Effect of Tungsten Valences on Gasochromic Coloration in Tungsten Oxide Thin Films

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Tungsten tri-oxide (WO_3) thin films are prepared by magnetron sputtering and subsequent thermal treatment. Ion irradiations with $^4He^+$ at 350 keV were performed for the films. Gasochromic coloration of the irradiated films was observed by a measurement of optical transmittance with the exposure of 1 % hydrogen. The extent of coloration level of the irradiated film with the fluence of 1×10^{17} ions/cm^2 is 7.5 times lager than that of non-irradiated film. W $4f$ photoemission spectra for the films were measured by x-ray photoelectron spectroscopy. From the fitting analysis for the spectra, the non-irradiated film has only W^{6+}. In the irradiated film with the fluence of 1×10^{17} ions/cm^2, it is estimated that 17 % and 4 % of the W^{6+} change into W^{5+} and W^{4+}, respectively. The irradiation for the films breaks the chemical bonds between tungsten and oxygen, and makes atomic sites of oxygen-deficient tungsten such as W^{5+} and W^{4+}. The improvement of the gasochromic coloration for the WO_3 films relates to the increment of the W^{5+} and W^{4+} sites induced by the irradiation.
Key words: Tungsten oxide, Hydrogen, Gasochromic coloration, Valences, XPS, Irradiation

1. INTRODUCTION

Tungsten tri-oxide (WO_3) thin films, whose color reversibly turn yellow into blue while in the exposure with hydrogen (gasochromic coloration), has been promised to be used as a detector of optical hydrogen sensors [1-6]. The optical sensors and its systems have less power, more lightweight, smaller size, and simpler structure than the electrical sensors which are used most at present [7]. The optical sensing characteristic is measuring the gasochromic coloration, i.e., the change of optical transmittance of WO_3 thin film. But the rate of the gasochromic coloration is not high enough to satisfy the specification for hydrogen sensors.

While the mechanism of the gasochromic coloration for the WO_3 films is still not fully understood in spite of the recent studies, the gasochromic coloration has been considered to relate to the double charge injection of electrons and protons into the films. This injection can be written in a simplified form as [8]

$$xH^+ + xe^- + WO_3 \longleftrightarrow H_x WO_3. \quad (1)$$
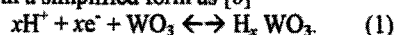
An existence of tungsten valences with W^{5+} and W^{4+}, or the oxygen vacancies [9-11] has been proposed to participate in the extent of coloration levels. During hydrogen or charge injection, charge are localized at tungsten sites thereby changing the valence of the tungsten ions from 6^+ to 5^+ or from 5^+ to 4^+. These localized charges accompany a lattice distortion that forms small polarons. These polarons can hop from sites A to adjacent sites B. This process which is responsible for color in tungsten oxide is referred to as inter-valence transfer and can be expressed as

$$W^{5+}(A) \text{ and } W^{6+}(B) \rightarrow W^{5+}(B) \text{ and } W^{6+}(A),$$
$$W^{4+}(A) \text{ and } W^{5+}(B) \rightarrow W^{4+}(B) \text{ and } W^{5+}(A). \quad (2)$$

Although this model is widely accepted, it still cannot explain some key experimental results [9].

Ion beam irradiation for WO_3 thin films has a possibility to create different tungsten valence or the oxygen vacancies through the breaking chemical bonds between tungsten and oxygen [12-14]. The rate of gasochromic coloration in WO_3 is expected to be improved by the irradiation due to the increment of the different tungsten valence. In this study, $^4He^+$ irradiation at 350 keV for WO_3 films is performed to make atomic sites of oxygen-deficient tungsten such as such as W^{5+} and W^{4+} valences. And then, a participation of the tungsten in the gasochromic coloration is investigates.

2. EXPERIMENTAL

The tungsten oxide thin films were prepared by the reactive r.f. magnetron sputtering with a target of W (purity 99.9 %). The deposition chamber equipped with two sputter sources was pumped down to a base pressure of about 5×10^{-4} Pa using a turbo-molecular pump. The sputtering gas of purity 99.999 % argon (Ar) and reactive gas of purity 99.99 % oxygen (O_2) were flowed into the deposition chamber through mass-flow meters to obtain the required Ar and O_2 mixture under the pumping condition. The deposition on quartz glass substrate was performed in $O_2/Ar = 16$ % atmosphere at room temperature. As-deposited films were annealed at 400 °C in air for 1 hour in order to form the WO_3. The crystal structure of the tungsten oxide films is expected to change with the annealing [15,16]. The structure for the films before and after annealing were characterized by x-ray diffraction (XRD) in which the x-ray source was operated at 40 kV and 30 mA for Cu-$K\alpha$ radiations. The thickness of the films was confirmed with a surface profiler.

$^4He^+$ irradiations were performed in the fluence range from 1×10^{15} to 1×10^{17} ions/cm^2 at JAEA/Takasaki. The incident energy was selected 350 keV due to give the

energy uniformly for the thickness direction [17,18]. In this energy region with $^4He^+$, dominant effect is electronic excitation rather than nuclear collision in WO_3 films. The incident direction of the ion beam was perpendicular to the surface of the film. The shape of the beam was squared to be the size of 5 mm x 10 mm using a slit. The current density of the beam was detected to be 4 $\mu A/cm^2$ at the film. The vacuum pressure kept under than $1x10^{-5}$ Pa during the irradiation.

To characterize the gasochromic coloration, a palladium (Pd) catalyst with the thickness of 15 nm was deposited on the surface of the WO_3 films using the sputtering. The gasochromic coloration were examined by time resolved optical spectroscopy at room temperature, as described in previous reports [6]. The experimental set up is composed of sealed gas cell to keep a concentration of hydrogen, light-emitting diode with the wavelength of 645 nm and optical spectrometer. The reduction of the transmittance T/T_{air} was measured with an exposure of the hydrogen of which the concentration is 1 % diluted by Ar gas. In this experiment, T_{air} and T are the intensity of light transmitted the film in air and during the hydrogen exposing, respectively. The background of the spectrometer is subtracted from T_{air} and T.

W 4f core-level XPS spectra have indirect implications on the valence band, and inform the tungsten valences in the material [19]. The W 4f doublet, 4$f_{5/2}$ and 4$f_{7/2}$ peak, has chemical shift according as the valence of the tungsten changes. To confirm the existence of different tungsten valences in the films, the W 4f XPS spectra were measured with an electron lens and a hemispherical electron energy analyzer under the pressure of $1x10^{-8}$ Pa. The x-ray source was used Al $K\alpha$ radiation, and the photoelectron pass energy was selected 20 eV. In this resolution, full width at half maximum of reference Au 4$f_{7/2}$ peak is measured to be 1.2 eV. The measurements of the XPS for WO_3 films are difficult, because the shape of spectra distort with an electrically charge up due to the insulator. Therefore, the films ware grounded by an aluminum electrode putted on the surface to avoid the charge-up. The measured W 4f spectra were analyzed by the curve fitting method [20]. An inelastic background of photoelectron and components for the W 4f doublet are estimated in the fitting procedure. In this analysis, it is assumed that the background at the kinetic energy, ε_a, given an attention is estimated to be the constant ratio for the area intensity above the ε_a. Lorentzian function was selected as the components of the W 4f doublet. The total components were convoluted with Gaussian function which is window function with the full width at the half maximum of 0.7 eV for the instrument.

3. RESULTS AND DISCUSSIONS
3.1 Structure
The XRD patterns for as-deposited and annealed films are shown in Fig. 1(a) and (b), respectively. The XRD pattern of as-deposited film has broad peak at 22 degree from amorphous structure of quartz glass substrate. The as-deposited films can not be observed crystalline structure. For the annealed film, many XRD peaks appear, and are assigned to be polycrystalline of
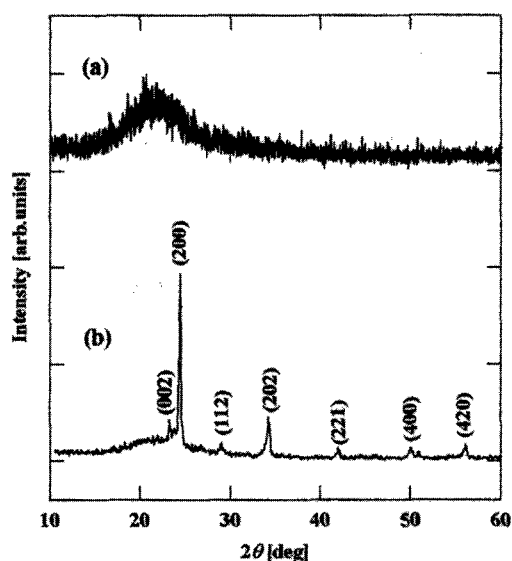

Fig. 1 XRD patterns of tungsten oxide films with 350 nm thickness, as-deposited (a), and after annealing at 400 °C for 1 hour in air (b). The indexes of monoclinic phase in WO_3 are assigned to the peaks of the annealed films.

monoclinic phase in WO_3 to be referred in Ref. 21 and the JCPDS file 43-1035. The XRD pattern indicates that the deposited tungsten oxide films transforms from amorphous or microcrystalline structure into polycrystalline structure of monoclinic phase with the annealing at 400 °C for 1 hour in air. The annealed films are expected to be fully oxidized such as stoichiometric WO_3. On the other hand, the thickness of the as-deposited and after annealed films was confirmed to be the same thickness of 350 nm.

3.2 Gasochromic coloration
Figure 2 shows gasochromic coloration, that is, the reduction of the transmittance with the exposure of 1 % hydrogen for non-irradiated film (a) and irradiated films at $1x10^{16}$ ions/cm^2 (b), $2.5x10^{16}$ ions/cm^2 (c), and $1x10^{17}$ ions/cm^2 (d), as the function of the exposure time. The transmittance of the non-irradiated film decreases gradually during the exposure. The reduction of transmittance is almost saturated approximately 200 seconds. The saturated value of the transmittance is 94 % at 1200 second. Therefore, the extent of coloration levels is 6 % in non-irradiated WO_3 film. The extent of coloration levels of irradiated films is almost similar to the non-irradiated film under the fluence of $1x10^{16}$ ions/cm^2. For the irradiated film at the fluence of $2.5x10^{16}$ ions/cm^2, the transmittance decreases to 84 % at 1200 seconds. The extent of coloration levels is 16 %. During the exposure of hydrogen, the transmittance decreases gradually and is expected to saturate soon. For the irradiated film at the fluence of $1x10^{17}$ ions/cm^2, the transmittance decreases drastically to 55 % at 1200 seconds. The extent of coloration levels is 45 %. The transmittance keeps decreasing during the exposure of hydrogen. The extent of coloration levels at 1200 second
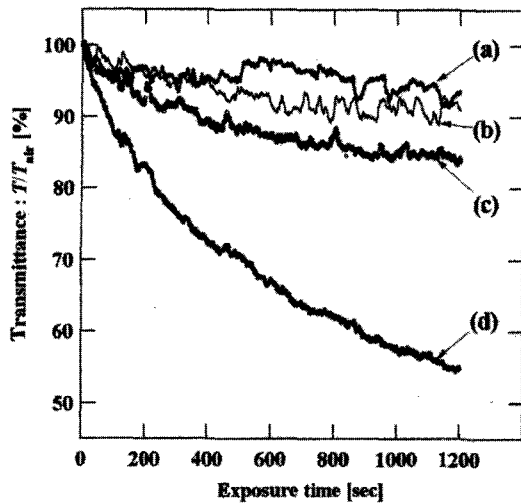
Fig. 2 Gasochromic coloration of tungsten oxide films, non-irradiated (a), and irradiated films at the fluence 1×10^{16} ions/cm^2 (b), 2.5×10^{16} ions/cm^2 (c), and 1×10^{17} ions/cm^2 (d) with ^{4}He$^+$ at the incident energy of 350 keV. T/T_{air} is the relative intensity of the transmitted light with the wavelength of 645 nm. T and T_{air} is intensity of the transmitted light during the exposure of 1 % hydrogen diluted by Ar gas and in air, respectively.

in the irradiated films with 2.5×10^{16} and 1×10^{17} ions/cm^2 is be 2.7 and 7.5 times larger than that of non-irradiated film. Thus, the rate of gasochromic coloration is recognized to be improved by ^{4}He$^+$ irradiation over the fluence of 1×10^{16} ions/cm^2.

3.3 XPS

Figure 3(a) shows the W 4f spin-split core levels XPS spectra of non-irradiated film without the capping of palladium catalyst. Through the fitting analysis, the spectrum can be assigned to the W^{6+} component as shown with dotted line. The 4$f_{7/2}$ and 4$f_{5/2}$ peak appears at the binding energy of 35.9 eV and 37.9 eV, respectively. Relative to the metal state in which the 4$f_{7/2}$ peak appears at a binding energy of 31.0 eV, the measured W 4f doublet is shifted to higher binding energies by 5 eV and represents the oxidation state W^{6+}. Therefore, the spectrum indicates that the tungsten oxide films annealed at 400 °C for 1 hour in air are completely oxidized and has stoichiometric WO$_3$ [10,19]. Performing the subsequent annealing, the stoichiometric difference on the deposition can be canceled out, and the deposited tungsten oxide films can be adjusted to stoichiometric WO$_3$. On the other hand, the shape of the spectrum in irradiated films change from that of non-irradiated film, as the intensity of low binding energy side for W 4$f_{5/2}$ and W 4$f_{7/2}$ increases slightly. The spectrum for the irradiated films at the fluence of 1×10^{17} ions/cm^2 shows in Fig. 3(b) as a typical example. The spectrum can not be fitted with only the W^{6+} component due to the chemical shift of the W 4f doublet. Then, the component of W^{5+} and W^{4+} was assigned at lower binding energy of 1 eV and 2 eV that that W^{6+}, respectively. The ratio of the W^{5+} and W^{4+} component is estimated to be 17 % and 4 %, respectively. The chemical shift of the spectrum is attributed the creation

of these atomic sites with oxygen-deficient tungsten. The irradiated film is suggested to transform from stoichiometric WO$_3$ into the sub- or non-stoichiometric WO$_{3-x}$. The ^{4}He$^+$ ion irradiation at 350 keV is considered to break the chemical bonds between tungsten and oxygen, and simultaneously make the atomic sites of oxygen-deficient tungsten in the films. The amount of the atomic sites is considered to be increased with the increase of the fluence. The reason of the larger coloration in the irradiated films with larger than the fluence of 1×10^{16} ions/cm^2 is the existence of the atomic sites of W^{5+} and W^{4+} which induces polaron hopping. The gasochromic coloration is expected to be enhanced with the increase of the atomic sites. It is mentioned that just surface configuration of the films is analyzed in XPS. The mean free path of W 4f photoelectron is approximately 0.5 nm [22,23]. In the gasochromic coloration, hydrogen injects through the interface
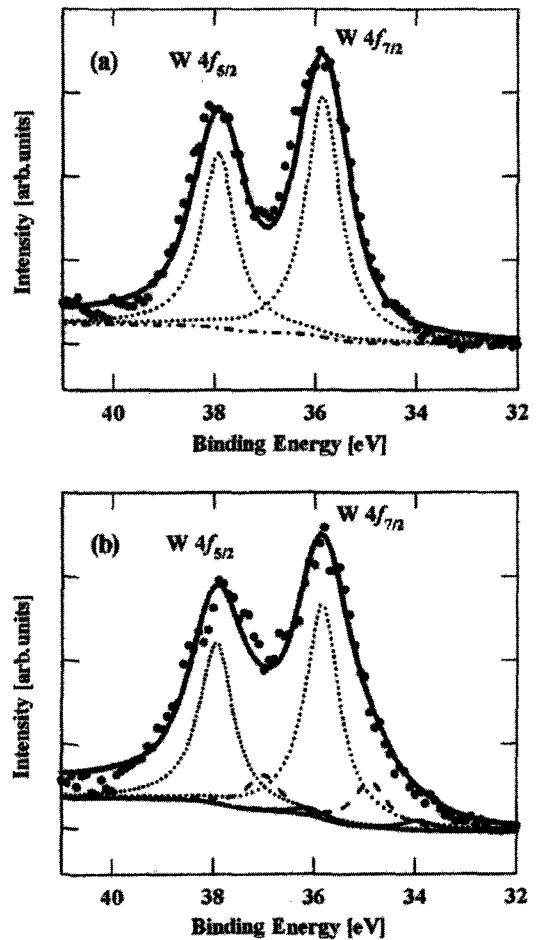

Fig. 3 W 4f core-level XPS spectra for tungsten oxide films, non-irradiated film (a), and irradiated film at the fluence of 1×10^{17} ions/cm^2 (b). Solid circles are the experimental data. Various lines are the result of the fitting analysis. Dotted, dashed, and solid lines are the component of W^{6+}, W^{5+} and W^{4+}, respectively. Dashed-and-dotted lines are the background. Bold solid lines are the result of the convolution for the total components.

between palladium and tungsten oxide. The atomic sites of oxygen-deficient tungsten are supposed to make the function to receive the injected hydrogen at the interface. The existence of the sites accelerates the double charge injection at the interface between tungsten oxide and palladium, and stimulates the polaron hopping. Ion irradiations for WO_3 films is suggested the possibility to improve the gasochromic coloration to select suitable energy and ion species. If suitable the tungsten valences are controlled by the ion irradiations, it is possible to indicate guidelines for high reproductively of the useful gasochromic materials with the WO_3 thin films. As other possibility, the increment of the atomic sites of oxygen-deficient tungsten inner the film is expected to distort or transform the crystal structure due to the braking of the chemical bonds with the irradiation.

For more investigation of the relation between the gasochromic coloration and the amount of the atomic sites with oxygen-deficient tungsten, it is required to analyze many films at different fluence. To discuss about tungsten valence and chemical bonds in more detail, an analysis for XPS spectrum of the oxygen and directly observation for the valence band are necessary. In the analysis, the surface of the films is required to be clean. Ion bombardments for the surface treatments are not appropriate, because chemical bonds are broken easily [12-14].

4. CONCLUSIONS

WO_3 thin films were prepared by magnetron sputtering and subsequent annealing. The crystalinity of the films were characterized by XRD to be polycrystalline monoclinic phase of WO_3. The irradiations for the films were carried out with $^4H^+$ at 350 keV to change the fluence. Non-irradiated films do not have almost the gasochromic coloration with the exposure of 1 % hydrogen. The rate of coloration is improved by the irradiation over the fluence of 1×10^{16} ions/cm^2. The extent of coloration level of the irradiated films at the fluence of 1×10^{17} ions/cm^2 is 7.5 times larger than that of non-irradiated films. By the irradiation, the chemical bonds between tungsten and oxygen are broken, and then oxygen-deficient tungsten atoms such as W^{5+} and W^{4+} are created in the films. At the fluence of 1×10^{17} ions/cm^2, 17 % and 4 % of the W^{6+} change W^{5+} and W^{4+}, respectively. The improvement of the gasochromic coloration in the irradiated WO_3 films relates to the increment of the atomic sites of oxygen-deficient tungsten in the films.

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