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Semiconductor Metal Oxides as Hydrogen Gas Sensors

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Abstract

Hydrogen (H_2) is a clean, portable and potentially inexhaustible energy source with the potential to become a panacea for clean energy generation. However, H_2 has wide explosive concentration range (4–75 vol%), low ignition energy (0.02 mJ) and large flame propagation velocity. Due to its ultra small molecular size, confinement and containment of this gas are difficult. Moreover, H2 cannot be detected by human senses because it is colorless and odorless. Thus, accurate detection and monitoring of hydrogen is an important issue. This presentation is a review of hydrogen gas sensors based on semiconductor metal oxides synthesized by a variety of synthetic techniques, namely RF magnetron sputtering, reactive RF sputtering, electro-spinning, Flame spray pyrolysis, hydrothermal and precipitation. The effect of synthetic methods and metal loading on the metal oxides on the response of hydrogen sensors will be discussed.

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Keywords: Hydrogen; Semiconductor metal oxides; Gas sensor

1. Introduction

Hydrogen (H_2) is a clean, portable and potentially inexhaustible energy source with the potential to become a panacea for clean energy generation. However, H_2 has a wide explosive concentration range (4–75 vol%), low ignition energy (0.02 mJ) and large flame propagation velocity [1]. Due to its ultra small molecular size, confinement and containment of this gas are difficult. Moreover, human senses cannot detect H_2 because it is colorless and odorless [2]. Thus, the ability to accurately detect and monitor hydrogen is important.

A review by Gu *et al*. [3] gave a comprehensive review of the hydrogen sensing properties of MOXs nanostructures, including thin films and 1D nanostructures. According to their sensing behaviour, the MOXs sensors can be divided into resistance, Schottky diode, MOSFET, MOS capacitor, optical and acoustic types. Some critical issues such as sensitivity, response time, recovery time, gas selectivity, limit of detection (LOD), temperature/humidity influence and long-term stability were discussed. Nanostructured MOXs thin film hydrogen sensors have the advantages of

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simple fabrication processes, good compatibility with integrated circuits for building integrated sensors, high sensitivity and short response/recovery times, *etc*. However, most thin film sensors still need to work at elevated temperatures, which results in poor long-term stability and high power consumption. The influences of grain size, porosity, orientation, doping and surface decoration as well as the device architecture on the sensing performance of hydrogen sensors have been widely investigated for improving gas selectivity and hydrogen response at low temperatures. In this review hydrogen gas sensors based on semiconductor metal oxides synthesized by a variety of synthetic techniques, namely RF magnetron sputtering, reactive RF sputtering, electro-spinning, flame spray pyrolysis, hydrothermal and precipitation. The effect of synthetic methods and metal loading on the metal oxides on the response of hydrogen sensors will be discussed.

2. Semiconductor metal oxides (MOXs)

Metal oxides play a very important role in many areas of chemistry, physics and materials science [4]. In technological applications, oxides are used in the fabrication of microelectronic circuits, sensors, piezoelectric devices, fuel cells, coatings for the passivation of surfaces against corrosion, and as catalysts. In the emerging field of nanotechnology, a goal is to make nanostructures or nanoarrays with special properties with respect to those of bulk or single particle species [5]. Oxide nanoparticles can exhibit unique physical and chemical properties due to their limited size and a high density of corner or edge surface sites. Particle size is expected to influence three important groups of basic properties in any material. The first one comprises the structural characteristics, namely the lattice symmetry and cell parameters [6]. The second important effect of size is related to the electronic properties of the oxide. Structural and electronic properties obviously drive the physical and chemical properties of the solid, the third group of properties influenced by size in a simple classification. In their bulk state, many oxides have wide band gaps and a low reactivity [7]. A decrease in the average size of an oxide particle in fact changes the magnitude of the band gap [8], with strong influence in the conductivity and chemical reactivity [9]. Surface properties are a somewhat particular group included in this subject due to their importance in chemistry.

Semiconductor metal oxides (MOXs) [10, 11] gained considerable attentions due to their low cost, high and fast response with relatively simplicity of use; and ability to detect a large number of gases. There are two types of MOXs namely n-type MOXs (zinc oxide, tin dioxide, titanium dioxide or iron (III) oxide responding to reducing gases (H_2, CH_4, CO, C_2H_2, and H_2S); p-type MOXs (nickel oxide, cobalt oxide responding to oxidizing gases (O_2, NO_2, and Cl_2).

2.1 Type of MOXs hydrogen sensors [3]

The MOXs hydrogen sensors can be divided into four types: resistance based, work function based sensors (Schottky diode type; MOS capacitor type; MOSFET), optical and acoustic sensors.

2.2 Gas sensing properties [12]

The gas sensing properties of unloaded and loaded-MOX nanoparticles sensing films are characterized in terms of response, response time and recovery time as a function of operating temperature, gas concentration and metal loading. Since the concentration of electrons on the surface of metal oxide increases and the resistance of n-type metal oxide layer decreases upon reaction with reducing gas. Thus, the gas-sensing response for n-type semiconducting oxide to reducing gas (S^n) is defined as:

$$S^n = \frac{R_a}{R_g} \tag{1}$$

On the contrary, the resistance of p-type metal oxide surface increases because generated electrons recombine with holes, decreasing in the hole concentration. The response for p-type semiconducting oxide to reducing gas (S^p) becomes:

$$S^p = \frac{R_g}{R_a} \quad (2)$$

where R_g and R_a are the electrical resistances of the sensors measured in the presence of reducing gas and pure dry air, respectively. The response time, T_{res} is defined as the time required to reach 90% of the steady response signal. The recovery times, T_{rec} denotes the time needed to recover 90% of the original baseline resistance [13]. Moreover, the selectivity defined as the response ratio of target gas to that of another gas is used to assess the relative performance of MOXs sensors towards different gases.

The majority of metal oxide–based gas sensors, suffer from low sensitivity and lack of selectivity. To solve these problems, a number of different strategies have been applied, such as the sensor's dynamic response analysis and mixed oxides sensors for gas detection [1]. The addition of a noble metal, such as gold (Au), platinum (Pt) or palladium (Pd), to a semiconducting oxide is an effective mean to enhance detection of specific gases because these metal catalysts increase the rate of interaction differently for distinct gases [13–21]. Platinum (Pt) is one of the most effective catalysts for sensing reducing gases, including hydrogen, carbon monoxide and hydrocarbon, by chemical sensitization via the 'spillover' effect [19, 20]. It effectively increases response and selectivity towards these reducing gases as well as reduces response and recovery times for various metal oxide materials such as WO_3 [1] ZnO [13], TiO_2 [21], MoO_3 [22] and Nb_2O_5 [23].

3. Factors affecting performance of hydrogen sensors

The characteristics of gas sensors strongly depend on base materials and preparation conditions [24]. Synthetic methods and metal loading will be discussed in more detail.

3.1 Synthetic methods

A variety of synthetic techniques, namely RF magnetron sputtering, reactive RF sputtering, electro-spinning, flame spray pyrolysis, hydrothermal and precipitation has been investigated as hydrogen sensors. WO_3 nanomaterials have proven to be the good candidate for MOXs hydrogen sensors. For WO_3 gas sensors, Pt-loaded WO_3 materials prepared by several synthetic methods have been widely studied and reported. A summary of H_2 gas sensing of differently prepared unloaded WO_3 and Pt-loaded WO_3 are listed in Table 1. A summary of H_2 gas sensing of differently prepared unloaded WO_3 and Pd-loaded WO_3 are listed in Table 2. Suitable Pt and Pd loading considerably improve the sensing characteristics of the WO_3 sensor. The gas-sensing properties of oxide semiconductors strongly depend on the surface of these materials. Hence, some research has concentrated on improving the specific surface area by introducing dopant/loading or decreasing particle sizes to nanoscale. It can be clearly seen from Table 1 that 1.0 wt% Pt-loaded WO_3 shows the highest response of 1.34 x 10^5 towards 1.0 vol% H_2 gas at 150^{o}C [1]. It is worth to mention that Pd/ SnO_2 nanowires synthesized from Pd nanoparticles deposited tin dioxide nanowires gave a very high response of 1.2 x 10^5 to 1.0 vol% of H_2 at room temperature [38].

Table 1 A summary of H_2 gas sensing of differently prepared unloaded WO_3 and Pt-loaded WO_3.

Method	Gas Concentration	Doping level	Response	Authors[ref.]
R.F. magnetron sputtering (sensors)	H_2; 0.125–1.0 vol%	Unloaded WO_3 Pt-loaded WO_3	9 to 1 vol% at 150°C 1600 to 1 vol% at 70°C, 200 at 150°C and no response at 200°C, 250°C and 300°C	Ippolito *et al.*[25]
Reactive rf sputtering (sensors)	H_2; 500 ppm	Unloaded WO_3 Pt-loaded WO_3	0.01 at 250°C 0.02 at 150°C	Penza *et al.*[26]
Reactive magnetron sputtering (sensors)	H_2; 1000 ppm	Unloaded WO_3	13.6 to 1000 ppm at 300°C	Shen *et al.*[27]
Radio frequency (r.f.) sputtering with subsequent two-step heat treatments	H_2; 30–200 ppm	0.5 at%Pt/WO_3	26 to 200 ppm at 95°C	Zhang *et al.*[28]
Electrochemical anodizing	H_2; 1000 ppm 20 ppm	WO_3 nanodots	79 at 200°C 3.1 at 200°C	Calavia *et al.* [29]
Anodization at elevated temperature	H_2; 6000 ppm 10000 ppm	Unloaded WO_3	2.56 at 500°C 14.9	Ou *et al.* [30]
Hydrothermal/impregnation (nanoparticles)	H_2 (0.01–1 vol%)	Unloaded WO_3	~102.4 to 1 vol.% at 250°C	Samerjai *et al.*[14]
Spin-coating (sensors)	H_2 (0.01–1 vol%) Temp.=250°C	1.0 wt% Pt-loaded WO_3	28 to 0.01 vol% 1.22 x 10^4 to 0.5 vol% 2.16 x 10^4 to 1.0 vol%	
Flame Spray Pyrolysis (nanoparticles) Spin-coating (sensors)	H_2; 0.01–1.0 vol%	1.0 wt% Pt-loaded WO_3	1.34 x 10^5 to 1.0 vol% at 150°C ~2.58 x 10^3 to 0.1 vol% at 150°C	Samerjai *et al.* [1]

Table 2 A summary of H_2 gas sensing of differently prepared unloaded WO_3 and Pd-loaded WO_3.

Method	Gas Concentration	Doping level	Response	Authors[ref.]
Hydrothermal (nanowires), Precipitation (WO_3 nanospheres), Flow through protonated ion exchange in acidic solution (WO_3 nanolamelle) Screen printing (sensors)	H_2; 50–200 ppm	0.75–3 at% Pd/WO_3(nanowires) 1.0 at%Pd/WO_3 (nanospheres) 1.0 at%Pd/WO_3 (nanospheres)	69 to 200 ppm at 180°C; 43 to 200 ppm at 200°C 41 to 200 ppm at 180°C; 27 to 200 ppm at 200°C 24.5 to 200 ppm at 180°C; 9 to 200 ppm at 200°C	Boudiba *et al.* [15]
Precipitation (WO_3 nanoparticles), annealed with 1 at% Pd at 400°C Screen printing (sensors)	H_2; 50–200 ppm	H_2; 25–200 ppm	16.2 to 150 ppm at 200°C 19.8 to 200 ppm at 200°C	Boudiba *et al.* [31]

Hydrothermal (WO_3 nnoparticles) and Decomposition of Pd and Pt (Pd/WO_3, Pt/WO_3)	H_2; 10–1000 ppm	Pd/WO_3 nanowires Pt/WO_3nanowires	Conductance increased with up to five order of magnitude to 1000 ppm of H_2 in air and even at RT	Kukkola *et al.* [16]
Electro-spinning	H_2; 500 ppm	10% mol Pd/WO_3	30 at 300ºC	Nikfarjam *et al.*[32]
Sol-gel process	H_2; 1300 ppm–0.1%	Pd/WO_3 films	100 to 1300 ppm at 200ºC 2.5 x 10^4 to 0.1% at RT	Fardindoost *et al.* [33]
Magnetron co-sputtering process	H_2/N_2; 0.5– 4%	Pd/WO_3 thin films	Pd/WO_3 thin films demonstrated better mechanical reliability than pure Pd layer	Yang *et al.* [34]
Focused ion beam-chemical vapour deposition (WO_3 nanowires) functionalized by Pd-Pt sputtering process	H_2: 1%	Pd-Pt/WO_3 nanowires	0.12 to 1% at RT	Choi and Kim [35]
Drop-casting of Pd-functionalized WO_3 nanowires	H_2: 0.1%	Pd/ WO_3 nanowires	3.1 to 0.1% at 300ºC	Chávez *et al.*[36]
Solvothermal method	H_2; 0.1–1.0%	Pd/WO_3 nanocomposite	34 to 0.1% at RT 173 to 1.0% at RT	Liu *et al.* [37]
Pd reduction on SnO_2 nanowires in Pd ion solution	H_2: 1.0 vol%	Pd/ SnO_2 nanowires	1.2 x 10^5 to 1.0 vol% at RT	Lee *et al.* [38]

3.2 Metal loading

Since Pt and Pd loading to WO_3 have proven to give high response towards H_2, Tables 1 and 2 show a variety of synthetic methods with different amount of loading. Pd-loading gave a highest response as compared to Pt and Ru-loading as reported by Chaikarn Liewhiran *et al.* [40] that sensors fabricated from FSP M-loading SnO_2 nanoparticles showing response in the order of 0.2 wt% Pd/SnO_2 > 0.2 wt% Pt/SnO_2 > 0.2 wt% Ru/SnO_2. 0.2 wt% Pd-loaded SnO_2 had response of ~ 10^4 to 1.0 vol% of H_2 at 200◦C.

3.2.1 Flame spray pyrolysis technique

Flame spray pyrolysis (FSP) is a versatile technique that can produce high purity nano-sized materials with well-controlled size and crystallinity. Therefore, FSP should be a very promising technique for sensor material fabrication since it enables excellent control of specific surface area. In FSP method, specific surface area can be increased by increasing an oxidant flow rate and reducing spray flame length, which lead to shorter residence times for particle growth [1, 39]. FSP has another key advantage of allowing one to completely manufacture the nanopowders in a single high-temperature step without affecting the microstructure and particle size in a subsequent annealing process.

Table 3 shows a summary of H_2 gas sensing of unloaded MOX and metal-loaded MOX synthesized by Flame Spray Pyrolysis technique. Among ZnO, SnO_2 and WO_3, 1.0 wt% Pt-loaded WO_3 showed the highest response towards H_2 with short response time and high selectivity towards CO, C_2H_2 and C_2H_5OH. The response (within seconds) and recovery (within minutes) times were very fast. It was found that 1.0 wt% Pt-loaded WO3 sensing films showed extremely excellent H_2 sensing performances at 150◦C with the highest sensor response (S ~1.34 x 10^5) to 1.0 vol% hydrogen.

Table 3 A summary of H_2 gas sensing of unloaded MOX and metal-loaded MOX synthesized by Flame Spray Pyrolysis technique.

Gas Concentration	Loading level	Response	Authors[ref.]
H_2; 0.01–1.0 vol%	1.0 wt% Pt-loaded WO_3	1.34 x 10^5 to 1.0 vol% at 150°C ~2.58 x 10^3 to 0.1 vol% at 150°C	Samerjai *et al.* [1]
H_2; 0.02–1.0 vol%	0.2 wt% Pd-loaded SnO_2	~10^4 to 1.0 vol% of H_2 at 200◦C	Liewhiran *et al.* [40]
H_2; 0.02–1.0 vol%	Unloaded SnO_2	16 to 1.0 vol% of H_2 at 350◦C	Liewhiran *et al.* [41]
	0.2– 2.0wt% Ru-loaded SnO_2	27 to 1.0 vol% of H_2 at 350◦C for 0.2wt% Ru-loaded SnO_2	
H_2; 0.02–1.0 vol%	0.2–2.0 at.% Pt-loaded ZnO	164 to 1.0 vol% of H_2 at 300◦C for 0.2 at% Pt-loaded ZnO	Tamaekong *et al.* [42]

3. Gas-sensing mechanisms of metal oxide sensors towards H_2 gas

Firstly, oxygen is absorbed on the MOX surface when it is heated in air. The adsorption of oxygen forms ionic species such as O_2^-, O^- and O^{2-}, which acquire electrons from the conduction band. The reaction kinetics may be explained by the following reactions [43, 44]:

$$O_2\,(\text{gas}) \Leftrightarrow O_2\,(\text{absorbed}) \quad (3)$$

$$O_2\,(\text{absorbed}) + e^- \Leftrightarrow O_2^- \quad (4)$$

$$O_2^- + e^- \Leftrightarrow 2O^- \quad (5)$$

$$O^- + e^- \Leftrightarrow O^{2-} \quad (6)$$

The electrons transfer from the conduction band to the chemisorbed oxygen results in the decrease in the electron concentration and an increase in the resistance of MOX film. The sensing of the MOX sensor to hydrogen gas normally arises from desorbing O^- and O^{2-}ions at the working temperature range of 250–350°C and >300°C, respectively. H_2 [2] sensing mechanisms of the MOX can be explained from following reaction paths:

$$H_2 + O^-(\text{ads}) \rightarrow H_2O + e^- \quad (7)$$

$$H_2 + O^{2-}(\text{ads}) \rightarrow H_2O + 2e^- \quad (8)$$

When the MOX film is exposed to hydrogen gas, hydrogen gas reacts with the chemisorbed oxygen species, thereby releasing electrons back to the conduction band. The reaction between hydrogen gas and the chemisorbed oxygen species may take place according to equations (7, 8). H_2 with small molecular diameter can easily penetrate through the surface dense layer. Oxygen with the larger molecular diameter is diffusion-controlled by the surface dense layer and hence both the oxygen gas concentration in the pores and the surface density of the adsorbed oxygen species are apt to decrease significantly while the reaction of oxygen with hydrogen is fast. The water produced via the oxidation of H_2 in the inner layer is supposed to pass through the dense layer and release easily out of the inner layer, because the water molecule has a somewhat small molecular size and is under vigorous thermal movement.

5. Conclusion

In this review, hydrogen gas sensors based on semiconductor metal oxides synthesized by a variety of synthetic techniques, namely RF magnetron sputtering, reactive RF sputtering, electro-spinning, focused ion beam-chemical vapour deposition, flame spray pyrolysis (FSP), hydrothermal, sol-gel and precipitation was presented. Sensor fabricated with Pt-loaded WO_3 nanoparticles synthesized by FSP has proven to give the highest response compared to the other materials and synthetic methods. An experiment to synthesize Pd-loaded WO_3 nanoparticles by FSP is in progress.

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