance state. If the film is now exposed to a reducing impurity, e.g., ethanol vapor, the latter reacts with the initially adsorbed oxygen. As a result, electrically neutral reaction products are formed that are desorbed from the SnO_2 surface, whereby the conductivity electron concentration in the layer becomes recovered to its initial level.

The quantitative differences in the gas sensitivity between the single-layer and bilayer samples are due, in our opinion, to the specific relief features of the film free surfaces. It is known [5] that the actual free surface area of thin films condensed on unheated surfaces is by several tens of times larger than the so-called apparent film surface, that is, the film projection area onto the substrate plane (Fig. 4). The thicker films formed at higher condensation temperatures show a more smoothened surface relief.

The mentioned free surface relief features of the thin and thick films provide a non-contradictory explanation for all the specific gas sensitivity characteristics of the bilayer films. The upper thin SnO_2 layer formed over the weakly heated thick underlayer provides a much higher specific free surface area of the bilayer film as compared to the single-layer thick film condensed at a higher temperature. As a result, due to improved adsorbing ability

caused by the developed surface relief, during oxygen absorption, the electron extraction from the conductivity zone of the bilayer composite reduces significantly the average charge carrier concentration in the whole volume thereof. That is why the upper thin layer of nanodispersed structure is not shunted with the thick coarsergrained layer.

The gas sensitivity independence of the nanodispersed layer thickness is explained, in our opinion, by the fact that the development extent of the free surface relief is not changed substantially as the SnO_2 film thickness is changed from 10 nm to 20 or 30 nm. This is confirmed by raster electron microscopy images of the films. It is to note that the experimentally confirmed gas sensitivity invariance of the bilayer films at the upper layer thickness changing by a factor of 2 or 3 evidences a good reproducibility of the properties for such bidispersed film composites.

The small delay of response to adsorption and desorption in the 2nd and 3rd group samples as compared to the 1st group ones can be due to the increased number of adsorption centers on the larger free surface area as well as to multiple adsorption/desorption phenomena in the open porosity labyrinths at the strongly developed free surface relief (Fig. 4) of the bilayer samples.

Thus, the bilayer bidispersed SnO_2 films are suitable as gas-sensitive elements of the gas sensors having an improved (by a factor of 2 to 4) and satisfactorily reproducible gas sensitivity characteristics as compared to the silgle-layer films of a comparable thickness. The improved gas sensitivity of the bilayer bidispersed SnO_2 films is shown to be due to the increased adsorption ability thereof caused by a higher specific free surface area that is provided by the thin upper layer of nanodispersed structure. This provides a significant depletion of the free charge carriers in the bilayer film.

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Структурний чинник підвищення газочутливості двошарових плівок діоксиду олова

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Виконано порівняльні дослідження електропровідності та газочутливості плівок діоксиду олова двох типів: одношарових та двошарових. Площа вільної поверхні двошарових плівок була умисно збільшена шляхом нанесення другого шару у формі тонкого нанодисперсного шару діоксиду олова з сильно розвинутим рельєфом. Показано, що при однаковій товщині газочутливість двошарових плівок у 2–4 рази вище, ніж одношарових. Цю та інші відмінності двошарових плівок пояснено їхньою підвищеною адсорбційною здатністю і, відповідно, більш значним збідненням шару вільними носіями заряду при адсорбції кисню.