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Gasochromic Property of Oriented Tungsten Oxide Thin Films

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The gasochromic properties of tungsten trioxide (WO_3) films covered with a thin Pd catalyst layer have considerable promise as the optical sensors for hydrogen, hydrogen-gas-leak detector using a fiber-optic. Tungsten oxide thin films were prepared by a reactive rf magnetron sputtering from a W target at various substrate temperatures (200 ~ 600 °C) and different oxygen partial pressures (0 ~ 90 mPa) with constant argon pressures (95 mPa). The crystallinity of the deposited films is strongly affected by the substrate temperature and the oxygen concentration in the sputtering gas. The results of XRD analysis of deposited films on SiO_2 glass substrate indicates that the highly oriented filmswere obtained at 600 °C. From atomic force microscope (AFM) observation, the film deposited at 600 °C was found to have a rough surface consisting of coarse grains with about 200 nm sizes. The measurement of gasochromic property of the oriented WO_3 films covered with 30 nm thick Pd layer for 1% hydrogen in argon indicate that it depend on the crystallinity of the films. The highly oriented films at substrate temperature of 600 °C exhibit good gasochromic properties.

Key words: gasochromic, hydrogen, WO_3, Pd

1. INTRODUCTION

Tungsten trioxide (WO_3) films covered with a thin Pd catalyst layer were known to be colored by dissociation of hydrogen in the catalysis layer (gasochromic). The films have considerable promise as the optical sensors for hydrogen, hydrogen-gas-leak detector using a fiber-optic, because it is considered to be operative at room temperature, highly sensitive, no-noise by electronic effects [1]. It is important to establish the preparation method of the WO_3 films that has good gasochomic property such as short response time, high coloring ratio and high stability, in order to advantage the optical hydrogen sensors. In previous reports, WO_3 films were often prepared by a sputtering, some types of evaporation, sol-gel method on substrates of several single crystals such as sapphire, MgO and $SrTiO_3$ [2-6]. In spite of many reports about preparation of the films, there are few reports about the gasochromic properties of these films because many experimental results are still not understood and often some of them are even not consistent [7, 8]. It is considered to be one of the guiding principles for understanding the film properties including gasochromic often in discord that the relation to the crystal structure of the WO_3 films

In this work, to study the relation the deposition condition and crystal structure of tungsten oxide films, the films were deposited on SiO_2 glass substrates systematically changing substrate temperature from RT to 700 °C, partial pressure of argon (40 ~ 280 mPa) and oxygen (0 ~ 90 mPa) in sputtering gas using a reactive R.F. magnetron sputtering. We characterize the crystal structure of the films with X-ray diffraction (XRD), the surface morphology with atomic force microscope (AFM) and scanning electron microscope (SEM), and the layer structure with Rutherford backscattering spectroscopy (RBS).

2. EXPERIMENTAL

Tungsten oxide thin films were deposited on SiO_2 glass substrates obtained commercially which are mirror-polished at both sides, and the typical size is $10 \times 10 \times 1$ mm^3. Deposition was done by a conventional reactive rf magnetron sputtering with a W target (purity: 3N, Furuuchi chemical corp.) in defined Ar/O_2 mixture. The deposition chamber was pumped down to a base pressure of about 5×10^{-4} Pa using a turbomolecular pump (TMP). Argon (purity: 5N) and oxygen (purity: 4N) mixture was flowed into the chamber through mass-flow meters controlled by an absolute pressure gauge (Baratron 626, MKS) under the pumping condition. In this study, the parameters of deposition were substrate temperature and sputtering gas. The deposition temperature was varied from RT to 700 °C. Argon and oxygen partial pressure was changed 40 ~ 280 mPa and 0 ~ 90 mPa, respectively. The typical sputtering conditions were as follows: The tungsten target to substrate distance of about 100 mm, a sputtering power of 50 W, a base pressure of less than 5×10^{-4} Pa, a sputtering time of 1 h. Heating the substrates was done using a TiB heater coated with SiC layer behind a substrates holder. Temperatures were monitored by a thermocouple placed next to substrates.

The thickness of the films was verified with a DEKTAK 3030 profilometer. Rutherford backscattering spectroscopy (RBS) analysis using a 3 MV single-stage-accelerator at JAEA / Takasaki was employed to characterize the thin films. The analyzing 2.0 MeV $^4He^+$ ions were incident and backscattered particles were detected at 165 ° scattering angle with a surface barrier detector. The crystal structure of tungsten oxide films was determined by X-ray diffraction measurements using a high-resolution diffractometer (X'Pert-MRD, PANalytical). The X-ray source was operated at 40 kV and 30 mA for Cu-Kα radiations. θ-2θ scans showed the degree of preferred orientation. The surface morphology of the deposited films was examined using a high-resolution field emission SEM (JSM6700F, JEOL) and AFM (SPA400, SII).

For the gasochromic measurements, the tungsten oxide films were coated with about 30 nm thick Pd layer by the RF magnetron sputtering. Deposition conditions of Pd were as follows: a working argon pressure of 130 mPa, a sputtering power of 50 W, and the sputtering time of 120 sec. For studies of the gasochromic properties, the transmittance of the samples was measured at a wavelength of 630 nm using a red light-emitting diode (LED) while an Ar gas including 1 % H_2 gas was exposed to the samples.

3. RESULTS AND DISCUSSION

3.1. Influence of the substrate temperature on the crystal structure of tungsten oxide film

To investigate the substrate temperature which tungsten oxide films can be oriented on the SiO_2 glass substrates, tungsten oxide films were deposited varying a substrate temperature in the range from RT to 700°C with maintaining a sputtering power of 50 W, partial pressures of Ar and O_2 gas of 95 and 20 mPa, respectively. The typical thickness of the films was about 400 nm. The crystal structure of tungsten oxide films was examined systematically by XRD. In Fig. 1 shows the XRD patterns from tungsten oxide films deposited at 200°C, 400°C and 600°C, respectively. The broad peaks of the XRD pattern were observed at lower substrate temperature than 400°C. It indicates that the crystal structure of tungsten oxide films deposited at lower substrate temperature than 400°C were amorphous or micro-crystallite structure. In the case of substrate temperature at 600°C, one can recognize a strong peak at almost 22.9°, and a weak peak at and 46.5°. These peaks might be attributed to a monoclinic or an orthorhombic phase of WO_3 [3]. These peaks can be assigned to the (002) and (004) planes, assuming to be the monoclinic phase in this report. The monoclinic phase WO_3 has lattice parameters that are nearly identical to the orthorhombic phase, these two phases cannot be distinguished within the accuracy of the XRD data. For simplicity, we will continue to refer to this orthorhombic/monoclinic phase as simply monoclinic. It is clarified that oriented tungsten oxide films can be oriented above the substrate temperature of 400°C during the deposition.

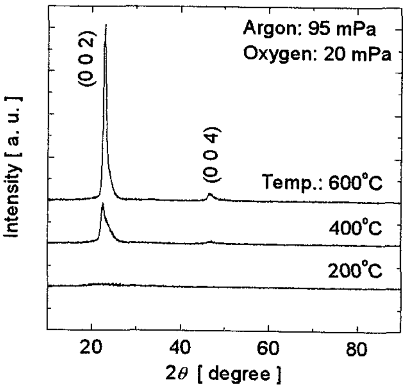

Fig. 1. XRD patterns of tungsten oxide films deposited at substrate temperature of 200 °C, 400 °C and 600 °C with partial pressures of Ar and O_2 gas of 95 and 20 mPa, respectively.

3.2. Influence of the partial pressure of oxygen in sputtering gas on the crystal structure of tungsten oxide film

To study the influence of the partial oxygen pressure in the sputtering gas on the crystal structure of tungsten oxide films, the XRD patterns of tungsten oxide films deposited changing partial pressure of oxygen from 10 to 80 mPa in sputtering gas were measured systematically. Fig. 2 shows the XRD patterns of tungsten oxide films deposited at substrate temperature of 600 °C in the sputtering gas containing argon of 95 mPa and changing

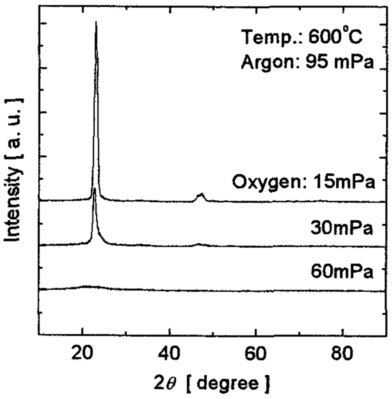

Fig. 2. XRD patterns of tungsten oxide films deposited at substrate temperature of 600 °C in the sputtering gas containing argon of 95mPa and changing oxygen of 15, 30 and 60 mPa, respectively.

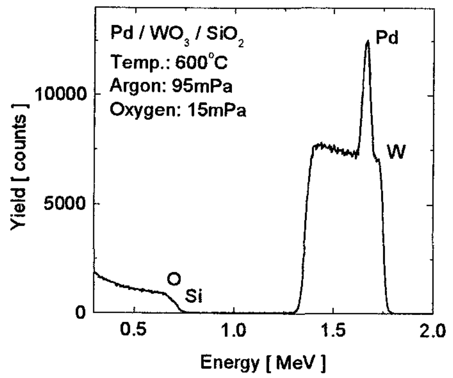

Fig. 3. RBS spectrum of the tungsten oxide film deposited at substrate temperature of 600 °C in the sputtering gas containing argon of 95 mPa and oxygen of 15 mPa.

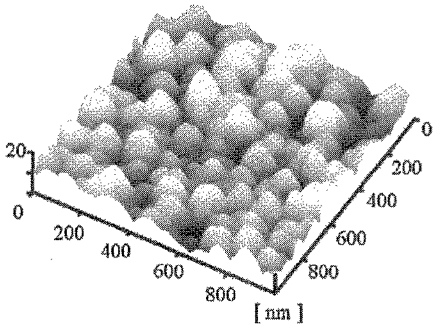

Fig. 4. AFM image of the tungsten oxide film deposited at substrate temperature of 600 °C in the sputtering gas containing argon of 95 mPa and oxygen of 15 mPa.

oxygen of 15, 30 and 60 mPa, respectively. Below the partial oxygen pressure of 15 mPa, the XRD patterns of the films indicated to the metallic tungsten (not figured). In a range of the oxygen pressure from 15 to 40 mPa, oriented tungsten oxide films were observed as shown in Fig. 2. But, above the pressure of 40 mPa, the broad peak of the XRD pattern was observed. It indicates that the films were formed amorphous structure or micro-crystallite structure.

The growth condition for highly oriented tungsten oxide films on SiO_2 glass substrate was optimized referring to the results of XRD measurements. The suitable condition for highly oriented tungsten oxide films was following conditions; substrate temperature: 600°C, sputtering gas: 15 mPa oxygen with 95 mPa argon, target species: W metal, sputtering power: 50 W.

3.3. Layered structure and surface morphology

To confirm layered structure and surface morphology of the tungsten oxide films, RBS analysis and AFM observation were carried. Figure 3 illustrates the 2.0 MeV $^4He^+$ RBS spectrum for the Pd/WO_3 on SiO_2 glass substrate. Tungsten oxide film was deposited at temperature of 600 °C in the sputtering gas containing argon of 95 mPa and oxygen of 15 mPa, and then Pd layer was deposited at 600 °C. The yield at 1.75 MeV regions is from the W component of the tungsten oxide film and the peak at 1.60 MeV corresponds to the Pd layer on the tungsten oxide film. It is confirmed that the film had clearly three-layer structure of SiO_2 substrate, tungsten oxide and thin Pd catalyst. Judging from the peak intensity, the tungsten oxide film is grown up from the interface and the interface is not mixed with each other within the depth resolution (~ 10 nm) of this technique. Figure 4 shows an AFM image of the tungsten oxide film deposited at 600°C in the sputtering gas containing argon of 95 mPa and oxygen of 15 mPa. The observation of surface morphology by AFM indicates that the tungsten oxide films are consisted of coarse grains with about 200 nm sizes.

3.4. Gasochromic properties of the tungsten oxide films

To study the relation between the crystallinity and the gasochromic properties of tungsten oxide films, the transmittance at 630 nm wavelength of tungsten oxide films was measured systematically during the exposure of 1 % hydrogen in argon gas at RT. The transmittance at 630 nm wavelength of non-oriented and oriented tungsten oxide films with 30 nm thick Pd layer varies with exposure time is shown in Fig. 5. These films were deposited at 600°C in the sputtering gas containing oxygen of 15 and 60 mPa. The transmittance of oriented film shows a rapid degrease down to 20 % and finally come to a minimum about 5 % after exposure of 15 min. But non-oriented film shows a monotonic degrease and come to about 80 % after exposure of 15 min.

The transmittance after exposure time of 15 min at 630 nm of the tungsten oxide films deposited at 600 °C in the sputtering gas containing argon of 95 mPa and the changing oxygen from 15 to 80 mPa were plotted against the partial pressure of oxygen in the sputtering gas in Fig. 6. The tungsten oxide film deposited in the oxygen partial pressure at 15 mPa exhibit a sharp drop in transmittance after exposed to hydrogen. In addition, the transmittance after exposure time of 15 min at 630 nm of the tungsten oxide films deposited varying a substrate temperature in the range from RT to 700°C shows in Fig. 7. The transmittance degreases markedly with increasing substrate temperature. The results indicate that the change of transmittance after exposed to hydrogen

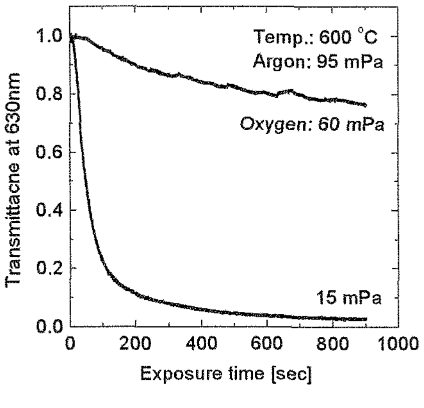

Fig. 5. The transmittance at 630 nm wavelength of tungsten oxide films deposited at substrate temperature of 600 °C in the sputtering gas containing oxygen of 15 and 60 mPa, respectively.

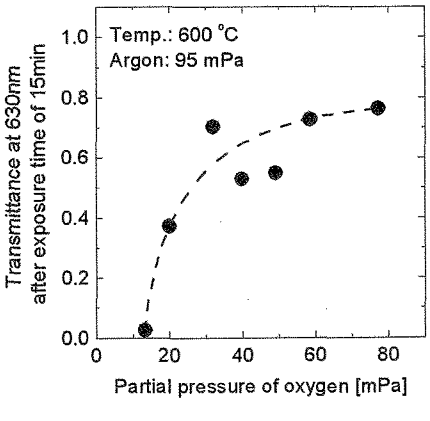

Fig. 6. The transmittance at 630 nm wavelength of tungsten oxide films deposited at substrate temperature of 600 °C in the sputtering gas containing argon of 95mPa and changing oxygen from 15 to 80 mPa.

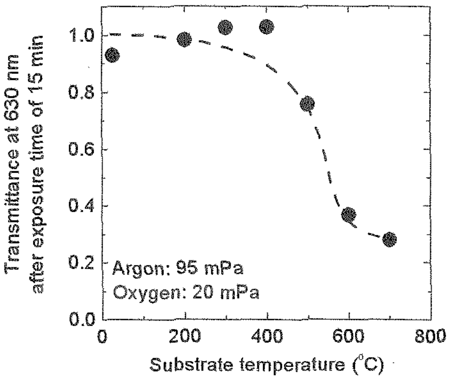

Fig. 7. The transmittance at 630 nm wavelength of tungsten oxide films deposited at substrate temperature from RT to 700 °C in the sputtering gas containing argon of 95mPa and changing oxygen from 20 mPa.

corresponding to gasochromic property is depends on the deposition condition of the films. Taking the results of XRD measurements as shown in Fig. 1 and Fig. 2, good gasochromic property of tungsten oxide was realized by the growth of highly oriented films.

4. SUMMARY

Tungsten oxide thin films were prepared by a reactive rf magnetron sputtering from a W target at different oxygen partial pressures and substrate temperatures. The highly oriented tungsten oxide films were obtained deposited at 600°C in the sputtering gas containing argon of 95 mPa and oxygen of 15 mPa. The highly oriented films on substrate with 30 nm thick Pd layer demonstrate good gasochromic properties for hydrogen.

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