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Electrochromic interference filters fabricated from dense and porous tungsten oxide films

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ABSTRACT

Smart windows offer an opportunity to reduce energy consumption. However, the use of multiple optical elements, such as low emittance coatings and electrochromic devices, is detrimental to the luminous transmittance of these high performance windows. Although the addition of antireflective coatings has helped to reduce this problem, some elements, such as high index of refraction materials still give rise to loss of light. We show that replacing the single WO_3 active coating, the main component of an electrochromic device, by an appropriately designed electrochromic interference filter can significantly increase the transmittance. This active filter is based on a stack of dense and porous WO_3 layers. We first study the effect of porosity on the physical and electrochromic properties of WO_3 prepared by radio frequency magnetron sputtering. We demonstrate that the overlying dense coating does not inhibit the coloration of the underlying porous coating. The best performing films are combined into a 27 layer quarter-wave interference filter which is shown to cycle between bleached and colored states, while providing attractive transmission. Finally, we discuss various filter designs which can increase the transmission of an electrochromic device in its bleached state, as well as the potential use of active filters for optical security devices possessing two levels of authentication.

1. Introduction

Faced with a growing population and increasing energy demands, society is faced with one of two options: produce more energy or find ways to reduce consumption. Very often, the former implies burning more fossil fuels with the adverse affects we all know too well. The latter starts with changing energy consumption habits, but can also be effectively tackled by the use of technology. For example, smart windows have been proposed as such a technology. In fact, the use of smart windows could lead to energy savings in cooling and lighting costs as well as offering adjustable lighting levels for user comfort [1].

High performance smart windows are nowadays very often based on a combination of multiple glass panes, each with its own particular function (low emittance, variable transmittance, etc.). Since the principal function of a window is to offer a clear outside view, ensuring a high optical transmittance is very important. Unfortunately, the high quantity of interfaces diminishes the transmission and, as a result, addition of antireflective (AR) coatings on each of the window components has become crucial [2,3]. Although this addition has helped, the presence of other elements, such as the high refractive index (n_H) materials present in electrochromic devices, results in losses due to their high reflectivity. This is the case with WO_3, the most popular electrochromic (EC) material. In this work, we propose a way to increase the transmittance by transforming the single WO_3 layer into an electrochromic interference filter (EIF). A similar concept has recently been explored for thermochromic VO_2 films, which intrinsically possess a low transmittance, by alternating TiO_2 and VO_2 layers [4].

In order to design and fabricate an interference filter [5], at least two constituents with different optical properties are necessary. Since the cost of interference filters is very often related to the total number of layers and their thickness, it is important to minimize these parameters by maximizing the difference of index of refraction (optical contrast) between the constituents. In the case of dielectric filters, maximizing the optical contrast results in a higher reflectivity at the interfaces, and thus in a more pronounced interference effect. The easiest method of obtaining two sets of optical properties is to use two different materials. In the present work, we have chosen WO_3 as the n_H material. Since there are no low index of refraction (n_L) cathodic EC materials, we propose the use of porous WO_3 as the n_L material.

One method to change the density of WO_3 deposited by magnetron sputtering is to vary the deposition pressure [6]. In fact, a higher pressure leads to an increased number of collisions between the sputtered atoms and the gas in the vacuum chamber,

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thus lowering the energy of energetic particles and augmenting their obliqueness. This oblique component is known to enhance the presence of voids in coatings due to atomic shadowing. For example, in glancing angle deposition, atomic shadowing is used to produce highly porous films [7]. Another approach is to use substrate bias modulation in order to obtain multilayer or graded layer single-material porous-dense optical filters [8].

In the present work, we first study the effect of the deposition pressure on the physical and electrochemical properties of WO_3 films. We then test simple configurations of alternating porous and dense coatings to assess their resulting behavior. Following these tests, a multilayer quarter-wave filter is fabricated and characterized. Finally, we discuss how the use of EIFs can increase the luminous transmittance of smart windows, and can also lead to innovative active optical security devices.

2. Experimental methodology

2.1. Deposition conditions

Coatings were deposited in a custom made vacuum chamber by radio frequency magnetron sputtering from a 50 mm diameter WO_3 target at a power of 150 W, while using an Ar and O_2 gas mixture (4:1 Ar to O_2 ratio). The base pressure was approximately 2.5×10^{-6} Torr.

The WO_3 coatings were deposited on 2.5 cm by 5 cm ITO-coated glass substrates with an average sheet resistance of 50 $\Omega/\square$. ITO substrates were cleaned with soap and de-ionized water, and in isopropanol for 15 min using an ultrasonic bath. Part of the substrate was masked during the deposition to allow access to the ITO electrode for cyclic voltammetry measurements.

2.2. Physical characterization

Samples were deposited on Si and on B270 glass for optical characterization. Variable angle spectroscopic ellipsometry (*VASE*, J.A. Woollam Co., Inc.) combined with transmission measurements using a Perkin Elmer *Lambda* 19 spectrophotometer, were used to obtain the samples' optical properties (refractive index and extinction coefficient), as well as their physical thickness. The data were analyzed with the *WVASE* 32 software (J.A. Woollam Co., Inc.). The interference filters were designed using the *OpenFilters* software [9].

Rutherford back scattering (RBS) measurements were performed in a tandem linear accelerator with a 2.042 MeV He^+ ion beam at a scattering angle of 170° (between the forward direction of the incident beam and the detector). The same accelerator was used for elastic recoil detection (ERD) measurements with a 1.5 MeV He^+ ion beam. The angle between the beam direction and the sample surface normal was 75° as well as between the detector and the sample surface normal (30° scattering angle). To stop all ions except hydrogen ions, a 6 μm–thick Mylar foil was placed in front of the detector [10].

To verify the crystalline or amorphous structure of the films, grazing incidence (1°) X-ray diffraction (XRD) was performed with a Philips X'pert diffractometer using Cu Kα (1.5406 Å) radiation. The acceleration voltage was set at 50 kV and the filament current at 40 mA. Finally, scanning electron microscopy images of the cross-sections of the samples were taken with a JEOL *JSM-7600F* at 5 kV electron beam acceleration voltage.

2.3. Electrochromic characterization

Cyclic voltammetry measurements were performed using an *Autolab PGSTAT302N* potentiostat/galvanostat in a 1 M aqueous solution of H_2SO_4. An exposed surface of 0.75 cm^2 of WO_3, a Pt foil, and a saturated calomel electrode (SCE) were used as the working, counter and reference electrodes, respectively. In order to perform optical transmission measurements, the cell was equipped with two windows: the first window consisting of the sample under evaluation, and the second window being an uncoated glass substrate. The cyclic voltammetry measurements were performed at a 50 mV/s scan rate between −0.6 V and +1.5 V.

In situ transmission measurements were performed during cyclic voltammetry to evaluate the coloration efficiency. The setup consisted of a stabilized deuterium tungsten halogen light source from Ocean Optics (*DH-2000*) equipped with an optical fiber outlet, a series of lenses to focus the beam onto the device and collect the transmitted beam into a second optical fiber connected to an Ocean Optics spectrophotometer (*USB2000*). This setup allows the acquisition of a complete spectrum (380–850 nm) approximately every 500 ms (30 averaged measurements of 3 ms plus signal treatment time).

3. Characterization of the dense and porous WO_3 material

3.1. Physical properties

We deposited a series of WO_3 films at different pressures ranging from 5 to 80 mTorr (see Table 1). As expected, the deposition rate decreases with increasing total pressure. For a better comparison, we prepared film thicknesses close to those required in the design of the interference filters.

Following spectroscopic ellipsometry measurements on both Si and B270 glass, we obtained the optical properties of as deposited samples (n and k at 550 nm) as presented in Fig. 1. To increase the

Table 1
Deposition conditions and thickness of the WO_3 films.

Pressure (mTorr)	Deposition rate (Å/s)	Thickness (nm)
5	1.8	79
10	1.3	82
15	1.1	86
20	0.8	73
40	0.4	93
80	0.2	95

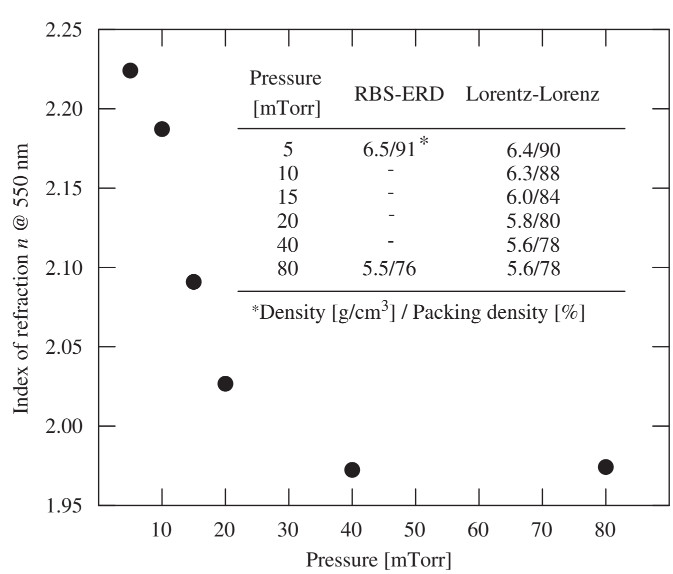

Fig. 1. Index of refraction at 550 nm as a function of the deposition pressure. The density and packing density of the films obtained by RBS–ERD measurements and calculated using the Lorentz–Lorenz effective medium approximation are also indicated.