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SURFACE AND OPTICAL PROPERTIES OF TINDIOXIDE NANO-FILMS INFLUENCED BY THE INITIAL SOLUTION COMPOSITION

The surface morphology and optical absorption results of nanostructured SnO_2 films, obtained using polymers are presented in the work. Optical densities dependencies and evaluation of electronic parameters of films are fulfilled for solutions with different contain of tin component. The forbidden zone width correlation is noticed for different compositions of solutions. The dimensional quantization energy, calculated by two different methods has similar results.

INTRODUCTION

Tin dioxide is one of few materials, which may be obtained and preserved in a nano scale. It has good chemical resistance in aggressive medias and is highly sensitive to the environmental changes. These properties define the preferable use of this material in a gas analysis as adsorptive-sensitive elements [1]. Quantum-dimensional effects, typical for nanosized grains' materials, allows to extend their application to electronic technique. Such materials' properties essentially depend upon the technique of their production and many technological parameters. The reagent composition, temperature and time peculiarities of the technology essentially influence the chemical methods of production.

Structure's difference and film materials' properties are practically well developed in the optical investigations.

An optical radiation interaction investigation results in transmission spectra of semiconductor films, allow to define forbidden zone width, optical transitions at the absorption edge, and to evaluate phonons' and electrons' dimensional quantization energy.

SAMPLES PRODUCTION TECHNIQUE AND THE INVESTIGATIONS METHODS

Transparent thin films of nanostructured tin dioxide were obtained using the polymer materials. The technique described in [2] comprised several stages, which include the polymer material solution preparation in the solvent and the thin containing organic compound insertion into it. The solution formed was deposited on the glass substrate, dried and annealed in a muffle. The temperature and time of annealing corresponded to the temperature and time of polymer's decomposition. After the polymer's decomposition products were fully taken away, and the oxidation was over, the thin tin dioxide layers were formed with developed nanoscale structure.

Aiming to determine the initial gels' composition influence (as a technological factor) upon their surface morphology the samples were prepared with different quantity of the tin containing filler in the initial solution. The four-valent tin acetyl acetonate ($Sn(acac)_4$) of 1%, 5% and 10% concentrations were used. The polymer concentration was one and the same in all types of films and was 0,1% of polyvinilacetate.

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. Measures were fulfilled by silicon probe with nominal radius ~10 nm (firm-producer NT-MDT, Russia), in a regime of a periodical contact (Tapping Mode ™). The investigated area surface was 500×500 nm^2.

The optical absorption for transitions in the waves' interval 300–750 nm was measured for SnO_2 layers aiming the evaluation the initial solutions' (acetyl acetonate of Sn (1, 5 and 10%) influence upon the layers electronic properties. The standard methods were used for spectrophotometer CF-46 measurements.

EXPERIMENTAL RESULTS

The 3-D AFM images for films' surfaces are given at Fig. 1. The least uniform structure is seen for the layers, obtained of the solvent with the initial content of $Sn(acac)_4$ (1%). The layers become more uniform with $Sn(acac)_4$ concentration growth in the initial solvents.

The optical density absorption spectra $D(\hbar\omega)$ are given at fig. 2, while analyzing the edge of absorption band form it is important to know, only the spectral changes of the absorption coefficient, but not it's value.

In the optical density spectrum there are two peaks: in the red region (1,85 eV for 1%, 1,88 for 5% and 1,84 eV for 10% $Sn(acac)_4$ and specific for tin dioxide peak in the nearest UV region (for 1% — 3,6 eV; for 5% — 3,5 eV; for 10% — 3,6 eV). The sharp break in the UV spectrum may be caused by different reasons. It is known [3] that tin dioxide is transparent for the nearest UV, and besides that, the glass substrate absorption gives principal changes to investigated films' spectrum.

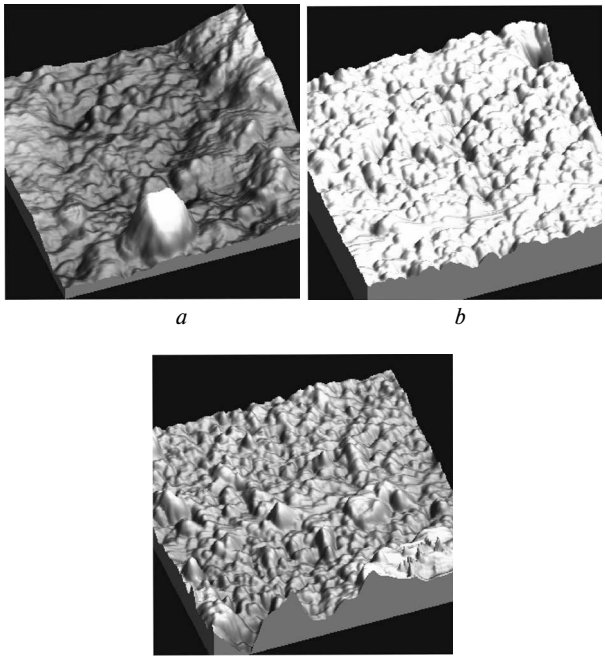

Fig. 1. 3-D AFM images of films' surfaces: *a* — 1%, *b* — 5%, *c* — 10% $Sn(acac)_4$ in the initial solvent (image size 500×500 nm²)

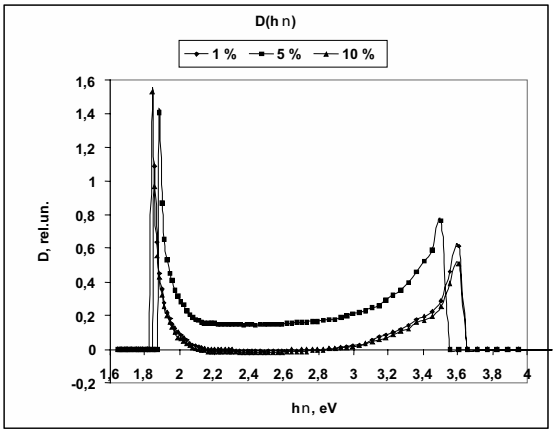

Fig. 2. The optical density spectra of nanostructured SnO_2 films, obtained from 0,1% PVA solutions and different $Sn(acac)_4$ content (1, 5 and 10 %)

DISCUSSION OF RESULTS

The AFM images analysis allows concluding about grain nanoscale structure in the films. Average grains' size, determined from the images, consists 10–15 nm. The least uniform films were obtained of low concentration $Sn(acac)_4$ solution.

The forbidden zone width and optical transitions character were defined using optical absorption edge investigation. The optical density in the absorption edge region is presented at fig. 3.

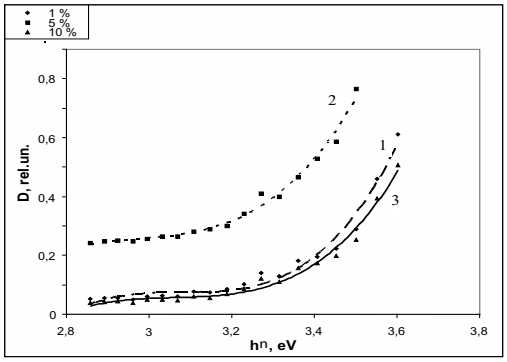

Fig. 3. Optical density spectra at the absorption edge region: 1 – 1%, 2 – 5%, 3 – 10% $Sn(acac)_4$ in the initial solution.

The results were replotted in $D_0^{1/s} = f(\hbar\omega)$ (s = 1/2, 3/2, 2,3) coordinates for the optical transitions types definition, and presented at fig. 4.

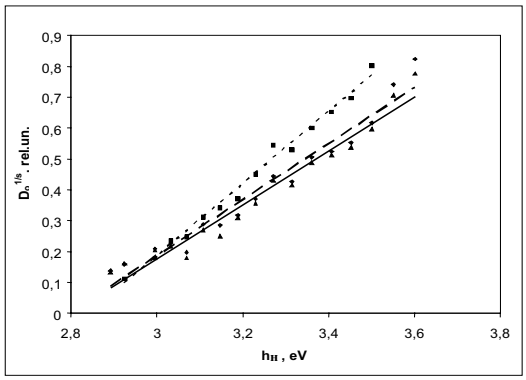

Fig. 4. The replotted optical density of the investigated layers in the absorption edge region at s=3. Dot and dash line corresponds to the same one at fig. 3

The best rectification of a curve takes place at 1/s =1/3 corresponding to optical density dependence $D_0^{1/s} = f(\hbar\omega)$; This corresponds to indirect forbidden transitions with phonons participation.

The nearest UV zone absorption, which corresponds to the absorption edge at calculation gives the forbidden zone width: for 1% — 2,96 eV, for 5% — 2,95 eV, for 10% $Sn(Acac)_4$ – 2,935 eV. Phonons' energy is — 0,14 eV for 1%, 0,07 eV for 5%, 0,135 eV for 10% $Sn(Acac)_4$.

The calculations results are given at a table

Table

$Sn(acac)_4$ content in the solution for films production	1%	5%	10%
E_g	2,96 eV	2,95 eV	2,935 eV
ħΩ	0,14 eV	0,07 eV	0,135 eV

The forbidden zone width values obtained for SnO_2 layers exceed the known values of amorphous layers of this material, which are 2,75–2,8 eV [3]. At the same time these values are lower E_g values of crystal tin dioxide. Thus, it may be supposed the considerable amount of nanosize crystal clusters in tin dioxide amorphous film.

As it may be seen from the table, the forbidden zone width decreases with the tin containing component concentration growth. This coincides with the conclusion in [4] that the zone width grows with pores' and grains' sizes decrease in nanoscale which is a specific one. Hence, it may be concluded about nanocrystals' sizes decrease in the investigated films, with $Sn(Acac)_4$ concentration decrease.

For the cases 1% and 10% $Sn(Acac)_4$in the initial solution phonons' energies are nearly similar 0,14 and 0,135 eV. For the second case it is divisible by 0,07 eV, which allows to suppose several phonons participation in the optical absorption. The possibility of phonon 34 meV in SnO_2 is reported in [5]. Taking this into account it is possible to say about multi phonons (2 and 4) transitions in the material at the light absorption.

The optical absorption character witnesses about density states tails in the forbidden zone, which defines the energy E_g difference, obtained in our research from the reported crystal SnO_2 value. The absorption peak for IR zone, which corresponds energies: (1,85 eV for 1%, 1,88 for 5% и 1,84 eV for 10% $Sn(Acac)_4$) is situated in the forbidden zone of the material. This may witnesses about some density states in the forbidden zone and is specific for amorphous or degenerated semiconductor [6].

The results obtained gave the possibility to calculate the dimensional quantization energy for the films. The effective mass values for SnO_2 carriers are different in different sources. The Bohr's exiton radius $\left(a_B = \frac{\varepsilon h^2}{\mu e^2}\right)$ for tin dioxide crystal calculation using data of [7] gives the value ~2,67 nm, and using data of [3] — ~1,28 nm. The holes localization on the quantum dimensional object was supposed, therefore a_B value practically approaches the Bohr's radius for electron in SnO_2 (~2,75 nm).

Using AFM data and m_e values from literature, the dimensional quantization energy may be estimated according formula in [8]:

$$E_{01}^e = \frac{0.71\hbar^2\varphi_{01}^2}{2m_e(\vec{r})^2}.$$

Nanocristallites' radius mean value in our case according to atom force microscopy data was 5–7 nm. By substituting these values to the dimensional quantization energy formula given in [9], we shall obtain dimensional quantization energy value E_{01}^e (for levels with $l = 0$ n = 1) using effective masses data from [7] ~0,63 eV, and from [3] - ~0,31 eV. If the same energy is calculated from the measured optical density spectra results, as a difference of the first absorption maximum energy value, corresponding to energy $E_g + E_{01}^e$, and forbidden zone energy values (2,96 eV – 1%, 2,95 eV – 5% and 2,935 eV – 10% $Sn(acac)_4$), then we shall obtain the following mean values [0,64±0,09] eV for 1%; [0,55±0,08] eV for 5%; [0,66±0,1] eV for 10%. The 15% error is considered.

In our case, the Bohr's mean radius for nanocrystallite is twice exceeds Bohr's radius value. At the same time, as it is shown in [8], holes dimensional quantization energy, practically did not influence the absorption spectra types. The calculations methods using optical absorption spectra give good matching of results.

CONCLUSIONS

After the surface morphology and optical absorption investigations of tin dioxide films obtained from solutions of various compositions, the following results were obtained:

— The forbidden band value dependence on the tin containing substance quantity in the initial solution. The band gap was 2,96 eV for 1%, 2,95 eV for 5%, 2,935 eV for 10% $Sn(Acac)_4$. Thus, the tin containing fuller concentration growth in the initial solution gives the forbidden zone value decrease in the obtained films. This may witnesses about nanocrystallites' sizes growth in the films.

— The phonons' component plays the principal role in the light absorption. The phonons' energies, which took part in the optical transitions were 0,14 eV for 1%, 0,07 eV for 5% and 0,135 eV for 10% of $Sn(Acac)_4$ and correspond to multyphonons transitions.

— The optical absorption character, witnesses about density states "tailes" in the forbidden zone. This defines energy E_g, difference between obtained in our work and for crystal SnO_2.

— 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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ВПЛИВ СКЛАДУ ВИХІДНИХ РОЗЧИНІВ НА ПОВЕРХНЕВІ Й ОПТИЧНІ ВЛАСТИВОСТІ НАНОПЛІВОК ДВООКИСУ ОЛОВА

У роботі представлені результати досліджень поверхневої морфології й оптичного поглинання наноструктурованих плівок SnO_2, отриманих з використанням полімерів. Розглянуто залежності оптичної густини і розраховані електронні параметри плівок з розчинів з різним вмістом олововміщуючої речовини. Помічено кореляцію ширини забороненої зони плівок і складу гелів для одержання плівок. Енергія розмірного квантування, розрахована по двох різних методиках, дає близькі значення.

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ВЛИЯНИЕ СОСТАВА ИСХОДНЫХ РАСТВОРОВ НА ПОВЕРХНОСТНЫЕ И ОПТИЧЕСКИЕ СВОЙСТВА НАНОПЛЕНОК ДВУОКИСИ ОЛОВА

В работе представлены результаты исследований поверхностной морфологии и оптического поглощения наноструктурированных пленок SnO_2, полученных с использованием полимеров. Рассмотрены зависимости оптической плотности и рассчитаны электронные параметры пленок из растворов с различным содержанием оловосодержащего вещества. Замечена корреляция ширины запрещенной зоны пленок и состава растворов для получения пленок. Энергия размерного квантования, рассчитанная по двум различным методикам, дает близкие значения.