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R. VITER, V. SMYNTYNA, I. KONUP, I. LYDINA, J. PUUSTINEN, J. LAPPALAINEN, V. IVANITSA.

Experimental physics department, Odessa I. I. Mechnikov University, Odessa, Ukraine,
+38067 66 39 327, viter_r@mail.ru
Microbiology department, Odessa I. I. Mechnikov University, Odessa, Ukraine
Department of Electrical and Information Engineering,
University of Oulu, Oulu, Finland

INVESTIGATION OF OPTICAL AND STRUCTURAL PROPERTIES OF TIN OXIDE-PORPHYRIN STRUCTURES FOR OPTICAL SENSORS APPLICATION.

Tin oxide-porhyrin structures deposited on glass substrates have been investigated for 2-Mercaptoethanol detection. Tin oxide layer was deposited by electro-spray pirolysis. Porphyrin layers were grown by dipping the substrates into porphyrin solution in water and toluene. Structural properties were characterized by XRD and AFM methods. Optical transmittance in range of 200–1100 nm of the structures was performed before and after adsorption of 2-Mercaptoethanol on their surfaces. Optical response of the structures to 2-Mercaptoethanol at room temperature is reported. The influence of 2-Mercaptoethanol adsorption to optical transmittance was discussed.

INTRODUCTION.

Tin oxide is well known material for sensor application. Tin dioxide sensitive properties were studied by many authors. In spite of good sensitivity to different compounds it has low selectivity, which was compensated by varying of operation temperature or using metal dopants.

Porphyrins are often used for optical sensor applications [1,2]. It was reported that adsorption of molecules on porphyrin structures changed absorption spectra in visible light [2]. Absorption maximum position shift was observed under gas molecules adsorption [2].

2-Mercaptoethanol is organic liquid used in some biological applications. 2-Mercaptoethanol is considered a toxin, causing irritation to the nasal passageways and respiratory tract upon inhalation and irritation to the skin.

The combination of tin oxide and porphyrins deposited by sol gel method was already successfully used for gas detection [3]. It is expected that layered SnO_2-porphyrin structure are suitable for 2-Mercaptoethanol detection.

In the previous works tin oxide-porphyrine sensors were based on resistivity measurements. In this case additional power was consumed to heat them up to operating temperatures of 200–350 ^{0}C. On the other hand, optical sensors based on absorbance and transmittance measurements operate at room temperatures.

In the present work, optical, structural characterization of tin oxide-porphyrine structures and sensitivity tests to 2-mercaptoethanol are reported.

EXPERIMENTAL.

Tin oxide layers were deposited by electro-spray pirolysis technique.Tin chloride ethanol solution with 0.01 mol/l concentration was used. Deposition of the layers was performed on glass substrates at 330 ^{0}C with 17 kV of applied voltage.

5, 10, 15, 20-tetrakis-(N-methyl-4-pyridyl)-porphynato-Cu-tetra iodide (Cu-Porph) and 5, 15-di –(N-methyl-4-pyridyl)-10,20-di (n-nonyl)-porphynato-tin dichloride (Sn-Porph) were deposited on top of tin oxide layer by dip coating into water and toluene solutions, correspondently.

Structural properties of the deposited films were investigated with X-ray diffraction (XRD) and Atomic Force microscopy (AFM) methods.

Phase identification of as deposited and annealed films has been studied by means of XRD (Philips MW 1380) instrumentation with CuKα radiation (λ=0,154 nm). The incident angle of X-rays was 2°. The measurements were performed with a constant speed 1/8 °/min in the 2θ range 20–60°.

Atomic force microscopy (Veeco Dimensions 3100) was used to investigate the surface morphology of obtained samples in tapping mode. The bearing area curves (BAC) and rms roughness R_q values have been calculated from AFM images to show surface morphology of the samples.

For optical characterization of the samples UV-1700 UV-VIS spectrophotometer has been used. Transmittance spectra have been measured at the range of wavelengths 200–1100 nm with 1 nm step.

RESULTS AND DISCUSSION.

XRD spectra of tin oxide films are plotted in fig.1. The one can see peaks at 26.5, 34.4 and 51.6, corresponding to tetragonal phase of tin oxide. By means of numerical methods average grain size d and lattice strain ε were estimated from XRD data. The obtained values for d and ε were 7 nm and 0.0027, correspondently.

The surface images of SnO_2 and SnO_2-porphyrin films are presented in fig.2. Tin oxide surface consisted of surface agglomerates with average dimension 100 nm (fig.2a). The roughness value Rq for tin oxide film was 26 nm.

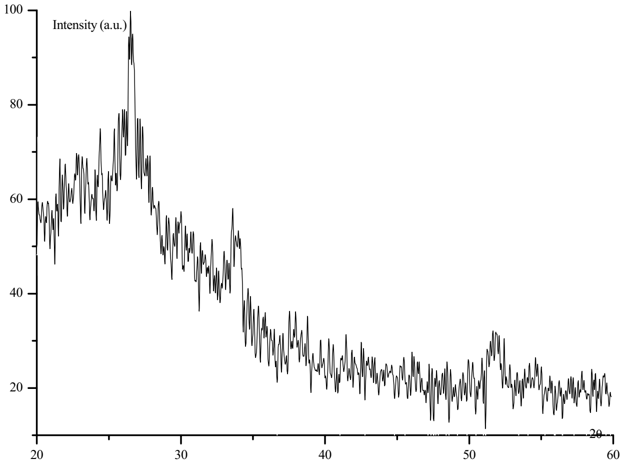
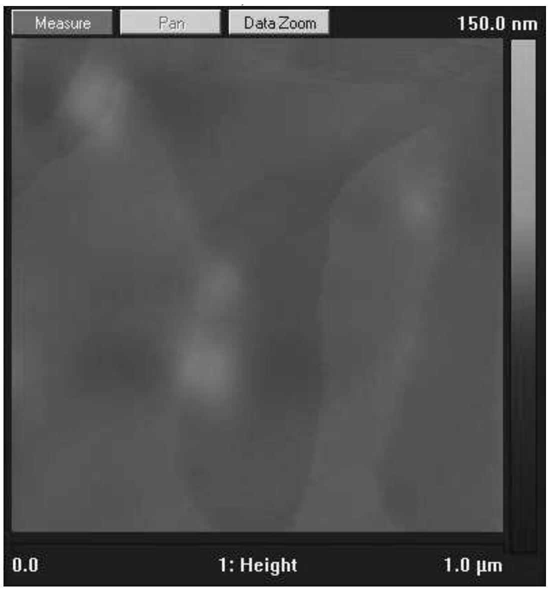
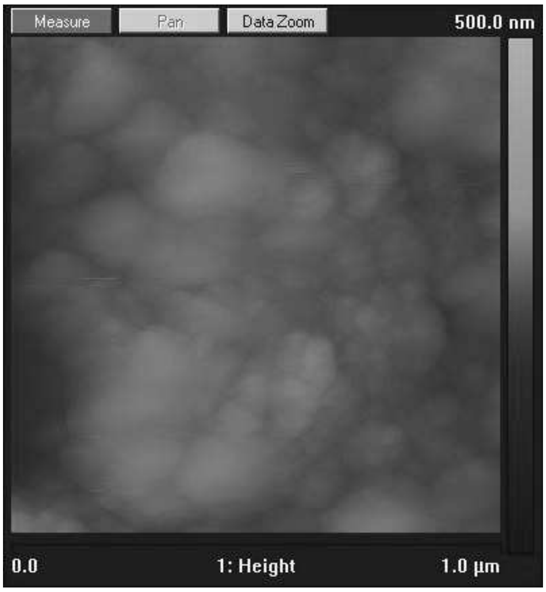


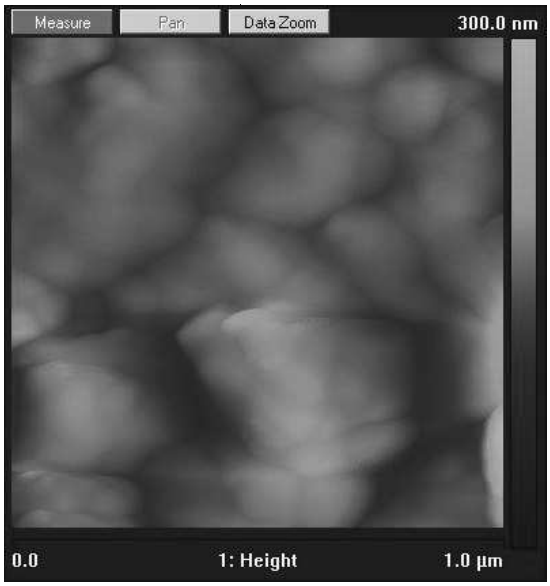
Fig.1. XRD spectrum of tin oxide layer.



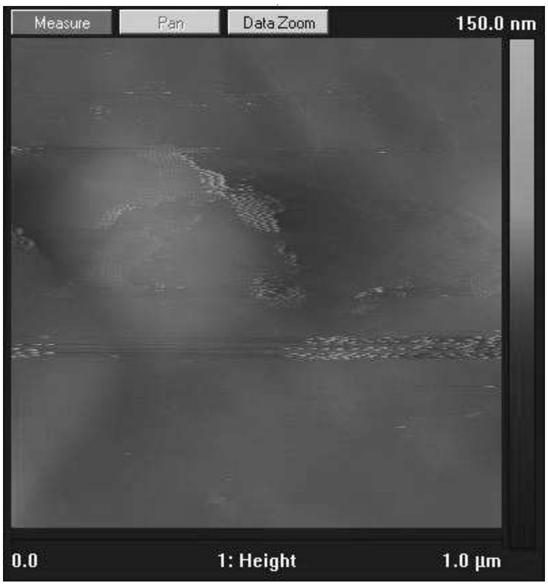
c)



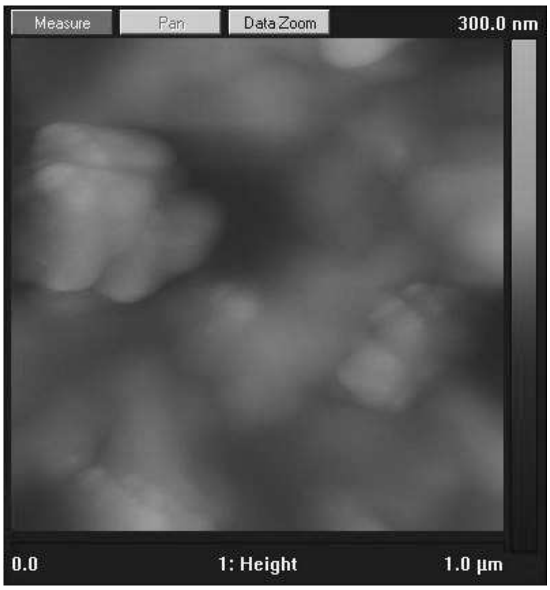
a)



d)



b)



e)

Fig. 2: AFM image: a) SnO_2, b) Cu-Porph, c) Sn-Porph, d) SnO_2-Cu-Porph, e) SnO_2-Sn-Porph.

Surface structure of porphyrins was really smooth (Rq=1.2ч1.4 nm) (fig.2b, 2c). After deposition of porphyrin layers on top of tin oxide the surface was still rough (fig.2d, 2e). The surface roughness (Rq) was about 21 and 18,5 nm for SnO_2-Cu-Porph and SnO_2-Sn-Porph, correspondently. It can be concluded that porphyrin layer 'smoothes' tin oxide surface.

Optical transmittance data of the samples are plotted in fig.3, 4. Both Cu-Porph and Sn-Porph transmittance spectra have minimums at 418 nm (fig.3b) and 440 (fig.4b) corresponding to the Soret band. The Q-band is absent for Cu-Porph but appears for Sn-Porph as transmittance minimums at 570 and 610 nm (fig.4b). After deposition of porphyrins on top of tin oxide film, blue shift of minimums was observed for Sn-Porph and red shift was Cu-Porph (fig3c, fig.4c). In case of Cu-Porph, minimum transformed to plateau (fig3c). This phenomenon is similar to the one observed in [4] where red shift of minimums was observed. The shift of the transmittance minimums indicates the occurrence of a strong interaction between tin oxide and porphyrin [4]. It was shown that porphyrins mostly exist as monomers on metal oxides. The heteroaggregates formation is possible between them what leads to optical properties changes [4].

Transmittance spectra of the sample were measured after 2-Mercaptoethanol adsorption on the their surface. The response of the samples to 2-Mercaptoethanol was different: the transmittance value dropped for SnO_2-Sn-Porph and enhanced for SnO_2-Cu-Porph structures in the range of 410–430 nm (fig. 3d, fig.4d).

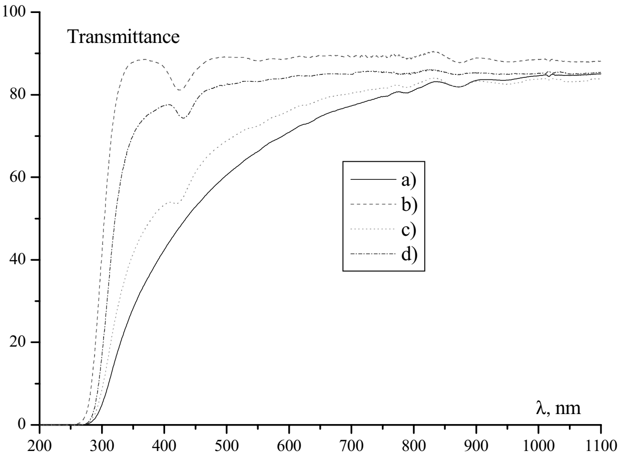


Fig. 3. Transmittance spectra: a) SnO_2, b) Cu-Porph, c) SnO_2-Cu-Porph, d) SnO_2- Cu-Porph-2-Mercaptoethanol.

It is known that tin oxide is poorly sensitive to organic compounds at room temperatures [3]. Therefore, porphyrine is key point in interaction between the structures with 2-Mercaptoethanol. As Soret bands correspond to ϖ-electrons transitions [5] the possible mechanism of 2-Mercaptoethanol adsorption comes through interaction adsorbed molecules with unsaturated bonds of porphyrins. It results to changes in heteroaggregates bonding and brings to optical changes.

However, it is necessary to perform additional measurements of electrical properties to reveal or contradict this interaction mechanism. Next works will be devoted to resolution of this problem.

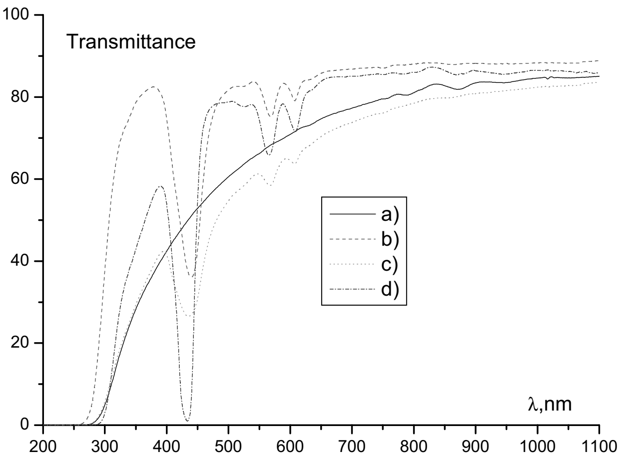


Fig. 4. Transmittance spectra: a) SnO_2, b) Sn-Porph, c) SnO_2-Sn-Porph, d) SnO_2- Sn-Porph-2-Mercaptoethanol.

CONCLUSION.

Porphyrins form heteroaggregates with tin oxide after their deposition on top of metal oxide surface what was proofed by Soret band shift and AFM data. 2-Mercaptoethanol adsorption on top of the surface led to transmittance changes what can be used in optical sensors. Adsorption mechanism can be explained by interaction of 2-Mercaptoethanol with unsaturated bonds of porphyrins.

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Tin oxide-porhyrin structures deposited on glass substrates have been investigated for 2-Mercaptoethanol detection. Tin oxide layer was deposited by electro-spray pirolysis. Porphyrin layers were grown by dipping the substrates into porphyrin solution in water and toluene. Structural properties were characterized by XRD and AFM methods. Optical transmittance in range of 200—1100 nm of the structures was performed before and after adsorption of 2-Mercaptoethanol on their surfaces. Optical response of the structures to 2-Mercaptoethanol at room temperature is reported. The influence of 2-Mercaptoethanol adsorption to optical transmittance was discussed.
Key words: tin oxide, porphyrin, optical sensors, 2-Mercaptoethanol detection.

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Р. В. Вітер, В. А. Сминитна, І. П. Конуп, І. Лидіна, Я. Пуустінен, Ю. Лаппалайнен, В. О. Іваниця.

ДОСЛІДЖЕННЯ ОПТИЧНИХ ТА СТРУКТУРНИХ ВЛАСТИВОСТЕЙ СТРУКТУР ОКСИД ОЛОВА-ПОРФІРИН ДЛЯ ОПТИЧНИХ СЕНСОРІВ.

Резюме
У роботі досліджено властивості структур оксид олова-порфірин для визначення молекул меркаптоетанолу. Оксид олова було нанесено методом електро-спрей піролізу на скляні підкладинки. Порфірини наносилися із розчинів органічних сполук. Структурні властивості зразків було досліджено за допомогою методів дифракції рентгенівського випромінювання та атомно-силової мікроскопії. Оптичні властивості було досліджено в діапазоні хвиль 200—1100 нм. Визначено вплив адсорбції меркаптоетанолу на оптичні властивості структур та обговорено механізм взаємодії молекул з поверхнею зразків.
Ключові слова: оскид олова, порфірин, оптичні сенсори, детектування меркапотетанолу.

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Р. В. Витер, В. А. Смынтына, И. П. Конуп, И. Лыдина, Я. Пуустиннен, Ю. Лаппалайнен, В. А. Иваница.

ИССЛЕДОВАНИЕ ОПТИЧЕСКИХ И СТРУКТУРНЫХ СВОЙСТВ СТРУКТУР ОКСИД ОЛОВА- ПОРФИРИН ДЛЯ ОПТИЧЕСКИХ СЕНСОРОВ.

Резюме
В работе исследованы свойства стурктур оксид олова- порфирин для определения молекул меркаптоэтанола. Оксид олова наносился на стеклянные подложки при помощи метода электро-спрэй пиролиза. Порфирины наносились из растворов органических растворителей. Структурные свойства образцов изучались при помощи методов дифракции рентгеновского излучения и атомно-силовой микроскопии. Оптические свойства были исследованы в интервале длин волн 200—1100 нм. Установлено влияние адсорбции меркаптоэтанола на оптические свойства структур и предложен механизм взаимодействия молекул с поверхностью образцов.
Ключевые слова: оксид олова, порфирин, оптические сенсоры, определение меркаптоэтанола.