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Influence of oxygen gas concentration on hydrogen sensing of Pt/WO_3 thin film prepared by sol–gel process

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ABSTRACT

High-performance hydrogen gas sensors are needed to ensure safe use of hydrogen gas as a clean energy resource. Pt catalyst-loaded tungsten oxide (Pt/WO_3), which shows gasochromism, is an excellent candidate for optical hydrogen gas sensor applications. Pt/WO_3 turns blue in a hydrogen gas atmosphere and its electrical conductivity also changes at the same time.

This study investigated the influence of partial pressures of hydrogen and oxygen gases on the gasochromism of Pt/WO_3. Using elementary gasochromic reactions as a basis, we estimated the concentration of hydrogen injected into a WO_3 lattice from the equilibrium of elementary reaction velocities. The estimation suggested that the inverse of the hydrogen concentration in WO_3 was inversely proportional to the partial pressure of hydrogen and was proportional to that of oxygen. Additionally, the estimation agreed well with the results of Pt/WO_3 gasochromic properties. Therefore, we were able to confirm the dependence of gasochromism on the partial pressures of hydrogen and oxygen gases, and substantiate that Pt/WO_3 is capable of detecting hydrogen gas concentrations in various atmosphere conditions where oxygen gas partial pressures change.

1. Introduction

Hydrogen is attracting much attention as a next-generation clean energy resource. Hydrogen gas is clean, storable, portable and highly efficient. However, hydrogen gas is dangerous because it is explosive between 4 and 74 vol.% in air and has a fast combustion rate. Moreover, it is highly diffusive because its molecule is very small and light. Therefore, a hydrogen gas leakage sensor capable of immediate detection is required for ensuring safety.

WO_3 is widely known as a chromic material that shows a reversible color change from light yellow to blue by means of its chromism. Electrochromism of WO_3, the most typical property, was discovered by S. K. Deb in 1972 [1,2]. Investigations of WO_3 thin films revealed that the electrochromic properties depended on the crystallinity, particle size and morphology [3–6]. In particular, the porosity and particle size affect the ion exchange at the interface between the electrolyte and the film. WO_3 thin films with numerous pores and large surface areas displayed the superior electrochromic coloration efficiency [4]. In contrast, the coloration efficiency of a highly crystallized film decreased due to the high density and small surface area.

In another development, a reducing gas has been found to color a Pt nanoparticle-dispersed WO_3 film. This phenomenon is called gasochromism. The gasochromism of Pt/WO_3 thin films has a similar structural dependence to that of electrochromism, where the Pt/WO_3 gasochromism properties also depend on film morphology, porosity, particle size and crystallinity. In a hydrogen gas atmosphere, the hydrogen molecules are dissociated into H atoms and ionized into protons and electrons by the Pt catalyst, which are injected into the WO_3 lattice. The H atoms diffuse through the WO_3 surface in what is called the spillover effect. The protons become stable in the interspace formed by WO_6 octahedral clusters and the electrons are trapped on the tungsten ions. Therefore, W^{6+} ions were reduced to W^{5+} by the injection of electrons. This leads to an intervalence charge transfer (IVCT) [6–8] and charge transfer from the valence band to a split-off W^{5+} state [8]. Then the hydrogen-injected WO_3 absorbs a broad wavelength range of light from the visible to the near infrared spectrum and changes to blue color. Therefore, the coloration of the Pt/WO_3 thin film indicates the presence of the colorless and odorless hydrogen gas.

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Additionally, the electrical conductivity of Pt/WO_3 increases under the hydrogen gas atmosphere due to the injection of protons and electrons, which work as electrical carriers. Thus, Pt/WO_3 thin films can detect hydrogen gas through the change of its electrical conductivity [9–13]. In this study, we also utilized Pt/WO_3 thin films as a hydrogen-gas leakage sensor.

WO_3 films were prepared by various methods such as rf-sputtering, chemical vapor deposition, and by a sol-gel process. The sol-gel process in particular can yield porous and low crystallized WO_3 film. Since the hydrogen gas (or protons and electrons) can diffuse into the film structure easily, the Pt/WO_3 thin films prepared by the sol–gel process showed fast response times to hydrogen gas exposure. In the case of physical vapor deposition, Pt catalyst nanoparticles are deposited on the films after WO_3 film fabrication, which means that Pt particles can only be deposited on the film surface and that sample preparation with the deposition method requires two steps (film fabrication and Pt deposition). In comparison, our proposed method is a very simple process that uses the sol–gel method [14,15]. Using the tungsten chloride and hydrogen hexachloroplatinate as starting materials and ethanol as the solvent, the ethanol solution was spin-coated onto the glass substrate. This process can simultaneously fabricate a WO_3 thin film and deposit Pt nano-particles. Pt nano-particles were dispersed in the film uniformly with 5–20 nm in size. The Pt/WO_3 thin film heat-treated at the appropriate temperature showed a very fast response to hydrogen gas, in which the normalized optical transmittance of the film changed 50% in less than 0.2 s when exposed to 100% hydrogen gas. In addition, the film can detect 100 ppm of hydrogen gas by electrical measurement in air. Further, the optical absorbance and the electrical conductivity respectively increased proportionally with increase of the hydrogen gas concentration. Using the both optical and electrical detections, the film can determine the concentration of hydrogen gas from 100 ppm to 4% in air [15].

Many studies of hydrogen gas sensor properties based on noble metal-loaded WO_3 films have reported the relationship between the gasochromic (hydrogen sensing) property and hydrogen gas concentration (partial pressure). Georg, Graf, Neumann, and Wittwer reported the linear relationship between the coloration velocity and the hydrogen gas concentration in argon [16]. Chan, W.C. Hsu, Peng, and Chang reported in 2007 that the absorbance of Pt/WO_3 films in pure nitrogen-diluted hydrogen gas is proportional to hydrogen gas concentration [17]. However, Chan, W.C. Hsu, Chang, and C.S. Hsu has further reported in 2011 that the absorbance plots against the partial pressure of the hydrogen gas in the nitrogen base gas reveal a nonlinear regression [18]. Sekimoto et al. and Ghosh et al. [19,20] reported that the absorbance of noble metal loaded WO_3 sensors was not proportional to hydrogen gas concentration. Nakagawa et al. reported that the electrical conductivity of Pt/WO_3 film is disproportionate to nitrogen-diluted hydrogen [9]. In comparison, Zhao and Ong reported that the electrical resistance of Pd/WO_3 film has a linear relationship with the hydrogen gas concentration in air [13].

The abovementioned studies indicate that the relationship between the gasochromic properties of noble metal-loaded WO_3 films and the hydrogen gas concentrations seem to depend on the condition, particularly the atmosphere, i.e., the partial pressure of oxygen gas. Actually, we have previously reported that the change value of optical transmittance or the conductivity by hydrogen gas exposure decreased in atmosphere that is 20% oxygen, since oxygen drives direct combustion with hydrogen on the noble metal catalyst surface and the protons and electrons are consumed by water formation [15].

In this study, we investigated the effect of oxygen partial pressure on gasochromic coloration of sol–gel-derived Pt/WO_3 thin film. We attempted to elucidate the relationship between the amount of hydrogen (protons and electrons) injected into a WO_3 lattice and oxygen gas partial pressure using the equilibrium of gasochromism based on elementary reactions.

2. Experimental

2.1. Sample preparation

Pt catalyst nanoparticle-dispersed WO_3 thin films were prepared by a sol–gel process using tungsten hexachloride (Kojundo Chemical Laboratory Co., Ltd., 99.99%) and hydrogen hexachloroplatinate (Kishida Chemical Co., Ltd., 98.5%) as starting materials [14,15,21].

In a dry box filled with pure nitrogen, 3.00 g of tungsten hexachloride and 0.303 g of hydrogen hexachlorideplatinate were dissolved in 42 mL of ethanol (Kanto Chemical Laboratory Co., Inc., 99.5%). The solution was stirred for several minutes until it cooled and the color of the solution turned light green. The solution was spin-coated onto an alkaline-free glass substrate (Corning EAGLE XG) and the samples were dried on a hot plate at 200 °C. Coating and drying were repeated 5 times and then the films were heat-treated at 400 °C for 10 min in a furnace.

2.2. Characterization

The morphology and thickness of the Pt/WO_3 was observed by field emission scanning electron microscopy (FE-SEM JSM-7600F, JEOL, Tokyo, Japan) using 15 kV of accelerating voltage. The crystal phase and crystallinity were confirmed by the X-ray diffractometer (UltimaIV, Rigaku, Tokyo, Japan) using CuKα radiation (40 kV, 40 mA). The atomic ratio of tungsten and platinum was measured by ICP-AES (ICPE-9000, Shimadzu, Kyoto, Japan). The resulting actual atomic Pt:W ratio was 1:10.2.

The optical gasochromic property was investigated by UV–Vis spectroscopy (UV-630, JASCO, Tokyo, Japan). For the optical measurement, the film was put in the transparent cell made of acrylic resin to flow the hydrogen gas. Transmission spectra were measured from 300 to 800 nm. The responses for hydrogen gas were evaluated by measuring the absorbance change at 800 nm against time. The electrical conductivity was measured in the steel cell filled with various hydrogen gas by the two-wire method using a digital multi-meter (ADCMT 7410E) and a comb-shaped gold electrode was deposited on the film by thermal evaporation. The optical absorbance and electrical conductivity were measured at various hydrogen and oxygen gas partial pressures, achieved by controlling the flow ratio of each gas. A mass-flow controller mixed the hydrogen, pure nitrogen and pure oxygen gases to prepare the experimental hydrogen gases. All experiments were measured under atmospheric pressure, optical absorbance was measured at room temperature and electrical conductivities were measured at 200 °C.

3. Results and discussions

3.1. Structural analysis

The Pt/WO_3 thin film prepared by the sol-gel method was heat-treated at 400 °C, the optimum temperature for obtaining superior hydrogen gas sensing properties [14,15]. As shown in Fig. 1, the diffraction peaks of the film were very low and broad, indicating small particles and low crystallinity of the film. SEM observation revealed that the film consisted of quite small WO_3 particles and the surface was porous. However, Pt particles were not observed, as they were likely smaller than 5 nm in size. The film thickness was about 400 nm. The obtained film seemed to have an ideal structure for detecting hydrogen gas, which has been previously reported in the literature.