

Comparison of Pt and Pd Modified TiO₂ Gas Sensors

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crossref <http://dx.doi.org/10.5755/j01.ms.20.4.6403>

Received 08 February 2014; accepted 05 November 2014

Pt and Pd have been widely used to improve response properties of TiO₂ based gas sensors. In this work, differences on response properties, especially the response time of Pt/TiO₂ and Pd/TiO₂ sensors, were carefully compared. TiO₂ sensing films were modified by dipping method using H₂PtCl₆ and PdCl₂, respectively. XRD, XPS and SEM were used to characterize the crystal structure, elemental composition and grain size of the sensing films. The defect state was characterized by the relationship between resistance and oxygen partial pressure. And the response transients to H₂ and O₂ were tested by voltammetry method. The difference on response properties of modified TiO₂ sensors were suggested to arise from activation energy.

Keywords: Pt/TiO₂, Pd/TiO₂, gas response transient, activation energy.

1. INTRODUCTION

As gas sensors, MOS (metal oxide semiconductors) are one of the most widely used sensing materials. They have various possible applications and attracted great interest of many users and scientists in gas sensing field [1–2], based on their advantages of low-cost, simplicity of use and sensitivity to many gases. The gas sensing mechanism of the most MOS-based sensing layer relies on variation of resistance when the layer exposed to target gases. Specifically, TiO₂ is one of the most popular and well commercialized materials for development of resistive type gas sensors [3–4]. Recently, TiO₂ with various geometries such as powders [5], thin and thick films [6], nanoparticles [7–8] and nanowires [9–11] have been fabricated and applied as gas sensors.

On the other hand, noble metals, such as Pt, Pd and Ag, have been widely used to improve response properties of MOS based gas sensing materials [12–16]. According to N. Yamazoe's [17] XPS studies, the mechanism of Pt modified TiO₂ is considered as chemical sensitization and Pd modified TiO₂ is electronic sensitization. Recent studies indicated that the incorporation of platinum and palladium has shown great improvement not merely on selectivity and sensitivity but also on the rate of response/recovery. Francioso [18] prepared Pt/TiO₂ sensing films by sol-gel method. This microsensor used as lambda probe was heat-treated at 500 °C and expressed a fast response speed (1.5 s–2.0 s) at 630 °C. A new network sensor which using Pd modified TiO₂ nanofiber was propounded by Moon [19] to improve the sensitivity of NO₂. The sensitivity (R_G/R_A) of this sensor reached 38 in NO₂ (2.1 ppm at 180 °C). R_G

and R_A were the sensor resistance exposed to target gas and air, respectively. Liewhiran [20] developed an ultra-sensitive H₂ sensor with well-controlled Pd-catalyzed SnO₂ nanoparticles by FSP (flame-spray-pyrolysis). This sensor showed fast response speed (seconds) and high sensitivity (104) to H₂ (1 vol%) at 200 °C.

Response time after the sensor being introduced to gases is another important parameter. From air-fuel ratio (A/F) feedback control system in engines to complex control systems in chemical industry, gas sensors used as safety monitoring, combustion control system and chemical process control system are all desired to possess a fast response speed [21]. Because of the potential as clean energy candidate, H₂ has aroused much interest around the world. Generally, the recent developments on H₂ gas leak detection are focus on accelerating the speed when the devices react with hydrogen [22].

Pt and Pd modified TiO₂ gas sensor has been successfully prepared in our previous work [23–26]. The goal of this paper is to further compare the response time of TiO₂ sensing film which was modified by dipping method using H₂PtCl₆ and PdCl₂, respectively. XRD, XPS and SEM were used to characterize the sensing films. The different response properties of Pt/TiO₂ and Pd/TiO₂ sensors were suggested to arise from activation energy.

2. EXPERIMENTAL DETAILS

TiO₂ based sensing films were fabricated by silk screen process, which is convenient, least expensive and simple. The preparation process can be seen in [25–26] in detail. TiO₂ nano-powder with the average diameter of about 50 nm was provided by TaiShan Chemical Factory Co., Ltd, China. Firstly, the paste of TiO₂ was prepared by ultrasonic dispersion coupled with nano-powder dispersion

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in the presence of ethyl cellulose. The prepared paste was then printed on an alumina substrate (35 mm×6 mm×1 mm) by thick-film technique. A Pt comb-type electrode was also fabricated by the screen-printing method on the Al₂O₃ substrate. Sensing film was calcinated at 1280 °C for 2 h. Thereby, a TiO₂ based thick-film was formed, which exhibited the thickness of about 30 μm.

Two types of noble metal precursors, palladium chloride (PdCl₂) and chloroplatinic acid (H₂PtCl₆·6H₂O) which provided by Northwest Institute for Non-ferrous Metal Research of China, were used to modify the TiO₂ thick films. In one group, TiO₂ films were dipped into chloroplatinic acid solution and were dried at room temperature. These films were then heat-treated at 900 °C for different time. Samples with the treatment time of 0, 2, 4, and 6 h were labeled as T0, T2, T4, and T6, respectively. In another group, sensing films were dipped into palladium chloride solution and were dried at room temperature, too. After that, the films were heat-treated at 900 °C for 0.5 h–5 h and named as D0.5, D1, D2, D3 and D5, respectively.

Crystalline structure of modified sensing films was investigated by X-ray diffraction (XRD, D/MAX-2400, Rigaku, Japan) with 2θ ranging from 20° to 70° at a step size of 0.02° and a speed of 0.12°/s. X-ray photoelectron spectroscopy (XPS, VG-MK-II, China) was used to detect the surface elements. The XPS experiment was realized at 1253.6 eV with a step size of 1.0 eV. Moreover, the micro-morphology of sensing films was examined using the scanning electron microscope (SEM, JSM-6700F, Jeol, Japan).

Thick-film sensors were tested at different temperatures in a tube furnace, in which the target gas (H₂ or O₂) with concentration of 1000 ppm and 99.999 vol% N₂ flowed through. The voltammetry method was used to characterize the dynamic properties of the sensing films. And the schematic drawing which illustrates the processing steps was shown in ref. [25].

3. RESULTS

The X-ray diffraction (XRD) of Pt-TiO₂ and Pd-TiO₂ thick films which treated at 900 °C for 2 h are shown in Fig. 1. Apparently, TiO₂ was in rutile phase, which dominated in both spectra. There are three peaks marked by squares and triangles, which can be attributed to cubic phase of metallic palladium (Pd) and platinum (Pt). The other peaks, which are marked by circular point at 34°, 42° and 55° (2θ), belong to palladium oxide (PdO).

The presence of palladium and platinum on TiO₂ thick films were also confirmed by XPS results, respectively. It is indicated that the content of Pd loading on the grain surface of TiO₂ was 4.48 at%, similar to the loading amount of platinum which was about 4.80 at%.

Metallic state Pd and Pt that dispersed on the TiO₂ grain surface were examined by scanning electron microscope. Fig. 2 shows the micrograph of modified TiO₂ sensing films, where the palladium and platinum particles are clearly visible. It is found that Pd agglomerated on the TiO₂ grain surface with a maximum diameter of about 400 nm, and the maximum diameter of Pt cluster was about 200 nm.

The resistance of modified TiO₂ films was measured as a function of oxygen content at 600 °C, as plotted in Fig. 3. Resistances of sensing films are characterized in terms of stabilization in oxygen [27].

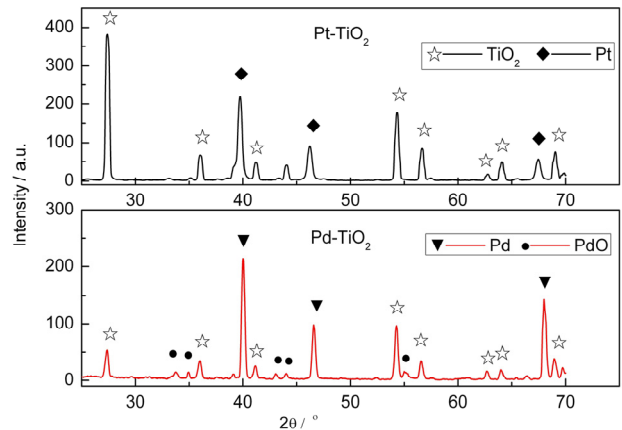


Fig. 1. XRD patterns of Pt-TiO₂ and Pd-TiO₂ which treated at 900 °C for 2 h

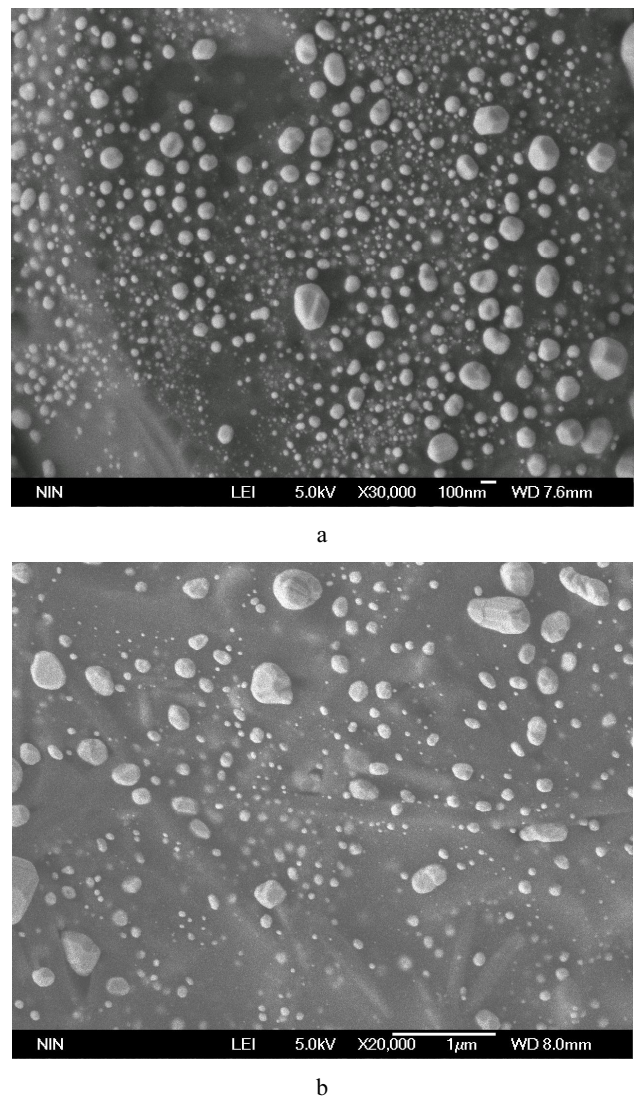


Fig. 2. SEM micrographs of T2 (a) and D2 (b)

Generally, the resistance (*R*) of metal oxide sensing material has a strongly connection with operating

temperature (T), activation energy (E) and oxygen partial pressure (P_O). For TiO_2 gas sensing film, the relationship between R and T , E , P_O can be expressed as following [20, 23–24]:

$$R = A \exp\left(\frac{E}{kT}\right) P_O^{-\frac{1}{m}}, \quad (1)$$

where A is a constant, k is the Boltzmann constant, and m is the defect constant which dependent on the nature of defects. For pure TiO_2 , the defect constant m is 6 according to Gao's work [28].

As shown in Fig. 3, the relationship between resistance and oxygen partial pressure of Pt/ TiO_2 was quite different from that of Pd/ TiO_2 . In Fig. 3, a, the resistance of Pt/ TiO_2 changed linearly with oxygen partial pressure under the logarithmic coordinates at 600 °C. It indicates that the conduction process of Pt modified TiO_2 sensing film was mainly controlled by transport of holes at 600 °C. The defect constant (m) of T2 sensing film was about 6.9.

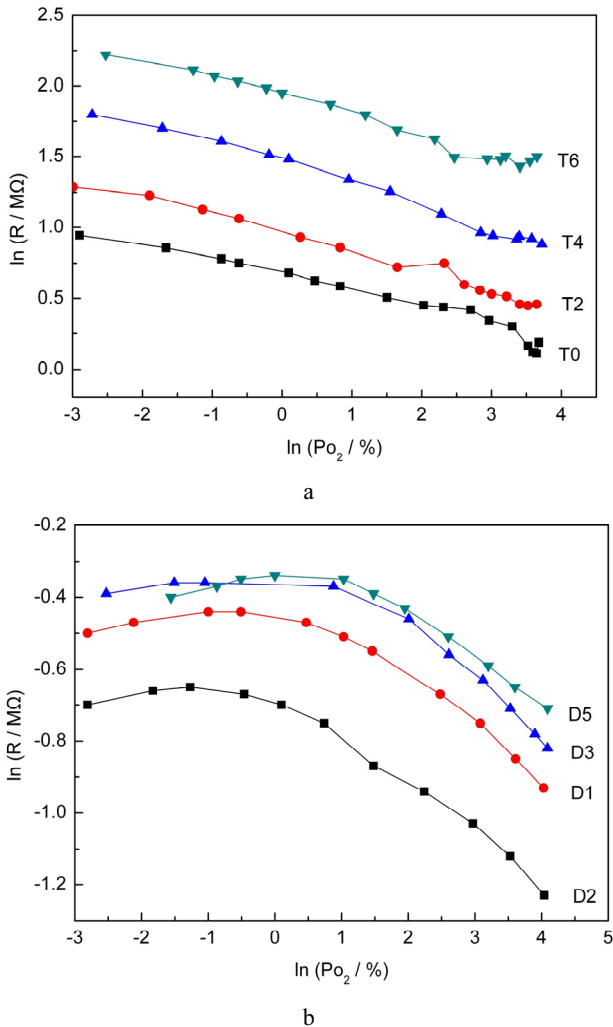


Fig. 3. Resistance response to oxygen partial pressure of Pt-TiO₂ (a) and Pd-TiO₂ (b) films at 600 °C

As comparison, a transformation can be observed in Fig. 3, b, which displays the relationship of resistance and oxygen partial pressure of Pd modified TiO_2 films. As can be seen, the conduction process of Pd/ TiO_2 film changed with oxygen partial pressure at 600 °C. At low oxygen partial pressure, the resistance of film increased with O₂

partial pressure. Probably the conduction process was dominated by the transport of electrons. On the contrary, it is found that resistance of the sensing-film decreased as P_O increased, at high O₂ partial pressure. This result indicates that the transport of holes in TiO_2 grain plays a major role in the conduction process. On the other hand, the defect constant (m) of Pd modified TiO_2 changed with O₂ partial pressure, too. The defect constant (m) of D2 was about 7.1 at high oxygen partial pressure.

Taking the natural logarithm of equation (1), the relationship between R and T , E , P_O can be expressed as following [23–24]:

$$\ln R = \ln A + \frac{E}{kT} - \frac{1}{m} \ln P_O, \quad (2)$$

When the sensor was operated at different temperatures (T_1 and T_2) and $P_O = 1$, we can obtain the following equation,

$$E = \frac{k(T_1 - T_2)}{T_1 T_2} (\ln R_1 - \ln R_2), \quad (3)$$

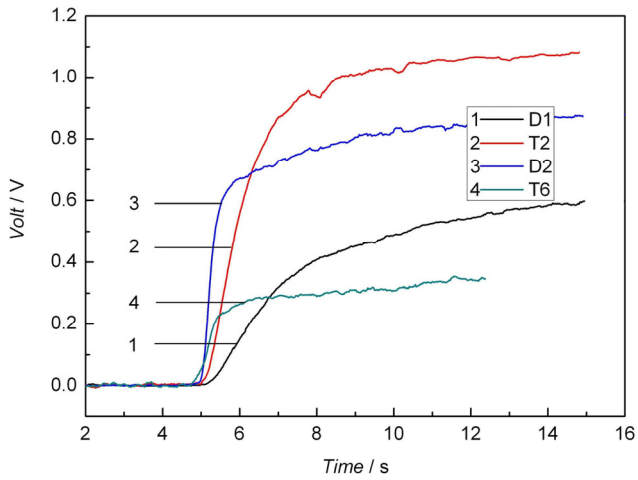
where R_1 and R_2 correspond to the resistance under T_1 and T_2 , respectively. It is obviously that equation (3) can be used to calculate the activation energy of Pd and Pt modified TiO_2 films. Fig. 4 shows the calculations of activation energy. The results indicate that the activation energy (E) of Pt modified TiO_2 sensing film was lower than that of Pd modified film. Especially, the sample T2 exhibits a minimum value of activation energy which is about 0.84 eV.

Gas sensing properties of modified TiO_2 thick films were recorded at different working temperatures when exposed to hydrogen or oxygen. It is found that response properties were almost the same at high temperatures (600 °C and above). The magnitude of expressed response was almost the same even though the sensors were modified by different precursors and treated under different conditions. Meanwhile, response times of Pd and Pt modified TiO_2 sensing films are stable over a very narrow region, when exposed to H₂ (20 ms–260 ms) and O₂ (20 ms–610 ms) at 600 °C, respectively.

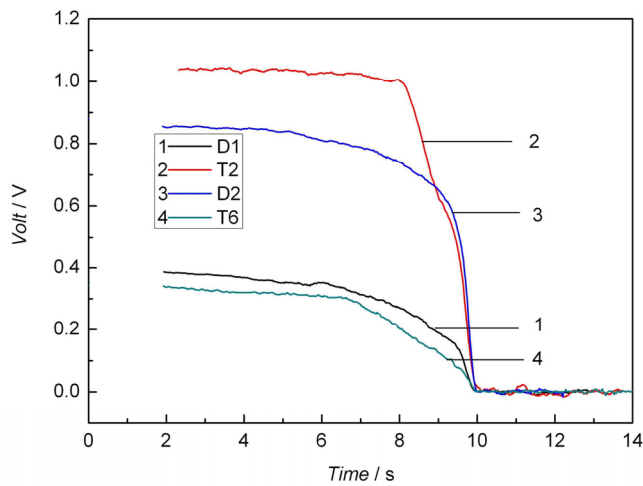
However, at low operating temperatures, response characteristics have been affected significantly by the type of modifying and treatment conditions. The response transients of representative sensors tested at 400 °C are shown in Fig. 4, when exposed to H₂ (a) and O₂ (b), respectively. It can be seen that the magnitude of response differed as the modified type changed even though the sensors were treated under the same conditions. Also, the magnitude of response was greatly affected by the treatment condition even if the sensing films were modified with the same noble metal. Likewise, there was a similar tendency towards the response time.

Among all the sensors modified by Pt comprised precursor, T2 which was treated for 2 h showed the best output with the fastest response rate, operating at 400 °C. As comparison, the sensor T6 which was treated for 6 h expressed extremely weak response at the same temperature. On the other hand, the sensor T2 took an extraordinary transient time before it reached the steady state, when operated at 400 °C for hydrogen (240 ms) and oxygen (180 ms). However, the sensor T6 expressed a long

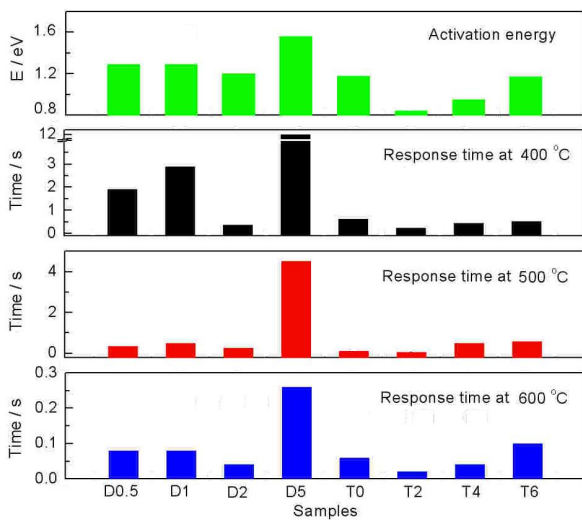
periods of time to get saturation state, which was about 510 ms and 520 ms for H₂ and O₂, respectively. Similarly, the sensors modified by Pd expressed the same trend.



a



b



c

Fig. 4. Response transients of different sensors tested at 400 °C when exposed to H₂ (a) and O₂ (b). Activation energy and response time of sensors when exposed to H₂ (c)

Response time of sensors exposed to H₂ in the range of 400 °C–600 °C, is shown together in Fig. 4, c. Here, the response time was obtained from the response transients in Fig. 4, a and b. The results showed that sensor T2 exhibited the shortest response time in the whole working temperature range (400 °C–600 °C) among all the sensors.

4. DISCUSSION

It is generally believed that the response properties of metal oxide based gas sensor are derived from grain size, gas diffusion coefficient, charge exchange interaction between gas and sensing film, gas surface reaction coefficient and electronic transmission in the grain [29]. In our previous work [23, 26], it is found that the sensing response characteristics of sensor D0.5-D5 and T0-T6 expressed no striking difference at high working temperatures ($T > 600$ °C) even if they had been treated by different precursor (PdCl₂ and H₂PtCl₆) for various heat treatment times. The results indicate that the gas sensing response properties of TiO₂ based sensors might be attributed to the interaction between target gas and material bulk defect [30], when operated at 600 °C and above.

However, the gas surface reaction and charge exchange play the major role at the temperature below 600 °C and grain bulk defect effect generally becomes very feeble. As the TiO₂ based gas sensing film exposed to atmosphere, several kinds of electronegativity adsorbed particles including O₂⁻, O⁻, O²⁻, and so on, are come into being by capturing free electrons from the conductance band of TiO₂ [31–32]. A space-charge region was built up on the surface of TiO₂ grains under the action of adsorbed electronegative particles, leading to an electron depletion layer. As a result, the resistance of TiO₂ film exposed to O₂ increased when the potential barrier developed between every TiO₂ grain boundary. When H₂ are introduced, hydrogen molecules can react with adsorbed oxygen particles and inject electrons into valence band of TiO₂ grain, resulting in a decrease of potential barrier. Then the resistance of TiO₂ film decreased in hydrogen.

The dispersed Pt and Pd particles on the TiO₂ grain surface provide several active sites promoting the gas sensing properties for the target gases [18]. When the incoming gas molecules get to the TiO₂ grain surface, they react with active sites (Pt and Pd) and become activated. Then, the activated gas molecules react with absorbates on TiO₂ grain surface, following the gas surface reaction coefficient (K_V) characterized by Arrhenius equation:

$$K_V = C \exp\left(-\frac{E}{kT}\right), \quad (4)$$

where C is the pre-exponential factor. Apparently, the surface reaction coefficient (K_V) increases with activation energy (E) decreases. This means that the response time which represents the change rate of conduction becomes short as activation energy decreasing when the sensor worked at the same temperature.

It is found in Fig. 4, c, that the activation energy of modified TiO₂ is directly associated with the type of modifying and the treatment conditions. Referring to these results and literature [26, 32], it can be inferred that the response time of TiO₂ sensing film is strongly affected by

the activation energy. As shown in Fig. 4, c, the tendency of response time was almost the same as the activation energy. Among all the modified films, sensor T2 that got the smallest activation energy displayed the shortest response time. By the same token, the sensor D5 expressed the longest response time with the largest activation energy.

5. CONCLUSIONS

The surface of TiO₂ thick films were modified with Pt and Pd containing solutions by dipping method. The incorporation of Pt and Pd on the TiO₂ surface was confirmed by XRD, XPS and SEM. Sensor T2 which exhibited the lowest activation energy (*E*) displayed the fastest response speed when exposed to H₂ and O₂. At high temperatures (600 °C and above), it was found that the response speed of sensing films had little concern with the types of modifying (Pt or Pd) and treatment conditions (temperature or time). However, at low working temperatures, the response speed which related to the surface reaction coefficient (*K_v*) was controlled by activation energy. TiO₂ thick film gas sensors with lower activation energy were more likely to express faster response speed.

Acknowledgments

Financial support by the Specialized Research Fund for the Doctoral Program of Higher Education (No: 20130203120016) and the Fundamental Research Funds for the Central Universities (No: K5051205010).

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