Improvement of Durability of Electrochromic Switchable Mirror in Environment

Kazuki Tajima*, Hiromi Hotta, Yasusei Yamada, Masahisa Okada and Kazuki Yoshimura
National Institute of Advanced Industrial Science and Technology (AIST), Shimo-shidami, Moriyama-ku, Nagoya 463-8560
Fax: 81-52-736-7305, e-mail: k-tajima@aist.go.jp

A durability of an electrochromic switchable mirror glass was evaluated in the accelerated degradation test with a constant temperature of 40°C and a relative humidity of 80% for improvement of the durability in the environment. A fluorocarbon polymer was also developed as a surface coating layer of the device to avoid environmental negative impact. Although the conventional device without surface coating rapidly degraded in the test, the device with surface coating exhibited high durability under high temperature and high relative humidity conditions and excellent optical switching properties with high transmittance of around 52.2% in the transparent state. Therefore, we achieved to develop the device with high durability in the environment.

Key words: thin film, sputtering, durability, environment, surface coating

1. INTRODUCTION
Conventional windows allow a considerable amount of infrared solar radiation to enter a room. Therefore, the energy costs of air conditioning increases in summer. A switchable mirror has been investigated and developed for use as a new energy-saving window [1-5]. The switchable mirror glass is expected to effectively control solar radiation incoming into a room.

These hydride complexes have higher transparency, resulting in a transparent state. In its reflective state, it can effectively control the solar radiation coming into a room.

For practical use of the device, it will be required for high durability in the environmental use and stable optical switching properties of the device. For example, it is well known that conventional windows are often affected by environmental factors such as temperature and humidity. In above mentioned, when we investigate the relationship between environment and the device properties, the conventional device has weakness for environment with high temperature and high relative humidity conditions [7]. For above reasons, it should be develop the device with high durability in environment in the viewpoint of commercial use of the device.

In this work, the relationship between environmental factors and device properties was investigated by an accelerated degradation test using a simulated environment with constant temperature and constant relative humidity controlled by a thermostat/humidistat bath in details. Moreover, a suitable surface coating layer to avoid these problems was researched and developed on the device for high durability in environment.

2. EXPERIMENT
2.1 Device fabrication
A commercial WO3/ITO/glass substrate (30×30×1.1 mm², Geomatec co.) was used as a substrate. First, the Ta2O5 thin film (thickness: 400 nm) was deposited by reactive direct current (dc) magnetron sputtering in a mixture gas of argon and oxygen at a ratio of 7:1, respectively. A 2-inch tantalum metal (purity: 99.99%) was used as target. The sputtering power was 70 W, and the working pressure was 0.75 Pa. After that, the sample was dipped into 0.5 M sulfuric acid solution to inject protons into the WO3 film across the Ta2O5 thin film under an applied voltage of 2.3 V, resulting in formation of H3WO4.

Then, an Al thin film (2 nm) was deposited by dc magnetron sputtering. A 2-inch aluminum metal (99.99%) was used as target. The sputtering power was 50 W, and the working pressure was 0.62 Pa. Next, the Pd and Mg-Ni thin films were prepared by dc magnetron sputtering with metal targets of palladium, magnesium and nickel, each with purity of 99.99%. To deposit the Pd thin film (4 nm), the sputtering power was 14 W, and the working pressure was 1.2 Pa. The Mg-Ni thin film (40 nm) was deposited on the Pd thin film by co-sputtering of magnesium and nickel targets using a sputtering power ratio for Mg and Ni of 1:88:1, respectively [3]. All processes were carried out at room temperature.

Finally, a commercial fluorocarbon polymer (DS-3320Z, Harves co.) was spin-coated onto the surface of the device at a rotational speed of 4000 rpm. After that, each sample was exposed to laboratory conditions, that is, 25°C and relative humidity of 40%. The fabricated layer had a thickness of around 10µm.
2.2 Degradation study
The as-prepared device was put in a thermostat/humidistat bath (PR-1K, Espec Co.) in order to investigate the impact of environmental conditions. Both the temperature and relative humidity in the bath could be controlled to maintain constant values. The fluctuations as well as the distribution of the temperature and relative humidity in the bath were controlled automatically by a computer. In this study, the temperature was set to 40°C and the relative humidity was set at 80%. Changes in surface morphology were induced after only few days. These results related to the degradation of the device without surface coating. Although the surfaces of the device showed a smooth surface with surface roughness of approximately Ra = 1.5 nm, as shown in Fig. 1(a). As the holding time in the bath increased, the surface of the device became rough, with the formation of large grains on the surface. Its grain size increased to approximately 400 nm with a surface roughness of Ra = 28.7 nm for after 14 days, as shown in Fig. 2(c).

2.3 Characterization of device
Changes in the optical switching properties of the device were measured with a 670-nm laser diode as well as a Si photodiode. Electrodes were connected between the Mg, Ni and ITO thin films on the device. The applied voltage was controlled via LabVIEW. The changes in the optical properties of the device were also measured via a scanning program of LabVIEW. The surface of the device was evaluated by atomic force microscopy (AFM, VN-8000, Keyence Co.) with optical microscopy.

3. RESULTS AND DISCUSSION
3.1 Surface images
Figure 1(a) to 1(f) show optical surface images of the device. Figs. 1(a) to 1(c) are results for the conventional device without surface coating and Figs. 1(d) to 1(f) show the results for the device with surface coating. All the as-prepared samples of the device had flat surfaces, as shown in Figs. 1(a) and 1(d). However, when the device was kept in the bath, the surface was damaged, as indicated by the appearance of many cracks under an optical microscope, as shown in Figs. 1(b) and 1(c). The changes in surface morphology were induced after only few days. These results related to the degradation of the surface metallic layer by the environmental factors of temperature and humidity [7]. In our previous work, high temperature and high relative humidity conditions became the Mg, Ni layer rougher because of the reaction with oxygen and moisture in the atmosphere. The layer changed to the non-metallic state of oxide and hydroxide. On the other hand, the device with surface coating did not show any typical structure on the surface even in same time kept in the bath.

![Fig. 1. Optical surface images of EC switchable mirror device. (a) to (c) are results for the conventional device without surface coating, (d) to (f) are results for the conventional device with surface coating.](image)

3.2 Optical switching properties
Figure 3 shows the optical switching properties of the device under an applied voltage of ±5 V. When the voltage was applied to the device with surface coating at time t = 5 s, its transmittance changed from 0.1% in the reflective state to 52.2% in the transparent state within 30 s. When the reversed voltage was applied to the device at time t = 65 s, the device switched from the transparent state to the reflective state within 20 s. Although these switching times were slightly slow, the device with surface coating exhibited high transmittance in the transparent state. The switching range was also improved compared with conventional device. In particular, the change in reflectance of the device with the new structure was between 59.7 and 6.8%. The device without surface coating had a range between 57.1 and 14.2%. The range improved by approximately 23%. These results appear to be related to interference multilayer. Thus, although the device with surface coating had thicker layer than the conventional device because it had more one layer of surface coating, it exhibited excellent optical switching properties.

![Fig. 3. Optical switching properties of the device under applied voltage of ±5 V. (a) Change in optical transmittance and (b) change in optical reflectance of device.](image)

Figure 4 shows the transmittance spectra of the device. Fig. 4(a) shows the results for the device with surface coating.
coating and Fig. 4(b) shows the results for the device without surface coating. The spectra were measured directly when a voltage was applied in situ. In comparison with the device without surface coating, notable changes in the spectra were observed in the wavelength range of 200 to 2500 nm. The device with surface coating exhibited high transmittance in the visible range, as shown in Fig. 4(a). The visible transmittance ($T_{vis}$) was calculated using the following equation:

$$T_{vis} = \frac{\sum \lambda V_\lambda \cdot T(\lambda)}{\sum \lambda V_\lambda} \quad (1)$$

where $D_\lambda$ is the spectral distribution of standard illuminant D65 defined by the International Commission on Illumination (CIE), $V_\lambda$ is the CIE standard luminosity factors, $T(\lambda)$ is the acquired optical transmittance. The calculated transmittance in the visible transmittance was 47.4%. This value was higher than that of the conventional device (42.4%), as shown in Fig. 4(b).

![Fig. 4. Transmittance spectra of the device. (a) with surface coating and (b) without surface coating.](image)

Figure 5 shows the results on the durability of the device in the bath. Fig. 4(a) shows the result for the device with surface coating and Fig. 4(b) shows the result for the device without surface coating in the bath at 40°C and relative humidity of 80%. In the test, the device without surface coating degraded rapidly. After being kept in the bath for 14 days, the switching speed of the device without surface coating became slow around 8 min and a maximum transmittance was also reduced to only 33% in the transparent state, as shown in Fig. 5(b). On the other hand, the device with surface coating had high durability, as shown in Fig. 5(a). Even after 30 days, the device with surface coating had a switching speed of 3 min. These results appeared to be related to degradation of the optical switching layer of the Mg$_2$Ni thin film. In our previous work, the optical switching layer of the Mg$_2$Ni thin film was degraded by the atmospheric negative impact [7]. The atmosphere includes high humidity degraded the layer, and the layer changed to a non-metallic state of magnesium and nickel observed by X-ray photoelectron spectroscopy. As a result, the optical switching properties of the device became poorer for the device without surface coating. On the other hand, the device with surface coating exhibited better optical switching property. These results indicate that the fluorocarbon polymer layer works as a surface coating layer to avoid the effect of the environmental negative impact on the device properties.

In our future work, we will investigate the relationship between the fabrication method of the surface coating layer and the device properties in detail under same test using thermostat/humidistat bath to understand the environmental effects.

4. CONCLUSIONS

We investigated the durability of EC switchable mirror glass under accelerated degradation test using thermostat/humidistat bath with constant temperature of 40°C and the relative humidity of 80%. Moreover, a surface coating layer of fluorocarbon polymer suitable for the device was also developed. Although the device without surface coating degraded and showed rougher surface in the test, the device with surface coating did not show any typical structure on the surface even if 14 days passed. The optical switching properties of the device in the environment were evaluated. The device without surface coating was not robust against the environment. On the other hand, although the switching speed from the reflective state to the transparent states became slower slightly for the device with surface coating, the maximum transmittance in the transparent state and the switching range was improved by interference of multilayer. These results suggest that the device with surface coating has high durability in the environment.

5. ACKNOWLEDGEMENT

This work was supported by Industrial Technology Research Grant Program in 2009 (Project No.09B35402a) from New Energy and Industrial Technology Development Organization (NEDO) of Japan.

References

(Received December 20, 2010; Accepted March 12, 2011)