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SEMICONDUCTOR PHYSICS INSTITUTE OF CENTRE FOR PHYSICAL SCIENCES AND TECHNOLOGY

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APPLICATIONS OF SCANNING PROBE MICROSCOPY FOR DEVELOPMENT AND INVESTIGATION OF GAS SENSITIVE NANOSYSTEMS AND HYBRID STRUCTURES INTEGRATED WITH THE ULTRA-THIN METAL OXIDE FILMS

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Virginijus Bukauskas

DUJOMS JAUTRIŲ HIBRIDINIŲ DARINIŲ IR NANOSISTEMŲ INTEGRUOTŲ METALO OKSIDO PLĖVELĖSE KŪRIMAS IR TYRIMAI SKENUOJANČIO ZONDO MIKROSKOPIJOS METODAIS

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Introduction

The state-of-the-art and the addressed problems. Bio-inspired artificial electronic systems for odor detection and recognition (an electronic nose) are typically based on non-selective sensors that are, however, characterized by individual set of parameters. Adaptability, effectiveness, reliability and the response time of these systems are highly dependent on the diversity of sensors included in an array of detecting module in the artificial system. Due to expanding areas of practical applications, there is still a great demand for methods and technologies acceptable for development of novel types of chemical sensors and tuning of the sensor parameters. At present, metal oxides (MO), particularly tin and indium oxides, are the most frequently used basic materials for the gas sensors in the electronic noses addressing the needs of real users. Fast response, high sensitivity, stability, reproducibility and cheap production are the most attractive advantages of MO sensors for the practical systems. In addition to that, MO are proved being acceptable for development of future detectors based on the nanoscaled and combined (e.g. with biomolecules) systems with unique mechanisms of conversion of chemical interaction into physical response. Despite the variety of the mechanisms, the chemical interactions on the surfaces typically produce the changes in the electrical properties in the MO sensors. The essence of the electrical response can be explained by a model commonly accepted for the polycrystalline MO film. In this film, the double-Schottky barrier defines the electron transport through the contact between the adjacent grains. Since the surface charge depends on the chemisorbed gases and the barrier depends on the surface charge, the electrical conductance of the film depends on the composition of the atmosphere. In the oxygen rich atmosphere, the oxygen species are dominant in the occupied chemisorption sites on the surfaces of MO films and, consequently, determine the surface chemical reactions with the gases. The dominating chemisorbed oxygen explains fundamental limitations of the selectivity in the MO sensors in typical practical applications. Development of MO based nanosystems and combined constructions offers novel basis in solving problems of odor recognition.

Formation of MO based nanosystems and combined constructions highly depend on the changes of the MO film structure during the growth. It is reasonable to expect that these changes will also modify the both electrical charge transport and the response to gas in thin and ultra-thin films. Since there is a lack in understanding of the relationship between the properties of the ultra-thin films and the response to gas, the film structure effect in the response is worthy of investigation.

Based on the gas diffusion study it was supposed that the response can be much faster in thin than in thick films. However, the response time in the nanoscaled films can be much more dependent on the processes specific to the nanosystems than on the commonly known effects. In addition, the factors defining the selectivity of the response can also be specific to the nanoscaled systems and especially to the combined constructions. Understanding of these aspects of the response picture is highly important for the technology and methods of application of newly emerging gas sensitive systems.

In the nanoscaled constructions, characterization of locale structure, electrical properties, a response to the external influences and the changes of the physical qualities in the surface-bulk system is crucial for the development of technology and application methods of these constructions. The Scanning probe microscope (SPM) is powerful tool for measurement of several physical parameters at a time in selected points and selected areas with the high position resolution. If specially enabled, the SPM can produce significant changes in the local properties of material that makes it applicable for specific processes in the nanotechnology. Fundamental aspects of application of the SPM in both the technology and characterization of gas sensitive structures are still have to be understood and defined.

The object of investigation. The objects of the investigation in this work are thin and ultra-thin gas sensitive metal oxide (MO), namely SnO_{2-x} and $In_{2-x}O_{3-y}$, films, metal oxide nanosistems and hybrid (organic/non organic) materials integrated with MO films.

Aim of the work. The aim of this work is to apply the methodologies of the SPM for characterization of the local point and local area properties in the gas sensitive MO films with the nanoscaled thickness that can be used for nanosystems and hybrid (combined) materials in novel types of chemical detectors.

Tasks of the work.

To investigate morphology and physical properties of metal oxide films with thickness from a few to about 50 nm and to describe a relationship between the gas response and film thickness.

To define the physical processes resulting in formation of controllable metal oxide nanostructures with the SPM.

To investigate the external influences such as electric field, atmosphere composition and force on the properties of the MO nanosystems.

To adapt SPM methods for investigation of electrical and mechanical properties of hybrid structures based on bio-molecular materials.

Methodology of research. Metal oxide films were grown by DC magnetron sputtering technique. Electrical properties of the metal oxide based samples and response to gas were evaluated from the dc-resistance measurements. The synthetic atmosphere with selectable composition of gases was produced by a special gas flow control system mixing fixed amounts of oxygen and nitrogen with fixed amounts of pure volatile compounds from special containers in special gas sensor testing chamber. Surfaces of the samples were investigated and modified by various methods of Scanning Probe Microscope (SPM).

Scientific novelty. Novelties of this work include the following results in the research area of gas sensitive materials and material science:

The special Veeco SPM TUNA method was originally adapted for the investigation of physical properties of ultra-thin MO films.

An original method based on the SPM probe controlled electrical current was proposed for the formation of nanosystems with various electrical properties on the surfaces of thin MO films.

It was proved that the specific oxygen transport in the MO based nanosystem results in the growth of the nanoobjects on the surfaces of MO films and the formation of these objects is sensitive to the composition of the atmosphere.

It was proved that a dependence of the magnitude and the kinetics of the response to gas on film thickness is related to the structural changes of MO films rather than to the diffusion of gases into the film.

It was shown that the surface properties in the nanoscaled areas of the MO films can be individually and intentionally modified by both the SPM driven nanoobject growth and deposition of the multimolecular 3D objects with/without the biochemicaly active centers.

Practical value. Based on the results of this study, the long term drift of the MO gas sensors is partly explained by the oxygen redistribution in the thin films under external voltage and the fundamental aspects valuable for an improvement of the sensor stability are described. Fundamental aspects of original method for nano-tuning of ultra-thin MO films in selected areas are described and the principles for formation of multi-component nano-assembly of solid state and hybrid material sensors is proposed.

Defended propositions

1. The electrical response to gas of tin oxide films with nanometer thickness depends on the film structure and the related mechanism of the charge carrier transport.
2. Effects of external influence on the properties of the surface nanostructures can experimentally be described by the specific characteristics of the scanning probe spectroscopy displaying the dependences of the probe contact electric current on both the probe potential and the probe pressing force.
3. In the thin metal oxide films an external electric field can transfer the oxygen from the bulk to the surfaces that results in formation of metal oxide nanoobjects if the redistribution exceeds a threshold level. The nanoobjects are characterized by the depth dependent electrical characteristics and the mechanical properties similar to that of the basic film.
4. The electrical and mechanical properties are characterized by the effective parameters measured by the scanning probe microscope in the dense and continuous hybrid materials while the component specific parameters are obtained in the comparatively low density discontinuous hybrid structures on the solid surfaces.

Structure of the dissertation

The dissertation (in Lithuanian) includes introduction, 6 chapters, general conclusions, list of publications and references.

The introduction contains relevance of the dissertation, aim and tasks of the work, methodology used for research, scientific novelty and propositions to be defended.

1. Thin gas sensitive films and formation of nanostructures on the surface of the film

A review of scientific reports about gas sensing properties of metal oxides and related gas sensors is presented in this chapter. The review includes information about typical techniques for detection of the MO response to gas, the models and mechanisms of electrical response to gas in polycrystalline MO films and the current trends in the investigations. It is also reviewed the advantages and disadvantages of MO in gas sensing, pros and coins of hybrid structures with biomolecular materials in gas sensing, and solid surface modifications by SPM techniques.

2. Samples and experimental methods

This chapter of dissertation is dedicated to the methods of our investigations, particularly those based on functions of Scanning probe microscope (SPM). The fundamental principles of these methods are discussed. The sample technologies and materials are reported.

3. Relationship of properties of nanometer size metal oxide films with their response to gas

In this chapter the results obtained in the experimental studies of electrical properties and the responses to gas in thin and ultra-thin (< 50 nm) SnO_x films are summarized.

Reduction in thickness of tin oxide films generally resulted in increase of the resistance of thinner films compared to the thicker ones. An unexpected minimum of the resistance was found within the narrow interval of the films thickness from about 4 nm to 7 nm (Fig. 1). This minimum was obtained for several series of the SnO_x films separately manufactured over individual periods of the work and at various temperatures from 525 K up to about 720 K.

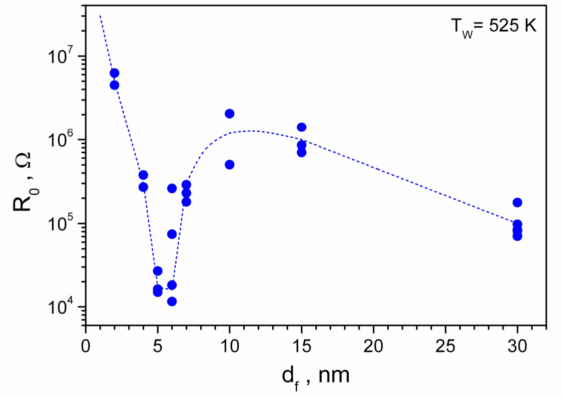


Fig.1. Clean air resistance measured in separated SnO_x films with individual thickness d_f, (working temperature was 525 K).

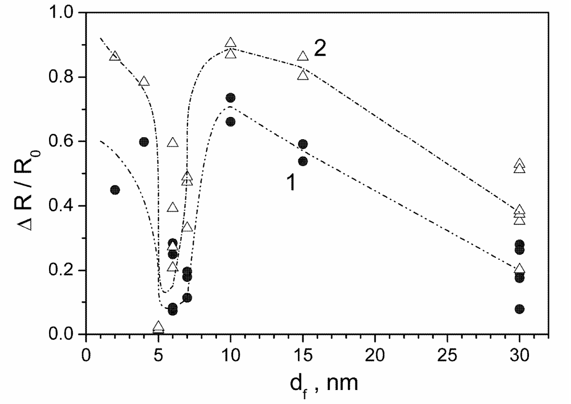


Fig.2. Relative resistance response to 12 ppm (1) and 60 ppm (2) of H_2 gas in air measured in separated SnO_x films with individual thickness d_f (working temperature was 525 K).

The resistance response to gas is also unusually dependent on the film thickness in the interval between 4 nm and 7 nm. Typical results obtained for a series of tin oxide films of individual thickness are shown in Fig. 2. The resistance response to H_2 gas was measured at the working temperature equal to 525 K. In general, the resistance response of relatively thinner tin oxide films to H_2 gas was higher if $d_f > 7$ nm. For the thinner films, a correlation between the response to gas and the film thickness seems complicated. The tin oxide films of thickness from 4 nm to 7 nm are considerably less sensitive than the sensors with relatively thinner and thicker films. The minimum of the response to H_2 gas was observed in the tin oxide films of about 5-6 nm. The thinner films are characterized by relatively higher responses to H_2 gas.

Measurements of the response to various concentrations of H_2 showed that there are no vast differences between the sensitivity of the thinner and the thicker SnO_x films (Fig. 3). On the other hand, the slope of the dependence in Fig. 3 is higher for thinner films and especially for the film thickness within the interval of 4-7 nm. In general, the dependence of the resistance response on gas concentration measured in the ultra-thin tin oxide films can be approximated by the same formulas that are commonly used for the description of the resistance response in thick tin oxide devices.

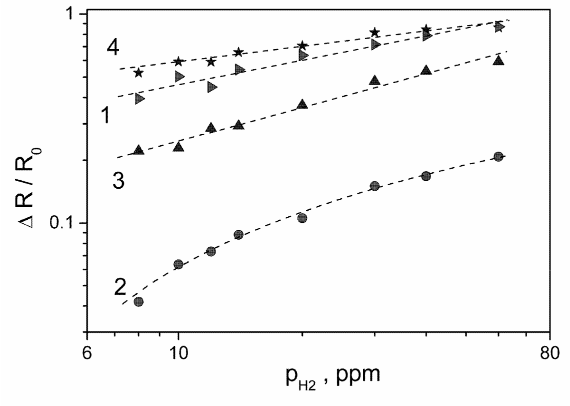


Fig.3. Dependence of the relative resistance response to H_2 gas in air on the gas partial pressure measured for individual tin oxide films thickness d_f of which are 2 nm (1), 5 nm (2), 6 nm (3) and 15 nm (4) (working temperature was 525 K).

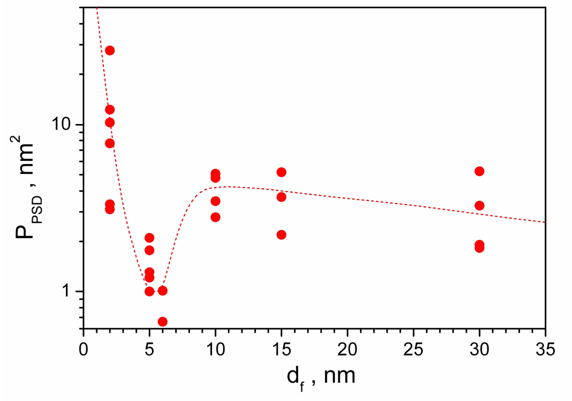


Fig.4. Integral power (P_{PSD}) obtained from the analysis of the power spectral density (PSD) for the surfaces of ultra-thin SnO_x films of individual thickness (d_f).

MO films topography of the surfaces of SnO_x films was analyzed by SPM. It was found that topography of the tin oxide film surfaces is dependent on the film thickness. In general, the surfaces seemed smooth with a few distinctive spot-like inclusions in ultra-thin films ($d_f \leq 6$ nm). In medium thin films (6 nm $< d_f \leq 15$ nm), the spot-like inclusions seemed emerging from smooth coverage, evenly spread over the surfaces. Comparably thick films ($d_f > 15$ nm) were clearly arranged in a granular structure.

Surface roughness measured by the SPM was characterized by power spectral density (PSD) that represents the amplitude of the surface's roughness as a function of the spatial frequency of the roughness. The function of the digitized surface profile (height z) is approximated by formula

$$P(f) = PSD(f) = \frac{2d_0}{N}\left|\sum_{n=1}^{N} z(n) e^{\frac{i2\pi}{N}(n-1)(m-1)}\right|^2, \; f = \frac{m-1}{Nd_0}, . \qquad (1)$$

In (1) the surface profile is digitized over length L that is sampled of N points at intervals of d_0. f is spatial frequency, $m = 1, 2, \ldots, N$. Total power is used as a characteristic of the surface roughness. The total power P_{PSD} is an integral of $P_{PSD}(f)$ over the total frequency interval. The square root of the integral equals the standard roughness R_q, i.e. root mean square (RMS) average of height deviations taken from the mean image data plane. The total power P_{PSD} is plotted as a function of the film thickness in Fig. 4. As it can be seen from Fig. 4, P_{PSD} significantly depends on the film thickness if $d_f <$ 10 nm. Higher magnitude of P_{PSD} in Fig. 4 can be explained by higher roughness of the surface while lower P_{PSD} characterizes smoother surfaces. As it follows from the results in Fig. 4, the roughest surfaces were obtained for the thinnest films. The minimum in the plot in Fig. 4 suggests that the smoothest surfaces are obtained for the films with a thickness of about 5–6 nm. The films thicker than about 10 nm are characterized by nearly the same P_{PSD} but a slight decrease of P_{PSD} in Fig. 4 can be supposed. This smoothening of the surfaces in the thicker films can be explained assuming more regular distribution of the grain shape objects in thicker films that, consequently, should result in column-like structure of relatively thick polycrystalline tin oxide films.

Such correlation between the $\mathrm{P_{PSD}}$ dependence on film thickness (Fig. 4) and resistance and the thickness (Fig. 1) has similar form to. It seems reasonable to suppose that an increase of the surface roughness in the films 6 nm < d_f < 10 nm should lead to reshaping of the electric current channel. A complex net of the connecting necks can be related to an increase of the channel length and decrease in the channel cross-section. Complex pathway for the electron transport can lead to an increase of the clean air resistance as it is in Fig. 1.

The resistance response to gas dependence on the tin oxide film thickness (Fig. 2) also qualitatively follows the line of the dependence of surface roughness and film thickness. A decrease in the response of the films 6 nm < d_f < 10 nm can be understood if suppose that smoothening of the film surfaces results in a decrease of the surface area which can be accessed by gas particles. Roughening of the film surfaces should result in increase of the surfaces exposed to gas and, consequently, these changes can lead to an increase in the resistance response.

The kinetics of the response was studied and specific parameters were extracted from the experimental results based on a transient of the response to a steep change in gas composition. The transients were described by a set of the time constants τ_i those define the response time of the gas sensitive film or sensor based on MO film. On the other hand, these time constants are determined by phenomenological rates of the surface chemical reactions, and are highly dependent on the surface properties of the films and the conditions of the surface chemical reaction. Typical time constants τ obtained for various $\mathrm{SnO_x}$ films of individual thickness are plotted as a dependence of the time constant versus films thickness in Fig. 5. It was obtained that the time constant of the sensor response is almost independent of d_f at all the sensor working temperatures from about 525 K to 720 K. And such correlation between the time constant and the film thickness was practically the same at any amount of the target gas. It was obtained from the experiments that the time constant generally decreases for all $\mathrm{SnO_x}$ films if amount of gas is increased as it is typically obtained for the metal oxide gas sensors.

It is important to note here that changes in the microstructure and thickness of the film do not produce a related change in the time constant of the response to gas. This result can be understood if suppose that the response time depends only on the rates of the surface chemical reactions but is independent on the migration of the chemisorbed gases over the surfaces of tin oxide film. Assuming that the gas particles can access all the reaction sites on the surfaces of the ultra-thin film without a delay it is understandable that the response time of the sensor is independent of the film thickness and even of the microstructure of the film.

Differences in the electrical parameters of tin oxide film gas sensors of individual thickness can not be adequately explained by gas diffusion based model. An increase of the film thickness when the columnar structure of the film is formed must result in increase of the diffusion time. Consequently, the response time of the sensor have to be longer for the sensors with thicker tin oxide film. This assumption is not supported by experimental results of the response kinetics. These results do not support the model of gas diffusion into the depth of the ultra-thin metal oxide films. The results are much more explainable in terms of the percolation theory assuming a dependence of the channel network parameters on the thickness of the films.

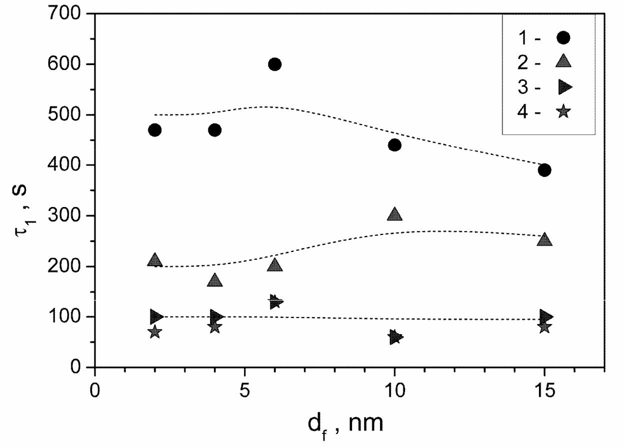


Fig.5. Time constant of the response of separated SnO_x films with individual film thickness d_f that were exposed to H_2 gas (12 ppm) in air at the working temperatures T (K): 1 – 525; 2 – 575; 3 – 625; 4 – 675.

4. Surface electrical current spot spectroscopy

This chapter presents applications of specific scanning probe spectroscopic techniques for the investigation of the properties of thin films and hybrid structures.

In films of thickness 5-10 nm the forward path of current I dependence on applied bias U_B does not correspond to the back path. The I-V dependences were represented by two lines corresponding to forward (from $-U_B$ to $+U_B$) and back ramping of the bias voltage. Typical splitting of the I-V dependences are shown in Fig.6 for the 6 nm thick SnO_x films. The split-path I-V dependences were obtained for the samples only if U_B exceeded a threshold magnitude that was about 2 V in the thicker SnO_x films ($d_f > 4$ nm). If U_B was ramped within the limits lower than the threshold magnitude, there was practically no splitting between forward and back paths in the I-V characteristics. The split I-V dependences in graphical representation have the shape of the number eight. These dependences can visually be divided into two parts corresponding to the lower branch of the curve (3 in Fig.6) and the higher branch (3’ in Fig.6). An increase of the bias voltage from $-U_B$ to $+U_B$ typically produces the lower current part in the I-V dependences. The part of the dependence corresponding to the higher curve branch is obtained during back ramping of the bias voltage from $+U_B$ to $-U_B$.

Differences in the I-V curves (Fig.6) can be explained by redistribution of oxygen vacancies in the nano-structure. The forward path of the I-V dependence is determined by a simultaneous transport of the conductance electrons and oxygen ions localized in the cell points of the metal oxide lattice. Since the MO films are non-stoichiometric, the oxygen ions can be transferred from the occupied lattice cell point to the location of the vacancy. With the negative bias voltage, the stoichiometry of the MOX film increases at the film surface to which the SPM probe is attached. As a result, the surface potential barrier increases in the contact area. In the depth of the film, the density of the vacancies (donor type defects) increases and, consequently, the density of the conductive electrons in the film also increase. The non-linear I-V characteristics describe the electron transport through the varying barrier at the MOX film surface. When the positive bias voltage exceeds the threshold magnitude the oxygen ions are forced to drift back to the volume of the MO film. Therefore the back ramping of the bias voltage results in the I-V dependence that displays the electron transport is limited by decreasing surface potential barrier.

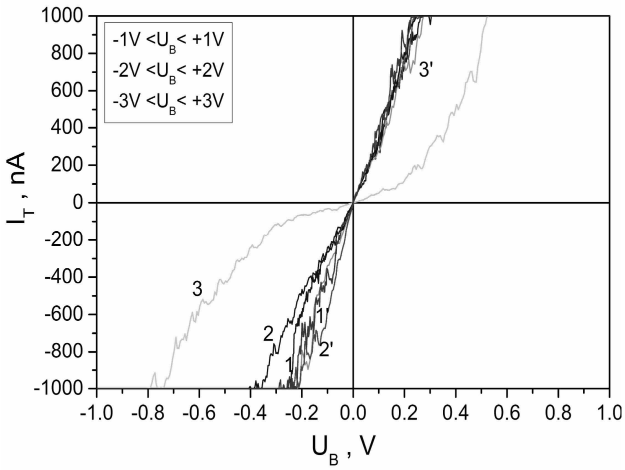


Fig.6. The SPM current-voltage dependences in a local point on the surface of SnO_x film (about 6 nm thickness). Numbers indicates voltage ramping intervals [$-U_B$, $+U_B$] and measurement path: forward (1, 2 and 3) and back (1’, 2’ and 3’) voltage ramping in clean air.

Gaseous surrounding is found to be important for SPM I-V characteristics of thin SnO_x films. Fig.7. illustrates typical I-V characteristics obtained for SnO_x films of 10 nm thickness at voltages between -5 V and +5 V in clean air and in air with CO impurity gas. The forward voltage ramping line (1 and 3) of I-V curve clearly does not match the back ramping line (2 and 4) in both atmospheres, but the difference between the two paths of the I-V curve is typically lower in CO contaminated surrounding than in clean air. For any U_B from the tested interval in the SnO_x samples, the current is always higher in presence of CO gas. Such increase in current is explained by the commonly known model of the response to reducing gases in metal oxide based sensors.

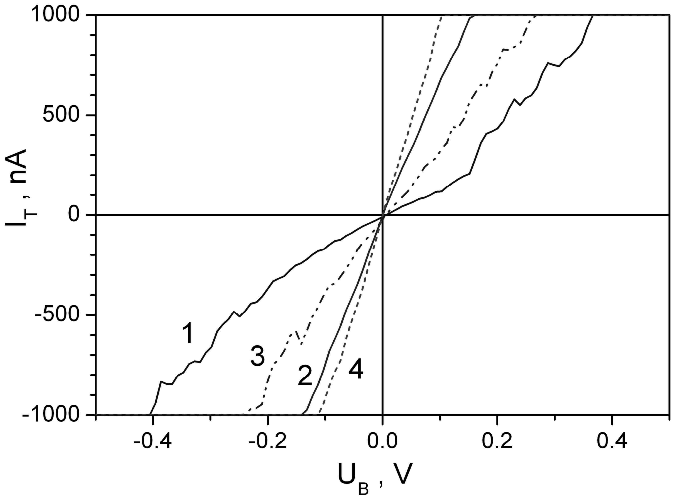


Fig.7. The SPM I-V dependences in a local point on the surface of SnO_x film of thickness about 10 nm, measured in clean air (1, 2) and in CO contaminated air (3, 4).

5. Tunneling current stimulated self assembly of the structures on nanometer thickness metal oxide films

Chapter 5 presents the formation of MO nanostructures under external electrical field. Qualitative model of formation of nanostructures on MO surfaces under electric field is presented.

As it was mention in chapter 4, electric field can cause the transport of oxygen ions in the metal oxide lattice and changes of the form of I-V dependences, but when the applied voltage amplitude is higher than threshold one, the structural changes on the surface of ultra-thin MO films can be detected. Typical changes of the structure after the SPM electric treatment are illustrated in SPM topography images (Fig.8). The results in Fig.8 were obtained on SnO_x film thickness of which was about 6.5 nm. The bias voltage U_B was applied between the SPM probe and the surface of the sample for time t. Several spots of the surface of SnO_x film were affected by electrical field with individual values of U_B and t. The experiment was carried on in the clean air atmosphere. The values of U_B and t, affected the surface shown in Fig.8, can be written in matrix form like:

$$a = \begin{pmatrix} -3V;1s & -4V;1s & -5V;1s & -7V;1s & -10V;1s \\ -3V;3s & -4V;3s & -5V;3s & -7V;3s & -10V;3s \\ -3V;5s & -4V;5s & -5V;5s & -7V;5s & -10V;5s \\ -3V;10s & -4V;10s & -5V;10s & -7V;10s & -10V;10s \\ -3V;50s & -4V;50s & -5V;50s & -7V;50s & -10V;50s \\ -3V;100s & -4V;100s & -5V;100s & -7V;100s & -10V;100s \end{pmatrix} \quad (2)$$

for the left image and

$$b = \begin{pmatrix} 3V;1s & 4V;1s & 5V;1s & 7V;1s & 10V;1s \\ 3V;3s & 4V;3s & 5V;3s & 7V;3s & 10V;3s \\ 3V;5s & 4V;5s & 5V;5s & 7V;5s & 10V;5s \\ 3V;10s & 4V;10s & 5V;10s & 7V;10s & 10V;10s \\ 3V;50s & 4V;50s & 5V;50s & 7V;50s & 10V;50s \\ 3V;100s & 4V;100s & 5V;100s & 7V;100s & 10V;100s \end{pmatrix} \quad (3)$$

for the right image in Fig.8.

In left image of Fig.8 the grains in surface topography are clearly seen, but there are no significant changes on the surface of SnO_x film on right image. The surface in left image was flat and smooth in the same area before the grain growth and was similar like surface in right one. From Fig.8 is clear that the grain forms only when the negative bias was applied to the sample. So it seems reasonable to suppose that the growth of the nano-sized structures on metal oxide films is controlled by specific mechanism that is different from that known in the surface nano-oxidation when positive bias is applied to the surface Si and isolating SiO_2 grows in the area of applied bias.

The grains of similar shape were obtained on SnO_x film surface, when thicknesses of the films were between 4 and 10 nm. Similar results were obtained on the surface of ultra-thin InO_x films, so it is reasonable to propose that such structure changes can be produced on the surfaces of ultra-thin non-stoichiometric MO films.

Such structural changes depend on the magnitude of applied bias U_B and the duration t of the bias has been applied. The height of grain linearly depends on the bias magnitude in bias interval $-10\ V < U_B < -2\ V$ and is proportional to ln(t) on duration of applied bias in interval $1\ s < t < 100\ s$.

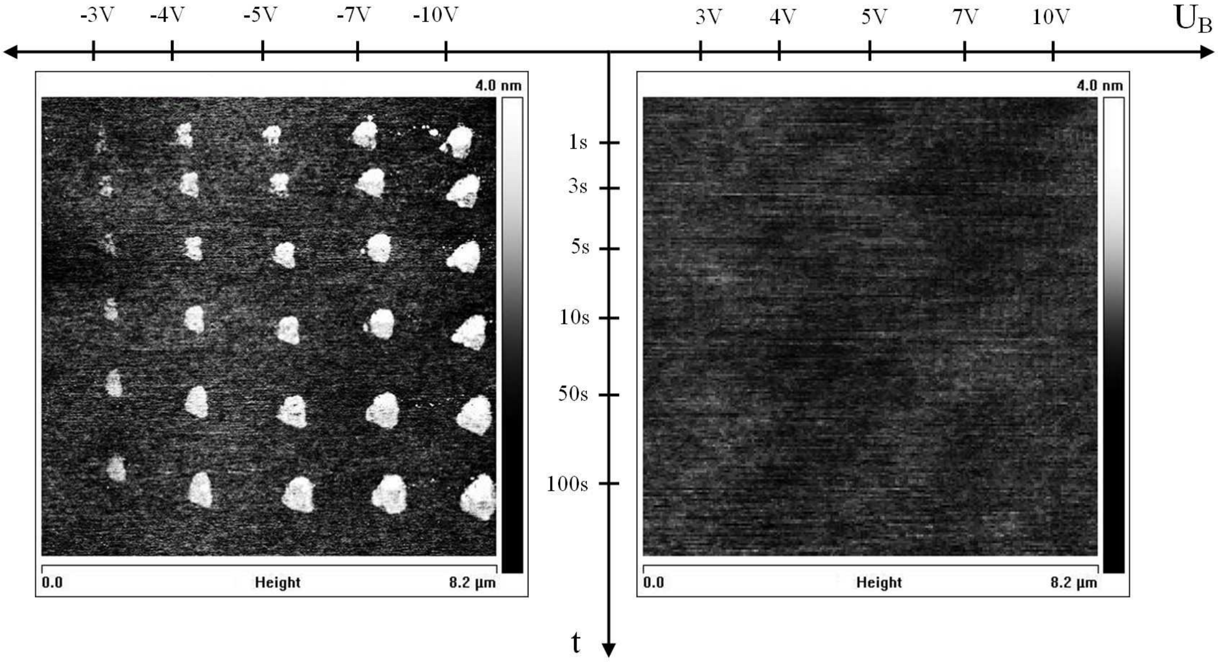


Fig.8. SPM topography images of surface after the SPM bias induced grain growth on the SnO_x film of about 6.5 nm thickness. Left image shows surface after negative bias was applied to the sample, right – positive. U_B on the scales means the magnitude of the bias, t – duration of bias was applied for.

Gaseous surrounding is found extremely important for the SPM induced nano-grain growth on the SnO_x films. Influence of the atmosphere on the volume of the grains is illustrated in Fig.9. In Fig.9 the cross sections of several grains are compared. These grains were grown in the SPM electric mode on individual areas of the same SnO_x film thickness of which was about 6 nm. The growth conditions were the same in all tests except for the surrounding gaseous mixture. The clean air, pure nitrogen atmosphere and the air with CO gas were the gaseous surroundings.

Typical results in Fig.9 demonstrate that the largest grains were obtained in the CO containing air. Comparatively large grains were also obtained in the pure nitrogen atmosphere. In rich oxygen atmosphere (the clean air) the SPM grown grains were typically much smaller compared to the CO and nitrogen surroundings. It seems reasonable to suppose that the reactive CO atmosphere is much more favorable for the growth of nano-grains on the surfaces of metal oxide films. An influence of gaseous surrounding on the SPM grain growth supports the assumption about redistribution of oxygen ions in metal oxide films. The growth of the structures in nitrogen atmosphere is stimulated by removal of the oxygen from the surface of the MO films. On the surfaces of MO films the density of chemisorbed oxygen species is controlled by adsorption and desorption of oxygen from and to the oxygen rich atmosphere. In nitrogen atmosphere desorption of oxygen effectively removes the oxygen species transferred by the electric field from the bulk to the surface. The growth of the agglomerates is much more effective in the air with reducing CO gas. The surface chemical reaction between CO and the oxygen species removes the oxygen from the metal oxide surfaces and increases an amount of the oxygen vacancies.

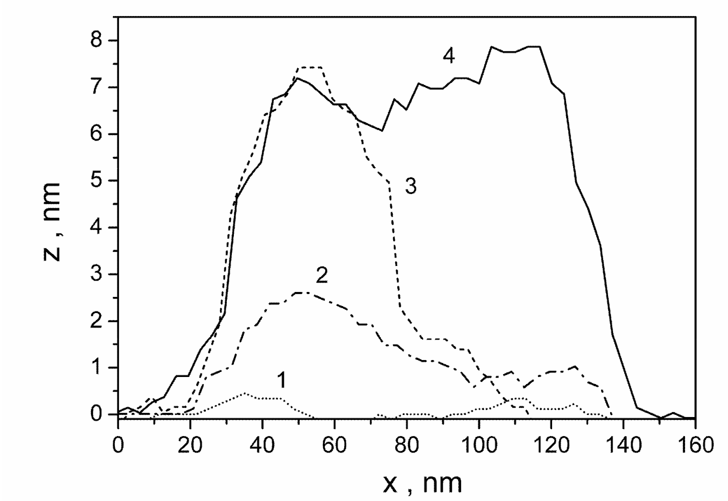


Fig.9. The cross section of the grains self-arranged on the SnO_X film characterized by the relief line (1) during the fixed point SPM tunneling current tests in clean air (2), pure nitrogen atmosphere (3) and air with 100 ppm CO (4).

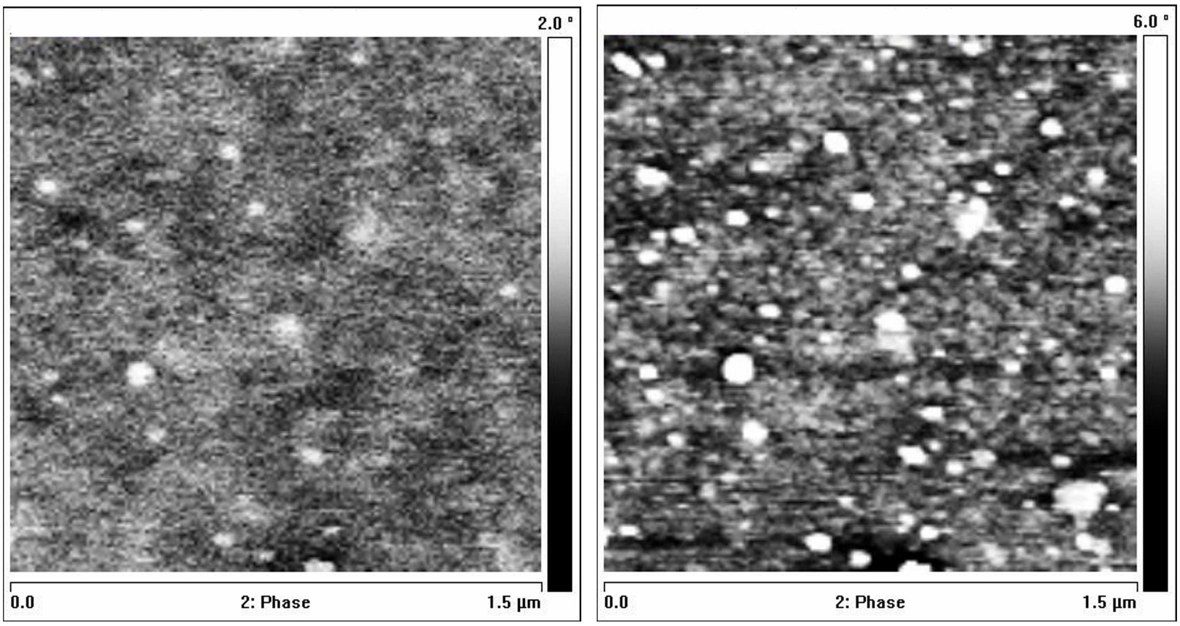
Mechanical properties of the SnO_x films and the grains formed by external electrical field were investigated by SPM force spectroscopy: force-distance curves were measured and analyzed. There were no differences in force-distance curves measured on the surface of SnO_x and grains formed by electric filed, so all mechanical properties of these two surfaces are the same.

The SPM mapping of the electric properties revealed that the local conductivity on the surface the tested films changes with enlargement of the grains. The area corresponding to the grains on the surface of SnO_x film was characterized by extremely low tunneling current. In contrast, the grains formed on the surface of thin InO_x films had higher tunneling currents comparing with currents on the surface of the rest of the film. The change in the surface conductance can be understood if significant structural changes of the films are considered. The experimental fact that the structures on MO films can be made with different electrical conductance let suppose that this method can be applied for making nanostructures on the surface MO films with various (or even selected) conductivity.

6. Investigation of hybrid structures by scanning probe microscopy

This chapter presents investigation of inner structure of continuous hybrid layers and individual components of hybrid films, which can be used for external influence detection.

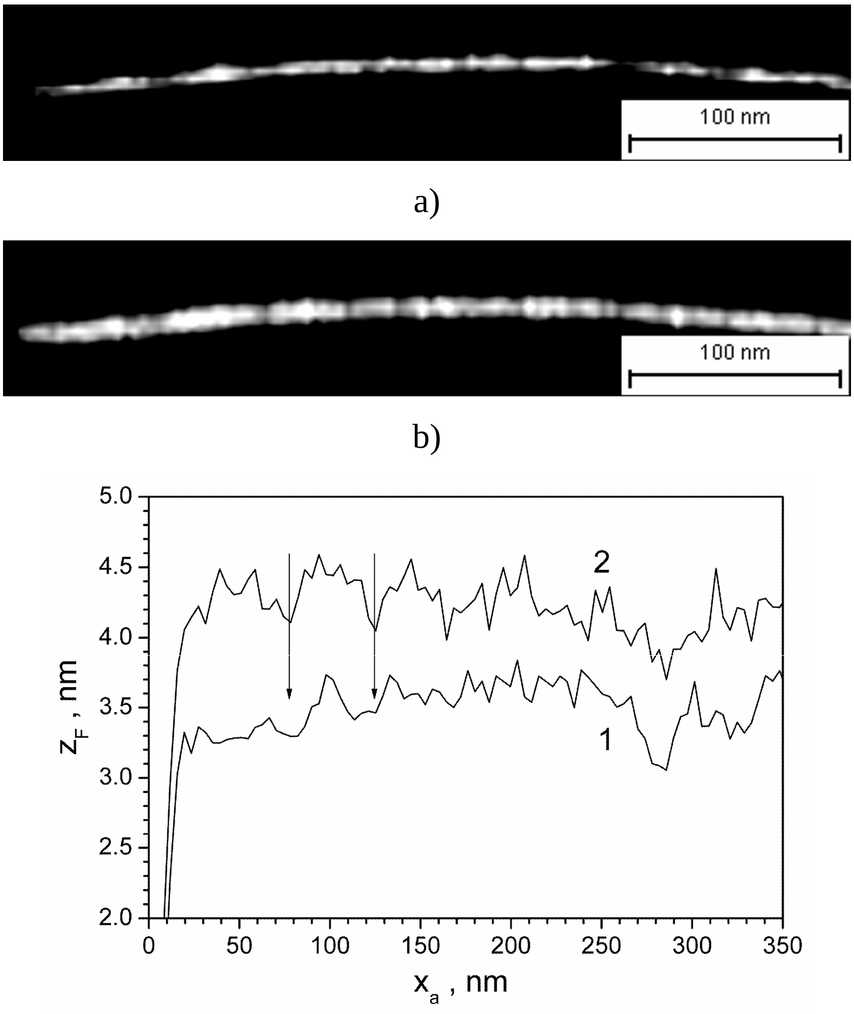
Possibility to detect inner structure of relatively thick continuous hybrid layers were shown experimentally by investigation of self-assembled DNA chains covered by silver (Ag) nanoparticles. First, there were made reference samples for each component of hybrid structures (DNA, and Ag nanoparticles). Components were deposited from colloidal solutions, dried for 15 min and rinsed with distilled water. Ag nanoparticles were deposited on mica surface and detected using Electric Force Microscopy (EFM) technique. Typical surface potential distribution over the scanned area is illustrated by electrical force sensitive phase images in Fig. 10. The bright spots represent the areas of locally charged domains of the sample surface. The two images in Fig.10 (a) and (b) were obtained for the same area of the sample between which and the tip the DC voltage difference is equal to +1 and +10 V, respectively. A larger DC voltage difference between the tip and the sample leads to a larger amplitude of oscillations of cantilever and, consequently, to a higher sensitivity to the charged domains. In Fig. 10(a), bright spots of low density can be associated with completely clean Ag nanoparticles on the top of DNA layer. Metallic nanoparticles that are partly or even completely covered by an isolating coating are explicitly displayed in the EFM phase image if the applied DC voltage is high enough. Based on comparison of the topography, standard phase and the EFM phase images, it seems that Ag nanoparticles can be visualized not only laying on the surface, but also covered by some coating or even in the bulk of the film.



a) b)

Fig.10. EFM images of the electric force phase distribution for a layer of Ag nanoparticles on mica substrate with base voltage a) +1 V and b) +10 V.

Inner structure of individual components of hybrid structures can be “seen” only when the density of elements on the surface is low. For SPM investigation of the inner structure of hybrid materials were selected Aβ40 fibrils. Typical topography images of individual fibril on the surface of mica are shown in Fig. 11. The images were obtained by scanning the sample in tapping mode. Fig. 11 (a) represents the scanning along the axis of fibril, and (b) – perpendicularly. Height distribution along the fibril is shown in section in Fig.11 (c). Section lines 1 and 2 shows similar distribution of the height of the fibril, so we can propose that height variation appears from the inner elements of the fibril, but not from mechanical damage of bio-molecules by SPM scanning. According to the Fig. 11 fibril consists of elements with the thickness of 10-20 nm and length the same as with of the fibril. Orientation of fibril inner elements is around 90 degrees to the axis of fibril.



a)

b)

c)

Fig.11. Topography of Aβ40 fibril on the surface of mica scanned along (a) and perpendicularly (b) the axis of fibril. (c) section along the fibril: line 1 taken from image (a), line 2 – from image (b).

Detection of electrical properties of individual elements of hybrid samples is showed in Fig.12. There are current distance curves plotted approaching and retracting SPM probe to or from the surface of the sample, when there were applied 20 mV voltage between the sample and the probes' tip. Curves 3 and 4 are measured on the surface of "clean" SnO_x and the curves 1 and 2 measured on the surface of SnO_x covered by the layer of streptavidin fibrils (SA). In curves 3 and 4 we can see current peaks that are almost at the same position in Z_S scale approaching and retracting SPM probe. Taking into account the pressure SPM tip creates at the surface contact area (up to 0.6 GPa), can be attributed to changing position of electronic states levels under the pressure. Current significantly decreases if the surface of MO is covered by the layer of SA (curves 1 and 2 in Fig. 12). The current measured retracting the tip is higher than the current measured approaching the surface. This can be explained by different position of the fibrils in the layer approaching and retracting the tip, and the current shown by curve 2 can be attributed to the current through the lifted fibril or/and response to external pressure.

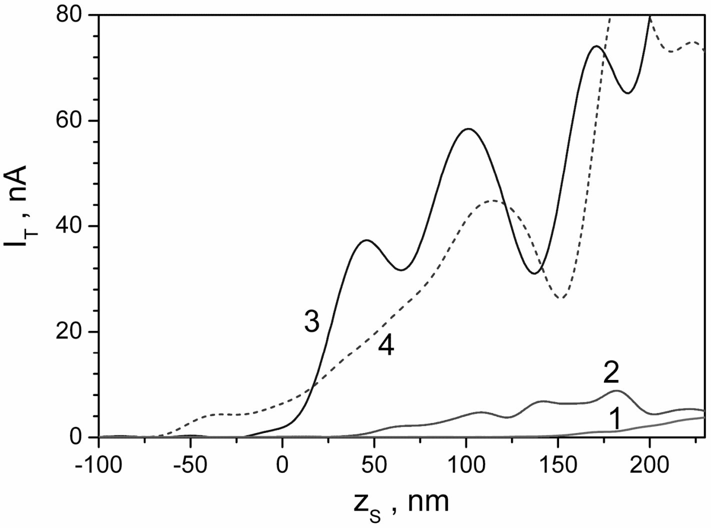


Fig.12. Dependences of electrical current through the sample on the distance of SPM probe from the surface: “clean” SnO_x 3, 4 surface, and SnO_x covered by the layer of streptavidin fibrils 1, 2.

General conclusions

1. Restructurisation of SnO_x films effects electrical response of the film to gas. Higher resistance response to gas of the SnO_x films with thickness < 4 nm and > 7 nm caused by higher ratio of surface area exposed to gas molecules and conductive cross-section of the film. Changes in the microstructure and thickness of the SnO_x film do not produce a related change in the time constant of the response to gas, i.e. time constant is independent on SnO_x film thickness (up to 40 nm). The response time depends only on the rates of the surface chemical reactions.

2. According to the experimental results on investigation of properties of thin SnO_x films morphology, electrical parameters and electrical response to gas, there were made gas sensors for detecting volatile components of propionic acid.

3. Electrical currents and changes of the currents in time that appear in nanosystems because of the charge transfer through or above the barrier depends on:1) properties of the nanosystem, 2) changes in the system caused by external factors of measurement system, such as electric field and mechanical effect and 3) interaction of nanosystem with surrounding atmosphere (air or gas).

4. It was created original method for formation of nanostructures of various conductivity on the surface of thin metal oxide films by SPM electric treatment, when negative bias is applied on the surface. Dimensions of formed nanostructures depend on electrical field magnitude and time it was applied during the formation, and also on the atmosphere composition above the metal oxide surface.

5. Combination of various Scanning probe microscopy methods were applied to investigate mechanical, electrical properties and structure of relatively thick continuous hybrid layers and individual components of noncontinuous hybrid films by making special hybrid samples.

List of Published Works on the Topic of the Dissertation
In the reviewed scientific periodical publications

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2. A. Šetkus, V. Bukauskas, A. Mironas, D. Senulienė, V. Strazdienė, Specific response of ultra-thin metal oxide films to gas, Physica status solidi (c), Vol. 6, 2753-2755 (2009).

3. V. Časaitė, S. Bružytė, V. Bukauskas, A. Šetkus, L. A. Morozova-Roche, R. Meškys, Expression and purification of active recombinant equine lysozyme in Escherichia coli, Protein Engineering, Design and Selection Vol. 22, 649-654 (2009).

4. V. Bukauskas, J. Babonas, A. Rėza, J. Sabataitytė, I. Šimkienė, A. Šetkus, Scanning probe microscopic and optical detection of DNA integration within multicomponent structures on Si surfaces, Lithuanian Journal of Physics, Vol. 48, 287-297 (2008).

5. V. Bukauskas, A. Olekas, D. Senulienė, V. Strazdienė, A. Šetkus, S. Kaciulis, L. Pandolfi, Effect of thickness in ultra-thin tin oxide film based gas sensors, Lithuanian Journal of Physics, Vol. 47, 475-483 (2007).

6. V. Bukauskas, A. Mironas, V. Strazdienė, A. Šetkus, V. Laurinavičius, R. Meškys, J. Razumienė, S. Kačiulis, and A. Mezzi, Metal-enzyme junction properties in gaseous surroundings: Conversion of biochemical reaction into electrical signal, Lithuanian Journal of Physics, Vol. 46, 513-517 (2006).

7. A. Galdikas, V. Bukauskas, S. Kaciulis, V. Laurinavičius, R. Meškys, A. Mezzi, A. Mironas, J. Razumienė, A. Šetkus, Properties of the planar ADH-dry-layer structures based on electrically controlled coupling between enzyme molecules and metal surfaces, Sensors and Actuators B: Chemical. Vol. 118, 60-66 (2006).

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1. V. Bukauskas, A. Šetkus, I. Šimkienė, J. Sabataitytė, A. Kindurys, A. Rėza, J. Babonas, DNA-controlled assemblage of Ag nanoparticles on solid surfaces, Interface controlled organic thin films, Springer proceedings in Physics, Vol. 129, 95-99 (2009).

2. V. Bukauskas, V. Strazdienė, A. Šetkus, S. Bružytė, V. Časaitė, R. Meškys, β-Sheeted Amyloid Fibril Based Structures For Hybrid Nanoobjects On Solid Surfaces, Interface controlled organic thin films, Springer proceedings in Physics, Vol. 129, 61-65 (2009).

3. A. Šetkus, V. Bukauskas, S. Pavliuk, S. Bružytė, V. Časaitė, R. Meškys, Self assemblage of beta sheeted structures on solid state film for biosensors, e-Journal of Surface Science and Nanotechnology, Vol. 7, 491-496 (2009).

4. V. Bukauskas, A. Šetkus, Lizocimo nanofibrilių savitvarka kietojo kūno paviršiuje, 11-osios Lietuvos jaunųjų mokslininkų konferencijos „Mokslas – Lietuvos ateitis“ medžiaga, Vilnius: Technika, 88-95 (2008).

5. V. Bukauskas, A. Šetkus, Dujoms jautrios SnO plėvelės formavimosi ir savybių kitimo tyrimas SZM metodu, 10-osios Lietuvos jaunųjų mokslininkų konferencijos „Mokslas – Lietuvos ateitis“ medžiaga, Vilnius: Technika, 126-132 (2007).

About the author

Virginijus Bukauskas was born in Kupiskis district the village of Aukstupenai, on the 16th of June 1979. The degree – bachelor of physics – he obtained in Faculty of Physics, Vilnius University, in 2002. In 2004 he received master degree in the material science in Faculty of Physics, Vilnius University. In 2005-2009 he was PhD student of Semiconductor Physics Institute. At present he is junior research assistant in Sensors Laboratory of the Semiconductor Physics Institute of Centre for Physical Sciences and Technology.

DUJOMS JAUTRIŲ HIBRIDINIŲ DARINIŲ IR NANOSISTEMŲ INTEGRUOTŲ METALO OKSIDO PLĖVELĖSE KŪRIMAS IR TYRIMAI SKENUOJANČIO ZONDO MIKROSKOPIJOS METODAIS

Tiriamoji problema ir darbo aktualumas.

Elektroninės sistemos skirtos kvapo detekcijai ir atpažinimui (dar vadinamos elektroninėmis nosimis) paprastai yra pagrįstos neselektyviais jutikliais, kurie, vis tik, charakterizuojami individuliais parametrų rinkiniais. Tokių sistemų pritaikomumas praktikoje, efektyvumas, patikimumas ir atsako trukmė ženkliai priklauso nuo jutiklių, atrinktų į atpažinimo modulio masyvą, įvairovės. Kadangi šių sistemų praktinio pritaikymo sritys sparčiai plečiasi, tai vis dažniau reikia metodų ir technologijų, leidžiančių kurti naujo tipo cheminius jutiklius bei modifikuoti jų parametrus. Šiuo metu metalų oksidai (MO), pvz. alavo ir indžio oksidai, yra dažniausiai dujų jutikliams, tinkantiems praktinėms elektroninėms nosims, gaminti naudojamos medžiagos. Pagrindiniai MO populiarumą lemiantys privalumai yra: greitas atsako laikas, didelis jautrumas, atkartojamumas, stabilumas, pigi gamyba. Pastarųjų metų tyrimų rezultatai rodo, kad MO išlieka perspektyvia medžiaga ateities jutiklių gamyboje, MO mažinant iki nanometrinių matmenų arba kombinuojant, pvz. su biomolekulėmis turinčiomis unikalų cheminės sąveikos keitimo į fizinį atsaką mechanizmą. Cheminė sąveika paviršiuje paprastai sukelia elektrinių MO jutiklio savybių pokyčius. Elektrinį atsaką galima paaiškinti remiantis modeliu taikomu polikristaliniuose MO sluoksniuose. Polikristaliniame MO sluoksnyje susiformavęs dvigubas Šotki barjeras lemia elektronų pernašą per kontaktą tarp granulių. Kadangi barjeras priklauso nuo paviršinio krūvio, o pastarasis nuo paviršiuje chemisorbuotų dujų, tai sluoksnio elektrinis laidumas priklauso nuo atmosferos sudėties. Ore, kuriame yra daug deguonies (~21%), deguonis dominuoja MO paviršiuje užimtose chemisorbuotuose būsenose ir lemia paviršines chemines reakcijas su dujomis. Dominuojantis chemisorbuotas deguonis lemia fundamentines MO jutiklių selektyvumo ribas. MO nanosistemų ir kombinuotų darinių kūrimas atveria naujas galimybes, sprendžiant kvapo atpažinimo problemas.

Remiantis dujų difuzijos tyrimais tikimasi, kad atsako trukmė turėtų būti mažesnė plonesniuose sluoksniuose lyginant su storesniais. Atsako trukmė nanometriniuose sluoksniuose gali daug ryškiau priklausyti nuo procesų vykstančių nanosistemose, negu nuo klasikinių efektų. Faktoriai lemiantys atsako selektyvumą gali būti itin specifiniai nanosistemose ir ypač kombinuotuose dariniuose. Šių atsako ypatybių supratimas yra svarbus kuriant naujas dujoms jautrias sistemas.

Nanometrinių darinių charakterizavimas: struktūros, elektrinių savybių, atsako į išorinį poveikį, fizikinių savybių kitimo, taip pat paviršiaus-tūrio sistemos ypatybių nustatymas yra svarbus vystant nanodarinių technologiją ir jų taikymo metodus. Skenuojančio zondo mikroskopas (SZM) yra instrumentas įgalinantis vienu metu matuoti keletą fizikinių parametrų pasirinktuose bandinio paviršiaus taškuose arba plotuose su nanometrine (subnanometrine) skiriamąja geba. Specialiai parenkant SZM valdymo parametrus, galima sukelti taškinius paviršiaus fizikinių savybių pakitimus, o tai leidžia pritaikyti SZM įvairiuose nanotechnologijos procesuose. Įvairius fundamentinius SZM taikymo, dujoms jautrių darinių technologijoje bei jų charakterizavime, aspektus vis dar reikia suprasti ir ištirti.

Darbo tikslas. Pritaikyti SZM metodus ultraplonųjų dujoms jautrių metalų oksidų (MO) sluoksnių, kurie gali būti panaudoti nanosistemoms bei hibridinėms medžiagoms konstruoti naujo tipo cheminiuose jutikliuose, taškinių ir paviršiaus savybių charakterizavimui.

Darbo uždaviniai.

Ištirti įvairaus storio MO sluoksnių morfologijos dėsningumus ir nustatyti jų sąryšį su elektriniu atsaku į dujas ir jo kinetika.

Nustatyti fizikinius procesus lemiančius SZM metodais kontroliuojamą nanodarinių formavimą MO paviršiuje.

Ištirti technologinių faktorių (elektrinio lauko, dujinės aplinkos, jėgos) įtaką MO plėvelių nanosistemų fizikinėms savybėms.

Pritaikyti SZM metodus hibridinių darinių, sudarytų iš bio-molekulinių medžiagų, morfologijos, elektrinių ir mechaninių savybių tyrimui.

Tyrimų metodika. Metalo oksidų (MO) sluoksniai buvo auginami DC magnetroninio garinimo metodu. Elektrinės MO savybės ir atsakas į dujas buvo tiriamas dc-varžos matavimais. Atmosfera su pasirenkamomis dujų koncentracijomis buvo sukuriama specialioje srauto kontrolės sistemoje, sumaišant fiksuotą deguonies arba azoto kiekį su tam tikru kiekiu grynų lakiųjų komponentų iš kalibruotų konteinerių, specialioje dujų jutiklių testavimo kameroje. Paviršiaus tyrimai ir modifikavimas buvo atliekami naudojant įvairius Skenuojančio zondo mikroskopijos (SZM) metodus. Hibridiniai sluoksniai formuoti savitvarkio formavimosi ant kietojo paviršiaus iš koloidinių tirpalų metodais.

Mokslinis naujumas. Rengiant disertaciją buvo gauti nauji moksliniu požiūriu rezultatai dujoms jautrių medžiagų ir medžiagų mokslo srityse:

Ultraplonųjų MO sluoksnių fizikinių savybių tyrimams pritaikytas Veeco SZM TUNA metodas.

Pasiūlytas originalus metodas SZM suformuoti, įvairiomis elektrinėmis savybėmis pasižyminčias, nanosistemas plonųjų MO plėvelių paviršiuje.

Įrodyta, kad specifinė deguonies pernaša MO nanosistemose lemia nanoobjektų augimą MO plėvelių paviršiuje, o šių objektų formavimasis priklauso nuo atmosferos sudėties.

Įrodyta, kad atsako į dujas amplitudės ir kinetikos priklausomybę nuo plėvelės storio labiau įtakoja struktūriniai pasikeitimai MO sluoksnyje negu dujų difuzija į sluoksnį.

Parodyta, kad paviršiaus savybes nanometriniuose MO paviršiaus plotuose galima individuliai ir tikslingai modifikuoti tiek SZM nanoobjektų auginimu, tiek daugiamolekulinių 3D objektų, su/be biochemiškai aktyviais centrais, nusodinimu.

Praktinė reikšmė.

Remiantis šių tyrimų rezultatais, ilgalaikis MO dujų jutiklių parametrų dreifas iš dalies gali būti paaiškinamas deguonies persiskirstymu plonosiose MO plėvelėse veikiant išoriniam elektriniam laukui. Darbe aprašomi fundamentalūs aspektai, vertingi siekiant pagerinti jutiklių stabilumą. Aprašomas originalus MO plėvelių, pasirinktose paviršiaus vietose, nanomodifikavimo metodas bei daugiakomponenčių nanojutiklių iš kietojo kūno ir hibridinių medžiagų formavimo principai.

Ginamieji teiginiai

1. Ginamasis teiginys:

Nanometrinių alavo oksido plėvelių elektrinis atsakas į dujas priklauso nuo sluoksnio struktūros ir jos lemiamo krūvininkų pernašos mechanizmo.

2. Ginamasis teiginys:

Išorinio poveikio įtaka paviršinių nanostruktūrų savybėms eksperimentiškai gali būti aprašomi specialiomis Skenuojančio zondo spektroskopijos charakteristikomis, pagrįstomis kontaktinių elektros srovių priklausomybe nuo zondo potencialo ir jo prispaudimo jėgos.

3. Ginamasis teiginys:

Plonosiose metalo oksido plėvelėse išorinis elektrinis laukas gali nulemti tūrinio deguonies judėjimą į paviršių ir su tuo susijusį metalo oksido nanoobjektų formavimąsi, jei charakteringųjų parametrų pokyčiai viršija tam tikrą slenkstinę vertę. Vientisosios medžiagos nanoobjekto ir pagrindo sluoksnio mechaninės savybės sutampa, kai tuo tarpu elektrinės savybės priklauso nuo medžiagos, išorinio poveikio bei formavimosi sąlygų ir gali būti nevienodos darinio tūryje.

4. Ginamasis teiginys

Skenuojančiojo zondo mikroskopijos metodai leidžia aprašyti santykinai vientisų hibridinių medžiagų apibendrintąsias elektrines ir mechanines savybes, o komponentų charakteristikos gali būti įvertintos tik santykinai mažo tankio, trūkiuose hibridiniuose dariniuose ant kietojo paviršiaus.

Darbo apimtis. Disertaciją sudaro 7 skyriai ir įvadas. Pirmame skyriuje apžvelgiami iki šiol atlikti tyrimai plonasluoksnių dujoms jautrių plėvelių srityje bei paviršiaus modifikavimas SZM metodais. Antras skyrius skirtas aprašyti naudojamoms matavimų bei bandinių gamybos metodikoms. Trečiajame skyriuje pateikiami plonųjų SnO_x sluoksnių morfologijos, elektrinių parametrų ir atsako į dujas eksperimentinių tyrimų rezultatai ir jų interpretacija. Ketvirtasis skyrius skirtas apibendrinti originalų būdą skirtą aprašyti plonųjų metalo oksidų sluoksnių bei hibridinių paviršių charakteristikoms, gaunamomis kombinuojant tunelinių srovių ir SZM jėgų spektroskopijas su taškinio kontakto srovių spektroskopija, pagrįsta srovės priklausomybėmis nuo prijungtos įtampos tarp zondo bei paviršiaus, ir nuo zondą veikiančios jėgos bei jos krypties. Penktajame skyriuje aptariamas sukurtas originalus metodas, tinkantis nanostruktūroms MO paviršiuje formuoti bei tų struktūrų elektrinėms savybėms keisti. Šeštajame skyriuje aptariami originalūs hibridinių paviršių tyrimų rezultatai, gauti pritaikant ir savitai kombinuojant kontaktines ir nekontaktines SZM metodikas. Septintame skyriuje pateikiamos bendrosios disertacijos išvados, ginamieji teiginiai ir publikacijų sąrašas disertacijos tema.

Darbo apimtis yra 137 puslapiai, tekste panaudotos 58 numeruotos formulės, 76 paveikslai.

Bendrosios išvados

SnO_x sluoksnių struktūros persitvarkymas dėl klasterizavimosi augimo metu iš tolydinės (d_f = 4-6 nm) į polikristalinę (d_f > 15 nm) padidina atsaką į dujas dėl to, kad padidėja santykis tarp paviršiaus ploto ir laidžiojo sluoksnio tūrio. Esant ženkliam atsako į dujas padidėjimui dėl struktūros pasikeitimo, atsako charakteringoji trukmė praktiškai nepasikeičia.

Remiantis plonųjų SnO_x sluoksnių morfologijos, elektrinių parametrų, bei elektrinio atsako į dujas tyrimų rezultatais, buvo pagaminti dujų jutikliai propioninės rūgšties lakiųjų komponentų detekcijai ir sumontuoti specialioje dujų atpažinimo sistemoje.

Nanosistemose dėl krūvininkų tuneliavimo per barjerą arba aktyvacinio pobūdžio krūvio pernašos atsirandančios taškinės elektrinės srovės ir jų kitimas laike priklauso: 1) nuo pačios nanosistemos savybių; 2) pokyčių toje sistemoje sukeltų matavimo metu atsirandančių veiksnių (elektrinio lauko, mechaninio poveikio ir pan.) ir 3) nanosistemos sąveikos su oru arba dujine aplinka.

Sukurtas originalus metodas, tinkantis nanostruktūroms MO paviršiuje formuoti bei tų struktūrų elektrinėms savybėms keisti. Šis metodas skiriasi nuo gerai žinomo paviršiaus nanooksidinimo, skirto cheminiam poveikiui atsparaus sluoksnio formavimui, tuo, jog gali būti pritaikytas formuoti įvairaus elektrinio laidumo nanostruktūras MO paviršiuje.

Eksperimentiškai pademonstruota, kad panaudojant matavimo įrangos poveikį į tiriamąjį objektą, galima aprašyti paties objekto savybes, pvz. kombinuojant mechaninį poveikį su elektriniais matavimais.

Pritaikius originalius pakeitimus ir savitas SZM metodų kombinacijas eksperimentais pademonstruoti būdai, gauti hibridinių paviršių charakteristikas, aprašančias struktūrines, chemines ir elektrines savybes įvairiais aspektais, priklausančiais nuo mikroskopo taikymo metodikos.

Įrodyta galimybė sukurti ant kietųjų paviršių (Si) periodiškai išsidėsčiusius tvarkingus hibridinius darinius, kurių savitvarka priklauso nuo apgalvotai pasirenkamų išorės faktorių, tokių kaip priemaišiniai jonai Fe^{3+} bei magnetinis laukas.

Įrodyta, kad nors ir esantys nestabilūs tirpaluose, nusodinti ant kietojo paviršiaus, dauguma biomolekulinių darinių išlaiko savo formą ir neyra ilgiau negu 0,5 metų, todėl iš jų suformuotus hibridinius darinius galima taikyti praktikoje.

Trumpos žinios apie autorių

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