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Si incorporated diamond-like carbon film-coated electrochromic switchable mirror glass for high environmental durability

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Abstract

Electrochromic switchable mirror glass is promising for energy-saving windows because it changes between a reflective and a transparent state when a voltage is applied. In our previous work, we confirmed that the device degraded at high temperatures and high relative humidity using an accelerated degradation test. The degradation was related to the reaction of the moisture in atmosphere with the surface optical switching layer of the Mg–Ni thin film. Therefore, we have developed a device with a Si incorporated diamond-like carbon thin film surface layer to improve the environmental durability. When the device was kept in a simulated environment at a constant temperature of 40 °C and a constant relative humidity of 60%, optical and atomic force microscopy showed that the surface did not degrade. Moreover, the surface coating repelled water, which prevented the reaction of the moisture with the Mg–Ni thin film. The optical switching speed from the transparent state to the reflective state of the device was slower than that of the uncoated device because of the fabrication conditions. The result seems to be related to the surface of the Mg–Ni layer which might be damaged by the conditions.

Keywords: Switchable mirror; Thin film; Diamond-like carbon; Environment; Durability

1. Introduction

High-performance smart windows can control the inflow of heat and lower the environmental impact of air conditioning during the summer months. Electrochromic (EC) materials, such as tungsten oxide (WO_3), are promising for practical applications because of their well-controlled light absorbance [1,2]. WO_3 can change between a transparent and an opaque blue state; when it is used in conventional windows, the opaque state can absorb the sunlight and control the inflow of heat. However, the window glass can be heated by the sunlight absorbed by the material, resulting in lower energy savings in houses and buildings.

Switchable mirror materials have been investigated for use in new energy-saving windows [3–5]. The material changes between a transparent and a reflective state through the hydrogenation and dehydrogenation of a Mg–Ni film [6,7]. Therefore, its use in energy-saving windows for houses and buildings would reduce the energy consumed by air conditioning during the summer more effectively because it would reflect away the solar radiation instead of absorbing it. Our EC switchable mirror glass consists of a $Mg_4Ni/Pd/Al/Ta_2O_5/WO_3$ (including protons)/indium-tin oxide (ITO) multilayer on a glass substrate [5]. The layers function as an optical switching layer, a proton injector, a buffer, a solid electrolyte, an ion storage layer and a transparent conductor, correspondingly. When a voltage is applied to the device, the protons in the ion storage layer move to the optical switching layer, and the Mg_4Ni thin film is hydrogenated to form MgH_2 and Mg_2NiH_4. These hydrides exhibit higher transparency, and the mirror switches to the transparent state.

We confirmed that the EC switchable mirrors degraded under environmental conditions [8,9]. The durability of the device under various conditions was evaluated using accelerated degradation tests in a thermostat/humidistat bath. High temperatures and high relative humidity strongly affected the optical switching properties and the surface of the device [8]. In particular, the surface optical switching layer of the Mg–Ni thin film was damaged and stopped functioning. Therefore, a

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device durable under various environmental conditions is required for practical use. Suitable surface coating materials were developed for the device [9]. However, the switching speed, transparency, and durability of the device were not sufficient. In the present study, we investigated as the surface coating layer of the device, Si incorporated diamond-like carbon (Si-DLC), which is a hard, low friction, low wear material, and it has gas-barrier property and also is relatively transparent in visible light [10]. The durability of the device was investigated in accelerated degradation tests at a constant temperature and relative humidity.

2. Experimental

2.1. Device fabrication

Commercial WO_3/ITO/glass ($30 \times 30 \times 1.1$ mm^3, Geomatec Co.) was used as a substrate. A Ta_2O_5 thin film (thickness: 400 nm) was deposited by reactive direct current (DC) magnetron sputtering using a 2 in. Ta metal target with a purity of 99.99%. The gas mixture flow ratio of argon and oxygen was 7:1, the sputtering power was 70 W, and the working pressure was 0.7 Pa. An electrical charge of 0.10 C was injected into the WO_3 thin film by applying a voltage of 2.3 V in 0.5 M sulfuric acid. The WO_3 film was hydrogenated to H_xWO_3, and bronzed. A Pd thin film (thickness: 4 nm) was deposited by DC magnetron sputtering using a 2 in. Pd target with a purity of 99.99%. The sputtering power was 14 W, and the working pressure was 1.2 Pa. Subsequently, a Mg–Ni thin film (40 nm) was deposited on the Pd thin film by co-sputtering Mg and Ni targets, both with a purity of 99.99%. The composition of the film was controlled by adjusting the Mg/Ni sputtering power ratio, as in our previous work [3].

Finally, the surface of the device was coated with a Si-DLC thin film using our PBII system. A description of our PBII system, which uses bipolar pulses, has been described elsewhere [10–12]. Tetramethylsilane (TMS, Si $(CH_3)_4$) was used as the precursor gas for fabricating the Si-DLC thin film. The coating conditions are as follows: TMS gas flow of 3.0 sccm at the pressure of 1.8 Pa with +pulse: +1.5 kV, 0.25 μs, and −pulse: −4.0 kV, 1 μs. The coating time was 1 min. The structure of the device is shown in Fig. 1(a). The structure was also observed by transmission electron microscopy (TEM).

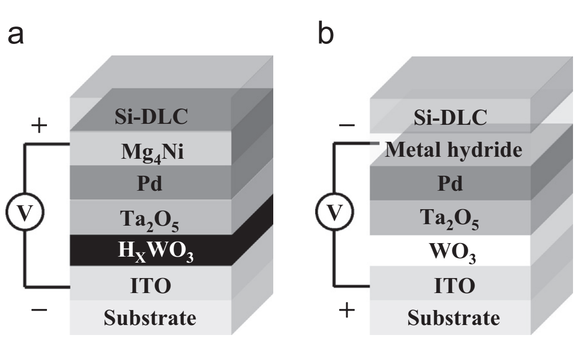

Fig. 1. Schematic image of the Si-DLC coated electrochromic switchable mirror glass.

The fabricated film contained approximately 30 at% of Si [13]. In our fundamental studies of the film, the typical transmittance of the film with a thickness of 185 nm was approximately 63% at the wavelength of 670 nm [10].

2.2. Accelerated test in a simulated environment

An accelerated test was carried out to investigate the effect of the environmental conditions on the optical switching properties of the device. A thermostat/humidistat bath (PR-1K, Espec Co.) with a constant temperature of 40 °C and relative humidity of 60% was used [8], which simulates typical conditions during the rainy season and summer in Japan, as well as common conditions in other high temperature and high humidity areas of the world.

2.3. Characterization of the EC switchable mirror

The surface state of the device was characterized by atomic force microscopy (AFM) with optical microscopy (VN-8000, Keyence Co.). The contact angle of the device was measured with an automatic contact angle goniometer (DMs-200, Kyowa Co.) in order to evaluate water repellence. Changes in the optical switching properties of the mirror device were measured with a combination of a laser diode (670 nm) and a silicon photodiode. A voltage was applied using electrodes connected between the Mg–Ni and ITO thin films. The applied voltage for evaluating optical switching properties was controlled using LabVIEW. This program was also used to measure the change in the optical switching properties of the device.

3. Results and discussion

Fig. 1 shows the structure of the Si-DLC coated EC switchable mirror glass. The initial structure is shown in Fig. 1(a). When a voltage was applied to the device, the protons in the ion storage layer moved to the optical switching layer, resulting in the transparent hydrogenated state (Fig. 1 (b)). This is a reversible reaction; when the reversal voltage was applied to the device, the device reverted to its initial mirror state. Fig. 2 shows low and high resolution cross-sectional images of the Si-DLC coated EC switchable mirror glass. The top of the surface of the device was coated with a 50-nm-thick Si-DLC thin film. The film was distorted by the solid electrolyte Ta_2O_5 layer of thin film, because of the sputter deposition conditions.

Fig. 3(a)–(f) shows optical surface images of the Si-DLC coated EC switchable mirror glass in the thermostat/humidistat bath. The surface of the as-prepared device was light yellow because of the interference of the Si-DLC thin film surface. When the device was kept in the bath conditions for times of up to 30 days, the optical microscope images of the device surface showed no damage. In our previous work, the uncoated device was easily damaged at these high temperatures and relative humidities [8]. This suggests that the surface coating layer of the Si-DLC thin film successfully protected the device. The dependence of the surface morphology on the duration of the exposure to the heat and humidity was also evaluated by AFM.

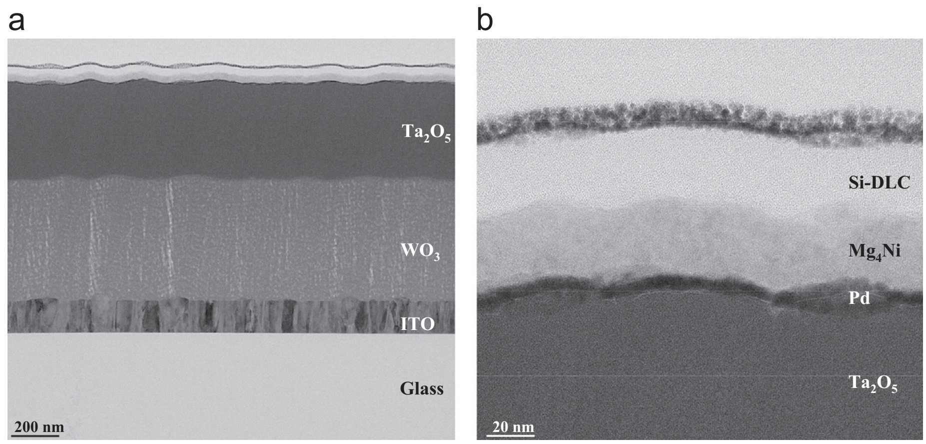

Fig. 2. Surface cross-sectional images of the Si-DLC coated electrochromic switchable mirror glass: (a) low resolution and (b) high resolution.

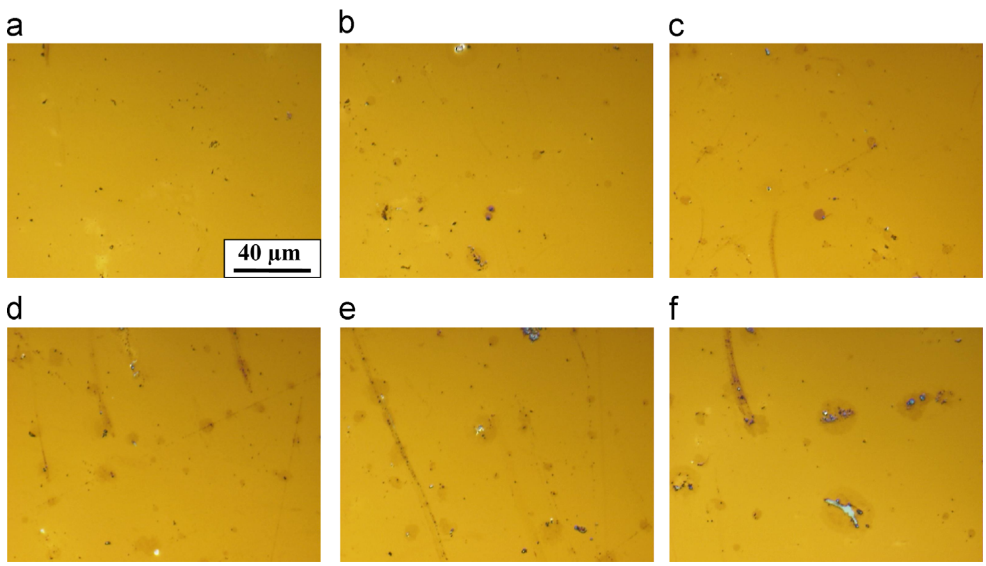

Fig. 3. Optical microscope images of the Si-DLC coated electrochromic switchable mirror glass surface after various times in the thermostat/humidistat bath: (a) the as-prepared film, (b) after 2 days, (c) after 6 days, (d) after 10 days, (e) after 20 days, and (f) after 30 days.

Fig. 4 shows the AFM surface images of the Si-DLC coated EC switchable mirror glass in the bath. The as-prepared device had a smooth surface with a surface roughness of $R_a = 3.2$ nm (Fig. 4(a)). When the device was kept in the bath conditions, the surface roughness of the device did not change significantly (Fig. 4(b)–(f)). The surface roughness of the device was $R_a = 2.8$ nm after 3 days, $R_a = 3.4$ nm after 6 days, $R_a = 3.3$ nm after 10 days, $R_a = 2.7$ nm after 20 days, and $R_a = 2.9$ nm after 30 days. Compared to the Si-DLC coated device, the uncoated device degraded rapidly and the surface optical switching layer reacted with the moisture in the atmosphere [8]. The Mg–Ni thin film was converted to the non-metallic oxide and hydroxide state. The metallic state of the Mg–Ni thin film is required to maintain the optical switching properties of the device. When the film was converted to the non-metallic state by the atmospheric conditions, the device lost its optical switching properties, because the metallic Mg–Ni thin film must be hydrogenated for the switching to occur. In contrast, the optical microscope images showed that the surface of the device with the Si-DLC surface coating was not damaged (Fig. 3). This indicates that the Si-DLC thin film protected the Mg–Ni thin film from moisture. We also confirmed the water repellence of the device by measuring the contact angle.

Fig. 5 shows the contact angle of the EC switchable mirror glass. Purified water (0.1 mL) was placed on the surface of the device, and the contact angle was monitored at intervals of 0.1 s. The images show the contact angle 0.1 s after the water was placed on the surface. Fig. 5(a) shows the contact angle of the uncoated device, and Fig. 5(b) shows the contact angle of the Si-DLC coated device. The uncoated device had a contact angle of 42.8°, and the value decreased with time. This suggests that the water reacted rapidly with the surface metal, and the water drop probably also penetrated the inside of the layer. The Si-DLC coated device showed a high contact angle of 92.8°, and repelled the water drop. Therefore, the Si-DLC layer repelled water efficiently.

Fig. 6 shows the switching speed of the Si-DLC coated EC switchable mirror glass between the reflective and transparent

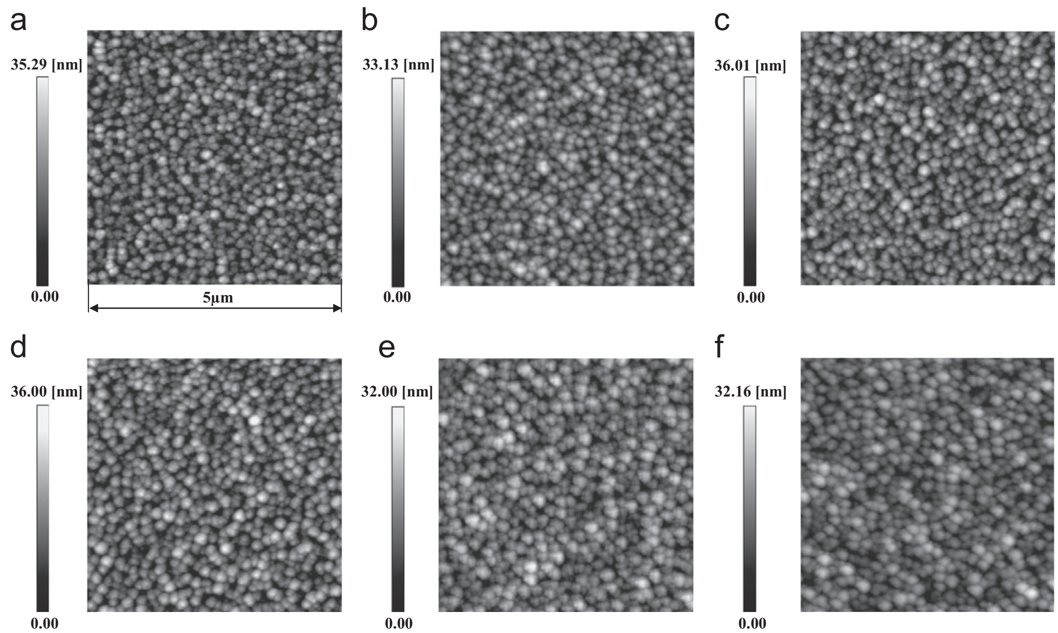

Fig. 4. AFM images of the Si-DLC coated electrochromic switchable mirror glass after various times in the thermostat/humidistat bath: (a) the as-prepared film, (b) after 2 days, (c) after 6 days, (d) after 10 days, (e) after 20 days, and (f) after 30 days.

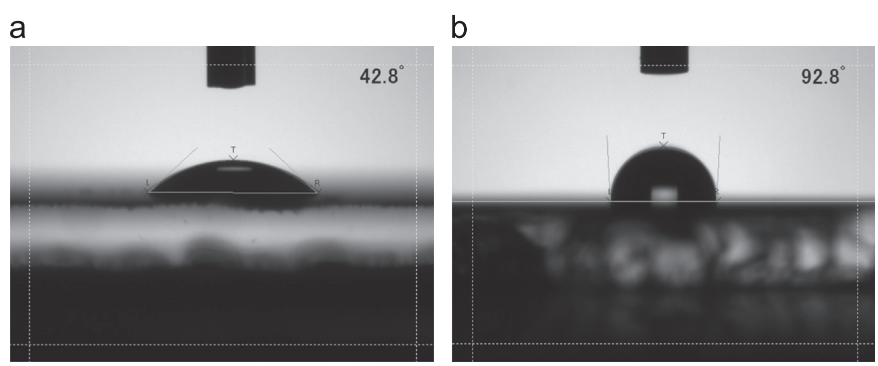

Fig. 5. Contact angle of the electrochromic switchable mirror glass for evaluating water repellence: (a) the uncoated device and (b) the Si-DLC coated device.

states at an applied voltage of ± 5 V. For example, when the voltage was applied at $t = 5$ s, the transmittance of the device changed from 0.1% (reflective state) to 42.1% (transparent state) within 30 s (Fig. 6(a)). When the reversal voltage was applied to the device at $t = 65$ s, the state changed to the reflective state. The reflectance also changed during switching, from 54.3% in the reflective state to 16.7% in the transparent state (Fig. 6(b)). Although the device with the Si-DLC coating also showed optical switching properties, the properties were inferior to the uncoated device. The reason seemed to be related to the surface of the Mg–Ni layer which might be damaged by PBII process dependeing on the fabrication conditions of a Si-DLC layer. When the voltage was applied at $t = 5$ s, the transmittance of the device changed from 0.1% in the reflective state to 36.3% in the transparent state within 120 s. Moreover, the reflectance of the initial metallic reflective state was 45.2% because of the absorption of light by the Si-DLC thin film, which is light yellow. The reflectance in the transparent state was higher than that of the uncoated device for the same reason. The durability of the device in the thermostat/humidistat bath for 20 days was also evaluated. Fig. 6(c) shows that the uncoated device had slower switching speed of around 1200 s that of the Si-DLC coated device in the bath conditions. The result suggested that the uncoated device was damaged by the bath conditions. In particular, the surface Mg–Ni layer changed to nonmetallic state of oxide and hydroxide in high temperature and high humidity conditions [8]. On the other hand, the Si-DLC coated device avoided the environmental negative effects by surface coating. The properties of the layer, such as the density, adhesion to the other layers, composition, and material, may also contribute to the optical switching properties. In order to improve the optical switching speed, the effect of the fabrication conditions on the structure of the device must be investigated for the surface coating layer. Furthermore, high transmittance, high reflectance, and a greater difference between the optical properties of the opaque and transparent states are required for practical applications of the device. Although we have developed a durable device using a Si-DLC layer surface coating, the optical switching properties are not yet sufficient. We intend to study the effects

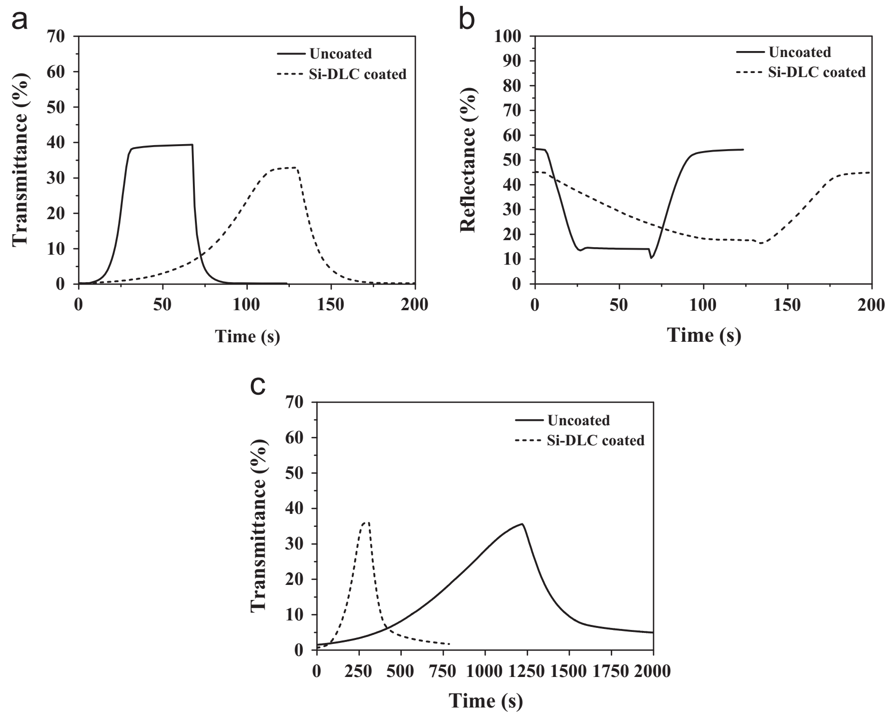

Fig. 6. Switching speed of the Si-DLC coated EC switchable mirror glass under an applied voltage of ± 5 V: (a) Change in transmittance, (b) change in reflectance and (c) durability in the thermostat/humidistat bath for 20 days.

of the surface coating layer on the optical switching properties of the device further.

4. Conclusions

A highly durable electrochromic switchable mirror glass was developed by using a Si-DLC thin film as a surface coating layer. The surface of the device was not damaged during the accelerated degradation test under a constant temperature and relative humidity in a humidistat/thermostat bath. The surface of the device was still very smooth after 30 days, with a surface roughness of $R_a = 2.9$ nm, which was similar to that of the as-deposited device. Furthermore, the water repellence of the Si-DLC thin film was confirmed by measuring the contact angle. The Si-DLC coated device showed a contact angle of 92.8°, which was higher than that of the uncoated device. These results suggest that the Si-DLC thin film protected the device from temperature and humidity. However, the speed of switching between the reflective and transparent states of the device with the Si-DLC coating was slower than that of the uncoated device. In future work, we intend to develop a highly durable device with better optical switching properties by optimizing the fabrication conditions for the Si-DLC coated device.

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