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Chapter 5
Optical Phenomena in Nanoscale Tin Dioxide Films Obtained by Means of Polymers

L. Filevska, A. Chebanenko, M. Klochkov, V. Ggrinevych, and V. Smyntyna

5.1 Introduction

Tin dioxide (SiO_2) is one of the principal nanoscale materials for sensors and electrodes which demonstrate a number of new properties that may expand its practical applications. One such novel property of SiO_2 at nanoscale is the photoluminescence (PL) registered at room temperature.

Requirements for modern electronic display devices stimulate the search for new luminescent materials. Nanoscale forms of tin dioxide 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 light emitting diode (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.

Low-temperature luminescence of crystalline tin dioxide was described in 1979 [5]. The intrinsic luminescence band of SnO_2 is located in the ultraviolet region of the spectrum (approximately 350–355 nm), [6, 7]. In the visible range, at low temperatures, wide photoluminescence (PL) bands in the range of 2 and 2.5 eV [8, 9] 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 PL decreases, and 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 [10].

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The number of observations of photoluminescence in a nanoscale SnO_2 at elevated temperatures increases [11–15].

Optical properties of SnO_2 films [16] are characterized by relatively high transmittance coefficients (80–90%). Optically colorless glass of mark K8, used as substrates, has a transparency of more than 90%. The maximum light absorption is no more than 20%, and the minimum is about 10%. A slight decrease in the thickness of the tin dioxide layer leads to a significant increase in the optical transmittance. At thicknesses of 0.07–0.09 μm, the average optical transmittance of tin dioxide films is 81–83%.

The study of the optical transmission spectra of SnO_2 films allows determining the coefficient of light absorption in the films. The form of the spectral dependence of the absorption coefficient makes it possible to determine the set of parameters. They are types of optical transitions, direct or indirect transitions, leading to the appearance of excess carriers in the conduction band, estimating the forbidden band as well as the degree of composition deviation from film stoichiometry.

The authors have obtained nanostructured films of tin dioxide by sol-gel method using polyvinyl acetate as a structuring additive. In this paper, the results of studies of optical absorption, reflection, and room temperature photoluminescence of the films, depending on the polymer content in the initial solution used for films' production, are presented.

5.2 The Sample Preparation Technology and Experimental Techniques

To obtain SnO_2 films by the sol-gel method, bis(acetylacetonato)dichlorotin (IV) was used as a precursor [17] and polyvinyl acetate (PVA) was used as a structuring substance [18]. The initial materials' solution in acetone was mixed in the required proportions. The resulting gel was put on glass substrates, and then high-temperature annealing was performed in air. As a result of annealing, which provides the removal of decomposition products of the PVA polymer, as well as additional oxidation, the thin layers of tin dioxide were formed. Surface profiles obtained using atomic force microscopy (AFM) showed that the surfaces of SnO_2 films have a porous columnar structure with an average transverse crystallite size of about 20 nm This indicates that the tin dioxide films obtained by the modified sol-gel method are nanostructured with a high degree of surface development.

The optical density spectra of samples of tin dioxide were measured on an SF-46 spectrophotometer. The measurement step was 10 nm in the spectral range from 350 to 1000 nm. The photoluminescence spectra were excited by the glow of a SVD-120 mercury lamp with a UFS-6 optical filter with $\lambda = 360$ nm.

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5.3 Results and Discussion

Figure 5.1 shows the optical density spectra of SnO_2 films with different contents of PVA. The band gap, estimated from the slope of the absorption edge, had different values for films obtained from solutions with different polymer contents. For a film from a solution with a PVA concentration of 1%, the size of the forbidden zone was $E_1 = 3.07$ eV and for a film from a solution with a concentration of PVA of 0.1% was $E_2 = 2.98$ eV. Since large values of the forbidden band are specific for smaller crystallites (which is typical for tin dioxide and other semiconductor materials [10, 19]), it can be assumed that the size of SnO_2 nanocrystals is smaller in the first case than in the second. The reason for this is that PVA in the initial solution plays the role of a matrix that divides the space into separate cells, where the synthesis of SnO_2 nanocrystals occurs. Obviously, it is the greater the concentration of PVA, the smaller the volume of the individual cell, which limits the size of SnO_2 nanocrystals. The straightening of the indicated dependence in the coordinates $D^{1/2} - h\nu$ indicates that the indirect allowed optical transitions take place in the studied films. The obtained numerical values of the energy of the forbidden band E_1 and E_2 are lower than those of single-crystal tin dioxide. This is due to the high degree of porosity of the layers under study and the presence of an amorphous phase in them [20]. The last statement is also supported by the presence of a plateau on the curve of the optical density spectrum from the long-wave side of the absorption edge. Processes at grain boundaries with a high density of barriers and boundary

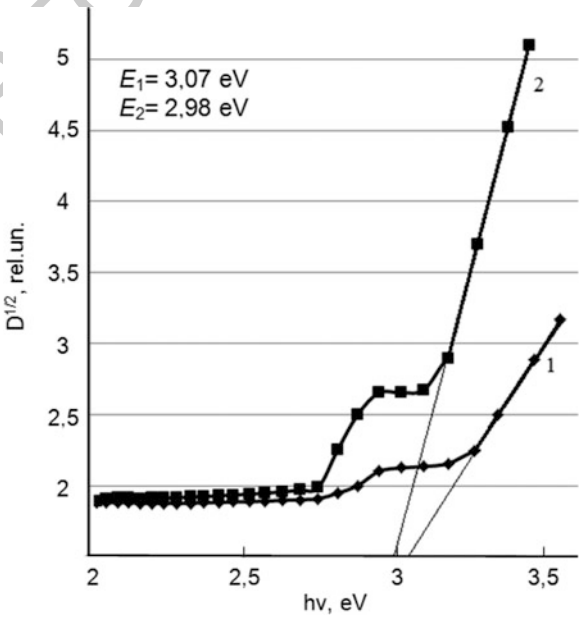

Fig. 5.1 Absorption spectra of SnO_2 films with different contents of PVA: (1) –1%, (2) –0.1%

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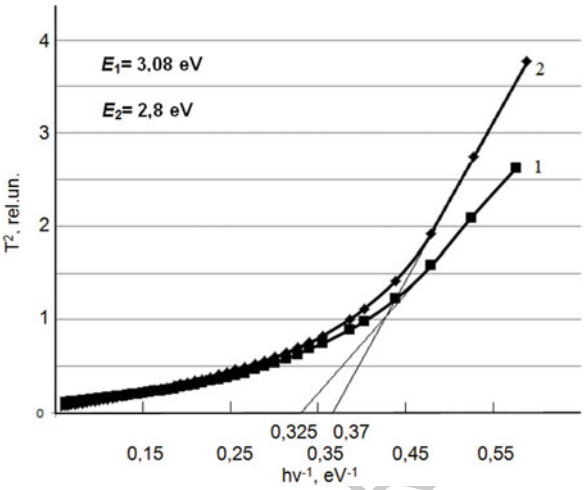

Fig. 5.2 Transmission spectra of SnO_2 films obtained from solutions with a PVA content: (1) –1%, (2) –0,1%

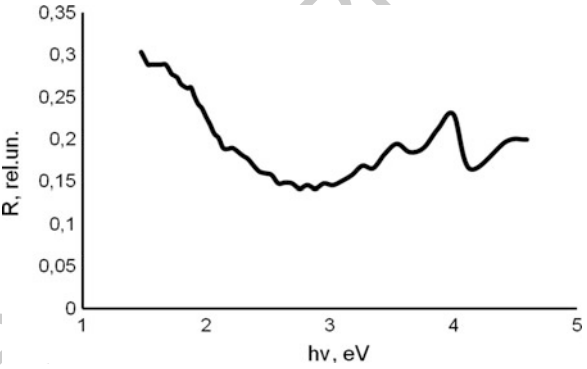

Fig. 5.3 Characteristic reflection spectrum of films SnO_2

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defects that affect optical absorption can also contribute to the narrowing of the band gap.

Figure 5.2 shows the optical transmission spectra of SnO_2 with different amounts of PVA in the initial solution. The numerical values of the band gap, estimated from the transmission spectra, were 3.08 eV (for films from a solution containing 1% PVA content) and 2.8 eV (0.1% PVA). As it can be seen, these values of the band gap agree well with those determined from the absorption spectra.

Figure 5.3 shows the specific reflection spectrum of tin dioxide films under study. In the energy range $h\nu > 3$ eV, it has an oscillating character. This may be due to the interference, which appears when the film thickness is comparable to the wavelength, as it was in the case, for example, of thin films of zinc sulfide [21].

The curve of the reflection spectrum shows a minimum at $E = 2.8$ eV, which corresponds to the frequency $\omega_{\min} = 4.25 \cdot 10^{15}$ s^{-1}. The minimum of reflection in films with a relatively high carrier concentration corresponds to the absorption

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of light by electron plasma with a plasmon frequency ω_p determined according to [22]

$$\omega_p = \sqrt{\frac{n_0 e^2}{m^* \varepsilon_s \varepsilon_\infty}} \tag{5.1}$$

In the above formula: m^* is the effective electron mass; e is the electron charge; and ε_s and ε_∞ are the static and dynamic dielectric constant of the semiconductor (tin dioxide in our case). The reflection minimum frequency, $\omega_{\min}$, is proportional to ω_p and is determined [23] as

$$\omega_{\min} \approx \omega_p \sqrt{\frac{\varepsilon_\infty}{\varepsilon_\infty - 1}} \tag{5.2}$$

Using (5.1) and (5.2), one can estimate the concentration of free electrons n_0 in the studied SnO_2. The following values were used for calculations [22]: $m^* = 0.59\ m_0$; $\varepsilon_s = 13{,}0$; and $\varepsilon_\infty = 24{,}0$. The obtained value of carrier concentration appeared to be equal to $n_0 = 9.4 \cdot 10^{12}\ \mathrm{cm}^{-3}$.

Figure 5.4 shows the photoluminescence (PL) spectra of two SnO_2 samples containing different concentrations of PVA. It can be seen that the spectral position of the maxima of the PL bands does not depend on the concentration of PVA, but the

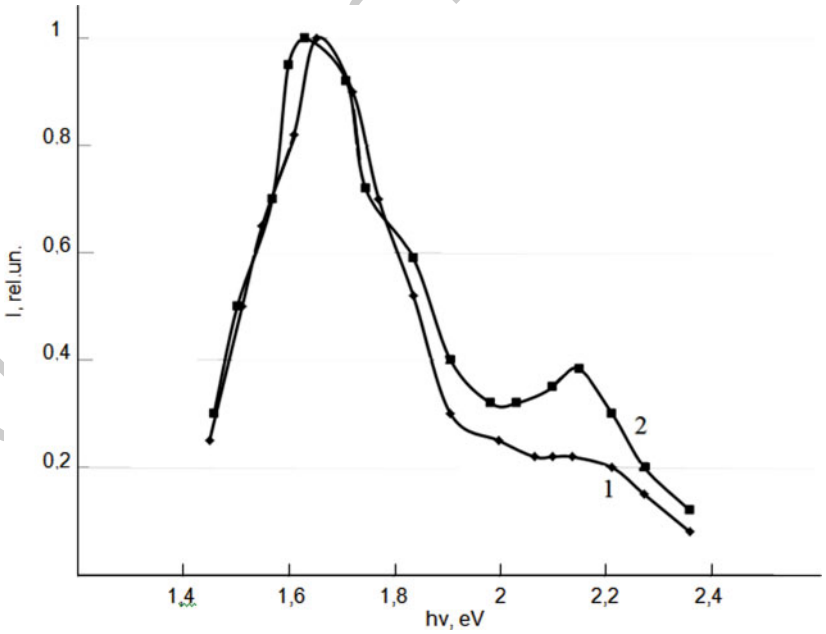

Fig. 5.4 Photoluminescence spectra of SnO_2 films with different contents of PVA in the initial solution: (1) –0.1%, (2) –1%

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intensity of the band at $\lambda_{max} = 580$ nm increases with PVA concentration growth. It is known [8] that in tin dioxide, oxygen vacancies (except for donor levels associated with V_0^+ and V_0^{++}) can be mutually located with tin atoms at angles of 100° and 130°, forming centers that participate in radiative recombination. The corresponding energy levels are located at an energy distance of 1.4 eV (V_0 (100°)) and 0.9 eV (V_0 (130°) from the top of the valence band. Taking into account the energy position of the maxima of the PL bands in the SnO_2 films (1.63–1.68 eV and 2.14 eV) under study, as well as the width of the forbidden band (about 3.1 eV), the observed PL bands can be attributed to radiative transitions of electrons from conduction bands of SnO_2 to V_0 (100°) and V_0 (130°) levels, respectively.

5.4 Conclusions

The band gap of the films estimated from the reflection spectra was 2.98 eV (for 0.1% PVA) and 3.07 eV (for 1% PVA). Therefore, the size of the nanocrystals of the film obtained from the solution with a higher polymer concentration is less due to the limitation of the crystallite size by the structuring polymer molecules at the film production.

The reflection spectrum of the investigated tin dioxide film has an oscillating character in the energy region $h\nu > 3$ eV. This may be due to interference, which manifests itself at a film thickness comparable with the wavelength, as it was in the case, for example, in thin films of zinc sulfide [6]. A minimum is observed on the reflection curve spectrum at a frequency $\omega_{min} = 4.25 \cdot 10^{15}$ s^{-1}. The calculated concentration of free electrons was $9.4 \cdot 10^{12}$ cm^{-3}.

The spectral position of the maxima of the PL bands does not depend on the PVA concentration; however, the intensity of the $\lambda_{max} = 580$ nm band increases with increasing PVA concentration. Taking into account the energy position of the maxima of the PL bands in the investigated SnO_2 films (1.63–1.68 eV and 2.14 eV), and also the band gap (about 3.1 eV), the observed PL bands may be associated with the radiative transitions of electrons from the conduction band of SnO_2 to the levels of V_0 (100°) and V_0 (130°), respectively.

The results obtained are valuable as good perspective for the possible application of nanosized tin dioxide as sensors for optical signal registration.

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