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Coloration and Depth Distribution of Cations Electrochemically-inserted into Electrochromic WO₃ Thin Films

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Abstract. Li⁺ and H⁺ ions were electrochemically inserted into amorphous WO₃ films prepared on an ITO-coated glass substrate by an R.F. magnetron sputtering method under Ar/O₂ flow ratios of 4/1 (SP1) and 1/1 (SP2). The cation distribution was estimated indirectly by depth profiles of refractive-index obtained from prism coupler measurements and was evaluated directly by glow discharge spectrometry (GDS). H⁺ ions inserted were segregated only at deeper region around ITO electrode, which was independent to the preparing condition. In the case of Li⁺ insertion into SP1 film, Li⁺ ions were initially segregated at around ITO electrode, and after further insertions, they were also distributed at around the surface of WO₃ film. In SP1 film, Li⁺ ions at around ITO electrode seemed to contribute to coloration. In SP2 film, however, Li⁺ ions subsequently inserted, which were uniformly distributed in the film, were only involved in coloration. The difference in depth distribution and coloration was due to the difference in atomic structure of WO₃ films.

1. Introduction

Amorphous tungsten trioxide (WO₃) film is a promising material for electrochromic device applications, and it has been researched widely. Electrochromism is a phenomenon that accompanies the electrochemical redox reaction together with the change in color and optical transmittance. Coloration and bleaching occur with insertion and removal of small cations according to the electrochemical reaction:



In the previous studies [1], insertion of monovalent cations such as Li⁺ and H⁺ has been investigated. In the authors' group, however, it was found that divalent cations such as Zn²⁺ and Cu²⁺ were successfully inserted to WO₃ films, and the WO₃ films were coloured in blue [2]. In this case, it was also found that the films were bleached gradually as time advances, which has never been observed in the case of Li⁺ and H⁺ insertions. As for the coloration and bleaching due to Zn²⁺ insertion, it was assumed as follows: H⁺ ions are also inserted from water present in minute amounts in a liquid electrolyte, segregating immediately at around a substrate. The diffusion of Zn²⁺ ions is much slower as compared with that of H⁺ ions, and as Zn²⁺ ions diffuse to the substrate side, electron transfer between W⁵⁺ and W⁶⁺ is inhibited, resulting in bleaching.

In this study, the distribution of inserted Li⁺ and H⁺ ions was evaluated to verify the assumption.

2. Experimental

WO₃ films were prepared on an ITO-coated glass substrate by an R.F. magnetron sputtering method. Ar/O₂ flow ratios were 4/1 (SP1) or 1/1 (SP2). The deposition parameters are shown in Table 1.

Li⁺ and H⁺ ions were inserted using 0.1 M LiClO₄/propylene carbonate and 1 M H₂SO₄ aqueous solution as electrolytes, respectively. A three-electrode system was constructed with the deposited film as the working electrode, Pt-wire as the counter electrode and Ag-wire or saturated calomel electrode as the reference electrode. Li⁺ and H⁺ ions insertion were carried out with a potentiostatic step method.

The cation distribution was examined indirectly by depth profiles of refractive-index obtained from prism coupler measurements and directly by glow discharge spectrometry (GDS). The thickness of deposited films was measured by prism coupler measurements.

Table 1. Sputtering conditions of WO₃ films preparation.

Substrate	ITO-coated glass (AGC)
Target	W metal (99.99% purity)
Working pressure	7.0×10^{-3} Torr (0.93Pa)
Sputtering atmosphere	Ar/O ₂ = 4/1 (SP1) or 1/1 (SP2)
RF power	30 W
Substrate temperature	Room temperature
Film thickness	400 (± 50) nm

3. Results and Discussion

Figure 1 shows the refractive-index profiles obtained from prism coupler measurements. Figures 1 (a) and (b) show the results of H⁺ insertion. With increasing H⁺ content, x in H _{x} WO₃, refractive-index decreases at deeper region 0.2-0.4 μ m near the ITO electrodes. The decrease in refractive-index is probably due to the segregation of cations with smaller polarizabilities, such as H⁺ and Li⁺ ions. Therefore, it is suggested that H⁺ ions inserted are segregated at around ITO electrodes. Figure 1(c) shows the results of Li⁺ insertion into SP1 film. At $x < 0.25$, refractive-index decreases only at around ITO electrode, and at $x > 0.25$, however, refractive-index decreases also at around the surface of WO₃ film. Figure 1 (d) shows the results of Li⁺ insertion into SP2 film. At $x < 0.25$, significant change in refractive-index profile is not observed. At $x > 0.25$, decrease in refractive-index is confirmed over the entire region. As the results, it is supposed that there are Li sites not-contributing the change in refractive-index in SP2 film.

Figure 2 shows Li⁺ distribution profiles in SP1 film obtained from GDS measurements. With the increase in x , amount of Li⁺ ions at around ITO electrodes increases. This result is consistent with the interpretation of Figure 1 (c).

It is inferred from the results of the refractive-index profiles and the element distribution profiles; In case of H⁺ ion insertion, H⁺ ion distribution is independent to the sputtering atmosphere. In case of Li⁺ ion insertion, at first, Li⁺ ions are segregated at around ITO electrodes. After further insertions, Li⁺ ions are also distributed at around the surface of WO₃ film.

Figure 3 shows the optical absorbance at $\lambda = 800$ nm as a function of the cation content x inserted into WO₃ films. In general, coloration is evaluated by the absorption at $\lambda = 800$ nm, and hence the wavelength was also chosen in the present study. As shown in Figure 3, the absorbance at $\lambda = 800$ nm increases commonly with the increase in x , and the change in slope is observed between $x = 0.2-0.4$ in all the films. As for H⁺ insertion, the difference in absorbance is small between Ar/O₂ = 4/1 and 1/1, and as for Li⁺ insertion, however, significant difference is confirmed between the films prepared under the different atmosphere.

In the case of H⁺ insertion, the coloration is independent to the sputtering atmosphere (Figure 3), and the similarity is also confirmed in the refractive index depth profile (Figures 1(a) and 1(b)). In the case of Li⁺ insertion into SP1 film, the absorbance at $\lambda = 800$ nm increases significantly up to $x = 0.25$

(Figure 3), and at the same time, Li^+ ions inserted are segregated at around ITO electrode (Figure 1(c) and Figure 2). Further Li^+ insertion ($x > 0.25$) results in the decrease in absorbance slope (Figure 3) and the uniform dispersion of Li^+ ions toward the surface (Figure 1(c)). These results suggest that coloration sites for Li^+ ions are present at deeper region of WO_3 films near ITO electrode, and Li^+ ions preferentially settle into the coloration sites. When the coloration sites are fully occupied by Li^+ ions, Li^+ ions begin to fill in other sites unrelated to coloration. In the case of SP2, however, Li^+ ions initially settle into the sites unrelated to coloration (Figure 1(d)), and then Li^+ ions enter the coloration sites present at the entire region of WO_3 film.

In the case of H^+ insertion, the depth distribution of H^+ ions and coloration seem to be independent to the sputtering atmosphere, and in the case of Li^+ insertion, however, they seem to be quite different between SP1 and SP2 films. These results suggest the difference in atomic structure between SP1 and SP2 films. It is actually reported that SP1 and SP2 films have structures similar to hexagonal- and tetragonal- WO_3 crystals, respectively [3]. Tetragonal- WO_3 has 3-dimensional path for ionic diffusion, and hexagonal- WO_3 has two 1-dimensional tunnels formed by three- and six-membered rings of WO_6 octahedra. The difference in depth distribution of cations and coloration is responsible for the difference in atomic structure between SP1 and SP2 films.

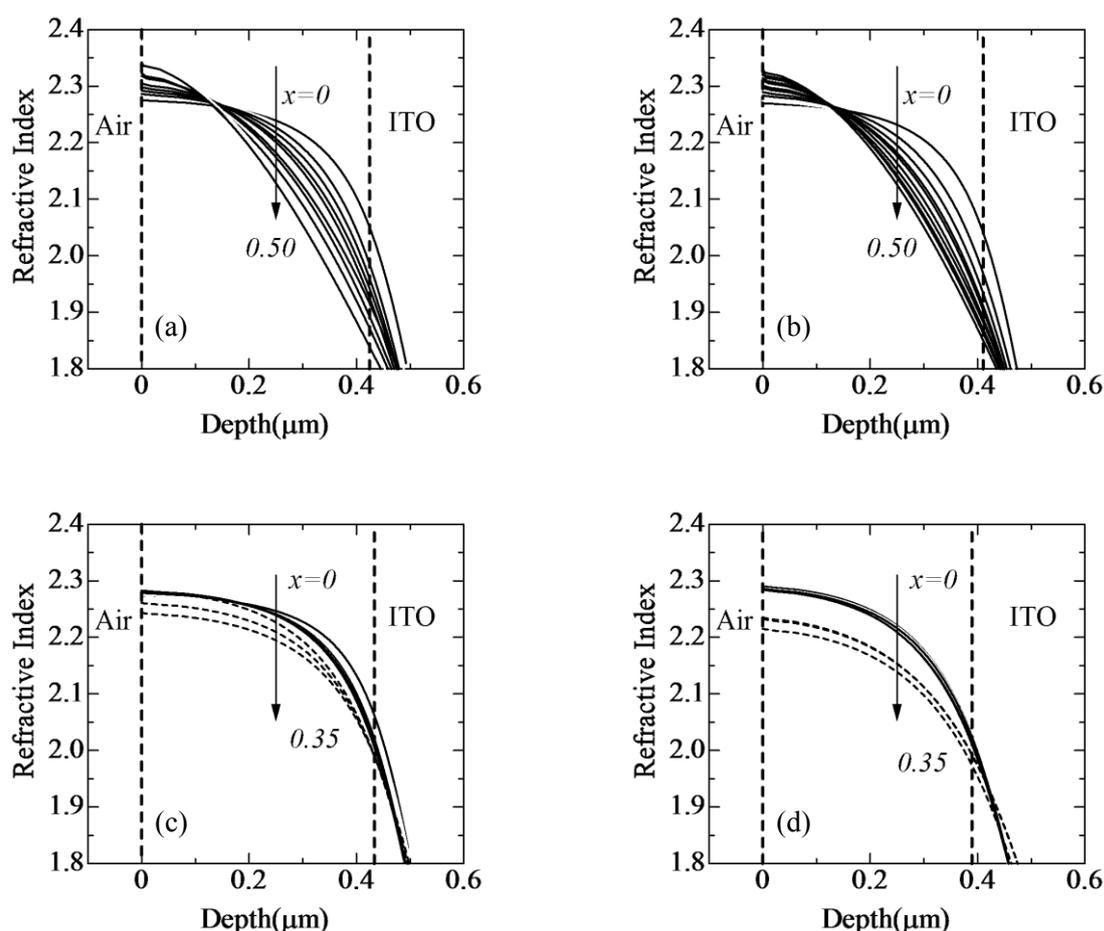


Figure 1. Refractive-index profiles obtained from prism coupler measurements at $\lambda = 473$ nm (a) H_xWO_3 ($x = 0 - 0.50$), $\text{Ar}/\text{O}_2 = 4/1$ (SP1), (b) H_xWO_3 ($x = 0 - 0.50$), $\text{Ar}/\text{O}_2 = 1/1$ (SP2), (c) Li_xWO_3 ($x = 0 - 0.35$), $\text{Ar}/\text{O}_2 = 4/1$ (SP1) and (d) Li_xWO_3 ($x = 0 - 0.35$), $\text{Ar}/\text{O}_2 = 1/1$ (SP2).

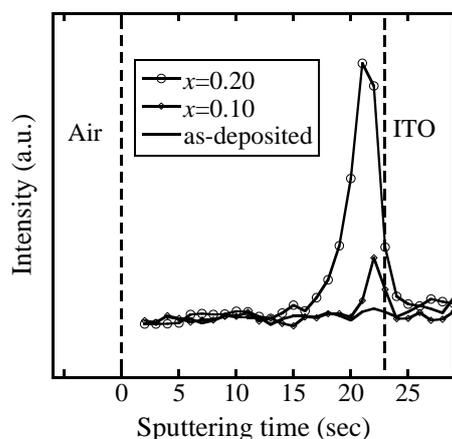


Figure 2. Distribution profiles of Li^+ ions obtained from GDS measurements for Li_xWO_3 ($x = 0 - 0.20$) films, $\text{Ar}/\text{O}_2 = 4/1$.

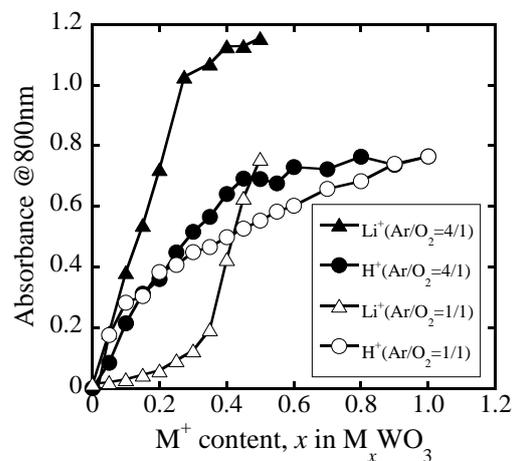


Figure 3. Change in absorbance at $\lambda = 800 \text{ nm}$ against cation content x .

4. Conclusion

The depth distribution of cations inserted into WO_3 films was examined indirectly by the depth profile of refractive-index obtained from prism coupler measurements and directly using GDS measurements. H^+ ions were segregated only at around ITO electrode, and distribution at around the surface of WO_3 film was not observed even after further insertion. As for WO_3 film prepared at $\text{Ar}/\text{O}_2 = 4/1$, Li^+ ions were initially segregated at around ITO electrode, and after further insertion, Li^+ ions were also distributed at around the surface, suggesting that Li^+ ions existed at around ITO electrode were the only species contributing to coloration. As for WO_3 film prepared at $\text{Ar}/\text{O}_2 = 1/1$, Li^+ ions initially inserted did not contribute to coloration, and those subsequently inserted contributed to coloration. It was also supposed that the difference in depth distribution and coloration was responsible for the difference in atomic structure of WO_3 films.

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