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Gasochromic Coloration of Non-stoichiometric WO_{3-x} Films

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We investigated the gasochromic coloration of amorphous tungsten oxide films having oxygen compositions between $WO_{0.25}$ and $WO_{3.0}$. The films were deposited by the reactive radio frequency (r. f.) magnetron sputtering with varying oxygen partial pressure. The oxygen and hydrogen concentration of the tungsten oxide films were determined using the Rutherford Backscattering Spectrometry (RBS) and the Elastic Recoil Detection Analysis (ERDA), respectively. The optical transmittance was examined for the films coated with palladium catalysis during the exposure of diluted hydrogen gas. Superior gasochromic properties were obtained for the films consisting of tungsten trioxide, WO_3. For the films with lower oxygen concentration than WO_3, the optical transmittance hardly changed during the hydrogen exposure. High concentration of hydrogen about 0.7 per a tungsten atom was found in the WO_3 films. The hydrogen retention drastically decreased with a decrease of the oxygen concentration.
Keywords: tungsten oxide, gasochromic, hydrogen, RBS, ERDA

1. INTRODUCTION

Tungsten oxide films covered with a thin palladium catalyst layer are colored by the exposure of hydrogen (gasochromic phenomenon). The gasochromic films can be used for the optical hydrogen-gas-leak detector using a fiber-optic, because it is considered to be operative at room temperature, highly sensitive and with no-noise by electronic effects [1, 2]. The two types of gasochromic coloration mechanisms are proposed. One is reported as double injection model [3]. In this model, dissociated hydrogen atoms and electrons in catalysis layer dissolve into the tungsten oxide film and the film is colored due to formation of tungsten oxide bronze (H_xWO_3). The other is the model proposed by Georg et al. [4]. The dissociated hydrogen atoms form H_3O^+ together with adsorbed water, allowed a fast diffusion. The diffused hydrogen atoms form H_2O together with oxygen of the WO_3 resulting in making oxygen vacancies in WO_3. The gasochromic coloration is caused by diffusion of the oxygen vacancies in the WO_3 as color centers. In both of these models, the gasochromic coloration of the tungsten oxide is influenced by oxygen and hydrogen concentration. Therefore, it is important for understanding the gasochromic coloration mechanism to investigate the relation between the compositions (oxygen and hydrogen concentration) in the tungsten oxide films and the gasochromic coloration for hydrogen gas.

In previous reports, Stolze et al. investigated the effects of the oxygen concentration on gasochromic coloration in tungsten oxide films deposited by reactive dc sputtering method using x-ray photoelectron spectroscopy (XPS) [5]. Ion beam analyses such as the Rutherford Backscattering Spectrometry (RBS) and the Elastic Recoil Detection Analysis (ERDA) are suitable to determine the oxygen and hydrogen concentration of the tungsten oxide films not only on the surface but also inside of the samples [6-10].

Therefore, in this study, we systematically investigated the effects of the oxygen and hydrogen concentration (O/W and H/W) in the tungsten oxide films on the gasochromic coloration for hydrogen gas, using the RBS and ERDA. The gasochromic coloration of various composition tungsten oxide films on quartz glass substrates was examined by optical transmittance in diluted hydrogengas.

2. EXPERIMENTAL

Samples were prepared by a reactive r. f. magnetron sputtering method with a W target (99.9 %, Furuchi) in a vacuum chamber evacuated up to a base pressure of 5×10^{-4} Pa using a turbo-molecular pump (TMP). The preparation was done in defined argon (purity: 6N) and oxygen (purity: 4N) mixture controlled by mass-flow meters and an absolute pressure gauge (Baratron 626, MKS) under the pumping condition. A distance between the tungsten target and the substrates was approximately 100 mm. The tungsten oxide films were deposited on quartz glass and glassy carbon substrates kept at room temperature. The working argon partial pressure was 150 mPa, and a sputtering power was 50 W. The oxygen partial pressure was changed up to 90 mPa, corresponding a sputtering rate from 2 to 15 nm/min. The crystalline structure of tungsten oxide films was determined by x-ray diffraction (XRD) using Cu-Kα radiations operated by a high-resolution diffract meter (X'Pert-MRD, PANalytical).

The RBS and the ERDA were performed for determination of the oxygen and hydrogen atomic

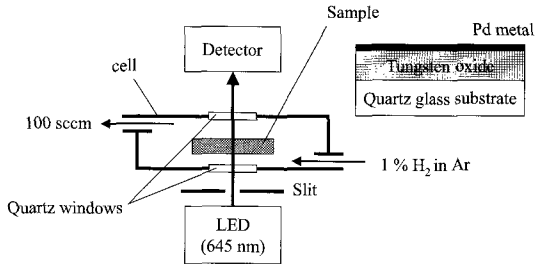

Fig.1. Experimental apparatus for examination of gosochromic coloration.

concentration ratio (O/W and H/W) of tungsten oxide films on glassy carbon, respectively. The RBS was performed using 2.0 MeV $^4He^+$ incident ions accelerated by a 3 MV single-stage-accelerator at JAEA/Takasaki. The backscattered particles were detected at 165 ° scattering angle with a surface barrier detector. The O/W of the tungsten oxide films was estimated by backscattered yields originating from the tungsten and oxygen atoms in the films. The thickness of the tungsten oxide films was estimated by simulation program "SIMNRA ver. 5.0" [11]. The hydrogen concentration in the films was measured by the ERDA, using 2.8 MeV $^4He^{2+}$ incident ions accelerated by a 1.7 MV tandem accelerator at Institute for Materials Research/Tohoku University. The incident ions were irradiated with an incident angle of 10 ° with respect to the sample surface normal. The recoiled hydrogen atoms were detected with an angle of 30 ° with respect to the incident direction normal using a surface barrier detector with 12 μm thick aluminum foil to avoid detecting backscattered He ions. The irradiation was performed with a flux of approximately 8 x 10^{12} ions/cm^2/sec and a fluence up to 1.6 x 10^{15} ions/cm^2. Absolute hydrogen concentration was estimated by yields of the recoiled hydrogen atoms with using titanium hydrate as standard sample in which hydrogen concentration was known ($TiH_{0.694}$).

For measuring the gasochromic coloration, the tungsten oxide films on quartz glass substrates were coated with approximately 15 nm thick palladium layers by the r. f. magnetron sputtering. The palladium layers were deposited under similar conditions. For examination of the gasochromic coloration of the samples, the transmittance of red light by the samples was measured at a wavelength of 645 nm, in Ar including 1 % H_2 (1 % H_2-Ar) with a flow rate of 100 sccm. An experimental apparatus for gosochromic coloration was consisted with a cell equipping quartz windows on both sizes, a red light-emitting diode (LED) and an optical fiber into a CCD detector, as shown in Fig. 1.

3. RESULTS AND DISCUSSIONS

Figure 2 shows the XRD patterns of 350 nm thickness tungsten oxide films deposited under the oxygen partial pressure of 5, 15 and 83 mPa. Three diffraction peaks are found when the deposition is performed under the oxygen partial pressure of 5 mPa, as shown in Fig. 2 (a). The peaks at 2θ of approximately 35.5, 39.9 and 43.7 ° correspond to the (2 0 0), (2 1 3) and (2 1 1) planes of beta-tungsten, respectively, identified by JCPDS file No. 47-1319. At the oxygen partial pressure of 15 mPa, the XRD pattern of the film shows a broad peak due to amorphous structure as the deposition as shown in Fig. 2 (b). At the pressure higher than 15 mPa, the XRD patterns of the films are the almost same, as shown in Fig. 2 (c). The amorphous tungsten oxide films are obtained in spite of varying the oxygen partial pressure, when the oxygen partial pressure is higher than 5 mPa.

Figure 3 shows the RBS spectrum of the film deposited on glassy carbon substrate with the oxygen partial pressure of 20 mPa. The peaks originating from tungsten, oxygen and carbon atoms of the sample are found in a backscattering energy range from 1620 to 1840 keV, from 530 to 700 keV and under 330 keV, respectively. The oxygen concentration per a tungsten atom (O/W) of the tungsten oxide film is estimated to be 3.0 ± 0.1, with counting total backscattered yields from the tungsten and oxygen atoms. On the other hand, the fitting curve simulated by the program is also shown by a solid line in Fig. 3. The thickness of the tungsten oxide layer is determined as approximately 320 nm by the simulation. From the fitting result, it is found that the oxygen concentration is homogeneous over the thickness.

Figure 4 shows the ERDA spectrum of the film deposited on glassy carbon substrate with the oxygen partial pressure of 20 mPa. The energy range of recoiled hydrogen from 720 to 1350 keV corresponds to hydrogen distribution in tungsten oxide film of 320 nm thickness. The simulated fitting curve shown by a solid line in Fig. 4 indicates that the hydrogen atoms are homogeneously distributed in the tungsten oxide film. The hydrogen concentration per a tungsten atom (H/W) in the tungsten oxide film is estimated to be approximately 0.7 (15 at. %) with using the standard sample, $TiH_{0.694}$.

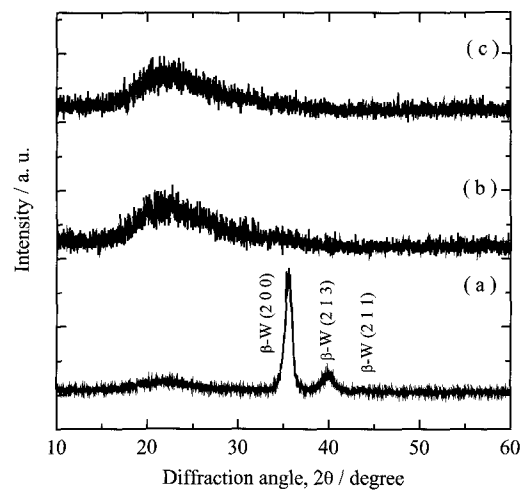

Fig. 2. XRD patterns of the tungsten oxide films deposited with the oxygen partial pressure of (a) 5, (b) 15 and (c) 83 mPa.

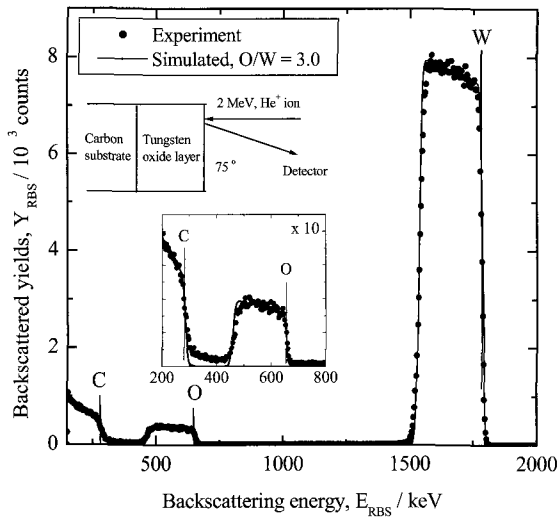

Fig. 3. Typical RBS spectrum of the tungsten oxide film deposited under the oxygen partial pressure of 20 mPa.

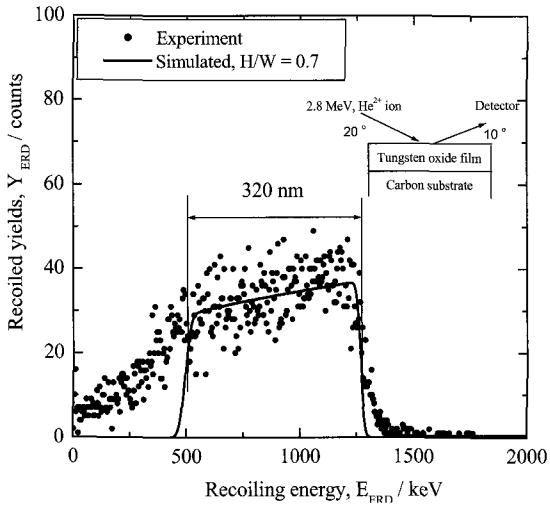

Fig. 4. Typical ERDA spectrum of the tungsten oxide film deposited under the oxygen partial pressure of 20 mPa.

The O/W and H/W are plotted against the oxygen partial pressure as shown in Fig. 5. Under the oxygen partial pressure lower than 15 mPa, the O/W and H/W drastically increase from 0.25 to 3.0 and from 0 to 0.7, respectively. Under the pressure higher than 15 mPa, the O/W and H/W are saturated at approximately 3.0 and 0.7, respectively. The O/W of a few films is higher than 3.0. It is found that the tungsten oxide films with lower oxygen concentration than WO_3 rarely contain hydrogen with comparing to stoichiometric WO_3 films. It is also confirmed that the hydrogen in all of the films is uniformly distributed over the thickness.

In previous reports, similar saturation characteristics of the oxygen concentration are reported from tungsten oxide films prepared by dc [5] and r. f. sputtering [12]. The high O/W over 3.0 is attributed to water (H_2O) [5, 6]. The water containing corresponds to the hydrogen found in this study.

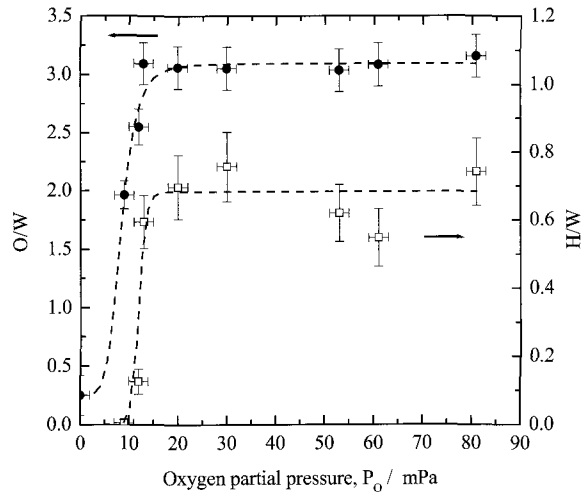

Fig. 5. O/W and H/W of the tungsten oxide films plotted against the oxygen partial pressure.

Considering that all of the hydrogen is contained as H_2O, it is suggested that the composition of the tungsten oxide films is $WO_{2.6}$ $(H_2O)_{0.4}$. But whether the hydrogen forms molecular H_2O or atomic H is not determined in this study.

To investigate the effect of the composition on the gasochromic coloration of the tungsten oxide films, the optical transmittance of the palladium-coated films on quartz glass substrates was measured during the samples in 1 % H_2-Ar. The spectrum of light transmitted by the sample is inserted as a solid line in Fig. 6. After 20 min from exposure of the hydrogen gas, the transmitted light is absorbed as drown by a broken line, that the sample caused gasochromic coloration. It is necessary to normalize the absorbance with the film thickness for evaluation of gasochromic coloration from this result, because the thickness of the films was different. For the normalization, the optical density before and after coloration is estimated using the follow equation [9].

$$\Delta OD_t = \frac{\Delta OD}{t} = \frac{-\log\left(\frac{I_C}{I_0}\right)}{t}, \qquad (1)$$

where t is thickness of the tungsten oxide films. I_0 and I_C are intensities of the light transmitted by non-colored and colored samples, respectively. ΔOD is changes of the optical density of between non-colored and colored samples, which can be calculated by I_0 and I_C. ΔODt is ΔOD normalized at the film thickness. The ΔOD_t at a wavelength of 645 nm is plotted against the O/W of the films as shown in Fig. 6. Below the O/W of 2.5, corresponding that the oxygen concentration is lower than that of WO_3, the films are hardly colored for the diluted hydrogen gas. Above the O/W of 2.5, corresponding that the composition is stoichiometric WO_3, ΔOD_t drastically increases with increasing the O/W. It is found that high gasochromic coloration of tungsten oxide requires the stoichiometric WO_3.

To release the hydrogen contained in the tungsten oxide

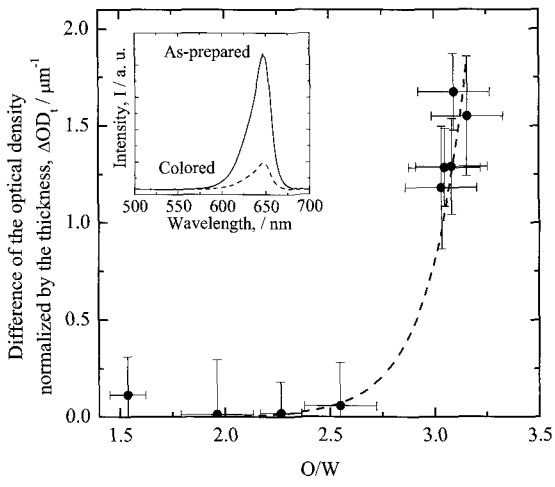

Fig. 6. Difference of optical density normalized at the film thickness before and after coloration plotted against O/W.

films, heat treatment at a temperature of 400 °C was performed for the deposited WO_3 films. The annealed tungsten oxide films, in which oxygen concentration unchanged with O/W of 3.0 and little hydrogen was contained, showed low gasochromic coloration (no shown). It is considered that the high gasochromic coloration of the tungsten oxide requires the hydrogen absorption. In this stage, we cannot decide the hydrogen states such as H_2O and H^+. Therefore, it is necessary to investigate the chemical bonding of the hydrogen in tungsten oxide using the infrared spectroscopy (IR).

4. CONCLUSIONS

We investigate the gasochromic coloration of the amorphous tungsten oxide films with various oxygen compositions in a range of O/W from 0.25 to 3.0. The stoichiometric WO_3 films have superior gasochromic properties. The films with lower oxygen concentration than WO_3 hardly shows the coloration. High concentration of hydrogen about 0.7 per a tungsten atom is found in the WO_3 films. The hydrogen is rarely contained in the tungsten oxide films in which the oxygen concentration is lower than WO_3.

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REFERENCE

[1] K. Itoh, T. Ohgami, *Appl. Phys. Lett.* **60 8** 938-940 (1992).

[2] K. Takano, S. Yamamoto, M. Yoshikawa, A. Inouye, A. Sugiyama, *Trans. Mater. Res. Soc. Jpn.* **31**, **1**, 223-226 (2006).

[3] Se-Hee Lee, Hyeonsik M. Cheong, Ping Liu, Dave Smith, C. Edwin Tracy, Angelo Mascarenhas, J. Roland Pitts, Satyen K. Deb, *Electrochimica Acta* **46** (2001) 1995–1999.

[4] A. Georg, W. Graf, R. Neumann, V. Wittwer, *Thin Solid Films*, **384** 269-275 (2001).

[5] M. Stolze, B. Camin, F. Galbert, U. Reinholz, L. K. Thomas, *Thin Solid Films* **409** 254-264 (2002).

[6] O. bohnke, G. Frand, M. Fromm, J. Weber, O. Greim, *Applied Surface Science*, **93** 45-52 (1996).

[7] Y. Yamada-Takamura, F. Koch, H. Marier, H. Bolt, *Surface and Coatings Technology*, **153** 114-118 (2002).

[8] P. Gérard, A. Deneuville, R. Courths, *Thin Solid Films*, **71** 221-236 (1980).

[9] K. Bange, *Solar Energy Materials and Solar Cells*, **58** 1-131 (1999).

[10] S. Nagata, S. Yamamoto, K. Tokunaga, B. Tuschiya, K. Toh, T. Shikama, *Nucl. Instr. and Meth. B* **242 1-2** 553-556 (2006).

[11] M. J. F. Healy, M. Torresa, J. D. Painter, *Nucl. Instr. and Meth. B* **249 1-2** 789-791 (2006).

[12] C. Bechinger, M. S. Burdis, J. –G. Zhang, *Solid State Communication*, **101-10** 753-756 (1997).

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