Nuclear Instruments and Methods in Physics Research B 268 (2010) 3151–3154

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

Ion irradiation effects on the optical properties of tungsten oxide films

S. Nagata [a,*], H. Fujita [a], A. Inouye [b], S. Yamamoto [b], B. Tsuchiya [a], T. Shikama [a]

[a] *Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan*
[b] *Japan Atomic Energy Agency, Takasaki 370-1292, Japan*

ARTICLE INFO

Article history:
Received 7 October 2009
Received in revised form 21 May 2010
Available online 1 June 2010

Keywords:
Ion irradiation
Oxygen
Tungsten oxide
Optical absorption

ABSTRACT

The optical changes in amorphous WO_3 film prepared by reactive RF sputtering and irradiated by 200–800 keV oxygen ions were measured to study the relationship between coloration and energy deposition. The color centers were effectively created by ion irradiation with contributions from nuclear collisions and electronic energy loss. The increase in the absorption coefficient was reasonably explained by a first order reaction, whose production rate depended roughly on the total deposited energy. During heat treatment in air atmosphere, transmittance recovery started at 400 K and completed at 550 K. No significant difference was found among films irradiated by different incident energies; therefore indicating that the ion-induced damage structure is not strongly influenced by the type of energy loss.

1. Introduction

Tungsten trioxide (WO_3) film is a well-known electrochromic material, which turns blue upon reduction and transparent upon oxidation. WO_3 film covered with a thin catalyst layer can be changed reversibly from transparent to deep blue by exposure to gas containing hydrogen. This optical switching behavior serves a wide range of industrial applications, such as smart windows and hydrogen gas sensors [1,2]. Although a variety of models have been proposed to explain the electrochromic and gasochromic phenomena in WO_3 film, a general model that explains the coloration mechanism has not been determined. Many experimental results have been reported supporting the various models, based on preparation methods, stoichiometry, the microstructure, film crystallinity, and coloration measurement techniques [3–5].

In contrast to the reversible coloration behavior, ion bombardment causes nonreversible effects in the film, such as the formation of tungsten bronze structures [6–8], color centers [9], and compaction [10]. In addition to electron and proton injection and polaron formation, oxygen vacancies in the WO_3 film play an important role in the coloration analogous to F-center formation in ionic crystals [2]. The present study investigates the changes in the optical properties of WO_3 film due to ion irradiation to clarify the relationship between ion-induced coloration and energy deposition in amorphous WO_3 films prepared by RF sputtering.

2. Experimental

Tungsten oxide films of about 400 nm thick were prepared by reactive RF magnetron sputtering using a W metal target (99.9% purity). A mixture of argon (999.999% purity) and oxygen (99.99% purity) gas was introduced through a mass flow controller into a chamber originally evacuated up to a base pressure of 5×10^{-4} Pa, adjusting the partial pressure of Ar and O_2 gas, to 150 and 20 mPa, respectively. The films were deposited on SiO_2 glass and glassy carbon at 473 K with an average growth rate of about 0.1 nm s^{-1}. The crystal structure of the film was examined by X-ray diffractometry using Cu-Ka radiation, and the chemical composition was measured by Rutherford backscattering (RBS) and elastic recoil detection (ERD). Oxygen ion irradiation was also performed in a scattering chamber connected with a 1.7 MV tandem accelerator at the Institute for Materials Research at Tohoku University. The sample was uniformly irradiated over an area of about 1 cm^2 by 200, 350, and 800 keV O^+ ions with a particle flux of about 2×10^{12} cm^{-2} s^{-1} up to a maximum fluence of 1×10^{16} cm^{-2}.

After ion irradiation, the optical absorption of the film was measured with a UV–Vis spectrometer at wavelengths between 190 and 900 nm. Isochronal annealing of the sample was performed for 600 s in air atmosphere in a temperature range between 283 and 573 K, and the UV–Vis spectrum was measured after each annealing stage.

3. Results and discussion

XRD pattern showed that the crystal structure of film prepared at 473 K had an amorphous structure showing a hollow peak at around $2\theta = 23°$. From RBS measurements of film deposited on

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* Corresponding author. Address: Institute for Materials Research, Tohoku University, 2-1-1, Katahira, Aoba-ku, Sendai 980-8577, Japan. Tel.: +81 22 215 2062; fax: +81 22 215 2061.
E-mail address: nagata@imr.tohoku.ac.jp (S. Nagata).

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doi:10.1016/j.nimb.2010.05.076

the glassy carbon substrate, the oxygen concentration was estimated at O/W = 3.0 ± 0.05 throughout the film. ERD measurements revealed that the hydrogen was also uniformly contained in the film at levels as high as H/W = 0.4–0.7. Although the chemical composition of the present films was similar to tungsten bronze H_xWO_3, the films had transparence in the wavelengths between 400 and 900 nm, as shown in Fig. 1. Therefore, the film consists of a large number of water molecules and oxygen deficiencies corresponding to the state of W^{4+} [11]. The large amount of hydrogen was probably taken from the atmosphere after preparation, because water molecules were retained on the substrate held at 470 K during deposition.

Fig. 1 shows optical absorption spectra of the WO_3 film between 300 and 900 nm for various incident fluences of 350 keV O^+ ions. The absorption coefficient increased in the visible and near infrared wavelengths with an increase in the fluence of the incident O^+ ions. The O^+ ions induced spectral changes resembling gasochromic changes during exposure to hydrogen gas. In general, no significant differences in the ion-induced changes of the absorption spectra were observed due to 200, 350, and 800 keV O^+ ion bombardments. The coloring efficiency in an electrochromic film is defined as

$$\mathrm{CE} = \frac{\Delta \mathrm{OD}}{Q} = (\alpha_c - \alpha_b)\frac{L}{Q \ln 10}, \tag{1}$$

where α_b and α_c are the absorption coefficients of the film in the bleached and colored states, respectively, Q is the charge injection per unit area corresponding to the optical density change ΔOD, and L is the film thickness. Assuming that the number of color centers per unit area (N_c) corresponds to the injected charge, we can replace Q with N_c, as given below:

$$\mathrm{CE} = (\alpha_c - \alpha_b)\frac{L}{N_c \cdot 1.6 \times 10^{-19} \cdot \ln 10}. \tag{2}$$

For an estimation of the ion-induced color centers, if we assume a typical value for the coloration efficiency of 50 $\mathrm{cm}^2\,\mathrm{C}^{-1}$ [1], we obtain about $4 \times 10^{16}\ \mathrm{cm}^{-2}$ color centers for the 350 keV O irradiation to a fluence of $5 \times 10^{13}\ \mathrm{cm}^{-2}$, where the change in the absorption coefficient was about 2 $\mu\mathrm{m}^{-1}$. SRIM [12] calculation estimated the number of displacements at about 500 per incident ion, with a displacement energy of 25 eV. This discrepancy suggests smaller displacement energy or the contribution of electronic energy loss to creating the color centers.

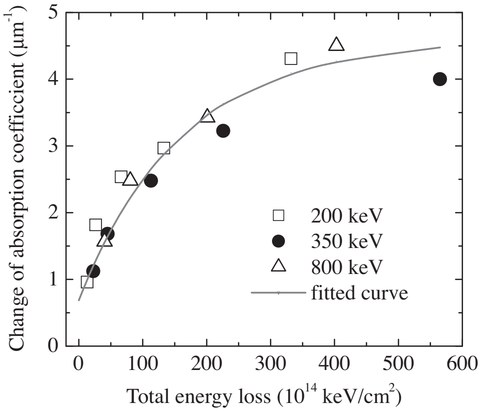

Fig. 2. Absorption coefficient averaged over the wavelengths from 600 to 900 nm for the film irradiated at different energies, plotted as a function of the incident ion fluence.

Fig. 2 shows changes in absorption coefficient averaged over wavelengths from 600 to 900 nm for film irradiated with different energies, plotted as a function of the deposited energy of the incident ions. The 200 keV O^+ ions are totally stopped in the film, and the projected range of 300 keV O^+ ions is slightly larger than the film thickness. Although the coloration mechanism is not clarified, a simple phenomenological model can be applied to describe the relation between the energy deposition and coloration. If the color center production rate is proportional to the energy deposition E_d, the number of color centers is

$$N(E_d) = N_0(1 - \exp(-\lambda \cdot E_d)), \tag{3}$$

where λ is the production rate of luminescence centers, and N_0 is the density of oxygen. Fig. 2 shows a least square fitting to the increase curve, plotted as a function of deposited total energy, where λ is estimated to be $1.2 \times 10^{-16}\ \mathrm{keV}^{-1}\ \mathrm{cm}^{-2}$. In the present experimental condition, electronic and nuclear energy losses in the WO_3 film for different incident O^+ energies calculated by SRIM [12] is shown in Fig. 3. Only a small fraction of energy was deposited by nuclear collision for 800 keV O^+ ions, in contrast to its higher electronic energy loss. To examine the effect of the type of energy deposition on changes in optical absorption, the changes in absorption coefficient were re-plotted as a function of the nuclear and electronic energy loss, as shown in Fig. 4a and b, respectively. Comparing the same nuclear energy deposition, the change in induced optical absorption from the 800 keV O^+ ions was most effective, suggesting that electronic energy deposition plays a role in vacancy formation. As shown in Fig. 4b, the curves for different incident energies are close to each other when plotted as a function of the electronic energy loss. A slightly higher absorption observed for

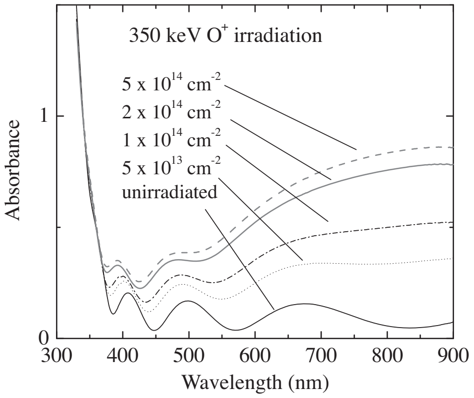

Fig. 1. Optical absorption spectra of the WO_3 film in the wavelengths between 300 and 900 nm for various incident fluences of 350 keV O^+ ions.

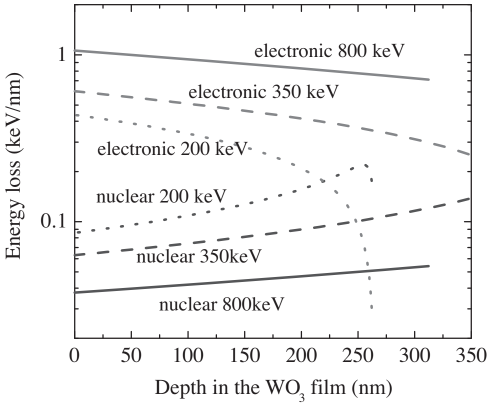

Fig. 3. Nuclear and electronic energy loss in the WO_3 film for different incident O^+ energies calculated by SRIM.