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Influence of cycling temperature on the electrochromic properties of WO_3//NiO devices built with various thicknesses

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ABSTRACT

Electrochromic smart windows, which are able to vary their optical transmittance by the application of a voltage, improve the indoor comfort in buildings by controlling light and temperature. Among electrochromic devices, ECDs, WO_3 and NiO are often associated leading to neutral color. This work focuses on the influence of the thickness of WO_3 and NiO single layers on the ECD electrochemical and optical properties. Initial characterizations in lithium-based liquid electrolyte, show a non-linear evolution of the electrochemical capacity for each oxides vs. thickness while for similar thickness, WO_3 thin films exhibit larger EC properties than NiO ones. The combinations of various WO_3 and NiO thicknesses lead to ECDs of which capacity appears limited by the one of NiO, while the switch to a neutral color always remain. Besides, the influence of each oxide on the ECD cyclic voltammogram shape is discussed. Finally, the study of the cycling temperature, in the range −40 °C to 80 °C on the electrochromic properties of ITO/650 nm-WO_3/$LiClO_4$-PC +PMMA/360 nm-NiO/ITO shows an increase in performance with temperature nevertheless associated with signs of degradation above 60 °C. At low temperature, the decrease in capacity is interestingly associated with a remaining significant optical contrast and the capacity recovery if the ECD is further cycled at RT.

1. Introduction

Nowadays, following architecture trends and comfort, surfaces assigned to windows on the buildings facades are getting larger and larger. In addition of day light, windows allow a flow of energy through them that must then be regulated in respect of heating or cooling. Global warming leads to extreme temperature forcing the population to increase their energy consumption, in air conditioning for instance. Consequently, smart windows [1,2], have received significant attention in the past few decades, in respect of their promising application as energy saving in building due to the control of solar light transmittance. Smart windows are commonly based on chromogenic devices and in particular electrochromic ones.

Electrochromic devices, ECDs, have the capability to change their optical properties in response to an electric field. In the visible, inorganic materials with a reversible color switch have been studied at least since the work of Deb at the end of the sixties [3]. Currently, the smart window technology is mostly based on the association of tungsten trioxide (WO_3) and nickel oxide (NiO) [4–11] separated with a solid electrolyte based on metal oxide [12] or a membrane containing lithium based electrolyte [13]. Indeed, WO_3 remains by far the most popular EC material. Upon reduction, WO_3 changes color from a transparent, to a dark blue state. Its stability, its high coloration efficiency of over 50 cm^2/C and fast switching times make it a reliable material. Despite over thirty years of study, anodically colored NiO still suffers from a lack of clear understanding of the mechanism from the scientific community in particular in the lithium based systems [14–16]. However, this anodic material is of particular interest as its brownish color, is very complementary to the blue color of WO_3 in order to built a smart window with a grey neutral color for a commercial purpose.

The purpose of this work is to better determine the contribution of each electrochromic layer on the WO_3//NiO ECD behavior, in terms of optical and electrochemical properties, considering in particular the influence of the thickness of each single layer. In the literature, the relationship between thickness and ECD performance has been discussed, but taking into account only one layer each time [17]. However, in 1994, Zhang et al. already pointed out the need of adjusting the thickness layers on a WO_3//V_2O_5 ECD [18]. In a first section of this paper, the EC properties of NiO and WO_3 thin films of various thicknesses are separately discussed prior to their association in a lithium based electrolyte membrane ECD.

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Despite limited literature [19–21], the stability vs. temperature is one of main criteria of ECD performance. The temperature may also play a role on the lifetime, the switching time or the optical contrast of the ECD. Herein, the evolution of the ECD performances in a temperature range from low temperature (− 40 °C) to high temperature (80 °C) is investigated.

2. Experimental details

2.1. Deposition of WO_3 and NiO thin film by DC magnetron sputtering

WO_3 and NiO thin films were deposited on $4 \times 5\ cm^2$ In_2O_3:Sn coated glasses (ITO glass, ~25 Ω/□) by reactive DC magnetron sputtering. The targets were 6 cm diameter pure tungsten (99.99%) and pure nickel (99.99%). During the deposition process, the slant angle of the target was 15°, the distance from the substrate to the target fixed at 30 cm, and the substrates (ITO glasses) were kept rotating by a constant speed at about 12° per second. The depositions are made at room temperature (without taking into account the heating of the substrate by the plasma). Such conditions led to the production of uniform films. The gas-flow ratio of Ar (99.99%) to O_2 (99.99%) was fixed by mass flow controllers at 160:100 (sccm) and 200:5 (sccm), corresponding to working pressures of 1.6 Pa and 2.6 Pa for WO_3 and NiO thin films growth, respectively. The power was maintained at 178 W and 132 W for WO_3 and NiO, respectively. Various durations of deposition were used for screening various thicknesses, leading to deposition rate of 12–13 nm/min and 6–7 nm/min for WO_3 and NiO thin films, respectively. Deposition parameters are summarized in Table 1.

2.2. Fabrication of the electrochromic device (ECD)

Five-layer ECDs, based on the ITO/x nm-NiO/$LiClO_4$-PC-PMMA/x nm-WO_3/ITO chain, were built by assembling NiO and WO_3 single layers in their initial states. The lithium based electrolyte was a kind of composite polymer gel made from polymethyl methacrylate (AR, 20% mass ratio), propylene carbonate (PC) and $LiClO_4$ (AR, 0.5 M). The devices were placed in a soft silicon capsule, and heated at a temperature of 80 °C and a pressure of 0.1 MPa.

Several ECDs were built, combining different thicknesses of WO_3 and NiO single layers, by either fixing the NiO thickness to 360 nm and varying the one of WO_3 from 130 nm to 860 nm or fixing the WO_3 thickness at 650 nm and varying the NiO thickness from 70 nm to 630 nm. For the study in temperature, 360 nm NiO and 650 nm WO_3 were chosen arbitrarily, each thickness corresponding to a deposition time of 50 min.

2.3. Characterization

The thin film morphology was characterized by scanning electron microscopy. The structure of NiO and WO_3 thin films was determined by X-ray diffraction (XRD) using a PANalytical X'pert MPD diffractometer with CuK_α incident radiation.

The optical transmittance was recorded in the visible, between 300 nm and 900 nm, with a spectrophotometer UviLine 9400.

The electrochemical properties of the single layer were carried out in 0.3 M LiTFSI in BMITFSI (Lithium bis(trifluoromethanesulfonyl) imide in1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide)) in a three-electrode cell using Pt as counter electrode and Satured Calomel Electrode (SCE) as reference electrode. Cyclic Voltammogramms (CV) were recorded using a scan rate of 20 mV/s. The voltage windows were −1.3 V/0.7 V vs. SCE for WO_3 and −0.7 V/1.3 V vs SCE for NiO. A two-electrode measurement was recorded for the ECD, with scan rate of 20 mV/s and a voltage window of −1.5 V to 1.5 V. Chronoamperometry (CA) was also performed, using the above CV limits of potential during 1 min each.

Table 1
Deposition parameters for sputtered WO_3 and NiO thin films.

Target	Working pressure (Pa)	Ar:O_2 (sccm)	Power (W)	Sputtering duration (min)
W	1.6	160:100	178	10; 30; 50; 70
Ni	2.6	200:5	132	10; 30; 50; 70; 90

2.4. Cycling in temperature

The 360 nm-NiO/$LiClO_4$-PC-PMMA/650 nm-WO_3 ECD was cycled in-situ in temperature. At higher temperature (T_{HIGH}) than room temperature (RT), the ECD was positioned inside an oven. T_{HIGH} of 45 °C, 60 °C and 80 °C were used. At lower temperature (T_{LOW}) than RT, the ECD was positioned inside an oil bath cryostat. T_{LOW} 0 °C and −40 °C were used. Between each cycling at T_{HIGH} and T_{LOW}, the ECD was cycled at RT more than 30 cycles in order to observe possible degradation after cycling at high or low temperature. After each cycling, the CIE L*a*b* colorimetric parameters were measured by Konica Minolta CM-700D spectrophotometer. CIE, L*, a* and b* were recorded in the colored and bleached states.

3. Results and discussion

3.1. XRD and SEM characterizations of WO_3 and NiO single layers

Whatever the thickness, the XRD pattern of WO_3 thin film is featureless, illustrating an amorphous structure. For all thicknesses, the X-ray diffraction patterns of NiO thin films show mainly two peaks (except the ITO substrate) indexed as the (1 1 1) and (2 0 0) of a cubic structure (SG: Fm-3m) (Fig. 1). The (1 1 1) preferred orientation observed for very thin films (i.e. 200 nm) disappears with increasing film thickness. Indeed, the (2 0 0) peak intensity strongly dominates for the 630 nm NiO thin film. All three thin films exhibit a cell parameter very close to 4.18 Å, similar to bulk nickel oxide of 4.176 Å (JCPDS: 01-089-3080). The crystallite size calculated using the Scherrer formula is of 18 nm for the thinnest film while it slightly increases to 25 nm for the 360 nm and 630 nm NiO thin films.

In first approximation, the SEM images of WO_3 and NiO thin films show a rather similar morphology consisting of a homogenous surface showing porosity in between agglomerated grains. The film morphology appears independent of the thickness (Fig. 2).

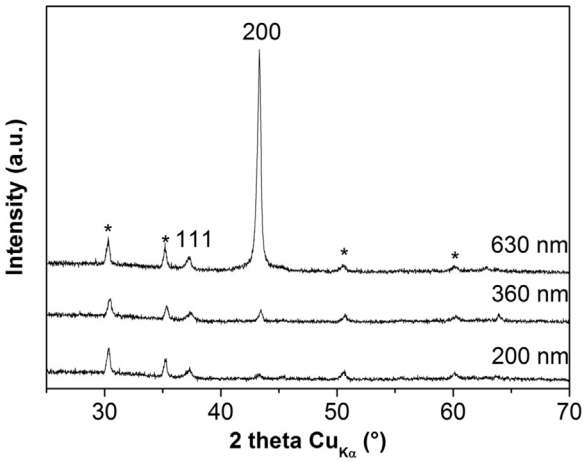

Fig. 1. X-ray diffraction pattern of various thicknesses (200, 360 and 630 nm) of NiO, ITO peak noted by *.