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All-Solid-Thin Film Electrochromic Devices Consisting of Layers ITO / NiO / ZrO_2 / WO_3 / ITO

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We have prepared an all-solid-thin film electrochromic device (ECD), consisting of layers ITO / NiO / ZrO_2 / WO_3 / ITO using the PVD method. The WO_3 is used as an electrochromic layer, NiO as an ion-storage layer, and ZrO_2 as a solid electrolyte layer in the all-solid-thin film ECD. The optical transmittance varied between 3-59 %. The device shows the coloration and bleaching time of 120 s and 2 s, respectively, with a good memory effect and desirable cycle-life.

Keywords: Physical vapor deposition, Electrochromic device, Transmission modulation

PACS numbers: 81.15.Ef, 85.60.Pg, 78.20.Ci

1. INTODUCTION

Electrochromic devices (ECD) are of considerable interest in many commercial applications due to their controllable transmission, absorption, and/or reflectance [1, 2]. The electrochromic (EC) phenomenon occurs due to the electrochemical redox reactions that take place in EC materials. There are many possible ECD structures reported in the literature [3, 4]. The ECD structure may have five layers (transparent conducting oxide (TCO) layer / ion-storage layer (IS) / solid electrolyte / EC layer / TCO layer) superimposed on one substrate or may be positioned between two substrates in the laminate configuration. On one side of the EC layer there is an ion-conducting layer and on the other side of it there is an ion-storage layer. In the complementary ECD structure both EC and ion-storage electrode layer show EC properties, one of them colored anodically while the other is colored cathodically. In such a device structure both layers are colored and bleached simultaneously, thus the optical modulation increases. Tungsten oxide (WO_3) is used as a cathodic coloration material [5] and Nickel oxide (NiO) is used as an anodic coloration material [6], because both materials show good EC properties [7, 8]. During the EC coloration and bleaching processes the following electrochemical reactions take place in WO_3 and NiO layers:

$$\underset{(Colorless)}{WO_3} + xe^{-1} + xM^{+} \leftrightarrow \underset{(Blue)}{M_xWO_3} \quad (1)$$

$$\underset{(Bleached)}{NiO} + OH^{-} \leftrightarrow \underset{(Colored)}{NiOOH} + e^{-}$$

$$OR \quad (2)$$

$$\underset{(Bleached)}{Ni(OH)_2} \leftrightarrow \underset{(Colored)}{NiOOH} + H^{+} + e^{-}$$

Zirconium oxide (ZrO_2) thin film is used as a "proton conducting" solid electrolyte [9] and Indium tin oxide (ITO) is used as a transparent conducting electrode [10]. A number of physical vapor deposition methods are reported for the deposition of the different thin film layers for the ECD structure.

In the present paper, we have prepared all-solid-thin film complimentary ECD structure consisting of layers ITO / NiO / ZrO_2 / WO_3 / ITO on a glass substrate using physical vapor deposition. The characteristic of the ECD devices like optical modulation, memory effect, switching time, and cycle-life are presented.

2. ECD FABRICATION

The different layers of all-solid-thin film ECD are deposited by different physical vapor deposition techniques in a high vacuum coating unit. The Indium tin oxide (ITO) thin films, having a sheet resistance of 5-10 Ω/□, are deposited at room temperature (RT) by RF magnetron sputtering on organically cleaned glass substrate [11]. Subsequently, NiO (250 nm) and ZrO_2 thin film (500 nm) are deposited by e-beam evaporation method on the ITO coated substrate held at 200 °C and RT, respectively. H^+ ions are injected into the NiO film, via ZrO_2 / NiO / ITO film structure by electrochemically cycling it in 0.1 M KOH electrolyte. After removing the film structure from the KOH electrolyte it is washed with distilled water to get rid of KOH and dried using dry air. Now the WO_3 thin film (250 nm) is deposited by thermal evaporation method on the above structure at 200 °C temperature. Finally, the ITO thin film is deposited on top of the above device structure.

The substrate was continuously rotated at 40 revolutions per minute (rpm) during the deposition to improve the film's uniformity. A frame-shaped shadow mask having an area 2×2 cm^2 is used to avoid short-circuiting between the different layers from the edge. The final configuration of the multilayered ECD structure is shown in Fig. 1.

The ECD can be characterized by the following: transmittance modulation, open-circuit memory effect, switching time, and cycle-life. The transmittance modulation of the ECD is measured by applying a constant voltage between both ITO electrodes to color and to

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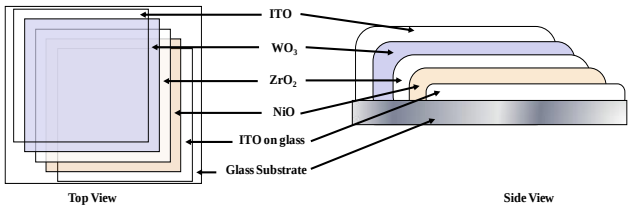


Fig. 1 – A schematic diagram of the ECD's structure with a frame-shaped shadow mask

bleach the device and concomitantly measuring the transmission spectra in 450-1100 nm wavelength ranges for both fully colored and bleached states. For the open-circuit memory effect measurement, a voltage pulse was applied for the coloration of the device and at the same time measured the optical transmittance spectra in an open-circuit condition. A square-wave pulse voltage was applied to the device for evaluating the switching time of the ECD and concurrently the optical measurements were performed using a laser diode (650 nm) and a Si photo-detector. For the cycle-life time measurement of the device, it was subjected to continually color-bleach cycling in the same way as for the switching time measurement.

3. RESULTS AND DISCUSSIONS

The transmittance modulation (i.e. change in the transmittance of bleached (T_b) and the colored (T_c) state of the ECD) is measured by applying a constant voltage (± 5 V) for color and bleach states of the device. When a positive potential is applied to the bottom ITO film, the color changes to dark from transparent and when a negative potential is applied, the color changes to transparent reversibly. During coloration, H^+ ions are intercalated electrochemically into the WO_3 film from NiO film via ZrO_2 electrolyte, while during the bleaching process H^+ ions are de-intercalated from the WO_3 thin film. The wavelength-dependence of the optical transmittance spectra in 400-1100 nm range for the as-deposited, colored, and bleached states of devices are presented in Fig. 2. The ECD shows 56 % transmission modulation with 59 % transmittance in bleach state and 3 % in colored state.

The memory effect is one of the excellent benefits of ECD. Open-circuit memory effect is defined as the time duration in which the material remains in steady state even after switching off the applied voltage. In the bleached state, the WO_3 and NiO thin film layers are electrochemically stable and thus no change is observed if ECD is initially in the bleached state. In this experiment, we applied a voltage of + 5 V for the coloration of the device and then measured the optical behavior in an open-circuit condition. The transmittance of the device was monitored after various open-circuit times and is presented in Fig. 3.

As shown in the Fig. 3, if the ECD is initially in the colored state, the transmittance of the device increases with time and reaches the bleach state. The ECD showed excellent long-term memory, with transmittance in colored state below 3 %, and the colored state remained constant up to 20 % after 170 min. This open circuit memory loss of the ECD was observed due to short-circuiting between WO_3 and NiO layer originating

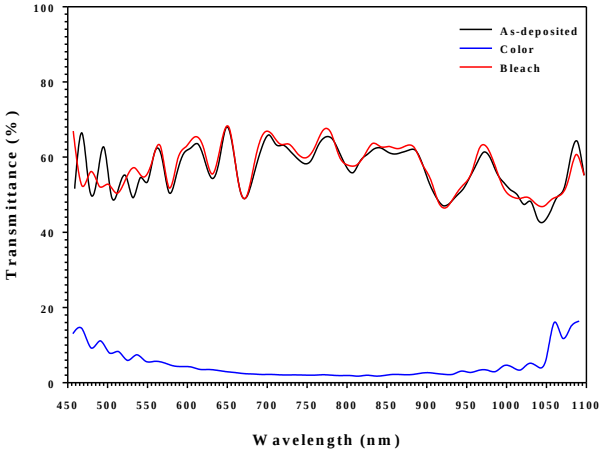


Fig. 2 – The transmittance spectra in the as-deposited color and bleach states of ECD

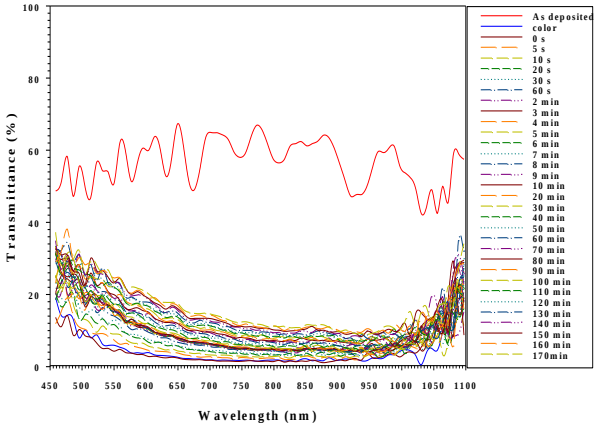


Fig. 3 – The change in the optical transmittance with time in open circuit conditions of ECD

from "pin-holes", which is produced during ZrO_2 film depositions or oxidation and reduction (de-intercalation and intercalation) of WO_3 and NiO, respectively [12].

The switching and stability of the devices were measured by applying a square-wave voltage to the device. In addition, concurrently, the variation in the optical transmittance with time was recorded. Fig. 4 shows the transmittance versus time, at 650 nm wavelength, subjected to different square-wave potentials at intervals of 60 s. The switching time, at 650 nm wavelength, is estimated from Fig. 4 for ECD under various applied voltages. The change in transmittance takes place within a few tenths of a second after application of the voltage pulse but coloration does not reach saturation even after several minutes.

The transmission modulation increases with increase in applied voltage. The maximum transmittance change was observed for an applied voltage of ± 5 V with coloration and bleaching time of 120 and 2 s, respectively. The photographs of the corresponding colored and bleached state are presented in Fig. 5. The application of high voltage leads to fast coloration but also increases the possibility of side reaction, and thereby reducing the device's performance and the life. Appling a low voltage makes switching safer, thereby increasing the life of the devices but the switching time increases and the optical

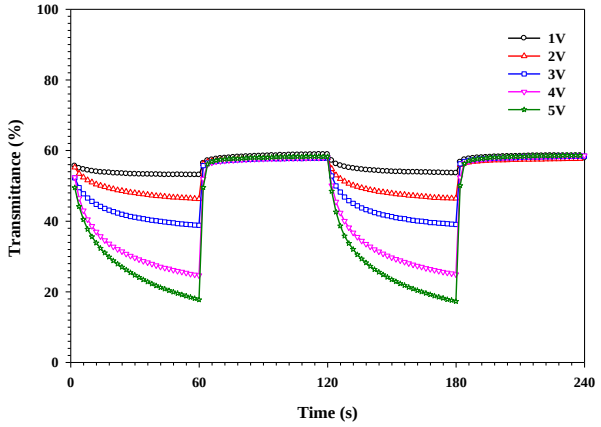
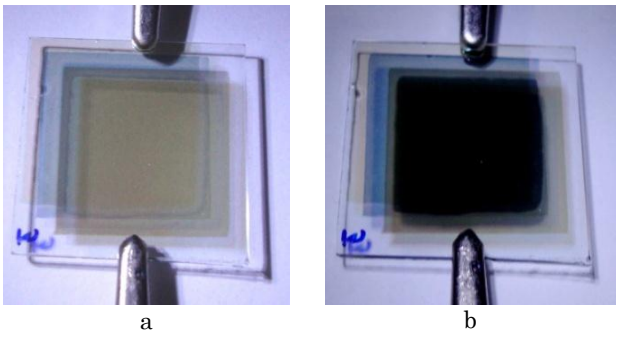


Fig. 4 – The variation in the optical transmittance at 650 nm wavelength at various applied voltages



a b

Fig. 5 – The photographs of the bleached (a), and colored (b) state of ECD

modulation is also less compared to that at a higher voltage. Thus, it is important to optimize the device's operating voltage to achieve a reasonable switching time and an optical modulation with a better lifetime.

For the cycle-life measurement of the device, the device was continually subjected to color-bleach cycles by application of ± 5 V at intervals of 60 s. Fig. 6 shows the color bleach cycle of transmittance modulation of ECD with time. One can see that there was no obvious

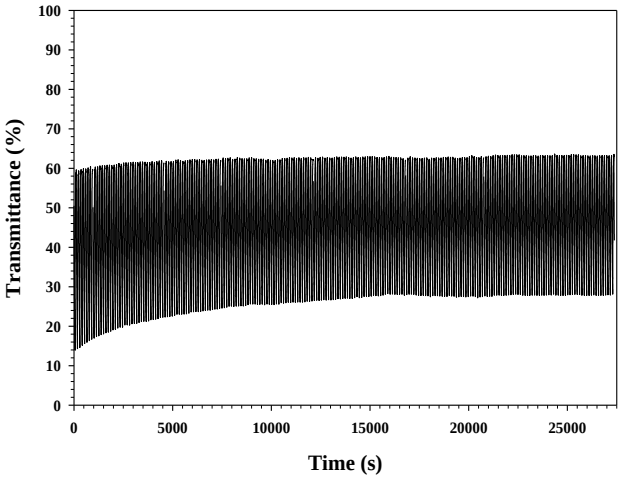


Fig. 6 – The transmittance modulation of ECD with time

decrease in transmittance modulation (60 %-20 %) even after 225 cycles or more, which indicates that this ECD has a good stability. Furthermore, the degradation of the device could not be observed until after a long time operation.

4. CONCLUSIONS

We have made an effort to fabricate all-solid-thin film ECD having a structure of ITO / NiO / ZrO_2 / WO_3 / ITO on a glass substrate. The ECD shows good transmittance modulation (56 %) in wavelength range of 450-1000 nm with good open-circuit memory effect of 170 min. The ECD has coloration and bleaching time of 120 s and 2 s, respectively, with a desirable cycle-life.

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