Extended Abstracts of the 2009 International Conference on Solid State Devices and Materials, Sendai, 2009, pp1318-1319

Evidence of Carrier Accumulation Effects on the Response Enhancement in Thin-Film Electrochromic Devices

Hideo Yoshimura[1], Yoshishige Tsuchiya[2], Hiroshi Mizuta[2], and Nobuyoshi Koshida[1]

[1]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
[2]Nano Group, School of Electronics and Computer Science, University of Southampton
Southampton, SO17 1, UK

1. Introduction

The electrochromic (EC) effect is attractive for photonic device applications such as shading windows and passive displays, since it enables reversible and nonvolatile coloration. In the previous papers [1,2], we reported that the dynamic response of a solid-state EC device can be significantly improved by introducing a carrier accumulation mechanism into the device operation. This approach works well with the fabrication process on the flexible polymer substrate [3].

The EC coloration is caused by proton generation and subsequent field-assisted diffusion into the coloration film. To clarify the underlying mechanism of accelerated EC coloration, the EC kinetics has been analyzed using simulation of the carrier distribution in the EC device.

2. Theoretical Analysis

The interfacial simulation was performed using ATLAS (by SILVACO) as in the case of MOS structure analyses. The EC device structures under analysis are shown in **Fig. 1**. The device and material parameters used for the present analysis are summarized in **Table 1**. The coloration film, WO_3, was assumed as an n-type oxide semiconductor based on the results of the first principle simulation by Cora et al [4]. The density-of-state profiles in the band gap and those of the band tail are shown in **Fig. 2** for three different films.

In the EC analysis, the mesh spacing near the hetero-junction structure was chosen to 0.1 nm so as to be small enough in comparison to the SiO_2 film thickness. Poisson's equation and the drift-diffusion based carrier transport equation which takes account of carrier recombination and generation effects were solved by using the 2-dimensional finite element method. Then the profile of the density-of-state in the band gap and the corresponding carrier density distribution were calculated under biased conditions. In this calculation, the continuous trap density model [5] was employed assuming the band tail state and the gap peculiar to the amorphous semiconductor (Fig. 2). Adapting the obtained interfacial carrier density to the kinetic equation, the EC coloration process was shown as the transient optical transmittance.

3. Results and Discussion

Calculated density-of-states in the band gap and the corresponding carrier density in the device are shown in **Fig. 3** at a bias voltage of V_b=3 V. In contrast to the conventional devices, Fermi-level pining was effectively dissolved by introducing a thin SiO_2 barrier film, and then the density of holes and electrons substantially increased at the SiO_2/Ta_2O_5 and the WO_5/SiO_2 interfaces, respectively. The increased density of holes found at the SiO_2/Ta_2O_5 interface is, in particular, very important to enhance the generation rate of protons leading to fast EC coloration.

The EC kinetics analysis was conducted by using the diffusion equation under a bias voltage with the interfacial holes density estimated above as an initial condition. The obtained transmittance is plotted in **Fig. 4** for the structures with and without the SiO_2 barrier film. The major fitting parameters are the diffusion coefficient of protons in WO_3 film and the final values of optical transmittance. We can see that the curves agree well with the experimental data indicated by open plots, and that the carrier accumulation accelerates the EC coloration. The final optical transmittance is consistent with that expected from the concentration of protons generated by accumulated holes.

4. Conclusion

The simulation quantitatively supports the hypothesis that the EC response time is significantly improved by carrier accumulation. The present results provide useful information to develop fast solid-state EC devices.

This work was partially supported by a Grant-in-Aid for the 21st Century COE Program of Future Nano-Materials Research from the MEXT.

References

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

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

[3] H. Yoshimura, T. Sakaguchi and N. Koshida, Jpn. J. Appl. Phys. **46** (2007) 2458.

[4] F. Cora, M.G. Stachiotti, and C.R.A. Catlow: J. Phys. Chem. B, **101** (1997) 20.

[5] P.M. Walker, H. Mizuta, S. Uno, Y. Furuta and D.G. Hasko, IEEE Trans. Electron Devices **51** (2004) 212.

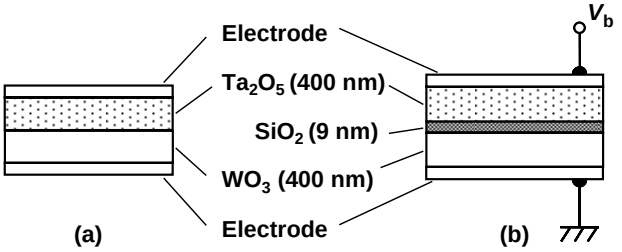

Fig. 1. Schematic cross section of solid-state EC devices. (a) Conventional structure. (b) Proposed structure with a thin SiO_2 film to accumulate carriers.

Table 1. Device parameters used for analyses.

	WO_3	SiO_2	Ta_2O_5
Structure	400	9	400
(Thickness [nm])	400	0	400
Dielectric constant	12	4	27.9
Band gap [eV]	3.2	9.0	4.3
Electron affinity [eV]	3.8	0.9	3.4
Doping [cm^{-3}]	2×10^{17} n-type	intrinsic	intrinsic

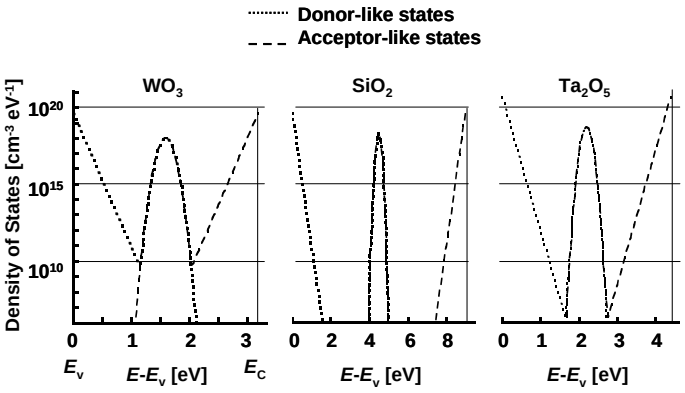

Fig. 2. Estimated continuous trap and tail state density distributions of constituent three films in EC device.

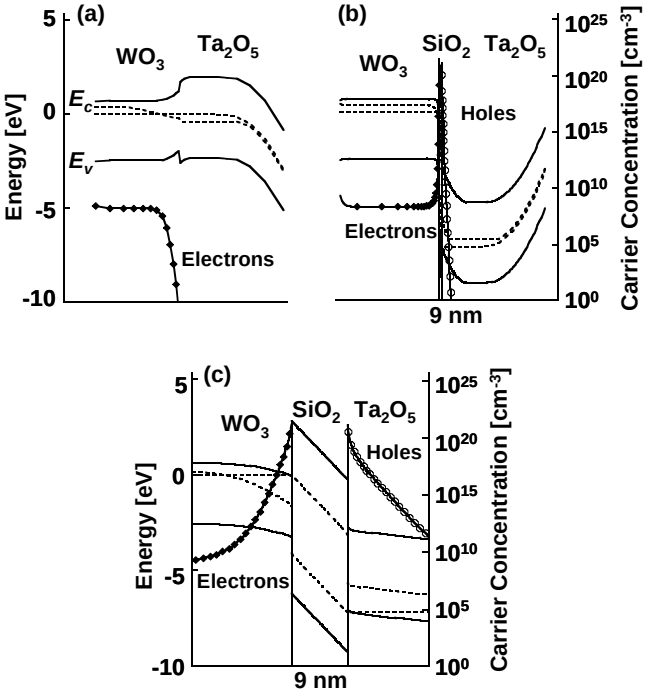

Fig. 3. Band diagram and calculated carrier density profiles in the EC device under a bias voltage of V_b = 3 V. (a) Conventional device. (b) Proposed device with an accumulating thin SiO_2 film. (c) Enlarged interfacial profile corresponding to the case (b). .

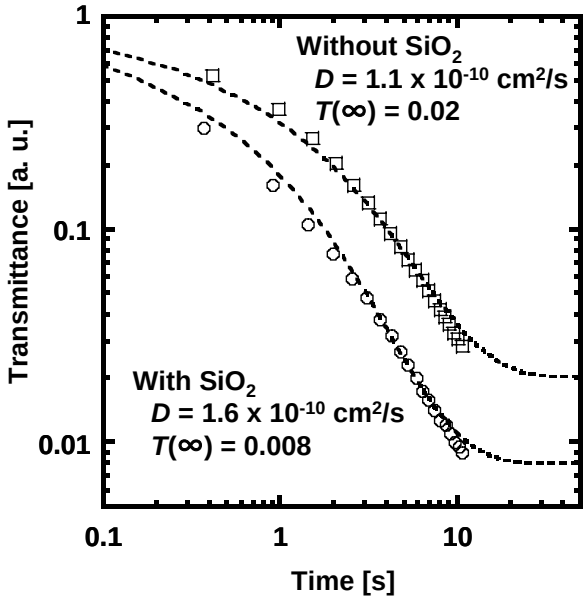

Fig. 4. Dashed curves: theoretical results of the EC-induced optical change with time obtained from the EC kinetic equation for the device with and without SiO_2 film. The respective experimental data are also shown by open plots. Both the validity of analysis and the accumulation effect on the EC response are confirmed.