Chapter 20
Characterization of SnO_2 Sensors Nanomaterials by Polarization Modulation Method

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Abstract The polarization characteristics for tin dioxide cluster films are studied by the method of modulation polarization spectroscopy. The galvanic conductivity presence in the films is the basis for registration in it the surface plasmon resonances. The spectral characteristics analysis by means of expansion in terms of Gauss components for the Stocks vector Q component of the probe radiation gave the parameters of the revealed resonances. The resonance excitation of polaritons and localized surface plasmons is established. The dispersion characteristics of non-radiative modes of surface plasmons are obtained which matches the cluster film structure. The numerical values comparison for resonances relaxation constants leads to the conclusion of application of one of them in sensors.

20.1 Introduction

The unique chemical resistance in an aggressive medium, specific adsorptive-catalytic, electrophysical and optical properties, cheapness in production and possibility to create Tin dioxide nano size forms secures its leading position among materials used for ecological monitoring [1, 2]. Nevertheless it is not the only sphere for application of this material. The resistance sharp decrease property for sensitive elements based on SnO_2 films at pressure decrease is successfully used in pressure transducers [2]. The conductive SnO_2 films are actively used as transparent electrodes in sun cells [3].

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J. Bonča, S. Kruchinin (eds.), *Nanomaterials for Security*, NATO Science for Peace and Security Series A: Chemistry and Biology, DOI 10.1007/978-94-017-7593-9_20

The nonstoichiometric oxides, SnO_x is among them, may become the basic material in the nearest future for new elements of computer energy independent memory-memristors, which modify their electric resistance under the current influence [4]. The application of nanoparticles of the dioxide composite material built in graphene nanoribbons, as anodes in Lithium Ions batteries in mobile electron technique were recently reported [5]. This may seriously enhance the productivity and effectiveness of such batteries and to achieve high initial charge and discharge potentials [6].

The use of optical methods of gas and biological objects detection in liquid and gaseous mediums became the new stage in nanosized tin dioxide application [7].

The tin-dioxide physical properties are principally dependent on the methods of its production. Among them are expensive ion-plasma, electron – beam deposition, magnetron spray and more cheap chemical methods – electric spray pyrolysis, chemical deposition from vapour phase, sol-gel method [8–10]. These methods are used for obtaining thin SnO_2 films of high defectness and as a result of high conductivity.

Free electrons presence in them secures the surface plasmon resonance (SPR) effects developing. The surface plasmons excitation by electromagnetic radiation (EM) is specific for nanosized structures, containing nanoparticles (NPs) of noble metals and may be registered by the plasmon adsorption in visible, nearest UV and IR wave length range [11]. The spectral and angular SPR characteristics of nanostructured metal-dielectric films are very sensitive to the dielectric permittivity variation of the contacting with them outer medium [12]. This is widely used for monitoring. Addition of gold (Au) on the SnO_2 surface in [13] enhances a sensor best performance due to response (s) and time of response (t).

Previously in our [14] the SPR existence in SnO_2 films without Au NPs was shown. At the same work the effectiveness of modulation-polarisation spectroscopy method (MPS) was shown, as an alternative method for diagnostics and characterization of SnO_2 films. The present work is a continuation of SnO_2 films characterization by MPS method aiming the determination of optimal resonance-optical SPR parameters in dependence on the resonance type (localized or polariton one) and also the structure morphology specificity aiming future application in sensors.

20.2 Samples and Experimental Details

Samples for the investigation were prepared by the technique described in detail in [15]. Bis(acetylacetonato)dichlorotin (BADCT) was used as a tin dioxide precursor [16]. Freshly prepared BADCT was dissolved in acetone at different concentrations, then equal volumes of each solution were mixed with the same volumes of polyvinylacetate (PVAC) solutions in acetone prepared at different concentrations. The mixtures were then sprayed onto the microscope cover glass of $22 \times 22\,mm^2$ size. Samples were kept at room temperature for about 15 min to allow the acetone

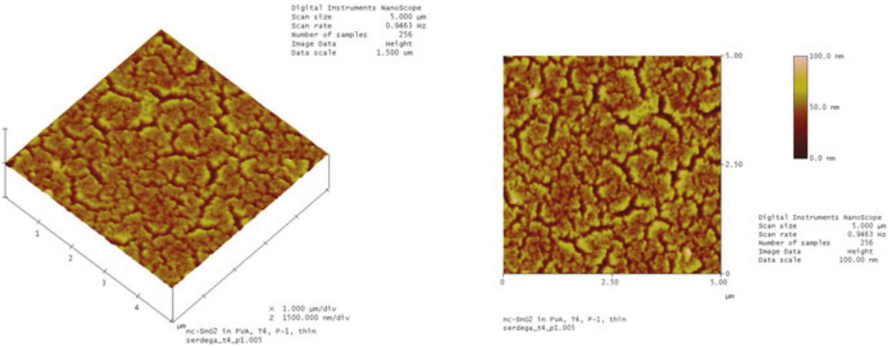

Fig. 20.1 AFM images of SnO_2 films

removing prior to annealing them at 600 °C for 6 h in air to achieve the thermal decomposition of the film organic components (BADCT and PVAC) and subsequent removing decay products. The organic components removing were confirmed by our thermogravimetric studies of the precursor [16] and by the data on the PVAC decomposition at temperatures above 200 °C, particularly in the presence of catalytic oxides (tin dioxide in our case). After annealing, the tin dioxide film was left on the substrate. PVAC was employed to structurize the film during removing its decay products. Force Microscopy (AFM) method (NanoScope IIIa, Digital Instruments). The tapping mode measurements were carried out with use of a silicon probe with nominal radius of about 10 nm. The AFM phase topology image of the sample T4.P1 (4 wt. % BADCT and 1 wt. % PVAC in the initial solution) is shown in Fig. 20.1a.

The optical scheme of experimental technique for spectral and angular SPR characteristics measurement based on the Kretchman [17] geometry and improved by the MPS method is described in details in [18]. The method is based on modulation of the EM radiation polarization. The idea of modulation is the periodical variation of probing radiation polarized state with constant intensity, frequency, phase and wave vector. The magnitude of the registered signal at the modulation frequency ($f = 60$ kHz) is equal to the intensities difference of the reflection coefficients s and p polarized radiations $\rho(\lambda, \theta) = R_s^2 - R_p^2$ – the polarization difference. According to the conventional terminology in polarimetry [19] this parameter is a Q-component of Stocks vector within the EM radiation which is reflected in this case by SnO_2 film fixed on a semicylinder surface and sensible to resonance. The phase locking detection of angular and spectral polarization characteristics increases the information ability of $\rho(\theta, \lambda)$ parameter, both due to the dynamic range extension of the measured quantity, and due to different signs of amplitude signals. The parameter ρ is more convenient in detection with high sensitivity to the peculiarities morphology of structure due to simultaneous measuring of R_s^2 and R_p^2 components under interaction between radiation and sample.

20.3 Results and Discussions

The angular characteristics of the internal reflection coefficients $R_s^2(\theta)$ and $R_p^2(\theta)$ and their polarization difference $\rho(\theta)$ at $\lambda = 500\,\text{nm}$ for SnO_2 films are shown at Fig. 20.2. For the incidence angles θ, more than the critical angle of total internal reflection $\theta_{cr} = 43°$, the presented characteristics minima, are caused by the surface plasmons excitation for both *s*- and *p* polarized radiation.

The effectiveness of the resonance interaction of *s*-polarization in the present case exceeds over *p*-polarization (R_{sp}^p and R_{sp}^s are oscillators' forces, excited by corresponding polarized radiation). The negative values of $\rho(\theta)$ characterize the SnO_2 films structure as cluster one and nonuniform, which corresponds to the results of investigation of ultra thin and cluster gold films in [20].

In dependence on the structure peculiarities of the films studied, the SPR excitation is subdivided to several types: the excitation of the surface plasmon-polaritons on the infinite plane boundary of the metal-dielectric surface and the excitation of surface plasmons, localized on separate not interacting NPs or between NPs of metal due to dipole-dipole interaction. The spectral characteristics of the polarization difference $\rho(\lambda)$ at different incidence angles $\theta = 45°, 55°, 65°$ are shown at the Fig. 20.3a for characterization of SnO_2 films, and SPR types definition. The complicated character of the parameter $\rho(\lambda)$ spectral contour is connected with different types of SPR in the films. The variable in signs form of curves $\rho(\lambda)$ caused by the resonance response from both polarizations at the phase-locked detection allows to interpret each extremum as a result of the resonant excitation of the surface plasmons of different nature.

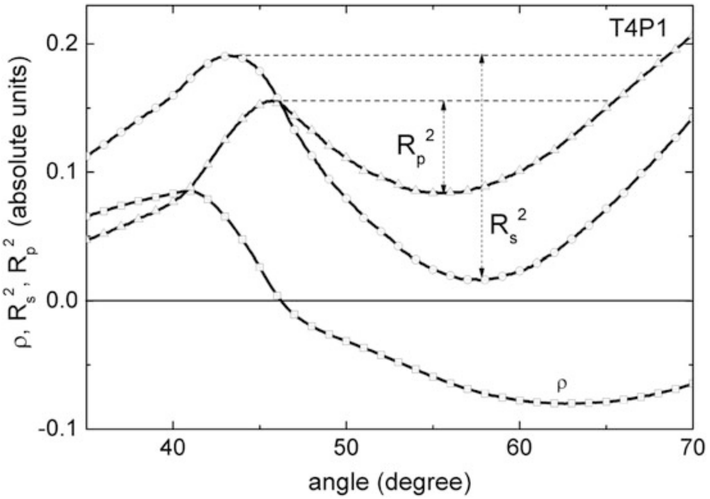

Fig. 20.2 Angular dependences of the internal reflection coefficients $R_s^2(\theta)$, $R_p^2(\theta)$ and polarization difference $\rho(\theta)$ at $\lambda = 500\,\text{nm}$

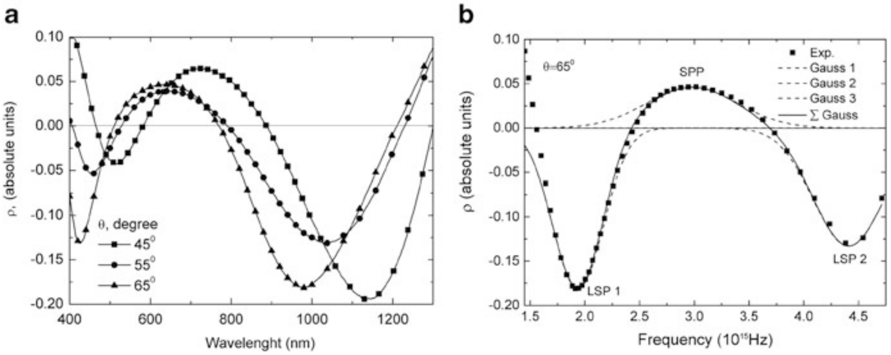

Fig. 20.3 (**a**) – spectral dependences of polarization difference $\rho(\lambda)$ for SnO_2 films at incident angles of $\theta = 45$ (*square*), 55 (*circle*), 65 (*triangle*), degrees. (**b**) – frequency dependence of polarization difference $\rho(\omega)$ at $\theta = 65°$ (*marks*) recalculated from the corresponding dependence of $\rho(\lambda)$ in comparison with the Gaussian distribution function (*solid line*) expanded into components (*dashed line*)

The negative sign extrema in $\rho(\lambda)$ spectra are conditioned by the resonant excitation of the localized surface plasmons in a short wavelength region ($\lambda_{\mathrm{LSP1}} \sim 500\,\mathrm{nm}$) on clusters or surface structure inhomogeneity, but in a long wavelength region ($\lambda_{\mathrm{LSP2}} \sim 1000\,\mathrm{nm}$) between clusters due to electrodynamic/ dipole-dipole interaction. In both cases, the simultaneous resonant interaction of both *s*-, and *p*-polarized radiation with SnO_2 film occurs. Extrema with positive $\rho(\lambda)$ values at $\lambda_{\mathrm{SPP}} \sim 650\,\mathrm{nm}$ are conditioned by the surface plasmon-polariton excitation in the interface film-air, consequently, as a result of resonant interaction only for p-polarized radiation. It is to be mentioned, that the “blue shift” occurs for corresponding extrema, which is conditioned by the considerable thickness $d = 230$–$400\,\mathrm{nm}$ of the SnO_2 films. Such peculiarities of $\rho(\lambda)$ curves are specific for cluster type and inhomogenous structure films [21].

Aiming the definition of every SPR parameters, the $\rho(\lambda)$ characteristics were studied by means of Gaussian functions approximation. As a result, the amplitude and relaxation resonance parameters were obtained. The frequency dependence of $\rho(\omega)$ of one of $\rho(\lambda)$ curves at $\theta = 65°$ was shown at Fig. 20.3b. The following principal frequencies and FWHM parameters (full width at a half maximum) are obtained: $\omega_{\mathrm{LSP1}} = 1.9 \times 10^{15}\,\mathrm{Hz}$, $\gamma_{\mathrm{LSP1}} = 0.73 \times 10^{15}\,\mathrm{s}^{-1}$; $\omega_{\mathrm{SPP}} = 2.86 \times 10^{15}\,\mathrm{Hz}$, $\gamma_{\mathrm{SPP}} = 0.994 \times 10^{15}\,\mathrm{s}^{-1}$; $\omega_{\mathrm{LSP2}} = 4.43 \times 10^{15}\,\mathrm{Hz}$, $\gamma_{\mathrm{LSP2}} = 0.544 \times 10^{15}\,\mathrm{s}^{-1}$. In all cases considered the surface plasmons excitation has non radiative nature and needs to secure phase-synchronous conditions, when both frequency (ω) and wave vector (k) of light excitation matches to those of the surface plasmon’s frequency and wave vector.

The resonances frequencies values, obtained from the components’ extrema (dash lines), both with the wave vectors magnitudes, considering the incidence angle (θ), permit to built the dispersion characteristics $\omega(k)$ of the surface plasmons (Fig. 20.4). The dispersion curves shape, their position in $\omega(k)$ coordinates, and

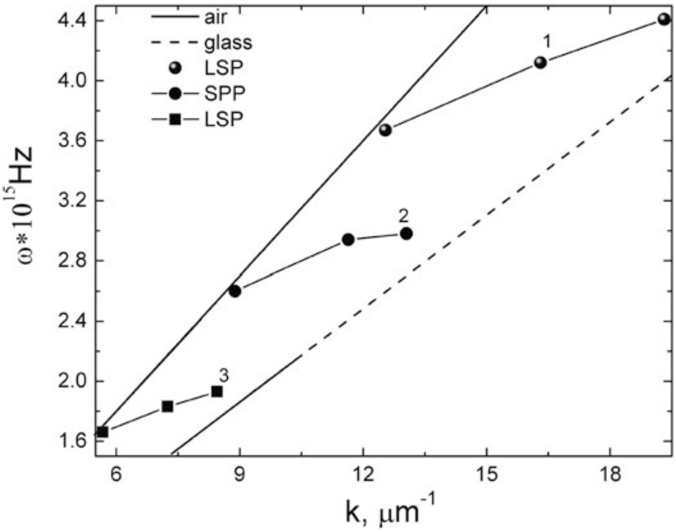

Fig. 20.4 Dispersion characteristics $\omega(k)$ of surface plasmons localized on isolated clusters (1), between clusters caused by dipole fields' interactions (3), and surface plasmon-polaritons (2) for SnO_2 films

also AFM images, makes it possible to identify two of them, correspondingly, as excitation of the surface plasmons, localized on separate, not interacting clusters, and interclusters interaction and the third – the excitation of surface plasmon-polaritons.

The angle dependencies of the relaxation parameters, γ, connected with SPR type is presented at Fig. 20.5. It is evident, that the biggest γ values corresponds to the surface plasmon-polariton excitation. According to the least γ parameter value rule, the SPR intercluster interaction dependence is the most appropriate for sensors applications. It is evident, the parameter value $\gamma_{\mathrm{LSP2}} = 0.472 \times 10^{15}\,\mathrm{s}^{-1}$ at the angel $\theta = 45°$, provides the maximum $\rho(\lambda)$ characteristic slope. It's shift as a result of the film interaction with an external detected medium, secures the maximum effectiveness in the sensors applications.

20.4 Conclusions

The characterization of resonant-optical parameters and morphology features of sensor – SnO_2 films is fulfilled by modulation – polarization spectroscopy method. Two SPR types are registered, which are conditioned both by the surface plasmon-polaritons excitation and localized surface plasmons on separate not interacting clusters and between clusters due to dipole interaction. The polarization analysis of SnO_2 research showed the inhomogeneity and cluster type of the structure

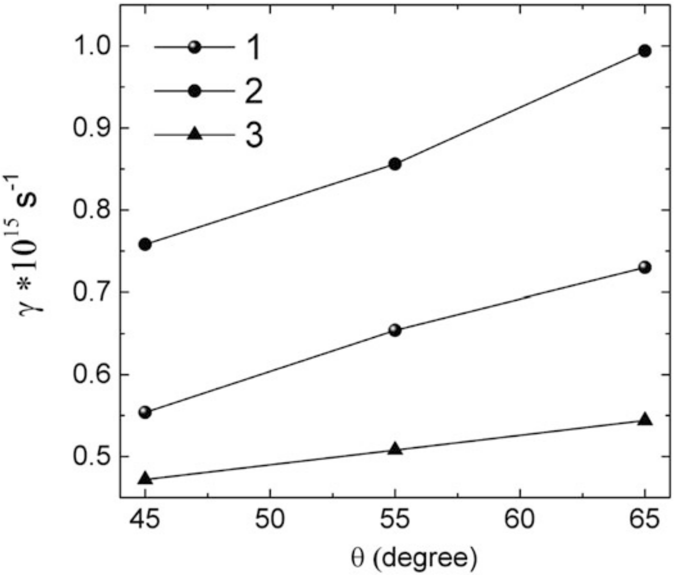

Fig. 20.5 Angular dependences of the relaxation parameters of SPR characteristics for SnO_2 films

morphology. The optimal resonance-optical parameters were obtained for SPR intercluster inter action, which supposes and secures their angular and spectral characteristics maximum effectiveness in the sensors applications.

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