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Degradation studies of electrochromic all-solid-state switchable mirror glass under various constant temperature and relative humidity conditions

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A B S T R A C T

We have developed an electrochromic switchable mirror that consists of all-solid-state thin films. The device can be switched between reflective and transparent states by applying a voltage. This device can potentially be applied to new energy-saving windows because the reflective state of the mirror can effectively control the solar radiation coming into a room. To realize such practical applications, the effects of environmental factors such as temperature and humidity on the optical switching properties of the device should be investigated in detail. In this work, we evaluated the effects of the environment on the device for various constant temperature and relative humidity conditions, which were controlled by a thermostat/humidistat bath. When the device was stored at 50 °C and 80% relative humidity (RH) for only 7 days, its surface became much rougher (R_a=21.9 nm) as a result of degradation of the Mg_4Ni thin film on the surface. Moreover, the degraded device lost its optical switching properties. The device was strongly affected by high temperatures and high relative humidity in the atmosphere, resulting in rapid degradation. To address this problem, a device with a protective surface layer was also fabricated, and its durability was evaluated by the same method. The device with the protective layer was found to retain its optical switching properties under a harsh environment.

1. Introduction

Switchable mirror materials have been investigated and developed as a new energy-saving window to reduce the environmental load of houses, buildings and automobiles [1–6]. These materials can switch their optical properties between transparent and reflective states via hydrogenation and dehydrogenation of their constituent films. The motivation behind this research was that conventional window glasses allow a substantial amount of solar radiation to enter a room, which in turn generates heat. This problem is particularly acute in summer, when increased use of air conditioning leads to higher energy costs. Although some energy-saving windows based on double glazing and low-emission glasses have come into widespread use, the heat shielding of such windows remains insufficient. On the other hand, use of the proposed switchable mirror material as a window material is expected to control the inflow of heat into a room effectively by reflection of solar radiation.

The electrochromic (EC) switchable mirror developed by our research group consists of all-solid-state thin films, with a multilayer structure of $Mg_4Ni/Pd/Al/Ta_2O_5/H_XWO_3$/indium tin oxide (ITO) on a glass substrate [7,8]. The layers of Mg_4Ni, Pd, Al, Ta_2O_5, WO_3, and ITO act as an optical switching, a proton injector, a buffer, a solid electrolyte, an ion storage layer and a transparent conductor, respectively. The as-prepared device is in the reflective state, and switches to the transparent state under an applied voltage of a few volts. When voltage is applied to the device, the protons in the ion storage layer (WO_3) flow into the optical switching layer (Mg_4Ni), and Mg_4Ni is hydrogenated to form MgH_2 and Mg_2NiH_4. The hydrides have higher transparency, effectively switching the device to a transparent state.

In our recent work, we investigated the effects of the environment on the optical switching properties of the device [8,9]. The surface layer consisting of the Mg_4Ni thin film was found to degrade when exposed to heat and humidity. The optical switching performance of the device deteriorated when stored under constant conditions of 30 °C and 80% relative humidity (RH) for an extended period in a thermostat/humidistat bath [9]. In a typical environment, window glasses are often exposed to various environmental conditions. Furthermore, Japan has four distinct seasons among which the temperature, relative humidity, solar radiation, and other environmental factors differ greatly. To improve the durability of the device, the relationship between various environmental factors and the optical switching properties of the device should be investigated in detail. In this work, we evaluated the effects of various simulated environmental

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conditions on the optical switching properties of the device through accelerated degradation tests.

2. Experimental

2.1. Device fabrication

A layered substrate of WO_3/ITO/glass ($30\times30\times1.1\ mm^3$, Geomatec Co.) was used. First, a Ta_2O_5 thin film (400 nm) was deposited by reactive DC magnetron sputtering using a 2-in tantalum metal target with 99.99% purity. The sputtering power was 70 W, and the working pressure was 0.7 Pa. The gas mixture ratio of $PH_2/(PAr+PO_2+PH_2)$ was set at 0.22. The protons involved in switching the state of the device were included in the Ta_2O_5 thin film [10]. An Al thin film (2 nm) was deposited by DC magnetron sputtering using a 2-in aluminum metal target with 99.99% purity. The sputtering power was 52 W, and the working pressure was 0.65 Pa. Finally, Pd and Mg_4Ni thin films were prepared by DC magnetron sputtering. The Pd thin film (4 nm) was deposited by DC magnetron sputtering using a 2-in palladium target with 99.99% purity. Here, 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 using co-sputtering of Mg and Ni targets, both of which had 99.99% purity. The sputtering power ratio of Mg/Ni was adjusted to 1.88 in order to properly form the Mg_4Ni thin film [5].

2.2. Degradation studies in simulated environment

The as-prepared device was placed in a thermostat/humidistat bath (PR-1K, Espec Co.) in order to evaluate the impact of environmental conditions on its optical switching properties. Both the temperature and relative humidity in the bath could be controlled to maintain constant values. In this study, the temperature was set to 30, 40 or 50 °C and the relative humidity was set at a constant value of 80%. These values mimicked typical rainy season conditions in Japan or high temperature and humidity areas such as Southeast Asia, Miami in USA, Cairns in Australia and so on. Some temperatures were mimicked from the surface temperature in the window warmed by solar radiation. The devices were stored in the bath at various constant temperatures and at 80% RH for 7 days to compare the environmental effects. The method used in the present study has been described in our previous report [9].

2.3. Characterization of electrochromic switchable mirror

The surface state of the device was evaluated by X-ray photoelectron spectroscopy (XPS; Sigma Probe, Thermo Scientific) with argon sputter etching. The surface was also observed by atomic force microscopy (AFM; VN-8000, Keyence Co.) and optical microscopy. The optical switching properties of the device were measured with a laser diode (670 nm) used in combination with a Si photodiode. Electrodes were connected between the Mg_4Ni surface layer and the ITO layer to switch the optical state of the device. The applied voltage and the change in the optical properties of transmittance and reflectance with an angle of incidence of 45° were directly controlled using LabVIEW.

3. Results and discussion

3.1. Surface observation of electrochromic all-solid-state switchable mirror glass

Fig. 1 shows optical microscopy images of the surface of the as-prepared device and the devices stored under various conditions in the bath. Although the as-prepared device did not exhibit any atypical structural features on its surface, the devices subjected to heat and humidity had surfaces damaged by the conditions in the bath, as shown by the appearance of a spotted pattern in Fig. 1(b)–(d). In particular, the surface of the device stored in the bath at 50 °C and 80% RH was heavily degraded, as shown in Fig. 1(d). Large cracks were also observed in the surface of the device, and the surface did not lost its electrical conductivity. Thus, the surface of the device was greatly affected by small differences in temperature.

Fig. 2 shows AFM images of the device surface for the as-prepared device and devices stored under various bath conditions. Again, the

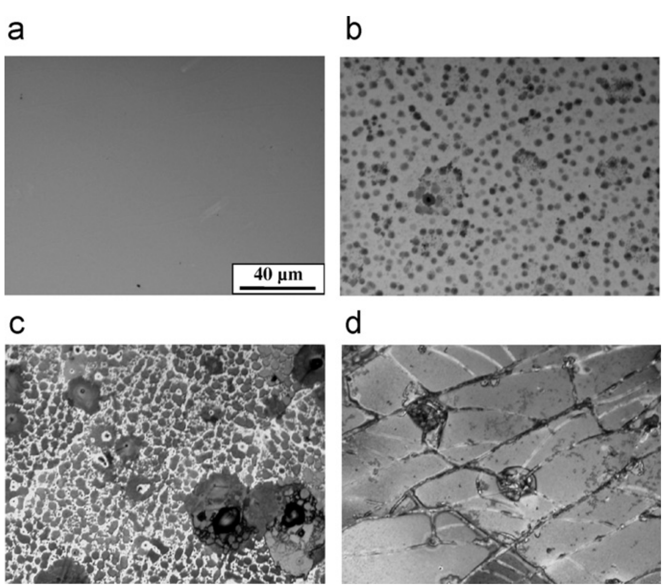

Fig. 1. Surface images of electrochromic all-solid-state switchable mirror glass observed with an optical microscope: (a) as-prepared, (b) 30 °C and 80% RH for 7 days, (c) 40 °C and 80% RH for 7 days, and (d) 50 °C and 80% RH for 7 days in the bath.

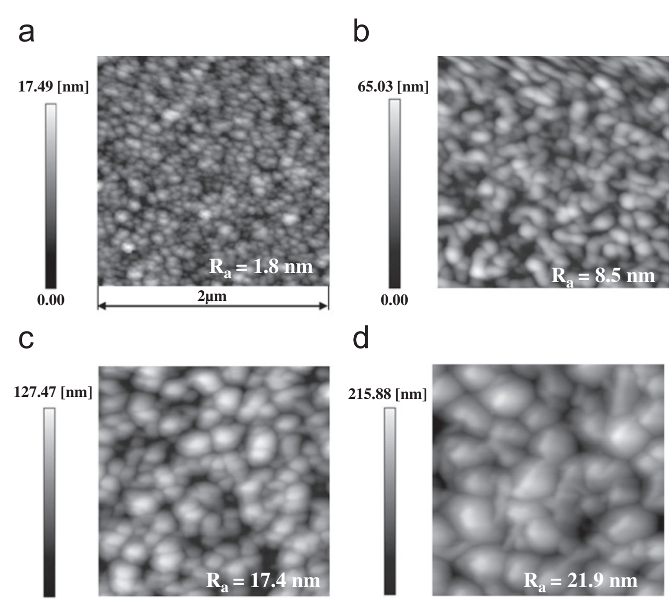

Fig. 2. AFM images of surface of the device: (a) as-prepared, (b) 30 °C and 80% RH for 7 days, (c) 40 °C and 80% RH for 7 days, and (d) 50 °C and 80% RH for 7 days in the bath.