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# Electrochromism of sputtered fluorinated titanium oxide thin films

A. Gutarra,<sup>a)</sup> A. Azens, and B. Stjerna

Physics Department, Chalmers University of Technology and University of Gothenburg,  
S-412 96 Gothenburg, Sweden

C. G. Granqvist

Department of Technology, Uppsala University, P. O. Box 534, S-751 21 Uppsala, Sweden

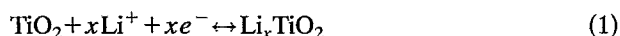
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Titanium-oxide-based films were prepared by reactive dc magnetron sputtering in Ar+O<sub>2</sub>+CF<sub>4</sub>. Pronounced electrochromism was found in LiClO<sub>4</sub>+propylene carbonate. The maximum coloration efficiency was 37 cm<sup>2</sup>/C at a wavelength of ~0.7 μm. Polaron hopping is believed to cause the absorption. Coloration/bleaching was performed for up to 2×10<sup>4</sup> cycles without apparent degradation.

This letter shows that reactive sputtering of titanium in a carbon-tetrafluoride-containing plasma can produce films with pronounced electrochromism and good cycling durability in a lithium conducting electrolyte.

Electrochromic materials change their optical properties persistently and reversibly under the action of voltage pulses.<sup>1-3</sup> Of particular interest are thin films of certain oxides that vary their absorbance when ions are intercalated/deintercalated from an adjacent ion conductor or electrolyte. Oxides of tungsten, molybdenum, niobium, and titanium become absorbing under ion insertion (cathodic coloration), whereas oxides based on iridium, rhodium, nickel, and cobalt can become absorbing under ion extraction (anodic coloration).<sup>2</sup> It appears<sup>3</sup> that the optical properties can be rationalized in terms of canonical band structures for metal ions surrounded by oxygen ions in octahedral coordination, and that the cathodic coloration is associated with small polaron hopping.<sup>3</sup> Electrochromic oxide films may have important applications in architectural ("smart") windows with variable transmittance of radiant energy, in nonemissive information displays, and in variable-reflectance mirrors.

TiO<sub>2</sub> is a semiconductor with a band gap  $E_g$  separating a filled O2p band from an empty Ti2s band. Its various phases are built from TiO<sub>6</sub> octahedral units sharing corners and edges. The anatase structure has  $E_g \approx 3.4$  eV and is hence transparent.<sup>4</sup> Ion intercalation proceeds jointly with electron insertion by the schematic reaction



for the case of lithium intercalation/deintercalation. The electrons enter the  $t_{2g}$  band and produce absorption, i.e., the material is electrochromic. This property was first demonstrated for anatase powder;<sup>5,6</sup> it has since also been found in films made by reactive evaporation<sup>7</sup> and sputtering<sup>8</sup> of Ti and by sol-gel preparation.<sup>9,10</sup> The coloration efficiency (CE) of the vacuum deposited films was <5 cm<sup>2</sup>/C, which is undesirably low for applications. However films made by evaporation of H<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> (Ref. 11) and by anodization<sup>12</sup> gave evidence for much larger CEs. The present work considers TiO<sub>2</sub>-based films made by magnetron sputtering, i.e., by a

technique suitable for large-area large-scale deposition, and shows that CEs up to 37 cm<sup>2</sup>/C can be achieved through proper fluorination.

Our films were made by reactive dc magnetron sputtering in a versatile deposition unit.<sup>13</sup> Evacuation to ~10<sup>-6</sup> Torr was followed by an inlet of Ar (purity 99.9997%), O<sub>2</sub> (purity 99.998%), and CF<sub>4</sub> (purity 99.995%) so that the total pressure was 10<sup>-2</sup> Torr. The gas flow rates, in standard cm<sup>3</sup> per minute (sccm), were 15 for Ar, 10 for O<sub>2</sub>, and 0–0.8 for CF<sub>4</sub> (denoted  $F_{\text{CF}_4}$ ). Sputtering took place from a 10-cm-diam Ti target onto 2.5×2.5×0.1 cm<sup>3</sup> glass substrates precoated with ~0.2-μm-thick indium tin oxide having a resistance/square of ~10 Ω. A stable discharge was obtained by setting the voltage to 460 V. The target-substrate separation was 6 cm. Films with thicknesses between 0.15 and 0.4 μm, as determined by surface profilometry (Tencor Alpha-Step), were prepared at rates between 1.5 and 4.5 nm/min. X-ray diffractometry did not indicate crystallinity. *Ex situ* atomic force microscopy (Park Scientific Instruments) showed surface roughness with a lateral extent between the protrusions of ~20 nm and a protrusion height that increased with the magnitude of  $F_{\text{CF}_4}$ .

Cyclic voltammetry, using an electrochemical interface (Solartron 1286), was carried out on films immersed in propylene carbonate with 1 M LiClO<sub>4</sub>. A three-electrode arrangement was adopted with Li foil serving as counterelectrode and reference electrode. All data were taken in a glove box with a water content of <2 ppm. Figure 1 shows cyclic voltammograms for ~0.2-μ-thick films sputter deposited at  $F_{\text{CF}_4}$  being 0, 0.4, and 0.8 sccm. With  $F_{\text{CF}_4}=0$ , the voltammograms show peaks at 2.25 and 1.6 V vs Li for the anodic and cathodic excursion, respectively. This is consistent with voltammograms for TiO<sub>2</sub> powder<sup>6</sup> and for sol-gel-prepared films<sup>9,14</sup> at low voltage sweep rates. An addition of CF<sub>4</sub> alters the voltammograms, and the lithium intercalation capacity is dramatically improved. The voltammogram for  $F_{\text{CF}_4}=0.4$  sccm is qualitatively similar to that for amorphous W oxide.<sup>15</sup>

Optical properties were measured in the 0.3<λ<2.5 μm wavelength range by double-beam spectrophotometry (Perkin-Elmer Lambda 9). We recorded normal transmittance  $T$  and near-normal reflectance  $R$  (using a calibrated reference mirror). Spectral absorbance  $A$  was obtained from

<sup>a)</sup>Permanent address: Facultad de Ciencias, Universidad Nacional de Ingeniería, Av. Tupac Amaru s/n, Lima, Peru.

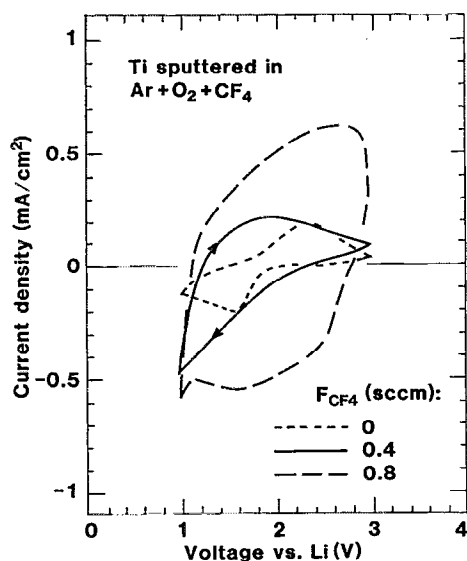


FIG. 1. Cyclic voltammograms for Ti-oxide-based films prepared by sputtering in Ar+O<sub>2</sub>+CF<sub>4</sub> with the shown values of the CF<sub>4</sub> rate ( $F_{CF_4}$ ). The voltage scan rate was 20 mV/s. Arrows denote scan direction.

$A=1-T-R$ . Figure 2 shows spectral absorbance for a 0.17- $\mu\text{m}$ -thick film, made with  $F_{CF_4}=0.6$  sccm, after coloration and bleaching for 20 s at 3 and 1.4 V vs Li, respectively. The film had undergone 200 color/bleach cycles prior to the measurement. The difference in absorbance is large, and the colored film has a broad absorption band centered at  $\lambda \approx 0.69$   $\mu\text{m}$  whereas the bleached film has a low and even absorbance. One may compare with optical data for sol-gel deposited Ti oxide films that had an absorption band at  $\lambda \approx 0.75$   $\mu\text{m}$ .<sup>9</sup> The optical changes in our studied film took place fairly rapidly, and 7 s was enough for inserting 84% of the maximum charge density or for extracting 99% of the charge.

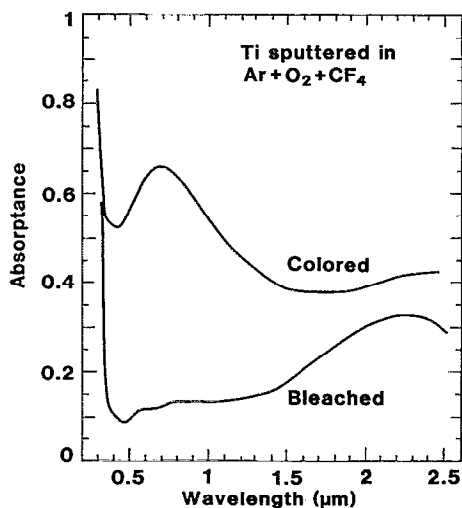


FIG. 2. Spectral absorbance for a Ti-oxide-based film, prepared by sputtering in Ar+O<sub>2</sub>+CF<sub>4</sub>, in colored and bleached states.

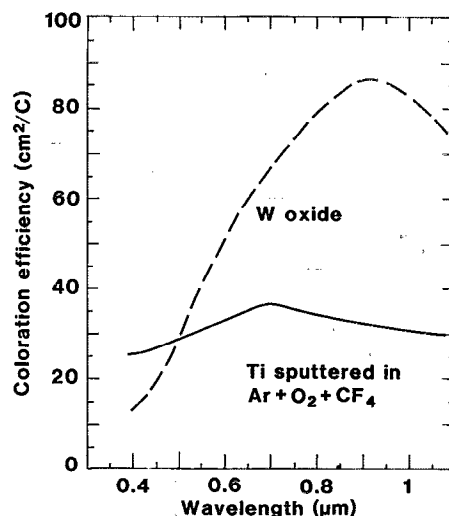


FIG. 3. Spectral coloration efficiency for a Ti-oxide-based film prepared by sputtering in Ar+O<sub>2</sub>+CF<sub>4</sub> and for an evaporated W oxide film (after Ref. 16).

The optical data allow a calculation of the CE by

$$CE = \left( \ln \frac{(1-R_b)^2 T_c}{(1-R_c)^2 T_b} \right) / \Delta Q, \quad (2)$$

where  $\Delta Q$  is charge per unit area, and  $b$  and  $c$  refer to bleached and colored states, respectively. The CE determines the practical usefulness of the films in electrochromic devices. Figure 3 displays the spectral CE for a 0.17- $\mu\text{m}$ -thick film made with  $F_{CF_4}=0.6$  sccm. A maximum CE of 37 cm<sup>2</sup>/C is seen to correspond to the peak absorption. The dashed curve in Fig. 3 puts this in perspective by showing the CE of "amorphous" evaporated W oxide films.<sup>16</sup> The latter data serve as a baseline against which the performance of any alternative cathodically coloring electrochromic material must be judged. In the luminous range, the CE of the Ti-oxide-based film is rather similar to the CE of W oxide, i.e., the two films are comparable with regard to their ability to modulate visible light. In the infrared, the W oxide film has a superior CE. It is noteworthy that the Ti-oxide-based film shows a smaller spectral dependence of the absorption than the W oxide film. Earlier work on films made by reactive evaporation<sup>7</sup> and sputtering<sup>8</sup> of Ti yielded the CEs less than 5 cm<sup>2</sup>/C, as noted above, and we therefore conclude that the CF<sub>4</sub> added to the sputtering gas is instrumental for making the Ti-oxide-based film of interest for applications.

The physical cause of the electrochromism is almost certainly small polaron hopping in the Ti  $t_{2g}$  band. This conclusion is reached from the analogy with substoichiometric Ti oxide crystals, specifically the Magnéli phases Ti <sub>$n$</sub> O<sub>2 $n$ -1</sub> with  $n$  being 4 and 6, for which polaron absorption led to an absorption band centered at  $\sim 1$  eV.<sup>17,18</sup> Hence we find a ratio of  $\sim 0.56$  between the polaron band centers for heavily disordered and crystalline Ti-oxide-based materials. Interestingly, W oxide films have approximately the same ratio.<sup>19</sup>

The durability under extended color/bleach switching was evaluated by applying alternately 1.4 and 3.0 V vs Li for 20 s periods to a 0.17- $\mu\text{m}$ -thick film prepared with  $F_{CF_4}=0.6$

sccm. The inserted and extracted charge density remained at  $34 \pm 2 \text{ mC/cm}^2$  with no sign of long-term degradation for  $\sim 2 \times 10^4$  full cycles. When the voltage span was increased so that it encompassed 1–4 V vs Li, degradation was noticeable after  $2 \times 10^3$  cycles. It seems that the durability is fully adequate at least for some applications.

Summarizing, we prepared Ti-oxide-based thin films by reactive sputtering in  $\text{Ar} + \text{O}_2 + \text{CF}_4$ . They showed pronounced cathodic electrochromism in a Li-conducting electrolyte with CEs up to  $37 \text{ cm}^2/\text{C}$  at a wavelength of  $0.7 \mu\text{m}$ . Polaron hopping is believed to cause the absorption. The films were capable of long-term color/bleach cycling.

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