

Ion conducting Properties of Hydrogen-Containing Ta₂O₅ Thin Films Prepared by Reactive Sputtering

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Abstract

Hydrogen-containing Ta₂O₅ (Ta₂O₅:H) thin films are considered to be a candidate for a proton-conducting solid-oxide electrolyte. In this study, Ta₂O₅:H thin films were prepared by reactively sputtering a Ta metal target in an O₂+H₂O mixed gas. The effects of sputtering power and post-deposition heat treatment on the ion-conducting properties of the Ta₂O₅:H thin films were studied. The ionic conductivity of the films was improved by decreasing the RF power and a maximum conductivity of 2×10^{-9} S/cm was obtained at an RF power of 20 W. The ionic conductivity decreased by heat-treatment in air, and no ion-conduction was observed after treatment at 300°C due to the decrease in hydrogen content in the films.

Keywords: proton-conducting solid electrolyte thin film, tantalum oxide, reactive sputtering, ionic conductivity

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1. Introduction

Thin-film solid electrolytes are used as ion transport layers in electrochemical devices such as microsolid-oxide fuel cells, thin film rechargeable batteries, gas sensors, micro-supercapacitors, and electrochromic devices. In the case of electrochromic devices, hydrogen-containing tantalum oxide ($\text{Ta}_2\text{O}_5\text{:H}$) thin films are considered to be a candidate for proton-conducting thin film electrolytes [1-3]. Reactive sputtering is one of the most widely used techniques for oxide film formation, and $\text{Ar}+\text{O}_2+\text{H}_2$ and $\text{Ar}+\text{O}_2+\text{H}_2\text{O}$ mixed gases have been used as reactive gases to deposit hydrogen-containing oxide thin films. From the viewpoint of experimental safety, H_2O gas (water vapor) seems to be preferable to H_2 gas, since H_2O has no risk of explosion. Residual water vapor in a sputtering chamber can also be used as a source of hydrogen; however, a well-controlled intentional H_2O supply seems to be better for reproducibility in experiments. In our previous paper [4], we reported the deposition of $\text{Ta}_2\text{O}_5\text{:H}$ films by reactive sputtering using $\text{O}_2+\text{H}_2\text{O}$ mixed gas and the incorporation of hydrogen into the films was confirmed. However, the ionic conductivity of the films was too low to be measured by AC impedance measurements. In this study, the effects of sputtering power and post-deposition heat-treatment were studied to examine the relationship between hydrogen content in the films and their ion-conducting properties.

2. Experimental

An RF magnetron sputtering system was used for sample preparation. Ta_2O_5 thin films with thicknesses of 200–400 nm were deposited on Si and indium tin oxide (ITO)-coated glass substrates by reactively sputtering a 2-inch disk Ta target (99.9% purity) in an O_2 and H_2O mixed gas atmosphere. The amount of H_2O gas introduced into the sputtering chamber was controlled using a flow-meter, and the H_2O flow ratio, $\text{H}_2\text{O}/(\text{O}_2+\text{H}_2\text{O})$, was maintained constant at 30%. The

total sputtering gas pressure and the total gas flow rate during the sputter deposition were 6.7 Pa and 5 cm³/min respectively. RF power during sputtering was varied from 20 to 50 W. The substrates were water cooled. Some of the samples were heat treated for 2 hours in air from 100°C to 300°C. The crystal structure and hydrogen content of the films were characterized by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) respectively. Samples with an Au/Ta₂O₅:H/ITO/glass structure as shown in Fig. 1 were used for AC impedance measurements in the frequency range of 10 mHz–1 MHz. An Au electrode was deposited by vacuum evaporation and the electrode area was 10 mm². Ionic conductivity was estimated by assuming an equivalent circuit shown in Fig. 2, wherein C_p and R_p are the parallel capacitance and parallel resistance respectively, and Z_w is the Warburg impedance, which is caused by a diffusion-controlled reaction at an electrode surface [5,6].

3. Results and discussion

3.1 Effects of RF power

The XRD measurements of the Ta₂O₅:H films indicated that all the films deposited in this study were amorphous. FTIR spectra of the Ta₂O₅:H films deposited on Si substrates under various RF powers are shown in Fig. 3. The broad absorption peaks at approximately 3400 cm⁻¹ are due to stretching vibrations of hydrogen bonded O-H groups [6,7]. Strong peaks at approximately 600 cm⁻¹ are due to Ta-O stretching [6,8]. Sharp peaks at approximately 1600 and 3700 cm⁻¹ are due to H₂O and those at approximately 2350 cm⁻¹ are due to CO₂ gas in the atmosphere during the FTIR measurements. The amount of hydrogen introduced into the films is thought to increase with decreasing RF power because the intensity of the peak due to the O-H groups increased with decreasing RF power. Substrate heating during sputtering was suggested to be the cause of the low

hydrogen content of the films deposited at high RF powers [4].

Impedance plots of the Ta₂O₅:H films deposited at RF powers of 20 and 50 W are shown in Fig. 4, where R and X are the real and imaginary parts of the impedance respectively. At high frequencies, the impedance is represented by a semicircle (a dotted line) and the intercept on the R axis indicates the value of R_p. At low frequencies, a linear segment is seen corresponding to the Warburg impedance. The ionic conductivity of the Ta₂O₅:H films calculated from the value of R_p is plotted as a function of RF power in Fig. 5. The ionic conductivity increased with decreasing RF power and a maximum conductivity of 2×10⁻⁹ S/cm was obtained at an RF power of 20 W.

3. 2. Effects of post-deposition heat-treatment

The Ta₂O₅:H film deposited at 20 W was heat-treated in air, and the FTIR spectra before and after the treatment are shown in Fig. 6. It is clearly seen that the intensity of the broad peak due to the O-H groups decreases after heat treatment at 200°C, and it almost disappears after heat treatment at 300°C. It is thought that hydrogen atoms are removed from the films as H₂O molecules. Corresponding to the change in the FTIR spectra, the ionic conductivity of the films decreased with increasing heat treatment temperature as shown in Fig. 7. This result clearly indicates that hydrogen atoms incorporated into the Ta₂O₅:H films contribute to the ionic conduction of the films, and the ionic conductivity decreases with decreasing hydrogen content. Although the exact chemical bonding state of hydrogen atoms is not clear, part of the hydrogen atoms are expected to be incorporated into the films as tantalum hydroxide and the remaining hydrogen atoms are present in the films as physisorbed and chemisorbed water [4].

4. Conclusion

Hydrogen-containing amorphous Ta₂O₅ films were prepared by reactive sputtering in an O₂+H₂O mixed gas. The ionic conductivity increased with decreasing RF power and the maximum conductivity of 2×10^{-9} S/cm was obtained at 20 W. The ionic conductivity of the films decreased by heat treatment in air due to the decrease in hydrogen content in the films.

Acknowledgements

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Figure captions

Fig. 1 Structure of a sample used for AC impedance measurements.

Fig. 2 Equivalent circuit used for estimating ionic conductivity.

Fig. 3 FTIR spectra of Ta₂O₅:H films deposited at various RF powers.

Fig. 4 Impedance plots of Ta₂O₅:H films deposited at RF powers of 20 and 50 W. The measurement frequency f was varied from 10 mHz to 1 MHz.

Fig. 5 Ionic conductivity of Ta₂O₅:H films as a function of RF power.

Fig. 6 FTIR spectra of Ta₂O₅:H films before and after heat treatment in air.

Fig. 7 Ionic conductivity of Ta₂O₅:H films as a function of heat-treatment temperature.

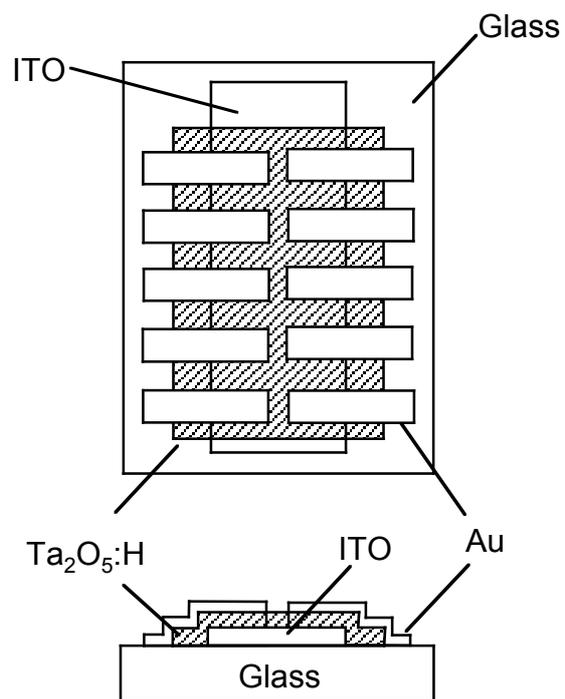


Fig. 1

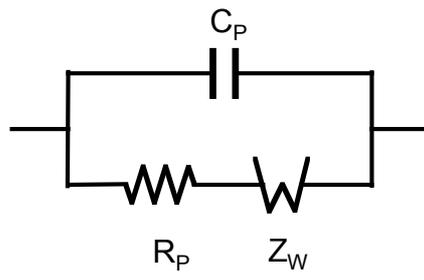


Fig. 2

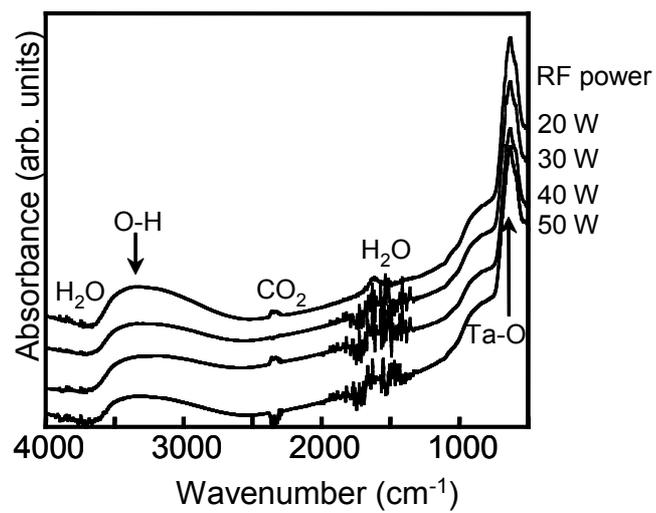


Fig. 3

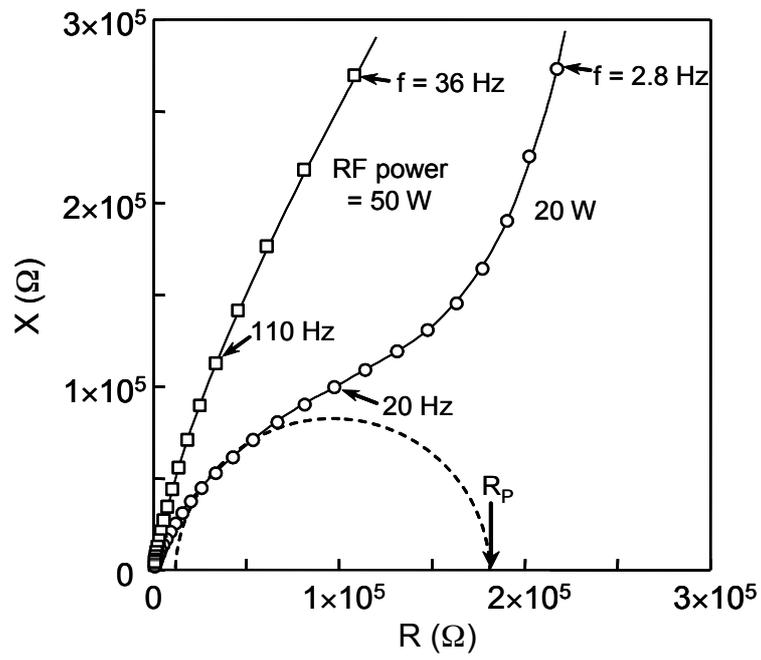


Fig. 4

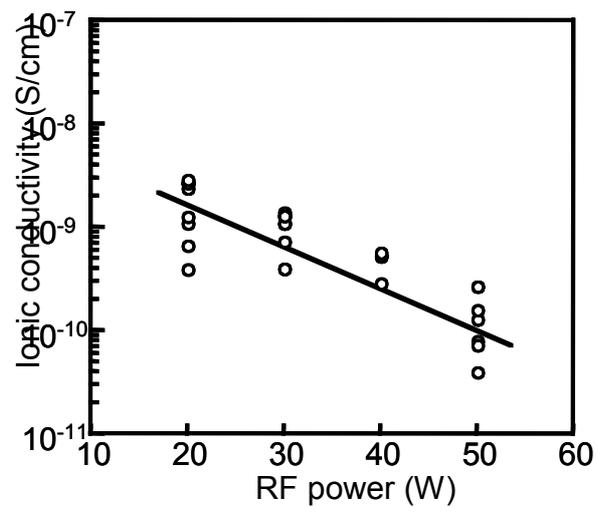


Fig. 5

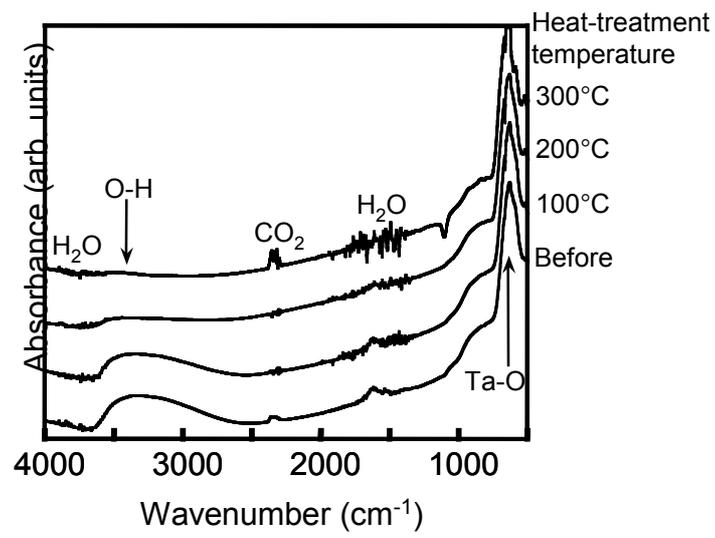


Fig. 6

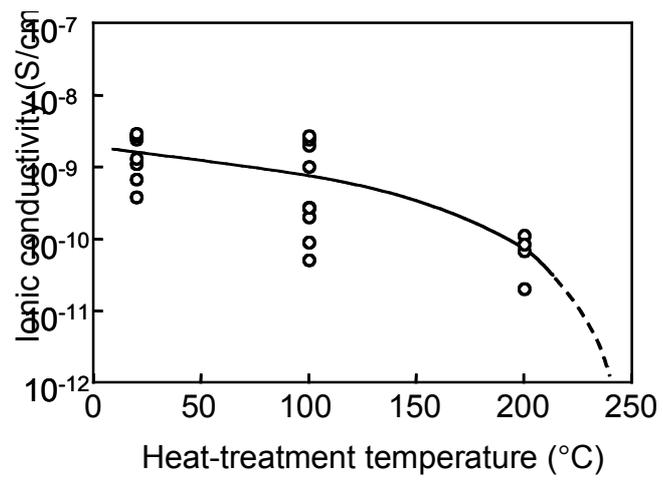


Fig. 7