Morphology and optical properties of SnO$_2$ nanofilms

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Abstract. Results of surface morphology and optical density investigations and the photoluminescence phenomenon were obtained for SnO$_2$ thin films. Films having nanosize of their grains ~ 10-15 nm were obtained using polymeric materials. Evaluation of a dimensional quantization is fulfilled by two methods: analytically using AFM data, and by means of optical density spectra; results obtained by these two methods are in a good agreement.

Keywords: tin dioxide, surface morphology, optical properties.

1. Introduction

Tin dioxide is one of the most stable and sensitive oxide semiconductors applied for detecting a surrounding atmosphere changes. At present time, it is one of the basic materials for adsorptive-sensitive elements in gases analysis [1]. The possibility of obtaining these materials' thin layers with a developed structure of a nanoscale broadens its already existing applications. It is conditioned by the appearance of new properties caused by quantum scale effects.

The surface state peculiarities investigations, optical density and thin SnO$_2$ film photoluminescence (PL) originally registered, together with a preparation of these films, obtained using polymeric materials are presented in this paper.

It is known that tin dioxide surface has high adsorptive and reaction abilities, which are defined both by presence of free electrons in the conductance band, bulk oxygen vacancies, and active chemisorbed oxygen [1]. The perfect knowledge of its morphology is necessary for the description of physical processes taking place on it. Electrons' and lattice ions' energy states define material interaction with the visible electromagnetic radiation, which is reflected in the absorption spectra.

The optical absorption investigation together with other electronic characteristics allows defining the forbidden band width of semiconductor and optical transition types near the absorption edge. The complex evaluation of morphology and optical peculiarities of a material permits the detailed description of behavior inherent to electron and ion subsystems. It was this attitude that defined the investigations of the surface morphology and optical properties of SnO$_2$ films obtained using polymer material.

2. Experimental methods and results

The technique using polymers as assisting structuring additives is applied for the obtaining of thin films with a developed surface and nanograins. The basics of the method are described in [2].

For the investigation, the SnO$_2$ films were obtained using gel that is PVA solution in acetone with a tin acetyl acetonate addition as the tin containing substance.

The tin dioxide layer surface morphology was investigated by the industrial atom-force microscope (AFM) NanoScope IIIa (Digital Instruments, USA) – Courtesy of V. Lashkaryov Institute of Semiconductor Physics of the National Academy of Sciences of Ukraine. Measurements were fulfilled using a 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 500×500 nm^2.

The investigated layers deposited on glass substrates were optically transparent. This gave the possibility to study optical transition in the wavelength range 300-750 nm. The standard methods were used for spectrophotometer СФ-46 measurements. The luminescence excitation was done by means of 337 nm N-laser.

The morphology studies results are summarized in Fig. 1. Figure 1 shows a top view and vertical profile of the layer surface. The higher points in Fig. 1 correspond to the lightest parts of the photo, and dark parts reflect the deepest regions.
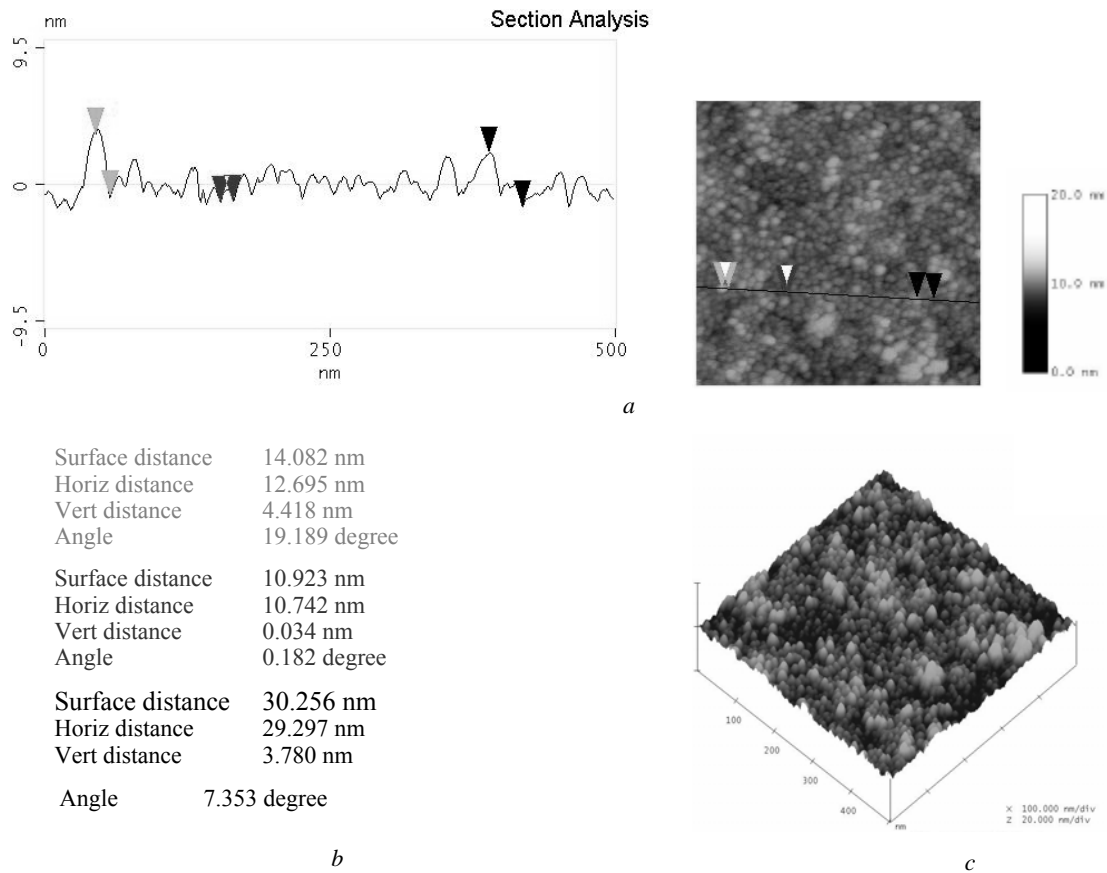
Surface distance	14.082 nm
Horiz distance	12.695 nm
Vert distance	4.418 nm
Angle	19.189 degree
Surface distance	10.923 nm
Horiz distance	10.742 nm
Vert distance	0.034 nm
Angle	0.182 degree
Surface distance	30.256 nm
Horiz distance	29.297 nm
Vert distance	3.780 nm
Angle	7.353 degree

b

c

Fig. 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; 3-D view of SnO_2 film surface(c).

As it may be seen, the film under investigation is enough uniform and consists of approximately equal-size nanograins. The depth affordable for the AFM probe at the given film is ~ 10.5 nm. The average size of a grain is 10-15 nm. Evaluating the grain size and depth of probe penetration, it is possible to say that the film is nanostructured and is continues for the gel used, but not of islet type. This is also confirmed by the 3-D view of a film surface, given in Fig. 1c.

The general view of the absorption spectra optical density $D(h\nu)$ is given in Fig. 2, as soon as the analysis of a form of an absorption band edge needs only an absorption coefficient spectra changes, but not its absolute value.

As it is seen in Fig. 2, there are two main 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 (3.757 eV). The sharp abruption in the UV spectrum may be caused by several reasons. It is known [3], that tin dioxide is transparent for the nearest UV. Besides, the glass substrate intrinsic absorption seriously increases in the UV, which gives principal changes to the investigated film 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 by the authors. 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 (Fig. 3, curve 1) in our case are probably connected with nano-sized grains in SnO_2 films. As it may be seen, two thin bands (halfwidth ~ 0.05 eV) 577 and 642 nm are present in the radiation spectrum.

The SnO_2 layer previously prepared by the electrosprayed pyrolysis (ESP) method was used as a basic sample for comparison (curve 2). In this case, peaks 577 and 642 nm are also present at its 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, similar structure of PL spectra is typical for nanosize materials [4]. It was established [5] that the layer obtained by ESP method was amorphous in principle with metallic Sn inclusions.
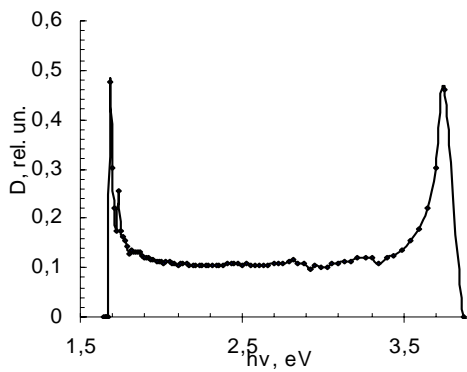
Fig. 2. The optical density spectrum of SnO_2 nano-structured films. Films were obtained on the base of gel (the PVA solution in acetone with tin acetyl acetonate) addition.
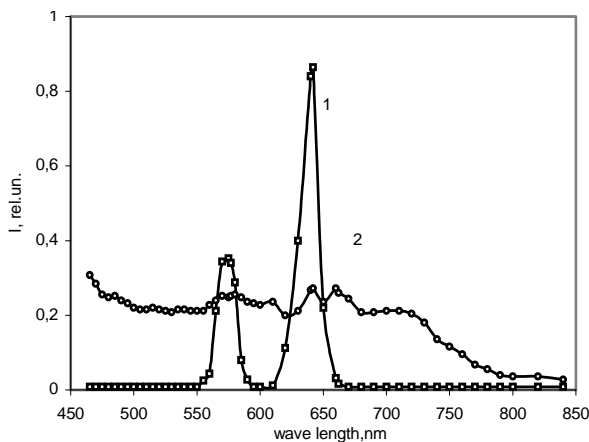

Fig. 3. SnO_2 radiation spectra: *1* – for the investigated samples; *2* – for the samples that were obtained using the ESP method.

3. Discussion

The surface morphology investigations results show that tin dioxide films have enough developed surface and consist 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 our films is on the contrary 3-6 MOhm·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 [6], 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 [6] in amorphous semiconductors, hence, its size may reach hundreds of nanometers.

The structural nature of the films may be illustrated by the calculations of tin dioxide films' parameters that are based on the optical density spectral data. Different literature sources give carriers effective masses data for tin dioxide, which notably differs from each other. Our calculation of the Bohr exciton radius ($a_B = \varepsilon h^2 / \mu e^2$) based on the data from [7] gives for tin dioxide crystal the value ~ 2.67 nm, but from [3] it is ~ 1.28 nm. With all that it was supposed the hole localization on the quantum-dimensional object, therefore, a_B value practically approaches to the Bohr radius value for electrons in SnO_2 (~2.75 nm).

The dimensional quantization energy may be evaluated according to formula [8]

$$E_{01}^{e,h} = 0.71 h^2 \varphi_{01}^2 / 2 m_{e,h} \left(\bar{r} \right)^2$$

by means of substitution of the known values $\bar{r}$, m_e, m_h.

Nanocrystallites' mean radius in our case is in correspondence with the Atom Force Microscopy data and gives ~ 5 nm. Substituting these values into the dimensional quantization energy formula [8], we shall obtain the dimensional quantization energy value $E_{01}^{e,h}$ (for $l = 0$ and $n = 1$ levels) ~ 0.63 eV, using the values for effective masses from [7], and using the similar values from [3] ~ 0.31 eV. If this energy is defined from the optical density spectra, as the difference between the first absorption maximum energy, which corresponds to the energy $E_g + E_{01}^{e,h}$ and the forbidden band width (~ 3.35 eV) that is obtained from the optical density data, then we shall obtain the value equal to ~ 0.40 eV.

In our case, the mean nanocrystallites radius nearly two times exceeds the Bohr radius value. However, as it is shown in the work [9] the holes' energy dimensional quantization practically did not tell on the absorption spectra type, and the calculation technique applied with using the optical absorption spectra gives a reasonable agreement with the results. As it may be seen comparing dimensional quantization energies values obtained by different methods, we have enough similar results. These results permits to use the optical density investigations data for the dimensional quantization energy definition, $E_{01}^{e,h}$, for the definition of nanocrystallite mean dimension.

The optical density spectra rebuilt in $D^{1/s} = f(h\nu)$ coordinates, where $s = \frac{1}{2}$, 3/2, 2, 3 depend on optical transitions types. 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, takes place not in the Brillouin zone centre, where $k = 0$, but in its vicinity. This conclusion may be useful in the future discussion of PL results.

The nearest UV band absorption corresponds to the absorption edge and gives the forbidden band width equal to 3.35 eV. The optical absorption character says about the "density of states tales" in the forbidden band, which defines the difference of E_g energy obtained in our work, from that in the crystalline SnO_2 forbidden band value. At the same time, the E_g obtained here is a bit

higher than the literature data for amorphous tin dioxide films, which witnesses in favour of crystalline structure of films' grains. The absorption peak (1.69 eV) corresponds to the middle part of the forbidden band defining some density of states with the energy $E_g / 2$, which is typical for amorphous or degenerated semiconductor [6]. Such spectrum type confirms the clusters existence supposition for the films discussed. Metallic Sn has 579 nm band in its spectrum, which is typical for single charged atoms [10]. Single charged oxygen atoms have series of spectral bands for the region of 645 nm [10]. Metal clusters' presence in SnO_2 films was also registered by authors [5, 11] 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 tin atoms or with clusters of these atoms.

Grains' nanosizes define a considerable potential hole density with a discrete level distribution. This assumption is supported by our PL results. 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 the Gauss function. This result permits to consider PL peaks to be of intercenter type. 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 PL results permits to connect 1.69 eV absorption peak with a 1.91 eV peak of PL. Both the energies difference and the radiation energy exceeding over the absorption energy may be interpreted as the anti-Stokes mechanism of PL in which 0.22 eV 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 band edge, as these transitions are not direct.

4. Conclusions

The main results of the presented work may be given as follows

− the SnO_2 films were obtained using the polymeric substance and have nano-sized grains;

− it was established that the principal surface morphology peculiarity is developed film surface having grains of 10-15 nm sizes;

− optical investigations showed that absorption and photoluminescence spectra give evidences of the cluster structure inherent to the films;

− the film optical density and PL joint analysis witnesses for phonons role in a overdistribution of absorbed electromagnetic energy;

− evaluation of a dimensional quantization is fulfilled by two methods: analytically using AFM data, and by means of optical density spectra; results obtained by these two methods are in a good agreement.

The film 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 film surfaces interact with different chemically active molecules, i.e. the film electronic subsystem interaction with the electron gas systems.

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