Extended Abstracts of the 2006 International Conference on Solid State Devices and Materials, Yokohama, 2006, pp. 638-639

P-7-3

Development of Flexible Electrochromic Device with Thin Film Configuration

Hideo Yoshimura, Tomonori Sakaguchi and Nobuyoshi Koshida

Graduate School of Engineering, Tokyo University of Agriculture and Technology
Naka-cho 2-24-16, Koganei-shi, Tokyo 184-8588, Japan
Phone: +81-42-388-7128, Fax: +81-42-385-5395, E-mail: koshida@cc.tuat.ac.jp

1. Introduction

The electrochromic (EC) effect is potentially useful for photonic devices such as paper-like display, since it shows reversible and nonvolatile coloration at low operating voltages. One of the important subjects to be pursued for practical applications of EC effect concerns the sufficient dynamic response. Another one is to fabricate the EC device on flexible substrates. These requirements should be met in the solid-state thin film configuration. Previously [1, 2], we reported that the solid-state EC response time can be significantly improved by introducing carrier accumulation concept into the coloration process. This approach has been applied here to a flexible polymer substrate in order to confirm its usefulness.

2. Experimental

The experimental EC devices were formed on ITO-coated flexible polyethylene-terephthalate (PET) films (0.2 mm in thickness). The basic structure is composed of a top semitransparent electrode (thin Au film or ITO), a electrolytic thin Ta_2O_5 film, a thin amorphous WO_3 film, and a PET substrate, as shown in **Fig. 1 (a)**. The thicknesses of WO_3 and Ta_2O_5 films are 400 and 400 nm, respectively. As the novel structure, a very thin SiO_2 film (7 nm thick) is inserted between WO_3 and Ta_2O_5 films, as shown in **Fig. 1 (b)**, to accelerate the EC kinetics in the same way as the case of glass substrates [1]. All these thin films were formed by RF sputtering or EB evaporation.

Under the forward bias condition that a positive voltage V_b is applied to the top electrode with respect to the substrate, the device acquires a dark-blue coloration by injection of H^+ ions and electrons into the working WO_3 film. This EC coloration was measured by a photodiode as a change in the transmittance for an incident He-Ne laser or white light. Besides the optical evaluation, the effect of inserted SiO_2 film on the EC efficiency was analyzed by cyclic voltammogram measurements separately, in which temporal changes in both the diode current and optical transmittance associated with the reversible EC effect were detected for the two devices as a function of V_b scanned in either the forward or reverse bias region.

3. Results and Discussion

Both devices shown in Figs. 1 (a) and (b) exhibited a definite EC effect. The corresponding experimental EC data at V_b=1-3 V are shown in **Fig. 2.** It can be seen that the EC coloration proceeds more quickly with increasing V_b. In particular, the response time was significantly improved in the device of Fig. 1 (b) with an inserted SiO_2 film, as observed in the case of glass substrates. The EC response time t_{70}, defined as a time at which the optical transmittance falls down to 70% of the initial value, reaches 370 ms at V_b=3 V. The coloration was bleached within a similar response time upon application of a reversed bias voltage.

In **Fig. 3** is shown the energy band diagram to explain the mechanism of the fast EC operation observed in the novel structure. The WO_3 and Ta_2O_5 films are supposed to be n-type and intrinsic, respectively. Under a forward bias, holes and electrons are blocked at the both sides of SiO_2 barrier. Consequent increase in the holes density accelerates oxidation of residual H_2O molecules in the Ta_2O_5 film. As a result, the generation rate of H^+ ions should be enhanced. In addition, electrons accumulated at the WO_3/SiO_2 interface attract H^+ ions and promote their intercalation into WO_3 through the SiO_2 film to form blue-colored H_xWO_3 (x=0-1). When a reverse bias voltage is applied, H^+ ions and electrons are extracted from H_xWO_3, and then the original semitransparent WO_3 film appears again.

Measured t_{70} values for the two devices with and without SiO_2 film are plotted as a function of V_b in **Fig. 4**. In this figure, previously reported data obtained from the glass substrate are also shown for reference. We can see that by introducing a SiO_2 barrier layer the EC response of the flexible device has been improved to a comparable level with that in the glass substrate case. In accordance with analyses of surface nanostructures, there remains some difference in the grain size distribution between the two films deposited on PET and glass substrates. More fast EC response could be attained in the flexible case by appropriate control of process parameters.

4. Conclusion

Carrier accumulation effect on the EC response time has been confirmed in the solid state device fabricated on a flexible substrate by low-temperature processing. The result provides very important step for development of practical EC devices.

Acknowledgments

This work was partially supported by a Grant-in-Aid for the 21st Century COE Program of Future Nano-Materials Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

References

[1] H. Yoshimura and N. Koshida, Appl. Phys. Lett. **88**, 093509 (2006).

[2] H. Yoshimura and N. Koshida, Jpn. J. Appl. Phys. **45**, 3479 (2006).

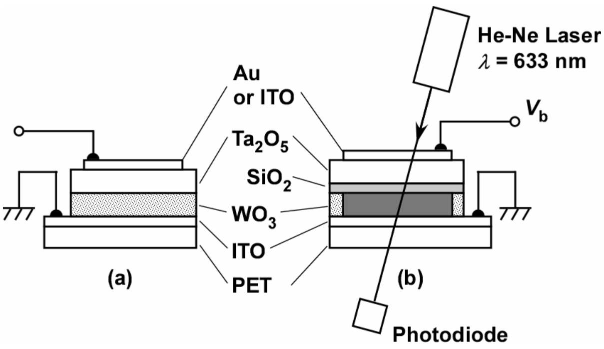

Fig. 1. Schematic cross-section of flexible EC devices and optical detection of EC coloration. (a): Conventional structure. (b): Proposed novel structure with a thin barrier layer (thin SiO_2 film in this case).

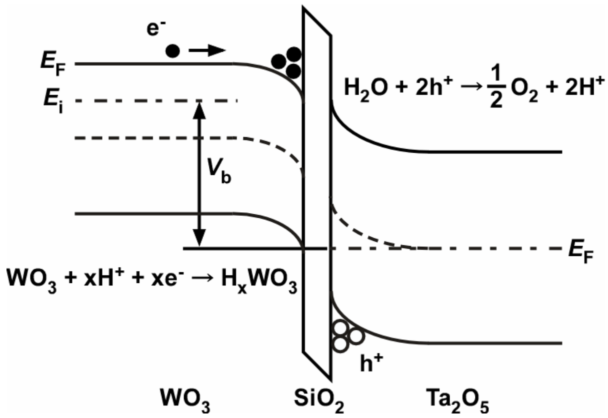

Fig. 3. Energy band diagram of solid-state EC operation in the proposed device with a carrier accumulating thin SiO_2 film.

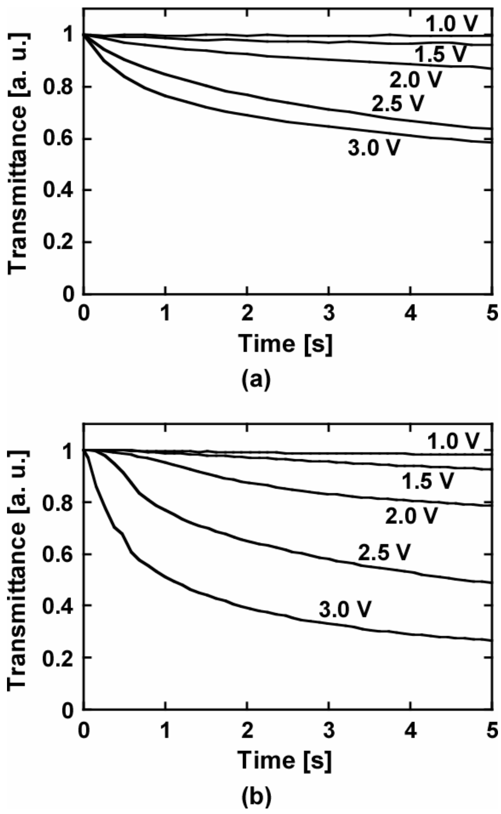

Fig. 2. Change in the optical transmittance due to EC coloration at different applied voltages for two devices (a) and (b) corresponding to Figs. 1 (a) and (b), respectively.

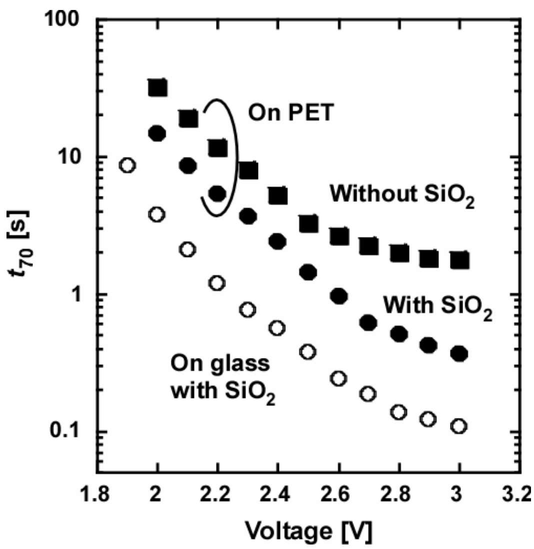

Fig. 4. The voltage dependencies of the EC response time t_{70} for three devices: conventional device on PET with no SiO_2, novel device on a PET with SiO_2, and novel device on a glass substrate with SiO_2. A significant improvement in the EC response has been attained in the flexible device.