

MORPHOLOGY OF NANOSTRUCTURED SnO₂ FILMS PREPARED WITH POLYMERS EMPLOYMENT

The gas sensitivity applied problems solutions needs a consideration and detailed investigation of the material's electronic and ionic subsystems' behavior. These systems' behavior at their own turn are tightly connected with the structure and morphology of surfaces. The morphology investigations results are given for the SnO₂ layers obtained with the polymers usage.

The nanoscaled materials have physical properties principally differing from the corresponding ones of microscaled objects, and are widely used in electronic, optical and magnetic devices such as gas, optical sensors, photodiodes, sun cells, monoelectron transistors and memory units. [1]. The nanomaterials' specific peculiarity is their great active surface which defines the crucial time and temperature decrease for the chemical reactions proceeding [2]. The mentioned property is widely used for the constructing of the new gas sensors' generation with perfect speed of response and low energy consumption. In connection with the said it is reasonable to elaborate the nanograins materials, with controlled development surface for the gas analysis. The technique using polymers as the components assisting in structuring is proposed for the aims of obtaining of well developed surface layers having the nanoscaled grains.

The nanocrystallized tin dioxide having the electroconductivity highly sensible to the state of the surface in the (300—800) K temperature region specific for the oxidizing-recollecting reactions has the most practical use in the gas analysis[3]. It is one of not many materials, which may be obtained in highly dispersed state (crystallite sizes 5—20 nm).

The tin dioxide surface has perfect adsorptive properties and reaction ability which are defined by the surface and bulk oxygen vacancies and active chemisorbed oxygen [3] and are tightly connected with the surface morphology. These ideas predefined the SnO₂ surface morphology investigation.

THE LAYERS PREPARATION METHODS

The transparent thin nanostructured Tin dioxide films were prepared using polymer materials in the sol-gel method. The production technique had several stages: preparation of the Tin containing organic fillers, preparation of polymer material sol in the solution and, finally, insertion the tin containing compounds into it. Further,

the gel obtained was deposited on the substrate and finally annealed in the muffle stove. The annealing time and temperature were chosen with the consideration of the polymer's decomposition time. After the polymer's decay products full removal during the annealing and the following it oxidation, the thin Tin dioxide layers with developed nanostructured surface were formed.

The films obtained had different degrees of transparency (from milk-white to fully transparent) and different adhesive properties. Having obtained these results, it is clear that the preparation of such films needs both different solvents (water, acetone), polymer materials (polyvinyl spirits, cellulose, poly-methyl-metacrylat and others) and Tin containing fillers. The films based on the polyvinyl spirits gel had weak coherence with substrates and were of milk-white color. This witnesses about presence in the film of not only Tin dioxide, but and other reaction's products. Films based on the cellulose had the dark brown color, which is specific for the bivalent tin oxide — SnO. The darkening of the films may be caused by the extremely great carbon contain, which stays in the film after the cellulose was burn away. The films based on polyvinyl-acetate (PVA) with the addition of acetyl-acetate of tin appeared to be fully transparent with tight adhesion with the substrate.

The initial sol was prepared as following. PVA was cleaned by 25% ammonia (NH₄OH) solution, was washed three times in a distilled water, then was dried by the CaCl₂ dryer, then was polymerized by means of 1% benzoyl peroxide solution and finally was grinded. Then the PVA obtained was inserted into the dissolver (acetone) at the room temperature. In a case of polymer's insolubility in the solvent, the monomer of the same substance may be used. The gel-type structure was formed after 20—60 minutes of thorough mixing. The solution of acetyl-acetate of tin powder in acetone was inserted into the gel obtained. After special preparations of the glass substrate it was covered by the mono layer of the film. Then it was kept for 5 minutes in the open air for the acetone may

evaporate. The annealing at 500 °C was provided in the muffle stove for 3 hours. The polymer, which was within the gel decomposed, and the decay products evaporated. The film's surfaces structural and morphology investigations were conducted after the preparations procedure was fulfilled.

EXPERIMENTAL RESULTS

The films obtained could not be investigated by the X-ray technique, because the films' thickness and their grains' nano scale were less than 100 nm which is critical limitation for the X-rays methods. The atomic force microscope (AFM) is being widely used to measure interatomic potentials of a sharp probe in the nearfield of a specimen overcomes the diffraction limit by nearfield observation of the specimen, thus permitting sub-micrometre of nanoscale measurement [4].

The tin dioxide layer's surface morphology was investigated by the industrial Atom Force microscope (AFM) Nano Scope 111a (Digital instruments, USA). The measurements were fulfilled by siliceous probe with a nominal radius ~ 10 nm (the production firm NT-MDT, Russia) in a regime of periodical contacts (Tapping Mode™). The investigated surface area was 500×500 nm². The film's surface top view (*a*) and the force probe oscillation phase change (*b*) are presented at Fig. 1. The higher points at Fig. 1, *a* correspond to the lighter parts of the snapshot, the dark parts reflects the deeper zones.

As it may be seen, the film investigated is enough uniform and consists of nanograins of approximately equal sizes. The AFM probe accessible deepness at the given film is $\sim 10,5$ nm. The mean grains' size is 10—15 nm. The oscillations phase changes allow to judge about relative uniformity of the material investigated. According to the picture it is possible to state that the film in whole consists of the grains with equal elastic-viscous properties. The film's vertical profile with the inter benchmarks sizes is presented at Fig. 2.

Evaluating the grain's size and the deepness of recording it is possible to conclude that the film investigated is nanostructured and for the used gel's composition is continues, but not of islet type. The 3D view of the film is given at Fig. 3.

The film's surface morphology investigations fulfilled give the possibility to predict the surface electrical potential distribution. Thus, this permits to show the regions of charge nonuniformity. Such regions' presence seriously defines charges exchange processes. Especially it becomes important when the film's surface interacts with different chemically active molecules. It means that the processes of chemisorption are taken into consideration. The understanding of the principal mechanisms of electronic subsystem behavior peculiarities at gas system contacts makes it the basis for sensitive elements construction principles.

References

1. H. Fissan, M. K. Kennedy, F. E. Kruis. Nanoparticles from the gas phase as building blocks for electrical devices

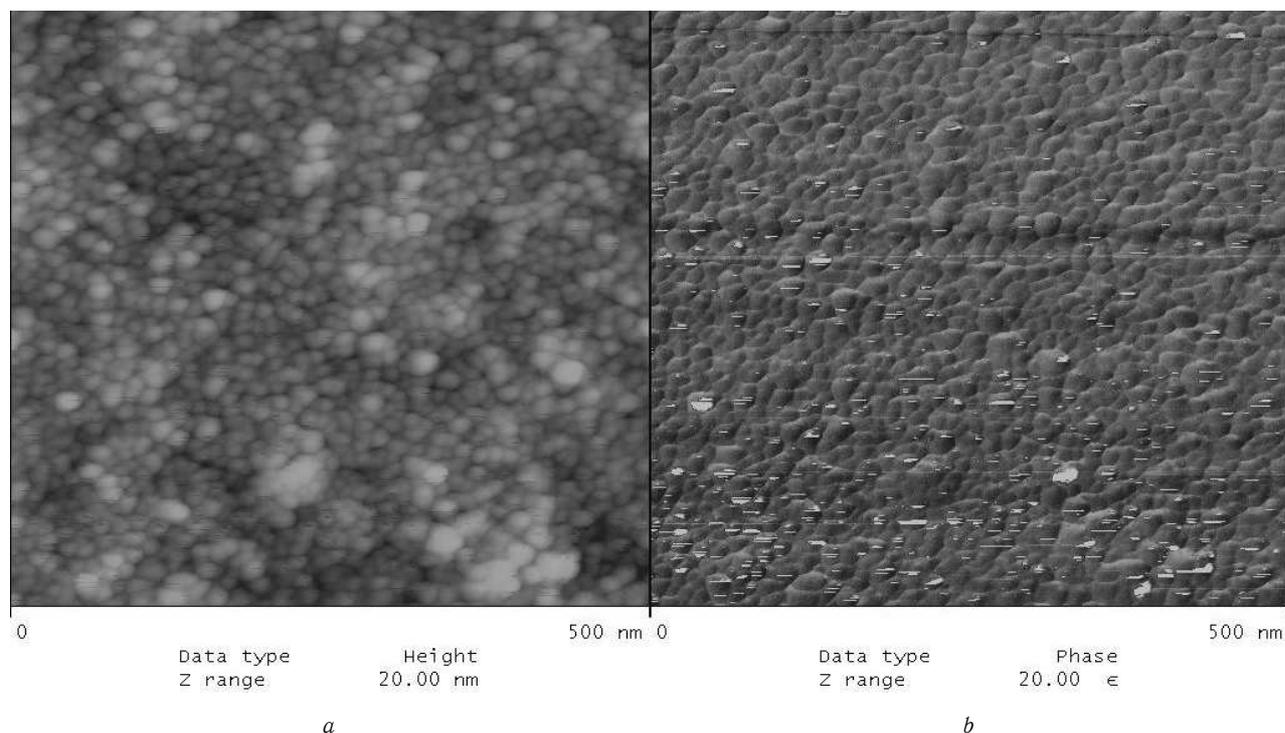
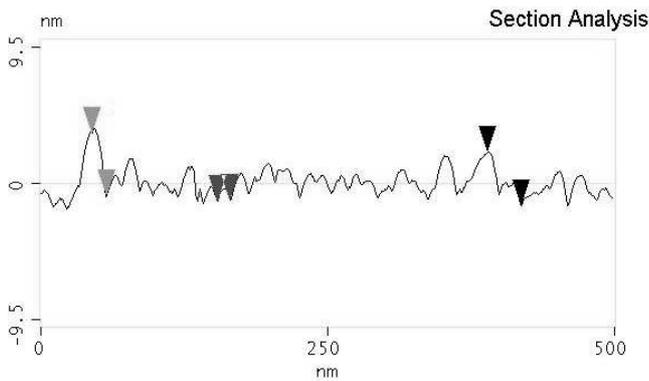
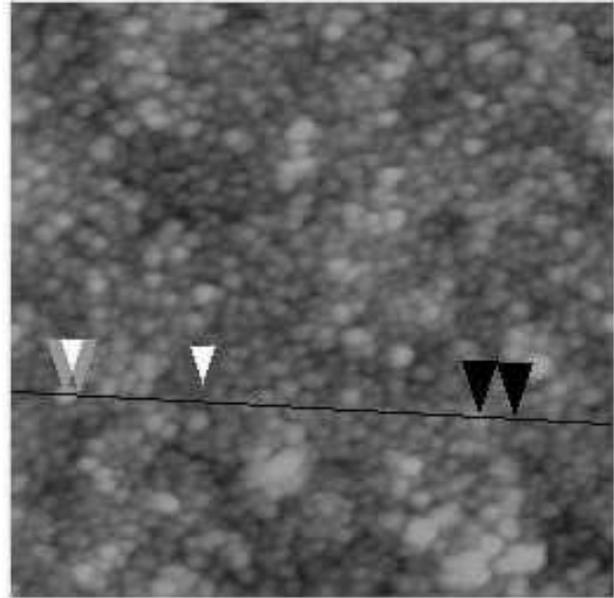


Fig. 1. Tin dioxide layer's surface (top view) (*a*) and the force probe oscillations phase changes (*b*)

Surface distance	10.923 nm	Surface distance	14.082 nm	Surface distance	30.256 nm
Horiz distance(L)	10.742 nm	Horiz distance	12.695 nm	Horiz distance	29.297 nm
Vert distance	0.034 nm	Vert distance	4.418 nm	Vert distance	3.780 nm
Angle	0.182 °	Angle	19.189 °	Angle	7.353 °



a



b

Fig. 2. The film's vertical profile (*a*), with interbenchmarks sizes indication (*b*): the text colour corresponds to the benchmarks colour

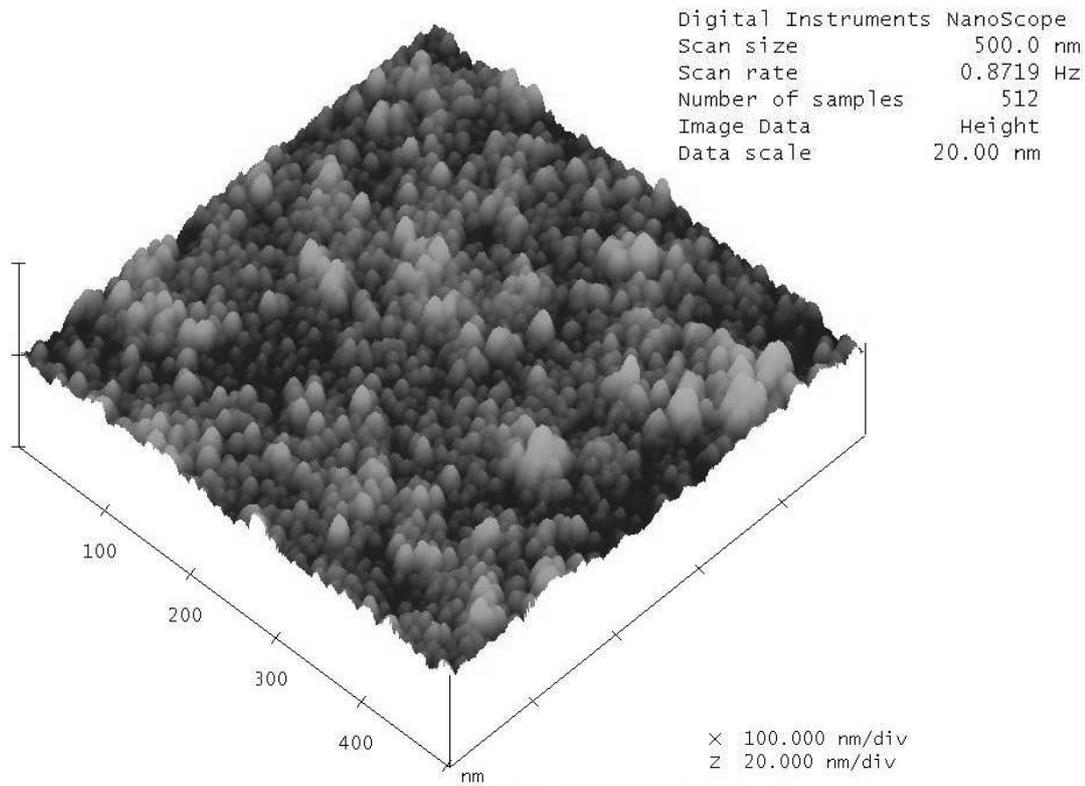


Fig. 3. Three dimensional tin dioxide film picture

// Book of abstracts of International Symposium on «Nanoparticles: Technology and Sustainable Development», Taipei, Taiwan, September 9–10, 2002. — P. 1–6 (2002).

2. Sergeev G. B. Nanohimiya. M. Moscow State University edition, Russia, 288 p. (2003)

3. Rumyantseva M. N., Safonova O. V., Bulova M. N., Ryabova L. I., Gaskov A. M. // Russian Journal «Sensor», 8, P. 27–35 (2003)

4. H. Xie, A. Asundi, Z. Liu, H. Shang, F. Dai. Micro- and Nano-Methods for Microscopy of Electronic Nanostructures // Microscopy and analysis. November 2005, P. 21–23 (2005).

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Л. Н. Филевская, В. А. Смынтина, В. С. Гриневиц

МОРФОЛОГИЯ ПОВЕРХНОСТИ НАНОСТРУКТУРИРОВАННЫХ ПЛЕНОК SnO₂, ПОЛУЧЕННЫХ С ИСПОЛЬЗОВАНИЕМ ПОЛИМЕРОВ

При решении задач улучшения газовой чувствительности адсорбционных элементов возникает необходимость детального исследования поведения электронной и ионной подсистем материала, которые в свою очередь тесно связаны с его структурой и морфологией поверхности. В работе приведены результаты исследования поверхностной морфологии применяемых в газовом анализе пленок SnO₂, полученных с использованием полимеров.

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Л. М. Філевська, В. А. Сминтина, В. С. Гриневиц

МОРФОЛОГІЯ ПОВЕРХНІ НАНОСТРУКТУРОВАНІХ ПЛІВОК SnO₂, ОТРИМАНИХ З ВИКОРИСТАННЯМ ПОЛІМЕРІВ

При вирішенні задач підвищення газової чутливості адсорбційних елементів виникає необхідність детального дослідження поведінки електронної та іонної підсистем матеріалу, що в свою чергу тісно пов'язані з його структурою та морфологією поверхні. В роботі наведені результати дослідження поверхневої морфології плівок SnO₂, отриманих з використанням полімерів.

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L. N. Filevskaya, V. A. Smyntyna, V. S. Grinevich

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