

## Electrochromic properties of iridium oxide thin films prepared by reactive sputtering in O<sub>2</sub> or H<sub>2</sub>O atmosphere

Satoshi Ito, Yoshio Abe, Midori Kawamura, and Kyung Ho Kim

Citation: *Journal of Vacuum Science & Technology B* **33**, 041204 (2015); doi: 10.1116/1.4923227

View online: <http://dx.doi.org/10.1116/1.4923227>

View Table of Contents: <http://scitation.aip.org/content/avs/journal/jvstb/33/4?ver=pdfcov>

Published by the AVS: Science & Technology of Materials, Interfaces, and Processing

---

### Articles you may be interested in

[Cyclic voltammetry on sputter-deposited films of electrochromic Ni oxide: Power-law decay of the charge density exchange](#)

*Appl. Phys. Lett.* **105**, 163502 (2014); 10.1063/1.4899069

[Electrochromic properties of large-area and high-density arrays of transparent one-dimensional  \$\beta\$ -Ta<sub>2</sub>O<sub>5</sub> nanorods on indium-tin-oxide thin-films](#)

*Appl. Phys. Lett.* **98**, 133117 (2011); 10.1063/1.3568896

[Optical properties of tungsten oxide thin films with protons intercalated during sputtering](#)

*J. Appl. Phys.* **103**, 063508 (2008); 10.1063/1.2887931

[Thickness-dependent microstructural and electrochromic properties of sputter-deposited Ni oxide films](#)

*J. Vac. Sci. Technol. A* **20**, 1468 (2002); 10.1116/1.1487871

[Preparation and properties of dc-sputtered IrO<sub>2</sub> and Ir thin films for oxygen barrier applications in advanced memory technology](#)

*J. Vac. Sci. Technol. B* **19**, 1857 (2001); 10.1116/1.1401750

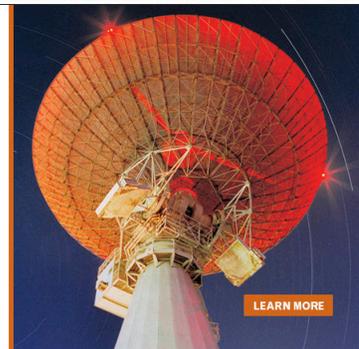
---

MIT LINCOLN  
LABORATORY  
CAREERS

Discover the satisfaction of  
innovation and service  
to the nation

- Space Control
- Air & Missile Defense
- Communications Systems & Cyber Security
- Intelligence, Surveillance and Reconnaissance Systems
- Advanced Electronics
- Tactical Systems
- Homeland Protection
- Air Traffic Control

 **LINCOLN LABORATORY**  
MASSACHUSETTS INSTITUTE OF TECHNOLOGY



# Electrochromic properties of iridium oxide thin films prepared by reactive sputtering in O<sub>2</sub> or H<sub>2</sub>O atmosphere

Satoshi Ito, Yoshio Abe,<sup>a)</sup> Midori Kawamura, and Kyung Ho Kim  
*Department of Materials Science and Engineering, Kitami Institute of Technology, 165 Koen-cho,  
Kitami 090-8507, Japan*

(Received 5 March 2015; accepted 15 June 2015; published 30 June 2015)

Iridium oxide is an electrochromic (EC) material, i.e., it shows reversible and persistent changes in optical properties. In this study, the authors investigated the effects of substrate temperature and sputtering gas on the structures and EC properties of iridium oxide thin films prepared by reactive radio-frequency magnetron sputtering. An Ir metal target was sputtered in an O<sub>2</sub> or H<sub>2</sub>O atmosphere at substrate temperatures between -30 and 130 °C. The crystal structures and chemical bonding states of the films were examined using x-ray diffraction and Fourier-transform infrared (IR) spectroscopy, respectively, and their EC properties were studied in 0.5 M aqueous H<sub>2</sub>SO<sub>4</sub> electrolyte solution. IrO<sub>2</sub> films were deposited at 70 and 130 °C, and amorphous films were formed at 20 and -30 °C in both O<sub>2</sub> and H<sub>2</sub>O atmospheres. IR absorption peaks from hydrogen-bonded OH groups were clearly observed for films deposited in an H<sub>2</sub>O atmosphere at substrate temperatures of -30 and 20 °C, which indicates that iridium oxyhydroxide or hydrated iridium oxide films were deposited. The amorphous iridium oxyhydroxide or hydrated iridium oxide films showed large variations in transmittance and high bleached-state transmittances, and they are considered to be suitable for use in EC devices. © 2015 American Vacuum Society.

[<http://dx.doi.org/10.1116/1.4923227>]

## I. INTRODUCTION

Electrochromic (EC) materials change their optical transmittance (darken and lighten) reversibly on application of a low voltage.<sup>1</sup> A typical EC device consists of an EC layer, an ion-conducting layer, and an ion-storage layer, all sandwiched between two transparent conducting electrodes. WO<sub>3</sub> is the most widely studied inorganic EC material; it turns dark blue on reduction and becomes transparent again on oxidation. Two other well-known EC materials, nickel oxide and iridium oxide, turn dark brown on oxidation and become transparent again on reduction; they are used as ion-storage layers to enhance transmittance variations of EC devices.<sup>2-5</sup> Such EC devices are used in displays, antiglare automobile rearview mirrors, and smart energy-efficient windows.<sup>6</sup>

Iridium oxide has high chemical stability in both acidic and basic electrolyte solutions and shows fast EC responses.<sup>7</sup> Iridium oxide thin films have been prepared by sputtering,<sup>8-15</sup> anodic oxidation,<sup>16-19</sup> electrodeposition,<sup>20-22</sup> thermal oxidation,<sup>23</sup> sol-gel,<sup>24</sup> and spray pyrolysis methods.<sup>25,26</sup> The chemical compositions of the films depend on the preparation method, and the films are considered to be iridium oxide in a broad sense, and include IrO<sub>x</sub> (binary compounds of iridium and oxygen), IrO<sub>x</sub>(OH)<sub>y</sub> (iridium oxyhydroxides), and IrO<sub>x</sub>·nH<sub>2</sub>O (hydrated iridium oxide).<sup>7,16</sup> For large-area device applications, sputtering is considered to be superior to other methods. Many researchers<sup>9,12-15</sup> have used pure O<sub>2</sub> or Ar + O<sub>2</sub> mixed gases and deposited iridium oxide thin films at substrate temperatures close to or above room temperature. However, Schiavone *et al.*<sup>8</sup> and Klein *et al.*<sup>11</sup> used O<sub>2</sub> saturated with water at room temperature and

Ar + H<sub>2</sub> + O<sub>2</sub> mixed gases with H<sub>2</sub>/O<sub>2</sub> ratios of 0.55–2.0, respectively, and deposited iridium oxide thin films on water-cooled or unheated substrates. Kang and Shay<sup>10</sup> sputter deposited iridium oxide films in an atmosphere consisting of Ar/O<sub>2</sub>, 80/20 onto substrates held at -35 °C. These results suggest that sputter deposition in an atmosphere that includes O and H and substrate cooling below room temperature are effective in improving the EC properties of iridium oxide thin films. However, systematic studies of the effects of substrate temperature and sputtering gas are scarce.

In our laboratory, a reactive sputtering technique using water vapor as the reactive gas has been developed and applied to nickel oxide and cobalt oxide thin films.<sup>27-29</sup> The films deposited in a water vapor atmosphere at a high sputtering gas pressure<sup>28</sup> and low substrate temperature<sup>29</sup> gave good EC performances. In the present study, we fabricated iridium oxide thin films in an O<sub>2</sub> or H<sub>2</sub>O atmosphere at various substrate temperatures, and examined the effects of sputtering atmosphere and substrate temperature on the structural, electrochemical, and EC properties of the films in detail.

## II. EXPERIMENT

Iridium oxide thin films were prepared by radio-frequency magnetron sputtering using an Ir metal target (99.9% purity, diameter 2 in.) in an O<sub>2</sub> or H<sub>2</sub>O atmosphere. The sputtering gas pressure and sputtering power were 6.7 Pa and 50 W, respectively. The substrate temperature was varied from -30 to 130 °C. Si and glass coated with F-doped tin oxide (FTO) were used as the substrates. The film thickness was measured using scanning electron microscopy (SEM; JEOL, JSM-6701F) at an accelerating voltage

<sup>a)</sup>Electronic mail: [abeys@mail.kitami-it.ac.jp](mailto:abeys@mail.kitami-it.ac.jp)

of 5 kV and working distance of 6 mm. The film deposition rate was calculated from the film thickness determined from the SEM observations and deposition time. The crystal structure and film density were determined using x-ray diffraction (XRD; Rigaku, Ultima IV) and x-ray reflectivity (XRR; PANalytical, X'Part PRO), respectively, with Cu K $\alpha$  radiation. Chemical bonding states were determined using Fourier-transform infrared (FTIR) spectroscopy (JASCO, FT/IR-6100). *Ex situ* FTIR measurements were performed in a sample chamber purged with dry N<sub>2</sub> to reduce absorptions of H<sub>2</sub>O and CO<sub>2</sub> in air. A bare Si substrate was used as the reference for calculation of the transmittance. Cyclic voltammetry (CV) and *in situ* optical modulation measurements were performed in 0.5 M aqueous H<sub>2</sub>SO<sub>4</sub> electrolyte solution to determine the electrochemical and EC properties of the films. The potential scanning range of the CV measurements, using a potentiostat/galvanostat (Hokuto Denko, HSV-100), was from  $-0.25$  to  $+1.25$  V, and the scanning speed was 20 mV/s. Ag/AgCl and Pt were used as the reference and counter electrodes, respectively. The optical transmittances of the films were determined using a multichannel charge-coupled device detector (Ocean Optics, S2000). The total transmittance of a sample with an iridium oxide/FTO/glass structure was measured using a quartz-glass cell filled with aqueous electrolyte as the reference sample.

### III. RESULTS AND DISCUSSION

Figure 1 shows the deposition rates of the films prepared in an O<sub>2</sub> or H<sub>2</sub>O atmosphere at different substrate temperatures. The deposition rates of the films prepared in an H<sub>2</sub>O atmosphere (referred to as H<sub>2</sub>O-deposited films) were approximately one-third of those of the films prepared in an O<sub>2</sub> atmosphere (referred to as O<sub>2</sub>-deposited films), and the deposition rate hardly changed with changes in substrate temperature. The smaller mass of H<sub>2</sub>O molecules compared with that of O<sub>2</sub> molecules is thought to be the reason for the lower deposition rate.

Figure 2 shows cross-sectional SEM images of films deposited on Si substrates in O<sub>2</sub> or H<sub>2</sub>O atmospheres at different substrate temperatures. The films deposited at substrate temperatures of  $-30$  and  $20^\circ\text{C}$  had flat, smooth surfaces, whereas those deposited at  $70$  and  $130^\circ\text{C}$  had rough

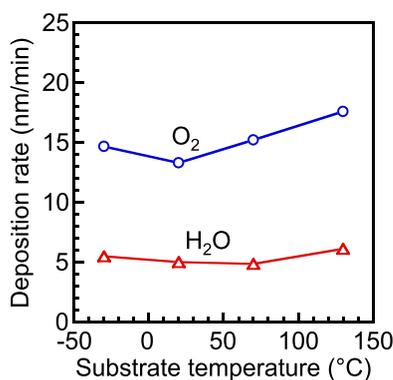


FIG. 1. (Color online) Deposition rates of films prepared in O<sub>2</sub> or H<sub>2</sub>O atmosphere as function of substrate temperature.

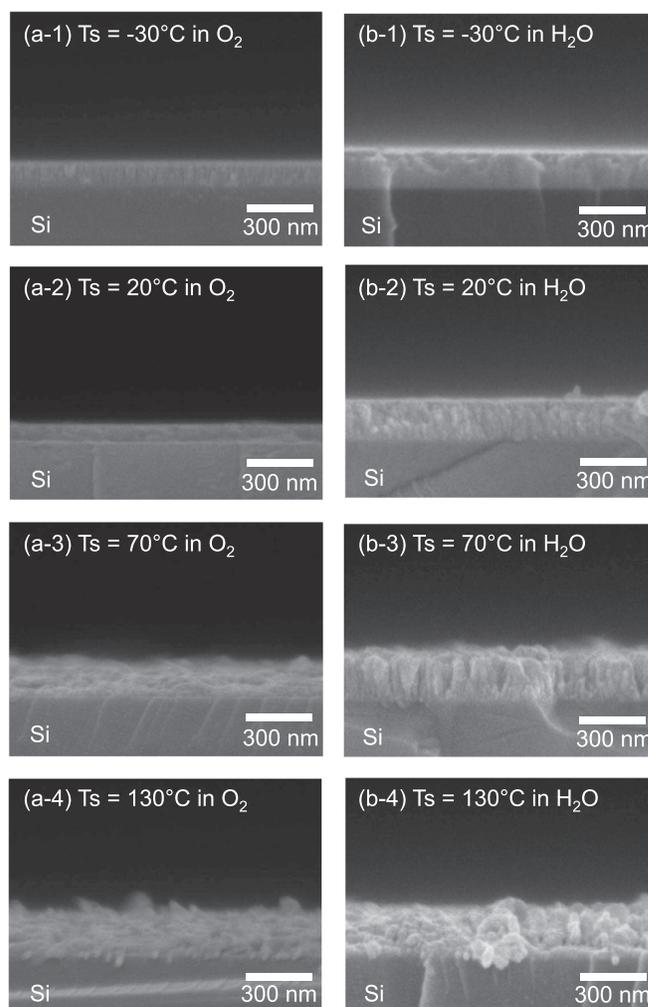


FIG. 2. SEM images of films prepared at various substrate temperatures in O<sub>2</sub> or H<sub>2</sub>O atmosphere.

surfaces. The rough surface morphologies of the films deposited at high substrate temperatures can be explained by the shadowing effect.<sup>30</sup> Under the relatively high sputtering gas pressure of 6.7 Pa used in this study, many sputtered atoms are expected to hit the substrate at oblique angles instead of falling normally on the substrate. If crystal grains grow on the substrate, the grains shadow the neighboring area from the incident atoms and the surface roughness is increased.

Figure 3 shows XRD patterns of films of thickness approximately 100 nm, deposited by adjusting the deposition time, using the deposition rate shown in Fig. 1, on Si substrates in an O<sub>2</sub> or H<sub>2</sub>O atmosphere at different substrate temperatures. Diffraction peaks from IrO<sub>2</sub> with the rutile structure<sup>31</sup> are clearly visible for the O<sub>2</sub>- and H<sub>2</sub>O-deposited films produced at  $70$  and  $130^\circ\text{C}$ ; the XRD peaks almost disappear for the films deposited at  $20$  and  $-30^\circ\text{C}$ , and these films are considered to be amorphous. The XRD peak intensities of the H<sub>2</sub>O-deposited films were much lower than those of the O<sub>2</sub>-deposited films. One reason for this is the low film density of the H<sub>2</sub>O-deposited films, as described below. In addition, the XRD peak widths of the H<sub>2</sub>O-deposited films were broader than those of the O<sub>2</sub>-deposited films, and the crystallites sizes of the H<sub>2</sub>O- and O<sub>2</sub>-deposited films

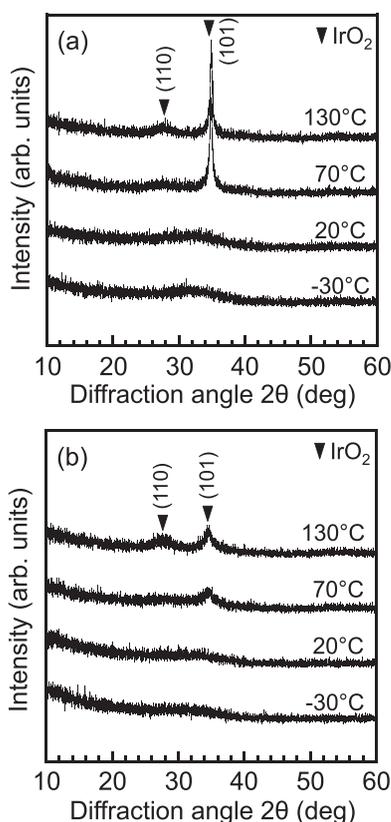


FIG. 3. XRD patterns of films prepared at various substrate temperatures in (a)  $O_2$  or (b)  $H_2O$  atmosphere.

produced at  $130^\circ C$  were estimated to be 6 and 22 nm, respectively, from Scherrer's formula.<sup>32</sup> It is thought that the film crystallinity deteriorated as a result of using  $H_2O$  as the reactive gas.

The film densities were estimated using XRR; the results are shown in Fig. 4. The  $H_2O$ -deposited films were less dense than the  $O_2$ -deposited films, and the densities decreased with decreasing substrate temperature. The minimum density obtained, that of a film deposited in an  $H_2O$  atmosphere at  $-30^\circ C$ , was nearly half the density of bulk  $IrO_2$  ( $11.666\text{ g/cm}^3$ ).<sup>31</sup> The critical angle for total x-ray reflection depends on the film density,<sup>32</sup> the film densities were estimated using curve-fitting software (X'PART REFLECTIVITY). The densities of the films deposited at higher substrate temperatures could not be estimated using XRR because the sample surfaces were rough, as seen in Fig. 2, and no clear total reflection was observed.

Figure 5 shows FTIR transmittance spectra of films of thickness approximately 100 nm, deposited on Si substrates at various temperatures in an  $O_2$  or  $H_2O$  atmosphere. The intensities of the broad infrared (IR) absorption peaks at around  $3400\text{ cm}^{-1}$ , from hydrogen-bonded OH groups, increased with decreasing substrate temperature for the  $H_2O$ -deposited films. In addition, absorption peaks assignable to Ir-O bonds ( $\sim 550\text{ cm}^{-1}$ )<sup>33</sup> were observed at  $510\text{ cm}^{-1}$ . In our previous studies of hydrated  $ZrO_2$  films reactively sputtered in  $H_2O$  and  $D_2O$  atmospheres, absorption peaks from O-D groups and an H/Zr atomic ratio close to 1.0 were

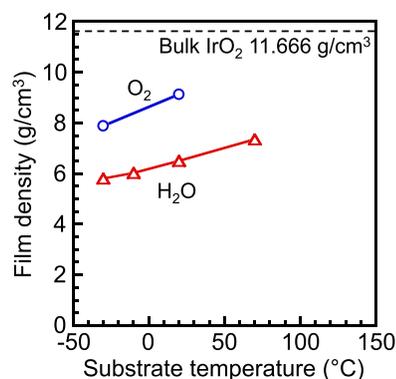


FIG. 4. (Color online) Density of films deposited in  $O_2$  or  $H_2O$  atmosphere as function of substrate temperature.

observed.<sup>34,35</sup> These results suggest that iridium oxyhydroxide or hydrated iridium oxide films were formed in an  $H_2O$  atmosphere at low substrate temperatures. The transmittances in the  $400\text{--}4000\text{ cm}^{-1}$  region decreased with increasing substrate temperature for the  $H_2O$ -deposited films and the transmittances of the  $O_2$ -deposited films were lower than those of the  $H_2O$ -deposited films. The low transmittances of the  $H_2O$ -deposited films at high substrate temperatures and of all the  $O_2$ -deposited films are considered to be caused by the metallic character of  $IrO_2$  [the bulk resistivity of  $IrO_2$  is  $35\ \mu\Omega\text{ cm}$  (Ref. 36)]. The Drude model<sup>37</sup> indicates that the optical reflectivity is unity when the light frequency is less than the plasma frequency, which is proportional to the free-electron density of a material, and decreases above the plasma frequency. If the free-electron density of the  $O_2$ -deposited films is high enough, high optical reflectivity and low transmittance are expected in the IR region. The

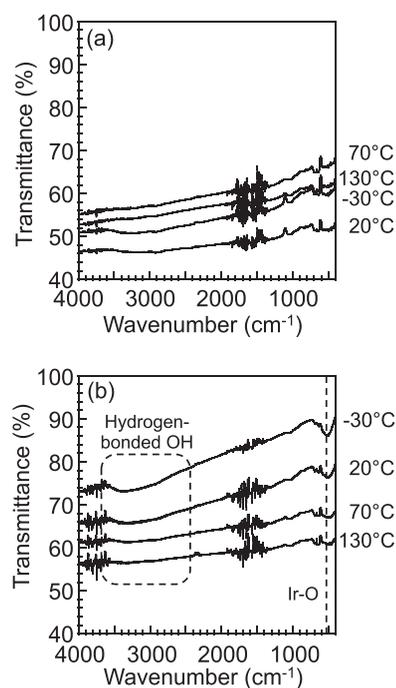


FIG. 5. FTIR spectra of films prepared at various substrate temperatures in (a)  $O_2$  or (b)  $H_2O$  atmosphere.

increased transmittances of the H<sub>2</sub>O-deposited films with decreasing substrate temperatures are considered to be caused by the decrease in their free-electron density.

The electrochemical and EC properties of the films deposited on FTO-coated glass of thickness approximately 100 nm in a 0.5 M aqueous H<sub>2</sub>SO<sub>4</sub> electrolyte were studied. Figure 6 shows the transmittance spectra of films in bleached and colored states measured after 100 CV cycles, obtained by applying constant voltages of  $-0.25$  and  $+1.25$  V (vs Ag/AgCl reference electrode) for 1 min. The width of the transmittance changes of the films increased with decreasing substrate temperature, and higher transmittances were obtained in the bleached state (particularly in the short-wavelength region) for films deposited in an H<sub>2</sub>O atmosphere at substrate

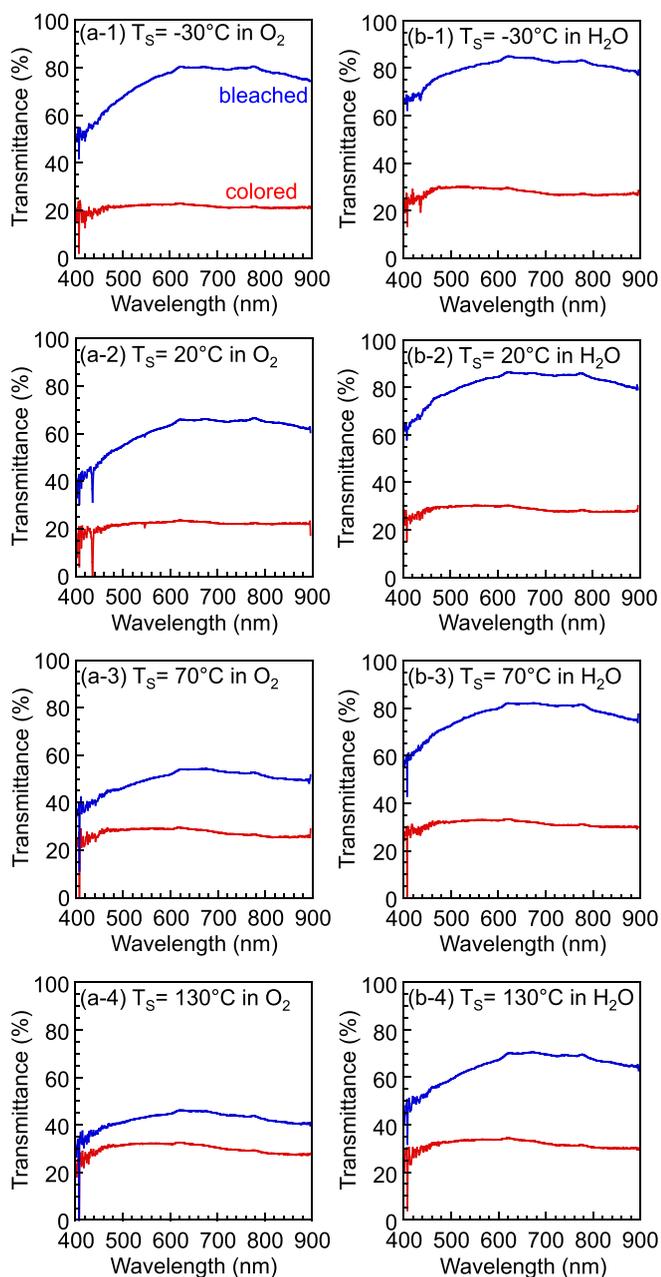


Fig. 6. (Color online) Bleached and colored transmittance spectra of films prepared at various substrate temperatures in O<sub>2</sub> or H<sub>2</sub>O atmosphere.

temperatures of 20 and  $-30$  °C. These properties are favorable for EC device applications. It is thought that the iridium oxide films have two-phase microstructures, namely, an IrO<sub>2</sub> core region, which is electrochromically less active and remains dark even in a bleached state, covered by iridium oxyhydroxide or hydrated iridium oxide layers, which are active and have higher bleached-state transmittances. A similar model has been proposed for the electrochromism of NiO.<sup>38</sup> Although the iridium oxyhydroxide or hydrated iridium oxide layers are bleached, the IrO<sub>2</sub> core region remains dark and the bleached transmittances of the O<sub>2</sub>-deposited films are lower than those of the H<sub>2</sub>O-deposited iridium oxyhydroxide or hydrated iridium oxide films. The bleached-state transmittance is expected to increase with decreasing size of the IrO<sub>2</sub> core region.

CV measurements up to 100 cycles were performed; the CV curves at the 100th cycle are shown in Fig. 7. The current density clearly increased with decreasing substrate temperature, and the CV curve shape changed depending on the atmosphere and substrate temperature. The triangular CV curves of the H<sub>2</sub>O-deposited films at 20 and  $-30$  °C are similar to those of films prepared by anodic oxidation<sup>18,19,23</sup> and electrochemical deposition,<sup>20,21</sup> and redox peaks are clearly observed. In contrast, the CV curves of the H<sub>2</sub>O-deposited films at 70 and 130 °C and all the O<sub>2</sub>-deposited films are rectangular and resemble those of sputtered iridium oxide thin films produced in O<sub>2</sub> or Ar/O<sub>2</sub> atmospheres reported in previous papers.<sup>8,9,11,15</sup> The variations in the CV curves from triangular to rectangular are thought to be caused by changes in the chemical composition from iridium oxyhydroxide or hydrated iridium oxide to IrO<sub>2</sub>. The increase in the current density with decreasing substrate temperature is considered to be caused by a decrease in the film density, which facilitates ion diffusion in the films, and a decrease in the crystal grain size, which results in an increase in the surface areas of the grains. The CV curves in Fig. 7 and the transmittance spectra in Fig. 6 were used to calculate the transferred charge density,  $\Delta Q$ , and optical density change,  $\Delta OD$  [ $\Delta OD = \log_{10}(T_b/T_c)$ , where  $T_b$  and  $T_c$  are the transmittances at 600 nm in the bleached and colored states, respectively]. The EC coloration efficiency,  $\eta$ , defined as  $\eta = \Delta OD/\Delta Q$ , was estimated to be approximately 13 cm<sup>2</sup>/C. The value of  $\eta$  was almost independent of the substrate temperature and sputtering atmosphere, and was comparable to the values reported in the literatures [17.9 cm<sup>2</sup>/C at 633 nm, measured in H<sub>2</sub>SO<sub>4</sub>,<sup>9</sup> and 11.5–16.3 cm<sup>2</sup>/C at 550 nm, measured in KOH (Ref. 15)].

#### IV. SUMMARY AND CONCLUSIONS

Iridium oxide thin films were prepared by reactive sputtering in an O<sub>2</sub> or H<sub>2</sub>O atmosphere at various substrate temperatures. Under both atmospheres, IrO<sub>2</sub> films were deposited at 70 and 130 °C, and amorphous films were formed at 20 and  $-30$  °C. The amorphous films deposited in an H<sub>2</sub>O atmosphere had low densities and contained a large number of hydrogen-bonded OH groups; these films are considered to consist of iridium oxyhydroxide or hydrated

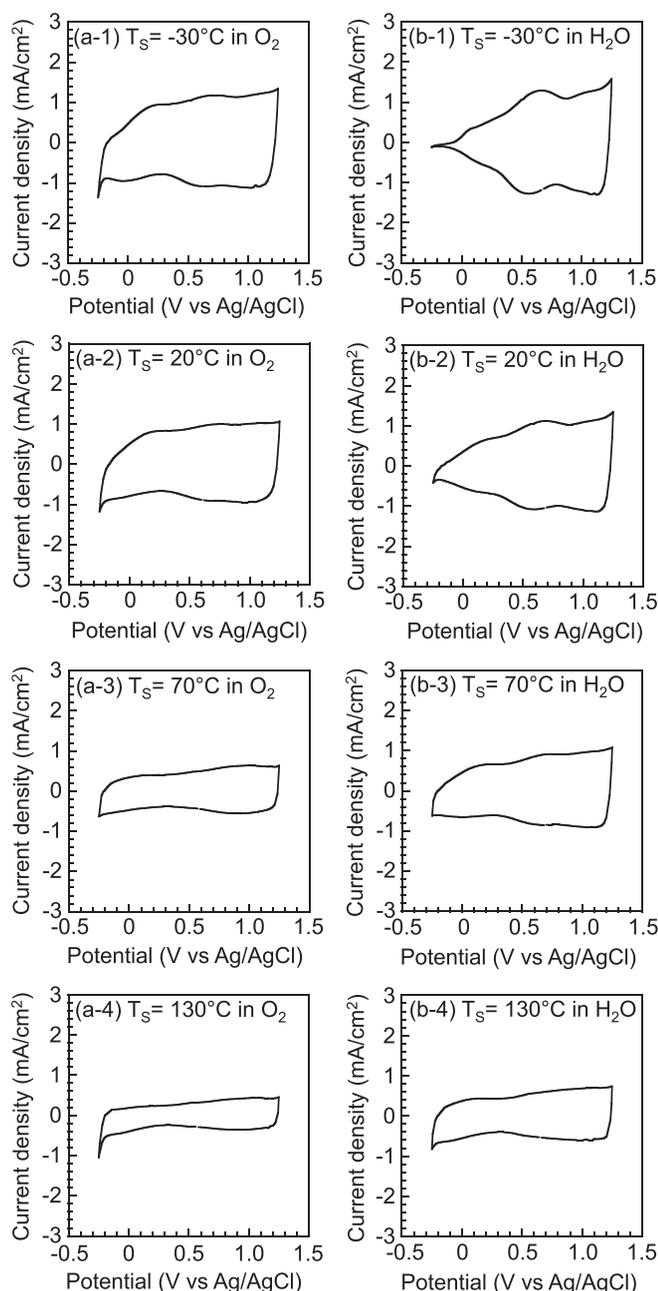


Fig. 7. Cyclic voltammograms of films prepared at various substrate temperatures in  $O_2$  or  $H_2O$  atmosphere.

iridium oxide. The amorphous iridium oxyhydroxide or hydrated iridium oxide films showed large transmittance variation and high bleached transmittances in the visible-wavelength region.

In summary, amorphous iridium oxyhydroxide or hydrated iridium oxide films deposited in an  $H_2O$  atmosphere at low substrate temperatures are considered to be suitable for EC device applications.

## ACKNOWLEDGMENTS

This work was supported by JSPS KAKENHI Grant No. 24550228. The authors thank Susumu Tokuda of the

Instrumental Analysis Center of the Kitami Institute of Technology for his assistance with SEM characterization.

- <sup>1</sup>C. G. Granqvist, *Handbook of Inorganic Electrochromic Materials* (Elsevier, Amsterdam, 1995), pp. 1–4.
- <sup>2</sup>S. F. Cogan, T. D. Plante, R. S. McFadden, and R. D. Rauh, *Sol. Energy Mater.* **16**, 371 (1987).
- <sup>3</sup>T. Niwa and O. Takai, *Thin Solid Films* **518**, 1722 (2010).
- <sup>4</sup>T. Niwa and O. Takai, *Jpn. J. Appl. Phys.* **49**, 105802 (2010).
- <sup>5</sup>T. Niwa and O. Takai, *Thin Solid Films* **518**, 5340 (2010).
- <sup>6</sup>C. G. Granqvist, *Thin Solid Films* **564**, 1 (2014).
- <sup>7</sup>W. C. Dautremont-Smith, *Displays* **3**, 67 (1982).
- <sup>8</sup>L. M. Schiavone, W. C. Dautremont-Smith, G. Beni, and J. L. Shay, *Appl. Phys. Lett.* **35**, 823 (1979).
- <sup>9</sup>L. M. Schiavone, W. C. Dautremont-Smith, G. Beni, and J. L. Shay, *J. Electrochem. Soc.* **128**, 1339 (1981).
- <sup>10</sup>K. S. Kang and J. L. Shay, *J. Electrochem. Soc.* **130**, 766 (1983).
- <sup>11</sup>J. D. Klein, S. L. Clauson, and S. F. Cogan, *J. Mater. Res.* **10**, 328 (1995).
- <sup>12</sup>B. Wessling, A. Besmehn, W. Mokwa, and U. Schnakenberg, *J. Electrochem. Soc.* **154**, F83 (2007).
- <sup>13</sup>J. Backholm, E. Avendano, A. Azens, G. de M Azevedo, E. Coronel, G. A. Niklasson, and C. G. Granqvist, *Sol. Energy Mater. Sol. Cells* **92**, 91 (2008).
- <sup>14</sup>J. Backholm and G. A. Niklasson, *Sol. Energy Mater. Sol. Cells* **92**, 1388 (2008).
- <sup>15</sup>R.-T. Wen, G. A. Niklasson, and C. G. Granqvist, *Sol. Energy Mater. Sol. Cells* **120**, 151 (2014).
- <sup>16</sup>R. O. Lezna, K. Kunitatsu, T. Ohtsuka, and N. Sato, *J. Electrochem. Soc.* **134**, 3090 (1987).
- <sup>17</sup>S. Gottesfeld, J. D. E. McIntyre, G. Beni, and J. L. Shay, *Appl. Phys. Lett.* **33**, 208 (1978).
- <sup>18</sup>G. Beni and J. L. Shay, *Appl. Phys. Lett.* **33**, 567 (1978).
- <sup>19</sup>S. Gottesfeld and J. D. E. McIntyre, *J. Electrochem. Soc.* **126**, 742 (1979).
- <sup>20</sup>T. Yoshino, N. Baba, and K. Arai, *Jpn. J. Appl. Phys.* **26**, 1547 (1987).
- <sup>21</sup>K. Yamanaka, *Jpn. J. Appl. Phys.* **28**, 632 (1989).
- <sup>22</sup>Y. Jung, J. Lee, and Y. Tak, *Electrochem. Solid-State Lett.* **7**, H5 (2004).
- <sup>23</sup>Y. Sato, K. Ono, T. Kobayashi, H. Wakabayashi, and H. Yamanaka, *J. Electrochem. Soc.* **134**, 570 (1987).
- <sup>24</sup>K. Nishio, Y. Watanabe, and T. Tsuchiya, *Thin Solid Films* **350**, 96 (1999).
- <sup>25</sup>P. S. Patil, R. K. Kaware, and S. B. Sadale, *Electrochim. Acta* **50**, 2527 (2005).
- <sup>26</sup>P. S. Patil, S. H. Mujawar, S. B. Sadale, H. P. Deshmukh, and A. I. Inamdar, *Mater. Chem. Phys.* **99**, 309 (2006).
- <sup>27</sup>H. Ueta, Y. Abe, K. Kato, M. Kawamura, K. Sasaki, and H. Itoh, *Jpn. J. Appl. Phys.* **48**, 015501 (2009).
- <sup>28</sup>Y. Abe, H. Ueta, T. Obata, M. Kawamura, K. Sasaki, and H. Itoh, *Jpn. J. Appl. Phys.* **49**, 115802 (2010).
- <sup>29</sup>K.-M. Lee, Y. Abe, M. Kawamura, and K. H. Kim, *Jpn. J. Appl. Phys.* **51**, 045501 (2012).
- <sup>30</sup>K. Wasa, M. Kitabatake, and H. Adachi, *Thin Film Materials Technology/ Sputtering of Compound Materials* (William Andrew, Norwich, NY, 2004), p. 26.
- <sup>31</sup>International Center for Diffraction Data (ICDD), Powder Diffraction File (PDF)-2, Release 2009, Reference Code 00-015-0870.
- <sup>32</sup>M. Birkholz, *Thin Films Analysis by X-ray Scattering* (Wiley, Weinheim, 2006), p. 108 and 160.
- <sup>33</sup>S. Musić, S. Popović, M. Maljković, Ž. Skoko, K. Furić, and A. Gajović, *Mater. Lett.* **57**, 4509 (2003).
- <sup>34</sup>N. Li, Y. Abe, M. Kawamura, K. Sasaki, H. Itoh, and T. Suzuki, *Jpn. J. Appl. Phys.* **50**, 045804 (2011).
- <sup>35</sup>N. Li, Y. Abe, M. Kawamura, K. H. Kim, and T. Suzuki, *Thin Solid Films* **520**, 5137 (2012).
- <sup>36</sup>W. D. Ryden, A.-W. Lawson, and C. C. Sartin, *Phys. Rev. B* **1**, 1494 (1970).
- <sup>37</sup>M. Fox, *Optical Properties of Solids* (Oxford University, Oxford, 2001), p. 143.
- <sup>38</sup>I. Bouessay, A. Rougier, P. Poizot, J. Moscovici, A. Michalowicz, and J.-M. Tarascon, *Electrochim. Acta* **50**, 3737 (2005).