Chapter 56 Nanostructured Metal Oxide Gas Sensor: Response Mechanism and Modeling

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ABSTRACT

This chapter provides a review of recent progress in gas sensor based on semiconducting metal oxide nanostructure. The response mechanism and development of various methods to enhancement of sensing properties receives the most attention. Theoretical models to explain the effects of morphology, additives, heterostructured composite and UV irradiation on response improvement were studied comprehensively. Investigations have indicated that 1D nanostructured metal oxide with unique geometry and physical properties display superior sensitivity to gas species. Also, the proposed conduction model in gas sensor based on 1D Metal oxide is discussed. Finally, the response mechanism of hierarchical and hollow nanostructures as novel sensing materials is addressed.

1. INTRODUCTION

Materials that change their properties depending on the ambient gas can be utilized as gas sensing materials. Nanostructured materials have the optimal combination of critical properties for gas sensor applications including high surface area due to small crystallite size, cheap design technology, and stability of both structural and electro-physical properties.

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Semiconducting metal oxide nanostructures such as SnO_2 , In_2O_3 , ZnO, and WO₃ are frequently employed in chemical gas sensors for various applications ranging from simple gas alarms to complicated electronic noises with potential applications in process control systems, medical diagnosis, security, and environmental monitoring. They have advantageous features such as simplicity in device structure and circuitry, high sensitivity, versatility and robustness (Huang & Choi, 2007; Kolmakov et al., 2005; Wang et al., 2009; Ashraf et al., 2008; Zeng et al., 2009).

The working principle of chemical gas sensor is based on change in resistance of semiconducting metal oxide induced by change in concentration of chemisorbed oxygen in the presence of target gas. Reducing gas such as CO and $CH₄$ cause to an increase of conductivity of n-type semiconductor by release of trapping electron to the bulk, while oxidizing gas (O_3, NO_2, etc) demonstrate opposite behavior. Gas response (sensitivity) is the ability of sensor to detect a certain amount of target gas and usually defined as the ratio of resistance measured in air and in atmosphere containing the target gas. Morphology of sensing layer, chemical components, surface modification, operating temperature and humidity can influence on the surface reaction and sensitivity of metal oxide (Korotcenkov, 2008; Wang et al., 2010). This chapter reviews the effects of morphology on gas sensing characteristics and summarizes the presented model highlighting the correlation between material structure and gas response. Different theories such as grain and neck controlled resistance model, electron tunneling transport, power laws and diffusion-reaction are presented for study of gas response to reducing gas. Control and improve of catalytic activity of gas sensor material is one of the most commonly used ways to enhance the performances of gas sensors. The introduction of second component changes the catalytic activity and chemical composition of base material and makes complicate the response mechanism (Hieu et al., 2010). Sensors based on metal oxides modified CNTs can detect gases such as $\mathrm{NO}_2^{\vphantom{\dagger}}, \mathrm{CO}, \mathrm{NH}_3^{\vphantom{\dagger}}$ and ethanol vapors at low operating temperature with improved sensing properties. The enhanced sensitivity of metal oxide/CNT thin film is studied by using Presented models. Conducting polymer/ metal oxide semiconductor hybrid device reveals a better sensing response than a bare metal oxide sensor due to the sorption nature of the polymer and synergetic effect. Mesoporous semiconducting oxides offer superior advantages, in comparison with merely nano-sized materials, in controlling the gas-diffusion process in sensors and in turn

achieving tailored and more excellent gas sensing properties. Hollow and hierarchical nanostructures with thin shell layers are also very attractive to achieve high surface area with a less agglomerated configuration. Thus, both a high gas response and a fast response speed can be accomplished simultaneously by using well-designed, hierarchical and hollow oxide nanostructures as gas sensor materials. UV irradiation is a very useful way to improve the gas-sensing properties and reduces the working temperature. Presented models for UV enhancement of gas sensing properties of nanograin metal oxide are reviewed. 1D metal oxide nanostructure with large surface-to-volume ratios and a Debye length comparable to their dimensions, have great potential to be used as chemical sensors. The working principle of 1D metal oxide nanostructures gas sensor has been investigated.

2. ADSORPTION OVER METAL OXIDE SEMICONDUCTOR SURFACES

2.1 Metal Oxide Semiconductor Surfaces

In order to better understanding the surface reactions of semiconductors with gases both chemical and physical view have to be considered. From a chemical point of view a surface can be divided into surface sites of varying reactivity. Usually, more active sites can be associated with heterogeneous surface regions or surface imperfections such as surface atoms with unoccupied or unsaturated orbitals (dangling bonds), crystallographic steps, intersections and interstitial defects. From a physical point of view the interruption of the crystal periodicity at the surface results in localized energy levels. These can exchange electrons with the non-localized energy bands in the bulk of the solid and act as acceptor or donor states. Surface energy levels in the band gap affect on the electronic properties of the solid, especially

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