Asian Journal of Chemistry; Vol. 26, No. 17 (2014), 5439-5441

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.18128

Preparation and Hydrogen-Sensitive Mechanism of Platinum-Doped Tungsten Trioxide Films†

ZELUN LI[1,2], CHUANDE ZHOU[2], YIKE TANG[1] and XIANLING DENG[2,*]

[1]College of Mechanial Engineering, Chongqing University, Chongqing 400044, P.R. China
[2]College of Mechanical and Dynamic Engineering, Chongqing University of Science and Technology, Chongqing 401331, P.R. China

*Corresponding author: Fax: +86 23 65023718; Tel: +86 23 65005216; E-mail: instru@163.com

AJC-15717

A tungsten trioxide (WO_3) nano-film was prepared by a sol-gel method using tungsten powder and hydrogen peroxide as the starting materials. Then, platinum was doped onto the WO_3 film surface by a magnetron sputtering method. A tunnel-atomic power microscope was used to characterize the WO_3. We theoretically analyzed the WO_3 film's hydrogen-sensitive mechanism as well as conducted research into the film's optical properties. The results indicate that the WO_3 nano-film mixed with Pt possesses a good hydrogen sensitivity and restorative quality.

Keywords: Tungsten trioxide, Nano-film, Optical properties, Hydrogen sensitive.

INTRODUCTION

Tungsten trioxide (WO_3) is an important functional material. It has been widely studied and applied because of its electro-chromic, gas-chromic and photo-chromic properties. In particular, WO_3's gas-chromic property has the potential to be especially applicable in the gas sensing industry[1,2]. For instance, numerous studies show that WO_3 has a strong gas-chromic effect and therefore, can be adopted as a gas sensing material for several different gases: H_2, H_2S, HCl, CH_4, NH_3, NO_x, *etc*. When doped with Pt or Pd, WO_3 has a highly selective response performance to H_2. Therefore, in recent years, research on a WO_3 hydrogen sensor has attracted great attention in both academia and industry[3,4].

Currently, hydrogen detection technology has two primary applications: one is the monitoring of the hydrogen concentration in the air surrounding a hydrogen container so that any potential hydrogen permeations, leakages, or failures can be identified and the second is the monitoring for hydrogen concentration changes in the air caused by metal corrosion[5,6]. A traditional gas-chromic film sensor is structurally complicated and is susceptible to electromagnetic waves, so it is not a good choice for conducting distant tests or for places where there is electricity[7,8]. However, a fiber hydrogen sensor has a strong resistance to corrosion and disturbance, so it is suitable for a long distance transmission. Worldwide, many countries are currently investing their resources into research on hydrogen-chromic film sensors[9-11].

The basic principle behind the fiber hydrogen sensor is to utilize the hydrogen-chromic material at the end of the fiber that changes its optical property when it absorbs hydrogen. By modulating the optical signal that is imported *via* the fiber and then processing and analyzing the optical signals that are imported, we can obtain information of the hydrogen changes. In this paper, we use a WO_3 film as the material for a hydrogen-chromic film and then characterize the film's crystal structure in addition to researching WO_3's hydrogen-chromic mechanism and optical properties.

EXPERIMENTAL

A certain amount of tungsten powder (98 %) and hydrogen peroxide (30 %) were mixed so as to induce their reaction. After the intense boiling reaction stopped, a filter paper and funnel was used to filter out the remaining small amounts of tungsten and impurities. There was a layer of yellow substance absorbed into the filter paper, from which we obtained a light yellow, transparent solution. Next, we used a platinum filament to decompose the uncreated hydrogen peroxide and added absolute ethyl alcohol to it. It was allowed to evaporate for 0.5 h at 80 ºC and then we obtained the orange transparent colloidal sol. It was sealed and placed aside. After a period of time, it became a sol. It was then coated on the spin coater (rotation speed 3000 r/min). Finally, the sample was dried for 0.5 h at 100 ºC to obtain the tungsten trioxide film.

†Presented at 2014 Global Conference on Polymer and Composite Materials (PCM2014) held on 27-29 May 2014, Ningbo, P.R. China

To serve as the catalyst, we sputtered a certain amount of Pt over the surface of the WO_3 thin film to prepare a platinum-doped WO_3 hydrogen-sensitive film using the magnetron sputtering method. The magnetron sputtering parameters are as follows: sputtering current 0.12 A, sputtering voltage 450 V, target distance 7 cm, argon flow 20 m^3 min^{-1} and sputtering pressure 1.6 Pa.

RESULTS AND DISCUSSION

Characteristics of platinum-doped WO_3 film: Tungsten trioxide films consist mostly of particles in the nano-scale or micro-nanoscale. Various methods used to characterize nano-film materials, such as X-ray analysis (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and tunnel-atomic force microscope energy dispersive spectroscopy (EDS), can all be used to characterize tungsten trioxide films. In this paper, in order to provide an analytical basis for its hydrogen-sensitive mechanism, we use XRD, SEM and a tunnel- atomic force microscope to test the film's optical performance and structural composition.

We then observed the film's shape and components with a Hitachi S-3700N scanning electron microscope, as exhibited in Fig. 1. From this picture, it is evident that the film's shape under this type of microscopy is similar to its shape under the tunnel-atomic power microscope; that is, they both assume an island structure. Moreover, by using the scanning electron microscope, we can clearly observe the film's component elements (Fig. 2).

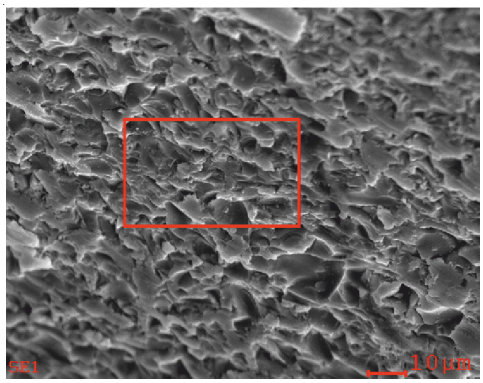

Fig. 1. Film's shape under a scanning electron microscope

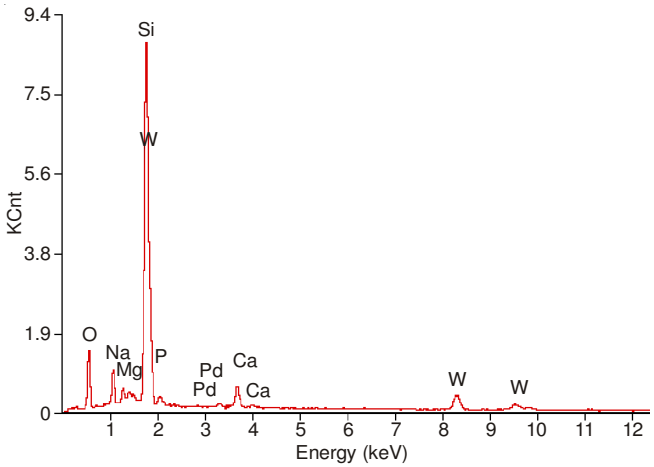

Fig. 2. Material components of film

Hydrogen sensitive mechanism of the platinum-doped WO_3 film: The principle behind the tungsten trioxide films' gasochromic properties can be briefly described as the following: the hydrogen molecules present on the film's surface decompose to hydrogen atoms in a catalyst role and then the hydrogen atoms diffuse into the nano-porous framework to enter the tungsten trioxide molecule. The colourless tungsten trioxide molecules change to a blue tungsten bronze structure H_XWO_3. The chemical formula is as follows:

$$H_2 \rightarrow 2H$$

$$WO_3 + xH \rightarrow H_XWO_3 \quad (1)$$

(Colourless) (Blue)

A fading mechanism is initiated when the blue tungsten bronze structure undergoes a condensation reaction and as it does so, the blue colour fades back to the previous colourless state.

Recent studies have published results that indicate that doping a noble metal such as Pd or Pt can improve the hydrogen-sensitivity of WO_3. Tungsten trioxide and platinum or palladium form a co-catalyst, which can then transfer the oxidation reaction of hydrogen to the tungsten bronze and the reaction equations are as follows:

$$WO_3 + xPt\text{-}H \rightarrow H_xWO_3 + xPt \quad (2)$$

$$H_xWO_3 \rightarrow xH^+ + xe^- + WO_3 \quad (3)$$

Through the continuous reaction above, the platinum crystal lattices can be released, which are favorable for the further dissociation chemisorptions of hydrogen.

Fig. 3 shows the microscopic processes of the colour causing during the nano-porous gasochromism. As can be seen from Fig. 3, there are seven processes, respectively: (a) The absorption and decomposition of the hydrogen gas in the platinum catalyst. (b) Hydrogen atoms transfer from the platinum to the surface of the tungsten trioxide. (c) Hydrogen atoms diffuse along the inner surface of the holes in the tungsten trioxide. (d) The formation of the intermediate state of the tungsten trioxide and two hydrogen atoms. (e) The formation of $WO_3 + H_2O$. (f) The diffusion of oxygen absence. (g) The escape of water (H_2O).

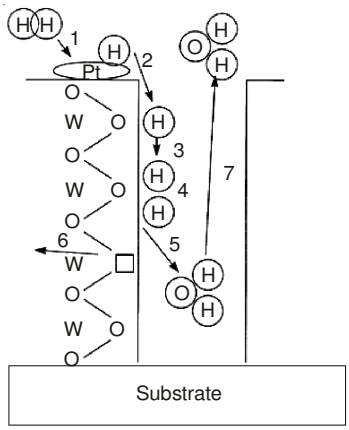

Fig. 3. Microcosmic coloring process of gasochromic films

In order to determine the film's hydrogen sensitivity, we detected the transmissivity of the platinum-doped WO_3 films, as shown in Fig. 4. We tested the film's transmissivity at

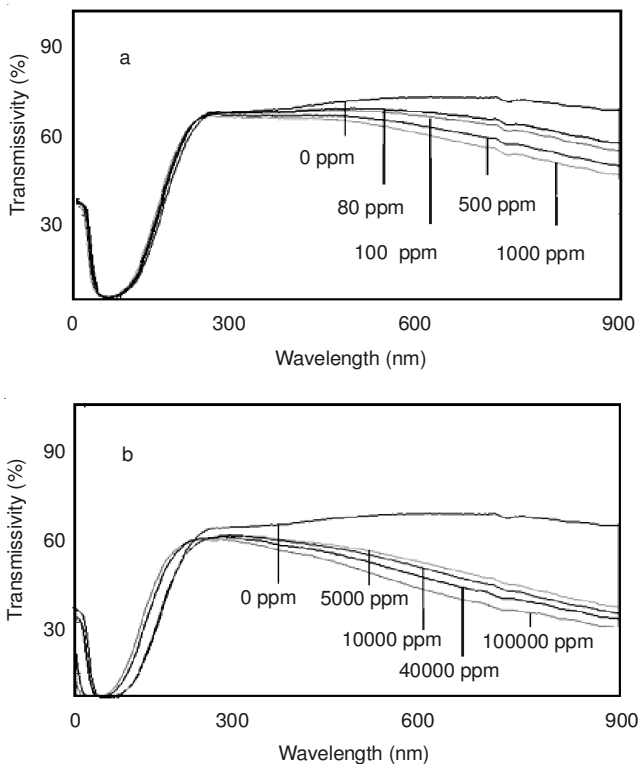

Fig. 4. Transmissivity of the platinum-doped WO_3 films

hydrogen concentrations of 80, 100, 500, 1000, 2000, 5000, 10000 and 40000 ppm. The results show that the transmissivity of the platinum-doped WO_3 films reaches 14 % at an 80 ppm hydrogen concentration and the balance time of hydrogen adsorption is 25 min. The transmissivity of the platinum-doped WO_3 films reaches 17 % at a 100 ppm hydrogen concentration and the balance time of hydrogen adsorption is 20 min. As the hydrogen concentration increases, the transmissivity of the platinum-doped WO_3 films changes and the film's hydrogen adsorption speed increases.

Conclusion

The WO_3 film is an important functional material. Because of its gas-chromic chemical property, the film is widely studied and applied. This paper uses tungsten powder and hydrogen peroxide as well as a Pt catalyst as the primary materials for preparing a Pt/WO_3 nano-thin film by combining the sol-gel method and magnetron sputtering. We characterized WO_3 with a tunnel-atomic force microscope and we theoretically analyzed WO_3's hydrogen-chromic mechanism as well as studied the film's optical properties. Our results indicate that a WO_3 nano-film mixed with Pt has a strong hydrogen sensitivity and restorative capabilities and, thus, has much potential in fiber sensor development.

ACKNOWLEDGEMENTS

This work is finically supported by the Project of National Science Foundation of China, NSAF (Grant No. 11076030), the Project of Postdoctoral Science Foundation of China (Grant No. 2012M511901) and the Project of Postdoctoral Science special Foundation of Chongqing (Grant No. XM20120053).

REFERENCES

1. W. Hsu, C. Chan, C.-H. Peng and C.-C. Chang, *Thin Solid Films,* **516**, 407 (2007).
2. J. Ederth, J.M. Smulko, L.B. Kish, P. Heszler and C.G. Granqvist, *Sens. Actuators B*, **113**, 310 (2006).
3. X. Bevenot, A. Trouillet, C. Veillas, H. Gagnaire and M. Clément, *Sens. Actuators B*, **67**, 57 (2000).
4. J. Villatoro, A. Diez, J. Cruz and M.V. Andrés, *Electron. Lett.,* **37**, 1011 (2001).
5. S. Sumida, S. Okazaki, S. Asakura, H. Nakagawa, H. Murayama and T. Hasegawa, *Sens. Actuators B*, **108**, 508 (2005).
6. K. Schroeder, W. Ecke and R. Willsch, *Optics Lasers Eng.,* **47**, 1018 (2009).
7. J.B. Beusink, A.M.C. Lokate, G.A.J. Besselink, G.J.M. Pruijn and R.B.M. Schasfoort, *Biosens. Bioelectron.*, **23**, 839 (2008).
8. Y. Jin and Y. Cho, *Trans. Korean Inst. Electrical Eng.*, **58**, 147 (2009).
9. M. Ando, R. Chabicovsky and M. Haruta, *Sens. Actuators B*, **76**, 13 (2001).
10. S. Okazaki, H. Nakagawa, S. Asakura, Y. Tomiuchi, N. Tsuji, H. Murayama and M. Washiya, *Sens. Actuators B*, **93**, 142 (2003).
11. M. Stankova, X. Vilanova, J. Calderer, E. Llobet, J. Brezmes, I. Gràcia, C. Cané and X. Correig, *Sens. Actuators B*, **113**, 241(2006).