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Hydrogen sensing characteristics of an electrodeposited WO_3 thin film gasochromic sensor activated by Pt catalyst

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Abstract

The hydrogen gas sensing performance of platinum (Pt) catalyst activated tungsten trioxide (WO_3) thin films were investigated in the present study. The WO_3 thin films exhibited a gasochromic effect; i.e., a reversible change in color from transparent when in air to blue when in hydrogen (H_2). All processes proceeded rapidly at room temperature. The films were prepared by the electrodeposition method under ambient conditions. A layer of Pt was then sputtered onto the surface of WO_3 film. The cycling of the coloration was obtained from UV–Vis spectra. The Pt catalyst dissociated H_2 into H atoms, which then diffused into the WO_3 thin film, which transformed from WO_3 to $H_xW^{VI}_{1-x}W^{V}_xO_3$ and changed the color of the WO_3 thin film. Therefore, we could detect the existence of H_2 by the coloration of the WO_3 thin film. Sensor properties of WO_3/Pt films were investigated at room temperature in H_2–N_2 gas mixtures containing 0–50 mol% of H_2. The results show that the transmittance change (ΔT) of the electrodeposited WO_3 hydrogen sensor was ~2% when the concentration of H_2 was 5 mol%, and ~20% when the concentration of H_2 was 50 mol%. Coloration and bleaching had good response and recovery times in the range of 5–60 s, respectively.

Keywords: Tungsten trioxide; Gasochromic; Hydrogen sensor; UV–Vis spectra

1. Introduction

A gas sensor is a device intended to transform gas concentration data to electric or optical signals. In general, gas sensors are used to detect toxic gases (e.g., H_2S, SO_2, CO, NO_x, …etc.) and inflammable gases (e.g., CH_4, H_2, C_2H_5OH,… etc.). Recently hydrogen fuel has been promoted as cleaner than petroleum. However, gaseous hydrogen leaked in air leads to an easily ignited explosive atmosphere when the concentration of hydrogen is more than the lower explosive limit (4%) at room temperature and pressure. Thus, accurate detection and monitoring of hydrogen concentrations is an important problem. Recently, the number of researchers studying hydrogen sensors has increased gradually [1–20]. Metal oxide semiconductors (MOS) were generally used as materials for the preparation of hydrogen sensors. Tungsten trioxide (WO_3) is known to interact with hydrogen and other alkaline metal ions in a unique manner and is the most commonly studied MOS material [6–20]. Many methods can be used to prepare WO_3 films, including sputtering [9–12], evaporation [13–15], sol–gel [16–19] and electrodeposition [21–24]. In general, the typical hydrogen sensor not only had a layer of WO_3 film but also needed a layer of catalyst. On contact with the catalyst, H_2 dissociated into two H atoms on the surface of the catalyst. The most common catalysts used are platinum (Pt) [9–17,20] and palladium (Pd) [18,19]. A bronze, $H_xW^{VI}_{1-x}W^{V}_xO_3$, forms when H atoms transfer from the catalyst onto the WO_3 surface. The reaction mechanism can be written as follows [17,20]:

$$H_2 \xrightarrow{Pt} 2H \tag{1}$$

$$\underset{\text{(colourless)}}{xH} + WO_3 \rightarrow \underset{\text{(blue)}}{H_xW^{VI}_{1-x}W^{V}_xO_3} \tag{2}$$

Accordingly, the electrochemical [6,8] and photochemical [10–20] properties of WO_3 changed when $H_xW^{VI}_{1-x}W^{V}_xO_3$ formed. The concentration of hydrogen gas was estimated from the changes of the electrochemistry or photochemistry of WO_3. The oxidation number of W^{6+} gradually reduced to W^{5+} due to the insertion of H atoms. The color of WO_3 then changed to blue when some of the W^{6+} reduced to W^{5+}. The reaction mechanism of these WO_3 gasochromic phenomena is similar to that of WO_3 electrochromic phenomena. The gasochromic reaction of WO_3 is reversible and the color of WO_3 will change back to transparent

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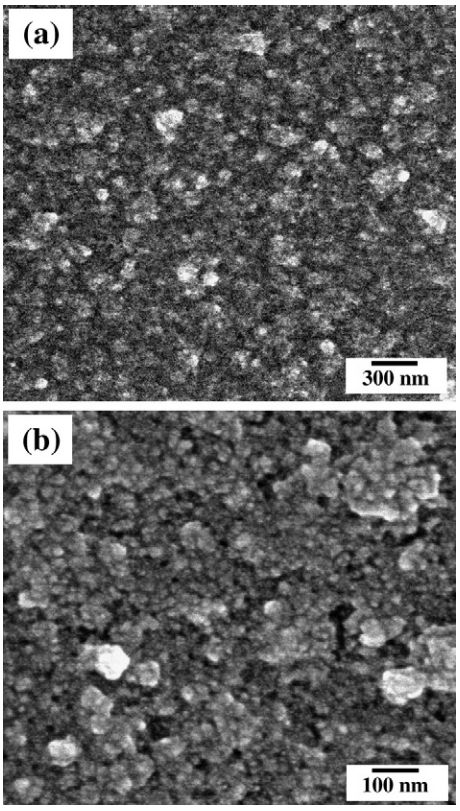

Fig. 1. The FE-SEM images of WO_3 film (a) ×30 K, (b) ×100 K.

when W^{5+} oxidizes to W^{6+} again. Therefore, it is possible to use this gasochromic characteristic to prepare a hydrogen sensor to detect the hydrogen concentration of a gas or to be used in gasochromic windows [20].

Among the preparation methods for WO_3 film, cathodic electrodeposition is simple, has the capability for mass production and is suitable for large area films. Therefore, electrodeposition was chosen for WO_3 film preparation in the present study. The hydrogen sensor was prepared by coating ITO glass with a layer of electrodeposited WO_3 film, followed by a layer of sputtered Pt film. Sensor properties of the WO_3/Pt films were investigated at room temperature in H_2–N_2 gas mixtures containing 0–50 mol% of H_2.

2. Experimentals

2.1. Preparation of substrate

Indium tin oxide (ITO) glasses (15 Ω/□, RITEK Corp., Taiwan) were used as the substrates for electrodeposition. The ITO glasses measured about 2.5 cm × 5 cm. All ITO glasses were cleaned with detergent soap, alcohol and de-ionized water before coating.

2.2. Preparation of electrodeposition solution

28% hydrogen peroxide (0.08 M, Union Chem. Co., Taiwan), H_2SO_4 (0.36 M, Union Chem. Co., Taiwan) and Na_2WO_4 (0.1 M, Sigma-Aldrich Inc. USA) were dissolved in de-ionized water to prepare the electrodeposition solution [22].

2.3. Preparation of gasochromic films and devices

A two-electrode cell system and constant potential technique were used in the electrodeposition process. ITO glass was used as the working electrode and platinum as the counter electrode. The deposition potential was controlled at −2.5 V and the deposition time was 500 s. After deposition, WO_3 film was dried at 80 °C for 30 min to obtain the gasochromic film. The sensor device was then prepared by sputtering a layer of platinum with thickness about 20 nm over the WO_3 film. All experiments were performed at room temperature. The proposed coating conditions gave the best mechanical stability and optical response of the electrodeposited WO_3 in the present study.

2.4. Measurement of gasochromic films and devices

The surface morphologies, thicknesses and elemental compositions of WO_3 and WO_3/Pt films were examined by Field-Emission Scanning Electron Microscope with Energy Dispersive Spectrometer (FESEM-EDS, HITACHI S4800, Japan). The crystal structure and phase identification of the films were investigated by transmission electron microscopy (TEM, model JEOL II 1200EX, Japan) operated at 120 kV and X-ray diffractometry (XRD, Bruker AXS D8 DISCOVER Advance Diffractometer, Germany, Cu K_α radiation) with a grazing incidence of angle 1°. The accelerating voltage and the applied current were 40 kV and 300 mA, respectively. The colorations of the gasochromic devices

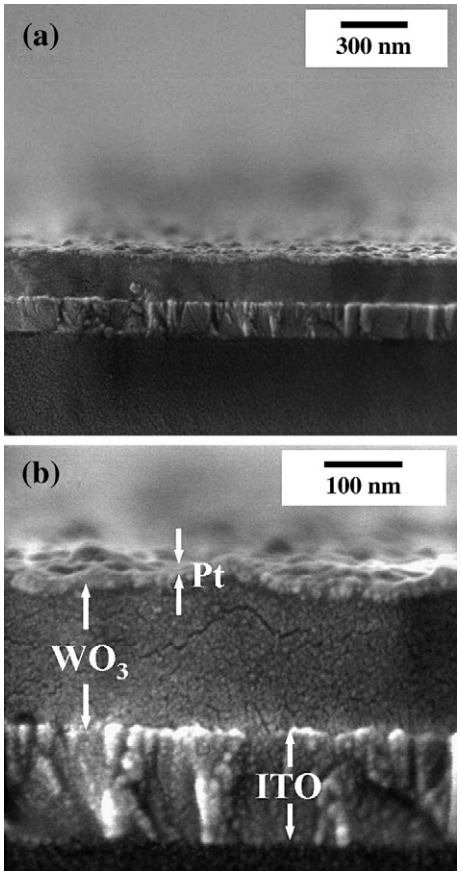

Fig. 2. The FE-SEM images of the cross-section of WO_3 film (a) ×30 K, (b) ×100 K.