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An ultra-fast response gasochromic device for hydrogen gas detection

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ABSTRACT

In the present work, gasochromic tungsten oxide (WO_3) thin films on glass substrate were fabricated by Pulsed Laser Deposition (PLD) system. Pt was sputtered on the surface of WO_3 thin films as a catalyst layer for hydrogen gas detection. The gasochromic properties of Pt/WO_3 thin films at room temperature were determined by examining their optical transmittance under various H_2–N_2 mixture gas exposures. The results show that in low H_2 atmosphere (0.5%) the room temperature grown Pt/WO_3 thin films still exhibited noticeable transmittance change, within the visible light (550–700 nm) range. WO_3 thin films have been characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and scanning electron microscopy (SEM). XRD and TEM confirmed that the morphology of the best performance WO_3 thin film is amorphous, and SEM investigations revealed that the thin films were composed of nanotextured grains.

1. Introduction

Recently, with increasing concern about renewable clean energy issue, using hydrogen as a clean energy source has attracted more attention than before. However, hydrogen gas is also known as a highly flammable gas, which has very wide explosion concentrations range (4–75%). In terms of its nature characteristics, hydrogen gas is colorless, odorless and tasteless which has high diffusion coefficient (0.61 cm^2/s in air) and very low density (0.0899 kg/m^3). Therefore, constant monitoring of hydrogen leak at storage and accurate hydrogen gas concentration measurement is essential to prevent the risk of an explosion. The need for hydrogen detection and concentration measurement can trace back to airship's air supplements around 100 years ago. Apart from air filling, hydrogen gas itself has a lot of applications in various areas of industry, such as chemical products synthesis and the production of rocket fuels. With the increasing concern about the global energy crisis, more attention is paid to hydrogen as a clean and renewable energy source. For instance, hydrogen can be harvested from water without producing other global warming gas. Although pure hydrogen fuel utilization is still in its beginning stage, fuel cells may be brought in a wide usage to automobile and home in near future. Therefore, some precautions are required for the safe use of hydrogen. More importantly, to avoid hydrogen explosion in a nuclear power station, which happened at Three Mile Island in 1979 and Fukushima in 2011.

Tungsten trioxide (WO_3) is a well-known metal oxide for its applications in gas sensing industry. WO_3 has been treated as a promising candidate for gasochromic platform based sensing device in many studies [1–3]. It has been widely reported that when WO_3 is coated with a catalytic layer such as Pt, Pd and Au, and exposed to hydrogen gas; it will undergo a reversible coloration process [4–7]. Although the origin of this coloration mechanism is still of some controversy, recently, the double injection model is widely accepted [8]. As for gasochromic devices, a very thin Pt catalyst is coated on WO_3 thin film, hence, hydrogen gas is dissociated on the catalyst into H ions (protons) and electrons, in which both protons and electrons are simultaneously affecting WO_3. This will reduce the valence state of W from 6^+ to 5^+ and color the thin film. As the hydrogen gas source is removed, the colored thin film will bleach back to original WO_3. Generally, there are various types of sensitive sensors and each of them has its own pros and cons on different monitoring purpose. In this study, we report hydrogen sensing performance of a gasochromic Pt/WO_3 thin film which is operated at room temperature.

2. Experimental

Gasochromic WO_3 thin films were fabricated by PLD method [9,10]. In order to make a good PLD target, high purity (99.999%)

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of WO_3 with 8 g total weight was prepared and well mixed for 3 h by a steady powder mixing machine. Afterward, it was compressed into a form of pellet with 25 mm diameter and 5 mm height and sintered at 600 °C for 12 h under the atmosphere [11]. Microscope slide glasses were used as the thin film substrates. The substrates were cut into 1 $cm^2 \times 1$ cm^2. All substrates were cleaned with detergent soap, alcohol and de-ionized water before PLD. A $\lambda = 248$ nm laser beam was provided by the KrF laser (Lambda Physik LPX Pro). The repetition rate is 2 Hz and laser intensity of about 5–6 J/cm^2. The deposition rate of thin film growth is about 0.05 nm/shot. The deposition chamber contained 0.2 Torr oxygen partial pressure and the temperature of substrates was set at room temperature, 250 °C and 500 °C. A platinum catalyst layer was sputtered at deposition rate of 8 nm/min, the catalyst was sputter for 20 s on the WO_3 thin film to complete a sensor device structure [12], and all measurements were performed at room temperature.

Surface morphology, thicknesses and elemental compositions of Pt/WO_3 thin films were examined by a Field-emission Scanning Electron Microscope with Energy Dispersive Spectrometer (FE-SEM-EDS, HITACHI S4800). The crystal structure and phase identification of the thin films were investigated by an X-ray diffractometry (XRD, Rigaku TTRAX III Diffractometer, Cu Kα radiation). The accelerating voltage and the applied current were 50 kV and 300 mA, respectively. A Transmission electron microscopy (TEM, JEOL JEM-2100F) was used to study the crystallinity of the films. The valence state of tungsten before coloration was verified by an X-ray photoelectron spectroscopy (XPS, ULVAC-PHI, Chigasaki). The colorations of hydrogen gas detection at room temperature were measured by an UV–vis spectrophotometer (BAL2000, Ocean Optics, Inc., USA). A small chamber with two view port windows opposite to each other and air venting valves is designed for gasochromic measurement. The sample is placed inside the chamber and aligned with light source and UV–vis spectrophotometer through two view port windows. The concentration of hydrogen gas is controlled by mole % ratio of H_2–N_2 mixtures gas.

3. Results and discussion

The morphology of the film is known as an important role in the gaschromic performance. Fig. 1 shows FE-SEM images of WO_3 films grown at room temperature (Fig. 1a, b), 250 °C (Fig. 1c, d) and 500 °C (Fig. 1e, f). Fig. 1a, c and e, highlights the homogeneous morphology of the WO_3 nanostructured thin films and the insert SEM image is the cross section of the sample, while Fig. 1b, d and f emphasize the compactness of the films. The results show thickness of films grown at room temperature, 250 °C and 500 °C WO_3 were 350–400 nm, 550–600 nm and 900–950 nm,respectively. Upon closer inspection, it is clear that the films grown at room temperature and 250 °C have a porous structure consisting of adjacent nanostructured clusters

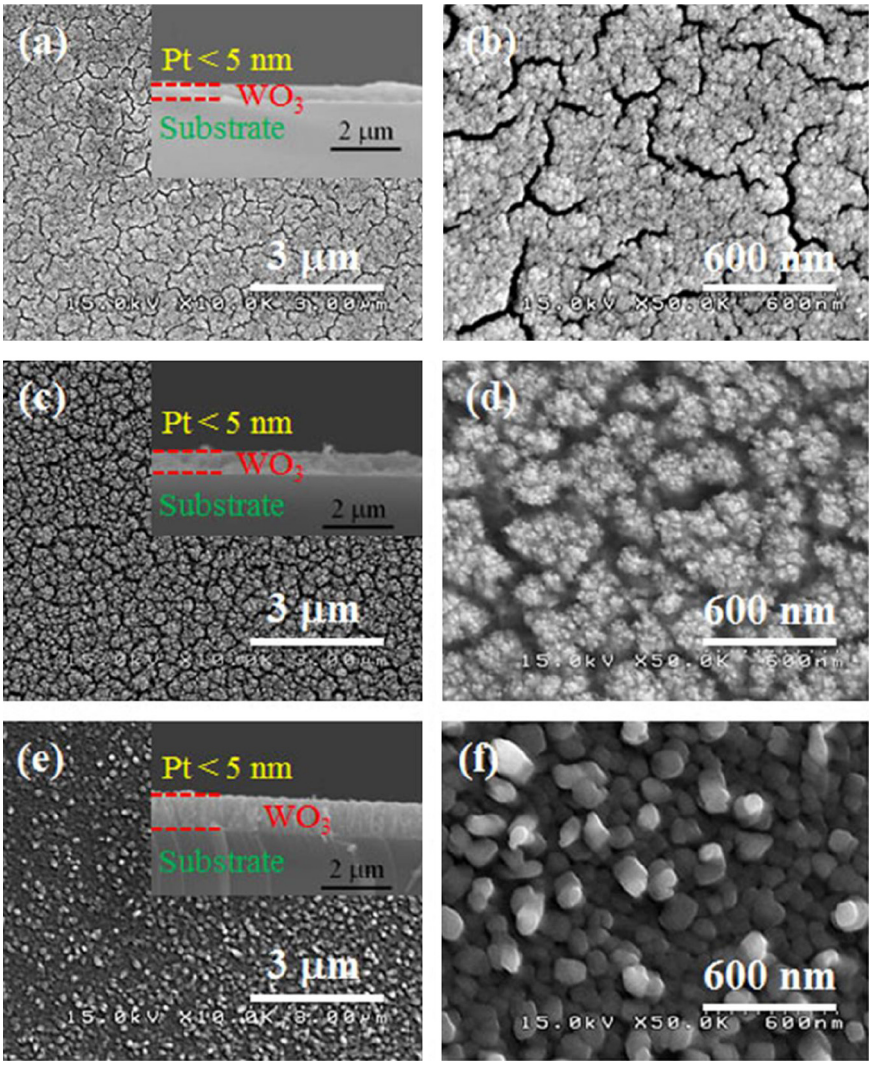

Fig. 1. FE-SEM images of WO_3 films and cross-section, grown at various temperature: (a) and (b) room temperature, (c) and (d) 250 °C, (e) and (f) 500.