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SPECTROSCOPY OF POLARISED AND MODULATED LIGHT FOR NANOSIZED TINDIOXIDE FILMS INVESTIGATION

The peculiarities of Surface Plasmons Resonance (SPR) in nanosized tin dioxide films, deposited on a prism of total interior reflection, were experimentally investigated using methods of the polarized and modulated radiation of light (PM). It was found that the layers, obtained by special technology using polymer materials as structuring additives are the combination of polycrystalline nanosized grains with air pores. This result has confirmed the supposition about the considerable porosity of the obtained layers. The obtained results confirm the considerable (PM) method's sensitivity for the aims of material's optical parameters detecting.

INTRODUCTION

In the modern gas analyses there is a natural transition to the thin films' adsorptive sensitive elements with a perfectly developed physical surface based on oxide nanodimensional materials. One of such a material is tin dioxide which has perfect sensitivity to a composition of a environmental atmosphere and chemical resistivity to a poisoning media. Transparent Tin dioxide films with nano sized grains may be applied as optical detectors of environmental compositions. It has become possible due to the noticed optical property of such films to answer the presence of different chemical compounds in the environment (both gaseous and liquid).

The later circumstance defined the urgency of the detailed researches of such films' optical properties.

Among possible diagnostic methods the surface plasmons resonance phenomenon (SPR) is a unique one because it is a basis of the most sensitive methods applied for the registration of media dielectric functions changes. The application of polarized and modulated light for detecting of SPR in oxide materials with nano grains is becoming proved and effective.

The peculiarities of the SPR in the nanosized Tin dioxide films deposited on the surface of total internal reflection prism were investigated using the technique of modulation of polarized light radiation (PM). The research supposed the presence of electrons' plasma in the obtained layers, which is indirectly confirmed by a property of a considerable electrons' degeneration in the films.

TECHNOLOGY OF SAMPLES PREPARATION AND THE INVESTIGATIONS TECHNIQUE

Transparent nanodimensional Tin dioxide films, obtained using polymer materials as structuring additives and Tin containing precursor of SnO_2 were used as samples. The samples' preparation methods described in [1] had several stages: preparation of tin containing organic filler, preparation of the polymer material solution, and introduction of tin containing compound into it. The resultant gel was deposited on a glass substrate and annealed in a muffle furnace. Temperature (500^0 C) and the annealing time (2 hours) were chosen as necessary parameters for both polymer and tin dioxide precursor decomposition. Thin tin dioxide layers with well developed nanostructure and considerable porosity were formed after the complete removal of decay products by means of annealing both of polymer and tin dioxide containing precursor and also after the complete oxidation of the films up to tin dioxide.

The nanostructure of the films was determined at the AFM [2] investigations and the typical surface of such films (AFM image) is shown on Fig. 1.

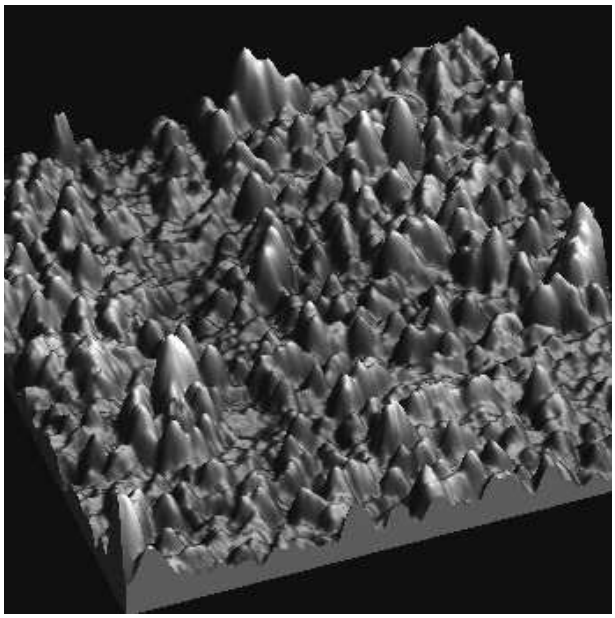

Fig. 1. The films investigated typical surface AFM image.

In the presented work the films were obtained from solutions having 0,03% of PVA as a structural additive and 1% of Tin containing SnO_2 precursor.

The total internal reflection on the border film-external environment was used as a detecting phenomenon. The theoretical evidence and the experimental

technique of the total internal reflection measurement are described in details in [3].

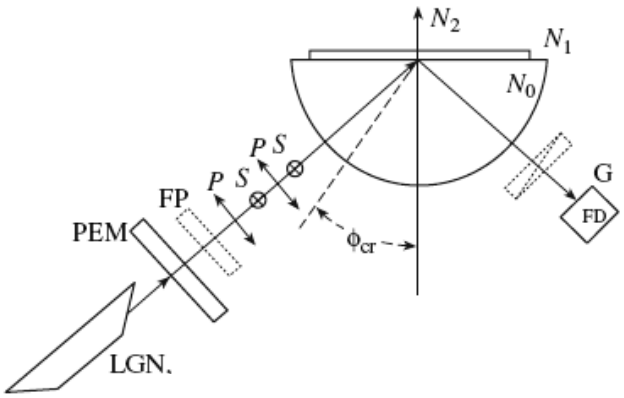

Fig. 2. The experimental equipment optical scheme for angles characteristics of a polarization difference measurements using modulation of polarization: LGN- Helium-Neon Laser, PEM-photo elastic modulator of polarization, FP- the phase plate, p,s linear polarizations, azimuths of them are parallel and perpendicular to the plane of incidence, G-Glann s prism, FD-photo detector, ϕcr the total internal reflection critical angle, N0, N1,N2- refraction indices of glass, films, air correspondingly.

The general optical scheme of the experimental equipment for measuring of both total internal reflection characteristics and polarization parameters difference is given at Fig.2. Hellium-Neon laser, LGN-113 with the fixed wave lengths 0,63 mkm and 1,15 mkm is used as a source of linearly polarized radiation, together with monochromator MDR-4 with a halogen lamp KGM-150 at the input and the polarizer on the out let. A modulator of polarization –REM was used as a dynamic phase plate functioning in two regimes. In the both cases, by rotating the modulator round the optical axe of the measuring device, it's position was chosen so, that the out let polarized radiation azimuth was parallel and perpendicular in turn to the plane of accident (p and s polarization, correspondingly).

After the interaction with the half cylinder and the surface of resonance sensitive Tin dioxide film, the radiation was directed to photo detector, FD (Silicium or Germanium photodiode) which after absorption of radiation generates a signal comprising an alternative component. It is proportional to the reflection indices difference of p and s polarization of the detected radiation.

Thus, the equipment with the modulation of polarized light permits to obtain not only the angle dependant reflection indices R_s and R_p correspondingly, but also their difference, ΔR. ΔR factor is not a result of mathematical act, but is the physical value independently and directly measured.

The investigated films were deposited on glass substrates which permited to supplement the glass segment to a half cylinder, using the contact of a substrate with a segment by immersion liquid (glycerin).

THE MEASUREMENTS RESULTS AND THEIR DISCUSSION

All the three characteristics (R_s, R_p and ΔR) for one of the samples are given at Fig.3 in relative, but comparable units. Wave length of the scanning radiation, λ =630 nm.

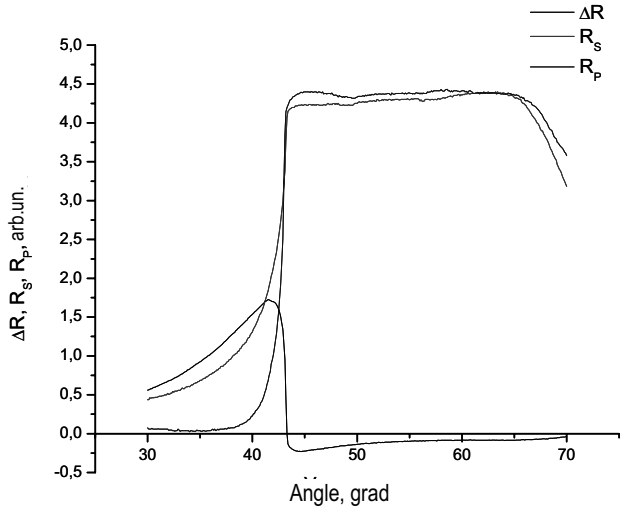

Fig. 3. Experimental dependencies for reflection indices Rs and Rp and their difference ΔR of the investigated samples.

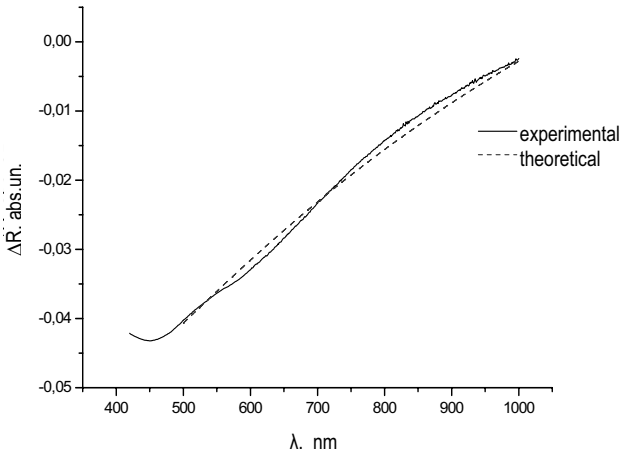

Fig. 4. The polarization difference vs wave length at a fixed angle, which is more than critical.

The most interesting is the angles' range where their values are more than critical ones where an inequality of R_s and R_p testifies about the broken total internal reflection, which is possible when an absorption has place in the sample. As soon as, the difference between R_s and R_p is registered on the background of considerable signals, then the big error is inevitable. This not favourable situation may be eliminated in a case when a polarization difference, which is measured relatively zero, may be amplified and, hence, fixed for sure. Thus, the polarization difference, $\Delta R=R_s-R_p$ certainly demonstrates the break of total internal reflection which change its sign at an angle equal to the critical one. It was a definite interest to retrace the differential difference dependence vs wave length at a fixed incidence angle which is more than critical. The experimental results at the incidence angle of 46^0 are shown at Fig.4 by the continues line in comparison with the theoretically calculated ones on the basis of Frehnels equations — by the broken line. The adjustment parameters were refraction and absorption indices for the Tin dioxide film.

As it is seen at Fig.4 the coincidence of experi-

mental and theoretical results is more than satisfactory in the wave length range 500-1000 nm. It is appeared, that n and k are linearly and uniquely dependent on the wave length: n=1, 28+0,000005$_*\lambda$; k= 0,223-λ/4700, λ in nm. Changes of n or k on more than 5_*10^{-3} gives the mismatch of experimental and theoretical data.

Changes of k move a theoretical curve higher or lower the experimental one, but variation of n changes the theoretical curve' slope.

The reflective index values obtained in our work are in good agreement with other authors' data [4]/

That is, the reflective index value obtained as a result of our samples investigation is within the indices values interval corresponding to indices of pure Tin dioxide (n=1,56) and for air (n=1,003).The pores existence was expected in the investigated layers which is resulted from polymers application at the films' production. Pores within the said technology are formed at polymer's decay during the annealing procedure.

Thus, the above discussed results confirm the considerable sensitiveness of the method for our material's optical parameters detecting.

CONCLUSION

The new technique for the Surface Plasmons Resonans parameters measuring by means of modulation of polarized light was applied to nanosized Tin dioxide layers in order to obtain their optical indices. The system's — porous layer of SnO_2 reflection index showed its satisfactory agreement with other authors' data. The obtained reflection index values characterize the object as a system of nanosize Tin dioxide with air pores. This result confirms the supposition of such pores presence in the films.

The polarized light modulation method has high sensitivity for optical parameters detecting at Plasmons Resonans in the investigated layers and, hence, gives good perspectives in gaseous environment detecting. Such a technique of PM in SPR of the layers is, besides all, is a perfect confirmation of electrons' plasma presence in them.

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Key words: polarizing modulation, thin film, tin dioxide.

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ПОЛЯРИЗАЦИОННО-МОДУЛЯЦИОННАЯ СПЕКТРОСКОПИЯ НАНОРАЗМЕРНЫХ ПЛЕНОК ДВУОКИСИ ОЛОВА

Резюме

Экспериментально с применением методики, основанной на поляризационной модуляции (ПМ) излучения, исследованы особенности поверхностного плазмонного резонанса (ППР) в наноразмерных пленках диоксида олова, нанесенных на поверхность призмы полного внутреннего отражения. Исследуемые слои являются сочетанием поликристаллических наноразмерных зерен с воздушными порами, что подтвердило первоначальное предположение о значительной пористости полученных с использованием полимеров пленок двуокиси олова. Полученные результаты свидетельствуют о значительной чувствительности метода ПМ в определении оптических параметров материала.

Ключевые слова: поляризационная модуляция, тонкие пленки, двуокись олова.

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ПОЛЯРИЗАЦІЙНО-МОДУЛЯЦІЙНА СПЕКТРОСКОПІЯ НАНОРОЗМІРНИХ ПЛІВОК ДВООКИСУ ОЛОВА

Резюме

Експериментально із застосуванням методики, заснованої на поляризаційній модуляції (ПМ) випромінювання, досліджені особливості поверхневого плазмонного резонансу (ППР) у нанорозмірних плівках діоксиду олова, нанесених на поверхню призми повного внутрішнього відбиття. Досліджувані шари є сполученням полікристалічних нанорозмірних зерен з повітряними порами, що підтвердило первісне припущення про значну пористість отриманих з використанням полімерів плівок двоокису олова. Отримані результати свідчать про значну чутливість методу ПМ у визначенні оптичних параметрів матеріалу.

Ключові слова: поляризаційна модуляція, тонкі плівки, двоокис олова.