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Review

Bulk doping influence on the response of conductometric SnO_2 gas sensors: Understanding through cathodoluminescence study

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ABSTRACT

Present paper is devoted to analysis of both cathodoluminescence (CL) and gas sensing properties of the SnO_2-based materials. For those purposes SnO_2 doped by Pt and Pd (0.01–10 wt%) during powders synthesis, and the SnO_2 films doped by Fe, Co, and Cu (0–16 at%) during spray pyrolysis deposition have been used. It is shown that there is correlation between cathodoluminescence and gas sensing properties of the SnO_2-based devices, in particular, between the CL intensity and magnitude of sensor response. It was concluded that while analyzing both the CL spectra and CL intensity, one can receive additional information on structural parameters of doped SnO_2 which could be used for better understanding of gas sensing effects. It is shown that heavily doped SnO_2 films had considerable structural disordering and reduced both sensor response and the CL intensity. It was also concluded that for achievement maximum response of doped SnO_2:(Pd, Pt, Co, Cu)-based sensors, concentration of additives during bulk doping should provide their full incorporation in the SnO_2 lattice without forming clusters at the SnO_2 grain surface, i.e. doping concentration should be less than the limiting solubility of dopants in the metal oxide.

Contents

1. Introduction

Numerous studies have shown that gas sensing properties of metal oxides depend tremendously on their structural parameters, such as a type and concentration of the point defects, which can be generated in metal oxide during the synthesis, doping and interaction with the surrounding gas [1–4]. Therefore, the study of both the structural properties of metal oxides and the regularities of their influence on gas sensing characteristics has special importance for designing gas sensors with optimal parameters. However, one should admit that at present, the number of methods used for detailed characterization of gas sensing materials at the stage of their synthesis, as well as during the process of either sensors design or fabrication, is very limited. Mainly for those purposes, the measurement of resistivity (or conductivity) and

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analysis of scanning and transmission electron microscopy images are being used. Recently, Fourier Transform Infrared (FTIR) [5–7] and micro Raman spectroscopy [8–11] methods were added to the list of methods, which could also be used in the characterizing gas-sensing materials. However, the application of indicated methods is not very extensive.

The main goal of the research discussed in this paper was to estimate the possibilities of cathodoluminescence (CL) measurements for characterization of metal oxides aimed for gas sensor applications. One should note that recently, few works targeted on analyzing cathodoluminescence spectra of metal oxides such as In_2O_3 and SnO_2 were published [3,12–17]. These works showed that cathodoluminescent spectra are sensitive to the technology of metal oxide synthesis and deposition, and, therefore, such spectra may contain information, which reflects the peculiarities of a particular technological route used in such an experiment. Moreover, it was established that depending on a technological route used, not only the intensity of cathodoluminescence, but also CL spectra are being changed. However, we should to note the insufficiency of results obtained during the above-mentioned studies for making a correct conclusion about possibilities of CL analysis for gas sensing materials characterization because authors of those papers did not try to find correlations between CL and gas sensor parameters. To close this gap, we were considering both cathodoluminescent and gas sensing properties of the SnO_2 powders doped by Pd and Pt, as well as the SnO_2 films doped by transition metals such as Cu, Co, and Fe. SnO_2 is one of the metal oxides most used during the design of gas sensors [1,18,19]. Therefore, obtaining the above mentioned information is very important for real applications of this material. Noble metals, such as Pd and Pt, and transition metals, such as Co, Fe, Cu, were chosen as additives since they are doping elements mostly used for optimization of conductometric gas sensors' operating characteristics [2,7,18,20–27].

The choice of doped samples for our study was also conditioned by the fact that until now, there is no one-valued opinion regarding mechanism of doping additives' influence on gas sensing properties. Also, there is no answer to the question as to how doping additives' phase state influences gas sensing properties of metal oxides and which state is optimal. In literature, there is a lot of uncompleted data, not analyzed yet and, therefore, it is not possible to have a clear idea of what happens with surface properties of gas sensing materials during bulk doping. One should also admit, that in the majority of works targeted on a study of gas sensing properties of doped metal oxides, the authors do not try to analyze the influence of doping additives' concentration, but rather they simply test sensors with one fixed concentration of doped additive. Obviously, such limited approach considerably narrows experimental base for analysis and formulation of some general conclusions.

At present, while considering gas sensing properties of metal oxides, the cluster model is used predominantly. In the frame of this model, catalytically active additives present on the metal oxide surface are in the cluster state. However, the predomination of this model, at our point of view, is mainly connected with the convenience of such objects study, but not with existence of established facts. The presence of clusters, which could be well observable during a scanning electron microscopy (SEM) and a transmission electron microscopy (TEM), does not mean yet that clusters determine sensors operation. In a present work, we have shown that while considering gas sensing properties of doped metal oxides, other approaches were also available.

We have to note that the results and conclusions made in this paper are related to the bulk doping only. Surface modification is not discussed here. Surface modification due to its specific regularities requires an individual consideration. Systems forming solid solutions such as SnO_2–TiO_2, SnO_2–In_2O_3 and In_2O_3–Fe_2O_3, where both components are conductive metal oxides with high sensitive to gas surrounding, are neither analyzed in a present paper. Analysis of electrophysical and gas sensing properties in those systems also requires a specific approach.

2. Features of samples analyzed: experimental details

Since a technology of metal oxides synthesis plays an important role in gas sensing properties forming, in our analysis we have mainly used data obtained for the samples, synthesized while using the same technology. We believe that only by using such approach one can expect a reliable conclusions, based on comparison of various properties of analyzed materials. In particular, SnO_2 powders doped by Pd and Pt were obtained by wet chemical route, starting from a $SnCl_4$ solution, using the process described elsewhere [4,24,25]. The ammonia solution was used for precursor precipitation. Additives in the form of chlorides were introduced in the precipitated solution before the thermal stabilization treatment. Pd and Pt were added with nominal concentrations from 0.01 to 10.0 wt%. The synthesized powders were washed, dried and calcinated (T_{cal}) in the air in temperature range from 400 to 1000 °C. It is necessary to note that described technology has been used for synthesizing powders, aimed for gas sensors manufacturing, by scientific teams of Prof. N. Yamazoe (Japan), Prof. J.R. Morante (Spain) and Tubingen University (Germany). That is why the results obtained by these teams in the field of structural and gas sensing properties study of the SnO_2 powders doped by Pd and Pt were basically used in present work for comparison with cathodoluminescence properties of given materials, and for the following analysis. Detailed information on structural, catalytic and gas sensing properties of analyzed materials one can find elsewhere [20,24–27]. However, we could not ignore data obtained at other samples. We have been trying to summarize all results one can get in this field of research. In particular, we have analyzed data obtained for the SnO_2 films doped by transition metals during film deposition. SnO_2 films deposited by spray pyrolysis from $SnCl_4$-water solution (T_{pyr} = 450 °C) had thickness from 40 to 400 nm. Technology of SnO_2 deposition and structural properties of deposited films were discussed in [28]. Transition metals Cu, Fe, Co, or Ni (0–16 at%) were added in sprayed solution in the form of chlorides. Detail description of structural properties of Cu-, Co-, and Fe-doped SnO_2 one can find in Refs. [29,30].

Avoiding ambiguity, in our analysis we did not consider results obtained for the samples having crystallites size less than 3–4 nm. Research has shown [31] that quantum effects, observed in such samples, have lead to the appearance of short-wave peaks in CL spectra in the range 290–330 nm, which location and intensity strongly depended on the crystallites size. Since crystallites, which size does not exceed 3–4 nm, are very sensitive to various thermal treatments [32], we were able to obtain results with small repeatability which would lead to ambiguity during observed effects interpretation. According to [2,33], the use of the SnO_2 powders with such small grain size is also undesirable when gas sensor are being introduced to the market, where high stability of characteristics and repeatability of parameters are highly rated and valued more than ultra-high gas sensitivity.

Results of the CL study used in present paper were reported in Refs. [12–17,34,35]. Room temperature cathodoluminescence measurements were conducted using a spectrometer, recording radiation in the spectral range from 300 nm to 850 nm. The CL spectra were excited in vacuum in the camera of a standard microprobe analyzer Camebax-4 [36]. The luminescence emitted was collected through the quartz window of the camera unit. The sample was excited by an electron beam with diameter up to 1 μm. The conditions of excitation were selected under the stipulation that at