Proton Conductive Tantalum Oxide Thin Film Deposited by Reactive DC Magnetron Sputtering for All-Solid-State Switchable Mirror

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Abstract. Our developed all-solid-state switchable mirror as a smart window is consisted in multi-layer of Mg,Ni/Pd/Ta_2O_5/WO_3/ITO/glass and can switch reversibly from the reflective state to the transparent one. The development of high performance solid electrolyte thin film of Ta_2O_5 is important for fast speed switching and high durability of the device. In this work, we have investigated the electrochemical property of Ta_2O_5 thin film deposited by reactive DC magnetron sputtering. The effect of thickness on electrochemical and proton conductivities of Ta_2O_5 thin film was investigated. The Ta_2O_5 thin film with a thickness of 400 nm had better proton conductivity of $1.5 \times 10^{-9}$ S/cm measured by AC impedance method. The transmittance at wavelength of 670 nm of the device with 400 nm thick Ta_2O_5 thin film was changed from 0.1% (reflective state) to 51% (transparent state) within 10 s by applying voltage of 5 V. The device showed high durability up to two-thousand switching cycles.

1. Introduction
A high performance smart window which controls light and heat is investigated and developed for low energy and low environmental load. It is well known that the glass with an electrochromic material of tungsten oxide (WO_3) controls its transmittance by changing its color because of the reversible intercalation and deintercalation of ions in the crystal structure of WO_3 [1,2]. However, the absorption-type smart window discharges radiant heat into the room.

Recently, we have developed and demonstrated the all-solid-state switchable mirror as a new smart window [3-8]. The device changes its optical property reversibly from a transparent state to a reflective one as a result of hydrogenation and dehydrogenation of the films by applying voltage. The heat can be effectively controlled because the reflective state can reflect the light almost completely, and radiant heat can not be discharged into the room. Our reflection-type device had the multi-layer structure of Mg-Ni/Pd/Ta_2O_5/WO_3/ITO/glass. Each material of Mg-Ni, Pd, Ta_2O_5 and WO_3 in the device plays optical switching, proton injector, solid electrolyte and ion storage, respectively. It is one of the key technologies to develop high performance solid electrolyte thin film for fast switching speed and high durability of the device.

In this work, we focused on the reactive DC magnetron sputtering to deposit solid electrolyte of Ta_2O_5 thin film. The effect of thickness on electrochemical property and proton conductivity of Ta_2O_5 thin film was investigated. Moreover, the film was applied to the device and optical switching property of the device was measured.
2. Experimental

2.1. Fabrication of the device
The all-solid-state switchable mirror was prepared by magnetron sputtering on a WO3/ITO/glass substrate (Geomatec). First, the Ta2O5 thin film was deposited by reactive DC magnetron sputtering using a 2-inch tantalum metal target with a purity of 99.99% in mixture gas of argon and oxygen. The ratio of Ar/O2 gas flow was set to be 4.7. A sputtering power was 65 W, and a working pressure was 0.8 Pa. The thickness of the film was varied from 100 nm to 400 nm. After deposition, the device was dipped in the 0.5 M sulfuric acid solution. The ITO film on the device and platinum wire were used for the electrodes. When a voltage of 2 V was applied to the electrodes, protons in the solution were injected into the WO3 film across the Ta2O5 film electrically and 0.1 C/cm2 were stored up the film. The WO3 film was changed to be HXWO3, and it showed dark blue color.

After the device was cleaned and dried, Pd and Mg-Ni thin films were deposited by DC magnetron sputtering. The deposition chamber has three magnetron sputtering guns with metal targets of palladium, magnesium and nickel with a purity of 99.99%. The Pd thin film with a thickness of 4 nm was coated the Ta2O5 thin film on the device. A sputtering power was 14 W, and a working pressure was 1.2 Pa. Then, the Mg-Ni thin film with a thickness of 40 nm was deposited on the Pd thin film by co-sputtering of magnesium and nickel targets. An adjusting sputtering power ratio of Mg/Ni of 1.88 was used to fabricate Mg4Ni thin film which had better optical switching property than other compositions [5].

2.2. Characterization
The conventional ac impedance method was carried out to characterize the Ta2O5 thin film. We evaluated the property referring to the previous research [9]. When the Ta2O5 thin film was characterized by ac impedance method, we used the sample of the Ta2O5 thin film coated ITO/glass substrate. The surface was coated by aluminum electrode. The sinusoidal potential modulation of 100 mV in the frequency range from 50 mHz to 20 kHz and dc bias of -400 mV were used for the measurement. A frequency analyzer provided the small amplitude ac modulation to the potentiostat (Solartron, 1280). The measurement system was controlled by computer using software of ZPlot (Scribner Associate). The measured impedance data was plotted on the complex plane to estimate the proton conductivity of the film using application software of ZView2 (Scribner Associate). The cyclic voltammetry was performed using a potentiostat (Hokuto Denko, HA-501G) and a function generator (Toho Tech. Research, FG-02) with a standard three-electrode configuration consisting of the device as a working electrode, a conventional Ag/AgCl (sat. KCl) electrode and a Pt counter electrode. The Ta2O5 thin film covered WO3/ITO/glass substrate was estimated in 0.5M sulfuric acid solution. Linear potential sweep cycling was performed in the range of -1 to 0.5 V at the sweep rate of 50 mV/s.

The change of optical transmittance and reflectance of the device was measured by the combination of a laser diode (λ=670nm) and a Si photo diode with applying voltage of ±5 V between the optical switching layer of Mg4Ni and ITO.

3. Results and discussion

3.1. Characterization of Ta2O5 thin film
The Ta2O5 thin film was fabricated on the ITO/glass substrate to evaluate its electrochemical property. The Cole-Cole plots were used to display the impedance of the film as shown in Fig. 1(a). The proton conductivity of the film was estimated by computer simulation using assumed equivalent circuit as shown in Fig. 1(b). In Fig. 1, $R_e$ is the resistance of the electrode, $R_p$ is the ionic resistance and CPE is the constant phase element, respectively. The values of proton conductivity were estimated by the measured impedance data. The proton conductivity of the films were $7.8 \times 10^{-10}$, $1.2 \times 10^{-9}$ and $1.5 \times 10^{-9}$ S/cm at the thickness of 100 nm, 200 nm and 400 nm, respectively. This result suggests that the proton conductivity of the film was increased with increasing the thickness of the film.
Figure 1. Impedance plot of Ta$_2$O$_5$ thin film and assumed equivalent circuit.

Figure 2 shows the cyclic voltammetry curve of the Ta$_2$O$_5$/WO$_3$/ITO/glass in 0.5 M sulfuric acid solution. The current density was small for the Ta$_2$O$_5$ with a thickness of 100 nm covered WO$_3$/ITO/glass substrate. On the other hand, the current density was large for the Ta$_2$O$_5$ with a thickness of 400 nm covered WO$_3$/ITO/glass substrates. This means that the Ta$_2$O$_5$ thin film with a thickness of 400 nm had higher proton conductivity than that of other films. The result was reasonably understood from the estimated proton conductivity by ac impedance method from the result of Fig. 1.

Figure 2. Cyclic voltammogram for the Ta$_2$O$_5$/WO$_3$/ITO/glass with a sweep rate of 50 mV/s.

3.2. Optical switching property of the device

Figure 3 shows optical switching property of the device. The state of the device was changed by applying voltage of ±5 V. When a voltage was applied to the device at 5 s, protons in the WO$_3$ thin film were transferred to the Mg$_4$Ni thin film across the Ta$_2$O$_5$ thin film and the Mg$_4$Ni thin film was hydrogenated to be hydrides of Mg$_2$H and Mg$_2$NiH$_4$. The hydride state showed the transparent state, resulting in the switching of the state of the device. The switching speed from reflective state to transparent one became faster with increasing of the thickness of the Ta$_2$O$_5$ thin film as shown in Fig. 3(a). The fast switching speed of 10 s and transmittance of approximately 51% was showed for the device with the 400 nm thick Ta$_2$O$_5$ thin film. The surface reflectance was also rapidly decreased from 64% to 16% as shown in Fig. 3(b).

The long-cycle switching test was carried out to investigate the durability of the device. The test was measured by a repetition of applying voltage of 5 V for 60 s followed by applying voltage of -5 V for 60 s. Figure 4 shows the switching durability of the device. The result showed that the devices with 400 nm thick Ta$_2$O$_5$ thin films had higher durability up to two-thousand switching cycles than that of other devices. Even after two-thousand switching cycles, the device showed the transmittances of 15% and 45% at the reflective state and the transparent one, respectively. On the other hand, the device with 100 nm thick Ta$_2$O$_5$ thin film showed faster degradation than that of other devices. These results suggest that the durability of the device was affected by the thickness of Ta$_2$O$_5$ thin film.
4. Conclusions
We have investigated the electrochemical property such as proton conductivity of Ta$_2$O$_5$ thin film for the development of high performance solid electrolyte to apply the all-solid-state switchable mirror. The film was fabricated by reactive DC magnetron sputtering and its thickness was varied from 100 nm to 400 nm for investigating the effect of the thickness of the Ta$_2$O$_5$ thin film on electrochemical property and optical switching property of the device. The Ta$_2$O$_5$ thin film with a thickness of 400 nm showed higher proton conductivity of $1.5 \times 10^{-9}$ S/cm than that with other thicknesses. The device using Ta$_2$O$_5$ thin film with a thickness of 400 nm was able to switch from the reflective state to the transparent state within 10 s by applying voltage. The transmittance at a wavelength of 670 nm was approximately 51% for the transparent state. The surface reflectance was also rapidly changed from 64% to 16% within 10 s. The device showed high durability of two-thousand switching cycles.

5. References
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