Available online at www.sciencedirect.com

SciVerse ScienceDirect

Procedia Engineering 25 (2011) 276 – 279

Procedia Engineering

www.elsevier.com/locate/procedia

Proc. Eurosensors XXV, September 4-7, 2011, Athens, Greece

Tin dioxide nanofilms as sensitive detectors for surface plasmon resonance phenomenon

V.S. Grinevich[a]a*, I.E. Matyash[b], L.S. Maximenko[b], O.N. Mischuk[b], S.P. Rudenko[b], B.K. Serdega[b], V.A. Smyntyna[a], L.N. Filevskaya[a]

[a]*Departmen of Experimental Physics, Odessa I.I. Mechnikov National University, 2 Dvoryanskaya str., Odessa 65082, Ukraine*
[b]*Lashkarev Inst. of Physics of Semiconductors, National Academy of Sciences of Ukraine, 45 prospect Nauki, Kiev 03028, Ukraine*

Abstract

Peculiarities of internal reflections, caused by surface plasmon resonance in nanosized composite films containing faulty tin dioxide clusters in stoichiometric matrix were studied. The angle and spectral characteristics of R_s^2 and R_p^2 reflection indexes of radiation with s- and p-polarization, both with their polarization difference $\rho=R_s^2-R_p^2$ are measured in the waves range of 400-1600 nm. The obtained experimental $\rho(\theta, \lambda)$ characteristics reflect the optical properties' peculiarities, connected with films' structure and morphology. The surface plasmon resonance investigation procedure is established to be sensitive for tin dioxide films' structure.

Keywords: Tin dioxide nanofilms, surface plasmon resonance

1. Introduction

Researches of nanosize films and tindioxide (SnO_2), in particular, is motivated by their numerous applications as a transparent material for electrodes, gas sensors, catalyst for oxidizing processes and others [1]. Surface plasmon resonance (SPR) became a method providing structural information for materials, in particular, metals. It is traditionally considered, that SPR is inherent to metals such as silver, gold, aluminum and copper, where a dielectric index has a negative sign ($n < 1$) in the visible range [2,3]. It is true, if the SPR is registered when reflection indexes are detected by means of widely spread optical scheme – geometry of Otto or Kretschman [4]. In a standard case (for metals) SPR is identified by sharply

* Corresponding author. Tel.: +38-048-731-7403; fax: +38-048-731-7403.
E-mail address: grinevich@onu.edu.ua.

1877-7058 © 2011 Published by Elsevier Ltd.
doi:10.1016/j.proeng.2011.12.068

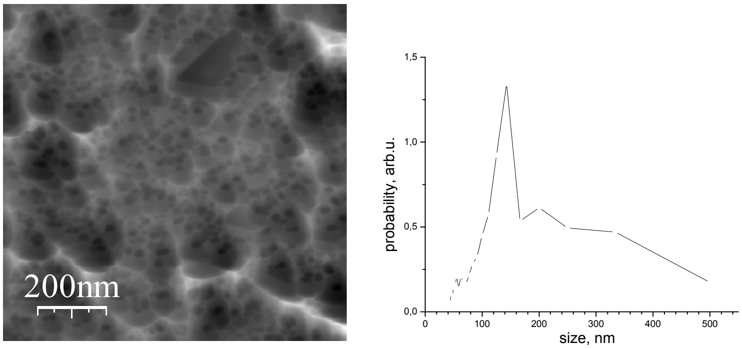
decreasing an internal reflection coefficient, in a narrow angular range for linearly polarized light. Surface plasmons excited by light in the films dissipate the energy to external space, causing the mentioned decrease. Thus, this energy is not present in the reflected light.

In the present work nanostructured tin dioxide films are considered as nanocomposite structures, which are clusters of nonstoichiometric tin dioxide (SnO_x) in a dielectric matrix of stoichiometric SnO_2. Detailed study of their properties is possible on elaborating the specific interpretation procedure, which is the aim of the presented work.

2. Samples preparation

Samples were prepared by a technique described in details in [5]. The principle samples' parameters are given in [6].

Average thickness of the films were obtained by the AFM method with an error of about 2 %, surface morphology of the tin dioxide layers was studied by the (AFM) NanoScope IIIa (Digital Instruments). The investigated surface area was 1000x1000 nm^2.



(a (b)

Fig.1 Phase AFM morphology of the sample T4.P1(a) and histogram of probable components' dimensions for the film composition (b)

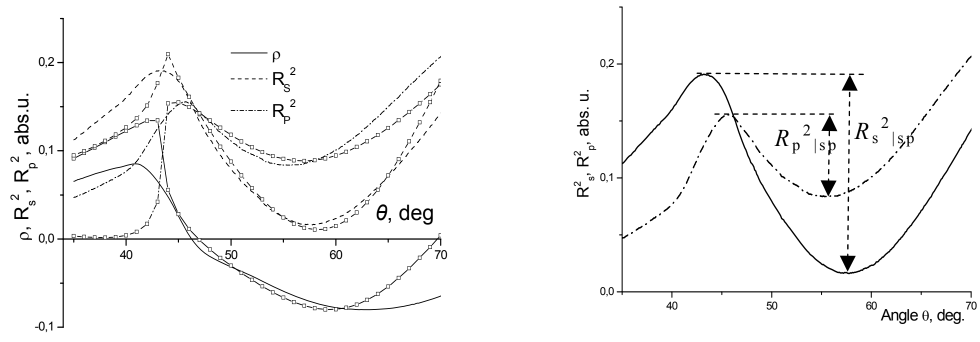
An AFM image for the sample T4P1 is given in Fig. 1(a). Employing Fourier analysis expansion to its surface profile a histogram was obtained, Fig. 1(b). It is seen that the film consists of two groups of clusters, which occupy approximately equal space on the histogram. One of them contains clusters of several nanometers to 200 nanometers, the other covers the sizes over 200 nm. As it will be shown below, such structural peculiarities of the films can influence the spectral characteristics. Clusters contain a large number of defects (boundaries between crystallites, and clusters), which are the electron sources in the films. On the other hand, nanoclusters determine the structure of the potential wells for charge carriers.

The $\rho = R_s^2 - R_p^2$ were measured as a function of incident angle and wavelength in the range 400-1600 nm. Modulated polarized light was used as detailed in [7].

3. Results and discussion

Results will be discussed here in terms of Fresnel's formulas describing the reflection indexes R_s^2 and R_p^2 and ρ as a function of incident angle [7]. Variation of R_s^2 and R_p^2, and the polarization difference ρ, with θ are shown at Fig. 2(a) for sample T4.P1 together with their theoretical estimations. The choice of 500 nm will be justified later. The figure shows that typical features of SPR are present at $R_s^2(\theta)$ curve downfall in the range $\theta > \theta_{cr}$.

The refractive index and absorption coefficient of tin dioxide cluster films, necessary for coefficients R_s^2 and R_p^2 and parameter ρ calculations were obtained from calculations and experimental results on condition of their coincidence achieved by means of adjusting several parameters.



(a) (b)

Fig. 2 (a) - experimental (lines) dependencies of the internal reflection indexes of $R_s^2(\theta)$, $R_p^2(\theta)$ and the parameter $\rho(\theta)$ in the sample T4.P1 in comparison with computed (dots) characteristics. The calculation was performed for the following parameters: $\lambda = 500$ nm; $N = n + I\times k$; $n = 1.61$; $k = 0.1$; $d_p = 290$ nm; $d_s = 300$ nm. (b) - illustration of different degrees of resonance interaction for $R_s^2{}_{|sp}$ and $R_p^2{}_{|sp}$ vs angle of light incidence in the sample T4.P1.

The angular dependencies disagreement may be justified by the film non uniformity within in the limits of light spot, which increases as the angle increases. The optical constants are in agreement with the data presented in [8]. Besides the clusters are not spherical, in general, which may be considered by an additional condition. Nevertheless, the agreement of the theoretical and experimental data in Fig. 2(a) is very satisfactory.

The resonant interaction is also evidenced by parameter $\rho(\lambda)$ spectral characteristics for samples with different thickness and concentration of tin dioxide, shown in Fig. 3. Here, absolute value of ρ is saved, which have been determined, in particular, for three dependencies by the negative sign of ratio $\rho = R_s^2 - R_p^2$, as actually measured values. It becomes clear from Fig. 3(a) that the reason for choosing the wavelength for the angular dependence of the $\rho(\theta)$ parameter, shown in Fig. 2 for sample T4.R1. It is seen that in the range 400–500 nm curves $\rho(\lambda)$ for all samples are characterized by extremums. The magnitude and the sign of the parameter ρ are in a correlation with the sample thickness and SnO_2 content in the initial solution.

The presence of another resonant interaction in the films is shown by curves in Fig. 3(b), which are the spectral curves of $\rho(\lambda)$ for two samples in the extended wavelength range. One of them shows an extremum at $\lambda \cong 950$ nm, typical for the resonance effect, and the second, due to a limited range, shows only a tendency to increase, which, leads to an extremum.

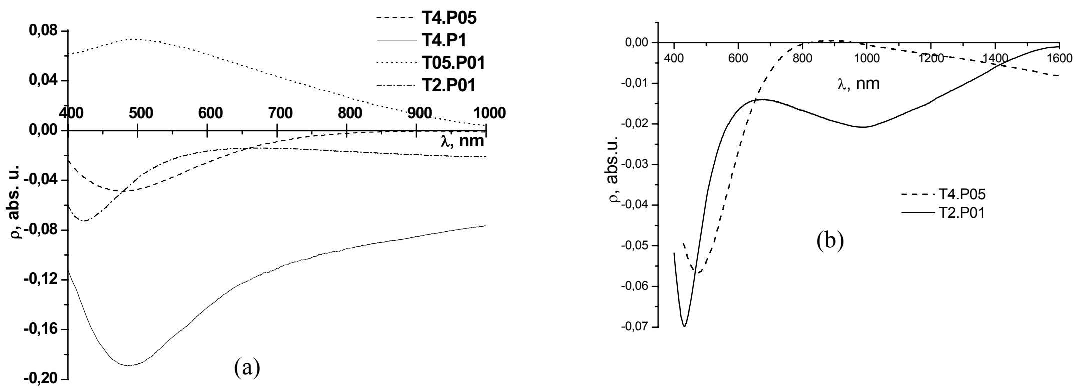


Fig. 3 (a) - the spectral dependence of the polarization difference □(λ) for samples T4.P05 (dot) T4.P1 (solid), T05.P01 (dots) T2.P01 (dashed line), measured at the incidence angle 55 º; (b) - the same for the samples T4.P1 T4.P05 in extended range wavelengths.

As for local plasmon resonance parameters then, under condition that the elementary oscillator resonance curve coincides with the curve of the normal distribution function, it becomes possible to determine not only the resonance frequency, but also, using its half width, the time of the oscillation relaxation, which is $\gamma = 1.3 \times 10^{-14}$c. For comparison, the value of this parameter in gold films with thickness d = 50 nm is reported as $\gamma_{Au} = 7.14 \times 10^{-13}$c [9], which indicates a great structural perfection of a metal film.

4. Conclusions

General principles of SPR phenomenon [3] do not forbid the possibility to detect it in conducting films of tin dioxide. Expediency of research in this direction is dictated by parameter ρ strong response to the variation both of films' optical properties and to the external environment.

As to the formulated aim of the work, it is shown, in particular, that the negative sign of polarization difference ("anomalous" reflection) $\rho = R_s^2 - R_p^2$ reveals a metallic nature of absorption in the films. The ρ negative values range and the shape of its angular dependence in this case are very different for continuous and cluster films. Thus, its greater extent in the angular range above the critical angle is exclusively related to the cluster structure of the material. In addition, the results obtained in this paper allow one, having an appropriate justification, to reconstruct clusters forms. The necessary information may be obtained from the ratio of $R_s^2{}_{|sp}$ and $R_p^2{}_{|sp}$, characterizing resonance interaction degree in their angular and spectral dependencies. Spectral analysis procedure used in this work gives an information on relaxation parameters, characterizing structural and crystalline perfectness of samples.

References

[1] Batzill M. and Diebold U. The surface and materials science of tin oxide. Progress in Surf. Science 2005; **79**:47-108.

[2] AgranovichV. M. and Mills D. L. *Surface polaritons. Electromagnetic waves on the surfaces and interfaces of mediums*. Moscow: Nauka, 1985.

[3] Dmitruk N. L., LitovchenkoV. G., Strizhevskiy V. L. *Surface polaritons in semiconductors and dielectrics*. Kyiv: Naukova dumka, 1989.

[4] Otto A. Excitation of nonradiative surface plasma waves in silver by the method of frustrated total reflection. Z. Physik. 1968; **216**:398-13; Kretschman E. Die bestimmung optischer konstanten von metallen durch anregung von oberflaschwingungen. Z. Physik. 1971 ;**241**:313-12.

[5] Filevskaya L.N., Smyntyna V.A., Grinevich V.S. Morphology of anostructured SnO_2 films prepared with polymers employment/ Photoelectronics. 2006.; № 15:11-4.

[6] Grinevich V.S., Matyash I.E., Maximenko L.S., Mischuk O.N., Rudenko S.P., Serdega B.K., et al. Polarization characteristics of surface plasmon resonance in SnO_2 nanocluster films. Semiconductors 2011, to be published.

[7] Berezhinskiy L. I., Maximenko L.S., Matyash I.E., Rudenko S.P., Serdega B.K., Opt. Spectrosc., Russian Acad. of Sciences Journal, 2008 ;**105:**281-9.

[8] Anastasescu M., Gartner M., Mihaiu S., Anastasescu C. , Purica M., Manea E. et al., Optical and structural properties of SnO_2-based sol-gel thin films. In Proceedings: International Semiconductor Conference, Sinaia, Romania, 27-29 Sept. 2006, Volume 1, Issue, pp.:163-4.

[9] Maximenko L.S., Matyash I.E., Minaylova I. A., Mischuk O.N., Rudenko S.P., Serdega B.K. Opt. and Spectrosc. Russian Acad. of Sciences Journal 2010;**109**, N.5:857-6.