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Review

Metal oxide hydrogen, oxygen, and carbon monoxide sensors for hydrogen setups and cells

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Abstract

Use of hydrogen, oxygen, and carbon oxide semiconductor sensors made of metal oxides allows controlling electronically the content of these gases in operation of many hydrogen setups, cells and devices. Present review-paper gives a general idea of achievements in this field.
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Keywords: Metal oxide; Semiconductor; Gas sensor; Hydrogen; Oxygen; Carbon monoxide

Contents

1. Introduction

The very exciting concept of hydrogen economy is developing more than 30 years. A. Fujishima, J. Bockris, T. Nejat Veziroglu, and many other researchers were at the beginning of solar–hydrogen economy. They and other scientists are working also on other methods of hydrogen production. Some researchers try to solve the problems of storage of hydrogen energy and production of electric energy using fuel cells, etc. [1–3]. Many achievements in all these directions were adequately presented in the Journal of Hydrogen Energy. Several National Programs on hydrogen are acting currently; Hydrogen Energy Economics is in the focus of many states [4,5]. I think that it is high time to draw attention of the JHE to also hydrogen, oxygen, and carbon oxide semiconductor sensors, which allow controlling electronically the content of these gases in operation of many hydrogen setups, cells and devices. The present review-paper summarizes the achievements in this field.

Research and development of gas-sensing devices is in the focus of activity of scientists and engineers in many countries in the last 20–30 years. Such detectors (including smoke-detectors) can be used for different applications—continuous

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monitoring of the concentration of gases in the environment and premises, detection of toxic dangerous gases, drugs, smoke and fire, energy saving, anti-terrorist defense, health, amenity, control of automotive and industrial emissions, as well as various technological processes in industry. Gas sensors can be manufactured using different materials, technologies and phenomena [6–13]. Sensing devices should be smaller and cheaper in comparison with analytical devices currently used which have sensitivities in the range from tens to several hundreds of ppm. I consider below only metal oxide semiconductor sensors, which got remarkable positions in science and technology, since they allow producing fast, reliable, non-expensive, low-maintenance devices using modern electron technologies. However, many gas-sensing micro-systems have not yet reached commercial viability because of high consumed electric power and working temperatures, inaccuracies, and the inherent characteristics of the sensors. So, suitable semiconductor materials are currently needed, which have the required surface and bulk properties and high sensitivity, stability, and selectivity.

Oxygen (O_2), hydrogen (H_2), carbon monoxide (CO), nitrous oxide (NO), nitrogen dioxide (NO_2), carbon dioxide (CO_2), methane (CH_4), ammonia (NH_3), hydrogen sulfide (H_2S), sulfur dioxide (SO_2), ozone (O_3), smoke and many others are among the important gaseous species.

Concentration levels of typical gas components are shown in Fig. 1 in Ref. [10]. They are limited in leading countries by corresponding standards(Environmental Standard, Ordinance on Health Standards in the Office, Offensive Odor Control Law, Working Environment Measurement Law, and Ordinance by Ministry of Health, Labour and Welfare, etc.) Gases like O_2 and N_2, and the humidity should be kept at adequate levels in living atmospheres, while hazardous gases should be controlled to be under the designated levels. One-tenth of lower explosion limit for lower hydrocarbons and H_2 gases is usually taken as an alarming level. Standards for toxic gases, volatile organic compounds (VOCs), odors, and other air pollutants are different. Some standards of VOCs such as benzene are seen to be less than 0.1 ppm, far out of the level reached by the present gas sensors.

Current trends in and promising materials for the manufacture of metal oxide hydrogen, oxygen, and carbon monoxide sensors, and different technologies are described in more details below after some general comments.

2. Semiconductor materials for gas sensors

First semiconductor gas sensors were made of tin oxide (SnO_2) and demonstrated in early sixties. Since that time, SnO_2 is the main material in sensorics. Sensors made of tin oxide became commercially available for detecting fuel gas, carbon monoxide, general purpose combustible gases, ammonia, water vapour, etc.

The demand for better environmental control and safety intensified the research into solid-state sensors of gases such as hydrogen and toxic gases, which have caused major accidents of last several decades (including Chernobyl catastrophe). General requirements to gas sensors are the following: high sensitivity and selectivity, small response and recovery times, room temperature operation, low power consumption and drift of parameters, robustness. They should be made preferable without expensive noble-metal materials. But the reality is rather far from such ideal demands.

Currently, the main materials for gas sensors are semiconductor metal oxides which are stable physically and chemically and widely investigated for gas and humidity detection. Sensing performances, especially sensitivity, are controlled by three independent factors: the receptor function, transducer function, and utility. Receptor function concerns the ability of the oxide surface to interact with the target gas. Chemical properties of the surface oxygen of the oxide itself are responsible for this interaction in an oxide device, but this function can be largely modified. A considerable change in the sensitivity takes place when an additive (noble metal, acidic or basic oxide) is (usually) loaded on the oxide surface. Transducer function concerns the ability to convert the signal caused by chemical interaction of the oxide surface (work function change) into electrical signal. This function can be realized by the measure of the current through a system containing a lot of semiconductor grains and boundaries between grains, to which a double-Schottky barrier model can be applied. The utility depends on the barrier height, size of pores in sensing work body, diffusion depth, film thickness, doping of the material and the concentration of target gas. Decrease in the grain size (diameter) below a critical value can lead to quantum-size effects and a dramatic increase in the sensor sensitivity [12].

In addition to SnO_2, different materials are used such as semiconducting oxides (ZnO, TiO_2, Fe_2O_3, $SrTiO_3$), catalytic oxides (V_2O_5, MoO_3, CuO, NiO), structures containing metals deposited on oxide substrates (Pt/SnO_2, Pt/ZnO, Pd/SnO_2), and mixed (or complex) oxides, exhibiting different physical properties when exposed to different gas species. Although the employed semiconductor oxides are catalytically active materials, a small amount of a catalytic metal or metal oxide is often added to improve the selectivity and sensitivity of the gas sensor. In practical applications, oxidation catalysts employed for sensing have a transition or a noble metal deposited on the oxide. Less attention is given to traditional single crystal and polycrystalline semiconductors like Si, Ge, etc. Silicon carbide, porous silicon, and GaN sensors are more promising in this series of materials [11,14,15]. For example, investigation of influence of gaseous hydrogen on the properties of field-effect transistors (FETs) made of SiC with Ru or Pt was carried out in [16,17]. It was shown that SiC sensors can operate at rather high ambient temperatures. Pt/Ga_2O_3/SiC metal-reactive insulator-silicon carbide devices operated as Schottky diodes. The sensors have been tested at different concentrations of hydrogen gas as a function of operating temperature. This study showed advantages of this structure compared to the pure thin film (90 nm) Ga_2O_3 conductometric sensor. Hydrogen sensing characteristics of a Pt-oxide–$Al_{0.3}Ga_{0.7}As$ MOS Schottky diode are reported in [18].

The search for new materials and sensitive devices made of those by various technologies is very important. Note that gas sensors in the form of thin or thick films are more promising

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