

PHOTOLUMINESCENCE OF TIN DIOXIDE THIN FILMS, OBTAINED WITH THE USE OF POLYMERS

Tin dioxide nanostructured thin films properties obtained by the photoluminescent methods are reported. As a result of the researches fulfilled the luminescence in the visible region of 577 nm and 642 nm was established which is not yet reported in the literature. The luminescent mechanism connected with the system of centers typical for nanostructured objects are analyzed. The radiation spectra types changes, caused by the thermal treatment of a nanoscale tin dioxide films were noticed, which may be connected with structural transformations. These transformations seems caused the luminescent mechanism change from the intercenters' type to the recombinational one.

Tin dioxide is used in microelectronics for a long time as the elementary basis for different types transducers of non electric quantities into the electric ones. Such type transducers' properties considerably depend upon the technology of their production, and hence, upon their structural perfectness [1]. The nanostructured SnO_2 obtained by the new methods, reveals specific properties, which need the research methods which were not used for traditionally electronics' materials. As soon, as the tin dioxide investigation by the photoluminescent technique is not yet reported in the literature, the attempt to analyze the SnO_2 layers by this method is done.

EXPERIMENTAL RESULTS

Tin dioxide transparent films were obtained with the help of polymeric materials by a sol-gel method [2]. The films' production technique consisted of several stages, which included: the polymeric sol production in a solvent, tin containing compounds introduction into it, coating of a substrate by the gel obtained, and subsequent annealing in a muffle furnace. The time and the temperature of annealing were selected taking into consideration the time and temperature of the polymeric's material decay. After the products of decay were fully removed as a result of the annealing and after additional oxidation of a film, the thin films of tin dioxide with a developed structure were obtained. The nanoscale of the film was confirmed by the electronic microscopy methods. The photoluminescence investigations of the nanoscale layers were fulfilled on SnO_2 films obtained with the gel usage. The gel is a 0,1% solution of PVA in acetone with the addition of acetyl acetonate of tin $[\text{Sn}(\text{AcAc})_4]$ — metal organic compound, which gives the possibility to obtain metallic and oxide particles of a nanoscale during a decay process). The experiment was realized according to the procedure described in [3]. The luminescent excitation was

realized by the nitrogen laser with the wavelength of 337 nm.

According to our information, there is a shortage of information describing the luminescence in SnO_2 . Probably, it may be connected with the usage of SnO_2 samples as contact layers, which were the degenerated semiconductors with a definite number of defects. The defects presence causes the existence of a considerable number of nonradiative recombination centers in the forbidden zone [3], which defines the luminescence absence. The luminescent measurements are given at the fig. 1, curve 1 for the room temperature of SnO_2 layers. As it may be seen, the radiation spectrum contains two thin bands (halfwidth $\sim 0,05$ eV) 577 nm and 642 nm. The sample SnO_2 previously obtained by the electrohydrodynamic spraying method (EHDS) was used as a standard one (curve 2).

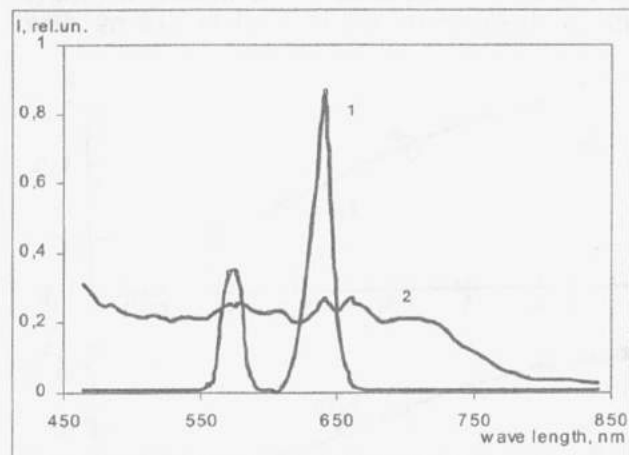


Fig. 1. The radiation spectra of SnO_2 :

1 — investigated samples; 2 — samples obtained by the EHDS method

It's spectrum also has two peaks 577 and 642 nm, but their intensity is much more weak. The luminescent peaks coincidence may witness about the centers of different nature presence in the layers obtained by different methods.

In the case of SnO₂ layers, obtained with polymeric materials use, the bigger intensity of radiation witnesses about bigger number of radiation recombination centers. Besides that, the similar luminescent spectra structure is typical for nanoscale materials [4]. It was established [5] that the SnO₂ layer, obtained by the EHDS method was mainly amorphous with the metallic Sn inclusions. The metallic Sn has a band 579 nm in it's spectrum, which is typical for it's single charged atoms [6]. The single charged oxygen atom has a series of spectral bands in the region of 645 nm [6]. The cluster of metal presence in SnO₂ layers was previously established by the authors [7, 8], where it was noticed their serious contribution to the SnO₂ layers adsorptive activity.

Comparing the mentioned facts it may be assumed about the correspondence of the 577nm band of both of the layers' types to the radiation centers, which are in accordance with metallic tin or with clusters of these atoms.

As the heating procedure usually stimulates the structural transformations in the layers, it may be supposed their influence on the luminescent results also. Similar to [1] the layer was heated with the subsequent analysis of the radiation spectra changes (fig. 2).

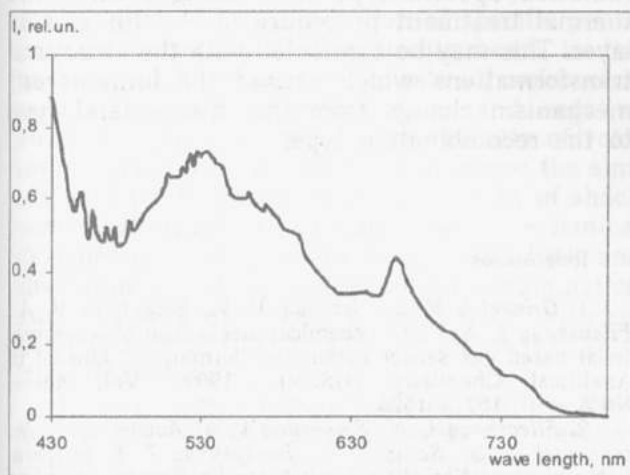


Fig. 2. The radiation spectra of SnO₂ after heating procedure

As it may be seen at fig. 2 the principal changes has taken place in the type of the spectrum. If the initial layers' luminescent spectrum has two enough thin bands (577 and 642 nm) then after the heating procedure the spectrum has several rather little peaks situated against the background of broad radiation band. The radiation may also be noticed in the nearest UV zone and at the edge of the visual zone, the tail of it may be noticed in the region of 430—480 nm of the spectrum. It may be done a supposition that the type of luminescence has changed from the intercenters' type to the recombination one as the little peaks are localized at the «tail» of the luminescence edge with the distance of 0,058 eV between them.

DISCUSSION OF RESULTS

The fulfilled E-microscopic investigations showed that the film studied is porous with a considerable part of amorphous component. The amorphous semiconductors are characterized by the presence of a considerable amount of structural defects. The concentration of them in the amorphous semiconductors is of the same order as the concentration of stoichiometrical atoms. The low resistance which may be expected for such samples is not realized. On the contrary, the samples obtained were of high resistance ($R \sim 10^6$ Ohm). This fact may be explained by the presence of potential holes which may have discrete levels but not of intrinsic nature [4]. These levels (so called fluctuation levels) may be created as a result of the arbitrary potential field of own structural defects. These levels may exist as discrete ones and may not be transformed into a zone, for electrons' transitions from one hole to another are complicated. Such transition could have taken place due to the tunnel effect, which needs the spatial closeness of these centers and the corresponding energy levels presence which seems to be hardly probable. This is the reason for the high resistivity of the layers. The nanosizes of the pores provides a considerable density of such potential holes with the discrete levels' distribution. In our case, such potential holes may be created by the tin clusters or by high concentrations of Oxygen near surface [7]. This supposition is supported by our luminescent investigations results.

It is convenient to present the spectra measured in the coordinates $I^* = \pm \left[\ln \left(\frac{I_0}{I} \right) \right]^{1/2} \sim E$,

where I_0 —radiation intensity at $\nu = \nu_0$. $I(h\nu)$ is a distribution normalized to 1. The SnO₂ radiation spectra replotted in the coordinates

$I^* = \pm \left[\ln \left(\frac{I_0}{I} \right) \right]^{1/2} \sim E$ are presented at the Fig. 3.

Plot (a) corresponds to 642 nm band, and plot (b) corresponds to the band 577nm.

As it may be seen at the Fig. 3 the spectra are well plotted by the linear dependence in the proposed coordinates and may be described by the Gauss function. This attitude gives the possibility to consider the mentioned peaks' luminescent as the intercenters' one and to describe it by the configuration coordinates model. The radiation spectra investigation of the films taken after the heating treatment procedure showed the luminescent mechanism change from the intercenters' to the recombination one. The carriers' recombination in this case takes place between the centers situated in the nearest proximity to each other. In other words, the inter donor-acceptors pair mechanism of recombination takes place. At this case, the energy position of the radiation centers depends upon the distance between the components of a donor-acceptor pair. Taking into consideration the little

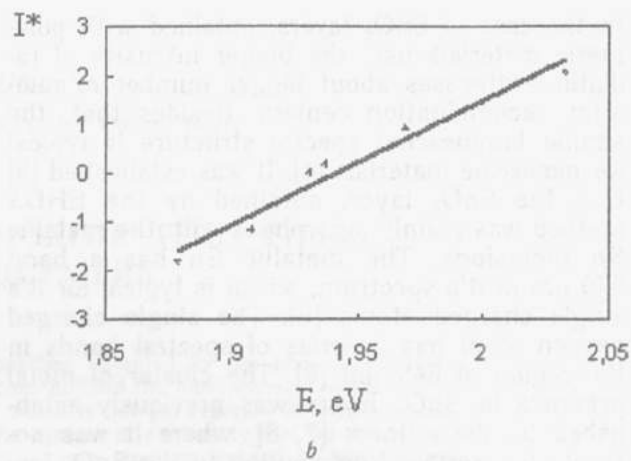
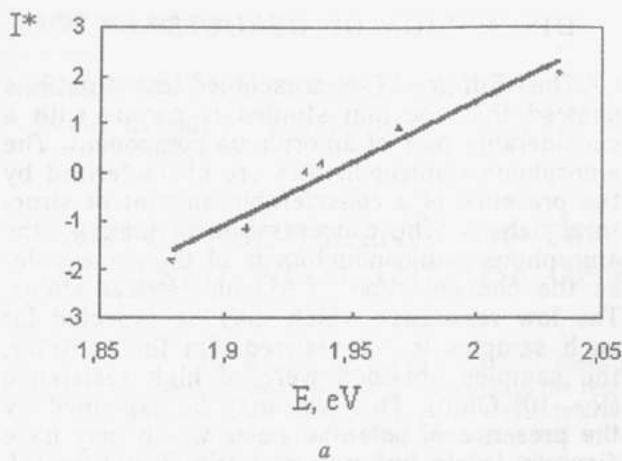


Fig. 3. Radiating intensity vs energy dependences drawn in $I^* = \pm [\ln(I_0/I)]^{1/2} \sim E$ coordinates:

a — for the peak with $E = 1.93$ eV; b — for the peak with $E = 2.15$ eV

value of donors' activation energy E_D , it may be calculated according to the equality (1)

$$E_a = E_g - hv + \frac{e^2}{\epsilon R}, \quad (1)$$

where R — distance between donor and acceptor within the pair. If it is taken into consideration that the radiation energy for the given luminescence type is described by the dependence (2) [3],

$$hv = E_g - \left(E_D + E_A - \frac{e^2}{\epsilon R} \right), \quad (2)$$

and the luminescent excitation energy (3,7 eV) is nearly equal to the forbidden zone width, then the mentioned mechanism of the luminescence may fully be registered at the given conditions.

The dark current temperature dependencies gave the possibility to determine the conductivity activation energy (0,36 eV), which corresponds to donors' depth in the material investigated. In such a case the acceptor centers' energy position, calculated according to the equation (1), gives the value of 1,56 eV order. This level corresponds to the deep level in the forbidden zone. Such a deep center may be an oxygen if the layers' structure and their developed surface influence would be taken into consideration. Oxygen could have been adsorbed by the surface earlier and then under the heating procedure influence had fulfilled a transition from the state of physical to the chemical sorption subsequently or due to the layers' initial nonstoichiometry was built into the SnO_2 structure. Thus, the donor-acceptor pair may be realized as two (oxygen and tin) atoms unit (cluster type) which are situated in the nearest proximity to each other. These atoms seems to be slightly displaced from their equilibrium states because of the structure's serious disorder. The structure changes were indirectly registered by two types of investigations and are indicating of the instability of a layer and, consequently, of the necessity to continue the investigations.

CONCLUSIONS

As a result of the investigations realized the tin dioxide layers luminescence in the visible region of 577 nm and 642 nm was registered which is not reported in the literature. The luminescence mechanism is analyzed for the system of centers, typical for the nanostructure. The radiation spectra type was changed after the thermal treatment procedure of the tin dioxide layer. This may be connected with the structural transformations which caused the luminescence mechanism change from the intercenters' type to the recombination type.

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