Academic Journal of Science and Technology
ISSN: 2771-3032 | Vol. 10, No. 1, 2024

Research Progress on Preparation of SnO_2 Gas-Sensing Materials and Modification by Metal Ions Doping

Xinyang Gao

University of Science & Technology Beijing, Beijing 100083, China

Abstract: This paper delineates the developmental trajectory of SnO_2-based gas sensing sensors and conducts an in-depth analysis of the prevalent preparation methodologies employed for nano-powder and thin film SnO_2 materials. Recent investigations underscore that the doping of metal ions primarily operates through atomic substitution and solid solution mechanisms, where partial distortions in the crystal structure and the creation of oxygen vacancies emerge as pivotal factors augmenting the gas sensing capabilities of doped SnO_2. Future research endeavors aimed at refining the modification of SnO_2 through doping are anticipated to pivot towards mitigating its susceptibility to cross-sensitivity when confronted with mixed gas environments, while concurrently exploring physicochemical and biologically inspired preparation methodologies to imbue the process with greater eco-friendliness.

Keywords: Modification by doping; synthesis method; n-type metal oxide semiconductor.

1. Introduction

SnO_2, as a direct wide-bandgap (3.6 eV) metal oxide semiconductor, has gained prominence as the most widely used gas sensing material in practical applications due to its relatively low resistivity and high surface activity. In recent years, a series of nanostructured SnO_2 materials (such as nanoparticles, nanowires, etc.) have been synthesized by controlling factors such as SnO_2 morphology, crystal structure, and surface defects, thereby increasing their specific surface area and enhancing gas adsorption performance. Consequently, the sensitivity, response speed, and selectivity of SnO_2 sensors have been improved. In addition to detecting common gases such as carbon monoxide and methane, doped SnO_2-based gas sensors have also been explored for detecting more complex gas environments, such as volatile organic compounds and biomolecule [1,2]. This paper primarily focuses on the preparation principles and methods of doping SnO_2 with metal ions, compares the advantages and disadvantages of various preparation methods, and summarizes the results and benefits brought by different doping components.

2. The Research Evolution of SnO_2 Gas Sensing Sensors

The development and application history of tin dioxide (SnO_2) gas sensing sensors can be traced back to the early 1960s. During this period, researchers discovered that SnO_2 exhibits variations in resistance upon adsorption and desorption of oxygen at specific temperatures, laying the groundwork for subsequent sensor designs. Throughout the 1970s, research efforts deepened our understanding of the performance, structure, and operational mechanisms of SnO_2 gas sensing sensors. Simultaneously, there were endeavors to apply SnO_2 gas sensing materials in gas detection applications, such as detecting carbon monoxide and methane.

With advancements in semiconductor technology during the 1980s, fabrication processes and performance of SnO_2 gas sensing sensors were refined and improved. Scholars began exploring novel fabrication methods and material modification techniques to enhance the sensors' selectivity, sensitivity, and stability. By the 1990s, SnO_2 gas sensing sensors entered the commercialization stage and found widespread applications in various fields, including environmental monitoring, industrial safety, and medical diagnostics. Furthermore, their performance continued to advance, solidifying their status as indispensable tools in gas detection.

Since the beginning of the 21st century, the application scope of SnO_2 gas sensing sensors has further broadened with advancements in nanotechnology and materials science. Through innovations in nanostructure design and composite material fabrication, the sensors' performance has been further enhanced, facilitating their deployment in additional domains such as smart wearable devices and smart homes.

In summary, after years of research and refinement, SnO_2 gas sensing technology has matured significantly and found extensive applications across various sectors, contributing to the convenience and safety of people's lives and work.

3. Doping Modification of SnO_2 Gas-Sensing Materials

Doping modification of SnO_2 gas-sensing materials serves as a strategic approach to manipulate the crystal and electronic structures, inducing lattice distortions and defects that augment the material's surface reactivity. Moreover, doping-induced alterations in the concentration of oxygen vacancies within both the bulk and surface regions of SnO_2 profoundly impact its gas adsorption capabilities. These tailored modifications intricately regulate the material's conductivity, gas sensing efficacy, selectivity, and stability, rendering it apt for diverse gas sensor applications. Notably, the current research spotlight revolves around the doping of metallic elements, which engenders multifaceted effects on gas sensing sensor performance, encompassing the following dimensions:

3.1. Sensor sensitivity

Metal element doping can modify the electronic structure of SnO_2, resulting in an increase in carrier concentration and

consequently enhancing sensor sensitivity. For instance, the incorporation of metals such as indium (In), tungsten (W), and cobalt (Co) has been shown to augment the conductivity of SnO_2, thereby amplifying the sensor's ability to detect target gases. Liu et al. [3] synthesized different concentrations of cerium (Ce) doped tin oxide (SnO_2) nanomaterials via a hydrothermal method. It was observed that Ce^{4+} doping could inhibit the growth of large SnO_2 crystallites and promote the uniform growth of large agglomerates. The 2% Ce-doped SnO_2 exhibited excellent gas sensing performance even at gas concentrations as low as 10ppm, with rapid response and good recovery rates. This enhancement was attributed to the increased oxygen adsorption capacity, with O^{2-} being the main oxygen species on the surface of SnO_2, although O^- may also play a more significant role in enhancing gas response.

3.2. Sensor selectivity

Metal element doping can also regulate the surface chemical properties of SnO_2, altering the interaction between adsorbed gas molecules and the sensor surface, thereby enhancing the sensor's selectivity towards specific gases. For instance, A.Salehi 's study [4] has demonstrated that thermally evaporated indium-doped SnO_2 gas sensors exhibit notably higher sensitivity, ranging from 50 to 300℃, and greater selectivity towards wood smoke within the concentration range of 500 to 3000 ppm, compared to hydrogen. The variation in sensitivity is mainly due to the microstructure of the film, especially the porosity.

3.3. Regulation of sensor operating temperature

Through the doping of metal elements, the electrical properties and surface activity of SnO_2 can be altered, thereby regulating the operational temperature range of the sensor. For example, sensors based on octahedral single-crystal nanoparticles of SnO_2 doped with dual elements Cu and Zn via a one-step hydrothermal method, as confirmed by Zhang et al. [5] , exhibited a significantly reduced optimal operating temperature from the previously reported 350°C to 110°C compared to the undoped material, while the minimum sensitivity limit decreased to 17 ppb.

4. Preparation Method of Nano SnO_2 Powder

When preparing sintered or thick-film SnO_2-based gas sensing devices, it is typically necessary to first prepare SnO_2 powder. Existing preparation methods have been able to control the particle size of the powder at the nanoscale, providing a richer specific surface area and superior adsorption performance compared to materials prepared at the micron level in earlier years. During the preparation of powder gas sensing materials, it is usually important to control reaction conditions, solvent selection, precursor choice, and heat treatment parameters to obtain the desired properties of the SnO_2 material. Powder materials are commonly prepared by the following methods.

4.1. Sol-Gel Method

The sol-gel method typically entails dissolving the precursor substance of the gas-sensitive material (often a metal salt or an organic precursor) in a solvent to generate a sol. Subsequently, additional gelling agents are introduced to initiate a hydrolysis or condensation reaction, leading to the conversion of the metal ions or precursors in the solution into a gel system. The resulting gel is subjected to drying and heat treatment processes to achieve the desired morphology and structure.

The technique is straightforward and user-friendly, allowing for precise control over the morphology and structure of the material through manipulation of precursor substances and treatment parameters. However, the stability and uniformity of the sol are susceptible to variation under different preparation conditions and thus necessitate meticulous regulation. Yogamalar et al. [6]synthesized pure SnO_2 and Ni^{2+}-doped SnO_2 with varying weight percentages using the sol-gel method, followed by high-temperature annealing to enhance crystallinity. High-resolution scanning electron microscopy (HRSEM) results showed in Fig.1 revealed a morphological transition from spherical to rod-shaped nanocrystals induced by doping. Furthermore, varying the concentration of nickel dopants allowed for control over the length, width, and thickness of the Ni-doped SnO_2 nanocrystals.

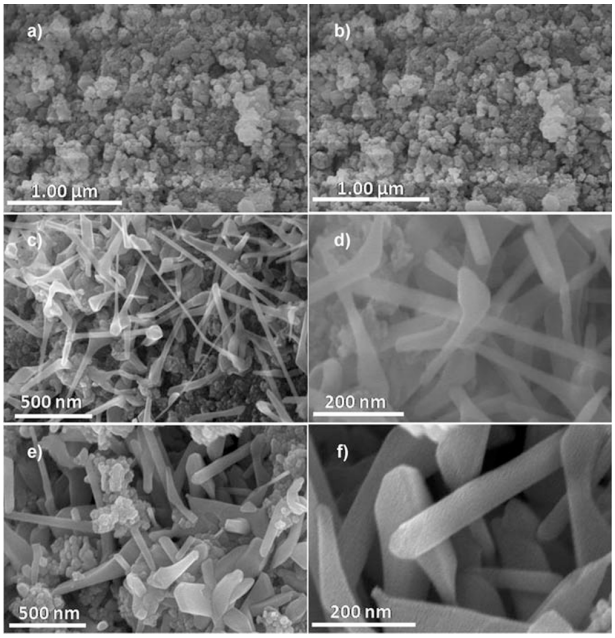

Figure 1. a-b）HRSEM photographs of 1 wt% Ni^{2+} doped SnO_2 materials prepared by sol-gel method

c-d）SnO_2 material doped with 1 wt% Ni^{2+} annealed at 500°C

e-f）SnO_2 material doped with 1 wt% Ni^{2+} annealed at 800℃

4.2. Hydrothermal Method solid-phase synthesis

This methodology involves the high-temperature, high-pressure reaction of metal precursors with water, leading to the formation of crystalline structures. By fine-tuning reaction parameters such as temperature, pressure, and duration, the crystallographic structure and morphology of SnO_2 can be precisely controlled. Zhang et al. [7]employed a hydrothermal approach to fabricate hierarchically mesoporous SnO_2 nanosheets. Subsequent thermal treatment yielded sensing materials characterized by mesoporous architectures, diminutive grain sizes, and a profusion of surface defects. Fig. 2 illustrates the microstructural features and morphology of the materials synthesized via the hydrothermal route. Gas

sensors utilizing these SnO_2 nanosheets demonstrated heightened responsivity, rapid response-recovery dynamics, and exceptional selectivity toward 1-1000 ppm ethanol vapor, even at relatively modest operating temperatures (165°C).

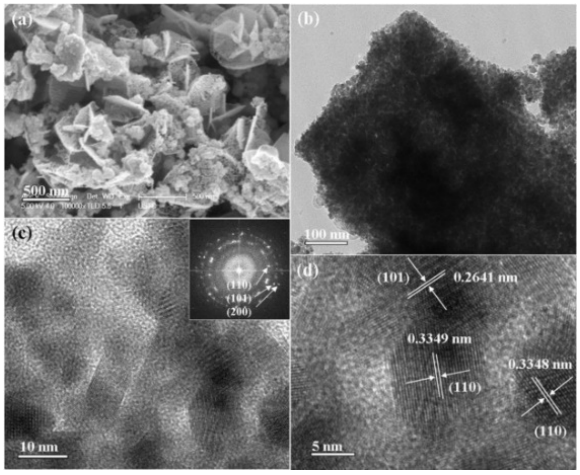

Figure 2. (a) Panoramic FESEM of SnO_2 nanosheets synthesized by hydrothermal method, (b) typical TEM, (c) magnified TEM and (d) HRTEM images of the SnO_2 nanosheets. Inset in (c): the corresponding fast Fourier transform (FFT) pattern.

4.3. Solid-phase synthesis

By employing tin salt and an oxidizing agent, chemical reactions at high temperatures can be utilized to control the crystal structure and morphology of SnO_2 materials by adjusting parameters such as temperature, duration, and atmospheric conditions during heat treatment. Additionally, preparation via ball milling is also feasible. Abe et al. [8]investigated the impact of different ball milling durations on the particle size of powders during the preparation of Co_3O_4-SnO_2 composite materials. Significantly enhanced response to CO was observed in thick-film devices prepared with sufficiently long ball milling time (6 hours).

4.4. Biosynthesis technology

To mitigate or eradicate the utilization of hazardous chemical substances, emerging bio-mediated green synthesis methodologies have garnered attention. These techniques rely on biologically derived materials, including plant extracts, bacteria, fungi, and other biomolecules such as proteins and vitamins. Reported studies [9] have demonstrated the synthesis of SnO_2 nanoparticles utilizing plant extracts and biological templates. These nanoparticles exhibit versatile applications in practical domains, including photocatalysis, gas sensing, and biomedical activities.

5. Preparation of thin-film SnO_2 gas-sensitive Materials

The preparation of thin-film type sensitive materials is based on the preparation process of powders, which are prepared by manipulating, for example, the following methods at completion or near completion to obtain thin-film gas-sensitive elements that are widely used today.

5.1. Physical Vapor Deposition, (PVD)

The typical procedure involves the deposition of gas-sensitive materials layer by layer on the substrate surface through methods such as evaporation or sputtering, resulting in the formation of thin films. This approach enables the fabrication of high-purity, highly crystalline films with rapid film formation rates. However, its drawbacks include high equipment costs and complex preparation processes, rendering it suitable for the production of small-area films. Zhu et al. [9] utilized plasma-enhanced chemical vapor deposition to prepare Sb^{3+}-doped SnO_2 conductive thin films. Research findings indicate that these films exhibit favorable sensitivity to NO_2 gas, with the optimal operating temperature being 170°C. Iizuka et al. [10] investigated porous thick-film gas sensors prepared via plasma spray physical vapor deposition (PS-PVD), observing that under constant conditions, thinner sensor films result in higher responses to 40 ppb formaldehyde concentration.

5.2. Solution Impregnation Method

The procedure entails immersing the substrate in a solution containing the precursor of the gas-sensitive material for a specified duration, followed by extraction and drying to form a thin film. This method offers advantages such as simplicity, cost-effectiveness, and compatibility with various substrate types. However, challenges include the difficulty in controlling film thickness and uniformity, necessitating precise adjustment of parameters such as solution concentration and immersion time. Wang et al. [10] employed the dip-coating technique to fabricate homogeneous porous SnO_2/TiO_2 composite photocatalytic films with a Sn/Ti molar ratio of 1%. The resulting film exhibited grain sizes ranging from 20-30 nm. Notably, this approach yielded films with the smallest grain size and the highest specific surface area compared to other doping preparation ratios. The resultant film surface displayed relative flatness with limited occurrence of larger island-like particles, indicative of a porous structure with particle aggregation.

5.3. Screen printing method

The method involves mixing powder materials with a binder in a certain proportion, uniformly coating the slurry onto a ceramic substrate through a stencil or other tool, and then sintering the substrate at low temperatures to volatilize the internal binder, thereby achieving the production of the film. This method is simple and feasible, yielding relatively uniform films. Chen et al. [11] utilized screen printing to deposit prepared Au-loaded, In-doped SnO_2 materials onto ceramic substrates connected with gold electrodes. Porous tin dioxide nanotubes doped with indium and modified with different Au/Sn molar ratios exhibited excellent ethanol sensing performance. The results showed that indium-doped tin dioxide porous nanotubes modified with 3% mol Au displayed high ethanol response (Ra/Rg = 316.8 at 100 ppm) and could detect 50 ppb ethanol at a relatively low operating temperature (150°C).

6. Synthesis and Outlook

Currently, significant progress has been made in the research of SnO_2 gas-sensitive sensors, but some challenges still exist. There is still a need to further improve the sensitivity, selectivity and stability of SnO_2 sensors to meet the needs of different application scenarios. At the same time, because in practice there are often multiple gas mixtures coexisting, which has higher requirements for the cross-sensitivity of gas sensors, how to distinguish different gases with the response results in the case of multiple gas components is gradually becoming a current research hotspot,

which also needs to be improved by means of material design and surface modification. Overall, SnO_2 gas sensors have a broad application prospect in the fields of environmental monitoring, intelligent manufacturing, and medical diagnosis. Future research will focus on improving sensor performance, expanding new application scenarios and realizing industrialized production of sensors.

References

[1] Wen Z, Tian-Mo L. Gas-sensing properties of 2-TiO_2-based sensor for volatile organic compound gas and its sensing mechanism[J]. Physica B-Condensed Matter, 2010, 405(5): 1345-1348.

[2] Lee D S, Kim Y T, Huh J S, Lee D D. Fabrication and characteristics of SnO_2 gas sensor array for volatile organic compounds recognition[J]. Thin Solid Films, 2002, 416(1-2): 271-278.

[3] Liu D, Liu T, Zhang H, et al. Gas sensing mechanism and properties of Ce-doped SnO_2 sensors for volatile organic compounds[J]. Materials Science in Semiconductor Processing, 2012, 15(4): 438-444.

[4] Salehi A. Selectivity enhancement of indium-doped SnO_2 gas sensors[J]. Thin Solid Films, 2002, 416(1-2): 260-263.

[5] Zhang W, Yang B, Liu J, et al. Highly sensitive and low operating temperature SnO2 gas sensor doped by Cu and Zn two elements[J]. Sensors and Actuators B-Chemical, 2017, 243: 982-989.

[6] Yogamalar R, Mahendran V, Srinivasan R, et al. Gas-Sensing Properties of Needle-Shaped Ni-Doped SnO_2 Nanocrystals Prepared by a Simple Sol-Gel Chemical Precipitation Method[J]. Chemistry-an Asian Journal, 2010, 5(11): 2379-2385.

[7] Zhang L, Yin Y. Hierarchically mesoporous SnO_2 nanosheets: Hydrothermal synthesis and highly ethanol-sensitive properties operated at low temperature[J]. Sensors and Actuators B-Chemical, 2013, 185: 594-601.

[8] Abe S, Choi U S, Shimanoe K, Yamazoe N. Influences of ball-milling time on gas-sensing properties Of Co_3O_4 -SnO_2 composites[J]. Sensors and Actuators B-Chemical, 2005, 107(2): 516-522.

[9] Gorai S. Bio-based synthesis and applications of SnO_2 nanoparticles-an overview[J]. Journal of Materials and Environmental Sciences, 2018.

[10] Iizuka K, Kambara M, Yoshida T. Highly sensitive SnO_2 porous film gas sensors fabricated by plasma spray physical vapor deposition[J]. Sensors and Actuators B-Chemical, 2012, 173: 455-461.

[11] Chen L, Shi H, Ye C, et al. Enhanced ethanol-sensing characteristics of Au decorated In-doped SnO_2 porous nanotubes at low working temperature[J]. Sensors and Actuators B-Chemical, 2023, 375.