

Formation of hydrated yttrium oxide and titanium oxide thin films by reactive sputtering in H₂O atmosphere and their electrical properties

Yoshio Abe^{1*}, Ning Li¹, Kosuke Nishimoto¹, Midori Kawamura¹, Kyung Ho Kim¹, and Tsutomu Suzuki²

¹*Department of Materials Science and Engineering, Kitami Institute of Technology, Kitami, Hokkaido 090-8507, Japan*

²*Department of Biotechnology and Environmental Chemistry, Kitami Institute of Technology, Kitami, Hokkaido 090-8507, Japan*

E-mail: abeys@mail.kitami-it.ac.jp

Hydrated yttrium oxide and titanium oxide thin films were prepared by reactive sputtering in H₂O atmosphere at substrate temperatures from -30 to +130 °C. The electrical conductivities of the yttrium oxide films increased with decreasing substrate temperature. The increase in electrical conductivity corresponds well to the increase in IR absorption intensity due to OH bonds, and it is considered that proton conduction is dominant in the yttrium oxide films. In contrast, the conductivity of the titanium oxide films increased with increasing substrate temperature, suggesting that electron conduction is dominant in the films.

Thin films of solid electrolytes are used as ion transport layers in electrochromic devices and switchable mirrors, which are expected to be applicable to energy-saving smart windows.¹⁻⁶⁾ Hydrogen-containing tantalum oxide and zirconium oxide are considered to be candidate proton conducting solid electrolytes, and some of their previously reported data are shown in Table I.⁷⁻¹²⁾ Although the proton conductivities of the sputtered films were relatively lower than those of the films prepared by ion plating and sol-gel techniques, the sputtering technique is considered to be suitable for forming large-area thin films with uniform thickness and quality. Our group has developed a new reactive sputtering technique using H₂O as a reactive gas and applied the technique to deposit hydrated Ta₂O₅ and ZrO₂ thin films.^{9,12)} OH radicals and atomic hydrogen formed in the H₂O plasma were incorporated into the growing films and hydrated oxide films were deposited. To clarify the applicability of the technique to various hydrated oxide films, yttrium (Y) oxide and titanium (Ti) oxide films were prepared by the H₂O sputtering technique on the basis of the reported proton conduction in Y₂O₃ and TiO₂ ceramics.^{13,14)} The effects of substrate temperature on the structural and electrical properties of Y oxide and Ti oxide films were examined in this study.

Hydrated Y oxide and Ti oxide thin films with a thickness of approximately 1 μm were deposited on silicon (<100>, boron-doped, CZ, and both-side-polished wafer with a resistivity of 0.01–1 $\Omega\cdot\text{m}$ and a thickness of 525 μm) and glass (Corning EAGLE 2000 with a thickness of 1 mm) substrates. These films were deposited from Y and Ti metal targets (2 inch diameter and 99.9% purity), in H₂O atmosphere, using an RF magnetron sputtering system. The schematic diagram of the sputtering system was reported in our previous papers.^{15,16)} The H₂O gas flow rate, sputtering gas pressure, and RF power were standardized to 2 cm^3/min , 6.7 Pa, and 50 W, respectively. The substrate temperature was changed from -30 to +130 $^{\circ}\text{C}$.

The crystal structure was characterized by X-ray diffraction (XRD) using Cu K α radiation. Chemical bonding states were studied by Fourier transform infrared spectroscopy (FTIR). Film thickness and refractive index were measured by ellipsometry at a wavelength of 633 nm. Electrical conductivity was measured by AC impedance measurements at frequencies from 10 mHz to 1 MHz in air at room temperature. Pt thin films were deposited by sputtering on glass substrates and used as electrodes. The length and gap of the coplanar Pt electrodes were 22 and 1–10 mm, respectively.

The XRD patterns of the films deposited on Si substrates are shown in Fig. 1. Diffraction peaks due to bcc Y₂O₃¹⁷⁾ and monoclinic YOOH¹⁸⁾ were observed in the Y oxide films

deposited at 130 and 70 °C, respectively, and the peaks disappeared in the films deposited at 10 and -20 °C. For the Ti oxide films, diffraction peaks due to anatase TiO_2 ¹⁹⁾ were clearly observed in the films deposited at a substrate temperature of 130 °C, and no peaks were found at substrate temperatures of -30–70 °C. The refractive index of the films is plotted as a function of the substrate temperature in Fig. 2. It is clearly seen that the refractive index of the films decreases with decreasing substrate temperature, and the values are much lower than those of bulk Y_2O_3 ($n=1.93$),²⁰⁾ YOOH ($n=1.845$),²¹⁾ and anatase TiO_2 ($n= 2.554$ for c-axis parallel and $n=2.493$ for c-axis perpendicular).²²⁾ These results indicate that low-density amorphous oxide films were formed at low substrate temperatures. On the basis of Thornton's structure model of sputtered thin films,²³⁾ it is thought that porous films with voided structures were formed at low substrate temperatures, resulting in the low film density and low refractive index.

Figure 3 shows the FTIR spectra of the Y oxide and Ti oxide films deposited on Si substrates. Broad absorption peaks due to hydrogen-bonded O-H are clearly observed in the wavelength range of 3000–3600 cm^{-1} in the films deposited at low substrate temperatures. The intensities of the absorption peaks decreased with increasing substrate temperature, and the peaks almost disappeared in the films deposited at 130 °C. These results are similar to those of Ta and Zr oxide thin films reported in the previous papers,^{9,12)} and it is considered that hydrated oxide films were prepared at low substrate temperatures. The absorption peaks at about 1600 cm^{-1} are due to H_2O in the films and in the atmosphere of the FTIR sample chamber. Absorption peaks corresponding to Y_2O_3 (557 cm^{-1}),²⁴⁾ YOOH (685 cm^{-1}),²⁵⁾ Ti-O (550–653 cm^{-1}), and Ti-O-H (1000–1300 cm^{-1}) bonds in anatase TiO_2 ^{26,27)} are also observed.

The electrical conductivities of the films were estimated from the plot of real and imaginary parts of AC impedance (Cole-Cole plot). If we assume a parallel equivalent circuit of resistance and capacitance, the electrical resistance of the film can be obtained from the semicircle of the Cole-Cole plot. The conductivities calculated from the resistances are plotted as a function of the substrate temperature in Fig. 4. The conductivities of Ta and Zr oxide films reported in our previous studies^{9,12)} are also plotted in the figure for comparison. The conductivities of Y, Ta, and Zr oxide films increased with decreasing substrate temperature, and the maximum conductivities of 10^{-6} – 10^{-5} S/m were obtained at the lowest substrate temperatures of approximately -30 °C. In contrast, the conductivity of the Ti oxide films increased with increasing substrate temperature.

Although the electrical conduction of these oxide films is thought to be a mixed

ionic-electron conduction, the increase in the conductivity of the Y oxide films corresponds well to the increase in absorption peak intensity due to OH bonds shown in Fig. 3. The proton conductivity increased with decreasing substrate temperature because of the increase in OH content and the decrease in film density. From these results, it is considered that the electrical conduction of the Y oxide films is mainly caused by proton conduction similarly to that observed in the Ta and Zr oxide films.^{9,12)} In contrast, the electrical conduction of the Ti oxide films is thought to be predominantly caused by electron transport rather than by proton transport because the highest conductivity was obtained in the film deposited at 130 °C, which has the smallest OH absorption peak. N-type semiconducting TiO₂ is thought to be formed by the incorporation of hydrogen into the films because hydrogen atoms can act as a donor.^{28,29)} The electrical conductivity of the Ti oxide films is thought to be improved by the increase in electron conductivity due to the improvement in crystallinity. The relatively low band-gap energy (3.2 eV) and high Hall mobility (0.5–3.9 cm²V⁻¹s⁻¹ for polycrystalline films and 30 cm²V⁻¹s⁻¹ for epitaxial films) of anatase TiO₂^{30,31)} seem to be the reasons why electron conduction is superior to proton conduction in the films.

In summary, hydrated Y oxide and Ti oxide thin films were prepared by reactive sputtering in H₂O atmosphere. The electrical conduction of the Y oxide films is considered to be proton conduction; however, that of the Ti oxide films is predominantly electron conduction. The low band-gap energy and high Hall mobility of Ti oxide are thought to be the reasons for the predominance of electron conduction.

Acknowledgments

This work was supported by a Grant-in-Aid for Scientific Research (C) (No. 24550228) from the Japan Society for the Promotion of Science. We would like to thank Mr. Yuki Kamiya for his assistance in sample preparation.

References

- 1) M. Kitao, H. Akram, K. Urabe, and S. Yamada, J. Electronic Mater. **21**, 419 (1992).
- 2) Y. Sone, A. Kishimoto, and T. Kudo, Solid State Ionics **70/71**, 316 (1994).
- 3) P. van der Sluis and V. M. M. Mercier, Electrochim. Acta **46**, 2167 (2001).
- 4) T. Niwa and O. Takai, Thin Solid Films **518**, 1722 (2010).
- 5) K. Tajima, Y. Yamada, S. Bao, M. Okada, and K. Yoshimura, Appl. Phys. Express **1**, 067007 (2008).
- 6) K. Tajima, Y. Yamada, S. Bao, M. Okada, and K. Yoshimura, J. Electrochem. Soc. **157**, J92 (2010).
- 7) T. Saito Y. Ushio, M. Yamada, and T. Niwa, Solid State Ionics **40-41**, 499 (1990).
- 8) N. Ozer and C. M. Lampert, J. Sol-Gel Sci. Technol. **8**, 703 (1997).
- 9) Y. Abe, F. Peng, Y. Takiguchi, M. Kawamura, K. Sasaki, H. Itoh, and T. Suzuki, Jpn. J. Appl. Phys. **47**, 7269 (2008).
- 10) K. Tajima, Y. Yamada, S. Bao, M. Okada, K. Yoshimura, Solid State Ionics **180**, 654 (2009).
- 11) S. H. Kim, J. H. Ko, S. H. Ji, J. S. Kim, S. S. Kang, M-J. Lee, and Y. S. Yoon, Jpn. J. Appl. Phys. **45**, 5144 (2006).
- 12) N. Li, M. Suzuki, Y. Abe, M. Kawamura, K. Sasaki, H. Itoh, and T. Suzuki, Sol. Energy Mater. Sol. Cells **99**, 160 (2012).
- 13) T. Norby and P. Kofstad, Solid State Ionics **20**, 169 (1986).
- 14) F. M. Vichi, M. T. Colomer, and M. A. Anderson, Electrochem. Solid-State Lett. **2**, 313 (1999).
- 15) N. Li, Y. Abe, M. Kawamura, K. H. Kim, and T. Suzuki, Thin Solid Films **520**, 5137 (2012).
- 16) Y. Abe, J. Vac. Soc. Jpn. **53**, 515 (2010) [in Japanese].
- 17) International Center for Diffraction Data (ICDD), Powder Diffraction File No. 00-041-1105.
- 18) International Center for Diffraction Data (ICDD), Powder Diffraction File No. 00-020-1413.
- 19) International Center for Diffraction Data (ICDD), Powder Diffraction File No. 00-021-1272.
- 20) W. J. Tropsch and M. E. Thomas, in *Handbook of Optical Constants of Solids II*, ed. E. D. Palik (Academic Press, San Diego, CA, 1998) p. 1079.
- 21) M. W. Shafer and R. Roy, J. Am. Ceram. Soc. **42**, 563 (1959).

- 22) M. Kiyono, *Sanka Titan* (Titanium Oxide) (Gakuzyutu Shuppan, Tokyo, 1991) p. 52 [in Japanese].
- 23) J. A. Thornton, J. Vac. Sci. Technol. **11**, 666 (1974).
- 24) H. Guo, W. Zhang, L. Lou, A. Brioude, and J. Muginer, Thin Solid Films **458**, 274 (2004).
- 25) R. F. Klevstova and P. V. Klevstov, J. Struct. Chem. **5**, 795 (1964).
- 26) M. Nakamura, L. Sirghi, T. Aoki, and Y. Hatanaka, Surf. Sci. **507-510**, 778 (2002).
- 27) T. Bezrodna, G. Puchkovska, V. Shymanovska, J. Baran, and H. Ratajczak, J. Mol. Struct. **700**, 175 (2004).
- 28) K. Xiong, J. Robertson, and S. J. Clark, J. Appl. Phys. **102**, 083710 (2007).
- 29) W. P. Chen, Y. Wang, and H. L. W. Chan, Appl. Phys. Lett. **92**, 112907 (2008).
- 30) T. Hitosugi, Y. Furubayashi, A. Ueda, K. Itabashi, K. Inaba, Y. Hirose, G. Kinoda, Y. Yamamoto, T. Shimada, and T. Hasegawa, Jpn. J. Appl. Phys. **44**, L1063 (2005).
- 31) N. Yamada, T. Hitosugi, N. L. H. Hoang, Y. Furubayashi, Y. Hirose, T. Shimada, and T. Hasegawa: Jpn. J. Appl. Phys. **46**, 5275 (2007).

Figure Captions

Fig. 1. (Black and white) XRD patterns of (a) Y oxide and (b) Ti oxide thin films deposited at various substrate temperatures.

Fig. 2. (Black and white) Refractive indices of Y oxide and Ti oxide thin films as a function of substrate temperature.

Fig. 3. (Color online) FTIR spectra of (a) Y oxide and (b) Ti oxide thin films deposited at various substrate temperatures.

Fig. 4. (Black and white) Electrical conductivities of Y oxide and Ti oxide thin films as a function of substrate temperature. The data on Ta oxide and Zr oxide thin films reported in our previous papers^{9,12)} are also shown for comparison.

Table I. Ion conductivities of Ta and Zr oxide thin films reported in previous papers.

Thin film	Ion conductivity (S/m)	Preparation method	Ref.
Ta ₂ O ₅	1.4×10^{-6}	Sputtering	7
Ta ₂ O ₅	1.5×10^{-3}	Ion-plating	7
Ta ₂ O ₅	3.2×10^{-4}	Sol-gel	8
Ta ₂ O ₅	4×10^{-6}	Sputtering	9
Ta ₂ O ₅	2.1×10^{-7}	Sputtering	10
ZrO ₂	1.67×10^{-4}	Sputtering	11
ZrO ₂	6×10^{-6}	Sputtering	12

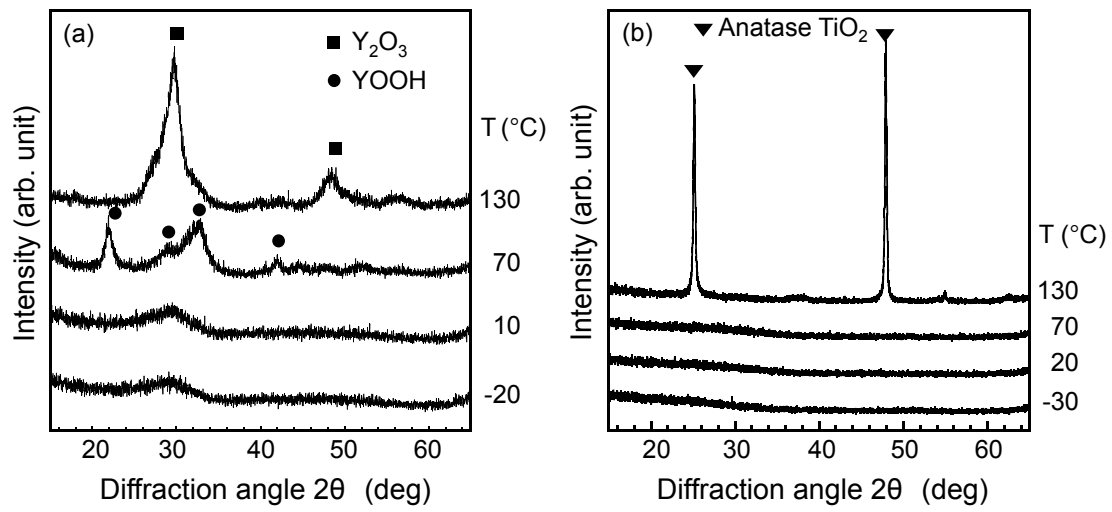


Fig. 1

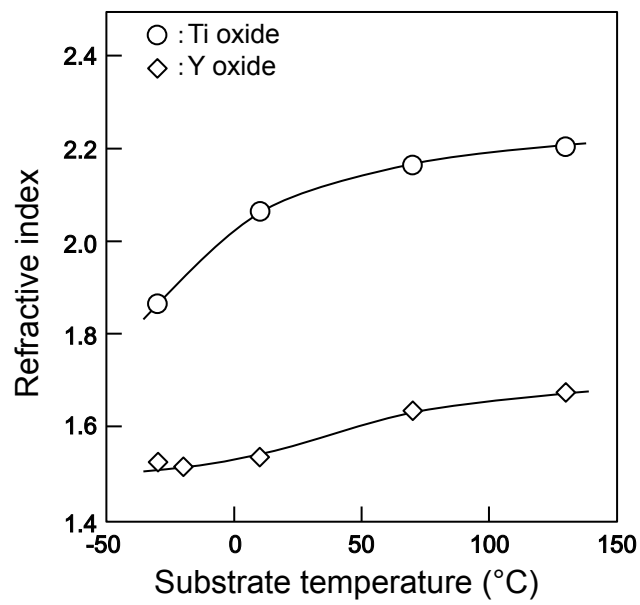


Fig. 2

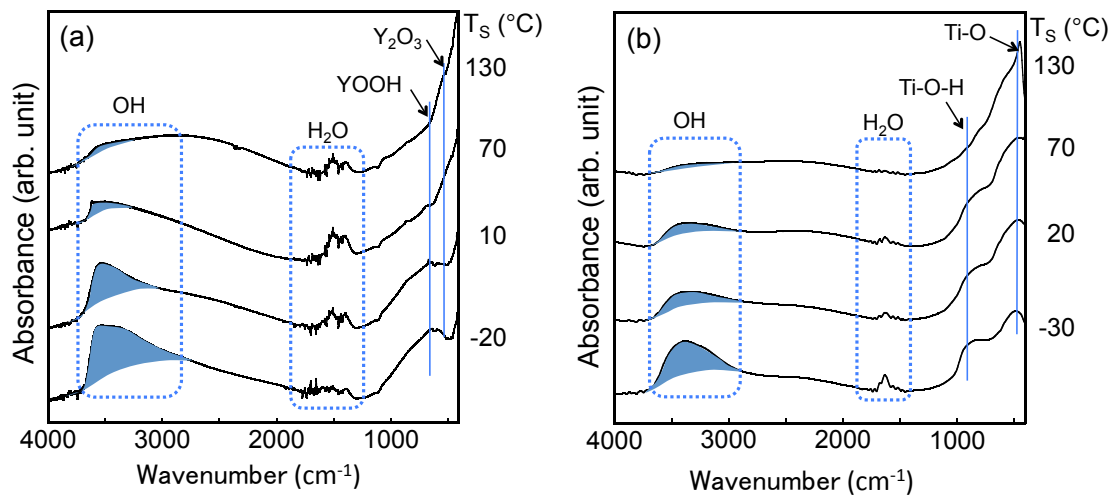


Fig. 3

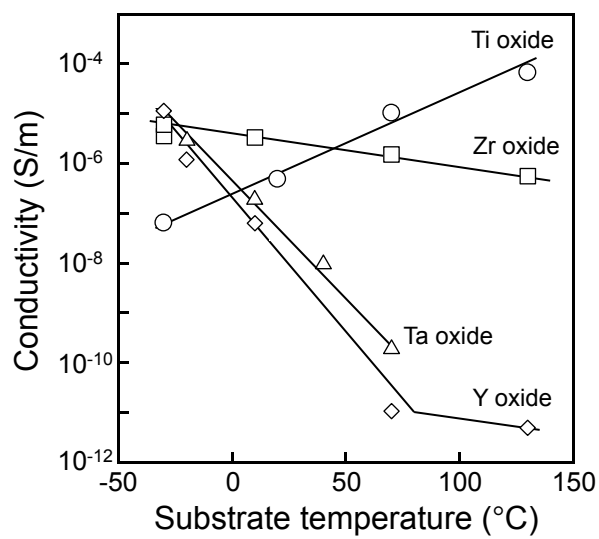


Fig. 4