Vacuum 87 (2013) 155–159

Contents lists available at SciVerse ScienceDirect

Vacuum

journal homepage: www.elsevier.com/locate/vacuum

Improved durability of electrochromic switchable mirror with surface coating in environment

Kazuki Tajima*, Hiromi Hotta, Yasusei Yamada, Masahisa Okada, Kazuki Yoshimura

National Institute of Advanced Industrial Science and Technology (AIST), Shimo-Shidami, Moriyama-ku, Nagoya, Aichi 463-8560, Japan

Keywords:
Switchable mirror
Sputtering
Durability
Environment
X-ray photoelectron spectroscopy
Degradation
Mg–Ni thin film

ABSTRACT

Electrochromic switchable mirrors can be reversibly changed between a reflective state and a transparent state by applying a voltage. In our previous work, the properties of the device were significantly affected by environmental factors such as temperature and relative humidity. In that work, the effects on the device properties were investigated through an accelerated degradation test in a thermostat/humidistat bath at a constant temperature of 40 °C and a relative humidity of 80%. The switching speed between the reflective state and transparent state increased as the duration of the simulated environmental exposure increased. The device stored for 7 days under the simulated environmental conditions showed a around 45-fold slower switching speed than that of the as-prepared device. In this work, a high-durability surface coating material constructed from a cyclo olefin polymer sheet and ultraviolet resin was developed to protect the device from environmental degradation. The device with surface coating kept under the simulated environmental conditions for 7 days showed almost the same switching speed as the as-prepared device with the surface coating.

1. Introduction

Switchable mirrors are a new material that could have potential applications as energy-saving windows for houses, buildings, automobiles, and airplanes. Their optical properties can be reversibly switched between a transparent state and a reflective one as a result of hydrogenation and dehydrogenation of the optical switching layer [1–3]. The material could potentially reduce the environmental impact of air conditioning if it is used for commercial windows, because the reflective state effectively reflects solar radiation.

We have previously reported the construction of electrochromic (EC) switchable mirrors with a multilayer structure of Mg_4Ni/Pd/Al/Ta_2O_5/WO_3/ITO on transparent substrate [4–6]. The layers in the device consist of an optical switching layer (Mg_4Ni), a proton injector layer (Pd), a buffer (Al), a solid electrolyte (Ta_2O_5), an ion-storage layer (WO_3) and a transparent conductor (ITO). The layers were fabricated by direct current (DC) magnetron sputtering. An applied voltage alters the optical properties of the device reversibly between the transparent and reflective states; when a voltage is applied to the device, the protons in the WO_3 ion-storage layer move to the Mg–Ni optical switching layer where the hydrides MgH_2 and Mg_2NiH_4 are formed. These hydride complexes have a higher transparency than Mg_4Ni, resulting in a transparent state.

We have investigated the effect of environmental factors such as temperature and humidity on the durability of an EC switchable mirror [6–8]. The device degraded under high humidity conditions and the optical switching properties disappeared after an accelerated degradation test using a thermostat/humidistat bath. If the device is to be used in practical applications, it must be durable under a variety of environmental conditions. In our recent work, we found that a surface coating for EC switchable mirrors to improve the durability in environment [7,8]. In this work, the purpose of the research was that we found a surface coating for EC switchable mirrors using a thermostat/humidistat bath in the first try to find new material suitable for the surface coating with resistance to degradation under environmental conditions.

2. Experimental

2.1. Device preparation

A WO_3/ITO/glass substrate (30 × mm 30 × mm 1.1 mm, Geomatec Co.) was used as a substrate. The Ta_2O_5 thin film (thickness: 400 nm) was deposited by reactive direct current (DC) magnetron sputtering at a sputtering power of 90 W in a 7:1 mixture of argon

* Corresponding author. Tel.: +81 52 736 7546; fax: +81 52 736 7406.
E-mail address: k-tajima@aist.go.jp (K. Tajima).

0042-207X/$ – see front matter
http://dx.doi.org/10.1016/j.vacuum.2012.08.003

and oxygen. A 2-inch tantalum target (purity: 99.99%) was used, and the working pressure was 0.8 Pa. After that, the sample was dipped in a 0.5 M sulfuric acid solution under an applied voltage of 2.3 V, in order to inject protons (0.05 C) into the WO_3 film across the Ta_2O_5 thin film, resulting in the formation of H_xWO_3.

The Al thin film (2 nm) was then deposited by DC magnetron sputtering at a sputtering power of 50 W, using a 2-inch aluminum target (99.99%) and a working pressure of 0.65 Pa. The Pd and Mg–Ni thin films were prepared by DC magnetron sputtering with palladium, magnesium and nickel targets (99.99% purity). The Pd thin film (4 nm) was deposited at a sputtering power of 14 W, and a working pressure of 1.2 Pa, and the Mg_4Ni thin film (40 nm) was deposited on the Pd thin film by co-sputtering of magnesium and nickel targets at a sputtering power ratio for Mg and Ni of 1.88:1 [9]. All processes were carried out at room temperature.

2.2. Surface coating layer

A combination of ultraviolet (UV)-cured epoxy resin and a cyclo olefin polymer (COP) sheet was chosen as a surface coating. The high transparency of COP allows the material to be used in lenses, displays and medical applications. In addition, COP has low moisture absorption and is resistant to solar radiation. A commercial UV-cured epoxy resin (XNR5541, Nagase ChemteX Co.) was spin-coated onto the surface of the device. Then, the surface was covered with a commercial COP sheet (ZF14-100, Zeon Co.), and the resin was hardened under UV irradiation at an intensity of 170 mW/cm^2 and a wavelength of 365 nm for 6 min. The device was stored in a thermostat bath at 100 °C for 1 h to stabilize the resin. The final structure of the device was COP/UV-resin/Mg_4Ni/Pd/Al/Ta_2O_5/WO_3/ITO/glass. The optical switching properties of a conventional device without surface coating were compared with the device with surface coating before and after the accelerated degradation test.

2.3. Accelerated degradation test

The durability of the device was investigated through an accelerated degradation test in a thermostat/humidistat bath (PR-1K, Espec Co.). The fluctuation and distribution of the temperature and relative humidity in the bath were controlled automatically by a computer. The device was held at a constant temperature of 40 °C and a relative humidity (RH) of 80% in order to test the durability of the device in the same simulated environment that was used in our previous work [7,8]. These values mimic typical rainy season conditions in Japan, as well as the conditions in high-temperature and high-humidity areas of the world.

2.4. Evaluation and characterization

Changes in the optical switching properties of the device were measured with a 670 nm laser diode and a Si photodiode. Electrodes were connected between the Mg_4Ni and ITO thin films on the device. LabVIEW software was used to control the applied voltage and to measure the changes in the optical properties of the device. The material was characterized by X-ray photoelectron spectroscopy (XPS; Sigma Probe, Thermo Scientific) with argon sputter etching. The surface of the device was evaluated by atomic force microscopy (AFM; VN-8000, Keyence Co.) and optical microscopy.

3. Results and discussion

3.1. Surface observation

Fig. 1 shows the optical and AFM surface images of the conventional device with no surface coating. The as-prepared device showed a flat, smooth surface (Fig. 1(a) and (d)). However, for the device that was kept in the bath, structures typical of environmental damage were visible in the optical microscope images (Fig. 1(b) and (c)). The surface morphology changed and some particle-like structures were observed after only few days in the bath (Fig. 1(e) and (f)); the device kept in the bath for 7 days showed a higher surface roughness of $R_a = 31.9$ nm. These surface changes were strongly related to the degradation of the surface Mg_4Ni layer in the conventional device with no surface coating.

However, the device with the surface coating did not show any surface structures typical of environmental damage after the same duration in the bath (Fig. 2). These changes in the surface structure were related to the reaction of the Mg_4Ni thin film optical switching layer with environmental factors of oxygen and humidity (moisture) [6]. The effects of the environment on the degradation of the device with no surface coating were evaluated by XPS analysis.

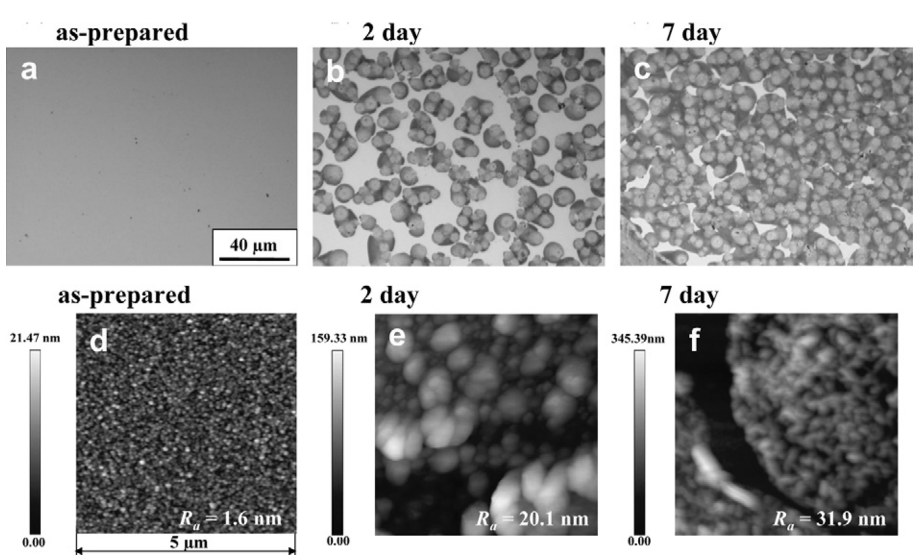

Fig. 1. Surface images of the electrochromic switchable mirror with no surface coating kept at 40 °C and 80% RH. (a)–(c) are optical images, and (d)–(f) are AFM images.