

CATHODOLUMINESCENCE EMISSION STUDY OF NANOSTRUCTURED SnO₂ FILMS DEPOSITED BY SPRAY PYROLYSIS

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Abstract

In this paper the results of cathodoluminescence (CL) emission study of undoped and doped SnO₂ films are discussed. SnO₂ films were deposited by spray pyrolysis method. It was shown that the study of CL emission is effective method for structural characterization of metal oxides aimed to gas sensor applications. It was concluded that the changes taking place in CL spectra are connected with the change of both the grain size and the crystallinity (stoichiometry) of the surface layer and the bulk of SnO₂. The shape of CL spectra depends on correlation between well-crystallized core and disordered surface layer. It was found that doping is accompanied by deterioration of film crystallinity and the growth of concentration of structural defects responsible for unradiative recombination of excited electrons and holes.

1. Introduction

At present there can be no doubt that both the structural properties and the peculiarities of energy spectrum of native defects in metal oxides, in many respects, determine gas-sensing characteristics of solid-state sensors [1-3]. However, one should admit that although the crystallographic properties of metal oxides have been studied in detail [4-7], the information about the bulk and surface structural disordering is very limited [8].

It means that obtaining of additional information about structural properties of metal oxides, including behavior of native defects, is the task of importance for material sciences of metal oxides. In this context, the object of this study, such as the cathodoluminescence emission of SnO₂ films deposited using different technological routes, presents interest. At present the measurement of CL emission is one of the most effective methods for study of powders' physical properties; and it is being widely used for characterizing metal oxide phosphors [9, 10]. Use of this method for metal oxides such as SnO₂ can give information necessary for better structural characterization of metal oxides aimed to gas sensor applications. It is necessary to note that the first results of research in this direction can be found in Refs. [11-13].

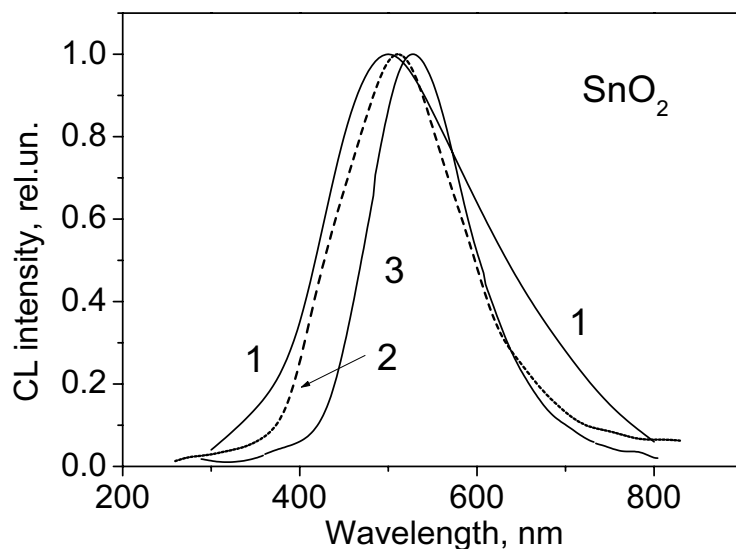
2. Experimental details

Studied undoped and (Cu-, Fe-, and Co)-doped SnO₂ films were deposited by spray pyrolysis from 0.2 M SnCl₄ water solution [14]. The doping was realized during the process of film deposition. The additives were embedded into a solution prepared for the spraying in the form of chlorides. The concentration of the doping elements in the sprayed solution was varied from 0 to 16 at %. As it was shown in Refs. [3, 15, 16], the concentration of additives, optimal for the gas sensor applications, is in the concentration range indicated before. Studied films had thickness varied in the range from 40 to 400 nm. Structural and gas sensing characteristics of studied SnO₂ films were discussed in detail in [3, 14, 17].

Room temperature cathodoluminescence (CL) was measured using spectrometer, recording radiation in the range 300-850 nm. The CL spectra were excited in vacuum in the camera of a standard micro-probe analyzer Camebax-4. The sample was excited by an electron beam with diameter up to 1 μm. Excitation energies of electron beam were in the range 10–15 kV, and electron current was varied from 30 to 100 nA. These conditions favored for both the maximum CL intensity and the absence of electron beam interaction with substrate. Differences in CL spectra were observed as a function of deposition parameters (T_{pyr} - 350-550°C), nature and concentration of additives (0-16 at %), and the following high temperature annealing. Annealing was carried out in temperature range from 600 to 950°C in the atmosphere of usual air or nitrogen. During our experiments we took special care to produce CL spectra in conditions, giving possibility to compare their intensities, which is fundamental to the reliability of our conclusions.

3. Results and discussion

In Fig. 1 typical CL spectra of SnO₂ films and powders are shown. It is seen that irrespective of technological routes, as-deposited SnO₂ films have CL spectra similar to CL spectra of as-synthesized SnO₂ powders [11, 12]. Spectra do not have edge emission band, and the intensity of CL is low, especially for films deposited at low pyrolysis temperature and for thin films with thickness less than 60 nm. CL spectra have alone broad band centered at $\lambda \sim 500$ nm. Analogous shape also was observed for spectra of radiative recombination, measured for SnO₂ nanostructures such as nanowires, nanoribbons, etc. [12, 18]. They observed broad



peak centered in dependence on synthesis temperature in spectral range from 510 to 570 nm. Taking into account the band gap of SnO₂ ($E_g \sim 3.6$ eV [19]), the edge-band luminescence must be picked at the wavelength of 340-360 nm.

Fig. 1. Typical CL spectra of as-deposited and as-synthesized (2,3) SnO₂ films and (1) powders: (2)- $T_{\text{pyr}} = 450^\circ\text{C}$; (3)- $T_{\text{pyr}} = 550^\circ\text{C}$; $d \sim 130\text{-}150$ nm.

The increase of pyrolysis temperature in the range 350-500°C is accompanied only by the narrowing of emission band (see Fig. 1) and by the increase of CL intensity (see Fig. 2). As it is seen from the results presented in Fig. 2, the CL intensity increases up to 10 times in the above-indicated temperature range of spray pyrolysis deposition. High temperature annealing at T_{an} higher than 700-800°C (see Fig. 3) also results in considerable growth of CL intensity.

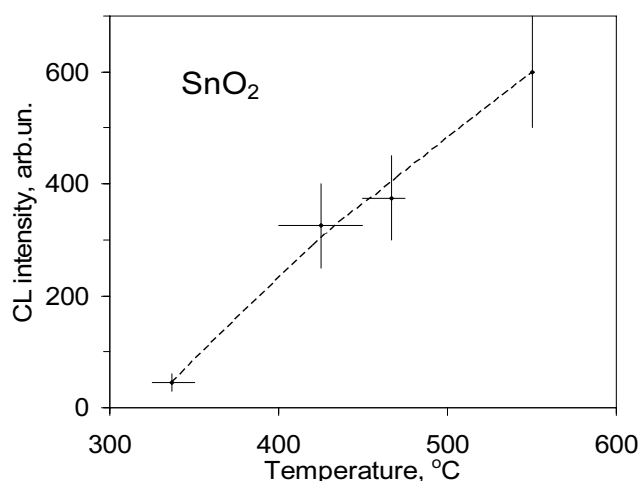


Fig. 2. Influence of pyrolysis temperature on the CL intensity of SnO₂ films ($d \sim 130-150$ nm).

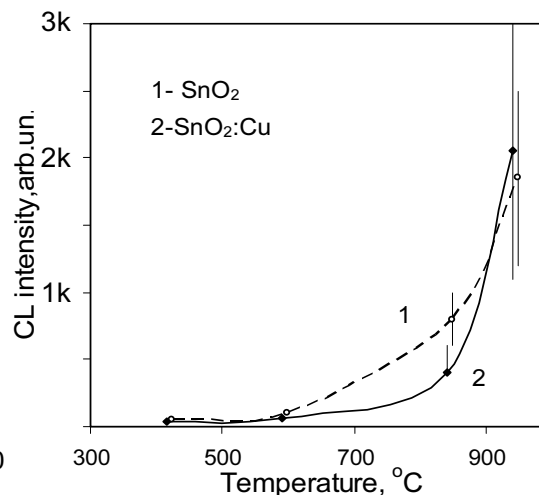


Fig. 3. Dependence of CL intensity of (1) undoped and (2) Cu doped SnO₂ films on annealing temperature ($T_{pyr} = 350^\circ\text{C}$; $d \sim 130-150$ nm).

The increase of the effectiveness of luminescence after high temperature annealing up to 1000-1200°C, accompanied by a considerable growth of crystallite size, is well known fact [9-20], and it is widely used in the technology of phosphorus. The same growth of the CL intensity was observed during calcinations of SnO₂ powders [12], aimed to gas sensor design. According to Refs. [9-20], only after $T_{an} > 1500^\circ\text{C}$ the decrease of the CL intensity takes place, which is accompanied by an essential increase of SnO₂ resistance, testifying to the decrease of concentration of oxygen vacancies responsible for electron nature of SnO₂ conductivity. Observed similarity in the behavior of CL properties in both powders and films during annealing process testifies to similarity of the processes taking place in those materials.

The absence of edge band emission and low intensity of CL spectra of as-deposited SnO₂ films indicates that they are highly imperfect films with lattice irregularity independent of both pyrolysis temperature and film thickness. Due to high concentration of structural defects in the films, they are characterized by high rate of nonradiative recombination and specific shape of CL spectra, where the radiative transitions with participation of shallow donor levels, associated with O-vacancies, and trapped centers, located in the midgap of SnO₂, predominate. According to Ref. [12] in SnO₂ there are three types of defects, forming deep levels, located at 0.8-0.9, 1.35-1.45 and ~ 1.6 eV from the top of valence band. Just for this reason the short-wave band is absent in experimental CL spectra of SnO₂ films.

After analysis of CL spectra transformation, taking place during thermal treatments, we concluded that the changes taking place in CL were connected with the change of both the grain size and the crystallinity (stoichiometry) of the surface layer and the bulk of SnO₂. For example, we assume that the shape of CL spectra depends on correlation between well-crystallized core and disordered surface layer. The latter due to high concentration of structural defects and high

density of the states near the conduction band bottom and the valence band top, caused by lattice nonstoichiometry, is characterized by high rate of nonradiative recombination of excited electrons and holes. The possibility of formation of these structures in SnO₂ nanograins was experimentally confirmed in Refs. [21, 22]. It means that depending on correlation between well-crystallized core and disordered surface layer, the intensity and the shape of CL spectra of SnO₂ would greatly differ from each other. As-deposited, especially at low temperature, SnO₂ grains have small diameter of well-crystallized core and extensive amorphous-like surface layer. It means that in these films due to high concentration of defects the nonradiative recombination of excited carriers can be dominating. Besides, the presence in the grain of a space charge region with thickness comparable with grain size, due to space separation of excitable electrons and holes, would contribute to the increase of the role of surface structural disordered area in the CL spectra forming. It is necessary to note that for SnO₂ being in oxygen containing atmosphere, the band bending could reach 0.5-1.0 eV [23].

As it is known, high temperature annealing in oxygen-containing atmosphere favors increase of the size of both crystallites and well-crystallized core and improvement of the surface layer stoichiometry [3, 5, 22, 24]. It means that high temperature annealing, due to such effects as the ordering of surface layer structure, the decreasing of structural defect concentration, and the removing of mechanical strains in bulk of grains, contributes to the strengthening of the role of well-crystallized core in the CL spectra forming and the weakening of the influence of non-radiative recombination on CL spectra. As one can see from the earlier presented results, precisely these regularities were observed during our research.

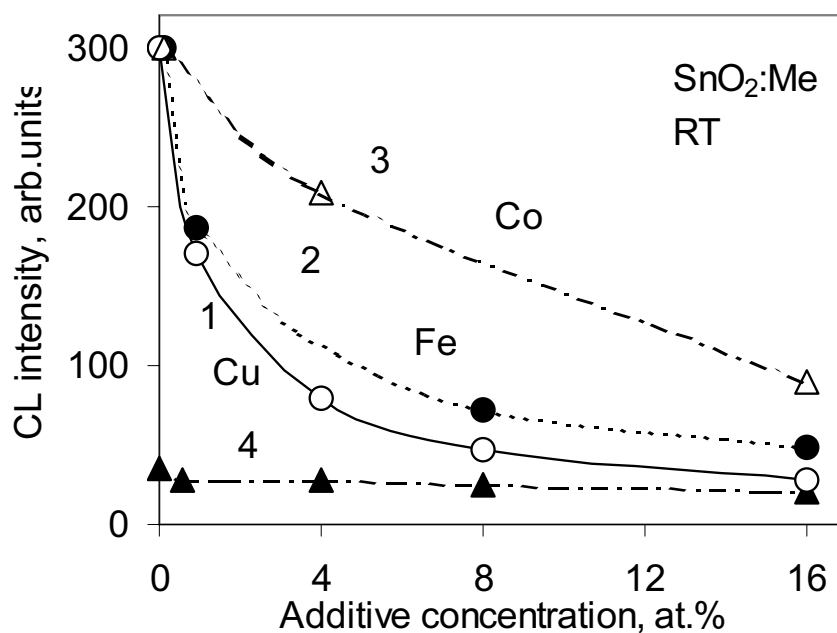


Fig. 4. Doping influence on CL intensity of SnO₂ films deposited by spray pyrolysis (1-3) - $T_{\text{pyr}} = 450^\circ\text{C}$; (4) - $T_{\text{pyr}} = 350^\circ\text{C}$, ($d \sim 120$ nm).

Experiments related to cathodoluminescence study of doped SnO₂ films confirm our assumption. As it is shown in Fig. 4, doping with even small concentrations of transition metal additives is accompanied by strong decrease of CL intensity. It means that the doping is accompanied by degradation of film crystallinity and the growth of the concentration of structural defects. Results of research presented in Ref. [3] are good confirmatory examples that in heavily doped SnO₂ the concentration of structural defects is increased. It was shown that in SnO₂ due

to doping with transition metals the tailing of band gap edge takes place, testifying to the appearance of tails of electronic states inside the band gap. Besides, the degree of the change in optical transmission near the band gap edge observed at SnO₂ doping (see [3]) is in a good agreement with earlier presented results of the doping influence on the CL intensity. If one compare the data presented in Ref. [3] for SnO₂:Cu, one can see that the stronger the tailing of band gap edge, the bigger the decrease of CL intensity. A possibility of appearance near SnO₂ valence band of the electronic states, introduced by lattice disordering, caused by SnO₂ doping, is also experimentally confirmed in Ref. [25] on the base on the results of X-ray Photoemission Spectroscopy (XPS) study of SnO₂ powders after Ar-ion bombardment and doping with Pd and Pt. As it was shown in Ref. [19] there are no states in the band gap of the stoichiometric SnO₂ surface.

The coincidence of CL emission intensities of heavily doped films deposited at high pyrolysis temperatures and SnO₂ films deposited at low temperature, which are structurally less perfect [25, 26], directly confirms the above said. As one can see from the results presented in Fig. 4, curve 4, at the maximum concentration of dopants the intensity of cathodoluminescence drops to the level corresponding to CL intensity measured for the samples deposited at low pyrolysis temperature. It is important that for films deposited at low temperatures the CL intensity is so low that the dopants practically do not influence the CL spectra. Apparently, the concentration of structural defects in SnO₂ films deposited at low temperatures is so high that probability of nonradiative recombination of excitable electrons and holes appreciably exceeds the probability of radiative recombination.

The similar situation took place during SnO₂ doping with noble metals, such as Pd and Pt. These metals are usually used for improvement of catalytic activity of gas sensing material [3]. Results of the above mentioned research were discussed in detail in Ref. [11]. However, in contrast to transition metal doping, during the doping with noble metals we observed very interesting effect. The decrease of CL intensity happened only for additive concentration higher than 0.1-0.2 wt %. At smaller additive concentrations the CL intensity even increased. It indicates that small concentration of both Pd and Pt additives in SnO₂ contributes to the decrease of non-radiating recombination rate, which can be considered an evidence of the material crystal structure improvement. It is important to note that this threshold concentration corresponds to the doping conditions when the maximum sensitivity of SnO₂(Pd,Pt)-based sensors is achieved [27]. It means that the good crystallinity of metal oxides is one of the important factors contributing to improvement the gas sensing characteristics of solid-state devices. One can assume that at small concentration of Pd and Pt additives, the oxygen dissociation on small Pd and Pt clusters with following spillover stimulates the increase of the concentration of atomic oxygen, which participates in the process of SnO₂ growth and promotes to improvement of its stoichiometry. The high level of nonstoichiometry may be the reason of high concentration of surface states pinning the surface Fermi level and limiting the Fermi level shift during interaction with gas environment.

Cathodoluminescence spectra for undoped and doped SnO₂ films after thermal treatments at T=950°C are shown in Figs. 5 and 6. It is seen that the high temperature annealing in addition to influence on CL intensity (see Fig. 3) is accompanied by considerable transformation of the spectra. The latter is conditioned by the fact that in CL spectra there appears the short-wavelength band, peaked at 375 nm, close to band-edge luminescence, which has not been observed on spectra of as-deposited samples. It testifies that only after high temperature annealing the crystal structure of SnO₂ films and powders tends to the structure of SnO₂ single crystals. However, it is necessary to note that the process of SnO₂ crystallinity improvement has its own peculiarities. Firstly, edge-band luminescence shows up only for films being thicker than 200-

300 nm (see Fig. 5, curve 3). For SnO₂ films with thickness less than 200 nm on the CL spectra the emission with maximum peaked at $\lambda \sim 500$ nm continues be dominating (see Fig. 5, curves 1 and 2).

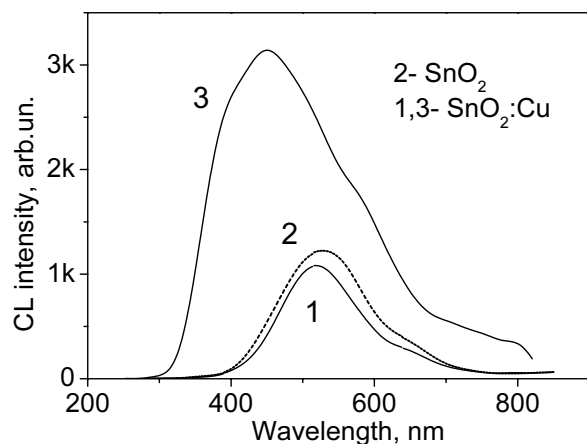


Fig. 5. CL spectra of undoped and Cu-doped SnO₂ films with thickness (1, 2) 200 nm and (3) 400 nm after annealing at 950°C ($T_{\text{pyr}} = 450^\circ\text{C}$).

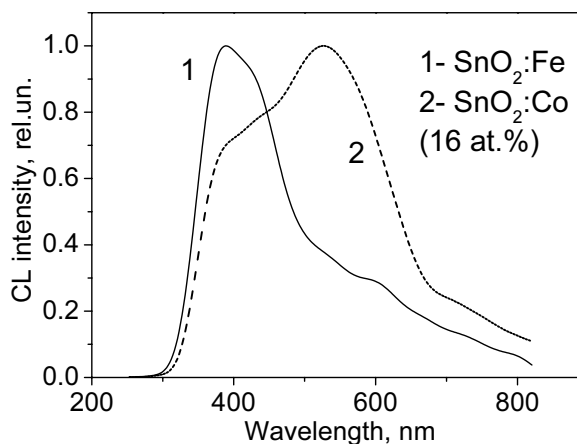


Fig. 6. CL spectra of (1) SnO₂:Fe and (2) SnO₂:Co films with thickness ~ 400 nm after annealing at 950°C ($T_{\text{pyr}} = 450^\circ\text{C}$).

It is known that the main difference between films with diverse thickness consists in the size of grains forming deposited film. Films with greater thickness have larger size of crystallites [4]. Moreover, it was established that the growth of grain size depends on film thickness and this change is greater in thicker films [24]. It means that the size of crystallites really plays an important role in obtaining of good luminescence properties of metal oxides. Secondly, although invariability of the structure of emission bands dominating in CL spectra, the correlation of the intensity of individual bands in CL spectra depends on nature of dopants (see Figs.5 and 6). In the case of the doping with iron in CL spectra of SnO₂ the band peaked at 380 nm dominates, at the doping with copper the band peaked at 450 nm has higher intensity, while at doping with cobalt the band with maximum intensity is peaked at 530 nm. It means that dopants have their own specificity of interaction with structural defects of SnO₂; that is, due to preferable interaction with structural defects of certain type doping could appreciably change their concentration in comparison with undoped material.

4. Conclusions

On the basis of the carried out research it was shown that the measurement of cathodoluminescence emission spectra could become an effective method for characterization of nanostructured metal oxides, aimed to gas sensor applications. There is a correlation between CL spectra peculiarities, crystallographic structure, and gas sensing properties of metal oxides.

As a result of the research we made the following conclusions: (1) The shape and intensity of CL spectra are sensitive to technological routes used for deposition of metal oxides; (2) As-deposited SnO₂ films are materials with lattice disorder and high concentration of point defects; (3) Only annealing at temperatures higher than 700-800°C contributes to considerable improvement of SnO₂ films crystallinity; (4) Doping with transition metal oxides (1-16 wt %) is accompanied by an increase of the structural defect concentration with appropriate decrease of CL intensity.

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