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Effect of Modification/Doping on Gas Sensing Properties of SnO_2

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Abstract

Modification and doping are both terms which used to display improvement of sensory characteristics of materials, particularly their selectivity. But these processes are different in the way how they influence on material's properties. This review concentrates on differences between modification and doping and their impact on parameters of sensitive materials for semiconductor gas sensors, in particular on characteristics of SnO_2 as one of the most promising sensor material.

Keywords: Tin (IV) oxide; Additives; Modification; Doping; Selectivity

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Introduction

Metal oxides SnO_2, ZnO, In_2O_3, CdO are wide-bandgap *n*-type semiconductors and the most frequently used as a sensitive material for the gas sensors. They belong to a class of transparent conductive oxides due to a number of unique functional properties, of which the most important are the electrical conductivity, the visibility in a wide spectral range and the high reactivity of the surface [1-3].

Metal oxides based gas sensors are widely used due to their high sensitivity to harmful for human health or hazardous gases (such as CO, NO, NO_2, H_2, etc.) in conjunction with easy fabrication methods and low manufacturing costs. Tin (IV) oxide is the most promising sensor material among a wide set of semiconducting metal oxides [4-7].

In the technology of manufacturing sensors based on SnO_2 the important place takes modification/doping of sensory material. This is due to the fact that pure SnO_2, despite it's obvious advantages (such as good surface adsorption properties, high chemical stability and mechanical strength, optical transparency in the visible region, good adhesion to glass and other surfaces, excellent electrical characteristic) [8,9] doesn't provide sufficient selectivity for sensor device.

There are several approaches for improving the selectivity of gas sensor include choosing appropriate operating temperature depends on analyte, using additives and using sensor arrays [10]. Using additives can provide new active centers on the material's surface or change electronic structure of material. In the first case, we are talking about modification of sensitive material, second variant belongs to the doping process.

There are a lot of papers devoted to study additives effect on selectivity of gas sensor devices [11-19]. However, there is a lack of attention on the difference between modification and doping processes. Therefore, the aim of this paper is to concentrate on differences and main principles of modification and doping processes.

Literature Review

Modification vs. Doping for selectivity improvement

Selectivity characterized the ability of sensor to respond selectively to a group of analytes or even specifically to a single analyte [20]:

$$Q(\%) = 100 \cdot \frac{dy / dx'}{dy / dx},$$

where *y*-an output signal or a change in the electrical resistance; *x*-given concentration of detected gas [21,22].

It is one of the most important parameters for gas sensor devices and creating of high-selective gas sensor is one of the most difficult tasks during device creation. One of the way for enhancing of sensor selectivity is introducing catalytically active additives in the sensing layer via doping or surface functionalization [23]. Additive can cause changing in the sensor performance depending

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on its doping concentration [11-14] ways of impregnating [24,25] sensor operating temperature [26,27] and the species of analyte gases [28].

Active components can be added in several different ways. Doping involves the addition of dopant to the prepared oxide. It can be due to the impregnation or mechanical mixing. Impregnation is related to ion-exchange/adsorption processes. It is the simplest method of preparing doped material. Solution containing the additive is contacted with powder of metal oxide and then the product is dried and/or heated at certain temperature. For example, to obtain gold/tin dioxide gas sensors Wang et al. dispersed SnO_2 powders in $HAuCl_4$ solution with further drying and calcinating procedures [29]. During the mixing process, the ready oxide and the compound of active component are mixed mechanically, after which the heat treatment is carried out to decompose the dopant compound. For instance, to obtain palladium-doped SnO_2 gas sensors for selective detection of CO and CH_4, SnO_2 and $PdCl_2$ powders were simply mixed in a mill, homogenized in a mixer and isostatically cold pressed. Then material was annealed in order to decompose the $PdCl_2$ and to sinter the SnO_2 crystallites [25]. In their work Choi and Oh synthesized La_2O_3-based SnO_2 thick film gas sensors by ball-milling of commercial SnO_2 and La_2O_3 powders in a ZrO_2 jar with ZrO_2 balls [30].

Modification is more complicated process. It comprises the addition of additives directly during the synthesis of the metal oxide. The so-called process of precipitation or coprecipitation. The undoubted advantage of this method is more uniform distribution of the active component. Precipitation is in principle a crystallization process and can occur in the bulk of the liquid. In almost all cases, the formation of a new solid phase in a liquid medium result from two elementary processes: formation of the smallest elementary particles of the new phase which are stable under the precipitation conditions; and agglomeration of the particles [31]. Gu et al. reported of obtaining Ni-doped SnO_2 microstructures using wet synthesis technique from $SnCl_4 \cdot 5H_2O$ and $NiCl_2 \cdot 6H_2O$ solutions [32]. For the preparation of Pd-doped SnO_2 nanofibers, the corresponding amount of $PdCl_2$ was added to the solution [28]. Shan et al. synthesized SnO_2-Fe_2O_3 interconnected nanotubes by mixing $Fe(NO_3)_3 \cdot 9H_2O$ and $SnCl_2 \cdot 2H_2O$ solutions under magnetic stirring at room temperature and calcinating of resulting composite nanofibers [33].

One of subtypes of precipitation techniques is gelation route or the sol-gel method. This is a homogeneous process which results in a continuous transformation of a solution into a hydrated solid precursor (hydrogel). Sol-gel methods have been recognized for their versatility which allows control of the texture, composition, homogeneity, and structural properties of the finished solids [31]. Pd-doped SnO_2-based sensor was obtained by Lim using sol-gel process. $PdCl_2$ was added to the gel of SnO_2 precipitates from the $SnCl_4$ solution and mixture was calcined at 550°C in air [24]. To synthesize indium-doped SnO_2 nanoparticles Kaur et al. prepared indium-doped sol by adding an appropriate amount of In_2Cl_3 in the tin oxide sol at its initial preparation stage [14].

Therefore, considering the processes of doping and modification from the point of view of synthesis technique, the difference between these two methods is in the ways and stages of the addition of active components. The process of doping is easier to implement. Although the modification allows to achieve a higher level of homogenization and homogeneity.

Additives can influence on material properties through two different mechanisms–chemical and electronic [20]. In chemical way, also known as catalytic, the reaction takes place at the material surface. Metal additive acts as catalyst from which compressed gas is transported to the surface of SnO_2, where reacts with absorbed oxygen. And released electron leads to a decrease in resistance [34]. This scheme represents modification process (**Figure 1a**). A modification is a change or alteration to improve characteristics of material or device. In the case of semiconductor gas sensors modification of material's microstructure means the creation of new active centers in relation of certain gases by using additives. The surface of nanostructures SnO_2 is characterized by the presence of oxygen vacancies, which are active centers but non-selective because they allow to interact with different molecules from gas phase at the same time [35]. Thus, for increasing of selectivity of gas sensors based on tin (IV) oxide the chemical modification of surface is used. In this instance, the surface acquires new active centers of "receptor selectivity" which respond only to target gases.

The electronic mechanism introduces doping process. Here the reaction involves dopant atoms (**Figure 1b**) [20]. Term doping is used to describe the adding of "impurities" into material's structure for improvement it's chemical and physical properties. In the case of the electronic mechanism (so-called Fermi energy control mechanism), reducing gas reacts with the surface of the metal additive. As a result, electron released and transported to SnO_2. Changes in the electron density near the surface of SnO_2 lead to a decrease in resistance [34]. Additives can cause changing in the charge concentration of the SnO_2 matrix, catalytic activities, the surface potential, formation of new donor or acceptor energy states and also influence on physical properties of material [20,36]. This in turn leads to changes in the electrical characteristics. Depending on impurities nature additives can result in increasing of conductivity because an extra electron is available in the lattice (donor impurities) or increasing of resistance because the effect of the oxygen vacancy donor levels is compensated by the acceptor levels (acceptor impurities) [37].

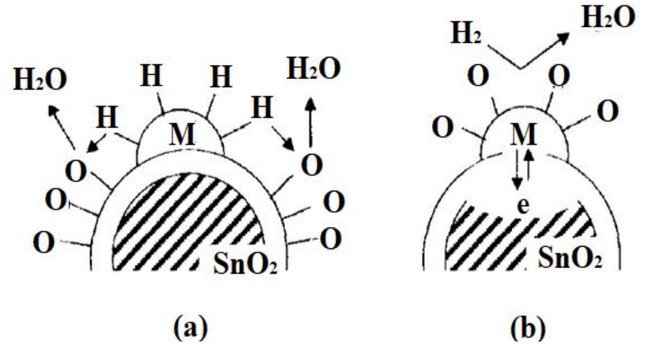

Figure 1 Chemical (a) and electronic (b) sensitization schemes in metal-doped SnO_2 gas sensor.

Thereby, the main difference between the electronic and catalytic mechanism is to transport particles between the additive and SnO_2. In the electronic model takes place the transfer of electrons; in the chemical model-transportation of atoms. **Figure 2** schematically shows both the detection mechanisms on metal oxide doped semiconductor.

But in principle, this division on two different mechanisms is quite conditional, because some additives have more broad impact and can influence on the electronic structure as well as create new adsorption sites [38].

Choose of additives for increasing selectivity of SnO2-based sensors

As dopants, most commonly used metals of platinum group-Pt, Pd, Ru, Rh [11,15,37,39], or oxide catalysts-Fe_2O_3, La_2O_3, Cr_2O_3, V_2O_5, NiO, CuO [16,17,30,33,40,41]. Important step-choice modifier for the gas and the change the reactivity of the material by changing the modifier concentration. The choice of dopant is carried out depending on the nature of the gas, clusters of noble metals used for doping sensor elements aimed at determining gas-oxidants (O_2, NO_2) and gases not have defined acid-base properties (CO, H_2, CH_4). For detection of basic and acidic gases using clusters of oxide catalysts-oxides of molybdenum and vanadium to identify the basic gases; oxides of copper, nickel, iron, lanthanum for detection of acid gases (**Figure 3**). However, some additives can increase selectivity and sensitivity to gases of different nature. For instance, indium-doped SnO_2 thin films are sensitive to both reducing and oxidizing gases, depending upon the doping concentration and the operating temperature [14,42].

Discussion

Even at very small dopant concentrations a bulk and a surface effect are observed. The reason for these findings can be attributed to a shift of the Fermi level position due to the presence of additional donor levels in the band gap and to the appearance of surface acceptor levels [43]. That's why usually, the additive loadings required for improved sensor performance are low (typically less than 10% mass or mole basis) [27]. For example, Choi et al. reported that selective detection of C_2H_5OH was observed with 0.08 wt% Pd SnO_2 hollow nanofibers [28]. In their work Hübner et al. showed increasing of sensing parameters towards H_2 and CO by using 0.2 wt% Pt: SnO_2 sensor [38]. Wagn et al. examined the effect of Au loading of Au/SnO_2 sensor for different CO concentrations. It was found that optimum Au loading was 2.86 wt%. Below this Au content the response to CO gas increased with the increase of the gold loading. But for Au loading more than 2.86 wt%. The response to CO gas decreased with the increase of the Au percentage [13]. In the case of PdO-SnO_2 nanocomposites the maximum sensor response to CO was obtained at 0.1 mol% Pd. And the rising of Pd contents causes decreasing of sensor response [12]. SnO_2-based sensors with good response to CO_2 were synthesized by addition of 2.2 wt% of La_2O_3 [30].

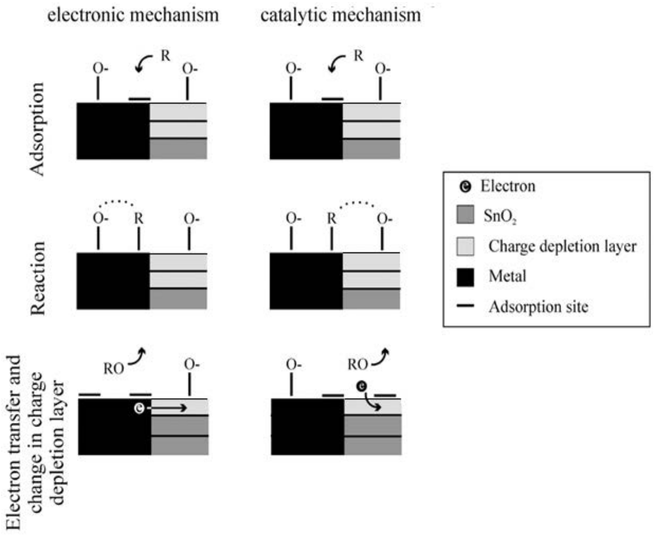

Figure 2 Schematic diagram indicating the sensing mechanism on the SnO_2 surface.

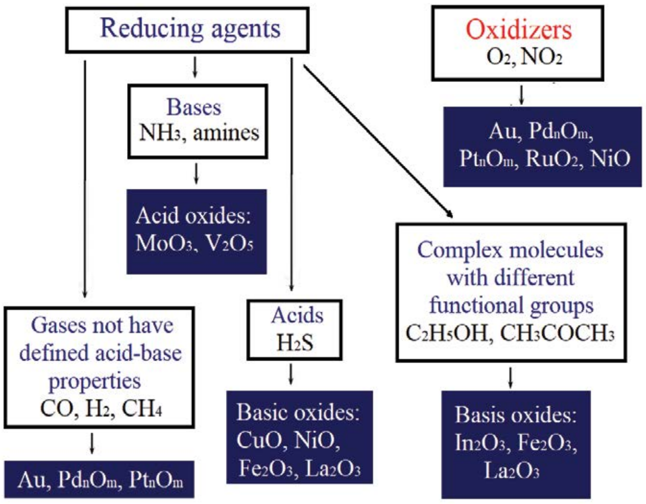

Figure 3 The choice of modifiers to increase the specificity of interaction with gases.

Thus, taking into account, presented results of different researches, it can be concluded that not only nature of additives, but also their concentration has a huge impact on sensor properties.

Conclusion

In terms of data presented in contemporary scientific literature, selectivity of gas sensors can be improved by using additives as it allows to create new active sites as well as to impact on electrical properties. Both these changes lead to increasing of selectivity, but in different way. For choosing of additive the nature of detected gas should be considered. No less important step is finding of the optimum loading concentration for which the best sensor response can be achieved.

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