

Optical Properties of WO₃-NiO Complementary Electrochromic Devices

Chih-Ming Wang, Chih-Yu Wen, Ying-Chung Chen, Chun-Chieh Wang, Chien-Chung Hsu, Jui-Yang Chang, Jyun-Min Lin

Abstract—In this study, we developed a complementary electrochromic device consisting of WO₃ and NiO films fabricated by rf-magnetron sputtered. The electrochromic properties of WO₃ and NiO films were investigated using cyclic voltammograms (CV), performed on WO₃ and NiO films immersed in an electrolyte of 1 M LiClO₄ in propylene carbonate (PC). Optical and electrochemical of the films, as a function of coloration–bleaching cycle, were characterized using an UV-Vis-NIR spectrophotometer and cyclic voltammetry (CV). After investigating the properties of WO₃ film, NiO film, and complementary electrochromic devices, we concluded that this device provides good reversibility, low power consumption of -2.5 V in color state, high variation of transmittance of 58.96%, changes in optical density of 0.81 and good memory effect under open-circuit conditions. In addition, electrochromic component penetration rate can be retained below 20% within 24h, showing preferred memory features; however, component coloring and bleaching response time are about 33s.

Keywords—Complementary electrochromic device, Rf-magnetron sputtered, Transmittance, Memory effect, Optical density change

I. INTRODUCTION

RECENTLY, the awareness of the need for global environmental conservation and the reduced use of electrical energy and decrease of CO₂ have led to the development of energy-saving systems. Electrochromism (EC) is defined as a phenomenon in which a change in color takes place in the presence of an applied voltage and which involves the reversible injection and extraction of ions within the crystal structure of a host by electric potential [1]. Electrochromic devices (ECDs) has recently attracted considerable attention since they has such advantages as low switching voltage, the ability to display various colors, high reflective contrast ratio, large viewing angle, memory effect, and possibility of viewing

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over long periods without eye strain [2]-[5]. ECDs have many potential applications including: architectural smart windows, car rear-view mirrors, sunroofs of automobiles, view angle-independent display, sunglasses, price labels, e-paper, variable-emittance surfaces for temperature control of spacecraft and passive and active optical switching devices, however high switching speed is not required [6]-[7].

A complementary ECD (CECD) is a device containing two electrochromic layers, one of which is anodically colored while the other cathodically colored both on an electronically conducting transparent substrate (ITO/Glass), which is separated by an electrolyte layer. Fig. 1 shows schematically the cross-section of a typical CECD with WO₃ as the cathodically colored layer and NiO as the anodically colored layer, together with the description of voltage application and transmission measurement. In such a dual-layer CECD, they are colored together and bleached together. The two materials can be switched simultaneously to provide higher optical contrast and coloration efficiency, and at the same time a proper charge balance can be maintained in the device, which results in better device performance, such as a higher open-circuit stability and long-term switching stability, than that of single-layer ECD.

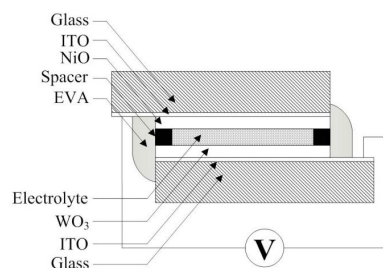


Fig. 1 Schematic configuration of CECD

Inorganic ceramics oxides in EC materials can be cathodically colored materials: MoO₃, WO₃, TiO₂ and Nb₂O₅ belong to n-type semiconductors, the anodically colored materials: NiO, IrO₂, Rh₂O₃ and CoO₂ belong to p-type semiconductors, are a result of the injection or extraction of both a cation (or an anion) and an electron (or a hole). Among these transition metal oxides, WO₃ and NiO are currently in widespread use as cathodic and anodic coloration materials, respectively. Electrochromic thin films can be prepared by a variety of methods, including sol-gel process [8], RF sputter deposition, electron-beam evaporation [9], spray pyrolysis [10]

and the chemical vapor deposition [11]. Out of which the electron beam evaporation technique, one of the physical vapor deposition methods, has been considered largely for the growth of device quality thin films [12]. However, the morphology and the coloration/bleaching behavior of the films are strongly related to the deposition conditions. Among the film deposition techniques, the sputtering is widely used in the glass industry and could enhance adhesion and large area deposition.

II. EXPERIMENTAL

WO₃ and NiO thin films were deposited by the rf magnetron sputtering technique. Ceramic WO₃ and NiO (2 inches in diameter, 99%) and ITO-coated glass (15 Ω/sq.) were used as the target and the substrate, respectively. The distance between the target and the substrate was 5 cm. The vacuum chamber is capable of achieving a base pressure of 7.5×10^{-5} Pa and the working pressure for sputtering was 3.1 Pa. The target was pre-sputtered at the working pressure for 5 min. The details deposition parameters of WO₃ and NiO thin film deposition is showed in Table I.

TABLE I
THE DEPOSITION CONDITIONS OF THIN FILMS

Material	WO ₃ , 99.5%	NiO, 99%
Base pressure (Pa)	7.5×10^{-5}	7.5×10^{-5}
Work pressure (Pa)	3.1	1.9
Deposition rate (nm/min)	3.3	1
Deposition temperature (°C)	Room temperature	Room temperature
Oxygen concentration (%)	60	60
RF power (W)	100	100

The CECD in the form of Glass/ITO/NiO/Eleetrolyte/WO₃/ITO/Glass was fabricated by the following process: two coated substrates were assembled together by separated the NiO/ITO/Glass and WO₃/ITO/Glass. The space between two electrochromic layers was controlled by placing an insulating spacer approximately 1.45 mm and then the eletrolyte was filled into the CECD through a small hole using by a syringe. The four edges of CECD was then sealed using ethylene vinyl acetate (EVA). The effective area of the device is 6.48 cm².

The characterization of the electrochromic properties was carried out in a two-electrode cell with an electrochemical analyzer (CHI, 611B), which the WO₃/ITO/Glass as a working electrode and a common NiO/ITO/Glass as a counter electrode and a reference electrode at the same time. The cyclic voltammogram (CV) measurements from -2.5 V to +2.5 V were made using potential sweeps of 50 mV/s. Optical transmittance spectra were measured using an ultraviolet visible near-infrared spectrophotometer (Jasco, V-570) in the 200-2500 nm wavelength range. Transmittance data were taken at or near the center of each cell, depending on the size of the sample. The transmittance of the devices was measured against air as reference. The memory effects of the devices were observed under open-circuit voltage conditions.

III. RESULTS AND DISCUSSION

The transmittance spectra of CECD Glass/ITO/NiO/Electrolyte/WO₃/ITO/Glass applied at different voltages are shown in Fig. 2. The bleached transmittance curve was very close to that of the other as-deposited transmittance.

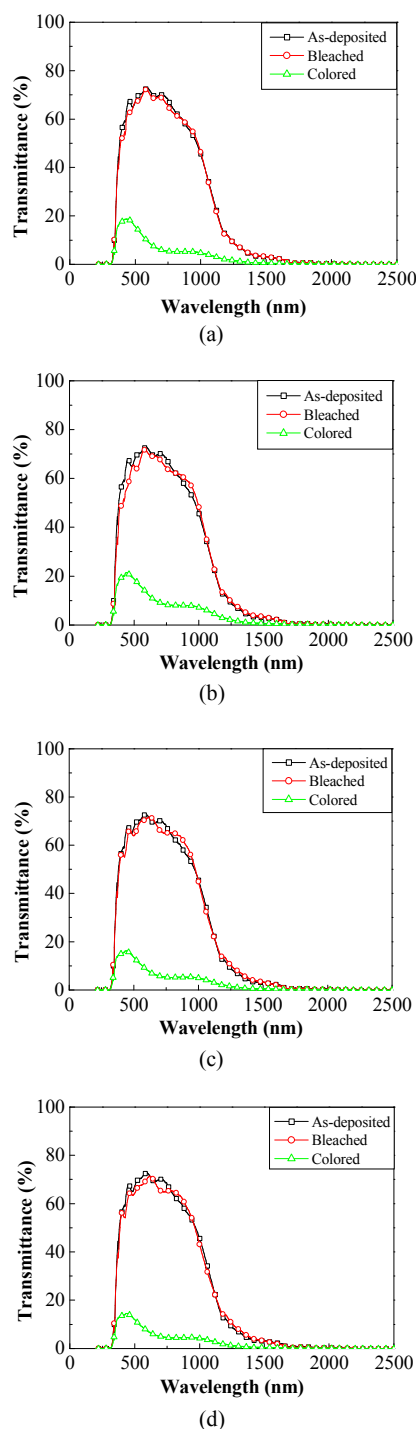


Fig. 2 Transmittance spectra of CECD applied at various voltages; (a) -2.1 V (b) -2.3 V, (c) -2.5 V, and (d) -2.7 V

This indicates good Li^+/e^- intercalation/deintercalation reaction during the coloring/bleaching process. Additionally, in its dark state, applied voltage of -2.5 V was effective in filtering out visible and near-infrared (NIR), i.e. it inhibited the passing of radiated heat; however, these optical properties were dependent on applied voltage.

Fig. 3 plots the $\Delta T\%$ and optical density change (ΔOD) as a function of applied voltage. The ΔOD is given as $\Delta OD = \log(T_{\text{Bleached}}/T_{\text{Colored}})$ at 550 nm in bleached and colored states, respectively. It can be seen that both $\Delta T\%$ and ΔOD increased significantly with an increase in applied negative voltage. This was due to the fact that the degree of insertion charge corresponded to the degree of coloration. Thus, it can be seen that applied voltage is a key parameter for controlling the optical properties of the devices. The movement of Li^+ ion into the WO_3 layer is accompanied by the oxidation reaction of NiO, which creates an internal electrostatic driving force for the diffusion of Li^+ down an ionic concentration gradient, towards WO_3 . As shown, CECD had a maximum $\Delta T\%$ at an applied voltage of -2.5 V. A high is able to provide wide optical modulation with relatively little insertion charge.

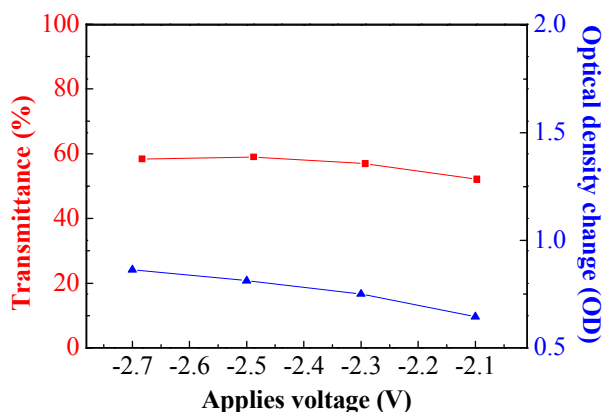


Fig. 3 The $\Delta T\%$ and ΔOD of CECD applied at various voltages

When the applied voltage is removed during the switch, at any point in the coloration, the momentary state of coloration remains unchanged. This phenomenon is known as the memory effect [13]. Fig. 4 (a) shows the transmittance spectra of the CECD, with -2.5 V applied voltage showed excellent long-term memory, with colored transmittance below 19.40% after 24 h, and the color state remained constant, even without supplied energy. Fig. 4 (b) shows the transmittance spectra of CECD exhibiting different degrees coloration after various open-circuit times. The device returned to its original colorless state when driven at +2.5 V, and the bleached transmittance approached that of as-deposited transmittance. In addition, it also shows the colored transmittance of λ at 550 nm after various open-circuit times. The colored transmittance gradually increased with open-circuit time. The colored transmittance at 2 h was 13.51%, and device coloration lightened, but increased slowly, as open-circuit time increased beyond 2 h. In contrast, CECD The memory effect succeeded in maintaining the colored state in intercalated (WO_3 , reduction

reaction)/deintercalated (NiO , oxidation reaction) states, and was therefore appropriate for use in energy-saving devices [14].

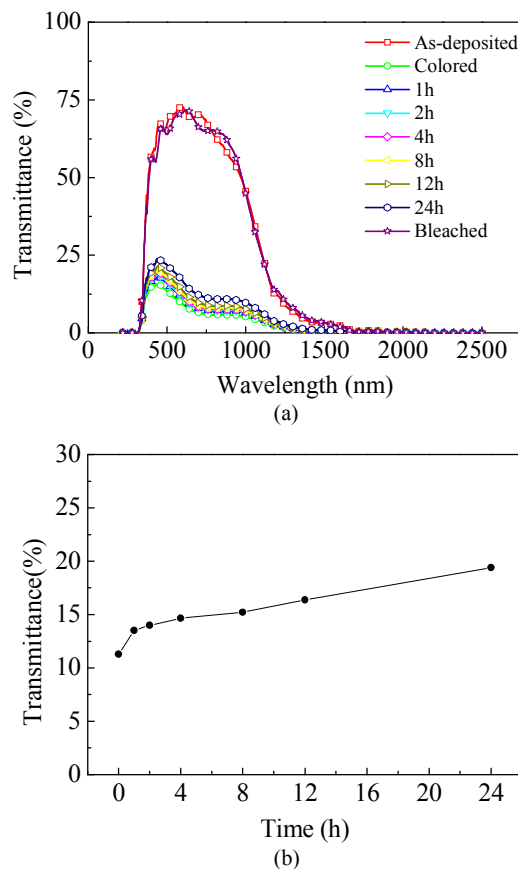


Fig. 4 (a) Transmittance spectra and (b) memory effect of CECD

Fig. 5 shows images of CECD after various open-circuit times. The device coloration lightened with an increase in open-circuit times, and background wording gradually became clear as the device became more transparent.

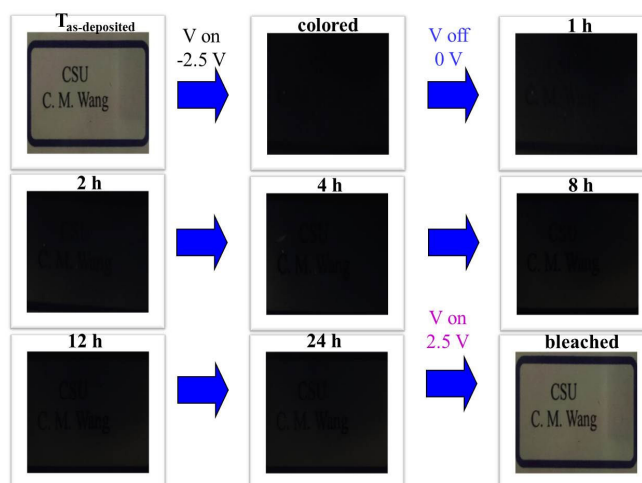


Fig. 5 The images of the CECD after various open-circuit times

IV. CONCLUSIONS

In summary, a CECD employed WO_3 as the cathodically colored layer and NiO as the anodically colored layer were fabricated by rf-magnetron sputtered on an ITO/Glass substrate. The experimental results from as follows: The maximum change $\Delta T\%$ of 58.96% varied from approximately 10.75% to 69.71% and the corresponding ΔOD was 0.81. An applied voltage of -2.5 V drove that the CECD exhibited excellent optical, electrochromic and long-term memory characteristics. Further studies on the physical and electrochemical behavior are underway, to improve η values of CECDs, and device cycle lifetime.

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