New switchable mirror device with a counter electrode based on reversible electrodeposition

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ABSTRACT

A new structure for a switchable mirror device based on reversible electrodeposition is proposed. This device does not contain Cu ions in the electrolyte and adapts a counter electrode. The feasibility of the device was evaluated with a WO_3 film, which is a well-known electrochromic material, as a counter electrode. Even in the absence of Cu ions, the WO_3 film facilitates a clean erase feature in the device. Furthermore, using a pre-deposited Ag film as a working electrode, Ag deposition can be driven at a substantially lower voltage than that in conventional devices. Moreover the deposition current decreases with the progress of Ag deposition, and stops after completion of the deposition process. The results clearly indicate that the tri-bromine ion, which makes the self-erasing circulation, is not generated during Ag deposition process. The new switchable mirror shows excellent bistability and size scale-up is possible because it does not consume continuous current in the mirror state. By appling the proposed technology, a switchable mirror device with a 7 cm × 9 cm active area was successfully fabricated.

1. Introduction

Efforts to reduce the use of fossil energy and energy consumption have been undertaken globally to realize a cleaner environment. New technologies are used to bring about a reduction in energy usage in buildings, and the smart window technology, in particular, is of special research interest [1–3]. The smart window technology is used to effectively reduce the consumption of heating, cooling, and lighting energy by controlling the amount of solar energy entering a building [1–3]. Smart window technologies include an electrochromic window that controls the transmission of light [4–10] and a switchable mirror that controls the reflection of light [11–19]. The smart windows based on the electrochromic technology are currently in the commercialization phase, but the switchable mirror technology is not yet. The switchable mirror technology has the advantage of controlling the transmission of solar energy effectively as it controls reflection and transmission while minimizing the absorption of light. The switchable mirror technologies have been studied mainly based on metal hydride transition [11–17], and applied to gasochromic devices [18,19]. Because there is a great demand for electrically driven devices, solid-state switchable mirrors, which are driven by electric current, are also under study [20,21]. Tunable metamaterials using plasmonic nanoparticles

are also emerging as candidates for the switchable mirror device [22].

Recently, device technologies based on reversible electrodeposition (RED) have been proposed as a light modulation technology and have attracted much attention [23–35]. Switchable mirror devices based on RED technology are expected to be applicable to smart windows, because they have a simple structure, can switch at relatively high speeds and show high transmittance in the transparent state. However, the RED-based switchable mirrors have a major drawback that they easily lose their mirror state when the power is turned off. Because of this poor bistability, current must be continuously supplied in order to maintain the mirror state of the device. This continuous current consumption not only increases the power consumption of the device but also causes a non-uniformity of the voltage distribution. It causes the voltage applied to the device to decrease from the edge of the device to the center, resulting in device non-uniformity. As a result, the scale-up of the device, which is indispensable for actual application as smart window, is very difficult. Therefore, the RED technology should address the issue of bistability improvement in the corresponding devices [36].

In this study, we propose a new structure to improve the bistability of the RED device. It is confirmed that Cu ions in the electrolyte deteriorate the bistability of the device. In order to obtain good bistability, it is essential to remove Cu ions from the electrolyte. However, the

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removal of the Cu ions makes erasing operation of the device difficult [23,25,28,29]. To solve this problem, we introduced a counter electrode material that can act as a mediator. In order to verify this device concept, we have applied a well-known electrochromic material, WO_3 thin film, as a counter electrode. By applying the counter electrode material, fast and clean erasing of the device could be achieved without Cu ions. Furthermore, a pre-deposited Ag film was applied to improve the bistability of the device. The bistability could be greatly improved by applying the pre-deposited Ag film to the working electrode. Superior bistability makes it possible to scale-up devices, and we have successfully fabricated a large sized device with a 7 cm × 9 cm active area by applying this structure.

2. Experimental

2.1. Fabrication of the device with a WO_3 counter electrode

A WO_3 film used as the counter electrode was deposited with a reactive DC magnetron sputtering with a W metal target in Ar/O_2 plasma [37]. The deposition pressure was 20 mTorr. ITO (sheet resistance of 7 $\Omega/\square$) on soda lime glass was used as the substrate, and the thickness of the WO_3 film was 1.8 μm. ITO (15 $\Omega/\square$) on soda lime glass was used as the working electrode. The working electrode was pre-cleaned with O_2 plasma to eliminate any residual organic contamination, before the construction of the device. The working electrode and counter electrode were assembled with melting films (Surlyn, Dupont Co.) to create the cell cavity. Two melting films with a thickness of 60 μm each were stacked to make a cell gap of 120 μm. $AgNO_3$ (0.05 M) with LiBr (0.25 M) in dimethyl sulfoxide (DMSO) was used as the electrolyte. The electrolyte was injected into the cell cavity with a syringe. The size of the active area of the device was 1.4 cm × 1.9 cm.

For a comparison, a conventional RED device was also prepared. The device cavity was fabricated with two ITO (15 $\Omega/\square$) on glass substrates via the previously described method. $AgNO_3$ (0.05 M) along with LiBr (0.25 M) and $CuCl_2$ (0.01 M) in DMSO was used as the electrolyte.

2.2. Fabrication of the device with a pre-deposited Ag film and a WO_3 counter electrode

The pre-deposited Ag film was deposited with the DC magnetron sputtering at a pressure of 5 mTorr on ITO (15 $\Omega/\square$) on glass substrate. The sheet resistance of deposited Ag film was 0.44 $\Omega/\square$, which is equivalent to 36 nm thickness. The WO_3 film used as the counter electrode was deposited to a thickness of 1.8 μm on a ITO (7 $\Omega/\square$) glass. The device cavity was created by the previously described method. $AgNO_3$ (0.05 M) with LiBr (1.0 M) in DMSO was used as the electrolyte. A higher concentration of LiBr was used to prevent the possible precipitation of Ag due to the additional Ag^+ ions from the pre-deposited Ag film. The size of the active area of the device was 1.4 cm × 1.9 cm.

To fabricate a large device with 5 cm × 7 cm active area, ITO glass with a sheet resistance of 7 $\Omega/\square$ was used as a substrate for the both electrodes. The cell gap of the device was adjusted to 420 μm with a Teflon spacer and melting films. All other parameters were same with those of the device with 1.4 cm × 1.9 cm active area.

2.3. Reflectance measurements

The reflectance of the fabricated devices was measured with an optical measurement system consisting of a light source (DH-2000-BAL, Ocean Optics Inc., USA), optical fibers, and a spectrometer (USB2000+UV–VIS, Ocean Optics Inc., USA). The measurements were made in back reflection geometry at the working electrode side where the Ag film is deposited or erased, and specular reflectances were measured.

2.4. Cyclic voltammetry

The cyclic voltammetry measurement was done with a potentiostat (CHI1030, CH Instrument Inc., USA). The sweep rate of voltage was 0.05 V/s. The reference electrode was a Ag/AgCl electrode and LiBr (1 M), $AgNO_3$ (0.05 M) in DMSO was used as the electrolyte, a Pt wire was used as the counter electrode.
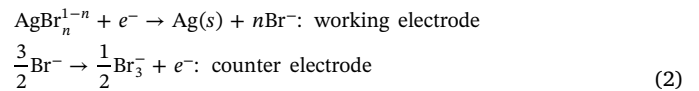
3. Results and discussion

3.1. Device concept

Typical RED devices contain Ag, Br ions and Cu ions in the electrolyte. It is known that Br ions aid in the deposition of a smooth film with good specular characteristics when Ag is deposited [29,34], while Cu ions help in removing the Ag film from the strip and keeping it clean during the erasing operation [23,25,28,29]. Cu ions dissolve Ag in the presence of halide ions such as Br^- (S1). Therefore, the Ag mirror film deposited in the RED device will have poor stability in the presence of Cu ions. The dissolution reaction can be expressed by Eq. (1):

$$Ag(s) + Cu^{2+} + nBr^- \rightarrow AgBr_n^{1-n} + Cu^+ \tag{1}$$
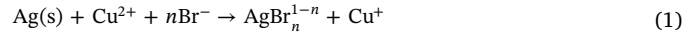
In order to maintain a mirror state in the RED device, Ag should be continuously deposited to compensate for that dissolved by the Cu ions. Since such a continuous deposition of Ag is accompanied by current consumption, the voltage applied to the electrode decreases from the edge area to the center of the device; this becomes a limiting factor for larger devices. In order to stabilize the deposited Ag film, the Cu ions must be removed from the electrolyte. However, Cu ions are very important constituents of the RED device, since they allow for effective erasing [23,25,28,29].
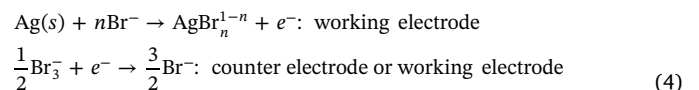
We focused on the structural characteristics of the device to probe the erasing characteristics in the absence of Cu ions. The RED device without Cu ions can be considered as a special type of electrochromic device in terms of its structure. The similar device concept with the electrochromic device composed with type I and type II electrochromes can be applied [38]. Fig. 1(a), (b), and (c) show the operation model for the device without Cu ions in the electrolyte. Fig. 1(a) shows the deposition of the Ag film. In order to deposit Ag on the working electrode, electrons should be supplied by oxidizing the Br^- ions at the counter electrode. This oxidation/reduction reaction is understood as the following pair reactions [24,25]:

$$AgBr_n^{1-n} + e^- \rightarrow Ag(s) + nBr^-: \text{ working electrode}$$
$$\frac{3}{2}Br^- \rightarrow \frac{1}{2}Br_3^- + e^-: \text{ counter electrode} \tag{2}$$

During Ag deposition, the Br_3^- ions generated at the counter electrode diffuse into the electrolyte; when one Br_3^- ion is generated, two Ag atoms are deposited to maintain charge balance. These Br_3^- ions diffuse toward the working electrode due to a concentration gradient, oxidize the deposited Ag atoms to Ag^+ ions, and are reduced to Br^- ions. This mechanism exhibits a self-erasing behavior, as shown in Eq. (3):

$$Ag(s) + nBr^- + \frac{1}{2}Br_3^- \rightarrow AgBr_n^{1-n} + \frac{3}{2}Br^-: \text{ working electrode} \tag{3}$$
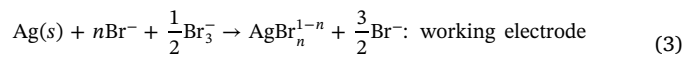
The steady state is reached when the self-erasing reaction and the Ag deposition are in equilibrium, and the concentration distribution of the Br_3^- ions in the cell becomes linear at this time. Fig. 1(b) shows the erasing operation. During the erasing operation, Ag dissolution must occur at the working electrode. The reactions can be described as below:

$$Ag(s) + nBr^- \rightarrow AgBr_n^{1-n} + e^-: \text{ working electrode}$$
$$\frac{1}{2}Br_3^- + e^- \rightarrow \frac{3}{2}Br^-: \text{ counter electrode or working electrode} \tag{4}$$