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Effect of the Humidity on EC Characteristics of Complementary Cells

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All-solid-state complementary electrochromic (EC) cells were fabricated. The EC cells consisted of two transparent conductive films (ITO), cathodic and anodic EC films (WO_3 and NiO, respectively) as active films and solid electrolyte (Ta_2O_5) film as ions conductor. All films were deposited by RF sputtering. For Ta_2O_5 and NiO films preparation, the hydration degree in the films was varied by using hydrogen-introduced sputtering. EC characteristics of the cells were measured in a humidity-controlled chamber. The effects of humidity in environment and hydration degree of Ta_2O_5 films on EC reaction were investigated. The maximum optical density change of the cells was obtained in humidity of 90%. The EC cells were able to color and bleach even in low humidity (~30%), when Ta_2O_5 films were hydrated.

Key words: electrochromism, Ta_2O_5, WO_3, NiO, all-solid-state EC cell

1. INTRODUCTION

Electrochromic (EC) phenomenon is to be given rise to reversible coloration and bleaching by electrochemical injection and extraction of ions and electrons. Recently, considerable attention on EC phenomena is paid to optical transmission-controlled devices (switchable windows, antidazzling mirrors, etc.) [1]. In order to realize these devices, all-solid-state complementary EC cells are available.

The most studied EC material is tungsten oxide (WO_3) film, which is colored in dark blue when negative voltage is applied to the film [2]. WO_3 is called cathodic EC material. EC reaction in WO_3 films is considered as follows:

$$\underset{\text{(bleached)}}{WO_3 + xM^+ + xe^-} \Leftrightarrow \underset{\text{(colored)}}{M_xWO_3},$$

where M^+ is cation like H^+, Li^+ and Na^+. WO_3 films are reversibly colored/bleached by injection/extraction of cations [3].

On the other hand, EC materials colored by positive voltage are called anodic. Nickel oxide (NiO) is one of anodic EC materials. NiO is colored in dark brown. EC reaction in NiO films is not clear so far. Two types of reaction are supposed [4].

$$Ni(OH)_2 \Leftrightarrow NiOOH + H^+ + e^-,$$
$$Ni(OH)_2 + OH^- \Leftrightarrow NiOOH + H_2O + e^-.$$
(bleached) (colored)

As seen from these equations, H^+, OH^- and H_2O play important roles for EC phenomena [5].

We fabricated the all-solid-state complementary EC cells and investigated EC characteristics of them in environment with various degree of the humidity.

2. EXPERIMENTAL

We fabricated all-solid-state complementary EC cells, whose configuration of the cells (bottom ITO / NiO / Ta_2O_5 / WO_3 / top ITO) is illustrated in Fig.1. All films constituted of the cells were deposited by RF sputtering. The preparation conditions are shown in Table 1. ITO (Indium Tin Oxide) films were used as transparent conductive electrodes. WO_3 and NiO were employed as anodic and cathodic EC films, respectively.

ITO and WO_3 films prepared by conventional

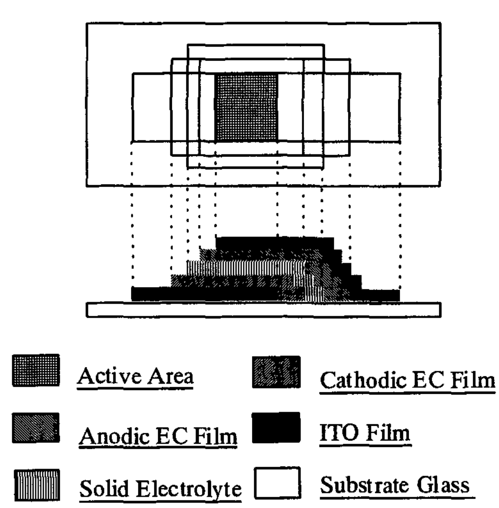

Fig.1 The configuration of all-solid-state complementary EC cells.

Table I Preparation conditions of sputtered films and color of as-deposited films.

	Input PW (W/cm^2)	Time (min)	Pressure (Pa)	Gas Content $Ar:O_2:H_2$	As-deposited color	Film thickness (nm)
ITO	2.55	10	6.7	100 : 0 : 0	Transparent	200
WO_3	1.28	60	8	50 : 50 : 0	Transparent	200
NiO	0.64	180	8	50 : 50 : 0 50 : 10 : 40	Brown Transparent	150
Ta_2O_5	2.55	60	6	50 : 50 : 0 to to 10 : 40	Transparent	400

sputtering. The as-deposited WO_3 films are usually colorless. The color of the as-deposited NiO films, which are prepared by conventional sputtering, is dark brown [6]. By using hydrogen-introduced sputtering method [7], it is able to make NiO films hydrated and transparent in as-deposited state. For practical construction of EC cells, the choice of electrolyte is one of important problems. H_2SO_4 ethanol and NaOH solutions are usually used as liquid electrolyte for WO_3 and NiO, respectively. The problem for the liquid electrolyte are its leakage and chemical stability. Solid electrolyte should be used. We employed Ta_2O_5 films as solid electrolyte in complementary EC cells. It has high ion conductivity and very low electron conductivity. Targets of a NiO compressed powder, a W metal and a Ta_2O_5 compressed powder for preparation of NiO, WO_3 and Ta_2O_5 film were employed, respectively. The respective masks for preparation of each film were employed to avoid electric leak from the film edge.

Schematic diagram for optical transmittance measurement of the EC cells is shown in Fig.2. In order to investigate the effect of humidity on EC reaction, we measured transmittance of the cells in a chamber where temperature and humidity were controlled. Humidity was controlled in the range between 30-90%. The coloration and bleaching were performed by applying DC voltage of $\pm 5V$ between two ITO electrodes. The amount of charges (Q) flowed through the EC cells was measured by a coulomb meter. Transmittance spectra were measured by a spectrometer with CCD detector. Optical density change (Δ OD) was estimated from transmission data:

$$\Delta OD = \log(T_B/T_C),$$

where T_B is the transmittance of EC cells in bleached state and T_C that of colored one at wavelength of 633nm. ΔOD_{max} is defined as Δ OD between the fully bleached and colored cells.

IR absorption spectra of Ta_2O_5 films were measured in order to investigate the degree of hydrogen in them. The configuration of the samples for IR measurement is (glass substrate / Au / Ta_2O_5). The spectra were measured in reflection mode.

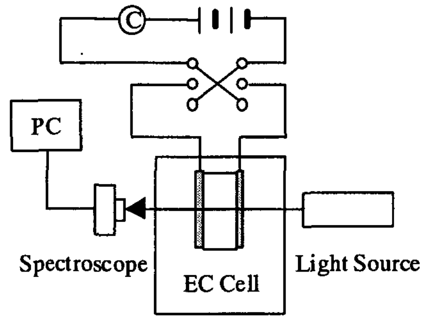

Fig. 2 Schematic diagram for transmittance measurement of the EC cells.

3. RESULTS AND DISCUSSION

3-1. NiO films

When all films in the complementary EC cells were deposited without using hydrogen-introduced sputtering, the cells hardly showed the EC phenomenon as shown in Fig.3. Fig.4 shows the transmittance spectra of the cells with hydrated NiO film. The cells with hydrated NiO films indicate large optical modulation. This is because that as-deposited WO_3 films were transparent (in oxide state) and as-deposited NiO films were colored (in oxide state). Transport ions might not move smooth in the cells. Therefore, as-sputtered NiO films should be deposited at the bleached state as well as WO_3 films. Thus, transparent NiO films deposited by the hydrogen-introduced sputtering were used in the following experiments.

3-2. The effect of humidity on EC reaction

The effect of humidity in environment on EC cells was investigated. Maximum optical density change (ΔOD_{max}) is shown as a function of humidity in Fig.5. ΔOD_{max} increased largely with increasing humidity. It indicates that humidity (water molecules) in the environment was adsorbed in EC cells. If the water molecules are decomposed to H^+ and OH^- ions in Ta_2O_5 films by applied voltage, these ions were considered to be injected into EC films during EC reactions.

3-3. The effect of hydration on Ta_2O_5 films

In order to change the degree of hydration in as-deposited Ta_2O_5 films, Ta_2O_5 films were prepared by hydrogen-introduced sputtering. The as-deposited Ta_2O_5 films were always transparent. IR absorption spectra of the films are shown in Fig.6. As seen from this figure, absorption intensity of O-H stretching increased with increasing hydrogen in sputtering atmosphere. The as-deposited Ta_2O_5 films prepared by hydrogen-introduced sputtering are considered to be hydrated.

Fig.7 shows ΔOD_{max} as a function of hydrogen content in sputtering atmosphere. When Ta_2O_5 films were not prepared by hydrogen-introduced sputtering, the cells gave EC reaction in high humidity environment but hardly in dry. When the hydrated Ta_2O_5 films were used, the effect of humidity decreased with increasing hydrogen content in Ta_2O_5 sputtering atmosphere. When the hydrogen content was 40%, the EC cell gave EC reaction in dry environment as well as high humidity. It is supposed that H^+ ions in Ta_2O_5 films were made by the hydrogen-introduced sputtering and could move during EC reaction even in dry environment.

3-4. Amount of charges injected in the cells

At first, we define injected charges as the charges flowed into the cells during coloration. Fig.8 shows the Δ OD as a function of the injected charge for the EC cells with non-hydrated Ta_2O_5 films. It was difficult to colcr the EC cells in dry environment even if a lot of charges were injected. In high humidity environment, on the other hand, the EC cells would be colored with a small amount of the injected charges.

Fig.9 shows Δ OD for the EC cells with hydrated Ta_2O_5 films, which were prepared in the sputtering atmosphere with hydrogen content of 40%. The effect of humidity on the EC cells was smaller than one shown in Fig.8. If hydrogen in as-deposited Ta_2O_5 films makes to exist enough by hydrogen-introduced sputtering, EC characteristics of the cells would be not influenced by humidity (water molecules) in environment. Therefore hydration to Ta_2O_5 films is considered to be valid for solid electrolyte in EC cells.

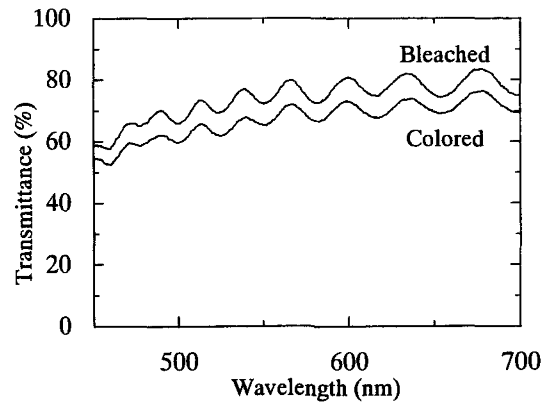

Fig. 3 Transmittance of the cell with non-hydrated NiO film.

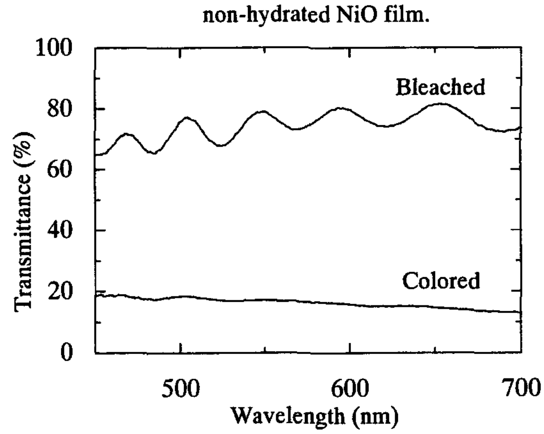

Fig. 4 Transmittance of the cell with hydrated NiO film.

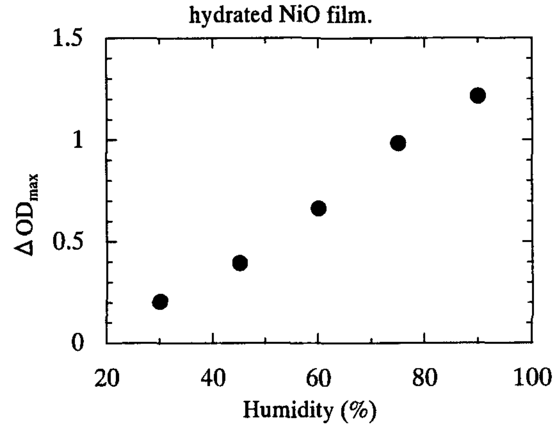

Fig.5 Δ OD as a function of humidity.

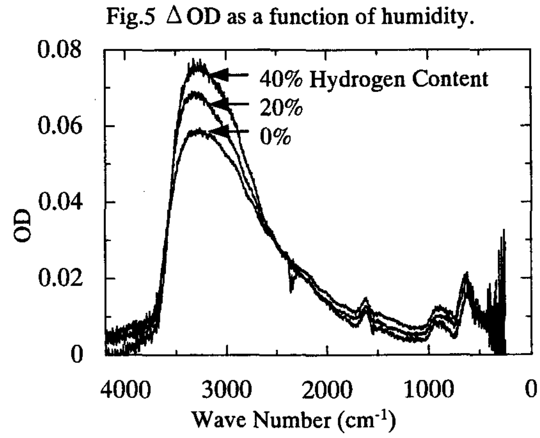

Fig.6 IR absorption spectra of the films.

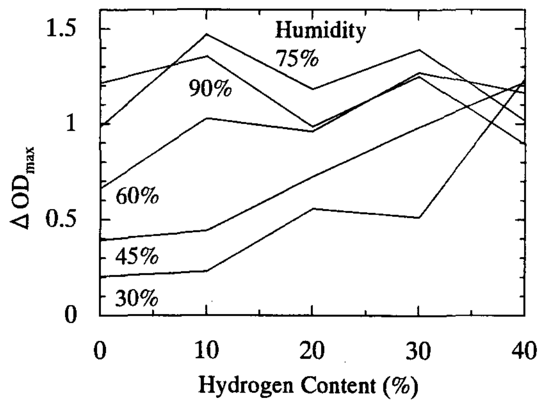

Fig. 7 Δ OD_{max} as a function of hydrogen content in sputtering atmosphere.

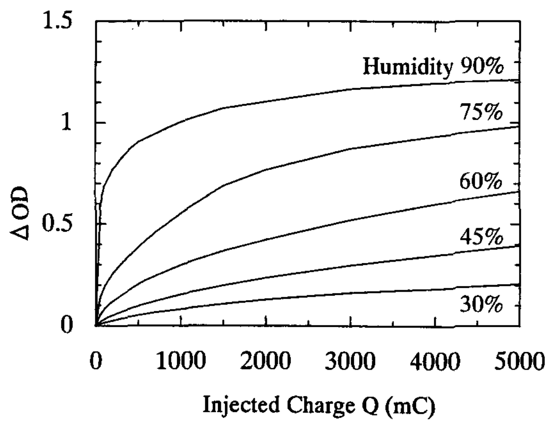

Fig.8 Δ OD as a function of the injected charge for EC cells with non-hydrated Ta_2O_5 films (0%).

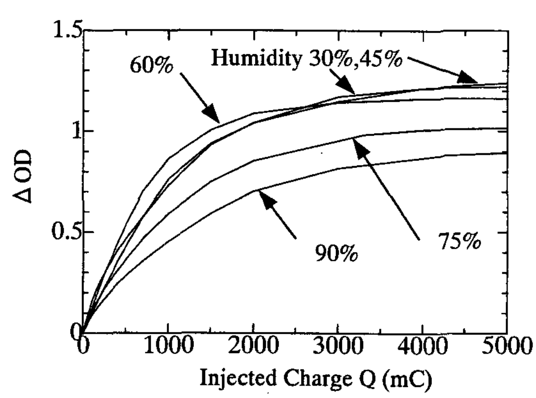

Fig.9 Δ OD as a function of the injected charge for EC cells with hydrated Ta_2O_5 films (40%).

4. CONCLUSION

All-solid-state complementary EC cells were fabricated. NiO and Ta_2O_5 films were prepared by hydrogen-introduced sputtering. The effect of humidity in environment on EC characteristics was investigated. The results were obtained as follows:

(1) The complementary cells gave good EC characteristics, when as-deposited NiO films were prepared at bleached (colorless) state as well as WO_3 films.

(2) The EC cells were largely influenced by humidity in environment. Δ OD_{max} increased with increasing the humidity in environment.

(3) When Ta_2O_5 films was hydrated by hydrogen-introduced sputtering, the effect of humidity in environment on the cells was small.

The water molecules in electrolyte films play the important roles in EC reaction. The future problem is to elucidate the EC mechanism by investigating the difference between the roles of the water from environment and pre-injected water in the Ta_2O_5 films (hydrated Ta_2O_5 films).

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