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Hydrogen incorporation and gasochromic coloration of tungsten oxide films

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Abstract

The retention and release of hydrogen were studied in connection with the gasochromic coloration and bleaching of tungsten oxide (WO_3) thin films prepared by RF magnetron sputtering at various substrate temperatures. The concentration depth profiles of hydrogen in the WO_3 film were measured by the Elastic Recoil Detection Analysis technique. The hydrogen was effectively incorporated and was uniformly distributed in the WO_3 films deposited at the higher substrate temperatures above 400 K, where crystalline structure was formed with a preferred orientation. Excellent gasochromic characteristics were found for the highly oriented crystalline WO_3 film covered with a Pd layer. In situ measurements of hydrogen retention and optical transmission of the WO_3 demonstrated that hydrogen concentration in the WO_3 film increased with decreasing the optical transmission during the exposure of hydrogen gas.

Keywords: Oxide materials; Thin films; Optical properties; RBS

1. Introduction

The electrochromic properties of the tungsten oxide film are of great interest from scientific and technological points of view [1]. It is known that optical absorption of a tungsten oxide film is drastically changed when the surface covered with catalyst layer of Pd is exposed by hydrogen gas. The optical switching of the gasochromic film based on an electrochromic layer offers wide range industrial applications such as smart windows, an optically based hydrogen detector [2,3]. There is a widely accepted model [4], in which protons and electrons are simultaneously injected into a WO_3 film and reduce WO^{6+} to WO^{5+}, changing the optical absorption in the oxide layer. In another model [5], dissociated hydrogen is transferred into a pore or grain boundary of WO_3 and subsequently creates water and an oxygen vacancy. Despite extensive investigations on the optical and electrical properties of tungsten oxides, the role of the hydrogen on the gasochromic mechanism is still not clearly understood. So far, hydrogen transport was measured mainly by electrochemical techniques and by infrared absorption measurements [6,7]. Besides, the gasochromic characteristics depended on the preparation methods of the WO_3 films, such as a sputtering evaporation and sol–gel coatings [8,9]. In this work, the hydrogen retention/release behavior in tungsten oxide films with different composition and structure prepared by RF magnetron sputtering was examined using ion beam analysis techniques. Moreover, in situ measurements of hydrogen during the coloration/breaching processes were performed to investigate the role of hydrogen on the gasochromic mechanism.

2. Experimental

Tungsten oxide thin films were prepared on a SiO_2 glass substrates by RF magnetron sputtering with a W target (purity: 3N, Furuuchi Chemical Corp.) in a deposition camber under the base pressure of about 5×10^{-5} Pa, at substrate temperatures varying from 300 to 970 K. A mixture of argon and oxygen gases was introduced into the chamber through a mass-flow controller and the $Ar:O_2$ gas flow ratio was adjusted to be about 4:1. The deposition rate of the tungsten oxide layer was typically about 0.1 nm/s. The thickness of the deposited tungsten oxide films was in the range of 400–600 nm, determined by a profilometer and also by conventional Rutherford Backscattering Spectroscopy (RBS) using

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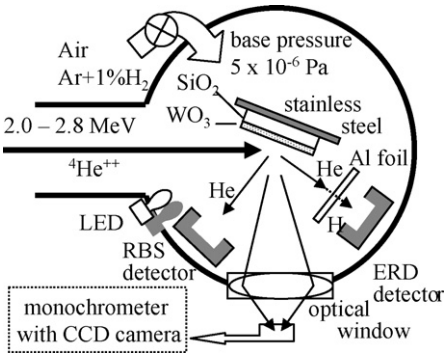

Fig. 1. A schematic illustration of the experimental setup for the RBS, ERDA and optical reflection measurements.

2 MeV He^{++} ions. The crystal structure of tungsten oxide films was examined by X-ray diffractometry using Cu Kα radiations. The concentration depth profiles of hydrogen in the near surface layer were determined by the Elastic Recoil Detection Analysis (ERDA) technique. The RBS and ERDA experiments were performed in a scattering vacuum chamber, connected to a tandem accelerator. The experimental setup for the ion beam analysis is schematically shown in Fig. 1. For the ERDA measurement, an analyzing beam of 2.8 MeV He^{++} was incident on the specimen at an angle of 75° to the surface normal and the recoiled hydrogen atoms were detected at an angle of 30° with respect to the analyzing beam. An Al foil of 12 μm thickness was placed in front of the detector to stop the forward scattered He ions. Since the probing depth of the ERDA in the present experimental condition was about 800 nm in the tungsten oxide, the whole thickness of the deposited films was analyzed. To evaluate the hydrogen concentration, a plate of titanium hydride was employed as a standard sample having a known content of hydrogen. For the measurements of gasochromic characteristics, the tungsten oxide films were coated with a thin Pd layer of about 20 nm. The coloration and bleaching processes of the $Pd/WO_3/SiO_2$ sample were examined in atmospheres of diluted hydrogen in Ar ($Ar + 1\%H_2$) gas and air, respectively. The optical transmittance as a function of time was measured at a wavelength of 640 nm using a red light-emitting diode (LED), by a CCD camera equipped with a monochrometer. In case of the in situ measurement of gasochromic coloration and hydrogen incorporation, the reflected light from the stainless steel foil placed on the backside of the $pd/WO_3/SiO_2$ sample was detected through an optical window of the vacuum scattering chamber as shown in Fig. 1.

3. Results and discussion

Fig. 2 shows ERDA spectra for tungsten oxide films of 400 nm thickness deposited at 295 and 873 K. The spectra indicated that a considerable amount of hydrogen was retained in the oxide film deposited at higher temperature, and the H atoms were uniformly distributed in the oxide layer in both samples. From the RBS measurement, the composition of W:O in the deposited oxide film in the present experiment was determined to 1:3, and did not depend on the substrate temperature. The additional hydrogen atoms were incorporated in the tungsten trioxide WO_3 film expressed as H_xWO_3. The hydrogen atoms seemed to be up-taken after the deposition, since hydrogen was not retained in WO_3 film at temperatures above 600 K as described later. The average H concentration, namely the x-value in the H_xWO_3 film was evaluated by the conventional analysis procedure [10], and was shown in Fig. 3, plotted as a function of the substrate temperature. The x-value increased with increasing the substrate temperature. In the XRD pattern, a broad small peak was observed for substrate temperature below 470 K, indicating amorphous or nano-crystalline structure. Above 700 K of the substrate temperature, a sharp diffraction peak appeared and can be assigned to (0 0 2) plane of the monoclinic or orthorhombic phase of WO_3 [11]. The formation of hydrogen tungsten bronze ($H_{0.33}WO_3$) with tetragonal crystalline structure was previously reported for annealed tungsten oxide films [12], but the hydrogen concentration in the present crystalline film was considerably higher than that of the hydrogen tungsten bronze. The highly oriented crystalline WO_3 film covered with a thin Pd layer showed excellent gasochromic properties; the light transmittance changed more rapidly and largely [11]. The results suggest that the hydrogen can be more easily incorporated in the oriented WO_3 crystalline film prepared at higher substrate temperature. If we assume the gas chromic mechanism is subjected to the double injection model [4], the excellent gasochromic characteristic can be attributed to a fast diffusion of proton in the crystalline WO_3 film with preferred orientation. A further

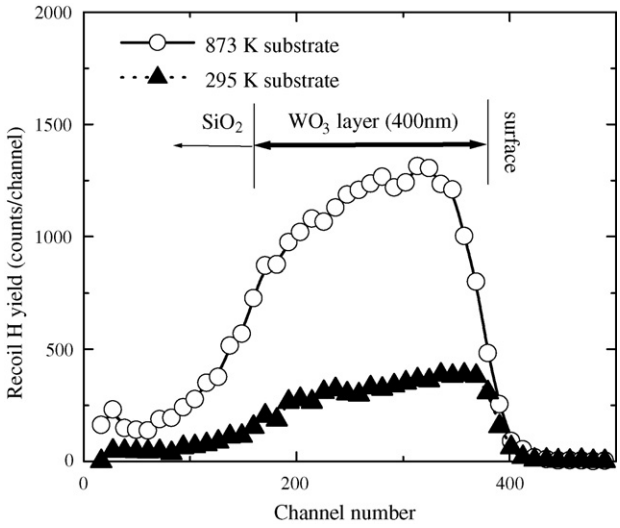

Fig. 2. Recoil hydrogen spectra for WO_3 films deposited at the temperature at 295 K (▲) and 873 K (◯).

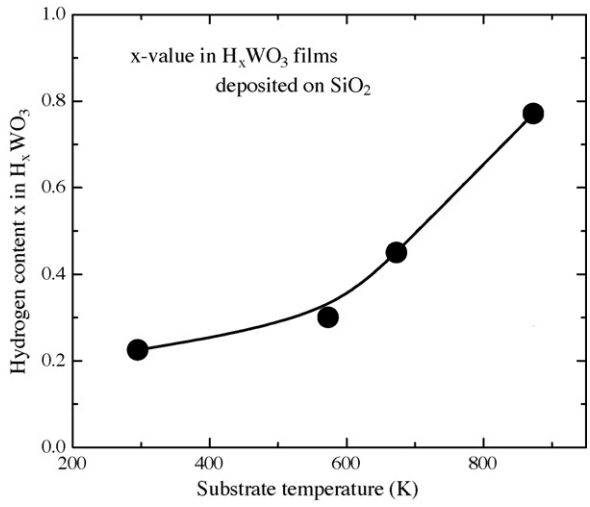

Fig. 3. Hydrogen content in the WO_3 films, namely the x-value in H_xWO_3, plotted as a function of the substrate temperature during the sputtering deposition.

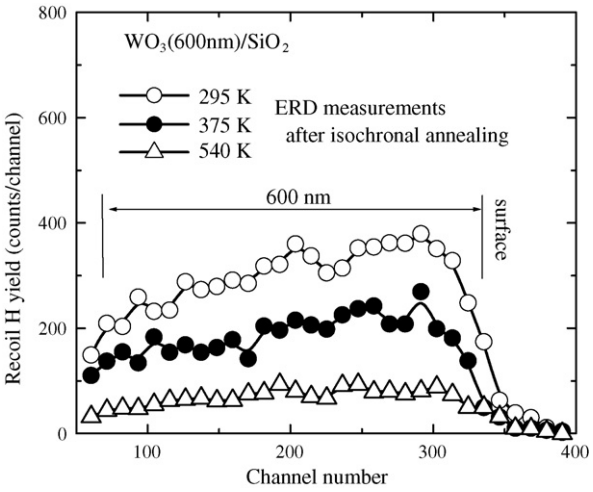

Fig. 4. Recoil hydrogen spectra of hydrogen in a WO_3 film of 600 nm thickness measured at room temperature for as prepared state (◯) and after the isochronal annealing at 375 K (●) and 540 K (△) for 500 s.

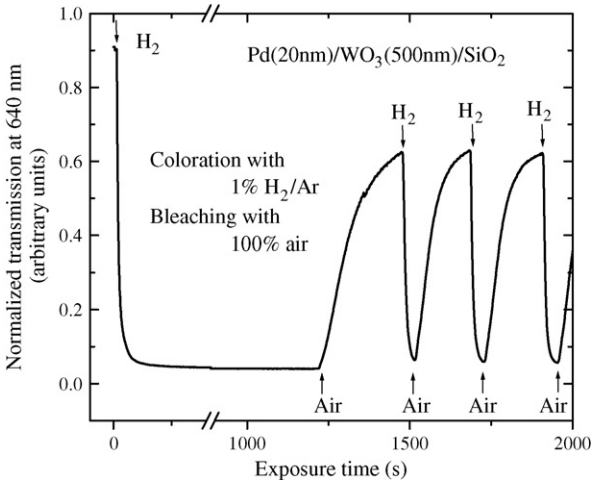

Fig. 5. The transmission at 640 nm wavelength of a WO_3 film covered with a thin Pd layer, plotted against the time during alternate exposures of Ar + 1% H_2 gas and air.

investigation is needed to clarify the relation between hydrogen incorporation and crystal structure.

The thermal release of the incorporated hydrogen in the WO_3 film was measured by the ERDA during the heat treatment in vacuum. Fig. 4 shows ERD spectra of hydrogen in the tungsten oxide of 600 nm thickness measured at room temperature after the each stage of isochronal annealing for 500 s. The hydrogen concentration decreased uniformly in the whole oxide thickness with increasing the annealing temperature. The result of the thermal release experiment of hydrogen suggests a fast diffusion of hydrogen in the WO_3 film and a recombination limited process of hydrogen release at the surface. The composition of tungsten and oxygen did not vary with the annealing temperature up to 600 K, at which almost all the hydrogen atoms were released from the WO_3 film. It is interesting to compare the thermal release behavior of up-taken hydrogen to that of ion-implanted one. The thermal release of the ion-implanted hydrogen [13] was accompanied with reduction of the tungsten oxide layer during the annealing procedure, and was completed at lower temperatures.

Typical gasochromic coloring/bleaching processes of a WO_3 film deposited on SiO_2 covered with thin Pd layer was shown in Fig. 5. The transmission at 640 nm wavelength of the sample was measured as a function of the time during exposures of diluted hydrogen in Ar and air. The coloring and bleaching of the WO_3 film was repeated regularly by the alternate exposure of hydrogen and air. The WO_3 film was colored immediately after the exposure of hydrogen, but the bleaching process took place slowly, presumably due to the smaller flowing rate of the air at the catalyst surface. Fig. 6 shows recoil hydrogen spectra in the WO_3 film of the sample exposed by hydrogen and air. After evacuating the scattering chamber to 1×10^{-4} Pa, 1% H_2 diluted in Ar or air was introduced into the chamber to 1 atm for 2000 s. Then, the chamber was evacuated to 1×10^{-5} Pa, and the ERDA measurement was carried out.

It is clearly seen that the hydrogen concentration increased after the hydrogen exposure, and was decreased after the air exposure. It should be also noted that the changes of the hydrogen concentration was uniformly occurred in the whole thickness of the WO_3 film. During the ERDA measurements, the reflected light from the stainless steel foil placed on the backside of the sample was monitored simultaneously. The changes of hydrogen content x in H_xWO_3 film and the reflection intensity at 640 nm wavelength were shown in Fig. 7. The gas exposure and evacuation was repeatedly carried out by the same procedure described above. The hydrogen concentration in the WO_3 film increased with decreasing the reflection for hydrogen exposure, and vice versa for air exposure. The changes of the optical reflection were smaller than those of the optical transmission as shown in Fig. 5. The transmission decreased by an order of magnitude after the hydrogen exposure, while the reflection varied about 20%. In the reflection measurement, the gas was not directly blown on the catalyst surface, but was slowly introduced by filling the volume of the vacuum chamber. The less effective gasochromic coloration/bleaching processes observed in the reflection measurement can be explained by the slower

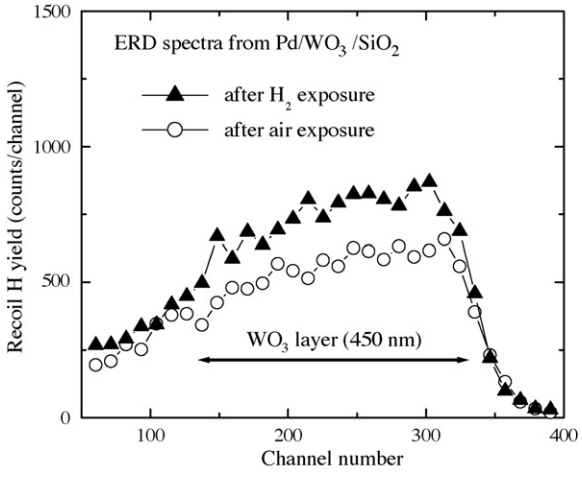

Fig. 6. Recoil hydrogen spectra in the WO_3 film covered with thin Pd layer, after the exposure of Ar + 1% H_2 gas (▲) and air (◯) for 2000 s.

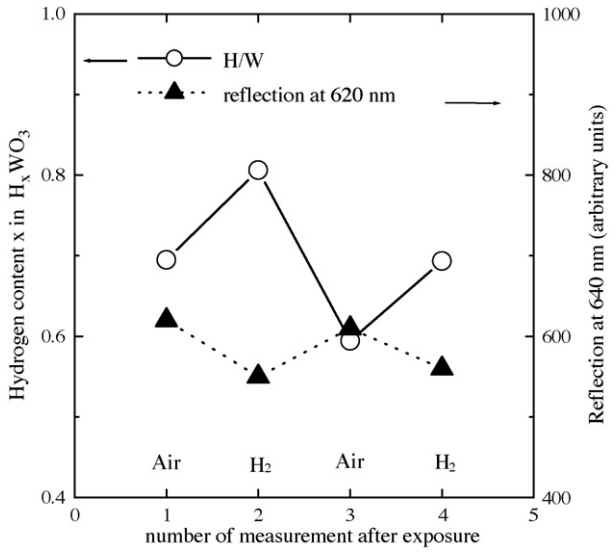

Fig. 7. Changes of hydrogen content x in H_xWO_3 (◯) and the reflection intensity at 640 nm wavelength (▲) from the $Pd/WO_3/SiO_2$ sample placed on the stainless steel foil, obtained after the alternate exposures of Ar + 1% H_2 gas and air.

gas flowing rate, which allows adsorption of impurities on the catalyst surface.

4. Conclusion

The hydrogen behavior and gasochromic characteristics were investigated for tungsten oxide films with different hydrogen content (H_xWO_3, $0.2 < x < 0.8$) and structure. A large amount of hydrogen was retained in the WO_3 films deposited at higher substrate temperature during the sputtering. The effective incorporation of hydrogen and better gasochromic characteristics can be attributed to the high diffusivity of the hydrogen in the oriented crystalline structure of the WO_3 film. The simultaneous measurements of the hydrogen concentration and optical transmission of the WO_3 film covered with a thin Pd layer showed that the gasochromic coloration/bleaching of the WO_3 films was directly related to the hydrogen retention/release in the film. The results support the double injection mechanism of the coloration process in the crystalline WO_3 film by hydrogen exposure.

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