

Quick Response Observed in Solid-State Electrochromic Device with an Interfacial Barrier Structure

Hideo Yoshimura and Nobuyoshi Koshida

Department of Electronic and Information Engineering, Faculty 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: +81-42-388-7128, E-mail: koshida@cc.tuat.ac.jp

1. Introduction

Electrochromic (EC) effect is a field-induced ion insertion into some kind of thin films followed by a significant change in their optical and electrical properties. Owing to its reversible and nonvolatile characteristics, the EC effect is potentially useful for photonic devices such as passive display. To date, however, the EC device has not been able to take solid-state type, because a sufficiently quick response can be obtained only from systems with liquid junctions [1].

From a practical viewpoint, a reliable solid-state EC composition would be desired for applications. It is presented here that the response time is significantly shortened by the introduction of a carrier accumulation layer into the interface between an EC film and a solid electrolyte film.

2. Basic EC Operation and Proposal

A conventional solid-state EC device is composed of a top semitransparent electrode, a thin amorphous WO_3 film, a thin electrolyte Ta_2O_5 film, and a ITO-coated glass substrate, as shown in **Fig. 1 (a)**. In the novel EC structure proposed here, a very thin SiO_2 film is deposited between WO_3 and Ta_2O_5 films, as shown in **Fig. 1 (b)**. All the components of the device are formed by RF sputtering or EB evaporation.

For the forward bias scheme in both structures, that is, under the situation that a positive voltage is applied to the top electrode with respect to the substrate, positive H^+ ions produced at the interface by oxidation of residual H_2O molecules in the Ta_2O_5 film are injected into the working WO_3 film. Also electrons are injected from the substrate into the WO_3 film at the same time. As a result, non-stoichiometric compound H_xWO_3 called tungsten bronze is formed, where $0 < x < 1$.

As illustrate in **Fig. 2**, M is inserted into a large space in the main lattice of WO_3 . The inserted H atoms act as color centers and donors optically and electrically, respectively. Then the originally transparent and insulating WO_3 film becomes colored (dark blue) and conductive. This effect is stored in the nonvolatile manner. When the device is biased by a reverse voltage, H^+ ions and electrons are extracted from the H_xWO_3 film, and then the original WO_3 film property appears again.

In the device structure shown in **Fig. 1 (a)**, there are two major limiting factors for dynamic response: production rate of M^+ ions and subsequent diffusion process. If the former factor should be enhanced factor is enhanced without affect on diffusion, the fast EC operation could be possible even in the solid-state scheme.

The energy band diagrams corresponding to the two EC devices in **Figs. 1(a)** and **1(b)** are shown in **Figs. 3(a)** and **3(b)**, respectively. In both cases, the devices are biased by a forward voltage. The WO_3 and Ta_2O_5 films are supposed to be n-type and intrinsic, respectively. Under the forward bias, holes drifted from the bulk Ta_2O_5 promote oxidation of H_2O molecules at the interface. In the conventional structure (**Fig. 1(a)**), the high production rate of H^+ ions cannot be expected, because holes concentration at the interface is limited by leakage towards the WO_3 film as suggested from **Fig. 3(a)**.

In the device structure proposed in **Fig. 1(b)**, in contrast, the production rate of H^+ ions at the interface should be enhanced by holes accumulation due to the barrier against diffusion as expected from **Fig. 3(b)**. Accumulated electrons at the WO_3 film side could also contribute to extraction of produced H^+ ions and accelerate the EC process as shown in **Fig. 3(b)**.

3. Experimental Results

The coloration speed of the WO_3 film associated with EC effect was measured by a time evolution of the transmittance for an incident white light. In **Fig. 4** are shown the experimental data at a applied voltage of 3 V for the conventional and proposed devices. We can see that the EC response is drastically improved by the introduction of a barrier layer. The response time defined as a time at which the optical transmittance drops to 70% of the initial value reaches 100 ms. The coloration was quickly bleached by a reverse bias voltage. This response is close to a practical level for some applications.

4. Conclusion

Carrier accumulation is very effective to promote efficient production of intercalation species and to enhance the dynamic response of the solid-state EC operation. The proposed device concept provides a promising means to overcome the most difficult problem in the development of solid-state EC devices.

Acknowledgments

This work was partially supported by a Grant-in-Aid from the Ministry of Education, Culture, Sports, Science and Technology of Japan, and the COE Future Nanomaterials Program.

References

- [1] M. Nagasu and N. Koshida, J. Appl. Phys., **71**, 398 (1992).

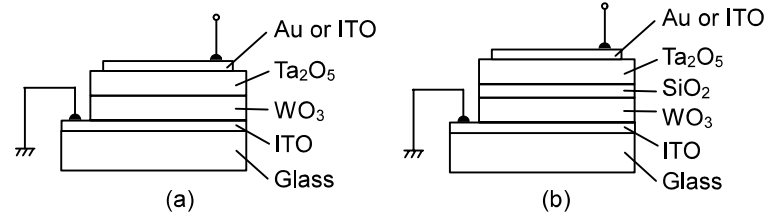


Fig. 1. Schematic crosssection of solid-state EC devices. (a): Conventional structure. (b): Proposed novel structure with a thin barrier layer (thin SiO₂ film in this case).

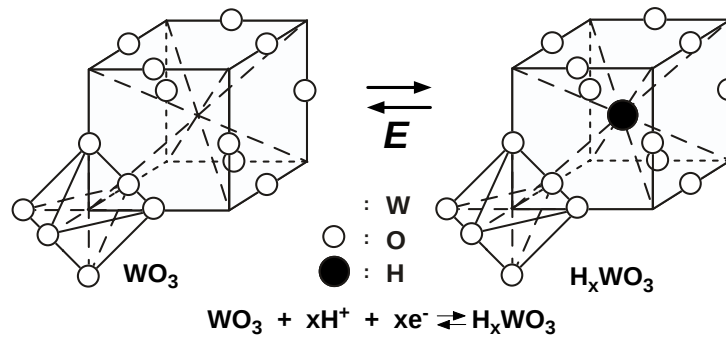


Fig. 2. Schematic illustration of the EC process. Protons reversibly inserted into a space in the main lattice of WO₃ with a perovskite structure produces a significant change in the optical and electrical properties.

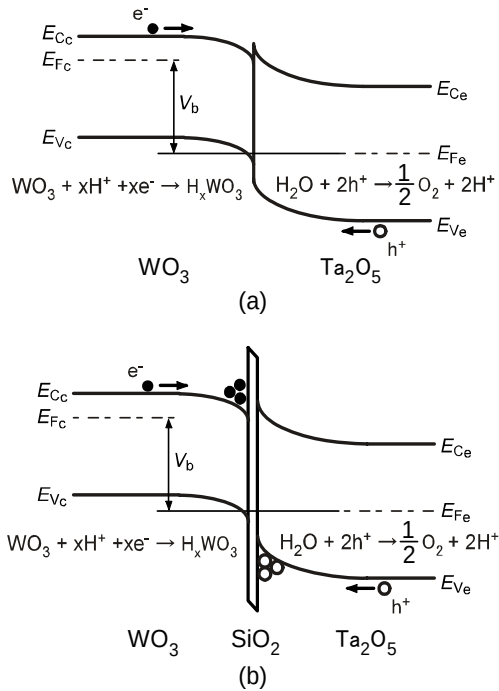


Fig. 3. Energy band diagrams of solid-state EC devices under operation. (a): Conventional structure. (b): Proposed novel structure with a thin barrier layer for carrier accumulation.

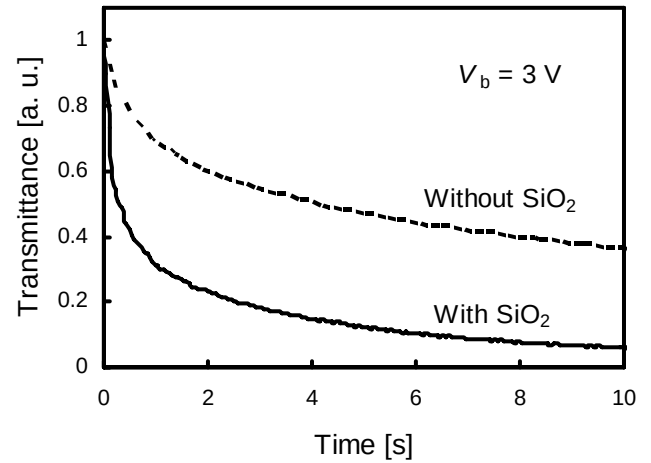


Fig. 4. Comparison of the optical response of the two solid-state EC devices at a applied voltage of 3 V. (a): Conventional structure (dashed curve). (b): Novel structure with a thin SiO₂ barrier film (solid curve). A drastic improvement in the EC response has been attained in the solid-state configuration.