Solar Energy Materials & Solar Cells 145 (2016) 76–82

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

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

Driving mechanism of high speed electrochromic devices by using patterned array

Tae-Youb Kim [a,b,*], Seong M. Cho [a], Chil Seong Ah [a], Hojun Ryu [a], Joo Yeon Kim [a]

[a] Smart I/O Platform Research Department, Components & Materials Research Laboratory, Electronics and Telecommunications Research Institute, Daejeon 305-350, Republic of Korea

[b] University of Science and Technology, Advanced Device Technology, Daejeon 305-350, Republic of Korea

ARTICLE INFO

Article history:
Received 7 January 2015
Received in revised form
1 September 2015
Accepted 17 September 2015
Available online 9 October 2015

Keywords:
Electrochromic devices (ECDs)
Patterned array cells
Nanoparticles
Driving mechanism

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 behavior of their devices was studied using 6×6 patterned array cells. The driving tests of 4 types were used to understand the exact driving mechanism and *to prevent the rapid blur problem.*

1. 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 [1–9]. 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 [10–15]. Especially, the suggested electrode structure of VTO minimizes the diffusion length of the Li^+ ion and sub-second switching speed is realized [16–18]. 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 [19]. Chen and Ho. [20–21] among others reported that the charge balance on the two electrodes was important for the optical and chemical stability of ECDs. Also, the dynamic behaviour of patterned array ECDs is important for the applications that require a fast driving speed such as light shutters and information display. However, the device structure of patterned array ECDs and the driving mechanism makes easily current flow between unit cells through the electrolyte. That phenomenon is observed as a blur of output image and induces cross-talk state of ECD. The isolation of electrolyte within unit cell could be a solution for rapid blur problem as with the bank structure, patterned gel type electrolyte, and LC electrolyte [22–24]. However, it makes the complicated process and the limitation of the cell resolution.

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 pre-reduction process takes place to change the initial oxidation state of ATO counter electrodes. This step is important for the charge balance of ECDs and makes an increase of cell stability [20–21]. 6×6 patterned array cells of ECDs are designed for understanding of the dynamic behaviour. The devices are formed by the silk screen printing. We study the driving methods of 4 types to understand the exact driving mechanism and to prevent the rapid blur problem.

2. Experimental details

The ECDs are basically composed of an electrochromic electrode, an ion storage electrode, and an electrolyte. FTO (fluorine-doped SnO2, 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 6×6 patterned array cells, FTO glasses were formed by the laser beam patterning

* Corresponding author. Tel.: +82 42 860 5267; fax: +82 42 860 5202.
E-mail address: youby@etri.re.kr (T.-Y. Kim).

http://dx.doi.org/10.1016/j.solmat.2015.09.024
0927-0248/

method as the finger-shaped conducting layer. A TiO_2 nanoparticle paste with an average diameter less than 20 nm was purchased from ENB Korea Co. TiO_2 thin films were prepared using the method of silk-screen printing and formed by the calcination process at 450 °C for 30 min in air. This heat treatment was performed adequately to burn off polymer materials and to form the nanostructured TiO_2 electrodes. The phosphate-anchored purple viologens (N,N′-4,4′-bis(2-phosphonylethyl)-bipyridium dichloride) were used as the electrochromic materials [14]. The nanostructured TiO_2 electrodes were dipped in the purple viologens-ethanol solution of a 0.5 mM concentration for 20 h. The VTO electrodes were rinsed in ethanol and dried with N_2 gas after completion of the reaction.

The ion-storage electrode was fabricated by 4 mol% ATO nanoparticles using a hydrothermal process [19]. The synthesized nanoparticles of diameters less than 10 nm were mixed with terpineol, lauric acid and ethyl cellulose to make slurry. The ATO thin films were formed on the finger-shaped FTO substrates by the method of silk-screen printing. The patterned thin films were calcined at 450 °C for 30 min in air to burn off the polymers and to make the nanostructured electrodes. The pre-reduction process took place to change the initial oxidation state of ATO counter electrodes. This step was used with a potentiostat (CHI1030, CH Instrument Inc., USA) before ECDs cell construction. For the pre-reduction, the Ag/AgCl was used as a reference electrode and the solution of 0.5 M $LiClO_4$ in propylene carbonate was used as an electrolyte.

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 μm (Surlyn, Dupont co.). The electrolyte solution of 0.5 M $LiClO_4$ in propylene carbonate was injected by vacuum pump into the cell cavities. The devices were $2.0 \times 2.0\ cm^2$ in size, of which $0.7 \times 0.7\ cm^2$ was the active area for a test of high driving speed and stability. Also, the devices were $3.2 \times 4.5\ cm^2$ in size, $1.4 \times 1.0\ mm^2$ of which was the active area for one pixel of the 6×6 patterned array.

The optical properties of the fabricated ECDs were measured using 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). Driving bias was applied by a function generator (Hewlett Packard co., 33120A), DC power supply (Protek co., OPE-303Q), and an isolation board with an operational amplifier. Switching currents during electrochromic operation were recorded using a digital multimeter (Agilent co., 34461A). The surface microstructures and the cross-section of the VTO and ATO layer were observed by FE-SEM (Hitachi S-4500).

3. Results and discussion

Fig. 1 shows the SEM micrographs, photographs, and transmittance spectra to observe the properties of nanostructured VTO and ATO electrodes. The images of Fig. 1(a) and (b) are the surface microstructures and the cross-section of the VTO and ATO layer. The prepared films have the nanostructured electrodes of large surface area. The thickness of VTO and ATO layer are 6 μm and 4 μm. Also, the value of the charge capacity is about 5.98 mC/$cm^2$and 7.1 mC/cm^2 respectively. The thickness of VTO and ATO layer is important for the charge balance of stable driving ECDs. Fig. 1(c) and (d) show photographs of the patterned VTO and ATO films on FTO glass. Two rectangular areas of a red dashed line in

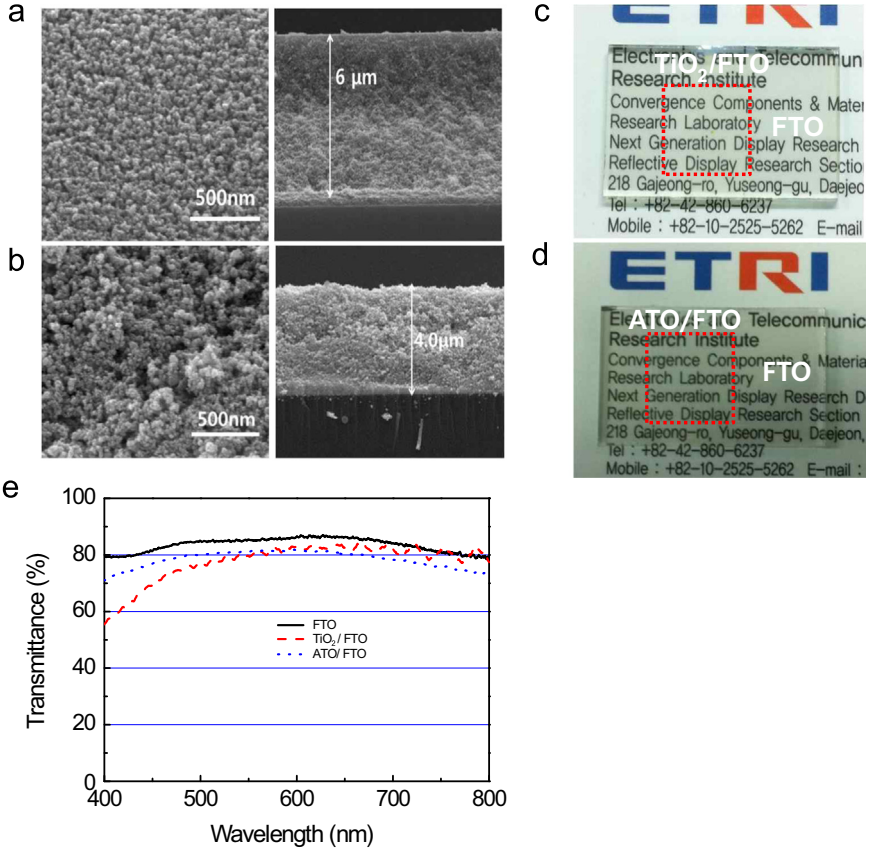

Fig. 1. SEM images of (a) a viologen-anchored TiO_2 (VTO) film and (b) an antimony-doped SnO_2 (ATO) film formed by the silk screen printing. Photographs of (c) the VTO thin film and (d) the ATO thin film coated on FTO (fluorine-doped SnO_2) conducting substrate. (e) Transmittance spectra of the VTO and ATO film on FTO glass.(For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)