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OPTICAL ABSORPTION AND ELECTRONC SYSTEM PARAMETERS OF NANO SnO₂ FILMS

Optical density investigation results were registered by authors for nano SnO₂ thin films. Films having nano size of their grains ~10—15 nm were obtained using polymeric materials by sol-gel method. 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.

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 having a developed structure of a nanoscale broadens it's already existing applications. They are conditioned by the appearance of new properties caused by quantum scale effects.

The optical density of nano SnO₂ thin films which were obtained using polymeric materials and evaluation of a dimensional quantization is fulfilled by two methods: analytically, using AFM data, and by means of optical density spectra. 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 SnO₂ films, obtained using polymer material.

EXPERIMENTAL METHODS AND RESULTS

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 SnO₂ films were obtained using gel which is PVA solution in acetone with tin acetyl acetonat addition as the tin containing substance.

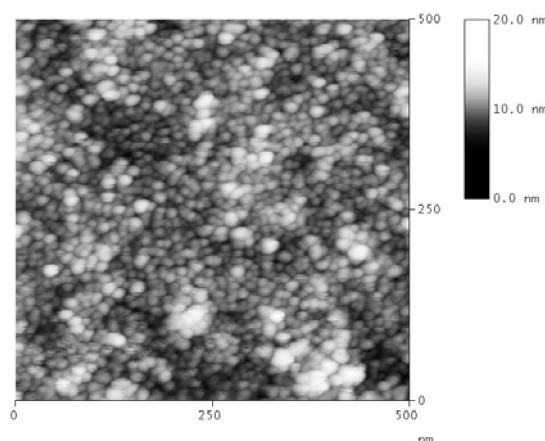The tin dioxide layers' surface morphology is presented at the figure 1 [3].

Fig. 1. Tin dioxide layer's surface (top view)

The films investigated are 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. Evaluating the grain's size and deepness 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.

The layers deposited on glass substrates were optically transparent. Theist gave the possibility to study optical transmissions in the wave's interval 300—750 nm. The standard methods were used for spectrophotometer CF-46 measurements.

The general view of absorption spectra optical density D($h\nu$) is given at the figure 2. Because the analysis of a form of an absorption band edge needs only an absorption coefficient spectra changes, but not it's absolute value.

As it is seen at the figure 2 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, [4], that tin dioxide is transparent for the nearest UV. Besides that, the glass substrate own absorption itself 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. The PL measurements of SnO_2 layers at room temperature are presented in the work [5]. Thin peaks of visible radiation in our case, probably, are necessary to connect with grains' nanosizes in SnO_2 films. Besides that, similar structure of PL spectra is typical for nanosize materials [6].
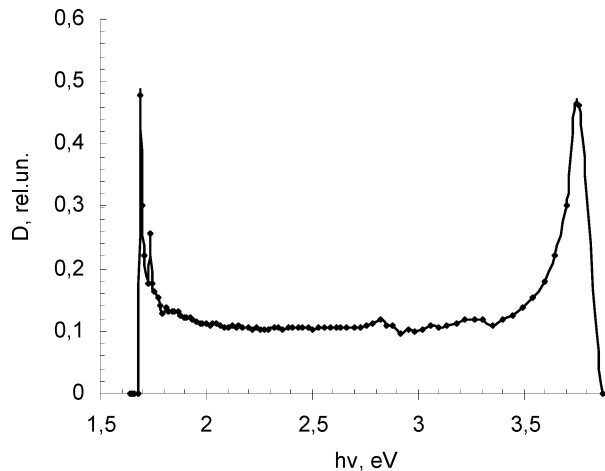

Fig. 2. The optical density spectrum of SnO_2 nano structured films. Films were obtained on the basis of gel (the PVA solution in acetone with tin acetyl acetonate) addition

DISCUSSION

The surface morphology investigations results [3] 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 carriers being localized in such holes are not able to take part in a current transport. The potential holes presence is connected, as in [7], with clusters which are 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 [7] 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 which are based on the optical density spectra data. Different literature sources give carriers effective masses data for tin dioxide, which notably differ from each other. Our calculation of the Bohr' exiton radius ($a_B = \varepsilon \hbar^2 / \mu e^2$) based on the data from [8] gives for tin dioxide crystal the value ~2,67 nm , but from [4] it is ~1,28 nm. With all that it was supposed the hole's localization on the quantum-dimensional object, therefore, a_B value practically approaches the Bohr's radius value for electrons in SnO_2 (~2,75 nm).

The dimensional quantization energy may be evaluated according to formula [9]

$$E_{01}^{e,h} = 0,71 \hbar^2 \varphi_{01}^2 / 2 m_{e,h} (\vec{r})^2$$

by means of substitution of the known values $\vec{r}$, 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 [9], we shall obtain the dimensional quantization energy value E_{01}^{eh} (for $l = 0$ and $n = 1$ levels) ~0,63 eV, using the values for effective masses from [8], and using the similar values from [4] ~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 $E_g + E_{01}^{eh}$ and the forbidden zone width (~3,35 eV) which is obtained from the optical density data (figure 2), then we shall obtain the value equal to ~0,40 eV.

In our case the mean nanocrystallites radius nearly two times exceeds the Bohr's radius value. However, as it is shown in the work [10] 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. They permit to use the optical density investigations data for the dimensional quantization energy definition, E_{01}^{eh}.

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 3.

As it is seen at the figure 3 the best linearization of optical density dependence has place when $1/s = 1/3$. This situation corresponds to indirect electrons' forbidden zone 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 with PL results discussion.

The nearest UV zone absorption corresponds to the absorption edge and gives the forbidden zone width equal to 3,35 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 579 nm band in its spectrum, which is typical for single charged atoms [11]. Single charged oxygen atoms have series of spectral bands for the region of 645 nm [11]. Metal clusters' presence in SnO_2 films was also registered by authors [12] together with the clusters' contribution to SnO_2 adsorptive activity. All these facts comparison supports the assumption of the correspondence between PhL band 577 nm in both films' types and the radiation centres which are connected with metal tin atoms or with these atoms' clusters.
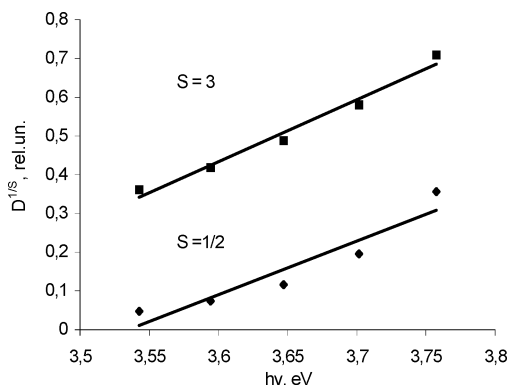

Fig. 3. The optical density vs. absorbed EM energy measured at the absorption edge region

Grains' nanosizes define a considerable potential holes' density with a discreet levels' distribution. This supposition is supported by our PhL researches. 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 PhL results permit to connect 1,69 eV absorption peak with a 1,91 eV of the PhL. Both the energies difference and the radiation energy exceeding over the absorption energy may be interpreted as the anti-Stokes mechanism of PhL in which 0,22eV phonon takes part. Developing this idea, the PhL intercentres at 1,91 eV may also be of anti-Stokes type. These conclusions are supported also by optical density spectra analysis which shows that 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
— 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 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.

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ОПТИЧЕСКОЕ ПОГЛОЩЕНИЕ И ПАРАМЕТРЫ ЭЛЕКТРОННОЙ СИСТЕМЫ НАНОПЛЕНОК SnO$_2$

В работе представлены результаты исследованного авторами оптического поглощения тонких нанопленок SnO$_2$. Пленки, имеющие нано размер зерен ~10—15 нм, были получены с использованием полимерных материалов в золь-гель методе. Двумя независимыми методами рассчитана энергия размерного квантования: с использованием данных атомно-силовой микроскопии и из спектров оптической плотности. Результаты этих двух расчетов хорошо согласуются между собой.

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ОПТИЧНЕ ПОГЛИНАННЯ ТА ПАРАМЕТРИ ЕЛЕКТРОННОЇ СИСТЕМИ НАНОПЛІВОК SnO$_2$

В роботі представлені результати дослідженого авторами оптичного поглинання тонких нано плівок SnO$_2$. Плівки, що мають нанорозмір зерен ~10—15 нм, були отримані з використанням полімерних матеріалів у золь-гель методі. Двома незалежними методами розраховано енергію розмірного квантування: з використанням даних атомно-силової мікроскопії та зі спектрів оптичної густини. Результати цих двох розрахунків добре узгоджуються між собою.