Chapter 18
Temperature Studies of Luminescence in Nanosize SnO$_2$ Films

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18.1 Introduction

Tin dioxide, widely used in various electronics industries, is not known as a luminophore material; however, low-temperature luminescence of crystalline tin dioxide has been described in the literature back to 1979 [1]. The band of intrinsic SnO$_2$ luminescence is located in the near-ultraviolet spectrum region. In the bulk tin dioxide samples in the visible range, wide photoluminescence (PL) bands are observed at low temperatures in the regions of 2 and 2.5 eV, which are associated with interstitial tin/oxygen vacancies electronic transitions [2, 3]. However, with temperature increasing, the intensity of such a photoluminescence decreases, and at a room temperature, the PL is practically invisible. The PL spectra of nanoscale tin dioxide samples differ from the bulk material spectra, which were shown by a number of researches [2–4]. The nanoscale forms of this material have recently been increasingly characterized as luminescing at the room temperature [5–8].

Photoluminescence of tin dioxide nanosized particles at the liquid nitrogen temperature was studied by Meier and colleagues [4]. PL was excited by GaN LED at a wavelength of 400 nm. The researchers detected a PL peak at a wavelength of 625 nm (E = 2 eV) independent of particles' size, which witnesses, according to the authors, about the group defect responsible for it, associated with oxygen vacancies. At the same time, the PL intensity increases with nanoparticle size growth from 5 to 20 nm and with the samples' composition approaching to stoichiometry

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from $SnO_{1.5}$ to $SnO_{1.7}$. This fact correlates with a high density of electrons' states within the gap width obtained from the absorption measurements presented at the same work. The authors associate this intensity increase with the low rate of nonradiative recombinations in $SnO_{1.7}$ due to the low total defect density. Obviously, in an ideal, in a defect-free SnO_2 crystal, there should be no defects responsible for PL. If the number of oxygen vacancies increases, the PL intensity will also increase until the processes of nonradiative recombination will begin to dominate, as in the case of $SnO_{1.5}$.

Korean researchers also explained the influence of oxygen vacancies on PL observed by them in the region of 2.5 eV for thin SnO_2 films deposited by the CVD method. Bonu et al. [7] also explained the observed luminescence at 2.54 eV and 2.42 eV by oxygen defects, namely, in-plane and bridging "O" vacancies. The broad luminescence peak, observed by [7], at about 1.96 eV in NPs SnO_2 was associated with the hydroxyl groups OH^- on the surface of particles. In [8], the broad luminescence bands observed in the 350–550 nm region were associated with defect states on the surface of SnO_2 nanoparticles. As it may be seen, the surface states play an important role in the luminescence of tin dioxide nanoforms.

This paper presents the luminescence low-temperature studies of nanostructured tin dioxide films obtained using polymers in order to establish the mechanisms of radiation and its temperature quenching.

18.2 Film Preparation and Research Methods

SnO_2 films were obtained by a sol-gel method using polyvinyl acetate (PVA) to improve structuring. In samples' series fabrication, the content of the precursor (bis (acetylacetonato) dichlorotin (BADCT)) in the initial solution varied from 1% to 10%. After deposition on the glass substrate, the samples were annealed until the organic components were removed and a transparent layer of tin dioxide was formed.

The experiment was carried out according to the standard procedure [9, 10]. A nitrogen laser with a radiation wavelength of 337 nm was used to excite the luminescence. The photoluminescence of the samples was studied in the temperature range 9–300 K.

18.3 Experimental Results and Discussion

The films of tin dioxide obtained with the use of polymers showed photoluminescence at room temperature in the orange-red spectrum region. The results of photoluminescence at room temperature on SnO_2 layers, depending on the amount of precursor, are shown in Fig. 18.1.
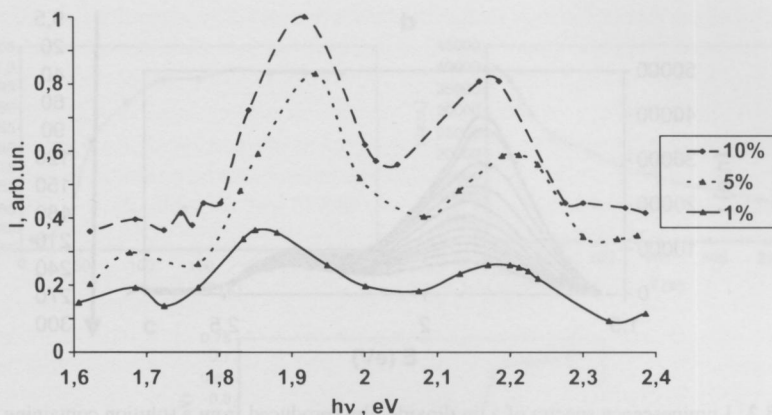
Fig. 18.1 The photoluminescence spectrum of SnO$_2$ films with different precursor concentrations (0.05% PVA) at room temperature

Table 18.1 Energy of maxima of PL bands for SnO$_2$ films with different precursor concentrations in the initial solution

Precursor concentrations	1%	5%	10%
The band in the 647 nm region	1.85 eV	1,88 eV	1,92 eV
The band in the 579 nm region	2,18 eV	2,2 eV	2,17 eV

As it can be seen (Fig. 18.1), in the emission spectrum, there are two intensive wide bands (1.92 eV for 10%, 1.94 eV for 5%, and 1.86 eV for 1% of BADCT and 2.17 eV for 10%, 2.2 eV for 5%, and 2.18 eV for 1% of BADCT). Moreover, the energy positions of the maxima of these bands are nonlinearly dependent on the concentration of tin dioxide precursor in the original gel. The bands themselves are quite wide and complex. Thus, the peak in the region 1.86 eV (for 1% of the precursor) is considered as a broadening of the bands 1.92 eV and 1.94 eV for films with high precursor content. The figure also shows an increase in the radiation intensity with an increase in the precursor concentration. This may indicate an improvement in the crystallinity of the SnO$_2$ film resulted in a decrease of nonradiative transitions. The values of both peaks in films of different compositions are presented in the Table 18.1.

Meier and colleagues [4] associate the detected photoluminescence peak at 625 nm (2 eV) at a liquid nitrogen temperature in nanoscale SnO$_x$ particles with a group defect formed by oxygen vacancies. The PL was established in the present work in nanostructured tin dioxide films at room temperature. It was supposed that the peak at 647 nm (1.9 eV) is also associated with oxygen vacancies in the samples studied. The difference in the peaks' energies may be due to the different energy of the PL excitation and the differences in the samples' structure. At the same time, according to Bonu's data [7] on hydroxyl groups on the surfaces of SnO$_2$ nanoscale particles, this peak may also be attributed to them. This supposition can be confirmed
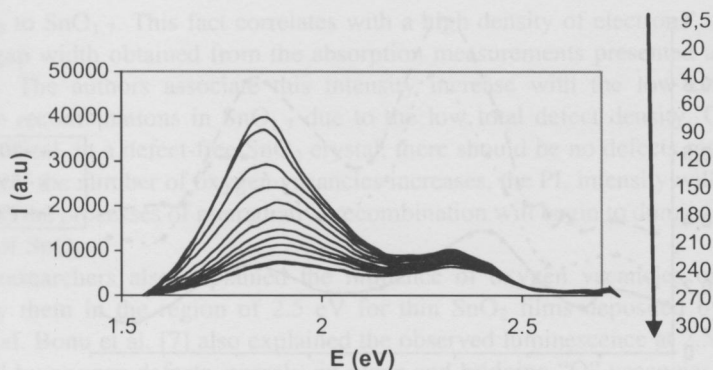
Fig. 18.2 Luminescence spectra of a tin dioxide film (produced from a solution containing 0.05% PVA and 1% precursor of tin), measured at temperatures from 9.5 to 300 K

by additional studies of PL in vacuum at elevated temperatures after additional annealing, but this was not the task of this paper.

It is known from the reference data [11] that a singly charged Sn has a band of 579 nm (2.15 eV) in its spectrum. Comparing these facts, it may be supposed the correspondence of the group of bands 2.17–2.2 eV in the films to the centers of luminescence, which are the interstitial tin atoms or clusters of these atoms. The presence of metal clusters in SnO_2 films was established earlier by the authors [12]. Their notable contribution was marked in the electrical conductivity and adsorption activity of SnO_2 layers. In addition, it was shown in [13] that at $T = 723$ K, there were at least three phases in tin dioxide films: Sn, SnO, and SnO_2. On the other hand, the presence of excess tin indicates the presence of vacancies in the oxygen structure. Having the reports of luminescence on oxygen vacancies in this region [2, 3, 5, 6], it is possible to associate the observed peak with them.

Figure 18.2 shows the temperature dependences of the luminescence of tin dioxide films studied in the temperature range from 9.5 to 300 K.

As it can be seen from the figure, two peaks are observed in the photoluminescence spectra: the first is in the region 1.85–1.9 eV, and the second is in the region 2.32 eV. The value of the second peak slightly differs from the previously measured value (2.18 eV). This may indicate the structural changes that occur in the layer in the process of research procedure, namely, the surface oxygen influence and its gradual incorporation into the crystal structure.

The results of studies in the forms of the peaks' energy, intensity, and half-width temperature dependencies are shown in Figs. 18.3 and 18.4.

The temperature dependences show a decrease in the peaks' luminescence intensity with temperature growth. The observed effect is explained by temperature quenching of luminescence as a result of nonradiative recombination. This is a consequence of a significant density of electron states in the forbidden band, specific for tin dioxide [14], especially for nanoscale structures and thin films with a
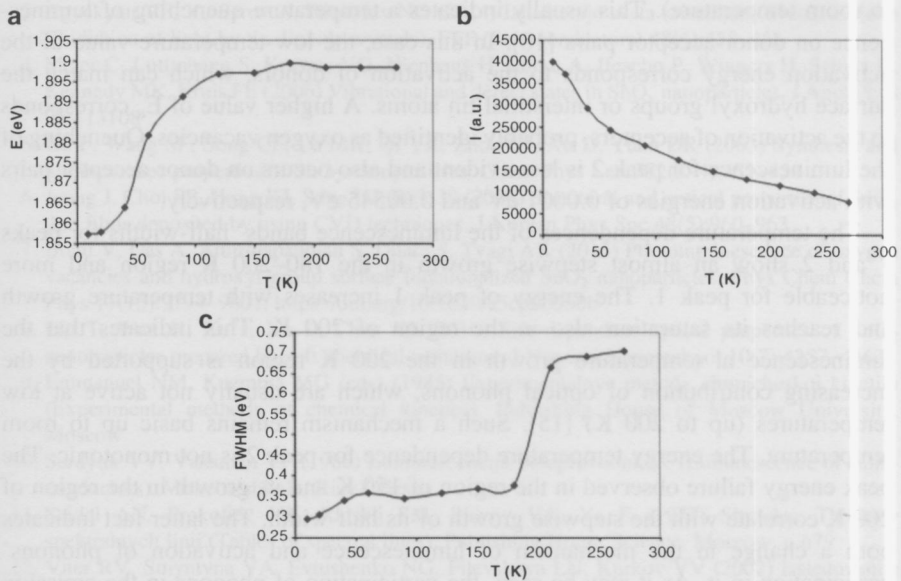
Fig. 18.3 Temperature dependences of the peak' energy 1 (a), its intensity (b), and half-width (c)
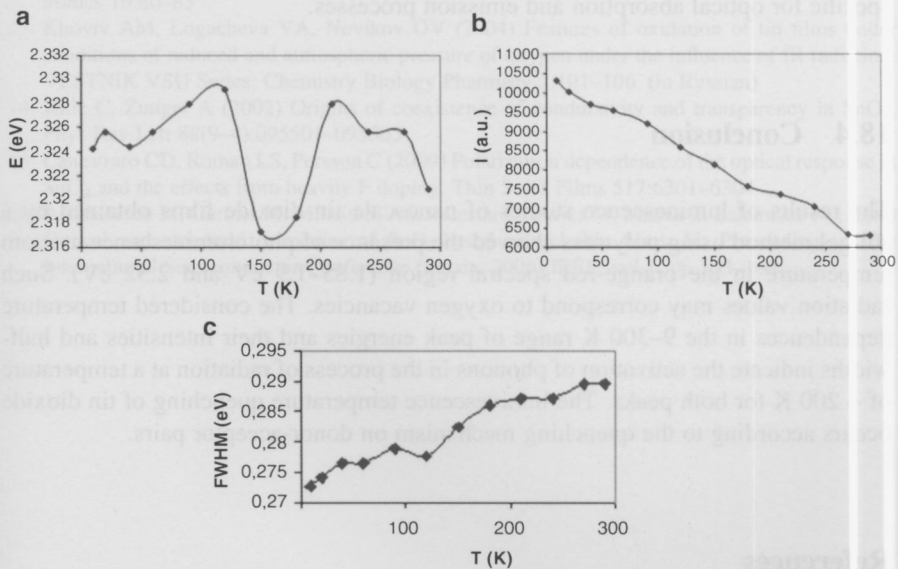

Fig. 18.4 Temperature dependences of the peak' energy 2 (a), its intensity (b), and half-width (c)

significant disruption of long-range order [2, 4]. The change in the peak' 1 temperature dependence of intensity built as a graph of semilogarithmic dependence on the reciprocal temperature showed the presence of two regions with activation energies $(E_a) \sim 0.0114$ eV (at a lower temperature up to ~ 50 K) and ~ 0.0156 eV (from 120 K

to room temperature). This usually indicates a temperature quenching of luminescence on donor-acceptor pairs [10]. In this case, the low-temperature value of the activation energy corresponds to the activation of donors, which can match the surface hydroxyl groups or interstitial tin atoms. A higher value of E_a corresponds to the activation of acceptors, probably identified as oxygen vacancies. Quenching of the luminescence for peak 2 is less evident and also occurs on donor-acceptor pairs with activation energies of 0.0001 eV and 0.00545 eV, respectively.

The temperature dependences of the luminescence bands' half-widths for peaks 1 and 2 show an almost stepwise growth in the 180–200 K region and more noticeable for peak 1. The energy of peak 1 increases with temperature growth and reaches its saturation also in the region of 200 K. This indicates that the luminescence at temperature growth in the 200 K region is supported by the increasing contribution of optical phonons, which are usually not active at low temperatures (up to 200 K) [15]. Such a mechanism remains basic up to room temperature. The energy temperature dependence for peak 2 is not monotonic. The peak energy failure observed in the region of 150 K and its growth in the region of 200 K correlate with the stepwise growth of its half-width. The latter fact indicates both a change in the mechanism of luminescence and activation of phonons' participation in it. As it may be seen, the participation of phonons in the emission process is specific for both peaks. In favor of this is also the fact that tin dioxide is an indirect-gap semiconductor [16], and the participation of phonons in such a case is specific for optical absorption and emission processes.

18.4 Conclusion

The results of luminescence studies of nanoscale tin dioxide films obtained by a sol-gel method using polymers showed the presence of photoluminescence at room temperature in the orange-red spectral region (1.85–1.9 eV and 2.32 eV). Such radiation values may correspond to oxygen vacancies. The considered temperature dependences in the 9–300 K range of peak energies and their intensities and half-widths indicate the activation of phonons in the process of radiation at a temperature of ~ 200 K for both peaks. The luminescence temperature quenching of tin dioxide occurs according to the quenching mechanism on donor-acceptor pairs.

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