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SURFACE AND OPTICAL PROPERTIES OF NANO SnO_2 FILMS FOR SENSOR ELECTRONICS

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Abstract:
Results of surface morphology, optical density and the photoluminescence phenomenon were registered by authors for SnO_2 thin films, used as gas sensors. Films having nano size of their grains ~ 10-15 nm were obtained using polymeric materials in sol-gel method.
Keywords: tin dioxide, surface morphology, optical properties.

INTRODUCTION

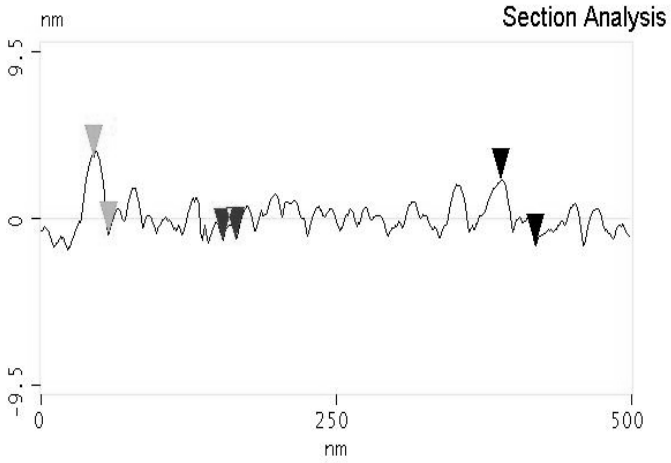
Tin dioxide is one of the most stable and sensitive oxide semiconductors for detecting a surrounding atmosphere changes. It is the basic material at the present time for adsorptive-sensitive elements in gases analysis [1]. The possibility of obtaining these materials' thin layers with a developed structure of a nanoscale broadens it's already existing applications. It is conditioned by the appearance of new properties caused by quantum scale effects.
The surface states' peculiarities investigations, optical density and thin SnO_2 films photoluminescence (PL) originally registered by authors, together with preparation of these films, obtained using polymeric materials are presented in the work.
As soon as tin dioxide surface has high adsorptive and reaction abilities, which are defined as by free electrons presence in the conductance zone, bulk oxygen vacancies, and active chemisorbed oxygen [1] the perfect knowledge of it's morphology is necessary for the description of a phenomena physical mechanisms taking place on it. Electrons' and lattice ions' energy states define a material interaction with the visible electromagnetic radiations, which is reflected in the absorption spectra.
The optical absorption investigation together with other electronic characteristics allows defining a forbidden zone width of a semiconductor and optical transitions types near the absorption edge. The complex evaluation of morphology and optical peculiarities of a material permits the detailed description of electron's and ion's subsystems behavior. This attitude was that which had defined the investigations of the surface morphology and optical properties of SnO_2 films, obtained using polymer material.

THE LAYERS' PREPARATION METHODS

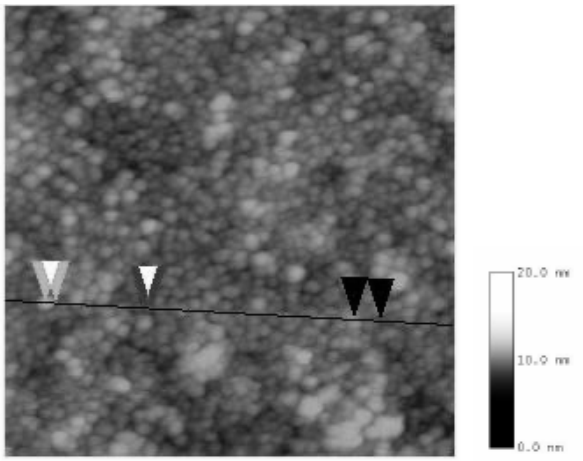
The technique using polymers as assisting structuring additives is used for the obtaining of thin films with a developed surface and nano grains. The basic elements of the method are given in the work [2].
For the investigation the SnO_2 films were obtained using gel which is PVA solution in acetone with tin acetyl acetonat addition as the tin containing substance.

EXPERIMENTAL METHODS AND RESULTS

The tin dioxide layers' surface morphology was investigated by the industrial atom-force microscope (AFM) NanoScope IIIa (Digital Instruments, USA) – Courtesy of Lashkarev Institute of Semiconductors Physics of Ukrainian National Academy of Sciences. Measuring was fulfilled by silicon probe with nominal radius ~10 nm (firm-producer NT-MDT, Russia), in the regime of a periodical contact (Tapping Mode ^{TM}). The investigated area surface was 500x500 nm^2.
The investigated layers deposited on glass substrates were optically transparent. This gave the possibility to study optical transition in the wave's interval 300-750 nm. The standard methods [3] were used for spectrophotometer CF-46 measurements. The experimental studies of photoluminescence of nanosized layers were realized according to methods in [4]. The luminescence excitation was done by means of N-laser with the wave 337 nm.
The morphology studies results are given at figures 1 and 2. Figure 1 shows top view and vertical profile of the layer's surface. The higher points at Figure 1 correspond to the lightest parts of the photo, and dark parts reflect the deepest regions.
As it may be seen the film investigated is enough uniform and consists of approximately equal sizes nanograins.
The deepness affordable for the probe AFM at the given film is ~ 10,5 nm. The average size of a grain is 10-15 nm.



a



Surface distance	14.082 nm
Horiz distance	12.695 nm
Vert distance	4.418 nm
Angle	19.189 degree
Surface distance	10.923 nm
Horiz distance	10.742 nm
Vert distance	0.034 nm
Angle	0.182 degree
Surface distance	30.256 nm
Horiz distance	29.297 nm
Vert distance	3.780 nm
Angle	7.353 degree

b

Figure 1. Vertical film's surfaces profile (a) with the indication of sizes between bench marks (b); the nuance of grey color corresponds to the nuance of bench marks.

Evaluating the grain's size and deepness of probe penetration, is possible to say that the film is nanostructured and is continues for the gel used, but not islet type. 3-D view of a film's surface is given at figure 2.

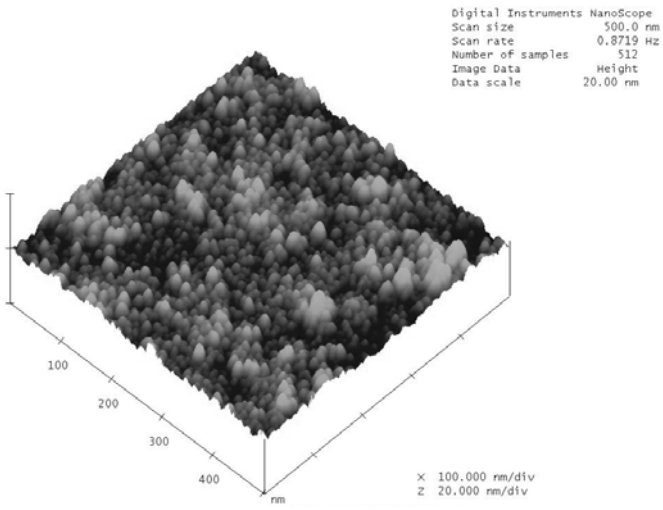


Figure 2. 3-D view of SnO_2 film surface.

The general view of absorption spectra optical density $D(h\nu)$ is given at the figure 3, as soon as the analysis of a form of an absorption band edge needs only an absorption coefficient spectra changes, but not it's absolute value.

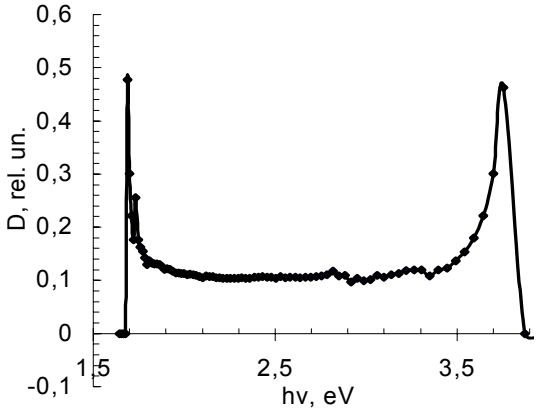


Figure 3. The.optical density spectrum of SnO_2 nano structured films. Films were obtained on the base of gel (the PVA solution in acetone with tin acetyl acetonate) addition.

As it is seen at the figure 3 there are two peaks present in the optical density spectrum: in the red region (1,69 eV) and specific for tin dioxide peak in the nearest UV region (3,757eV). The sharp abruption in the UV spectrum may be caused by several reasons. It is known, [5], that tin dioxide is transparent for the nearest UV. Besides that, the glass substrate own absorption seriously increases in the UV, which gives principal changes to the investigated film's spectrum.
The photoluminescent investigations of tin dioxide nano structured films make it possible to register the visible spectrum radiation, previously not described for amorphous and polycrystalline SnO_2 layers. The PL

absence for SnO_2 like in a degenerated semiconductor was usually explained by the great amount of non radiating recombination centers. Thin peaks of visible radiation in our case, probably, are necessary to connect with grains' nanosizes in SnO_2 films. The PL measurements of SnO_2 layers at room temperature are presented at figure 4 curve 1. As it may be seen, two thin bands (half width ~ 0,05 eV) 577 nm and 642 nm are present at the radiation spectrum. The SnO_2 layer, previously prepared by electrosprayed pyrolysis (ESP) method was used as a basic sample for comparison (curve 2).

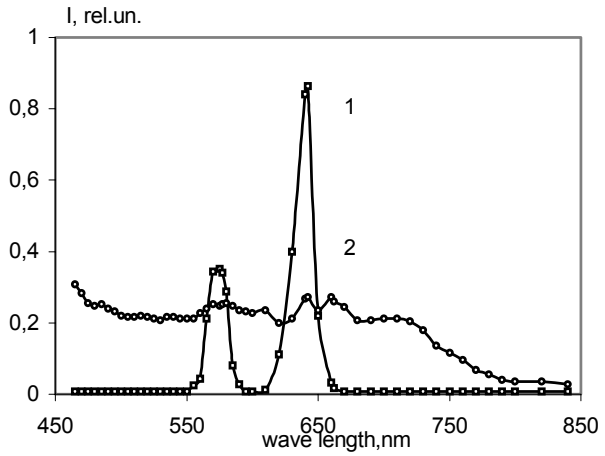


Figure 4. SnO_2 radiation spectra: 1 – for the investigated samples; 2 - for the samples which were obtained by the ESP method

Peaks 577 and 642 nm are also present at it's spectrum, but their intensity is much less. The coincidence of PL peaks' positions may witnesses for the identical nature of the centres in the samples obtained by different methods. The great radiation intensities in the case of SnO_2 films, obtained using polymer materials, witnesses for a considerable amount of radiative recombination centers. Besides that, similar structure of PL spectra is typical for nanosize materials [6]. It was established [7] that the layer obtained by ESP method, was amorphous in principle with metallic Sn inclusions.

DISCUSSION

The surface morphology investigations results show that tin dioxide films have enough developed surface and are consisted of grains with the average size 10-15 nm. Tin dioxide films with a structure of such type have usually low resistivity because of a great number of amorphous phase presence. The resistivity of the films is 3-6 $Ohm \cdot cm^{-2}$. This fact may be explained by the existence of a complicated potential structure which is characterized by a great amount of potential holes presence arbitrary distributed in the film. The charge carrier being localized in such hole is not able to take part in a current transport. The potential holes presence is connected, as in [8], with clusters which is typical for amorphous solid state. The crystal type clusters presence in the films is indirectly supported by the grain sizes of 10-15 nm, as it was established from AFM methods. The clusters' dimensions may vary from several to 1000 atoms [8] in amorphous semiconductors, hence; its size may reach hundreds of nanometers.

The structural nature of the films discussion will be continued on the basis of our optical results.

The optical density spectra rebuilt in $D_o^{1/s}=f(h\nu)$ coordinates, where s=1/2; 3/2; 2; 3 depend on optical transitions types, are presented at the figure 5.

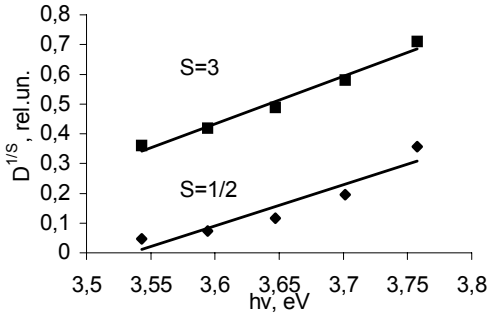


Figure 5. The optical density vs. absorpted EM energy measured at the absorption edge region.

As it is seen at the figure 5 the best linearization of optical density dependence has place when 1/s=1/3. This situation corresponds to indirect electrons' forbidden transitions with phonons participation, which, evidently, take place not in a Brillouin zone centre, where k=0, but in it's vicinity. This conclusion may be useful in future PL results discussion.

The nearest UV zone absorption corresponds to the absorption edge and gives the forbidden zone width equal to 3,3 eV. The optical absorption character says about the "density of states tales" in the forbidden zone, which defines the difference of E_g energy obtained in our work, from such in the crystalline SnO_2 forbidden zone value. At the same time, the E_g obtained here is a bit higher the literature data for amorphous tin dioxide films, which witnesses in favour of crystal structure of films' grains. The absorption peak (1,69 eV) corresponds to the middle part of the forbidden zone hence defining some density of states with the energy $E_g/2$, which is typical for amorphous or degenerated semiconductor. Such spectrum type confirms the clusters existence supposition for the films discussed. Metallic Sn has 579nm band in its spectrum, which is typical for single charged atoms [9]. Single charged oxygen atoms have series of spectral bands for the region of 645 nm [9]. Metal clusters' presence in SnO_2 films was also registered by authors [7, 10] together with the clusters' contribution to SnO_2 adsorptive activity. All these facts comparison supports

the assumption of the correspondence between PL band 577 nm in both films' types and the radiation centres which are connected with metal tin atoms or with these atoms' clusters.
Grains' nanosizes define a considerable potential holes' density with a discreet levels' distribution. This supposition is supported by our PL researches. If a PL spectra is rebuilt in coordinates $\pm[\ln(I_0/I)]^{1/2} \sim E$ then they shall be perfectly described by a linear dependence and by Gauss function. This result permits to consider PL peaks to be of intercenters' type and to describe the PL by means of configurative coordinates [4]. As it follows from our previous discussion, lattice vibrations play a noticeable role in tin dioxide electronic processes. Thus, the joint evaluation of optical absorption and the PL results permit to connect 1,69 eV absorption peak with a 1,91 eV of the PL. Both the energies difference and the radiation energy exceeding over the absorption energy may be interpreted as the antiStokes mechanism of PL in which 0,22eV phonon takes part. Developing this idea, the intercentres PL at 1,91 eV may also be of anti-Stokes type. These conclusions are supported also by optical density spectra analysis in connection with which lattice vibrations take also their part in the optical transitions near the forbidden zone edge, as these transitions are not direct.

CONCLUSIONS

The main results of the presented work may be given as following
– the SnO_2 films were obtained using the polymeric substance and have nanosizes;
– it was established that the principal surface morphology peculiarity is a developed films' surfaces having grains of 10-15 nm sizes;
– optical investigations showed, that absorption and photo luminescence spectra give evidence of the cluster structure of the films;
– the films' optical density and PL joint analysis witnesses for phonons role in a overdistribution of absorpted electromagnetic energy.
The films' surface morphology investigations make it possible to foresee the surface electric potential distribution. Thus, regions of charge nonuniformity may be shown. Such regions' presence perfectly influences charges exchange processes. Especially it becomes important when films' surfaces interact with different chemically active molecules, i.e. the films' electronic subsystem interaction with gases electronic systems.
It means that chemisorption's mechanism peculiarities may be the basis for sensitive elements construction.

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