Dynamic Behaviour of Patterned Array Electrochromic Devices

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***Abstract*—Electrochromic devices (ECDs) having a high switching speed and a good durability were developed with viologen-anchored TiO_2 (VTO) nanoparticles and antimony-doped SnO_2 (ATO) nanoparticles. The fabricated ECDs showed a good stability after 30,000 cycles driving at 4 Hz speed. Also, the dynamic behaviour of their devices was studied using 6 x 6 patterned array cells. The driving tests of 4 types were used to understand the exact driving mechanism and to prevent the rapid blur problem. The driving method of VTO cell is good choice in order to obtain blur-free images.**

Keywords - electrochromic devices (ECDs); patterned array cells; nanoparticles; driving mechanism

I. INTRODUCTION

Electrochromic devices (ECDs) have been attracting much interest for several decades because of their unique property of being able to control the transmittance of visible light [1-3]. Among these devices, ECDs with viologen-anchored TiO_2 (VTO) nanoparticles have attracted attention in various applications, such as information displays, light shutters, automobile mirrors, and smart windows due to the characteristics of the high coloration efficiency, the large viewing angle dependence, and memory effects under open-circuit status [4-5]. Especially, the suggested electrode structure of VTO minimizes the diffusion length of the Li^+ ion and sub-second switching speed is realized [6]. The antimony-doped SnO_2 (ATO) nanostructure is one of the promising counter electrodes for the devices because it can perform as a good ion storage layer [7].

In this work, we study ECDs having a high driving speed and a good durability with VTO nanoparticles and ATO nanoparticles. To fabricate high speed ECDs, VTO electrodes and ATO electrodes are prepared separately, then joined together to form ECDs. Also, the reduction step of ATO counter electrodes is processed before the devices construction. 6 x 6 patterned array cells of ECDs are designed for understanding of the dynamic behavior. The devices are formed by the silk screen printing. The driving methods of 4 types are tested to grasp the driving mechanism. The driving of VTO cell is good choice in order to obtain blur-free images.

II. EXPERIMENTAL

The ECDs are basically composed of an electrochromic electrode, an ion storage electrode, and an electrolyte. FTO (fluorine-doped SnO_2, sheet resistance of 15 Ω/□) coated glasses (TEC-15, Pilkington co.) were used as substrates and were cleaned with acetone, methanol, and pure water. For the 6 x 6 patterned array cells, FTO glasses were formed by the laser patterning method as the finger-shaped conducting layer. TiO_2 thin films were prepared using the method of silk-screen printing and formed by the calcination process at 450 ^oC for 30 min in air. The nanostructured TiO_2 electrodes were dipped in the purple viologens-ethanol solution of a 0.5 mM concentration for 20 hours. The ion-storage electrode was fabricated by 4 mol% ATO nanoparticles using a hydrothermal process [7]. The synthesized nanoparticles of diameters less than 10 nm were mixed with terpineol, lauric acid and ethyl cellulose to make slurry. The full cell ECD was prepared as follows : The electrodes of VTO and dried ATO were joined by a melting film of thickness of 100 □ (Surlyn, Dupont co.). The electrolyte solution of 0.5 M $LiClO_4$ in propylene carbonate was injected by vacuum pump into the cell cavities.

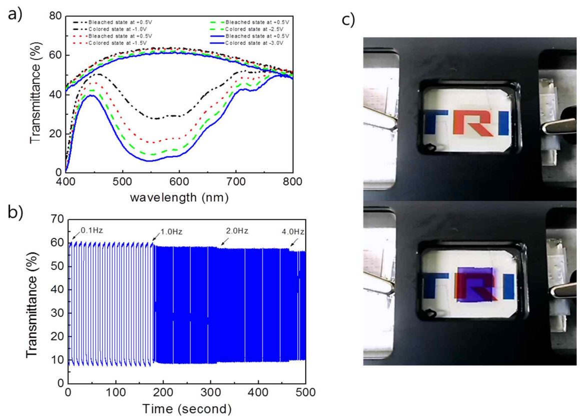

Figure 1. (a) Transmittance spectra at the various coloration voltages (-1.0, -1.5, -2.5, and -3.0 V) and at a bleached voltage of +0.5 V, (b) Transmittance changes in the driving speed increase from 0.1 Hz to 4 Hz at 550 nm, and (c) photographs of a fabricated device in its transparent bleached and purple colored states (coloration voltage : -2.5 V, device size : 2.0 x 2.0 cm^2).

III. RESULTS AND DISCUSSION

Figure 1 shows the transmittance spectra as a function of the applied voltages and the photographs of a fabricated device. The coloration voltages of Figure 1(a) were applied as -1.0, -1.5, -2.5, and -3.0 V. Also, the applied voltage was +0.5 V for the bleached state of devices. The transmittances in the colored states were decreased with increasing voltages drastically. On the other hand, those of the bleached states were slightly decreased. Figure 1(b) shows periodic transmittance changes, obtained at 550 nm wavelength for the repetition test of the ECD. In order to confirm the driving stability at different speeds, a switching frequency was used in 0.1 Hz (-2.5 V, 5sec / +0.5 V, 5 sec), 1 Hz (-2.5 V, 500 msec / +0.5 V, 500 msec), 2 Hz (-2.5 V, 250 msec / +0.5 V, 250 msec), and 4 Hz (-2.5 V, 125 msec / +0.5 V, 125 msec).

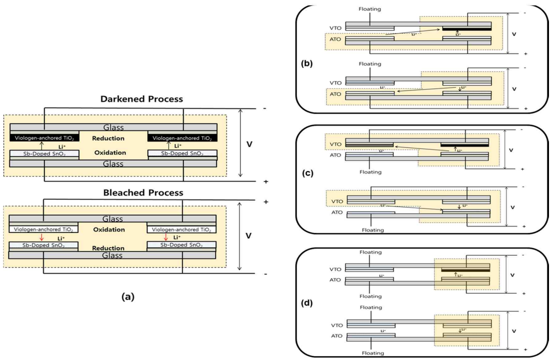

Figure 2. Schematic diagrams of 4 type driving method for the patterned array ECDs. (a) Full cell driving method, (b) VTO half cell driving method, (c) ATO half cell driving method, and (d) quarter cell driving method.

Figure 1(c) shows the optical images of a full cell ECD. The coloration state in the applied voltage -2.5 V had a dark blue colour and the bleached state in the applied voltage +0.5 V was highly transparent. To understand the dynamic behaviour of ECDs, the finger-shaped conducting layer was formed by a laser patterning process. 4 type driving methods were tested with 4 finger-like electrodes. The first driving method was the full cell driving method using all driving electrodes. Figure 2(a) shows the schematic diagram of the full cell driving method. Second was the VTO half cell driving method showed in Figure 2(b). This method was used with VTO driving cell having the floating electrode. As show in the Figure 2(c), the third method was the ATO half cell driving method. This method was used with the ATO cell having the floating electrode. Finally, Figure 2(d) was the quarter cell driving method with two driving electrodes. For a more understanding of the driving mechanism, the operation of the VTO half cell and the ATO half cell has been described through the bead model. Figure 3 shows beads model diagrams and corresponding photo images. Figure 3(a) and Figure 3(b) were the method of VTO half cell driving in the initial bleached state and the initial colored state, respectively. The switching charges of the ATO cells were fully maintained to the VTO half cells as shown in the black beads of Figure 3(a). Also, the switching charges of the initial colored state were dropped to exactly in half from Figure 3(b). The blurring of square images did not appear even though the black beads were remained in other ATO cells because of the discoloration characteristic of the ATO material. Figure 3(c) and Figure 3(d) present the method of ATO half cell driving in the initial bleached state and the initial colored state, respectively. The charges in ATO half cell driving were reduced to about 50 % of the switching charges for the coloration. Furthermore, the switching charges did not transfer to the one side of the VTO cell completely. This phenomenon was the cause of blurring the images. Figure 3(d) shows the method of the ATO half cell driving in the initial colored state. The switching charge did not fully maintain to the bleached state. The black beads remained in the VTO cell. Therefore, the driving method of the VTO half cell is a good choice in order to obtain blur-free images.

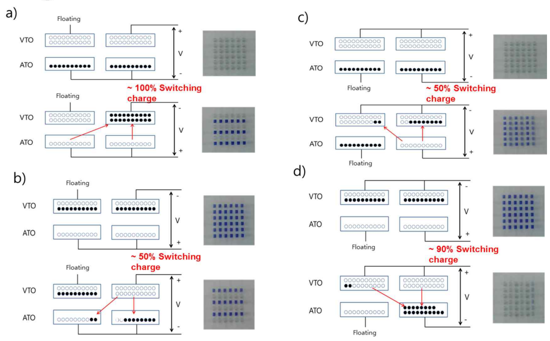

Figure 3. Beads model diagrams for the interpretation of driving mechanism and corresponding photo images. (a) VTO half cell driving (initial state : bleached state), (b) VTO half cell driving (initial state : colored state), (c) ATO half cell driving (initial state : bleached state), and (d) ATO half cell driving (initial state : colored state).

IV. CONCLUSION

Electrochromic devices (ECDs) having a high switching speed and a good durability were developed with viologen-anchored TiO_2 (VTO) nanoparticles and antimony-doped SnO_2 (ATO) nanoparticles. Also, the dynamic behaviour of their devices was studied using 6 x 6 patterned array cells. The driving test of 4 types and the beads model were used to understand the exact driving mechanism. The switching charges using the ATO half cell did not transfer to the one other side completely. Therefore, the driving method with the VTO half cell is a good choice in order to obtain blur-free images.

ACKNOWLEDGMENT

This work was supported by Institute for Information & communications Technology Promotion(IITP) grant funded by the Korea government(MSIP) (B0101-15-0133, The core technology development of light and space adaptable energy-saving I/O platform for future advertising service)

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