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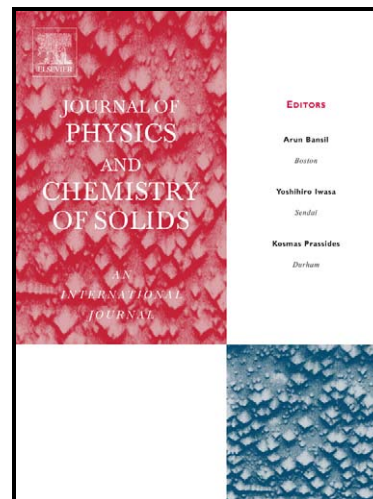
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## Electrochromic properties of $\text{WO}_3$ as a single layer and in a full device: from the visible to the infrared.

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### ABSTRACT

Most of the applications of electrochromic devices (ECDs) concern the visible whereas there is a significant need for ECDs active in the infrared (IR) region. After optimization,  $\text{WO}_3$  thin films show significant variation in emissivity, as high as 78 % and 49 % in the MW (3-5  $\mu\text{m}$ ) band and LW (8-12  $\mu\text{m}$ ) band, respectively. The incorporation of the EC  $\text{WO}_3$  layer in ECDs is discussed in terms (i) of device configuration (i.e. position of the active layer on top or bottom of the device), (ii) of the choice of materials including the transparent conductive layer, electrolyte, counter electrode, and (iii) of the thickness of each layer. Initial trends in optical modulation of the ECDs are deduced from simulation of the optical indexes (n and k). Experimental data based on half-cell assembly confirm the modulation in emissivity in the IR region for  $\text{WO}_3/\text{Ta}_2\text{O}_5/\text{NiO}$  based devices with however lower values than the predicted ones.

*Keywords:* A. Thin Films; D. Optical Properties; A. Oxides

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### 1. Introduction

Common electrochromic materials and devices (ECDs), which present the capability of modifying their optical properties under an applied voltage, generally work in the visible and near-infrared region [1-2]. Examples of such devices include dimmable rearview mirrors in car, smart energy-saving windows, sunglasses, helmet visors [3]. Recently there has been a growing interest in emissivity modulators for satellites thermal control or for infrared furtivity [4,5]. The military camouflage application implies to prepare coatings for vehicles or soldiers which would be able to blend them in their surrounding and become therefore invisible to an infrared imager. Focusing on tungsten oxide, the typical electrochromic material, which switches from a transparent/insulator to a colored/metallic state under proton/lithium insertion, we recently demonstrated promising

modulation in emissivity in band II (3-5  $\mu\text{m}$ ) and III (8-12  $\mu\text{m}$ ) for  $\text{WO}_3$  thin films deposited by radio-frequency sputtering and laser ablation [6]. However, the characterization of a single layer remains a preliminary step as our main objective concerns the realization of full devices. ECDs are typically based on multi-layered systems, consisting of optically and electrochemically active layers separated by an electrolyte sandwiched between two electrodes. Herein, the optimization of the EC behavior of  $\text{WO}_3$  thin films in the IR domain will be shortly discussed whereas their integration in a full device will be reported. Significant parameters, such as the position of the active layer, the choice of the various materials and the thickness of the layer on the optical response of the device will be addressed. Theoretical calculations based on the simulation of the optical indexes of each layer will be used as a guiding tool for the ECD realization.

### 2. Experimentals

Using Radio Frequency Sputtering technique  $\text{WO}_3$  thin films (referred here after as RFS-films) were deposited at room temperature on various substrates, namely FTO (F doped

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SnO<sub>2</sub>), Au, and Si, from a metallic W target, at 250 W with a 90 mm target-substrate distance in a 45 mTorr environment consisting of 15 sccm Ar and 3.75 sccm (20%) O<sub>2</sub>. The deposition time from 45 to 240 mins corresponds to film thickness in the 200 to 650 nm range as determined by profilometry using a Dektak instrument or by optical measurement with a spectroscopic ellipsometer (Sentech) over the 350 to 800 nm visible range.

For the optical properties in the 2.5 – 25 μm range, both the reflectance and the transmittance, were measured using an Infrared spectrophotometer SOC-100 HDR (Surface Optics Corporation), giving the Hemispherical Directional Reflectance (HDR) and Hemispherical Directional Transmittance (HDT) values. For the HDR and HDT measurements, the thin film is irradiated with a beam at 10° and 0° angle of incidence, respectively. The infrared source is a blackbody heated at 700°C to emit in the infrared region. A gold specular reference ( $R \approx 99\%$  in IR) is used to determine the HDR values whereas the air is used as the reference for the HDT ones.

Measurements in the IR domain were performed using two CEDIP infrared cameras equipped with an InSb detector for the MW band and a microbolometer for the LW band. The system consisted in heating at 60 °C a copper foil on which the films and a “simulated black body”, based on a piece of silicon substrate painted in black, are positioned. IR imagers recorded digit levels expressed in terms of either luminance ( $L = \epsilon\sigma T^4$ ) or temperature. For the latter, it corresponds to an apparent temperature and not to the real one as the emissivity of the films is different from the one of the black body ( $\epsilon=1$ ).

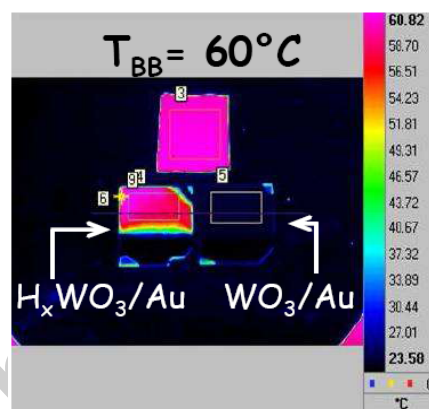
The electrochemical experiments were performed with a VMP automatic cycling/data recording system (Biologic S.A., Claix, France). Upon electrochemical cycling using a Pt/H<sub>3</sub>PO<sub>4</sub> 0.1 M/WO<sub>3</sub> cell, RFS-WO<sub>3</sub> films are reduced as a result of the injection of protons and electrons:  $\text{WO}_3 + x\text{e}^- + x\text{H}^+ \rightleftharpoons \text{H}_x\text{WO}_3$ . The contrast in reflectance  $\Delta R$ , defined as the difference between the integrated R value in the deinserted state and the one in the inserted state ( $\Delta R = R_{\text{deinserted}} - R_{\text{inserted}}$ ), was deduced from the reflectance recorded after having applied either the insertion (-1.9 V) or deinsertion (+1V) voltage for 180 s. The variation in emissivity was then calculated using the simple formula  $\epsilon = 1 - R$ , for non-transparent systems.

### 3. Results and Discussion

#### 3.1 RFS-WO<sub>3</sub> thin film as single-layer

Earlier studies indicated a strong dependence of the evolution of the reflectance with the depositions conditions and in particular with the oxygen pressure for RFS-WO<sub>3</sub> thin films [7]. Fixing the pressure to its optimized value, namely 45 mTorr, for both FTO and Au substrates, an increase in film thickness leads to an increase of the optical modulation in the LW band (Table 1). For instance, R doubles from 25 to 50 % for RFS-WO<sub>3</sub> films deposited on FTO of 320 and 650 nm, respectively. However independently of the deposition conditions, contrasts in reflectance always remain of smaller values in the LW band as compared to the MW one. In the current conditions (Table 1), R maximum values reach 73 % and 50 % in the MW band and LW band, respectively. Interestingly, the promising IR optical properties of RFS-WO<sub>3</sub> thin films were confirmed using infrared imagers. Using an infrared imager in band II and fixing the black body reference temperature to 60 °C, Fig. 1 shows the variation in luminosity of a 320 nm WO<sub>3</sub> film, deposited on Au at 45 mTorr, in the

inserted state and in the deinserted state. Upon proton insertion, the black appearance of WO<sub>3</sub> turns to a reddish-purple one for H<sub>x</sub>WO<sub>3</sub>, close to the purple appearance of the BB. This luminance modification is associated with a decrease in the apparent temperature from 59 °C, for the inserted state, to 24 °C, for the deinserted one. This variation in apparent temperature of 35 °C was correlated to a variation of emissivity,  $\epsilon$ , of 0.78 between an inserted state of high emissivity (0.86) and a deinserted state of very low emissivity (0.08) (Table 1). As expected from the smaller contrast in reflectance ( $R_{\text{LW}} = 15\% < R_{\text{MW}} = 73\%$ ), the variation of the apparent temperature of 5 °C in the LW band is of smaller amplitude (Table 1). In agreement with higher contrast in reflectance, a maximum variation in apparent temperature in the band III of 21 °C is obtained for thicker film (i.e. 650 nm). Having optimized the single-layer of WO<sub>3</sub>, its incorporation in the full device was our next step.



**Fig. 1.** Thermal camera picture, using an IR imager working in the MW (3-5 μm) band, of a 320 nm RFS-WO<sub>3</sub> thin films (deposited in 45 mTorr chamber pressure) in the inserted state (H<sub>x</sub>WO<sub>3</sub>) and deinserted one (WO<sub>3</sub>). T<sub>BB</sub> refers as the black body temperature, of which temperature is 60 °C, and appears in purple in the luminance color scale. Variation of the

Conditions of deposition at PO <sub>2</sub> = 45 mTorr								
Substrate	FTO				Au			
Thickness [nm]	320	650	320	650	320	LW	MW	LW
Optical behavior								
Band	MW	LW	MW	LW	MW	LW	MW	LW
$\Delta R_{\text{integrated}}$	25	25	25	50	73	15	43	34
$\Delta T_{\text{apparent}} [^{\circ}\text{C}]$	12	15	12	27	35	5	30	29
$\Delta\epsilon$	0.39	0.27	0.19	0.49	0.78	0.19	0.51	0.38

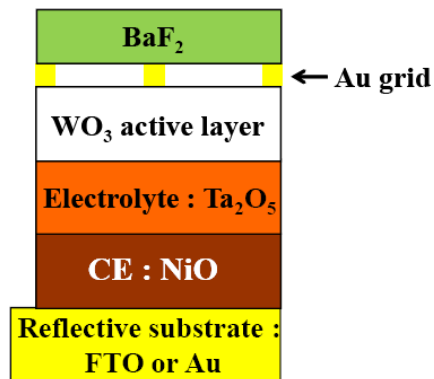
apparent temperature is added.

**Table 1:** Evolution of the contrast in reflectance and in apparent temperature for RFS-WO<sub>3</sub> thin films deposited in 45 mTorr chamber pressure on either FTO or Au substrates and for two thicknesses, 320 and 650 nm.

#### 3.2 WO<sub>3</sub>-based devices

Investigation of inorganic ECD active in the IR region is still scarcely reported. Our initial step was to start from existing devices working in the visible and to extend their characterization in the IR domain. Figure 2 gathers the choices corresponding to the various layers of a reflective ECD device, in the top configuration (i.e. WO<sub>3</sub> as top layer), using Au or FTO as supporting reflective layer. The success of the ECD device lies on the facility to ensure the electronic conductivity on the top of the device and therefore to synthesize transparent

conductor in the IR. To avoid the lack of available materials, Au grids were deposited by photolithography on  $\text{BaF}_2$  substrates, which show transparency of about 90 % from 2 to 11  $\mu\text{m}$  and of about up to 12  $\mu\text{m}$ . A transparency as high as 90 % was estimated for Au grids constituting of lines of 10  $\mu\text{m}$  separated by voids of 500  $\mu\text{m}$ . Keeping  $\text{WO}_3$  as the main active electrochromic layer, all-solid-state devices, based on its association with  $\text{Ta}_2\text{O}_5$  as electrolyte and NiO as counter electrode were initially chosen. In the IR domain (i.e. from 2.5 to 20  $\mu\text{m}$ ), and upon cycling in KOH medium, RFS NiO thin films exhibit a small modulation in absorbance/reflectance corresponding to a contrast between the oxidized (deinserted) and the reduced (inserted) state, R, lower than 10 % [8]. 300 nm RFS- $\text{Ta}_2\text{O}_5$  thin films show a transmittance of more than 70 % in the IR domain [8].

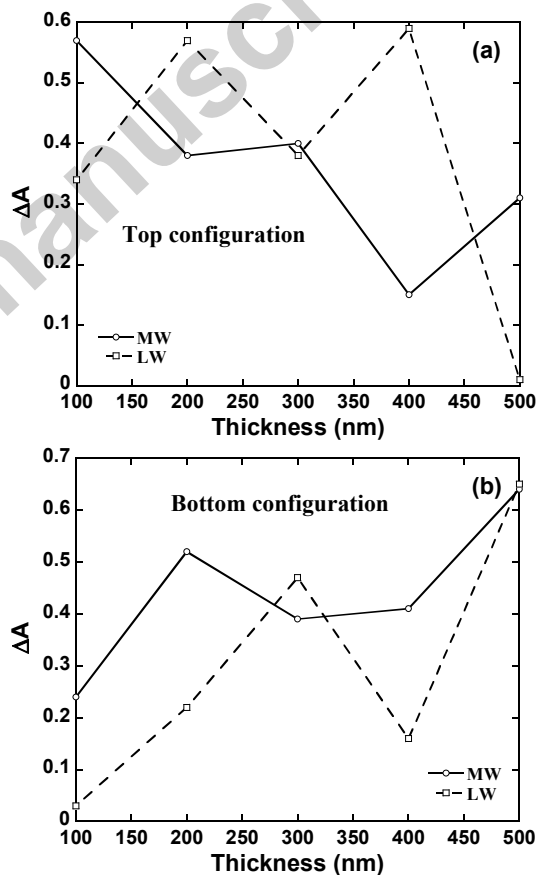


**Fig. 2.** Schematic cross section of a multilayer device built on a reflective substrate. Choice of the materials are included.

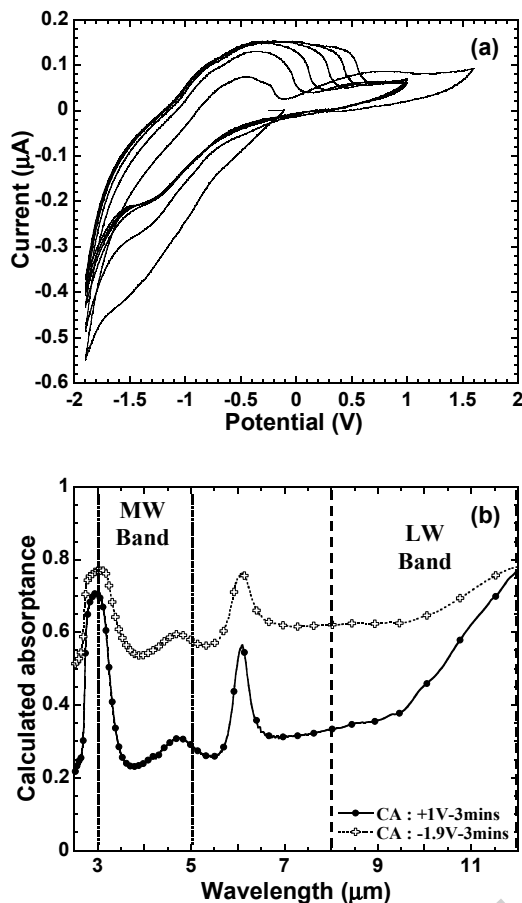
As a preliminary step of the experimental work, simulation of the films optical data was performed. The whole simulating process was based on the simulation, using the Film Wizard software [9], of the optical indexes,  $n$  and  $k$ , of each layer including the substrate prior to their incorporation in the multi-layer stack for the determination of the contrast in reflectance of the full device. For each layer, various states, namely as-deposited, inserted and deinserted were considered. In first approximation, in the following, we consider that the refractive indexes are not modified with the film thickness (< 650 nm). On the contrary as transmittive device, the optical response of reflective ECDs depends on the position of the active electrochromic layer. Having determined the various optical indexes, two types of ECD configurations, depending on the position of the  $\text{WO}_3$  electrochromic active layer were considered. In the first one,  $\text{WO}_3$  layer was placed at the top of the device whereas in the second one it corresponded to the bottom layer. The latter requires that the above electrolyte, counter electrode and conducting layers are IR transparent. In Fig 3 are compared the “simulated” modulation in Absorbance ( $\Delta A_{\text{MW}}/\Delta A_{\text{LW}}$ ) of NiO/ $\text{Ta}_2\text{O}_5$ / $\text{WO}_3$  device in the top (Fig. 3a) and bottom (Fig. 3b) configuration. The largely dispersed values confirm the key role played by the layer thickness, meanwhile it shows the advantage of offering a wide diversity of devices for various applications. In our group, realization of the multilayer devices in a single shot was experimentally limited. To overcome this difficulty, devices were built from half-cells assembly. Cyclic voltammograms of ECD realized by assembling two half-cells of  $\text{BaF}_2$ /Au grid/ $\text{WO}_3$ -650nm on one side and  $\text{Ta}_2\text{O}_5$ /NiO-100nm/FTO on the other side are presented in Fig. 4a. To ensure the ionic conductivity, two drops of water were added in-between the two half-cells before the assembly. The cycling properties, which are rather poor in respect probably of a poor electronic contact between the two electrodes, are visibly associated with

a limited optical modulation from transparent to a blue/grey color. The absorbance in the “colored” state, measured after a chronoamperometry at -1.9V for 180 s and the one in the “transparent state” after a chronoamperometry at 1.0 V for 180 s are shown in Fig. 4b. Despite the two bands located at 3 and 6  $\mu\text{m}$  due to the presence of water, the absorbance modulation reaches 0.27 in MW band, from 0.33 to 0.60 and 0.18 in LW band from 0.49 to 0.67. Such values remain quite low as compared to the ones predicted by the simulation namely 0.40 and 0.38 for MW band and LW band, respectively. Such discrepancy gives some hope on further improvements. Our next step was to integrate in the ECD a Au reflective grid located just below the  $\text{WO}_3$  active layer allowing therefore to consider the electrolyte and counter electrode as a reservoir electrochemically active but not optically. Such approach, allowing to consider a large range of materials for the electrolyte or counter electrode, leads to better optical performances.

For instance “ $\text{BaF}_2$ /Au grid/ $\text{WO}_3$ -400nm/R-AuGrid/ $\text{Ta}_2\text{O}_5$ /NiO-100nm/FTO device exhibits simulated contrast in absorbance of 0.60 and 0.42, in MW and LW band, respectively.



**Fig. 3.** Variation of the emissivity in MW and LW bands for the top (a) and bottom (b) configurations, in respect of  $\text{WO}_3$  and NiO thickness for  $\text{Ta}_2\text{O}_5$  thickness fixed to 100 nm.



**Fig. 4.** (a) Cyclic voltammograms of “(1)BaF<sub>2</sub>/G-TiR/WO<sub>3</sub><sub>650 nm</sub>/(2)Ta<sub>2</sub>O<sub>5</sub>nH<sub>2</sub>O<sub>300 nm</sub>/NiO<sub>100 nm</sub>/FTO” two-half cell assembly device. (b) Variation of the Absorbance (deduced from the measured Reflectance  $A = 1 - R$ ) after a chronoamperometry at -1.9 V for 180 s and at 1 V for 180 s. The two large

absorbance peak correspond to the drop of water added for improving the ionic conductivity.

#### 4. Conclusion

Thanks to a careful optimization of the deposition conditions, strong contrast in reflectance, emissivity and apparent temperature, in the IR domain are shown for electrochromic WO<sub>3</sub> thin films. Values as high as 75 % in MW band (3-5 µm) and 50 % in LW band (8-12 µm) are reached. Incorporation of the WO<sub>3</sub> layer in a complete device was successfully performed. However, the experimental results remain lower than the simulated ones giving hope for improvement.

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