



ERNEST ORLANDO LAWRENCE BERKELEY NATIONAL LABORATORY

CONF-970706--

Effective Medium Approximation of the Optical Properties of Electrochromic Cerium-Titanium Oxide Compounds

RECEIVED

FFR 1 / 1998

OSTI

K. von Rottkay, T. Richardson,
M. Rubin, and J. Slack

Environmental Energy
Technologies Division

July 1997

Presented at the
SPIE Annual Meeting,
San Diego, CA,
July 27-31 1997,
and published in
SPIE Proceedings,
Vol. 3138 (1997)

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor The Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or The Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof, or The Regents of the University of California.

Ernest Orlando Lawrence Berkeley National Laboratory
is an equal opportunity employer.

DISCLAIMER

Portions of this document may be illegible electronic image products. Images are produced from the best available original document.

SPIE, Vol. 3138 (1997), 9-19.

Effective Medium Approximation of the Optical Properties of Electrochromic Cerium-Titanium Oxide Compounds

K. von Rottkay, T. Richardson, M. Rubin, and J. Slack

Building Technologies Program
Environmental Energy Technologies Division
Ernest Orlando Lawrence Berkeley National Laboratory
University of California
Berkeley, California 94720

July 1997

This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Building Technology, State and Community Programs (BTS), Office of Building Systems of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

Effective Medium Approximation Of The Optical Properties Of Electrochromic Cerium-Titanium Oxide Compounds

K. von Rottkay, T. Richardson, M. Rubin, and J. Slack,

Lawrence Berkeley National Laboratory,

University Of California, Berkeley, CA 94720, USA

E. Masetti,

Thin Film Laboratory, ENEA Casaccia, G. Dautzenberg,

University Of Rome "La Sapienza", 00060 Rome, Italy

Abstract

Cerium titanium oxide samples derived from a solution have been compared against sputtered films over a wide range of different compositions. X-ray diffraction was used to investigate the structural properties of the compound material existing in a two-phase mixture $M_AO_2 \cdot M_BO_2$. The optical properties were evaluated over the whole solar spectrum by variable angle spectroscopic ellipsometry combined with spectrophotometry. The spectral complex refractive index was determined for CeO_2 and TiO_2 , as well as for their compounds. To reduce the large number of permutations in composition of multi-component oxides it would be useful to be able to predict the properties of the mixtures from the pure oxide components. Therefore these results were compared to those obtained by effective medium theory utilizing the optical constants of CeO_2 and TiO_2 . In order to investigate the performance as passive counter-electrode in Li^+ based electrochromic devices the films were tested by cyclic voltammetry with in-situ transmission control. Chemical composition was measured by Rutherford backscattering spectrometry. Surface morphology was analyzed by atomic force microscopy.

Keywords: electrochromic, cerium titanium oxide, optical constants, effective medium theory

Introduction

Among a plethora of variations in electrochromic device configurations there are mainly two different approaches for the choice of the counter-electrode. It can either act as an active or a passive electrochromic layer. Granqvist [1] compiled a review of the different materials used in inorganic devices. CeO_2 - TiO_2 is widely used as passive counter-electrode. Both components are used in optical thin films due to their high transparency in the visible and near-infrared spectrum. Since the band edge of CeO_2 coincides with the lower limit of the visible, it also finds use as UV absorbent coating (e.g. in automobile windows).

The binary mixture CeO_2 - TiO_2 aims to combine the good electrochemical stability of CeO_2 with the high ion diffusion coefficient of H^+ and Li^+ in TiO_2 . Camino et al. assume that for low cerium contents intercalated ions move along TiO_2 channels to CeO_2 sites [2]. XRD and TEM results indicate CeO_2 crystallites embedded in an amorphous TiO_2 matrix [3,4,5]. CeO_2 - TiO_2 films for

electrochromic applications have mostly been produced by sol-gel methods [2,3,4,6,7,8,9,10,11,12,13,14] and only recently by sputtering [15].

Deposition of $\text{CeO}_2\text{-TiO}_2$ by reactive dc-sputtering from metallic cerium and titanium targets constitutes an industrially viable technique. The high sputter rates (see experimental section) can be further increased by sputtering from multiple targets [16]. Adjusting the power of the sputter guns provides an easy means of varying relative film composition taking into account that the sputtering rate from the cerium target is about four times higher than from titanium.

Optical constants of TiO_2 [17,18,19,20,21,22,23,24,25,26,27], CeO_2 [25,28,29,30,31,32,33,34,35,36] and $(\text{CeO}_2)_{0.5}(\text{TiO}_2)_{0.5}$ [37, 38] deposited by different methods and under varying conditions have been reported. To reduce the large number of permutations in binary materials it would be useful to predict the optical properties by using the dielectric constants of their components. In two-phase compound films this can theoretically be achieved by using effective medium theory. Microstructure may strongly influence the optical properties of compounds unless the optical constants of the components are very similar [39] as in the case of TiO_2 and CeO_2 . On the one hand this allows the accurate modeling the $\text{CeO}_2\text{-TiO}_2$ system despite lack of microstructural information. Quite narrow bounds on the dielectric function can be constructed even without assumptions about composition or isotropy. On the other hand there is an elevated sensitivity to deviations in sample growth conditions. Precise control of deposition is necessary, because even slight changes affect the film refractive index and will therefore lead to erroneous results in effective medium theories.

Experimental

Films were co-deposited by dc-magnetron reactive sputtering using Ti (99.9%) and Ce (99.9%) targets. The Ar (99.9995%) flow rate was 220 sccm, delivered into the chamber through the sputter guns, flowing first under the anode shields and across the targets. O_2 (99.998%) flow was varied between 5.4 and 6 sccm, delivered through a manifold at the substrate. Deposition pressure ranged from 20 to 30 mTorr, this variation achieved by throttling the turbo pump gate valve. The chamber was pumped with a 450 l/sec LH turbomolecular pump backed by a LH D40B roughing pump. The typical base pressure was below 2.0×10^{-6} Torr. Two Angstrom Sciences 2" sputter sources inclined 20 degrees off normal to a common focal point were used for co-deposition, with a target-to-substrate distance of 17 cm. Compositional variation was achieved by varying power to each gun between 33 and 320 Watts, with the combined power throughout the sequence maintained at approximately 320 W. Peak deposition rates were 0.6 nm/sec and 2.4 nm/sec for TiO_2 and CeO_2 respectively. Low Ce content films were easily achieved as the Ce deposition rate per Watt (nm/sW) at 35 W gun power was only 3% of the rate per Watt at 307 W. This disproportionate decrease in rate as Ce power declined is presumably a function of surface oxidation of the target, and was most pronounced at power levels below 90 W. The rate/W at 96 W was 52% of the rate/W at peak power.

Films were deposited on $\text{In}_2\text{O}_3\text{-Sn}$ or $\text{SnO}_2\text{-F}$ glass. The sheet resistances of the transparent conductors were $20 \Omega/\text{square}$ and $15 \Omega/\text{square}$ respectively. Prior to deposition the substrate holder was heated to 120°C with the intention of driving moisture from the substrate surface. Deposition began after the holder had cooled to approximately 50°C. The deposition process maintained the temperature at approximately 50°C for the duration of the run. Film thickness ranged from 170 nm to 510 nm as was determined by ellipsometry.

Solution-derived films were prepared by a variation of the method of Baudry et al. [8]. 0.25 M stock solutions of titanium isopropoxide and ceric ammonium nitrate in anhydrous ethanol were mixed in the desired proportions and spin-coated on ITO glass substrates. After drying at room temperature for 1 h, the samples were inserted into a furnace at 450°C and densified in air for 20 min.

Optical measurements were made with a variable-angle spectroscopic ellipsometer (VASE) from 280 nm to 1700 nm using an instrument from the J. A. Woollam Co.. Ellipsometric data was taken at three different angles in order to provide data with good signal to noise ratio at each wavelength as well as to over-determine the system of unknown model parameters. To extend the covered spectral range to the whole solar spectrum, transmittance and reflectance measurements from 250 nm to 2500 nm were added; these measurements were taken at near-normal incidence on a Perkin-Elmer Lambda 19 spectrophotometer. The substrate backside was not roughened for ellipsometry to allow later in-situ transmission control during electrochemical current -voltage cycling. Therefore backside reflections had to be accounted for in the optical model used to extract the optical constants.

Sputtered and solution-derived films were tested by cyclic voltammetry in 1M LiClO₄/propylene carbonate electrolyte at 1 mV/s over the range 1.8 to 4.0 V using lithium foil for both reference and counter electrodes. The optical transmittance of the films in the visible range was monitored during testing.

Composition and thickness of the samples were characterized by Rutherford backscattering spectrometry (RBS) using a 1.95 MeV ⁴He⁺ beam in the 165° backscattering geometry. Ellipsometry was used not only as part of the optical analysis but also to measure film thickness. Other types of structural analysis were performed with x-ray diffraction (XRD), infrared spectroscopy and atomic force microscopy (AFM).

AFM measurements were performed with a Molecular Imaging instrument. Typical scans were taken over 2 x 2 μm at scan frequencies of 1-2 Hz. A 0.6 μm Si₃N₄ tip was operated at repulsive forces between 10 and 30 nN in contact mode. Whole images were corrected for slope in fast and slow scan directions and analyzed without filtering.

For XRD measurements bulk powder samples of the mixed oxide sols were prepared by heat treating the dried precursor mixtures under the same conditions as those used for the films. X-ray diffraction patterns were collected using a Siemens D5000 powder diffractometer at 0.1° resolution.

Results

Optical Properties

Amorphous stoichiometric CeO_2 and TiO_2 have similar optical properties over the solar spectrum. They show dielectric dispersion with a bandgap lying in the ultraviolet. The value of the bandgap of TiO_2 around 3.4 eV is somewhat larger than the 3.1 eV of CeO_2 . Two-phase mixtures of both materials are expected to have a bandgap lying in between those limits. Variations may occur due to different stress levels or slight variations in stoichiometry in films of different compositions.

Ellipsometry is an indirect technique requiring the evaluation of an optical model fitted to the experimental data in order to extract physically significant information. Details of the procedure can be found in [40].

Knowledge of the optical constants of the substrate is crucial to the accurate determination of the thin film refractive index. The substrate optical properties had been investigated in previous work [41,42].

We assumed a parametric semiconductor model for the dispersion of the CeO_2 - TiO_2 films [43,44]. It essentially constitutes a Kramers-Kronig consistent oscillator model with Gaussian instead of Lorentzian broadening as in the case of the common Lorentz oscillator model. It is more appropriate to model the abrupt onset of absorption in the case of CeO_2 and more accurately represents the strongly inhomogenous broadening in amorphous TiO_2 [45].

Optical constants ranging from pure CeO_2 to pure TiO_2 are shown in figure 1 a, b.

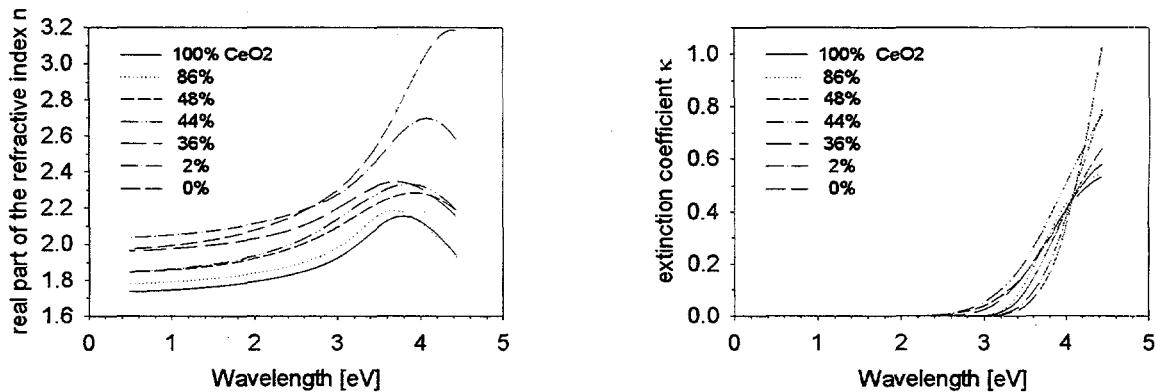


Figure 1. Spectral optical constants for CeO_2 - TiO_2 thin films ranging in composition from pure CeO_2 to pure TiO_2 : a) real part and b) imaginary part of the refractive index

To obtain good fits it was necessary to include surface roughness into the model. This was achieved by adding a surface layer consisting of an effective medium of the film material and a fixed portion of 50% void [46,47]. Bruggeman effective medium theory was used [48]. This improved the fit to experimental data significantly. In doing this one has to make sure that correlation of fit parameters does not lead to physically irrelevant results. Correlation between fit parameters can be evaluated by calculating cross-correlation coefficients [49]. Highest correlation coefficients found between thickness of surface roughness layer and thickness of thin film layer were found to be always less than 0.25 indicating high sensitivity of the optical model to roughness

induced changes in light polarization and therefore in ellipsometric data [50]. Atomic force microscopy confirmed the relative magnitude of optically detected roughness. However, root mean square values of roughness determined from microscopy lie systematically lower than those from ellipsometry in agreement with similar findings by other researchers [28,51].

Figure 2 a, b, c shows an example of a fit on ellipsometric and transmittance data of a 282 nm thick $(\text{CeO}_2)_{0.48}(\text{TiO}_2)_{0.52}$ film. The biased mean squared error (MSE) in this case is 14.9. Without the addition of a surface roughness layer of 6.5 nm it is 21.0.

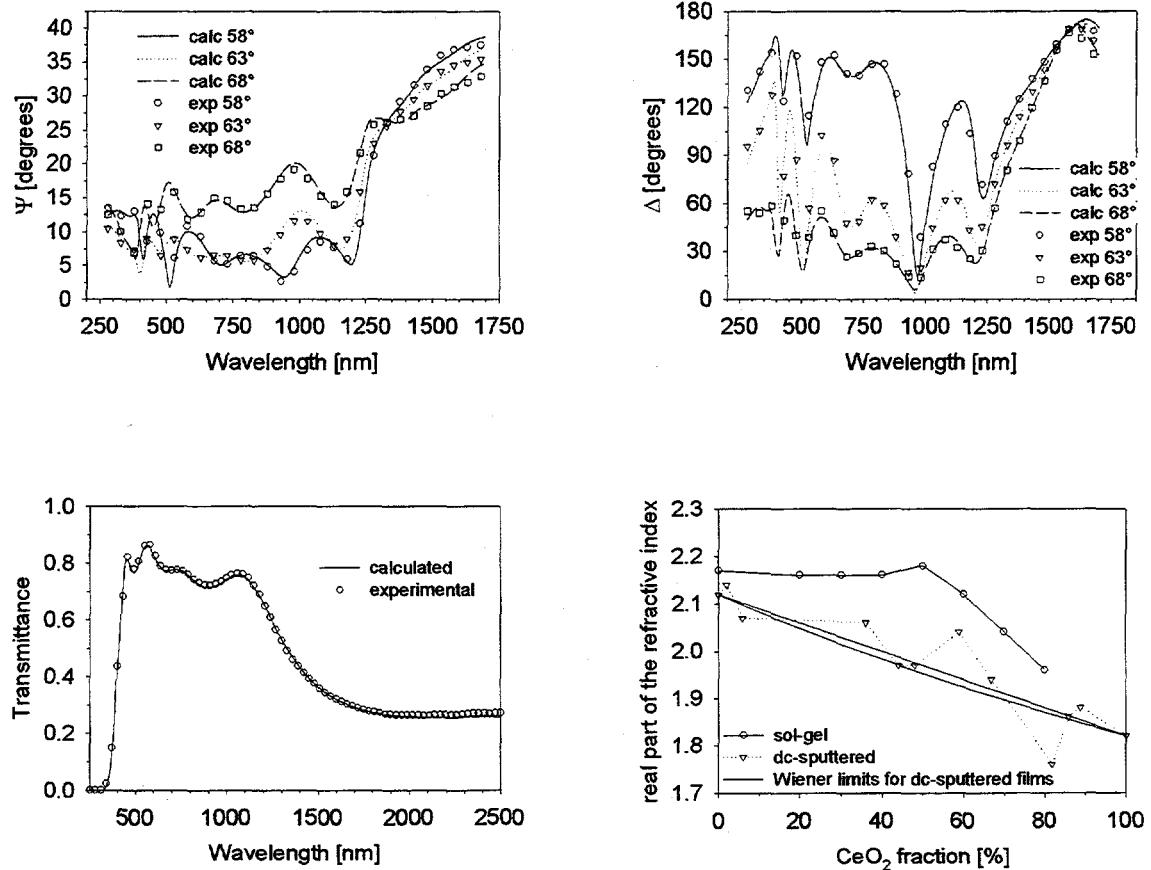


Figure 2. Fit on spectral optical data of a 282 nm thick $(\text{CeO}_2)_{0.48}(\text{TiO}_2)_{0.52}$ film on ITO coated glass: a) ellipsometric Ψ -data, b) ellipsometric Δ -data, c) transmittance data. For better readability only every fifth experimental data point is shown. Intermediate data also lie on the lines calculated from the optical model. d) Refractive index at 550 nm of sol-gel and dc-sputtered $\text{CeO}_2\text{-TiO}_2$ thin films versus molar CeO_2 fraction, Wiener limits for the sputtered films are drawn as solid lines.

Once the optical constants of all films were determined we investigated the possibility to evaluate all data in terms of effective medium theory. Wiener first gave the limits to the dielectric function of compound materials if no additional information regarding relative composition or microstructure is available [52]:

$$\epsilon_{\text{eff}} = f_a \epsilon_a + (1 - f_a) \epsilon_b \quad (1)$$

and

$$\frac{1}{\epsilon_{\text{eff}}} = \frac{f_a}{\epsilon_a} + \frac{1 - f_a}{\epsilon_b}, \quad (2)$$

where f_a is the volume fraction of material a and ϵ_i ($i = a, b, \text{eff}$) is the real dielectric constant for component a, component b and the effective mixture.

At 550 nm the extinction coefficient for all films was less than 10^{-3} . Therefore it is a very good approximation to set the imaginary part of the dielectric constant zero at this wavelength. However bounds can of course also be obtained on the complex dielectric function [53,54].

Figure 2d illustrates how narrow the Wiener limits are in the visible for $\text{CeO}_2\text{-TiO}_2$. Some values of the refractive index obtained from a direct fit of the parametric oscillator model to ellipsometric and transmittance data lie outside bounds. This explains why the application of effective medium approximation was not successful for all samples. Using Bruggeman effective medium theory assumes an isotropic material in three dimensions. This is a stronger assumption about the materials properties than those used to derive the Wiener limits. Therefore even more narrow bounds apply. In the graph they almost reduce to the upper line of the Wiener bounds and are omitted for better readability. We ascribe the variations of the refractive indices of compound samples to irrepeatabilities in the deposition process rather than deviations from a two-phase mixture. Good fits by effective medium theory were obtained for films with 44%, 48% and 86% CeO_2 content as expected from figure 2d.

Solution-derived films containing more than 80% cerium were of poor optical quality, with islands of opaque, white material. The thicknesses of single-layer films decreased with cerium content. This effect could be due to decreased viscosity of the coating solutions or to increased densification. Therefore no attempt of effective medium approximation was undertaken, because good optical constants for pure CeO_2 could not be obtained. But as can be seen from figure 2d the solution derived films do neither follow a rigid behavior as expected from the narrow bounds for sputtered CeO_2 and TiO_2 .

Structural Analysis

Due to the small crystallite sizes of the phases present in these films, it was not possible to obtain useful phase information from the films themselves, especially in the case of sputtered films, which were prepared at or near room temperature. In the case of solution-derived films, the only phases detectable were cerium oxide and indium oxide. To try to identify the nature of the titanium oxide phase, 2 g of bulk powder were prepared from an equimolar mixture of the solution precursors, and examined by XRD following 1 h heat treatments in air between 400 and 1000°C (figure 3). At 400°C, only CeO_2 can be seen in the pattern. The particle size is about 5 nm, and the lattice parameter is identical to that of pure CeO_2 . Above 500°C, a peak due to the anatase form of TiO_2

begins to appear at $2\theta \approx 26^\circ$, increasing in intensity and becoming sharper up to 700°C (particle size for both CeO_2 and TiO_2 ca. 10 nm). By 800°C , anatase is beginning to be converted to rutile TiO_2 , as evidenced by the low-angle shoulder on the strongest CeO_2 peak at 28.6° . At 1000°C , anatase is no longer present, and the pattern is that of an approximately equimolar mixture of CeO_2 and rutile. No evidence for Ti substitution in the CeO_2 structure or of any known cerium titanium oxide was found.

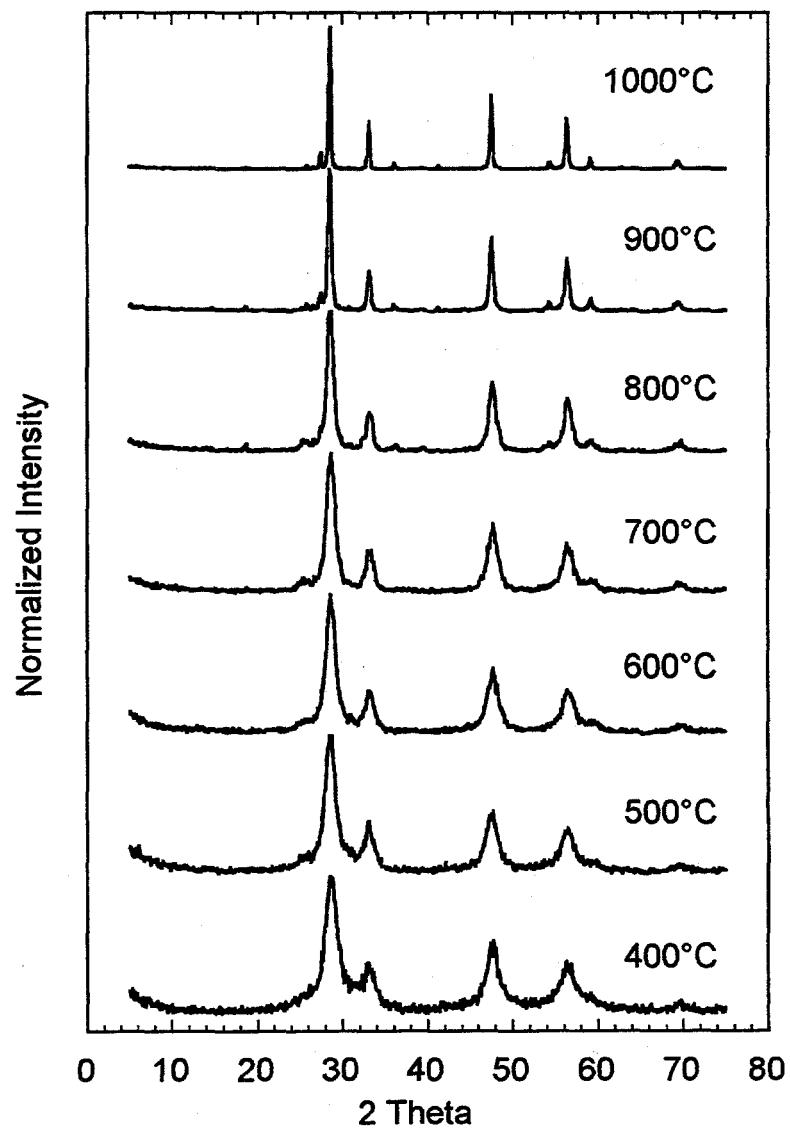


Figure 3. XRD data on dried powder of $(\text{CeO}_2)_{0.5}-(\text{TiO}_2)_{0.5}$

Electrochemical Analysis

The solution-derived films generally had low capacities for lithium insertion. The shapes of the CVs (figure 4a) for intermediate compositions resembled more strongly that of pure cerium oxide, suggesting that the titanium phase is largely inactive in these films. In addition, these samples were only very weakly electrochromic, typically coloring by no more than 1 or 2 percent. In contrast, the sputtered films had high lithium insertion capacities in the order of $40 \text{ mC cm}^{-2} \text{ nm}^{-1}$. The CVs of films of intermediate composition (figure 4b) were not characteristic of either end member, and films with high titanium content were strongly electrochromic.

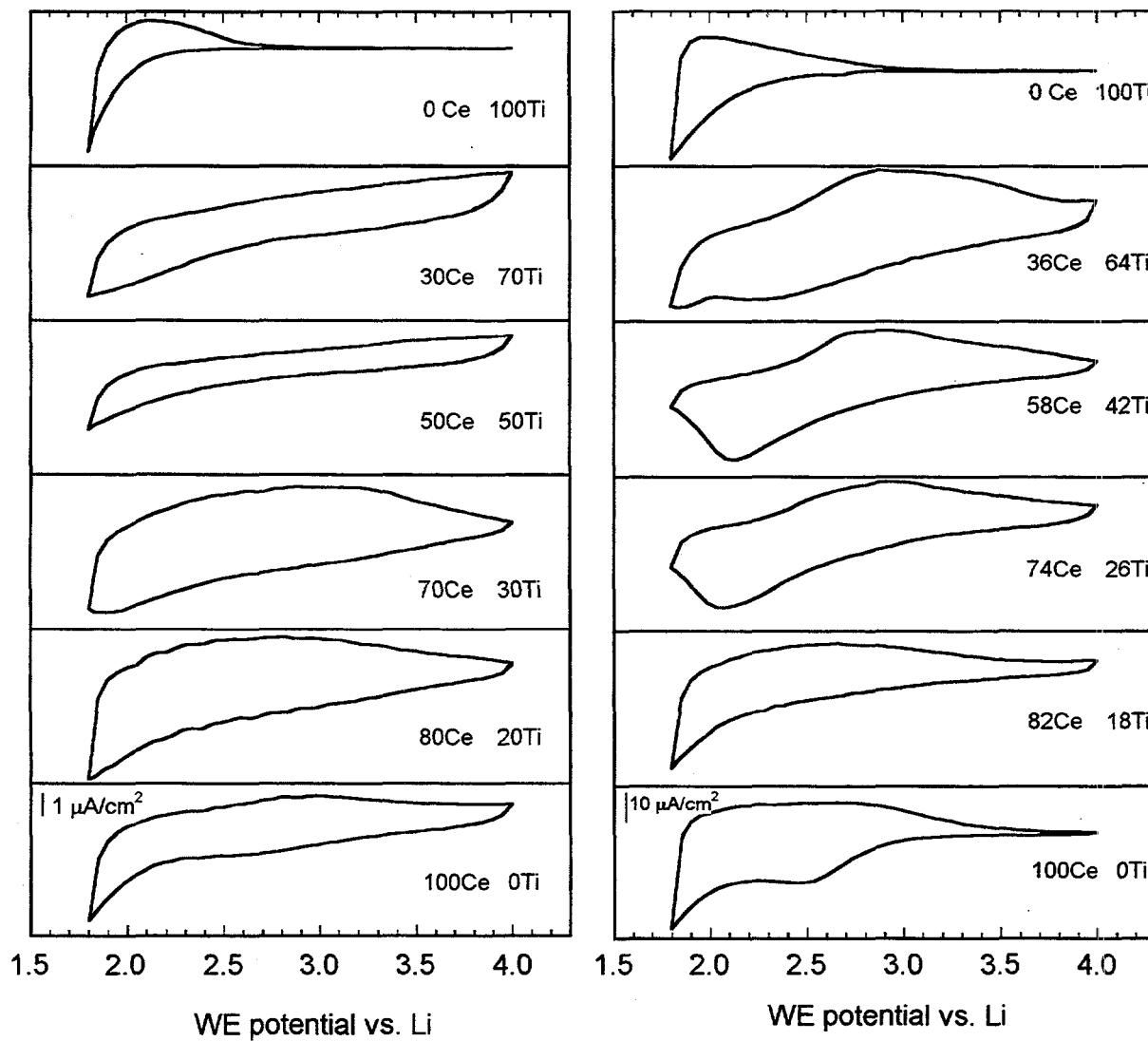


Figure 4. Cyclic voltammograms on a) solution-derived and b) on sputtered CeO₂-TiO₂ films

The pure sputtered TiO_2 films, though all of high visible transparency, behaved quite differently during cycling. For a film deposited at 4 sccm oxygen, 90 sccm argon and 18 mTorr run pressure we obtained a coloration efficiency of $23 \text{ cm}^2/\text{C}$ in the visible. This is much higher than reported by Seike et al. and Cogan et al., but in agreement with results by Gillet et al. and Gutarra et al. as mentioned by Granqvist [55,56,57,58,59]. Being 470 nm thick it had a wide switching range of 74% visible transmittance and remained stable over many cycles. Other TiO_2 films deposited at higher oxygen flow rates required some initial formatting associated with an irreversible Li^+ uptake reducing it partly to Ti^{3+} . Then they achieved the same coloration efficiency. This may indicate that a slight oxygen substoichiometry could enhance the electrochromic activity of TiO_2 . A more detailed study is underway to investigate this assumption.

Results of coloration efficiency of sputtered $\text{CeO}_2\text{-TiO}_2$ films of different composition are shown in figure 6. The coloration efficiency strongly increases for titanium rich films. Films with CeO_2 fractions above 35% were found to be almost passive upon Li^+ intercalation.

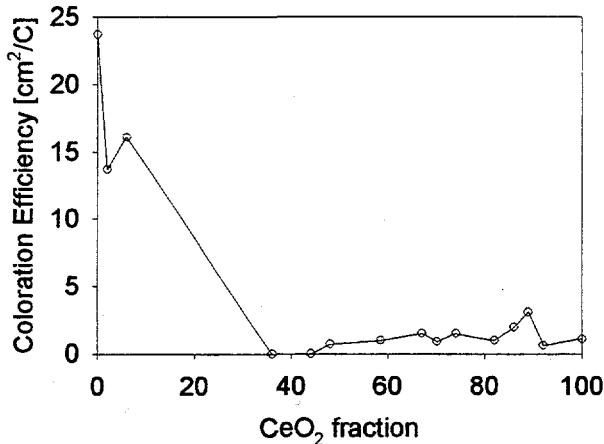


Figure 6. Coloration efficiency of dc-sputtered $\text{CeO}_2\text{-TiO}_2$ films versus atomic CeO_2 fraction

Conclusions

Clear and uniform $\text{CeO}_2\text{-TiO}_2$ films were deposited by dc-sputtering from metallic cerium and titanium targets. Film composition spanned the complete range from pure CeO_2 to pure TiO_2 . The sputtering rate from cerium was about four times higher than from titanium. Specular $\text{CeO}_2\text{-TiO}_2$ films by sol-gel could only be produced up to 80% CeO_2 . Films of higher CeO_2 content were either diffuse or very porous. The complex refractive index of all $\text{CeO}_2\text{-TiO}_2$ films was determined over the whole solar spectrum. Practical application of effective medium theory in the solar spectral region was found to be limited in this system because of very similar dielectric functions of CeO_2 and TiO_2 .

Sputtered films had higher lithium insertion capacities than solution derived films. $\text{CeO}_2\text{-TiO}_2$ did not color more than a few percent up to titanium contents higher than 70%. Sputtered TiO_2 deposited at lower oxygen flow rate was found to be highly electrochromic.

Acknowledgment

This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Building Technology, State and Community Programs (BTS), Office of Building Systems of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

We are grateful to L. Kullman and Prof. C.-G. Granqvist for helpful discussions and exchange of samples. The help of A. Lyon with the building of the sputtering system is thankfully acknowledged. Furthermore we thank N. Ozer and S.-J. Wen for the deposition of some early $\text{CeO}_2\text{-TiO}_2$ samples.

References

- [1] C.G. Granqvist, *Handbook of Inorganic Electrochromic Materials*, Elsevier Science, Amsterdam, 1995, p.225
- [2] D. Camino, D. Deroo, J. Salardenne, N. Treuil, *Solar Energy Materials and Solar Cells*, 39 (1995) 349-366
- [3] D. Keomany, C. Poinsignon, D. Deroo, *Solar Energy Materials and Solar Cells*, 33 (1994) 429-441
- [4] D. Keomany, J. Petit, D. Deroo, *Solar Energy Materials and Solar Cells*, 36 (1995) 397-408
- [5] A.R. Gonzalez-Elipe, A. Fernandez, J.P. Holgado, A. Caballero, G. Munuera, *J. Vac. Sci. Technol. A*, 11 (1993) 58-65
- [6] A. Makishima, M. Asami, K. Wada, *J. Non-Cryst. Solids*, 121 (1990) 310-314
- [7] M.A. Sainz, A. Duran, J.M.F. Navarro, *J. Non-Cryst. Solids*, 121 (1990) 315-318
- [8] P. Baudry, A.M. Rodrigues, M.A. Aegerter, L.O. Bulhöes, *J. Non-Cryst. Solids*, 121 (1990) 319-322
- [9] B. Valla, J.C.L. Tonazzi, M.A. Macêdo, L.H. Dall'Antonia, M.A. Aegerter, M.A.B. Gomes, L.O. Bulhöes, *SPIE 1536* (1991) 48-62
- [10] M.A. Macêdo, L. H. Dall'Antonia, B. Valla, M.A. Aegerter, *J. Non-Cryst. Solids*, 147&148 (1992) 792-798
- [11] U.Lavrencic Stangar, B. Orel, I. Grabec, B. Ogorevc, *SPIE 1728* (1992) 118-129
- [12] U.Lavrencic Stangar, B. Orel, I. Grabec, B. Ogorevc, K. Kalcher, *Solar Energy Materials and Solar Cells*, 31 (1993) 171-185
- [13] Z. Crnjak Orel and B. Orel, *Phys. Stat. Sol. (b)* 186 (1994) K33-K36
- [14] Z. Crnjak Orel and B. Orel, *Solar Energy Materials and Solar Cells*, 40 (1996) 205-219
- [15] A. Azens, L. Kullman, D.D. Ragan, C.G. Granqvist, B. Hjörvarsson, G. Vaivars, *Appl. Phys. Lett.*, 68 (1996) 3701-3703
- [16] M. Kharazzi, A. Azens, L. Kullman, C.G. Granqvist, *Thin Solid Films* 295 (1997) 117-121
- [17] H. K. Pulker, G. Paesold, E. Ritter, *Applied Optics* 15, (1976) 2986-2991
- [18] H. Küster, J. Ebert, *Thin Solid Films*, 70 (1980) 43-47
- [19] S. Y. Kim, *Applied Optics*, 35 (1996) 6703-6707
- [20] N. Özer, H. Demiryont, J. H. Simmons, *Applied Optics*, 30 (1991) 3661-3666
- [21] M. Gilo, N. Croitoru, *Thin Solid Films*, 283 (1996) 84-89
- [22] K. Bange, C. Ottermann, O. Anderson, U. Jeschkowski, M. Laube . R. Feile, *Thin Solid Films*, 197 (1991) 279-285
- [23] C. Ottermann, K. Bange, W. Wagner, M. Laube, F. Rauch, *Surf. Interface Anal.*, 19 (1992) 435-438
- [24] M. H. Suhail, G. M. Rao , S. Mohan, *J. Appl. Phys*, 71 (1992) 1421-1427
- [25] J.-S. Chen, S. Chao, J.-S. Kao, H. Niu, C.-H. Chen, *Appl. Optics*, 35 (1996) 90-96

- [26] H.-W. Zhang, S.-X. Liu, *Thin Solid Films*, 209 (1992) 148-149
- [27] G. Atanassov, R. Thielsch, D. Popov, *Thin Solid Films*, 223 (1993) 288-292
- [28] S. Guo, H. Arwin, S. N. Jacobsen, K. Järrendahl, U. Helmersson, *J. Appl. Phys.*, 77 (1995) 5369-5376
- [29] L. Shivalingappa, R. Narasimha, S. Mohan, *Vacuum*, 44 (1993) 1031-1035
- [30] R. M. Bueno, J. M. Martinez-Duart, M. Hernandez-Velez, L. Vazquez, *J. of Mat. Science*, 32 (1997) 1861-1865
- [31] S.-Y. Zheng, A. M. Andersson-Fäldt, B. Stjerna, C. G. Granqvist, *Applied Optics*, 32 (1993) 6303-6309
- [31] L. Shivalingappa, R. Narasimha, S. Mohan, *Vacuum*, 44 (1993) 1031-1035
- [32] S. Mansour, K. Al-Robaee, R. Narasimha, S. Mohan, *Thin Solid Films*, 221 (1992) 214-219
- [33] S. Mansour, K. Al-Robaee, R. Narasimha, S. Mohan, *J. Appl. Phys.*, 71 (1992) 2380-2386
- [34] V. Craciun, D. Craciun, M. C. Buescu, R. Dabu, I.W. Boyd, *Appl. Surf. Science*, 109/110 (1997) 354-358
- [35] F. Horowitz, S.B. Mendes, *Applied Optics*, 33 (1994) 2659-2663
- [36] S. Amirhaghi, A. Archer, B. Taguiang, R. McMinn, P. Barnes, S. Tarling, I. W. Boyd, *Appl. Surf. Science*, 54 (1992) 205-209
- [37] N. Özer, S. de Souza, C. M. Lampert, *SPIE Proceedings*, 2531 (1995) 143-151
- [38] M. Rubin, K. von Rottkay, S.-J. Wen, N. Ozer, J. Slack, presented at the Int. Symp on Opt. Mater. Technol. (Freiburg, Germany, Sept 1996) and to be published in Proceedings
- [39] D. E. Aspnes, *SPIE Proc.* 276 (1981) 188-195
- [40] R.M.A. Azzam and N.M. Bashara, "Ellipsometry and Polarized Light" (North-Holland, Amsterdam, 1977)
- [41] K. von Rottkay, M. Rubin, N. Ozer, *Mat. Res. Soc. Symp. Proc.*, 403 (1996) 551-556
- [42] K. von Rottkay and M. Rubin, *Mater. Res. Soc. Symp. Proc.*, 426 (1996) 449-454
- [43] C. Herzinger and B. Johs, Guide to Using WVASE32™, J.A. Woollam Co., Lincoln, NE, 1996, p. 347
- [44] C.C. Kim, J.W. Garland, H. Abad, P.M. Raccah, *Physical Review B*, 45 (1992) 11749-11767
- [45] X.-F. He, *J. Opt. Soc. Am. B*, 14 (1997) 17-20
- [46] D.E. Aspnes, J.B. Theeten, *Phys. Rev. B*, 20(8) (1979) 288-298
- [47] C. Pickering, R. Greef, A.M. Hodge, *Mater. Sci. Eng. B*, 5 (1990) 295
- [48] D.A.G. Bruggeman, *Annalen der Physik*, 24 (1935) 636-664
- [49] G.E. Jellison Jr., *Thin Solid Films*, 234 (1993) 416-422
- [50] I.L. Morrison, T.E. Jenkins, *Europhys. Lett.*, 34 (1996) 55-61
- [51] J. Koh, Y. Lu, C.R. Wronski, Y. Kuang, R.W. Collins, T.T. Tsong, Y.E. Strausser, *Appl. Phys. Lett.*, 69 (1996) 1297-1299
- [52] O. Wiener, *Abh. d. Königl. Sächs. Ges. d. Wiss., math.-phys. Kl.*, 32 (1912) 509
- [53] D.J. Bergman, *Phys. Rev. Lett.*, 44 (1980) 1285-1287
- [54] G.W. Milton, *Appl. Phys. Lett.*, 37 (1980) 300-302
- [55] T. Seike, J. Nagai, *Solar Energy Mater.*, 22 (1991) 107-117
- [56] S.F. Cogan, E.J. Anderson, T.D. Plante, R.D. Rauh, *Proc. Soc. Photo-Opt. Instrum. Engr.*, 562 (1985) 23-31
- [57] P.A. Gillet, J.L. Fourquet, O. Bohnke, *Mater. Res. Bull.*, 27 (1992) 1145-1152
- [58] A. Gutarra, A. Azens, B. Stjerna, C.G. Granqvist, *Appl. Phys. Lett.*, 64 (1994) 1604
- [59] C.G. Granqvist, *Handbook of Inorganic Electrochromic Materials*, Elsevier Science, Amsterdam, 1995, p.275