Title

ELECTROCHROMIC MATERIALS FOR THE REGULATION OF SOLAR ENERGY TRANSMISSION THROUGH WINDOWS

Author

Lampert, CM.

Publication Date

1984-02-01

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

APPLIED SCIENCE DIVISION

Invited Lecture presented at the 2nd International Workshop on the Physics of Semiconductor Devices, Delhi, India, December 5-10, 1983; and to be published in the Proceedings

ELECTROCHROMIC MATERIALS FOR THE REGULATION OF SOLAR ENERGY TRANSMISSION THROUGH WINDOWS

C.M. Lampert

February 1984

APPLIED SCIENCE DIVISION

Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

DISCLAIMER

LBL-17393
EEB-W 84-04
W-160

Based on an invited lecture given at the 2nd International Workshop on the Physics of Semiconductor Devices, December 5-10, 1983, Delhi, India, and to be published in the proceedings. Sponsor: Solid-State Physics Laboratory, Delhi.

ELECTROCHROMIC MATERIALS FOR THE REGULATION OF SOLAR ENERGY TRANSMISSION THROUGH WINDOWS

Carl M. Lampert

Materials and Molecular Research Division and
Applied Science Division
Lawrence Berkeley Laboratory
University of California
Berkeley CA 94720, U.S.A.

FEBRUARY 1984

This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Solar Heat Technologies, Passive and Hybrid Solar Energy Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

ELECTROCHROMIC MATERIALS FOR THE REGULATION OF SOLAR ENERGY TRANSMISSION THROUGH WINDOWS

Carl M. Lampert

Materials and Molecular Research Division and
Applied Science Division,
Lawrence Berkeley Laboratory
University of California, Berkeley, California 94720
U.S.A.

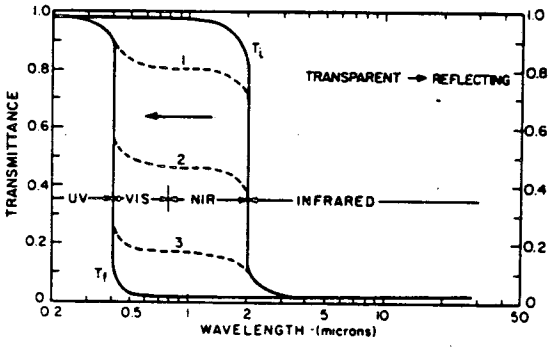
ABSTRACT

The concept of an architectural switching film based on solid-state electrochromism is introduced. Electrochromic films have the ability to dynamically control solar transmission through a glazing and to alter the energy conduction properties of the window. Switching properties of transition metal oxides based on tungsten and iridium are detailed. The properties of WO_3-based films, which can modify both the visible and near-infrared portions of the solar spectrum, are given.

1. INTRODUCTION

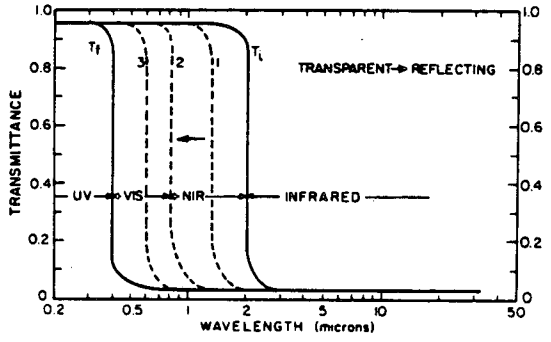
Electrochromism, also known as electrochemichromism, has been observed in many materials. Materials displaying this property include a number of organic compounds and a smaller group of inorganic materials comprised chiefly of transition metal oxides. Electrochromism has been used for electronic information displays, but as a technology has yet to capture a significant portion of the market, which is dominated by liquid crystals and light-emitting diodes.

In this study electrochromism is suggested for a new application, large-scale optical switching elements for building glazings. Due to the initial cost of such a device, research is directed toward the large-commercial building market, displacing exterior shutters, blinds, drapes, solar control films, and other types of aperture control.[1,2-4] An optical shutter, if designed properly, can effectively control glare, light levels, and passive solar heating in a building. An idealized spectral response for such a device is shown in Figure 1. Also for proper regulation of solar energy a material should respond to the visible and the near-infrared portions of the solar spectrum, as shown in Figure 2. There are other optical switching processes under study for this use; they include chromogenic, electrooptic, and kinetoptic processes.[5,2] But electrochromism offers many advantages over other processes.



XBL 828-6452

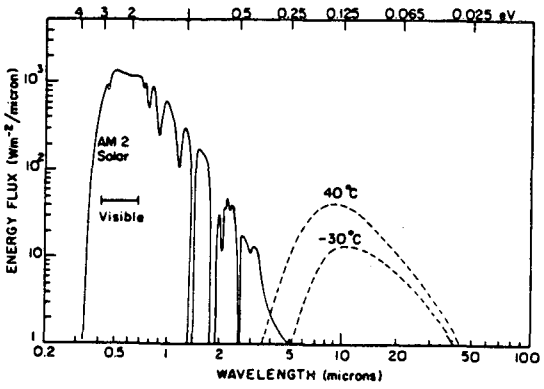
(a)



XBL 828-6453

(b)

Figure 1. Idealized spectral responses for broad-band optical switching material: (a) formation of a broad adsorption band, (b) adjustable Drude-like transmission edge.



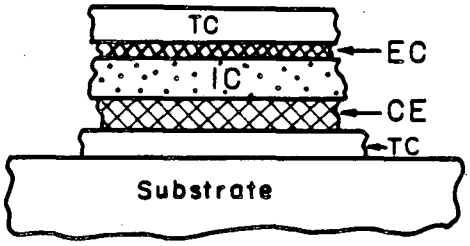
XBL 808-5758E

Figure 2. Energy spectra for airmass 2 solar radiation and blackbody thermal infrared distribution (-30°C, 40°C).

2. ELECTROCHROMIC DEVICES

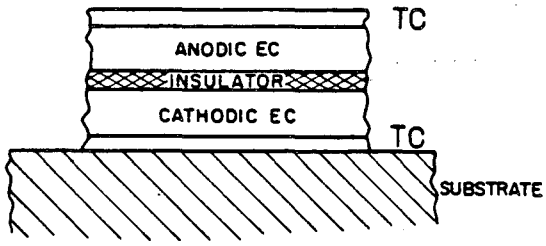
Electrochromism is a reversible color change in a material induced by the injection of ions under an applied electric current. This change in color can be due to the formation of adsorbing color centers or by forming Drude-like conduction, giving reflecting characteristics. An electrochromic material must exhibit both ionic and electronic conduction. Electrochromism is seen in both reduction (cathodic) and oxidation (anodic) conditions. Before introducing the theory it is important to describe device structures, To help clarify the theoretical considerations. Device structures can vary greatly, but generally consist of four to five layers of materials, the electrochromic film being one of the layers.

There are at least three configurations for the device. All three have a center layer that is an ion conductor, either a fast-ion conductor or a slower-ion conducting oxide barrier. On each side of the ion conductor is the electrochromic material and the counter electrode. The counter electrode must be able to store ions and be electrically conductive (shown in Fig. 3a), or be another electrochromic material (shown in Fig. 3b). The final layers are transparent electronic conductors, such as heavily doped tin or indium oxides. The third variation is to incorporate the electronic conductor and counter electrode together, such as with gold films. Two of these configurations are shown in Figure 3. The third configuration can be visualized by incorporating the transparent conductor (TC) and counter electrode (CE) together in figure 3a.



XBL 805-9714b

(a)

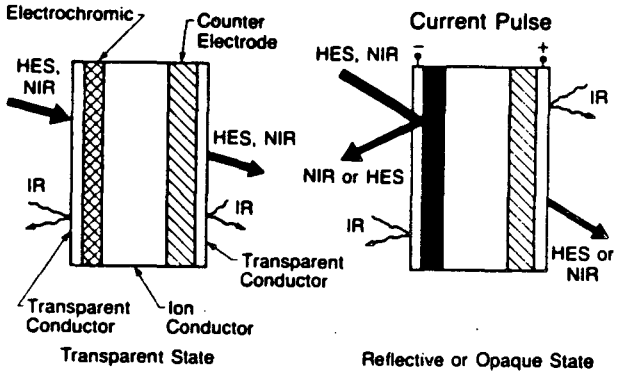


XBL 831-5135

(b)

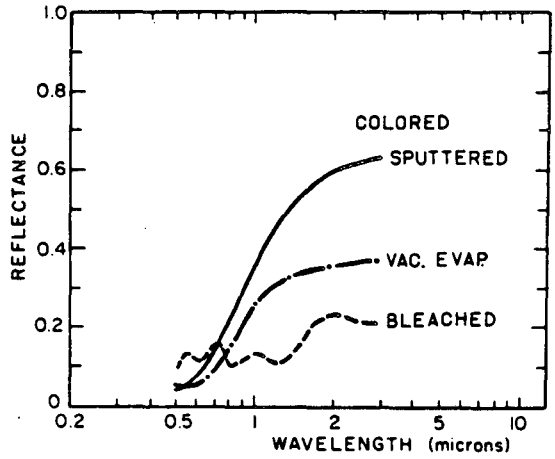
Figure 3. Structures for electrochromic switching devices: (a) non-electrochromic counter electrode; (b) anodic-cathodic design with two electrochromic layers (Notation, TC: transparent conductor, CE: counter electrode, EC: electrochromic, IC: ion conductor).

A schematic of an electrochromic device used as a solar optical shutter is shown in Figure 4. In this figure both the transparent (bleached) and colored (activated) states are shown. Depending on the nature of the electrochromic layer the colored state can be opaque or reflecting. The optical properties of a reflecting polycrystalline WO_3 electrochromic are shown in Figure 5. Thin film was made by RF sputtering and colored by proton insertion.[6] With further research, this film has potential for a solar control device.



XBL 842-10105

Figure 4. Schematic of an electrochromic optical shutter for passive solar use. Notation: HES: high energy solar, NIR: near-infrared, IR: thermal infrared.



XBL 842-812

Figure 5. Change in reflectance for RF sputtered polycrystalline WO_3 film compared to a vacuum evaporated film.[6]

3. THEORY OF ELECTROCHROMISM

From a mechanistic viewpoint tungsten oxide is best known, although still poorly understood. In tungsten oxide the color center is formed by insertion of a proton or ion into an interstitial site in the perovskite structure. The localization of the injected electron associated with the ion is not exactly known: It may be (a) delocalized in the conduction band of WO_3, (b) be trapped by W^{6+} forming W^{5+} ,or (c) be trapped by the interstitial ion. Recent work has shown Drude-like conduction in polycrystalline films, which favors electron delocalization.[6] However, in amorphous films intervalence transfer theory has been proposed.[7] In fine-grained material, modified Drude theory with conderation of localized electrons in deep donors in grain boundaries has also been proposed.[8]

The electrochromic layer is characterized by its internal electromotive force:[9] E(o), which is defined as $E(o) = -eu(o)$, where e is the electronic charge and u(o) is the chemical potential. The chemical potential is a function of ion occupancy (o) in the electrochromic layer. Ion occupancy is the ratio of ions stored per unit volume in the electrochromic relative to the total ion capacity of the material. In reference to Figure 3a, if we assume that the transparent conductors (TC) have identical properties and that the electrochromic (EC) and counter electrode (CE) have similar properties, then the potential difference for the device is

$E_d = e(u(o_c) - u(o_e))$, at fixed temperature and,

u (o_c) is the chemical potential for the CE layer and u(o_e) is the chemical potential for the EC layer.

Now if we assume that $o_c + o_e$ and $o_c + o_e + 1$, and then electrically connect the conductor layers, ions will be transferred across the ion conductor until equilibrium is established and $E_d = o$, and $o_c + o_e = 0.5$. The device is now bleached. If an external voltage is applied and electrons are injected, then ions will retransfer and $o_c = o_e$ again. In this condition the device is colored to a degree that depend on magnitude of change injected and number of ions transferred and color centers formed. The device will remain colored until the electrodes are shorted or external voltage is applied. During coloration the type of ion-insertion chemical reactions that might take place are:

$$MO_y + xA^+ + xe^- \rightarrow A_xMO_y \quad , \quad O < X < 1, \text{ where } A = H^+, Li^+, Na^+, Ag^+$$

This is known as cathodic coloration or coloration by reduction of Mo Another reaction is known as anodic coloration, or coloration by oxidation:

$$MO_y + xA^- + xh^+ \rightarrow A_xMO_y, \quad O < X < 1, \text{ where } A : F^-, CN^-, OH^-$$

2. MATERIALS CLASSES

The kinetics of bleaching and coloration are limited in these devices by the transfer of ions across the ion conductor/electrochromic interface (characterized by over-voltage) and by bulk diffusion of the ion into the electrochromic material. Diffusion rates are depend greatly upon the degree of hydration, film porosity, and microstructure of the electrochromic.

For solid-state devices, inorganic transition metal oxides have been used exclusively. The majority of materials research has been on cathodic electrochromic materials based on tungsten oxide, WO_3, and anodic iridium oxide, IrO_x. A list of experimental devices appears in Table 1.

Table 1

ELECTROCHROMIC DEVICES USING SOLID ELECTROLYTES

MATERIAL	PREPARATION TECHNIQUE	ION CONDUCTOR	INSERTION ION	REF
WO_3	Vac. Evap	Poly-AMPS: Hup;NASICON	H+;Na+	10, 11, 12
WO_3	e-b Evap	ZrO_2;Ta_2O_5	H+	13
a-WO_3	Vac. Evap	$RbAg_4I_5$	Ag+	14
WO_3	Vac. Evap, Sput	a-$LiAlF_4$:Li_3N	Li+	15, 16
Na_xWO_3	Vac. Evap, Sput	Na+-b-Al_2O_3	Na+	17
IrO_x	Anodize	$PbSnF_4$;PbF_2	F-	18
IrO_x	Anodize	NAFION	H+/OH-	19

Tungsten oxide devices can be classified according to the type of insertion ion used. The nature of a-WO_3 films depend greatly upon deposition technique and resulting film microstructure.

The presence of water is significant to the operation of proton-based devices. The importance of water in $WO_3/SiO_x/Au$, WO_3/ZrO_2, and WO_3/Ta_2O_5 has been researched.[20-21] Under vacuum (10^{-5} torr) cells of these designs

do not function. Also they exhibit threshold characteristics that correlate to the dissociation of water, providing protons for the reaction. Switching times on the order of seconds have been observed in proton based devices. Switching time can be reduced by optimization of porosity and microstructure. Faster switching cells of WO_3/LiF, independent of hydration, have been studied.[22] Devices using trapped water have been devised with WO_3/Cr_2O_3/Au layers.[23] A trapped water design based on a hermetically sealed device may be useful for a passive solar shutter, provided acceptable transmission can be obtained in the bleached state.

Some of the best proton conductors belong to the class of hydrated sulfonic acid polymers, such as polymerized 2-acrylamido - 2-methylpropane sulfuric acid (Poly-AMPS).[10]

Solid state WO_3 cells do not have to depend only on protons for their operation. Other metallic tungsten bronzes based on Li+, Ag+ and Na+ ions also exhibit electrochromism. But in these systems a fast-ion conductor is needed to obtain reasonable switching times. For solar use this condition may be relaxed. Ion conductors such as Na+-b-Al_2O_3, hydronium -b- Al_2O_3 (HUP), $LiAlF_4$, Li_3N, $RbAg_4I_5$, and NASICON have been studied.[12,14-17] By proper control of porosity and grain size in polycrystalline WO_3, ionic diffusion and switching speed can be enhanced. There is considerable current research on Li^+ based systems.

Solid-state anodic electrochromic devices are based mainly on hydrated IrO_x produced by anodization. Also with liquid electrolyte devices

considerable research has been performed on sputtered IrO_x films and, to a lesser degree, on hydrated Rh_2O_3, NiO_2, Nb_2O_3 , and CoO_x. Devices using IrO_x exhibit high stability over a wide temperature range with low cycle energy, compared to WO_3 devices. Active ions in these devices can be F^- or OH^-.

The major disadvantage to IrO_x -based switches for solar use is their high material cost. Although they are suitable for small area electronic displays, they would be to expensive for large windows.

Also of interest are the device concepts based on anodic-cathodic electrochromism. The cell structure can be WO_3/TaO/MOH, were MOH is one of the platinum groups hydroxides such as $IrO_x.nH_2O$. But, as with IrO_x cost restrictions apply. A schematic of this device is given in Figure 3b. Depending on the exact materials used, the anode and cathode of this device can color and bleach at the same time.

Comparative properties of IrO_x and WO_3 based devices are shown in Table 2. Here, a range of performance data from liquid electrolytes and solid-ion conductors are compiled.[24] The lower values are for the solid-state systems. Lifetimes are for liquid electrolyte systems.

TABLE 2

CHARACTERISTICS OF ELECTROCHROMIC DEVICES[24]

PROPERTY	TUNGSTEN OXIDE	IRIDIUM OXIDE
Device Response Time (mS), 22°C	0.3 - 3000	40 - 250
Optical Efficiency (cm^2c^{-1})	75 - 115	30
Energy Required Per Cycle ($mJcm^{-2}$)	8 - 50	17 - 20
Cyclic Lifetime (cycles)	1×10^7	2×10^7
Voltage (V)	1.5	1.5

SUMMARY

Electrochromic devices and materials have been discussed in the context of using solid-state devices for large-area solar switching. Devices based on WO_3 in three different configurations appear to have promise. The reflective phase of WO_3 may have ideal characteristics for control of near-infrared energy. Devices based on other electrochromic material may offer the spectral characteristics needed for solar energy control. Additional research is needed to understand the coloration mechanism in these materials and to further develop solid-state devices. Devices incorporating IrO_x appear to be too expensive for large-area solar use.

ACKNOWLEDGEMENTS

This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Solar Heat Technologies, Passive and Hybrid Solar Energy Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

Also I wish to thank Dr. S.C. Jain, (National Physical Lab, Delhi), Prof. J.J. Loferski (Brown University) and O. Shinaishin (National Science Foundation) for arranging travel support to give this paper at the 2nd International Workshop on Semiconductor Devices in India.

REFERENCES

1. C.M. Lampert, Electrochromic Materials and Devices for Energy Efficient Windows. LBL-16073 to be published, 1984.

2. C.M. Lampert and S. Selkowitz, Optical Switching Materials for Energy Efficient Windows, LBL-15378 to be published 1984.

3. R.B. Goldner and R.D. Rauh, Proc. of SPIE 428, 38 (1983).

4. S.A. Agnihotry, S.S. Bawa, A.M. Biradar, C.P. Sharma and S. Chandra, Proc. of SPIE 428, 45 (1983).

5. C.M. Lampert and M. Li, Photochromic and Thermochromic Phenomena for Switchable Glazings. LBL-16886 to be published, 1984.

6. R.B. Goldner et al., Appl. Phys. Lett., 43, 1093 (83).

7. B.W. Faughnan, R.S. Crandall and D.M. Heyman, RCA Rev. 36, 177 (1975).

8. W.C. Dautremont-Smith, M. Green and K.S. Kang, Electrochem. Acta 22, 751 (1977).

9. G. Beni from lectures given. Electrochromism and Electrochromic Display Seminar, Rome, Italy, November 1982.

10. R.D. Giglia and G. Haacke, Proc. of SID 23, 41 (1982).

11. A. Howe, S. Sheffield, P. Childs and M. Shilton, Thin Solid Films, 67, 365 (1980).

12. G. Barna, J. Electron, Mat., 8, 153 (1979).

13. Y. Hajimoto, M. Matsushima and S. Ogura, J. Electron. Mat., 8, 301 (1979).

14. M. Green and D. Richman, Thin Solid Films, 24, S45 (1974).

15. M. Miyamura, S. Tomura, A. Imai and S. Inomata, 3, 149 (1981).

16. T. Oi, K. Miyanchi, and K. Uchara, J. Appl. Phys., 53, 1823 (1982).

17. M. Green and K. Kang, Thin Solid Films, 40, L19 (1977).

18. C.E. Rice and P. Bridenbaugh, Appl. Phys. Lett. 38, 59 (1981).

19. G. Beni and J. L. Shay, Fast Ion Transport in Solids, Yashita, Monday and Sherinoy eds, Elsevier/North Holland, Amsterdam (1979).

20. A.J. Hughes, and P. Lloyd, Proc. of the Electronic Materials Conf., Cornell Univ. (1977) p. 44.

21. Y. Hajimoto, M. Matsushima and S. Ogura, Proc. of Electronic Materials Conf., Santa Barbara, CA (1978) p. 12.

22. H.J. Stocker, S. Singh, L.G. Van Uitert and G. Zydik, Proc. of Electronic Materials Conf., Santa Barbara, CA (1978) p. 12.

23. I. Shimizu, M. Shizukuishi and E. Inone, J. Appl. Phys., 19, 2121 (1980).

24. W.C. Dautremont-Smith, Displays, Jan 3, (1982); April, 67 (1982).

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720