Electrochromism is the reversible color change of electrochromic materials by applying a small voltage or current and, thus, it has drawn interest for optical devices such as smart windows, automotive mirrors, and light shutters. In electrochromic devices (ECDs), the selection of electrochromic materials is an important factor for effective coloration bleaching. Two typical electrochromic materials are metal oxides (e.g., IrO₂, WO₃, NiO, V₂O₅) and conducting polymers (e.g., polypyrrole and polythiophene). Among electrochromic metal oxides, iridium oxide shows a remarkably fast response to anodic coloration and cathodic bleaching, but its electrochromic properties of IrO₂ thin films are dependent on iridium oxides. In situ method, characterization using cyclic voltammetry and surface analyses such as X-ray photoelectron spectroscopy, Auger electron spectroscopy, and scanning electron microscopy. Prior to pulsed anodic current electrodeposition of IrO₂ thin film on indium-tin oxide substrate (total anodic charge 100 mC/cm²), IrO₂ islands, which work as good adhesive seeds, were prepared by cyclic voltammetry. In phosphate buffered saline solution, IrO₂ exhibited blue and black anodic electrochromic behavior at two oxidation potentials of +0.5 and +0.9 V (vs. a saturated calomel electrode). Surface analysis and mass variations of IrO₂ thin film indicated that the ejection of H⁺ and the injection of Na⁺ caused the cracks in the film and resulted in coloring behaviors.

**Experimental**

Electrochemical preparation of IrO₂ thin films.—Before IrO₂ deposition, an AT-cut 9 MHz indium-tin oxide (ITO) quartz crystal (Seiko Instruments Inc.) with a sheet resistance of 15 Ω/cm² was thermally treated at 500°C for 3 h and cleaned with acetone in an ultrasonic bath.

IrO₂ coating solution was prepared by the following six successive steps (by Yamanaka): (i) 4.5 mM of IrCl₄·xH₂O (Aldrich 99.9+% ) was dissolved in deionized water by magnetic stirring for 30 min, (ii) 1 mL of H₂O₂ (30 wt %) was added for lower current deposition and the coating solution was stirred for 10 min, (iii) 55.5 mM of oxalic acid ([COOH]₂·2H₂O) was added to prevent IrO₂ precipitation, (iv) the pH of the solution was adjusted to a value of 10.5 by adding K₂CO₃, (v) the resulting solution was aged for 5 days at room temperature, (vi) aging, insoluble materials in the deposition solution were filtered out and the resulting solution was stored at 5°C.

Electrochromic IrO₂ layers were formed on ITO by two successive electrodeposition techniques, i.e., CV and pulsed anodic electrodeposition. According to a previous study, CV performed between open-circuit potential (OCP) and oxygen evolution potential, i.e., −0.05 and +0.55 V (vs. a saturated calomel electrode [SCE]), respectively, produced good adhesion of IrO₂ films. Then, pulsed electrodeposition with a deposited charge of 100 mC/cm² was followed by anodic current of 0.07 mA/cm² for an on-time of 0.5 s and zero current for an off-time of 0.5 s in each cycle.

**Characterization of iridium oxides films.**—All electrochemical measurements were performed in phosphate buffered saline (PBS) electrolyte composed of 0.126 M NaCl, 0.1 M NaH₂PO₄, and 0.1 M Na₂HPO₄. Prior to electrochemical analysis, PBS solution was adjusted to pH 7.2 and deoxygenated with nitrogen gas for 1 h to confirm the air-free solution.

Electrochromic redox behavior of the IrO₂ thin films was carried out by CV experiment. Current response and long-term stability of the IrO₂ on coloration and bleaching were investigated with different pulse voltammetry.

Reference electrode was the SCE and a large platinum plate was used as the counter electrode. All electrochemical measurements were executed by a potentiostat/galvanostat (EG&G PAR 273A) connected with an oscilloscope (Tektronix TDS 350). Mass change of cathode was measured by a sensitive piezoelectric device, in situ EQCM (Seiko EG&G, QCA917). Surface morphology, crystallinity, binding energy, and depth profile of as-deposited, colored, and bleached IrO₂ films were observed with scanning electron microscope (SEM, Hitachi S-3300), X-ray diffraction (XR, Philips DYS616), XPS (AG ESCALAB 250), Au-

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ger electron spectroscope (AES, Physical Electronics PHI 600), and energy-dispersive X-ray (EDX) analysis, respectively.

Results and Discussion

Figure 1a shows the morphology of the pretreated ITO-coated glass, which was used as the substrate for the preparation of IrO$_2$. In Fig. 1b, the IrO$_2$ deposited by pulsed anodic electrodeposition has cracks and small crystallites with a diameter of ca. 0.4 μm on the entire surface. Cracks may be developed by the mechanical stresses generated during growth of the IrO$_2$ crystallites. Figure 1c is an enlargement of Fig. 1b and the deposited material is composed of larger crystals of ca. 50 nm compared with ITO crystals shown in Fig. 1a. Figure 1d is an EDX structural analysis of the Fig. 1c sample. One can clearly observe an Ir element on the ITO substrate and, thus, we assume that iridium (hydro)oxides are formed on the ITO anode.

A cyclic voltammogram of electrochromic IrO$_2$ films with electrodeposited charges of 100 mC/cm$^2$ is shown in Fig. 2a. Electrodeposited IrO$_2$ films exhibited anodic blue and black electrochromism at two oxidation potentials of +0.5 and +0.85 V, respectively, while on the cathodic scan, black thin films became colorless. In the first (i) and second (ii) anodic peak, partial Ir$^{3+}$ ions are oxidized to Ir$^{4+}$ and the remaining Ir$^{3+}$ ions are oxidized to Ir$^{4+}$ ions, respectively. This supports that the ejection of H$^+$ ions during anodic electrochromism induces the changes in iridium valence, i.e., from amorphous Ir(OH)$_3$ films to IrO$_2$.

For a better understanding of the colorization of iridium oxide, pulse potential experiments were performed. Figure 3 shows the current density response of IrO$_2$ films when pulse potential is applied in PBS solution. Analyzing Fig. 2, we select an appropriate coloring potential of +0.9 V and bleaching potential of −0.7 V. The electrolysis time required for full coloration ($t_c$) and full bleaching ($t_b$) is ca. 9 and 5 s, respectively. During coloration, i.e., when the potential of +0.9 V is applied, current density reaches a constant value of +1.6 mA/cm$^2$, while current density is nearly zero for bleaching at −0.7 V after 5 s. This observation indicates that the deposited material in coloration is conductive metallic oxides (i.e., IrO$_2$), but it becomes insulating materials (i.e., Ir(OH)$_3$) in the bleaching process. In addition, we observed that, during bleaching, deposited materials undergo two successive steps. IrO$_2$ changes partly into Ir(OH)$_3$ at the first current peak [marked with (i)] and

Figure 1. SEM images of the IrO$_2$ films; (a) ITO coated glass substrate, (b) as-deposited IrO$_2$, Pulsed anodic electrodeposition condition, (c) enlargement of b, and (d) EDX analysis of c: Anodic bias current = +0.07 mA/cm$^2$; anodic bias time = 0.5 s; current off-time = 0.5 s; total anodic charge = 100 mC/cm$^2$.

Figure 2. (a) Cyclic voltammogram and (b) in situ EQCM response of the IrO$_2$ film prepared by pulsed anodic electrodeposition (100 mC/cm$^2$) in PBS solution with a scan rate of 50 mV/s at room temperature.

Figure 3. (a) Applied pulse potential and (b) current response of IrO$_2$ films in PBS electrolyte. Anodic potential = +0.9 V for 20 s, cathodic potential = −0.7 V for 15 s.
phenomena are supposed to be the result of volume changes of the In the colored state, the thickness of the films is different, i.e., there is a cracked-mud structure and larger grain size compared to the colored IrO2 film oxidized at 5 kV; beam current density = 400 nA; analysis area = 40 × 40 μm. Ion gun: high voltage = 3 kV; ion beam current density = 27.5 μA/cm².

Figure 4a and b shows the surface morphology of the colored (black) IrO2 and bleached (transparent) Ir(OH)3, respectively. Colored IrO2 film oxidized at +0.9 V in PBS solution is not uniform, i.e., there is a cracked-mud structure and larger grain size compared with films of as-deposited IrO2 (see Fig. 1b), while uniform and smooth thin film is obtained on bleached IrO2 at −0.7 V. These phenomena are supposed to be the result of volume changes of the films near the crack sites and they may be due to the ejection and injection of H+ and/or Na+ in each cycle. This result is in good agreement with the result shown in Fig. 2.

Figure 4c and d shows AES depth profiles of the IrO2 films in colored and bleached states, respectively. Figure 4c indicates that a small amount of sodium ion is present in colorless films, while a relatively higher concentration of sodium ion is observed in colored films, as shown in Fig. 4d, and the relative ratio of O/Ir in the bleached state is lower than the ratio in the colored state. The thickness of the films is different, i.e., sputtering time to reach the substrates (ITO) in the colored state is longer than sputtering time in the bleached state. This result indicates that geometrical factors (e.g., the structure) of the IrO2 films were changed due to the well crystallinity and the insertion of the sodium ions into crack-mud structure (see Fig. 4a).

Figure 5 shows XPS spectra for O 1s, Ir 4f1/2, and Ir 4f3/2 electrons for (a) IrO2 and (b) Ir(OH)3. The vertical lines indicate the positions of the peaks in the spectra.

Conclusions

IrO2 thin films prepared by anodic pulse electrodeposition on ITO substrate showed coloring and bleaching phenomena when appropriate anodic and cathodic potentials of +0.9 V and −0.7 V were applied, respectively. We obtained the interesting morphological observations, i.e., the cracking and swelling of IrO2 at an anodic potential of +0.9 V. Analyzing surface characterization by XPS, SEM observation, and in situ mass change by EQCM, we clearly demonstrated that electrochromic mechanism of IrO2 was due mainly to proton injection and ejection. According to the measurement of AES depth profiles, we assumed that the sodium ion could also affect the colorisation of IrO2, but further investigations should be considered.

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