Hydrogen Sensing Behavior of Pt-coated Mesoporous Anodic Titania

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Abstract

We report on excellent hydrogen sensing properties of a Pt/TiO₂ system based on mesoporous titania grown by plasma electrolytic oxidation of a Ti metal substrate. The Pt phase is deposited onto the titania surface as an electrically continuous Pt nanomesh layer with an e-beam process. Resistive sensor response between the Pt and Ti terminals of the resultant structure is studied at room temperature for different partial pressures of H₂ gas (0.003-3 Torr) and different source voltages (0.5-2.0 V). A maximum resistance effect, reaching four orders of the magnitude for 3 Torr H₂ in 160 Torr O₂ is obtained at the bias voltage 1.4 V, and a strong effect is detected for only 0.003 Torr, or 20 ppm H₂ concentration. For voltages in the range 1.0-1.4 V, electrical conductance of the sample is about a linear function of the H₂ partial pressure in the gas phase. Influence of the background atmosphere (O₂, N₂ and vacuum) and the effect of bias reversal were investigated also, leading to a conclusion that the sensing mechanism can be related to ionic transport in the TiO₂ layer.

Keywords: nanostructures; oxides; semiconductors; chemisorption; electrical conductivity; transport properties

1. Introduction

Due to volatility and flammability of hydrogen gas, a small leakage of hydrogen-containing gases could lead to disastrous consequences. In the recent years, many groups have reported hydrogen sensors with different mechanisms and structures [1-6]. Fedtke

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et al. [7] reported electrical and optical changes of thin palladium layer (40 nm) during the hydrogen adsorption. This sensor showed a good behavior up to 4% hydrogen in nitrogen. Many groups have reported that metal-semiconductor (MS) Schottky diodes work well as hydrogen sensors [8-10]. Platinum or palladium Schottky diodes based on *n*-type GaN semiconductor revealed significant changes in the electrical characteristic of the sensor upon exposure of hydrogen in Ar or air mixture at room [11] and elevated temperature [12]. Metal-insulator-semiconductor (MIS) Schottky diodes, Pt/SiO₂/GaN, has been studied over a wide range of temperatures in the normal air atmosphere which demonstrated high sensitivity and a fast response time [13].

TiO₂ nanotubes and nanoporous structures have also been studied as hydrogen sensors, showing reversible responses in both air and N₂ atmospheres [14-20]. Shimizu et al. [18] outlined the important factors affecting the H₂ sensing performance of anodically oxidized TiO₂ films, including film morphology, oxidation temperature and electrode materials. The influence of nanotube diameters on the resistance variation of the TiO₂ has been tested and a three order of magnitude resistance variation was observed with exposure of 100 ppm hydrogen to N₂ ambient [20]. For higher concentration of hydrogen (500 ppm), a four order of magnitude change has been reported. In the previous work, the sensitivity of TiO₂ sensor has been studied at various operating temperatures, ranging from 250°C to 450 °C [21].

In this work, we discuss hydrogen sensing properties and mechanisms of a Pt/TiO₂/Ti type device based on anodically grown mesoporous titania. The device is simple to fabricate and it demonstrates extreme changes in its electrical resistance due to hydrogen exposure at *room temperature*. Here, the Pt catalyst was finely dispersed as an electrically continuous nanometer thickness mesh supported by the TiO₂ layer, and the anodized Ti metal substrate served as a base support and back contact, see Figure 1. Dependence of response characteristics on the source voltage is discussed. In order to understand basic mechanisms of the observed sensing performance, the experiments have been carried out in vacuum, oxygen and nitrogen gases at 160 Torr, and at bias reversal conditions. Hydrogen sensing behavior of this system is demonstrated, showing remarkable responses down to 0.003 Torr of H₂ partial pressure (20 ppm).

2. Sample Preparation and Experimental Setup

In order to prepare samples with a Pt/TiO₂ interface based on mesoporous titania, a 36x12x0.5 mm³ strip of standard (ASTM B265) 0.989 pure Ti metal was inserted in an aqueous 3M H₂SO₄ solution and anodically oxidized at a current density of 93.2mA/cm² for 3 min at room temperature until the anode potential reached 155 V. Measured thickness of the resultant TiO₂ was 10-11 μm. In the next step, a Pt layer of 15 nm thickness was obtained by sputtering of 0.9995 pure Pt through a 34x10 mm² mask on top of the porous TiO₂ surface via a wide-angle PVD in 10⁻⁷ Torr vacuum at the rate 0.02 nm/s. Finally, in order to complete the electrical contact of the structure, an SEM grade Ag paste was applied to attach two Ag wires (0.5 mm diameter) to the two opposite ends of the Pt surface. These fabrication steps are shown schematically in Fig. 1(a). XRD analysis data for the bare TiO₂ surface, and FESEM imaging of the Pt-coated TiO₂ surface are shown in Figs. 1(b) and 1(c), respectively. An RTD sensor of dimension 2x2x0.8 mm³ (Omega F2020-100) was attached in the middle of Pt surface for surface temperature monitoring. The sample was mounted inside a stainless steel 4.5 L vacuum chamber using a copper clamp attached to one of the pins of an electrical feedthrough flange.

Prior to the hydrogen sensing measurements, the sample surface was activated by oxyhydrogen reactions. The activation procedure has been described elsewhere [22]. Upon completion of the activation process, a repeatable baseline for resistance reading was obtained by exposing the sample to 160 Torr atmosphere of pure O₂ during 65 h, while a constant source voltage was kept applied to the sample. The resistance data recording started after 41 h of the exposure. Such a long pre-exposure with the source voltage in the background atmosphere was employed to eliminate a slow memristor effect [30-31], due to oxygen vacancy diffusion in the TiO₂ layer, which the system showed in hydrogen-free atmospheres.

In the beginning of each cycle of the hydrogen sensing studies, a particular amount of H₂ gas was admitted to the chamber and retained in it during 6 h resulting in a sharp decrease of the sample resistance. During the next 30 min, the chamber was evacuated to

a 10^{-6} Torr vacuum, followed by admission of 160 Torr oxygen retained in the chamber for 16 h to recover resistance of the sensor. Such a complete cycle of measurements is represented with a peak in Figure 1 plot. All the cycles reported in this paper were performed at room temperature (26-28°C). Sensor resistance was recorded continuously at a rate of 5 readings per minute with a Keithley 2400 sourcemeter in the voltage source mode.

In order to understand the effect of recovery gas on the sensor performance, oxygen gas was also replaced by nitrogen, which will be discussed below. The sensor tests were conducted at different hydrogen pressures and applied voltages in the range of 0.003-3 Torr and 0.5-2.0 V, respectively.

3 Results and Discussion

3.1 Sensitivity and response *properties*

The variation of the Pt/TiO₂/Ti structure resistance with time in different concentration of hydrogen in the presence of oxygen at room temperature were studied by applying different voltages at the Pt layer relative to the Ti substrate terminal (Fig. 2). Response of the sensor to different partial pressures of H₂ gas under 0.5 V is shown in Fig. 3(a). Upon admission of 3 Torr of hydrogen, the initial resistance of $4.5 \cdot 10^8$ Ohm jumped abruptly down within less than one minute, and then went more gradually down to the final value $7.5 \cdot 10^5$ Ohm within 6 h. By removing H₂ from the chamber during the next 30 min and adding pure O₂ gas at 160 Torr, the sensor resistance rapidly increased to form an inverted peak; this recovery was completed by reaching into the high resistance close to the initial value within the following 16 h. It should be noticed that the somewhat smaller resistance in pure O₂ compared to the initial value is due to a shorter exposure of the sensor to the background atmosphere in between two successive additions of hydrogen gas. According to Fig. 3(a), qualitative behavior of the sensor resistance is the same for three other partial pressures of hydrogen, 0.3, 0.03 and 0.003 T, although the lower peak value is different for each specific concentration.

In addition, the sensor response was also measured under 1, 1.4 and 2 V for different concentration of H₂ by the same procedure as it is explained above for 0.5 V, see Fig. 3. Increasing the applied voltage decreased the initial resistance of the sensor in pure oxygen. Otherwise, the sensor showed similar behaviors during the alternating exposure to hydrogen and oxygen gases. A four order of magnitude change in the resistance is typically seen due to exposure to 3 Torr of hydrogen. Also, the sensor resistance was notably decreased when it was exposed to only 0.003 Torr H₂, corresponding to a concentration of H₂ molecules of only 3.9 ppm in a normal atmosphere, or 20 ppm in the 160 Torr atmospheres used here. A solid-state sensor reacting to such small amounts of molecular hydrogen has not been reported earlier in the literature.

A formal *sensitivity measure* of the type

$$S = \frac{R_{O_2} - R_{H_2}}{R_{H_2}} \quad (1)$$

was investigated. Here, R_{O_2} is the resistance of the sensor in the background (reference) atmosphere of pure O₂ at 160 Torr, and R_{H_2} is the resistance in the end of the hydrogen exposure, represented by magnitudes of the inverted peaks in Fig. 3 plots. Dependences of the value S on source voltage and H₂ partial pressure are shown in Fig. 4. For a specific voltage, the sensitivity increases with the H₂ concentration. It also increases slightly with the source voltage, except for the lowest studied hydrogen pressure (0.003 Torr), for which better results were observed at smaller voltages. The highest values S were obtained for 3 Torr of H₂, varying from 550 at 0.5 V to 11670 at 2V. In Fig. 4(a) it can be also noticed that the sensitivity saturates for the voltages above 1.4 V. A sharp sensitivity drop, not shown in the figure, was observed at all hydrogen concentrations for voltages higher than 2 V. A prolonged exposure of the sensor to such voltages may lead to an irreversible decrease of the sensitivity.

Peak resistance values on each of the Fig. 3 curves can be fitted within a 20% or better accuracy with a power function of H₂ partial pressure, p ,

$$R(p) = a \cdot p^b \quad (2)$$

where the parameter b varies from -0.73 to -1.18 , depending on the source voltage, see Table 1.

Table 1. Value of the power function parameter b in Eq. (2) for different source voltages.

Bias (V)	0.5	1.0	1.4	2.0
b -value	-0.73	-0.96	-1.12	-1.18

Thus, electrical conductance of the sample can be a *linear* response function of H_2 partial pressure for a properly selected source voltage in the range 1.0-1.4 V. This provides opportunities for practical utility of the present solid-state system in hydrogen-selective pressure gauges and transducers.

3.2 Response time

Reviewer 1

2) “The author listed the response time for resistance drops 5%, 20% and 50%. However, the response time of gas sensors are always defined for the resistance drops 90% (t_{90}) in other literatures. Therefore, the author should provide the information of t_{90} to evaluate the response rate of this sensors. Moreover, the recovery time is also important for gas sensors. However, it is not considered in this work.”

We were able to extract the t_{90} (s) data from the existing resistance kinetics on the original manuscript. The data column t_{90} (s) in Table 2 was replaced with a column t_{90} (s). Also, the following pieces have been added or changed to provide the t_{90} (s) discussion:

In order to compare response time of the sensor under different voltages, the parameters t_{20} , t_{50} and t_{90} were defined to represent, respectively, periods of time during which the sensor resistance drops 20%, 50%, and 90% from its initial value, see Figure 3. These parameters are listed in Table 2 for 3 Torr H_2 exposure at different source voltages. It can be mentioned that the response time has a notable dependence on the source voltage. Upon exposure to 3 Torr of hydrogen under 1.4 V, the sensor resistance dropped to 90% of initial value within about 4 minutes. Thus, in the view of both sensitivity (Figure 4) and response time (Table 2) data, a source voltage around 1.4 V is optimal for this device in hydrogen sensing applications.

Table 2. Response time for 3 Torr H₂ exposure
at different source voltages.

Voltage (V)	t_{20} (s)	t_{50} (s)	t_{90} (s)
0.5	12	38	546
1.4	19	47	223
2.0	31	49	385

Reviewer 2

1) "The device has a good performance on the detection of hydrogen, the detecting limitation, detecting range, response time and sensitivity of the device should be compared with the published results, for example the results of the study and previous results are listed in a Table."

Thank you for this comment. We have added the following piece with the new Table 3:

The operating conditions (temperature, hydrogen concentration, and background atmosphere), sensitivity, and response time of this and typical earlier sensors based on TiO₂ are shown in Table 3. As can be seen, the present sensor device can be advantageous to the nanotube and sol-gel based sensors for its lower operating temperatures (26-28°C) and a lower sensitivity threshold (20 ppm). It also provides response times better than in the nanotube sensors, and sensitivity comparable with the sol-gel type sensors.

Table 3. Comparison of operating conditions, sensitivity, and response time of current sensor and previous sensors.

Sensor type	Temperature (°C)	H ₂ (ppm) / background gas	Sensitivity	t_{90} (s)
Mesoporous anodic TiO ₂	26-28	20-20000 / O ₂ , N ₂	0.35-11528 (1.4 V)	223-546
TiO ₂ prepared by sol-gel method [15]	100-350	300-10000 / air	10-10000	45-130
Highly ordered TiO ₂ nanotubes [19]	20-150	100-5000 / O ₂ , N ₂	10-35	1800-3900

3.3 Sensing mechanism

Reviewer 1

3-4) “Fig. 5 shows the hydrogen sensing behavior in O₂ and N₂ atmospheres, the author suggested that the order of magnitude variation in the sensor resistance was similar. However, according to Fig. 5, the response time and recover time for full response/recover is much different. Can you make some explanation of this phenomenon.

Fig. 6 shows the sensing behavior in vacuum background atmosphere. It can be found that the variation of sensitivity with the hydrogen concentration did not follow the rules shown in Fig. 5. Can you explain this phenomenon.”

The following piece (blue font below) has been amended to address these phenomena:

The mechanisms of hydrogen sensing in semiconducting catalytic systems remained unclear for a long time and different mechanisms have been introduced [16-19, 24-29]. Some studies revealed that the presence of oxygen species on the surface is necessary for the sensitivity of TiO₂ based devices to hydrogen gas [24]. It has been suggested that trapping of electrons from the conduction band of a metal oxide semiconductor by adsorbed oxygen molecules and return of these electrons to the conduction band by a reducing gas (H₂) are responsible for the hydrogen sensitivity [25]. In a quest for information about the correct sensing mechanism, the effect of *background atmosphere type* and *source voltage polarity* on the performance of present hydrogen sensor was investigated. The response of the sensor to different concentrations of H₂ under 1 V in 160 Torr O₂ and N₂ backgrounds is shown in Fig. 5. In contrast to the redox mechanism [24-25], by comparing the O₂ and N₂ curves shown in Fig. 5, it can be concluded that the presence of oxygen molecules was *not* an essential factor for the hydrogen sensing measurements. On the contrary, the initial resistance, recovery values and flatness of the curves (at 0.3 and 3 Torr H₂) were higher for the O₂ atmosphere. This fact could be explained by partial blockage of the active sensor surface with products of a slow oxyhydrogen reaction (water and OH radicals). These authors earlier showed that the oxyhydrogen reaction can be initiated on a similar catalytic surface at 16 Torr H₂ even at room temperature [22-23]. On the other hand, the order of magnitude variation in the sensor resistance in Fig. 5 data was similar for the two background gases at all H₂ partial pressures.

Fig. 6 shows variation of the sensor resistance versus time for a *high vacuum* background (10⁻⁷ Torr) under the voltage 1 V. It can be seen that the sensor responded to and

recovered from all the different concentrations of H_2 approximately at the same order of magnitude variation. This result provides further evidence toward the slow oxyhydrogen reaction hypothesis of the previous paragraph, because in this experiment the sensor surface remains free of any compound molecules of radicals at all times. Thus, the background gas (O_2 or N_2) only diminishes the sensor response, especially at the lower H_2 concentrations. Furthermore, independence of the response on the gas type, Fig. 5, suggests that molecules of the background gas participate only in physisorption processes on the sensor surface.

Recent studies show different mechanisms in which the hydrogen molecules dissociate and form atomic hydrogen on the metal surface. These hydrogen atoms will then diffuse through the metal and precipitate at the metal/semiconductor interface, decreasing the metal work function, and therefore reducing the Schottky barrier height [18, 26]. Fig. 7 shows the sensor responses when it was exposed to 3 Torr of hydrogen in high vacuum (10^{-7} Torr) under +1.4 and -1.4 V at room temperature. It can be seen that the order of magnitude variation in the sensor resistance under the positive source voltage is noticeably greater compared to the response at the negative voltage. This result indicates that the barrier reduction mechanisms based on electronic conductance is not fully applicable to the present sensor type. We suggest that *ionic transport* in TiO_2 serving as a solid electrolyte, also plays an important role in the sensing performance reported here. In particular, hydrogen ions (H^+) generated on the Pt nanomesh under positive bias in the presence of hydrogen adsorbate species are drifting toward the back Ti contact of the sensor to recombine there with electrons arriving from the external circuit, Fig. 2. A negatively biased catalytic electrode, on the contrary, cannot produce a significant amount of hydrogen ions, and therefore the sensor response was minute at the negative source voltage. It is also possible that the mechanism of oxygen vacancy (V_O) drift in TiO_{2-x} areas under electrical potential [30-31] is intertwined with the H^+ diffusion process in the present sensor type.

4. Conclusion

The transient response of a Pt/TiO₂/Ti sensor based on anodically grown mesoporous titania was studied at room temperature for different hydrogen concentrations and applied source voltages, and in three different background (reference) atmospheres: 160 Torr O₂, 160 Torr N₂, and 10⁻⁷ Torr vacuum. Comparable results were obtained in these atmospheres to reveal that the response of the sensor is not influenced by adsorbed O⁻ species [24], and the background gas molecules are likely to participate only in physisorption processes on the sensor surface. The applied source voltage in the range of 0.5-2 V had a great effect on the sensor sensitivity with the highest sensitivity observed at 1.4 V. For the 0.03-3 Torr H₂ exposures, the sensitivity increased with the source voltage until 1.4 V and then saturated at about 2 V. Irreversible changes of the sensor behavior occurred for voltages higher than 2 V, at which the sensitivity decreased significantly. For a source voltage in the range 1.0-1.4 V, electrical conductance of the sensor can be a linear response function of the H₂ partial pressure. The obtained data suggests that ionic conductance and vacancy diffusion processes in the mesoporous titania contributes to the resistive response of the sensor during hydrogen exposure.

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Figures (with captions)

Fig. 1: (a) Sample fabrications steps, (b) XRD analysis of the mesoporous TiO₂ layer, and (c) and FE SEM scan (at viewing angle 45°) of the Pt-coated TiO₂ surface.

Fig. 2: Sample wiring and the setup for resistance (R) measurements; V_S is a fixed source voltage.

Fig.3: Response transients of the mesoporous Pt/TiO₂ hydrogen sensor in the background atmospheres of 160 Torr oxygen at various source voltages: (a) 0.5 V (a), (b) 1.4 V (b), and (c) 2 V.

Fig.4: Sensitivity of the sensor versus voltage (a) and concentration of hydrogen (b) based on Fig. 3 data.

Fig.5: Comparative behavior of the sensor in the background atmospheres of 160 Torr oxygen and nitrogen under source voltage 1 V.

Fig.6: Sensor resistance variations in 10^{-7} Torr vacuum background for different concentrations of H_2 under source voltage 1 V.

Fig.7: The variation of sensor resistance versus time in high vacuum (10^{-7} Torr) for 3 Torr of H₂ under source voltages +1.4 and -1.4 V.