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LUMINESCENCE OF NANOSCALE TIN DIOXIDE. REVIEW

The article presents a brief review of luminescence in nanoscale tin dioxide. The luminescence caused by its intrinsic defects, the luminescence associated with impurities, the mechanisms of luminescence in tin dioxide are considered. The results of research by various authors presented in this review show the promising use of tin dioxide in optoelectronics and LED technology.

Introduction

Requirements for modern electronic display devices stimulate the search for new luminescent materials. Nanoscale forms of compounds that are not classical phosphors help in solving new electronics' problems. One of these compounds is tin dioxide. In recent years, studies of the luminescence of various nanoscale forms of pure and doped SnO_2, as well as composite compounds and heterojunctions using it, have been activated. This interest is due to the promising use of such materials as phosphors [1], in LED applications [2], in solid-state optical amplifiers and tunable lasers [3], etc. Thermoluminescence of tin dioxide doped by Europium [4] is used as a detection phenomenon for dosimetry purposes. Stannates of calcium, barium and strontium with a perovskite-like structure have attracted the attention of researchers to create IR phosphors as an alternative to expensive phosphors. [5].

Low-temperature luminescence of crystalline tin dioxide was described in 1979 [6]. In the ultraviolet spectrum region (~ 350-355 nm), the intrinsic luminescence band of SnO_2 is located. In the visible range, at low temperatures, wide photoluminescence (PL) bands in the range of 2 and 2.5 eV [7, 8] are observed in bulk samples of tin dioxide, which are associated with electron transitions in the interstitial tin/oxygen vacancy. With increasing temperature, the intensity of such a PL decreases, the PL becomes almost invisible at room temperature. The PL spectra of nanoscale samples of tin dioxide differ from the spectra of the bulk material, which was shown by a number of researchers [9]. Photoluminescence in nanoscale SnO_2 is increasingly observed at higher temperatures [10-12].

A brief review of luminescence in nanoscale tin dioxide will be presented in this paper.

Luminescence in nanoscale forms of tin dioxide

Glow due to its intrinsic defects. The edge luminescence of tin dioxide nanoscale forms was recorded by researchers in the ultraviolet region of the spectrum. For example, in [13] it was observed in transparent conductive thin films at 4.18 eV (~ 300 nm), and in [14] - at 333 nm. The differences in values are explained by the difference in the sizes of the nanocrystallites that form the film – the smaller it is, the greater is the energy of the peak of the edge luminescence.

In addition to the main UV peak of its intrinsic luminescence, the researchers report a whole set of radiation peaks in the visible region. As a rule, researchers observe bands in the blue-violet and orange-red regions of the spectrum. For example, Meier and colleagues [9] observed a PL peak at a wavelength of 625 nm (E = 2 eV) in SnO_x nanoparticles at liquid nitrogen temperature. Korean researchers [11] observed in thin films of SnO_2 PL in the region of 2.5 eV, Bonu and colleagues [12] observed at 2.54 eV and 2.42 eV and about 1.96 eV in SnO_2 nanoparticles. In

[15], photoluminescence measurements in thin SnO_2 films at room temperature with excitation at 280 nm show two broad emission peaks (400 and 430 nm). In thin undoped tin dioxide films on silicon substrates in [3], a broad emission peak at 395 nm was observed. The behavior of the peak at 590 nm depending on the diameter of tin dioxide nanowires was investigated in [16]. In addition to the edge luminescence at 333 nm, the authors of [14] observed a band of 480 nm at 13 K in thin SnO_2 films deposited by the MOCVD method on α-Al_2O_3 substrates. In [17], luminescence in the visible region (577 nm and 642 nm) of nanosized tin dioxide films was detected at room temperature. Violet (371-382) nm and blue (400-415 and 430-470 nm) luminescence bands in nanorods and tin dioxide nanocrystals were studied in [18].

Luminescence associated with impurities. The luminescence was often observed by researchers in tin dioxide with various additives, as well as in complex compounds, ceramics and heterojunctions with its use. For example, [19] found a violet photoluminescence band of about ~ 404 nm and weak red emission of about 700 nm in fluorine-doped films of tin dioxide deposited by spray pyrolysis on glass substrates. The SnO_2 quantum dots doped by Mn obtained using the solution combustion synthesis show the emission of orange radiation at about 590 nm [20]. The effect of doping by Mn and Ce on the luminescence associated with oxygen vacancies (400 nm) was studied in [21]. The properties of the intense peak of ultraviolet luminescence about 392 nm observed in SnO_2:Sb films at room temperature were studied in detail [22]. The use of nanoscale tin dioxide as a doping luminescent material used to enhance radiation in conjunction with other additives in glass or other similar structures has been reported in the literature. In [23], strontium phosphate glasses were doped with SnO_2 and Gd_2O_3, and they detected enhanced blue emission at 421 nm. The authors of [24] used tin dioxide nanocrystals to enhance the fluorescence of Eu^{3+} in SiO_2 glass by more than 150 times. The luminescence of SnO_2 was modified in [25] by doping with Cr. The normalized emission spectra from [25] are shown in Fig. 1. In the doped Cr nanostructures, a new emission with a center of 1.5 eV was detected; Cr doping also contributes to the enhancement of luminescence associated with oxygen vacancies (1.94 eV).

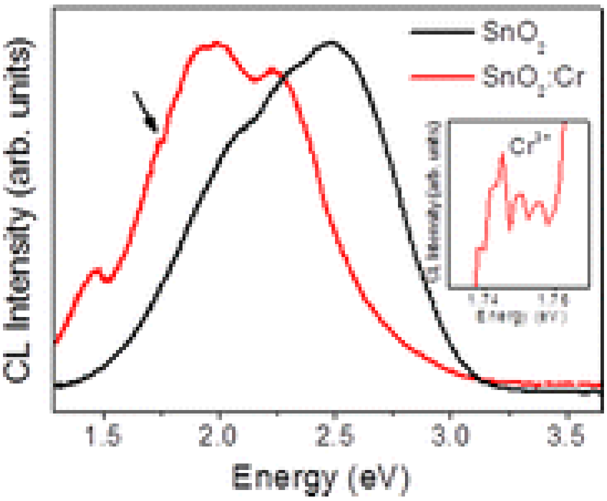

Fig 1. The normalized emission spectra SnO_2 and SnO_2: Cr.[25]

Luminescence mechanisms in tin dioxide. The variety of radiation centers provides the possibility of widespread use of the material, but it causes difficulties in unambiguous associating of bands with specific defects and luminescence mechanisms.

The authors of [26] attributed the PL peak to approximately 3.307 eV (at 10 K) to the donor – acceptor transition in high quality tin oxide nanowires. The observed by Chen and colleagues phonon replicas of this band indicated a high crystallinity of the samples. With an increase of temperature, donor energy of 32 meV was observed and the nature of the luminescence changed to recombination of a free electron on an acceptor with a shift in the emission maximum towards lower energies. They also observed an emission band with a maximum of 3.355 eV, the nature of which the authors attributed to radiative recombination on neutral donors. The relative intensity of this band decreases faster and disappears completely at about 70 K, which is the characteristic behavior of excitons associated with neutral donors and their transition to a free state with increasing temperature. At room temperature (300 K) all PL bands form a broad emission band at 3.18 eV. Unfortunately, the authors did not associate the observed luminescence with specific defects — interstitial tin, dangling bonds, or oxygen vacancies.

Radiation in the region of about 400 nm has several explanations in the literature. Thus, in [27], a broad peak of about 396 nm (~ 3.14 eV) was reported in thin SnO_2 films, the origin of which was associated with the nanodimension of crystallites and defects in the film. The radiation at 400 nm [28] was explained by an electron transition to the levels of defects in the band gap, such as oxygen vacancies. At the same time, they considered three different charge states of oxygen vacancies in the oxide: V_o^0, V_o^+ and V_o^{++}. The model of visible radiation at 400 nm thin SnO_2 films included the formation of an exciton upon photoexcitation. After tunneling deep into the film previously trapped on the surface or on the center of V_o^+ hole, recombination occurs with an electron in a deep trap with the formation of center V_o^{++}:

$$V_o^+ + h \rightarrow V_o^{++}$$

Thereafter, the visible emission at 400 nm can appear due to the recombination of a conduction band electron with the V_o^{++} center:

$$V_o^{++} + e \rightarrow V_o^+ + hv$$

A decrease in the peak intensity of 400 nm with the annealing temperature increase is in favor of this mechanism, since it increases the size of the films' crystallites. As a result, the ratio of surface to volume, and the number of surface defects and the number of oxygen vacancies decreases as a result of their recombination with oxygen diffusing into the film volume. In another paper, these authors [21] successfully proposed to introduce Ce^{3+} and Mn^{2+} ions into particles of tin dioxide to increase the number of oxygen vacancies and to increase the luminescence intensity.

In [29], in the photoluminescence spectra of cubic SnO_2 nanocrystals, a double peak was observed in the violet region between 360 and 400 nm. The energy separation between the two sub- peaks increased with the size of the nanocrystals. According to the authors, this is due to the edge recombination of the strip caused by different depths of oxygen vacancies. The conducted Density functional theory calculations showed that changes in the depth of oxygen vacancies lead to splitting of the peak of the valence band, which leads to the observed splitting and shift of the double peak[29].

In [30], the photoluminescence of the 417 nm band of a SnO_2 nanocrystalline powder obtained by direct chemical deposition was studied. The emission was associated with the recombination of electrons on oxygen vacancies with photoexcited holes of the valence band. With an increase in the annealing temperature, red mixing and a decrease in the luminescence intensity were observed, due to a decrease in the number of oxygen vacancies with an increase in the crystallite size from 9 to 43 nm. As we see, in this case, and in the case of 400 nm luminescence in thin nanoscale films of tin dioxide [28], the reason for the decrease in intensity is the same – a decrease in the number of oxygen vacancies in the samples.

Meier and colleagues [9] detected the PL peak of nanosized tin dioxide particles at liquid nitrogen temperature at a wavelength of 625 nm (E = 2 eV). The radiation wavelength did not depend on the particle size, which indicates the group defect responsible for it, according to the authors, associated with oxygen vacancies. Interestingly, the PL intensity increased with an increase in the size of nanoparticles from 5 to 20 nm and as the samples approached stoichiometry from $SnO_{1.5}$ to $SnO_{1.7}$ (Fig. 2).

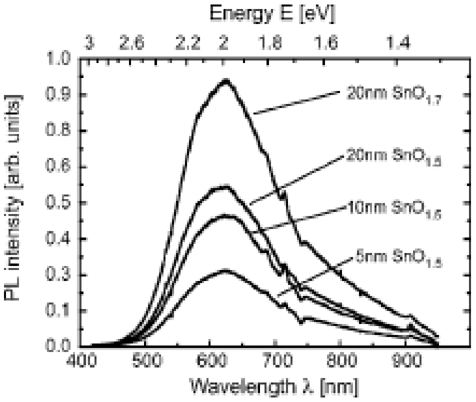

Fig. 2. The results of PL measurements for particles of various sizes and degrees of oxidation [9].

This fact correlated with the observation of a high density of electronic states inside the band gap from absorption measurements presented by the researchers there. The authors of this work associate this increase in intensity with a low rate of nonradiative recombination in $SnO_{1.7}$ due to the low total density of defects. Obviously, ideally, in a defect-free SnO_2 crystal, there are no defects providing PL. If the number of oxygen vacancies increases, the PL intensity will increase until nonradiative recombination processes dominate, as in the case of $SnO_{1.5}$.

The PL observed in nanostructured tin dioxide films obtained using polymers [31] was detected at room temperature. The authors also associated a peak at 647 nm (1.9 eV) with oxygen vacancies in samples whose PL results are shown in Fig. 3.

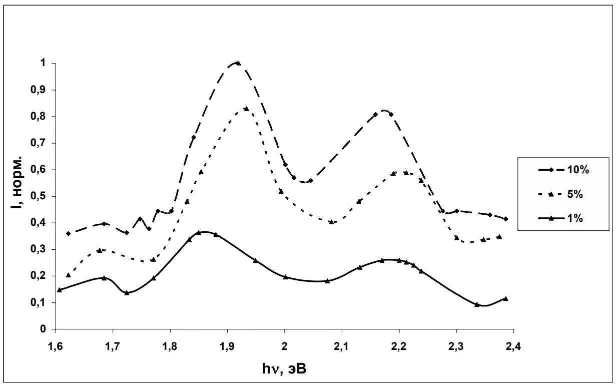

Fig. 3. The photoluminescence spectrum of SnO_2 films with different concentrations of the precursor (0.05% PVA) at room temperature.

The difference in the energy values of the luminescence peaks in the films obtained by the authors [9] and [31] may be due to both different temperatures during the experiments and differences in the structure of the samples studied by different authors. The authors of [31] also made the assumption that the band groups 2.17-2.2 eV in the films correspond to the luminescence centers representing interstitial tin atoms or clusters of these atoms, since it is known from reference data [32] that the free singly charged Sn atom has the spectrum band is 579 nm (2.15 eV). The presence of metal clusters in SnO_2 films was previously established by the authors of [33], and their significant contribution to the electrical conductivity and adsorption activity of SnO_2 layers was noted. In addition, it was shown in [34] that, at T = 723 K, at least 3 substances exist in films of tin dioxide: Sn, SnO, SnO_2.

The authors from Korea [11] also associated their observed peaks in thin SnO_2 films deposited by using CVD techniques in the 2.5-eV region with oxygen vacancies. Bonu and colleagues [12] also explained their observed luminescence at 2.54 eV and 2.42 eV with oxygen defects, namely in-plane and bridging 'O' vacancies. The authors observed a broad luminescence peak at about 1.96 eV in SnO_2 nanoparticles, the authors associate with OH^- hydroxyl groups on the surface of the particles. In work [35], the wide luminescence bands observed in the region of 350–550 nm were associated with defect states on the surface of SnO_2 nanoparticles. As we see, surface states play an important role in the luminescence of tin dioxide nanoforms.

Radiation at 421 nm was explained by the authors [23] as the Sn band. Moreover, the addition of Gd_2O_3 to the strontium phosphate glasses doped with tin dioxide they studied increases the Sn^{2+}/Sn^{4+} ratio, which contributes to enhanced blue emission of SnO_2-such doped glasses. The band at 430 nm in [28] was explained by the contribution of interstitial tin.

Based on experimental results, Indian researchers [18] proposed a schematic model for various relaxation processes in SnO_2 nanocrystals during photoexcitation (Fig.4). Visible radiation of SnO_2 nanocrystals was attributed by the authors to the transition of an electron from a level close to the edge of the conduction band to a deeply trapped hole in the volume (V_0^{++}) of SnO_2 nanocrystals. It was also shown that surface defects are more noticeable in smaller nanocrystals than in nanorods. It was found that the PL emission time and the decay time strongly depend on the shape of the nanocrystals.

Studying the cathode luminescence of tin dioxide nanowires, [36] found that the CL bands centered at 1.90 and 2.20 eV belong to the surface oxygen vacancies coordinated with tin atoms at an angle of 100°, and the CL bands centered at 2.37 and 2,75 eV, are associated with vacancies on the surface of oxygen, coordinated at 130°. The model of radiative transitions in the tin dioxide nanosized forms studied in [37] also takes into account the participation of coordinated oxygen vacancies in photoluminescence (Fig. 5).

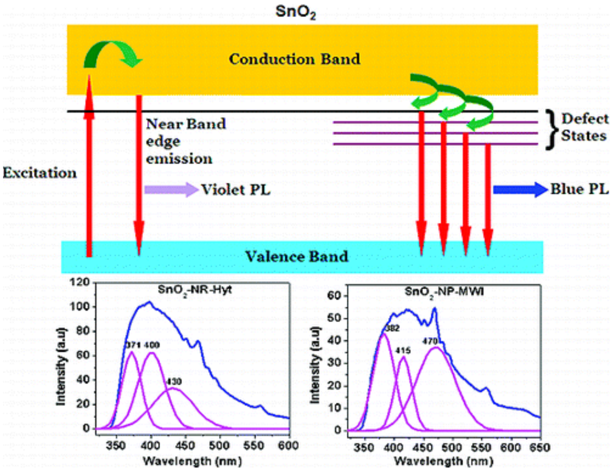

Fig. 4. A schematic model for various relaxation processes in SnO_2 nanocrystals upon photoexcitation [18].

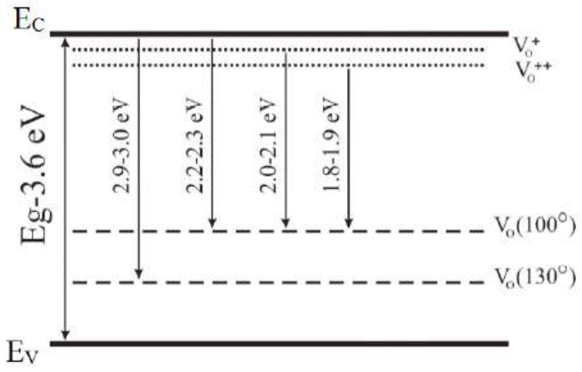

Fig. 5. Generalized scheme of levels and radiative transitions in photoluminescence of SnO_2 [37].

The results of research by various authors, presented in this review, allow us to consider tin dioxide not only one of the most popular and promising materials in sensorics, but also having wide applications in optoelectronics and LED technology.

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Summary

The article presents a brief review of luminescence in nanoscale tin dioxide. The luminescence caused by its own defects, the luminescence associated with impurities, the mechanisms of luminescence in tin dioxide are considered. The results of research by various authors presented in this review show the promising use of tin dioxide in optoelectronics and LED technology.

Key words: tin dioxide, nanoscale, luminescence.

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ЛЮМІНЕСЦЕНЦІЯ НАНОРОЗМІРНОГО ДІОКСИДУ ОЛОВА. ОГЛЯД

Резюме

У статті подано короткий огляд люмінесценції в нанорозмірному диоксиде олова. Розглядається світіння, обумовлене його власними дефектами, люмінесценція, пов’язана з домішками, механізми люмінесценції в діоксиді олова. Результати досліджень різних авторів, представлені в цьому огляді, показують перспективність застосування двоокису олова для широке застосування в оптоелектроніці і світлодіодним техніці.

Ключові слова: діоксид олова, нанорозмір, люмінесценція

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ЛЮМИНЕСЦЕНЦИЯ НАНОРАЗМЕРНОГО ДИОКСИДА ОЛОВА. ОБЗОР

Резюме

В статье представлен краткий обзор люминесценции в наноразмерном диоксиде олова. Рассматривается свечение, обусловленное его собственными дефектами, люминесценция, связанная с примесями, механизмы люминесценции в диоксиде олова. Результаты исследований различных авторов, представленные в этом обзоре, показывают перспективность применения двуокиси олова в оптоэлектронике и светодиодной технике.

Ключевые слова: диоксид олова, наноразмер, люминесценция