

# **Effects of Substrate Temperature on Electrochromic Properties of Cobalt Oxide and Oxyhydroxide Thin Films Prepared by Reactive Sputtering Using O<sub>2</sub> and H<sub>2</sub>O Gases**

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## **Abstract**

Cobalt oxide and oxyhydroxide thin films were prepared by reactive sputtering of a Co target in O<sub>2</sub> and H<sub>2</sub>O gases at substrate temperatures from -20 to +200 °C. Co<sub>3</sub>O<sub>4</sub> films were formed at all the substrate temperatures in O<sub>2</sub> gas and at 200 °C in H<sub>2</sub>O gas, and amorphous CoOOH films were formed in the range from 10 to -20 °C in H<sub>2</sub>O gas. A large transmittance change of approximately 26% and high electrochromic (EC) coloration efficiency of 20 cm<sup>2</sup>/C at a wavelength of 600 nm were obtained for the CoOOH thin films deposited at -20 °C in 0.1 M KOH aqueous solution. The good EC performance of the CoOOH film is attributed to the low film density and amorphous structure.

## 1. Introduction

Electrochromic (EC) materials change their optical properties (darken and lighten) reversibly with the application of low voltage. An EC device generally consists of an ion-conducting layer sandwiched between an EC layer, an ion storage layer, and two transparent conducting layers.  $\text{WO}_3$ ,  $\text{MoO}_3$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{V}_2\text{O}_5$ , and  $\text{TiO}_2$  are typical inorganic EC materials that are colored by reduction processes, and Ni oxide, Co oxide, and Ir oxide are used as ion-storage and second EC layers, which are colored by oxidation.<sup>1-3)</sup> Such EC devices have been developed for applications in displays, antiglare automobile rearview mirrors, “smart” energy-efficient windows, and sunroofs because of their low operation voltage and low power consumption.<sup>1-5)</sup>

Various methods have been developed for preparing Co oxide films. Švegl *et al.*<sup>6)</sup> reported Co oxide films, prepared by the sol-gel process, that exhibited transmittance change of 25% ( $\lambda = 634\text{nm}$ ) and EC coloration efficiency of approximately  $25 \text{ cm}^2/\text{C}$ . Polo da Fonseca *et al.*<sup>7)</sup> reported Co oxide films, prepared by anodic electroprecipitation, that exhibited transmittance change of 40% ( $\lambda = 632.8\text{nm}$ ) and EC coloration efficiency of  $20 \text{ cm}^2/\text{C}$ . Spray pyrolysis<sup>8)</sup> and chemical bath deposition<sup>9,10)</sup> have also been used to form Co oxide films. Estrada *et al.*<sup>11)</sup> reported Co oxide films prepared by sputtering, and Maruyama and Arai<sup>12)</sup> reported the EC coloration efficiency of  $21.5 \text{ cm}^2/\text{C}$  for Co oxide films prepared by chemical vapor deposition.

The electrochromism of Co oxide is similar to that of Ni oxide, where the oxidized form ( $\text{NiOOH}$ ) produces a dark brown coloration whereas the reduced form  $[\text{Ni}(\text{OH})_2]$  is transparent. Co hydroxide  $[\text{Co}(\text{OH})_2]$  and Co oxyhydroxide ( $\text{CoOOH}$ ) thin films have been

prepared by wet-processing techniques, such as electrodeposition<sup>13,14)</sup> and chemical bath deposition.<sup>15)</sup> However, applications of dry-processing techniques to form hydroxide thin films are very scarce. Sputtering is one of the most typical dry-processing techniques and has been widely used to fabricate thin films,<sup>16,17)</sup> because it is superior in its ability to form large-area films with high productivity, and it is easy to control the stoichiometry of the deposited films.

In our laboratory, Ueta *et al.*<sup>18)</sup> prepared NiOOH thin films by reactive sputtering using O<sub>2</sub> + H<sub>2</sub>O mixed gas, and obtained an EC coloration efficiency of 29 cm<sup>2</sup>/C in 1 M KOH aqueous electrolyte solution. Moreover, Li and coworkers<sup>19,20)</sup> prepared hydrated ZrO<sub>2</sub> thin films by reactive sputtering in H<sub>2</sub>O atmosphere, and found that substrate cooling was very effective in increasing the H<sub>2</sub>O content and decreasing the film density, which resulted in the high proton conductivity of the films.

In this work, we studied the formation of Co oxide and oxyhydroxide thin films by sputtering in O<sub>2</sub> and H<sub>2</sub>O gases, and examined the structure and electrochemical properties of the films. The EC properties of the films are discussed with the aim of clarifying the applicability of the sputtering technique.

## **2. Experimental Procedure**

Thin films with a thickness of 100 nm were prepared by RF magnetron sputtering. A 50 mm disk Co target (99.9% purity) was sputtered in O<sub>2</sub> and H<sub>2</sub>O gases. The total sputtering gas pressure and sputtering power were maintained at 6.7 Pa and 50 W, respectively. The substrate temperature was varied from -20 to 200 °C. Si and indium tin oxide (ITO)-coated

glass were used as substrates.

Film thickness was measured by multibeam interferometry. The crystal structure and film density of the deposited films were characterized by X-ray diffraction (XRD) analysis and X-ray reflectivity (XRR), respectively. The chemical bonding state was evaluated by Fourier transform infrared spectroscopy (FTIR). The plasma state during sputtering was characterized by plasma emission spectroscopy. Cyclic voltammetry (CV) and *in situ* optical modulation measurements were carried out in 0.1 M KOH aqueous electrolyte solution in a potential scan range from -0.44 to +0.56 V and at a potential scan rate of 20 mV/s using Ag/AgCl and Pt as reference and counterelectrodes, respectively.

### 3. Results and Discussion

Figure 1 shows the plasma emission spectra obtained in O<sub>2</sub> and H<sub>2</sub>O gases. The emission peaks corresponding to O<sub>2</sub><sup>+</sup> ions and O atoms are observed in O<sub>2</sub> plasma. Furthermore, in H<sub>2</sub>O plasma, there are additional peaks that may be attributed to H atoms and OH radicals in accordance with the results published elsewhere.<sup>21,22</sup> This indicates that some H<sub>2</sub>O molecules are decomposed into active species such as O and H atoms and OH radicals by the following reactions in the H<sub>2</sub>O plasma.<sup>23,24</sup>



We expect that OH radicals and H atoms are incorporated into the films and promote the formation of Co oxyhydroxide.

The deposition rates of the films prepared in O<sub>2</sub> gas were 0.6–0.7 nm/min and no

noteworthy temperature dependence was observed. However, deposition rates of the films deposited in H<sub>2</sub>O gas decreased from 1.2 nm/min at a substrate temperature of -20 °C to 0.5 nm/min at a substrate temperature of 200 °C. The higher deposition rate at lower substrate temperature in H<sub>2</sub>O gas suggests the incorporation of hydroxyl groups in the films. This conclusion is supported by the results of a comparison of the molar volumes of CoO<sub>4/3</sub> (13.25 cm<sup>3</sup>), CoOOH (17.50 cm<sup>3</sup>), and Co(OH)<sub>2</sub> (24.76 cm<sup>3</sup>), which may be calculated using the bulk densities of Co<sub>3</sub>O<sub>4</sub> (6.056 g/cm<sup>3</sup>),<sup>25)</sup> CoOOH (5.254 g/cm<sup>3</sup>),<sup>26)</sup> and Co(OH)<sub>2</sub> (3.753 g/cm<sup>3</sup>),<sup>27)</sup> respectively. Therefore, the deposition rate is expected to increase with increasing amount of Co hydroxide.

The structure of the films deposited on Si substrates was studied by XRD analysis using Cu K $\alpha$  radiation. As shown in Figs. 2(a) and 2(b), diffraction peaks due to the spinel Co<sub>3</sub>O<sub>4</sub> phase<sup>25)</sup> are observed in the films prepared in O<sub>2</sub> gas at all substrate temperatures and in the films prepared in H<sub>2</sub>O gas at substrate temperatures of 100 and 200 °C. The XRD peak intensity decreased with decreasing substrate temperature, and no marked peaks were observed for the film deposited in H<sub>2</sub>O at 10 and -20 °C, indicating that the films were amorphous.

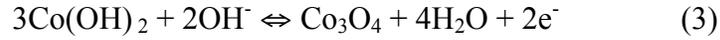
Figures 3(a) and 3(b) show FTIR spectra in a low-wave-number region for the films deposited on Si substrates at various substrate temperatures in O<sub>2</sub> and H<sub>2</sub>O gases. Absorption peaks at 564–566 and 664 cm<sup>-1</sup> were observed for the films deposited at 100 and 200 °C in O<sub>2</sub> gas and for the film deposited at 200 °C in H<sub>2</sub>O gas. The intensity of the peaks became lower with decreasing substrate temperature. For the film deposited at -20 °C in H<sub>2</sub>O, the higher-wave-number peak at 664 cm<sup>-1</sup> almost disappeared and the

lower-wave-number peak at  $566\text{ cm}^{-1}$  shifted to  $575\text{ cm}^{-1}$ . These results indicate that all the films prepared in  $\text{O}_2$  and the film deposited at  $200\text{ }^\circ\text{C}$  in  $\text{H}_2\text{O}$  are  $\text{Co}_3\text{O}_4$  because their absorption peak wave numbers are close to the reported values of  $558\text{--}570\text{ cm}^{-1}$  and  $661\text{--}663\text{ cm}^{-1}$  for  $\text{Co}_3\text{O}_4$ .<sup>28-30)</sup> The film deposited in  $\text{H}_2\text{O}$  at a substrate temperature of  $100\text{ }^\circ\text{C}$  has a mixed structure of  $\text{Co}_3\text{O}_4$  and  $\text{CoOOH}$ , and those deposited at  $10$  and  $-20\text{ }^\circ\text{C}$  are  $\text{CoOOH}$ , because their absorption peak wave numbers are close to the reported value of  $584\text{ cm}^{-1}$  for  $\text{CoOOH}$ .<sup>30)</sup>

Film density was estimated by XRR measurement and the result is shown in Fig. 4 as a function of substrate temperature. It is clear that the film density decreases with decreasing substrate temperature and the density of the film deposited in  $\text{H}_2\text{O}$  is lower than that deposited in  $\text{O}_2$ , which is similar to the results obtained for hydrated  $\text{ZrO}_2$ .<sup>21)</sup> The density of the film prepared at a substrate temperature of  $-20\text{ }^\circ\text{C}$  in  $\text{H}_2\text{O}$  gas was estimated to be approximately  $4.2\text{ g/cm}^3$ , which is much lower than those of bulk  $\text{Co}_3\text{O}_4$  ( $6.056\text{ g/cm}^3$ )<sup>25)</sup> and  $\text{CoOOH}$  ( $5.254\text{ g/cm}^3$ )<sup>26)</sup>, and it indicates that the film has highly porous structure.

The electrochemical properties of the films deposited on ITO-coated glass substrates were studied in  $0.1\text{ M KOH}$  aqueous electrolyte solution. Figures 5(a) and 5(b) show the CV curves of the films deposited at substrate temperatures of  $-20\text{ -- }+200\text{ }^\circ\text{C}$ . The current density increases with decreasing substrate temperature, which corresponds to the decrease of the film density. The shapes of the CV curves for the films deposited in  $\text{O}_2$  and for the films deposited in  $\text{H}_2\text{O}$  at high substrate temperatures of  $100$  and  $200\text{ }^\circ\text{C}$  are rectangular and redox peaks are not clearly observed. In contrast, redox peaks, which correspond to the following reactions,<sup>6,10,15)</sup> are clearly observed in the CV curves for the films deposited at

substrate temperatures of 10 and -20 °C in H<sub>2</sub>O.



The film deposited at -20 °C shows the highest current density, which indicates the enhancement of electrochemical activity.

Figure 6 shows the bleached and colored transmittance spectra of the films obtained by applying constant voltages of -0.44 and +0.56 V for 5 min. The transmittance change of approximately 10% was obtained for the Co<sub>3</sub>O<sub>4</sub> thin films deposited at -20 °C in O<sub>2</sub> gas and that of 26% was obtained for the CoOOH thin films deposited at -20 °C in H<sub>2</sub>O gas.

However, the width of the transmittance change decreased with increasing substrate temperature and no marked transmittance change was observed for the films deposited at 200 °C both in O<sub>2</sub> and H<sub>2</sub>O.

Figure 7 shows 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 a wavelength of 600 nm in bleached and colored states, respectively] of the films deposited in O<sub>2</sub> and H<sub>2</sub>O gases as functions of substrate temperature. A stable transmittance change was observed from the first cycle up to the 100th cycle. The  $\Delta Q$  and  $\Delta OD$  shown in Fig. 7 were obtained from the cyclic voltammograms after 10 cycles and were found to increase with decreasing substrate temperature. The  $\Delta Q$  and  $\Delta OD$  of the films deposited in H<sub>2</sub>O gas were higher than those of the films deposited in O<sub>2</sub> gas, and the highest  $\Delta Q$  (18 mC/cm<sup>2</sup>) and  $\Delta OD$  (0.372) were obtained for the CoOOH film deposited at -20 °C in H<sub>2</sub>O. EC coloration efficiency  $\eta$  is defined as  $\eta = \Delta OD / \Delta Q$ . An EC coloration efficiency of approximately 20 cm<sup>2</sup>/C, which

was similar to the reported values for Co oxide films,<sup>6,7,12)</sup> was obtained, and the value was almost independent of substrate temperature.

#### **4. Conclusions**

Co<sub>3</sub>O<sub>4</sub> and CoOOH thin films were prepared by reactive sputtering using O<sub>2</sub> and H<sub>2</sub>O gases with various substrate temperatures. The highest transmittance change of 26% and EC coloration efficiency of 20 cm<sup>2</sup>/C were obtained for the CoOOH film deposited at -20 °C in H<sub>2</sub>O gas. The substrate temperature has a great influence on the structure and chemical composition of the deposited films, and the CoOOH thin films, which exhibit better electrochromic properties than Co<sub>3</sub>O<sub>4</sub> films, were prepared at lower substrate temperatures in H<sub>2</sub>O gas. It is considered that the low film density and amorphous structure of the CoOOH film are responsible for the enhancement of electrochromic performance. Reactive sputtering using H<sub>2</sub>O gas at low substrate temperature is found to be a promising method for fabricating CoOOH thin films with good EC properties.

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Figure caption

**Figure 1.** Plasma emission spectra in O<sub>2</sub> and H<sub>2</sub>O gases.

**Figure 2.** XRD patterns of the films prepared at various substrate temperatures in (a) O<sub>2</sub> and (b) H<sub>2</sub>O gases.

**Figure 3.** FTIR spectra of the films prepared at various substrate temperatures in (a) O<sub>2</sub> and (b) H<sub>2</sub>O gases.

**Figure 4.** Density of the films deposited in O<sub>2</sub> and H<sub>2</sub>O gases as a function of substrate temperature.

**Figure 5.** Cyclic voltammograms of the films prepared at various substrate temperatures in (a) O<sub>2</sub> and (b) H<sub>2</sub>O gases.

**Figure 6.** Bleached and colored transmittance spectra of the films prepared at various substrate temperature (T<sub>S</sub>) in O<sub>2</sub> and H<sub>2</sub>O gases.

**Figure 7.** Transferred charge density  $\Delta Q$  and optical density change  $\Delta OD$  of the films deposited in O<sub>2</sub> and H<sub>2</sub>O gases as functions of substrate temperature.

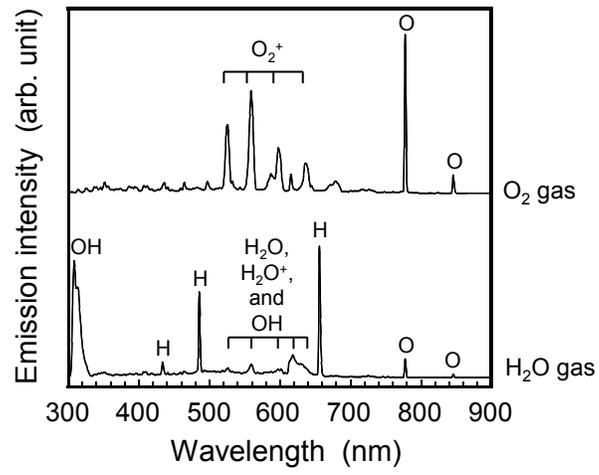


Fig. 1

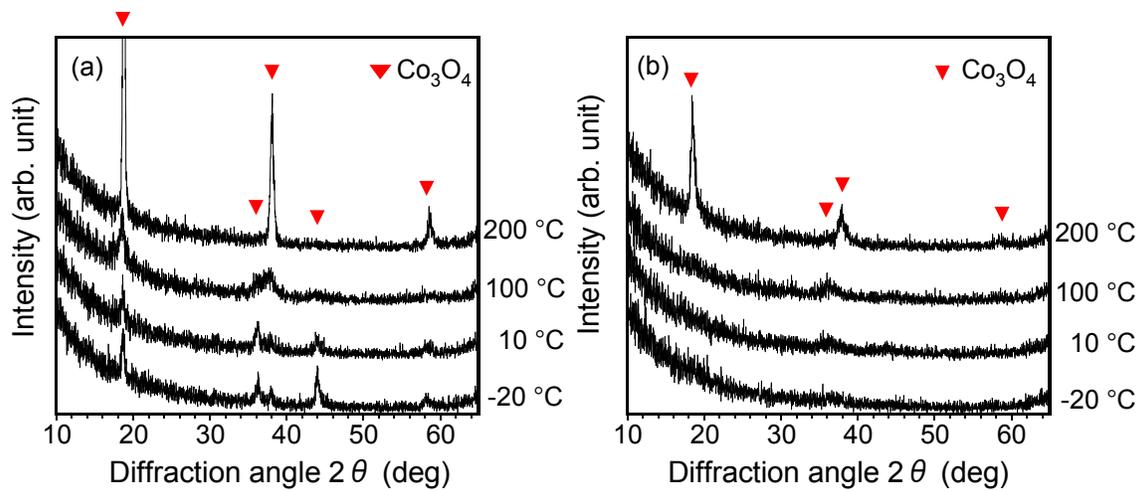


Fig. 2

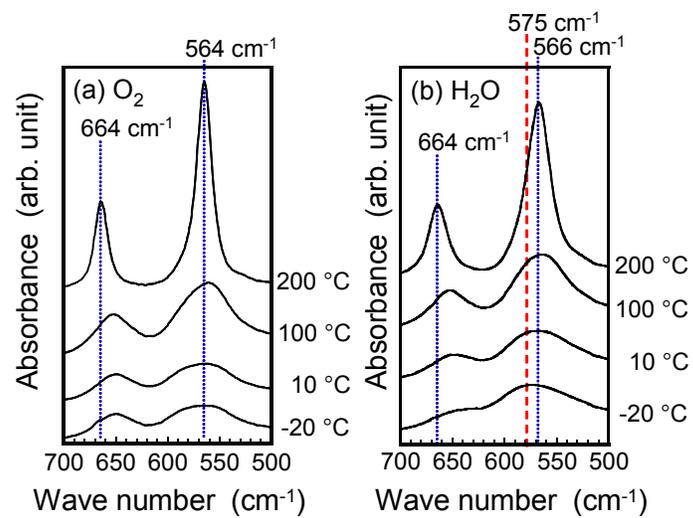


Fig. 3

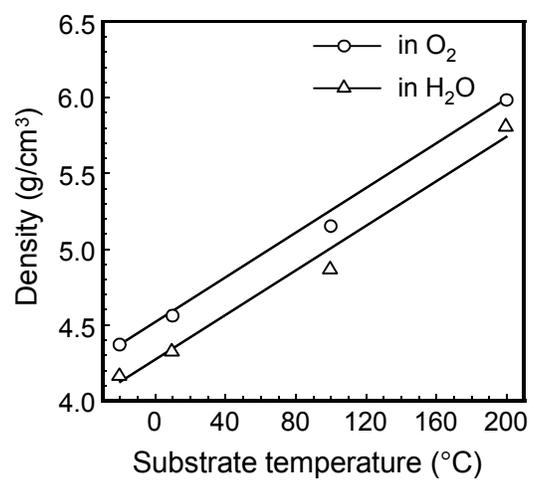


Fig. 4

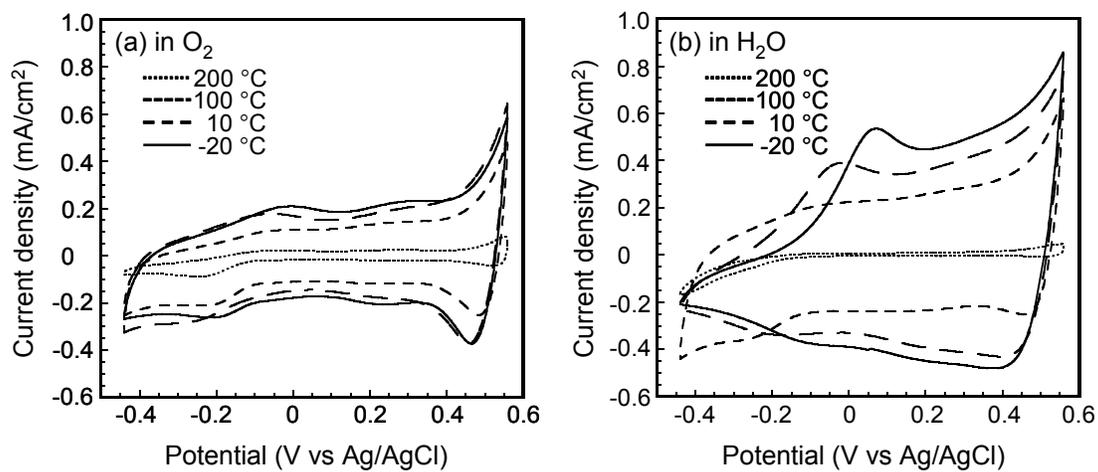


Fig. 5

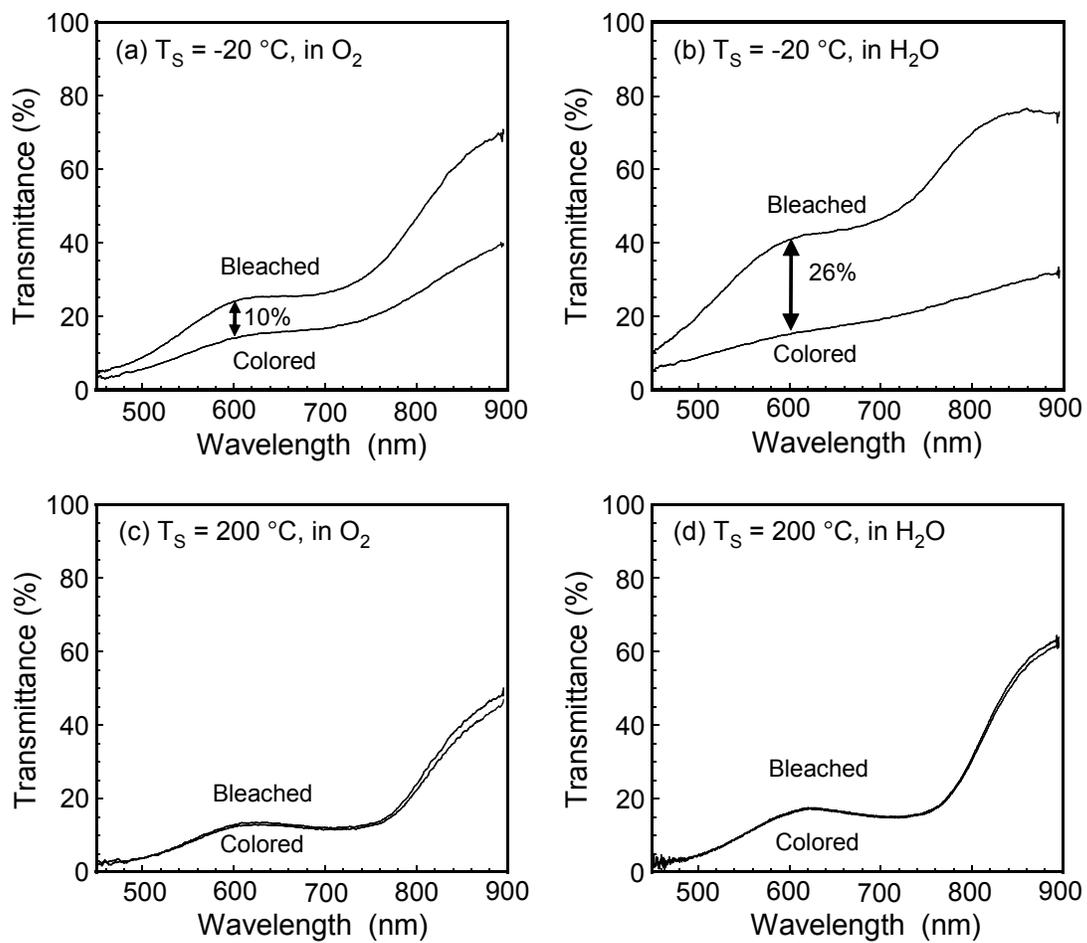


Fig. 6

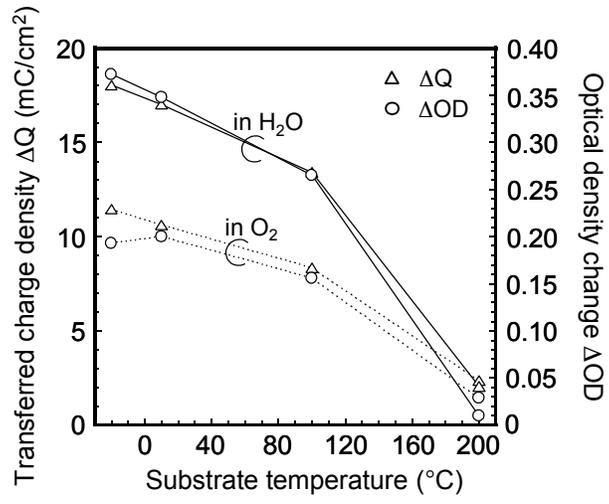


Fig. 7