| Title | Fast operation of a WO3-based solid-state electrochromic transistor |
|-------|---------------------------------------------------------------|
| Author(s) | Onozato, Takaki; Nezu, Yukio; Cho, Hai Jun; Ohta, Hiromichi |
| Citation | AIP Advances, 9(2), 025122 |
| Issue Date | 2019-02 |
| Doc URL | http://hdl.handle.net/2115/75112 |
| Rights | © 2019 Takaki Onozato, Yukio Nezu, Hai Jun Cho, and Hiromichi Ohta |
| Rights(URL) | https://creativecommons.org/licenses/by/4.0/ |
| Type | article |
| File Information | 1.5089604.pdf |

Hokkaido University Collection of Scholarly and Academic Papers: HUSCAP
Fast operation of a WO$_3$-based solid-state electrochromic transistor

Takaki Onozato, Yukio Nezu, Hai Jun Cho, and Hiromichi Ohta

ARTICLES YOU MAY BE INTERESTED IN

Effects of vacuum annealing on the electron mobility of epitaxial La-doped BaSnO$_3$ films
APL Materials 7, 022507 (2019); https://doi.org/10.1063/1.5054154

Large thickness dependence of the carrier mobility in a transparent oxide semiconductor, La-doped BaSnO$_3$
Applied Physics Letters 112, 232102 (2018); https://doi.org/10.1063/1.5033326

Peculiar magnetotransport properties in La$_{0.67}$Sr$_{0.33}$MnO$_3$/LaAlO$_3$/SrTiO$_3$
AIP Advances 9, 035129 (2019); https://doi.org/10.1063/1.5079898
Fast operation of a WO$_3$-based solid-state electrochromic transistor

Cite as: AIP Advances 9, 025122 (2019); doi: 10.1063/1.5089604
Submitted: 21 January 2019 • Accepted: 18 February 2019 • Published Online: 26 February 2019

Takaki Onozato, $^1$ Yukio Nezu, $^1$ Hai Jun Cho,$^{1,2}$ and Hiromichi Ohta$^{1,2,a,16}$

AFFILIATIONS
$^1$ Graduate School of Information Science and Technology, Hokkaido University, N14W9, Kita, Sapporo 060-0814, Japan
$^2$ Research Institute for Electronic Science, Hokkaido University, N20W10, Kita, Sapporo 001-0020, Japan

$^a$ Correspondence should be addressed to: H.O. (hiromichi.ohta@es.hokudai.ac.jp)

ABSTRACT
Electrochromic transistors (ECTs) have attracted attention as advanced memory technology because one can use both electrochromism and switching of electrical conductivity in a nonvolatile manner. Although several solid-state ECTs have been proposed so far, their operating speed is still slow (operating time $>$ 1 min) as compared to liquid-based ECTs ($\sim$ 20 s) due to their asymmetric gate-source electrode configuration. Here we demonstrate a fast operation of a solid-state ECT. We fabricated a solid-state ECT with three terminal gate-source-drain electrodes using an amorphous WO$_3$ film as the electrochromic material and amorphous TaO$_x$ as the solid electrolyte. By the insertion of a thin ZnO layer between the source and drain electrodes to achieve pseudo symmetric gate-source electrode configuration, we greatly reduced the operation time to less than 1 s at $\pm$ 3 V application while keeping the on-to-off ratio of $\sim$ 30. The present approach is effective to improve the operating speed of ECTs and may be practically used in advanced memory technologies.

© 2019 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/). https://doi.org/10.1063/1.5089604

I. INTRODUCTION
Electrochromic transistors (ECTs), which are the combinations of electrochromic displays (ECDs) and three terminal transistors, have attracted attention as advanced memory devices because ECTs have advantages against conventional data storage devices, which can store 1 bit of information as 0 or 1. For example, WO$_3$-based ECT channel turns from high resistive to low resistive state when the positive gate voltage is applied. At the same time, the color of the ECT channel turns from almost colorless transparent into dark blue. Thus, ECT can store the information of electrical resistance and color simultaneously in a nonvolatile manner.

Although many EC materials including organic materials are reported thus far, WO$_3$ has been considered as one of the best EC materials to develop ECT because WO$_3$ has several advantages such as large on/off ratio of the electrical conductivity and the large color contrast ratio. Several researchers have investigated the structural phase transition and metal-insulator transition using a liquid electrolyte and an epitaxial WO$_3$ film thus far. In 2015, Barquinha et al. demonstrated amorphous WO$_3$-based ECT prepared on a paper substrate. Very recently, neuromorphic transistor, which imitated synaptic movements, has been developed using WO$_3$-ECTs. Previously, most researchers used liquid electrolytes to fabricate WO$_3$-based ECT, however, the use of a liquid is not suitable for the practical application due to the leakage problem. To overcome this problem, several researchers used solid electrolytes to fabricate WO$_3$-based ECTs, which are free from the leakage issues. However, the operating speed of solid-state WO$_3$-based ECTs is slow (operating time $>$ 1 min) as compared to liquid-based ECTs ($\sim$ 20 s), most likely due to that the ionic conductivity of liquid electrolytes is higher than that of solid electrolyte.

In order to overcome this issue, we compared to the device structure of WO$_3$-based ECTs and WO$_3$-based electrochromic displays (ECDs) because ECDs can be operated within several milliseconds. Figure 1 schematically illustrates the structural difference between an ECD and an ECT. Both devices are composed of WO$_3$, electrolyte, and NiO, which are sandwiched by two transparent conducting oxides (TCOs). Protonation of WO$_3$ occurs when the electric field is applied to the multilayered structure composed of the top TCO electrode, NiO, electrolyte, WO$_3$, and the bottom electrode. Therefore, the multilayers are sandwiched by the two ITO electrodes with fully overlapped parallel plate electrode configuration in the
FIG. 1. Electrochromic devices. Schematic device structures of (a) electrochromic displays (ECDs), (b) reported electrochromic transistor, and (c) present electrochromic transistor. All devices are composed of $\text{WO}_3$, electrolyte, and NiO, which are sandwiched by two ITO (a transparent conducting oxide, ITO). Since there is a parallel plate electrode configuration, the operating speed of (a) is much faster than that of (b), of which the electrode configuration is asymmetric. Although one can use the resistance change in the case of (b), it cannot be used in the case of (a). In order to overcome this dilemma, we would like to propose the device structure (c), which is three terminal thin film transistor structure with parallel plate electrode configuration. We expected that the device (c) exhibits both fast transistor-like characteristic as well as the electrochromic display characteristics.

(a) Operating speed: Fast
Parallel plate electrode configuration
Resistance change cannot be used

Bleached state

\[ \text{WO}_3 \quad \text{Electrolyte} \quad \text{NO}_x \]
Transparent substrate

Colored state

\[ \text{Oxidized NiOOH} \quad \text{Electrolyte} \quad \text{Protonated } \text{H}_x\text{WO}_3 \]
Transparent substrate

(b) Operating speed: Slow
Asymmetric electrode configuration
Resistance change can be used

Bleached & high resistance state

\[ \text{TCO} \quad \text{Gate} \quad \text{Source} \quad \text{Drain} \]
Transparent substrate

Colored & low resistance state

\[ \text{Oxidized NiOOH} \quad \text{Electrolyte} \quad \text{Protonated } \text{H}_x\text{WO}_3 \]
Transparent substrate

(c) Operating speed: Fast
Parallel plate electrode configuration
Resistance change can be used

Bleached & high resistance state

\[ \text{Gate} \quad \text{Source} \quad \text{Drain} \]
Bottom TCO

Colored & low resistance state

\[ \text{TCO} \quad \text{Gate} \quad \text{Source} \quad \text{Drain} \]
Bottom TCO

The on to off current ratio depends on the sheet conductance ratio of $\sigma_c \text{H}_x\text{WO}_3 / \sigma_b \text{Bottom TCO}$

We inserted thin oxygen deficient ZnO layer, which is known as an n-type wide bandgap ($E_g = 3.4$ eV) semiconductor, as the bottom TCO between the source and drain electrodes to achieve pseudo symmetric gate-source electrode configuration. As a result, we greatly reduced the operation time to less than 1 s at ±3 V application while keeping the on-to-off ratio of ~30. The present approach is effective to improve the operating speed of ECTs and may be practically used in advanced memory technologies.

II. EXPERIMENTAL

The ECT devices were fabricated on an alkaline-free glass substrate (Corning EAGLE XG, $10 \times 10 \times 0.7$ mm) by pulsed laser deposition (PLD) with KrF excimer laser (248 nm, 10 Hz)
using stencil masks as shown in Figs. 2(a) and 2(b). All film fabrication processes were conducted at room temperature. (see experimental section for the detail). At first, a 30-nm-thick oxygen deficient ZnO film with the sheet conductance of \( \sim 150 \) \( \mu \)S, which is more than two orders of magnitude smaller than that of protonated \( \text{WO}_3 \) (\( \sim 70 \) mS), was deposited on the substrate as the bottom TCO layer. The electrical conductivity, carrier concentration, and Hall mobility of the ZnO layer were \( \sim 50 \) S cm\(^{-1} \), \( \sim 5 \times 10^{-19} \) cm\(^{-3} \), and \( \sim 6.6 \) cm\(^2\) V\(^{-1}\) s\(^{-1} \), respectively, at room temperature. Then the source and drain electrodes (a-ITO), a-WO\(_3\) active layer (100 nm), a-TaO\(_x\) electrolyte (250 nm), NiO counter layer (20 nm), and gate electrode (a-ITO) were deposited sequentially using the stencil masks [Fig. 2(a)]. The active channel size was 800 \( \mu \)m in length and 400 \( \mu \)m in width as schematically shown in Fig. 2(b). The ITO, WO\(_3\) and TaO\(_x\) films were amorphous, whereas the ZnO and NiO films were polycrystalline [Fig. 3], which was analyzed by glancing incidence (\( \omega \)-fixed 2\( \theta \) scan) X-ray diffraction (Cu K\( \alpha _1 \), ATX-G, Rigaku Co.).

Since we inserted a thin ZnO layer as a thin TCO, the electrical resistance switching ON/OFF ratio should be lower than reported without bottom TCO layer ECT device (ON/OFF ratio \( \sim 10^6 \)). The ON/OFF ratio can be controlled using the following equation, which describes the relationship between \( t_{\text{WO}_3} \) and \( t_{\text{TCO}} \): 

\[
\log \left( \text{ON/OFF} \right) = \log \left( \frac{t_{\text{WO}_3}}{t_{\text{TCO}}} \right) + \log \left( \frac{\sigma_{\text{WO}_3}}{\sigma_{\text{TCO}}} \right)
\]

Figure 2(c) shows the calculated ON/OFF ratio as a function of the thickness ratio of \( t_{\text{WO}_3}/t_{\text{TCO}} \). Since we used a 30-nm-thick ZnO (\( \sim 50 \) S cm\(^{-1} \)), the maximum ON/OFF ratio was calculated be \( \sim 50 \) (filled red circle). It should be note that there is a trade-off relationship between the ON/OFF ratio and the operating time. In order to increase the operating speed while keeping moderate ON/OFF ratio, we used a 30-nm-thick ZnO film.

III. RESULTS AND DISCUSSION

The present ECT with the TCO layer could be operated very fast. Figure 4(a) shows the changes in the sheet resistance (\( R_s \)) of the present ECT (w/TCO) as a function of time for both the protonation (gate voltage, \( V_g = +3 \) V, left) and deprotonation (\( V_g = -3 \) V, right) stages at room temperature. The gate current (\( I_g \)) during \( V_g \) application was measured by using a source measure unit (Keithley 2450). \( R_s \) was measured by the d.c. four probe method in the van der
FIG. 4. Change in the sheet resistance and the optical transmission before and after the protonation. (a) The decay of the sheet resistance (R_s) when +3 V is applied (left) and recovering of R_s when −3 V is applied. The result without the bottom TCO is also shown for comparison (dotted lines). The R_s drops within 1 s when +3 V is applied, whereas the R_s increases within 1 s when −3 V is applied. The operation time of the present device is much faster than the device without the TCO layer. (b) Optical transmission spectra of the present device. The transmission (T) of the deprotonated state (gray line) is 67 % at 550 nm whereas the protonated state shows 28 % at λ = 550 nm. The inset shows the photographs of the device. After the protonation, the device becomes dark blue whereas the device was transparent at the deprotonated state.

FIG. 5. Sheet resistance of the device as a function of the integrated electron density (Q). Details of the calculation process of charge electron-density are described elsewhere. To achieve 100 % protonation/oxidation, Q = 1.5 × 10^{22} cm^{-3} is required based on our electrochromic reaction: WO_3 + xH^+ + xe^- → HxWO_3. The present ECT device obeys the Faraday’s laws of electrolysis. (a) The R_s gradually decreases from 3 × 10^{3} Ω sq.\(^{-1}\) to 8 × 10^{1} Ω sq.\(^{-1}\) with increasing Q and saturates when Q is 4 × 10^{22} cm^{-3}. (b) The R_s increases from 8 × 10^{3} Ω sq.\(^{-1}\) to 3 × 10^{4} Ω sq.\(^{-1}\) with increasing Q and saturates when Q is 4 × 10^{22} cm^{-3}. 
Then, we measured the optical transmission change of the present ECT [Fig. 4(b)]. The transmission (T) of the deprotonation state was 67% at the wavelength (λ) of 550 nm and has a high overall transmittance in the visible region. After a gate voltage application of +3 V, the transmittance dramatically decreased to 28% at λ = 550 nm, and the average transmittance in the visible region was greatly reduced (see the video of the optical transmission spectrum during the device operation at supplementary material). To check the cyclability of the present ECT, we applied alternating $V_g = \pm 3$ V at 4 s period (i.e. 2 s at +3 V and 2 s at −3 V) and monitored the sheet resistance (Fig. 6). Cyclability over 90% was achieved after 500 repetitions, which ensures the good reversibility of the present ECT device.

Figure 7 shows a comparison between the present WO$_3$-based ECT and the reported WO$_3$-based ECTs (solid-state ECTs$^{3,13,18}$ and liquid electrolyte ECTs$^{2,7,10,19,20}$). The operating voltage and the operating time of the present ECT were ±3 V and ~1 s, respectively. Since there is an inverse proportional relationship between the operating voltage and the operating time, our result shows that the insertion of a thin TCO in solid-state WO$_3$-based ECTs is effective to greatly reducing both operating voltage and speed. Although current operating time (~1 s) is difficult to use as the memory cell of the flash memory (~μs), the operating time would be enough fast for smart display applications. Thus, the present approach may be practically used in advanced memory technologies.

**IV. CONCLUSIONS**

In conclusions, we have demonstrated that a solid state WO$_3$-based ECT with TCO bottom layer can be operated faster (~1 s) than the reported WO$_3$-based ECTs (solid-state: ~1 min, liquid electrolytes: ~20 s) at low operation voltage (±3 V) keeping the ON/OFF ratio ~30. Since all fabrication processes were performed at room temperature, the present ECT can be fabricated not only on glass substrates but also on flexible substrates such as plastics, which will have significant economic advantages. We envision that this new EC device structure will move the EC technology forward and be utilized in advanced memory devices.

**SUPPLEMENTARY MATERIAL**

See supplementary material for the movie showing fast operation of the electrochromic transistor.

**ACKNOWLEDGMENTS**

This research was supported by Grants-in-Aid for Scientific Research A (17H01314), the Asahi Glass Foundation, and the Mitsubishi Foundation. Student aids from JSPS (T.O., 17J01281) is also greatly appreciated.

**REFERENCES**

1. H. Akinaga and H. Shima, Proc. IEEE 98, 2237–2251 (2010).
2. P. Barquinha, S. Pereira, L. Pereira, P. Wojcik, P. Grey, R. Martins, and E. Fortunato, Adv. Electron. Mater. 1, 1500030 (2015).
3. T. Katase, T. Onozato, M. Hirono, T. Mizuno, and H. Ohta, Sci. Rep. 6, 25819 (2016).
4. D. Y. Tu, D. Nilsson, and R. Forchheimer, J Disp Technol 9, 755–759 (2013).
Z. Li, Y. Zhang, A. L. Holt, B. P. Kolasa, J. G. Wehner, A. Hampp, G. C. Bazan, T.-Q. Nguyen, and D. E. Morse, New J. Chem. 35, 1327 (2011).

V. Jain, H. M. Yochum, R. Montazami, and J. R. Heflin, Appl. Phys. Lett. 92, 033304 (2008).

M. Wang, S. Shen, J. Ni, N. Lu, Z. Li, H. B. Li, S. Yang, T. Chen, J. Guo, Y. Wang, H. Xiang, and P. Yu, Adv. Mater. 29, 1703628 (2017).

S. G. Altendorf, J. Jeong, D. Passarello, N. B. Aetukuri, M. G. Samant, and S. S. Parkin, Adv. Mater. 28, 5284–5292 (2016).

X. Leng, J. Pereiro, J. Strle, G. Dubuis, A. T. Bollinger, A. Gozar, J. Wu, N. Litombe, C. Panagopoulos, D. Pavuna, and I. Bozovic, Npj Quantum Mater 2, 35 (2017).

C. ViolBarbosa, J. Karel, J. Kiss, O. D. Gordan, S. G. Altendorf, Y. Utsumi, M. G. Samant, Y. H. Wu, K. D. Tsuei, C. Feber, and S. S. Parkin, Proc. Natl. Acad. Sci. USA 113, 11148–11151 (2016).

J. T. Yang, C. Ge, J. Y. Du, H. Y. Huang, M. He, C. Wang, H. B. Lu, G. Z. Yang, and K. J. Jin, Adv. Mater. 30, 1801548 (2018).

T. Tsuchiya, M. Jayabalan, K. Kawamura, M. Takayanagi, T. Higuchi, R. Jayavel, and K. Terabe, Jpn. J. Appl. Phys. 57, 04fk01 (2018).

P. Grey, L. Pereira, S. Pereira, P. Barquinha, I. Cunha, R. Martins, and E. Fortunato, Adv. Electron. Mater. 2, 1500414 (2016).

T. Niwa and O. Takai, Thin Solid Films 518, 1722–1727 (2010).

T. Minami, H. Nanto, and S. Takata, Appl. Phys. Lett. 41, 958–960 (1982).

R. E. I. Schropp and A. Madan, J. Appl. Phys. 66, 2027–2031 (1989).

T. Katase, Y. Suzuki, and H. Ohta, Adv. Electron. Mater. 2, 160044 (2016).

S. Thakoor, A. Moopenn, T. Daud, and A. P. Thakoor, J. Appl. Phys. 67, 3132–3135 (1990).

X. Meng, F. Quenneville, F. Venne, E. Di Mauro, D. Işık, M. Barbosa, Y. Drolet, M. M. Natile, D. Rochefort, F. Soavi, and C. Santato, J. Phys. Chem. C 119, 21732–21738 (2015).

H. Kalhori, M. Coey, I. Abdolhosseini Sarsari, K. Borisov, S. B. Porter, G. Atchison, M. Ranjbar, H. Salamati, and P. Stamenov, Sci Rep 7, 12253 (2017).