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Evaluation of ion conductivity of ZrO_2 thin films prepared by reactive sputtering in O_2, H_2O, and $H_2O + H_2O_2$ mixed gas

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ABSTRACT

Hydrated ZrO_2 thin films were prepared by reactive sputtering in O_2, H_2O, and $H_2O + H_2O_2$ mixed gas, and the effect of the sputtering atmosphere on ion conductivity of the films was investigated. The results showed that the films deposited in O_2 gas exhibited poor ion conductivity; however, the ion conductivities of the films deposited in the other two kinds of atmosphere were similar and 300–500 times higher than that of the films deposited in O_2 gas. It was indicated that the higher ion conductivity of the films was caused by lower film density and higher water content.

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1. Introduction

Electrochromic (EC) materials change their optical properties during electrochemical oxidation and reduction through ion insertion. A standard EC device typically consists of five layers [1], including an anodic EC layer, an ion-conducting layer, a cathodic EC layer, with these three layers sandwiched between two transparent conducting layers for optical modulation. The electrolyte plays an important role as the ion-conducting layer in EC systems. Nowadays, liquid electrolytes are widely used due to their high ion conductivities; however, dissolution of the EC layers by the liquid electrolyte and leakage limit the application and development of liquid electrolytes [2]. Instead, the development of solid electrolytes [3] has been pursued by various groups. Among the different types of solid electrolytes, proton conductors have been the focus of recent attention because of their high ion conductivities due to the ease of proton migration. In view of the high ion conductivity [4,5] and poor electronic conductivity [6], hydrated $ZrO_2 \cdot nH_2O$ thin films are promising proton conductor candidates in EC devices [7–9].

Oxide thin films with proton conductivity have been deposited by RF magnetron sputtering using $Ar + O_2$ [10] or $H_2 + O_2 + Ar$ [11] as reactive gas. Although the films deposited in $H_2 + O_2 + Ar$ have high ion conductivities, there is danger of explosion (the range of explosion for H_2 in O_2 is 4.65–93.9 vol.% at 1 atm). In an earlier study, we prepared hydrated ZrO_2 thin films by sputtering using H_2O, and the results showed that the ion conductivity of the films increased with decreasing substrate temperature and a high ion conductivity of 6×10^{-8} S/cm was obtained for the thin films deposited at a substrate temperature of −30 °C [12]. Bando et al. [13] anticipated that H_2O_2 produces higher amount of OH radicals than H_2O, and they used $Ar + H_2O_2$ gas as the sputtering atmosphere to prepare amorphous indium tin oxide (ITO) transparent conductive electrode films. In this study, O_2, H_2O, and $H_2O + H_2O_2$ mixed gas were used, and the effects of the reactive gas atmosphere on the ion conductivities of hydrated ZrO_2 thin films prepared by RF magnetron sputtering were investigated in detail.

2. Experimental details

Hydrated ZrO_2 films with thickness of approximately 100 nm and 0.5–1 μm were deposited by RF magnetron sputtering. A 50 mm diameter Zr target disk (99.9% purity) was sputtered in O_2, H_2O, and $H_2O + H_2O_2$ mixed gas, respectively. Fig. 1 shows the reactive RF magnetron sputtering system used in this study. A liquid source tank was loaded with pure water or 30% hydrogen peroxide to supply H_2O or $H_2O + H_2O_2$ mixed gas, respectively. The inside of the tank was coated with polytetrafluoroethylene (PTFE) and a PTFE tube was used for the transportation of gas to avoid the decomposition of H_2O_2. The background pressure, sputtering gas pressure, sputtering power, and substrate temperature were maintained at 1.1×10^{-4} Pa, 6.7 Pa, 50 W, and 20 °C, respectively. During sputtering, the flow rates of O_2, H_2O, and $H_2O + H_2O_2$ mixed gas were maintained at 1, 0.33, and 0.33 ml/min, respectively. Indium tin oxide (ITO)-coated glass and Si were used as substrates. The thickness and refractive index of the deposited films were characterized by ellipsometry (Mizojiri DVA-FL) at a wavelength of 633 nm. The film density and crystal structure were characterized by X-ray reflectivity and X-ray diffraction (XRD) (PANalytical X'Pert diffractometer) using

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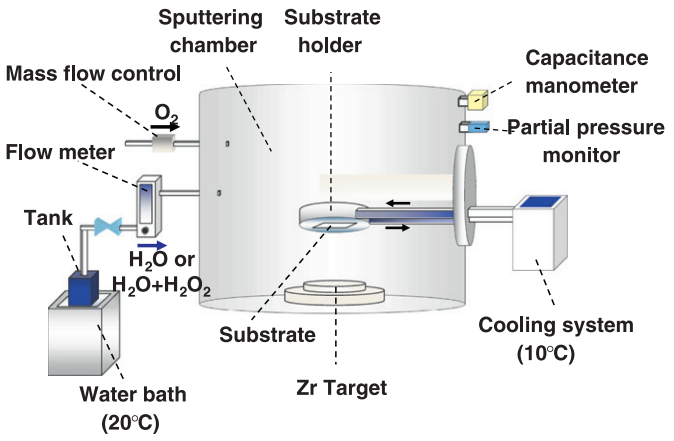

Fig. 1. Schematic diagram of the reactive RF magnetron sputtering system used in this study.

Cu Kα radiation (λ = 0.154 nm) operated at 40 mA and 45 kV in the symmetric θ/2θ configuration. The chemical bonding state was evaluated by Fourier transform infrared spectroscopy (FTIR) (JASCO FT/IR-6100) with a resolution of 16 cm^{-1} in the air. The plasma state during sputtering was characterized by plasma emission spectroscopy (Ocean Optics S2000 fibre optic spectrometer). The elemental composition of the hydrated ZrO_2 films was measured by Rutherford Backscattering Spectrometry (RBS) and Hydrogen Forward Scattering Spectrometry (HFS), which were carried out by the Evans Analytical Group. He^{++} ion beam with the energy of 2.27 MeV was used for the RBS and HFS experiments, and expected uncertainties were ±1, ±3, and ±2 at.% for Zr, O, and H, respectively. Ion conductivity was measured by AC impedance measurements (Solartron SI 1260 impedance/gain-phase analyzer and 1296 dielectric interface) at frequencies from 10 mHz to 1 MHz in air at room temperature with a relative humidity of approximately 20% for the sample with the Au/ZrO_2/ITO structure. The structure of the samples used for the AC impedance measurements and the equivalent circuit for the calculation of ion conductivity were the same as those used in a previous study [12,14].

3. Results and discussion

The deposition rate, refractive index, and density of thin films with thickness of 100 nm prepared on Si substrates in the different atmospheres are listed in Table 1. The deposition rate of the films deposited in H_2O, and $H_2O + H_2O_2$ was higher than that of the films deposited in O_2 gas, which suggests the incorporation of H_2O molecules in the films deposited in H_2O and $H_2O + H_2O_2$ atmosphere. The refractive index and density of the films deposited in O_2 gas were higher than those deposited in the other two kinds of gas, and the values for films deposited in H_2O gas were a little lower than those deposited in $H_2O + H_2O_2$ mixed gas. The reason for this result is considered to be that porous structure was formed in H_2O gas and $H_2O + H_2O_2$ mixed gas.

XRD patterns of the deposited films with a thickness of 1 μm prepared on Si substrates are shown in Fig. 2. Diffraction peaks due to monoclinic-ZrO_2 [15] are clearly observed. However, the crystal structure of the films did not change when alternating the three reactive atmospheres.

Table 1
Deposition rate, refractive index, film density and ion conductivity of the films deposited in different reactive gas atmospheres.

Sputtering gas atmosphere	Deposition rate (nm/min)	Refractive index	Density (g/cm^3)	Ion conductivity (S/cm)
O_2	0.54	2.09	5.50	6.7×10^{-11}
$H_2O + H_2O_2$	1.42	1.92	4.20	2.2×10^{-8}
H_2O	1.43	1.90	4.05	3.3×10^{-8}

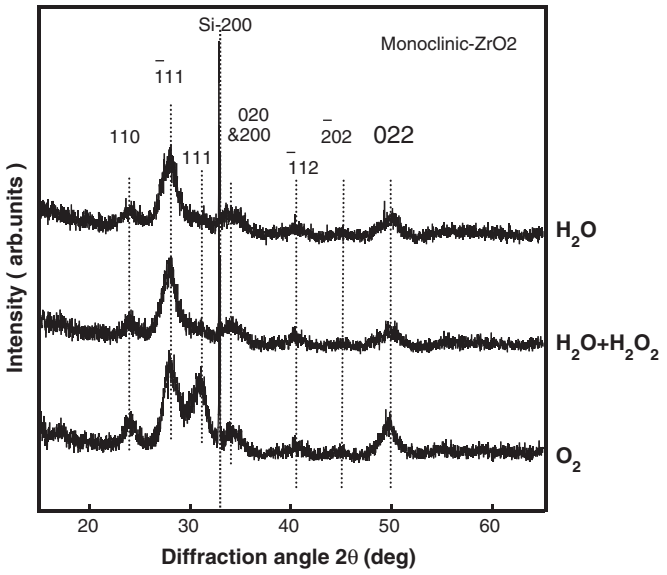

Fig. 2. XRD patterns of the films with a thickness of 1 μm deposited on Si substrates in different reactive gas atmospheres. The substrate temperature was maintained at 20 °C.

FTIR spectra of the films deposited on Si substrates in different atmosphere were measured in transmission mode, and are shown in Fig. 3. The films were thick enough to cause the optical interference oscillations in the FTIR spectra. Absorption peaks due to Zr–O groups [16,17] were seen around 740 cm^{-1} for all the films, indicating the formation of ZrO_2. Absorption peaks due to hydrogen bonded OH groups [18] were also observed in the region from 2800 to 3700 cm^{-1} for all the films. However, the peak intensity of the film deposited in O_2 gas was low, and the highest peak intensity was obtained for the film deposited in H_2O gas. The observed H_2O molecules in the film deposited in O_2 gas are thought to be introduced from the air after the film was taken out from the sputtering chamber. However, the H_2O molecules in the films deposited in the two other kinds of atmosphere are considered

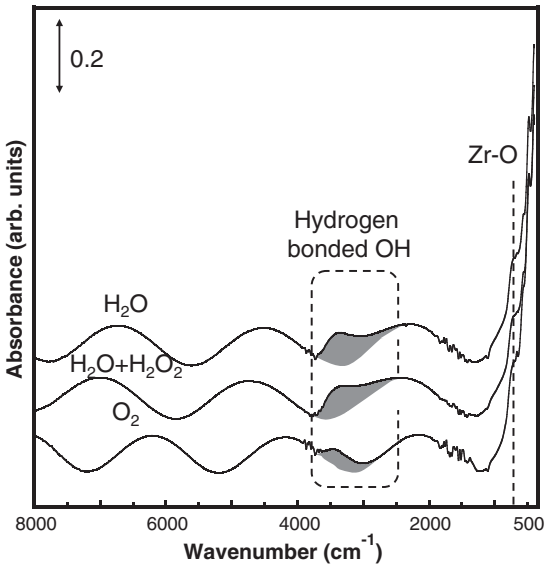

Fig. 3. FTIR spectra of the films with a thickness of 1 μm deposited on the Si substrates in different reactive gas atmospheres. The substrate temperature was maintained at 20 °C.

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