

Electrochromic Properties of Sputtered Iridium Oxide Thin Films with Various Film Thicknesses

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Abstract

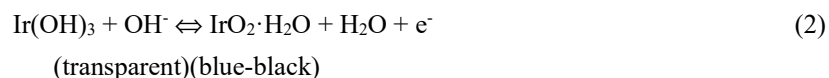
Iridium oxide is an anodic electrochromic material, which takes on a blue-black color through electrochemical oxidation and turns to transparent via reduction. Hydrated amorphous Ir oxide thin films with various thicknesses from 20 to 400 nm were prepared by reactive sputtering in a H₂O atmosphere, and their transmittance spectra in both the bleached and colored states as well as their response times were examined in this study. The bleached and colored transmittances decreased with increasing film thickness according to Lambert's law, and the absorption coefficients in the bleached and colored states were estimated to be 3.2×10^3 and 1.1×10^5 cm⁻¹, respectively, at a wavelength of 600 nm. The results point to almost all the Ir atoms being electrochemically active and contributing to the color change. A maximum transmittance change of 81% was obtained for the 400 nm-thick film. Further, there was a trade-off between the response speed and the transmittance change. The response speed slowed down with increasing the film thickness, while the coloring and bleaching response time for the thick films was several tens of seconds.

Keywords: electrochromic, iridium oxide, optical transmittance

1. Introduction

Electrochromic (EC) materials change their optical transmittance reversibly via electrochemical oxidation and reduction (Granqvist, 1995). A typical EC device consists of an EC layer, an ion-conducting layer (electrolyte), and an ion-storage layer, which are all sandwiched between two transparent conducting electrodes. WO₃ is the most widely studied inorganic EC material; it turns dark blue upon reduction and becomes transparent upon oxidation. Two other well-known EC materials, nickel oxide and iridium (Ir) oxide, turn brown and blue-black upon oxidation and become transparent upon reduction; they are used as ion-storage layers to enhance the transmittance variation of EC devices (Granqvist, 1994; Granqvist, 2012). Such EC devices are used in displays, antiglare automobile rearview mirrors, and smart energy efficient windows (Granqvist, 2014; Motimer, Rosseinsky, & Monk, 2015).

Ir oxide has been reported to possess a superior chemical stability in both acidic and basic electrolyte solutions, a long cycle durability, and a fast optical response (Dautremont-Smith, 1982). The coloration mechanism of Ir oxide has been proposed to be governed by the following equations (Mortimer, 1997).



IrO₂ has a rutile-like structure and is a conducting oxide with a bulk resistivity of 35 μΩ·cm (Ryden, Lawson, & Sartani, 1970). Its electronic structure has been studied using X-ray photoelectron spectroscopy and theoretical band calculations (Mattheiss, 1976; Kahk et al., 2014). Ir atoms are surrounded by a nearly octahedral array of six

oxygen atoms, with the metal d level split into triply degenerate t_{2g} and doubly degenerate e_g components due to the effect of the crystal field. Five $5d$ electrons in Ir^{4+} partly fill the t_{2g} bands while the e_g bands are empty. The optical properties of IrO_2 can be explained via free-carrier and intraband transitions within the t_{2g} bands below ~ 2.5 eV as well as interband transition from the filled O $2p$ to the Ir d bands above ~ 3 eV (Goel, Skorinko, & Pollak, 1981). Transitions between t_{2g} and e_g states are partly-forbidden. When Ir^{4+} is reduced to Ir^{3+} , the t_{2g} bands are filled with six d electrons, which results in optical transparency.

Ir oxide thin films have been prepared by sputtering (Schavone, Dautremont-Smith, Beni, & Shay 1979; Schavone, Dautremont-Smith, Beni, & Shay, 1981; Backholm & Niklasson, 2008; Wen, Niklasson, & Granqvist, 2014), anodic oxidation (Shay, Beni & Schiavone, 1978), electrodeposition (Yoshino, Baba, & Arai, 1987; Yamanaka, 1991; Jung, Lee, & Tak, 2004), thermal oxidation (Sato, Ono, Kobayashi, Wakabayashi, & Yamanaka, 1987), sol-gel (Nishio, Watanabe, & Tsuchiya, 1999), and spray pyrolysis methods (Patil, Mujawar, Sadala, Deshmukh, & Inamdar, 2006). The EC properties of the Ir oxide thin films were found to be dependent on the preparation methods and conditions, which determine the structure and composition of the Ir oxide thin films. Their EC performances also depend on the cell structures, such as film thickness and cell area. The properties of other components, such as the ion conductivities of the electrolytes and the electrical resistances of transparent electrodes, also affect the EC properties, which makes it difficult to quantitatively compare the characteristics of the EC films.

In our laboratory, a reactive sputtering technique using water vapor (H_2O) as a reactive gas was developed (Ueta, et al., 2009; Li et al., 2012, Lee et al., 2012), and the technique was applied to Ir oxide thin films (Ito et al., 2015). The hydrated Ir oxide thin films deposited in an H_2O atmosphere on cooled substrates at -30 °C were found to have good EC properties, namely a large transmittance variation and high bleached transmittance in the visible wavelength region. In the present study, we prepared Ir oxide thin films with various thicknesses and examined the effects of film thickness on the bleached and colored transmittances as well as the response times. We believe that these data are useful in order to quantitatively compare the EC performances of Ir oxide films prepared with different methods and under different conditions and to design EC devices with appropriate optical properties.

2. Method

2.1 Sample Preparation

Hydrated Ir oxide thin films were prepared using a radio-frequency (RF) magnetron sputtering system with an Ir metal target (99.9% purity, 2 inches diameter) in an H_2O atmosphere. A glass coated with fluorine-doped tin oxide (FTO) with a sheet resistance of $200 \Omega/\text{sq}$ was used as the substrate, and the substrate was cooled to -30 °C with a Peltier device during sputtering. The sputtering gas pressure and RF power were 6.7 Pa and 50 W, respectively. These were the optimum conditions for our sputtering system to deposit Ir oxide thin films with good EC properties. The films deposited under these conditions were found to consist of highly hydrated amorphous Ir oxide. The film density was estimated to be approximately 6 g/cm^3 , which is nearly half the density of bulk IrO_2 , 11.666 g/cm^3 (ICDD, 2009). The low density amorphous structure of the hydrated Ir oxide thin films is considered to be the reason for their high electrochemical activity. The details of the structure as well as the electrochemical and electrochromic properties of the films have been reported in our previous paper (Ito et al., 2015). In this study, Ir oxide thin films with various thicknesses from 20 to 400 nm were prepared by changing the deposition time assuming a constant deposition rate of 5.5 nm/min . The size of the FTO-coated glass substrate was $3 \times 1 \text{ cm}^2$, and the active area of the Ir oxide films was 1 cm^2 .

2.2 Characterization Methods

The EC properties of the Ir oxide thin films were studied in an electrolyte ($0.5 \text{ M H}_2\text{SO}_4$ aqueous solution), while Ag/AgCl and Pt were used as the reference and counter electrodes, respectively. A potentiostat/galvanostat (Hokuto Denko, HSV-100) was also used, and a constant voltage of either -0.15 or $+1.25 \text{ V}$ (vs Ag/AgCl) was applied to bleach and color the Ir oxide working electrodes, respectively. The optical transmittance of the films was measured in situ using a tungsten halogen light source and a multi-channel charge coupled device (CCD) detector (Ocean Optics, USB2000+). The total transmittance of a sample with an Ir oxide/FTO/glass in a quartz-glass cell filled with the aqueous electrolyte was measured using a quartz-glass cell filled with the aqueous electrolyte as a reference.

3. Results and Discussion

3.1 Bleached and Colored Transmittance

The bleached and colored transmittance spectra of the Ir oxide thin films with different thicknesses are shown in Figure 1. The spectra were measured after bleaching at -0.15 V and coloring at $+1.25 \text{ V}$ for 10 min. The colored

transmittance spectra of all the samples are almost flat in a visible wavelength region, which means that the films' color was gray or black. The thinnest film has a very high transmittance and a flat transmittance spectrum in the bleached state; the film looks fairly transparent. However, the bleached transmittance in the short wavelength region decreased and the color of the films became yellow with increasing film thickness. Slight oscillations in the bleached transmittance spectra are thought to be caused by optical interference originating from the multi-layered structure of the samples (Ir oxide/FTO/glass).

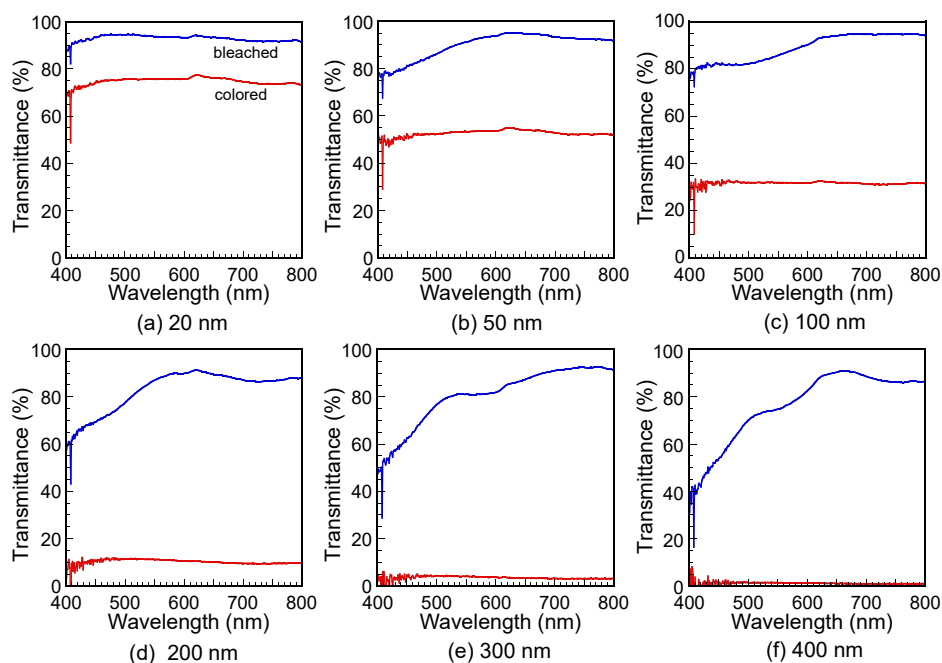


Figure 1. The bleached and colored transmittance spectra of Ir oxide thin films with various film thicknesses. The spectra were measured after bleaching at -0.15 V and coloring at $+1.25$ V for 10 min

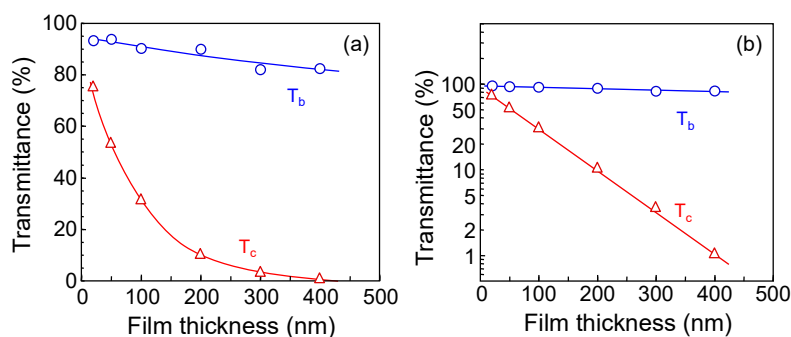


Figure 2. Bleached and colored transmittances (T_b and T_c) at a wavelength of 600 nm as a function of film thickness. Transmittances are plotted on a linear scale (a) and a logarithmic scale (b)

Figure 2 shows the bleached and colored transmittances of the films as a function of film thickness at a wavelength of 600 nm, at which the bleached transmittances almost reached their maximum values. Figure 2(a) shows that the colored transmittance, T_c , decreases steeply with increasing film thickness; in contrast the bleached transmittance, T_b , remains high, and the maximum transmittance change, $T_b - T_c$, and the maximum contrast ratio, T_b/T_c , were obtained (81% and 79, respectively) for the 400 nm-thick film. A logarithmic plot of the bleached and colored transmittances are shown in Figure 2(b), and a linear relationship between the transmittance and the film thickness was clearly obtained. This result indicates that the transmittance of the films, T , can be described by Lambert's law.

$$T = \exp(-\alpha \cdot d), \quad (3)$$

where d is the film thickness and α is the absorption coefficient. The absorption coefficients of the films in the bleached and colored states were estimated to be 3.2×10^3 and $1.1 \times 10^5 \text{ cm}^{-1}$, respectively, from the slope of the straight lines shown in Figure 2(b). The extrapolated transmittances at zero film thickness (approximately 94%) correspond to the loss of the transmitted light by the absorption of the glass substrates and the reflection at the interfaces between the aqueous electrolyte and the samples.

The absorption coefficient can be expressed by the following equation:

$$\alpha = 4\pi k / \lambda, \quad (4)$$

where k is the extinction coefficient (imaginary part of the refractive index) and λ is the wavelength. The extinction coefficients of the Ir oxide films in their bleached and colored states were calculated to be 0.015 and 0.5, respectively. The extinction coefficient of single-crystal IrO_2 for the electric field vector of the light polarized parallel and perpendicular to the c -axis were reported to be approximately 1.1 and 0.8, respectively, at a wavelength of 600 nm (2.07 eV) (Goel et al., 1981). These values are comparable to those of our Ir oxide thin films in the colored states. Gottesfeld and Srinivasan reported extinction coefficients of 0.01 and 0.10 for the Ir oxide films formed on the Ir electrode via electrochemical reduction and oxidation, respectively, in 0.5 M H_2SO_4 (Gottesfeld & Srinivasan, 1978). Backholm & Niklasson reported extinction coefficients of 0.12 and 0.19 for the bleached and colored states, respectively, of the IrO_x films prepared by reactive sputtering in an Ar + O_2 atmosphere at a wavelength of 660 nm (Backholm & Niklasson, 2008). The larger difference of the extinction coefficients in the bleached and colored states in our study indicates a much higher proportion of Ir atoms that are electrochemically active. These results demonstrate that almost all the Ir atoms in our Ir oxide thin films can be considered to be contributing to the coloration change. These optical constants are useful to estimate the EC activity of devices using Ir oxide films.

3.2 Response Time

The transmittance change of the Ir oxide films after applying constant voltages of -0.15 V for bleaching and $+1.25 \text{ V}$ for coloring is shown in Figure 3. The transmittance was measured at a wavelength of 600 nm. The bleaching and coloring response times were defined as the time required to obtain a 90% transmittance change from the fully colored state to the fully bleached state, and vice versa. Figure 4 shows the response times as a function of film thickness. From these figures, we found that the response time increased from 2–3 s to several tens of seconds with increasing film thickness.

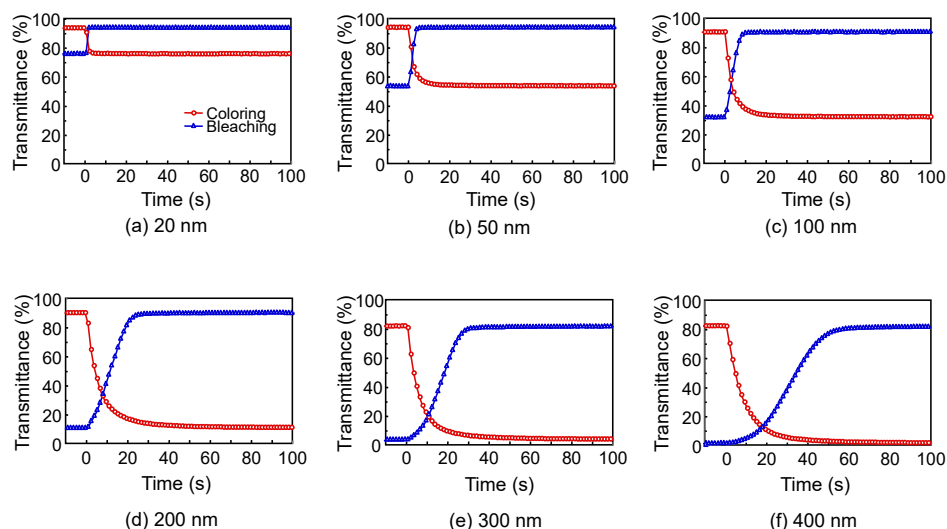


Figure 3. Transmittance change of the Ir oxide films with various film thicknesses by applying a constant voltage of -0.15 V for bleaching and $+1.25 \text{ V}$ for coloring. The measurement wavelength was 600 nm

Compared with the very fast response reported in previous papers, such as $\sim 0.2 \text{ s}$ (Shay et al, 1978) and less than 50 ms (Schivone et al, 1979), the response speed of our samples is much slower. This discrepancy can be explained by the high sheet resistance of our FTO electrode. The electric charge required to color and bleach the Ir

oxide films increases with increasing film thickness; however, the maximum current is restricted by Ohm's law, which results in longer response times for EC cells using transparent electrodes with high sheet resistances.

The response times of EC cells depend on the properties of the EC materials, such as the porosity and surface area, which affect the diffusion coefficients of ions in the films. The ion conductivity of the electrolyte, the electrical resistance of the transparent electrodes, and the device structure, such as the thickness of the EC layer and the device area, also affect the response times of EC devices (Viennet, Randin, & Raistrick, 1982; Kamimori, Nagai, & Mizuhashi, 1987). Although quantitative discussions of the response times are difficult, Figures 2 and 4 clearly show that there is a trade-off between the response time and the optical contrast ratio. These data are considered to be useful for the design of EC devices with appropriate performances.

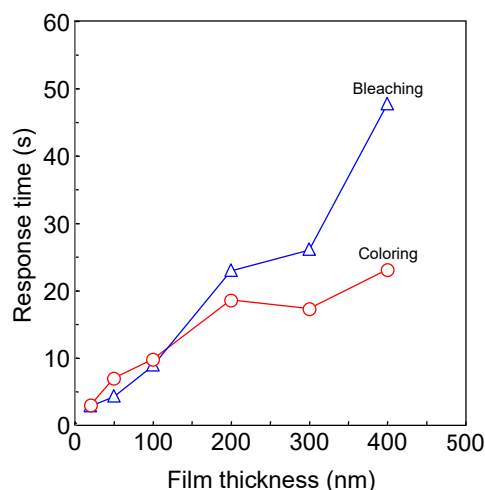


Figure 4. Bleaching and coloring response times as a function of film thickness

4. Conclusions

Hydrated Ir oxide thin films with thicknesses from 20 to 400 nm were prepared by reactive sputtering in a H₂O atmosphere, and their transmittance spectra in the bleached and colored states as well as their response times were studied. The bleached and colored transmittances decreased with increasing film thickness according to Lambert's law, and the absorption coefficients in the bleached and colored states were estimated to be 3.2×10^3 and 1.1×10^5 cm⁻¹, respectively, at a wavelength of 600 nm. These results demonstrate that almost all the Ir atoms in the oxide thin films can be considered to be electrochemically active and to be contributing to the color change. The transmittance change and the contrast ratio of the bleached and colored transmittances increased with increasing film thickness with maximum values of 81% and 79%, respectively, obtained for the 400 nm-thick Ir oxide film. We found that there is a trade-off between the response speed and the transmittance change, i.e., the response is slower with increasing film thickness.

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