IN SITU PHOTOELECTRON SPECTROSCOPY: A POWERFUL TOOL TO DEVELOP ELECTROCHROMIC MATERIALS

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ABSTRACT

In the building sector, a highly glazed envelope can lead to overheating in summer. In return, it increases daylighting and provides passive solar heating in winter. In order to make the best use of the solar resource, the use of a window with dynamic solar gain would be advantageous. Electrochromic coatings can darken on demand and thus modulate the solar gains. Some products are on the market but there are still several drawbacks with existing technologies such as the dynamic range, the switching speed, the color, the energy efficiency and the durability. Nanomaterials can improve the properties of such coatings.

In this work, thin film materials for electrochromic glazing are studied in detail using X-ray photoelectron spectroscopy. The thin films are deposited via reactive magnetron sputtering and transferred to the analysis equipment without breaking the vacuum. The surface of the samples is therefore characterised as deposited, ex situ contamination is avoided and the surface state is not modified because no additional argon sputtering is required. X-ray photoelectron spectroscopy (XPS) provides information on the electronic structure of the sample. The quantification of the chemical composition can be determined through integration of peak areas. Information on stoichiometry can thus be obtained precisely on the same day of sample preparation and provides feedback to improve deposition parameters rapidly.

In this study, an electrochromic material, tungsten oxide, is deposited by reactive magnetron sputtering and studied by XPS. Elemental compositions of the deposited films have been determined by in situ core-level photoelectron spectroscopy. The influence of deposition parameters, such as working pressure and O_2/Ar mass flow ratio, on the electronic, electrochromic and optical properties has been studied. It was shown that in situ analysis by X-ray photoelectron spectroscopy is a powerful tool to investigate and develop new nanomaterials for electrochromic windows.

Keywords: In situ X-ray photoelectron spectroscopy (XPS), electrochromism, tungsten oxide, nanomaterials, magnetron sputtering.

INTRODUCTION

Electrochromic windows are useful for regulating the solar gains. They allow some solar gains in winter and reduce undesired heat in summer. Commercial electrochromic windows are starting to enter the market. However, they still suffer several drawbacks in terms of switching time, durability or color rendering [1, 2].

Magnetron reactive co-sputtering is a widespread method to deposit coatings. Despite the fact it needs vacuum and therefore expensive equipment, it allow precise control of deposition parameters. This deposition technique is used for low emissivity coatings which are now of general use in new windows [3].

In order to develop new electrochromic materials with improved performances, one needs to obtain a feedback on the deposited material. The stoichiometry, for instance, is an important parameter. X-ray photoelectron electron spectroscopy (XPS) allows the determination of the elemental composition of a sample. The stoichiometry can be found by integration of the areas of the core level peaks corresponding to the elements present in the sample.

In this study, reactive magnetron sputtering was used to deposit electrochromic materials. The samples were then transferred to the XPS measurement chamber without taking the sample out of the vacuum. Likewise, in situ XPS analysis could be performed immediately. No sputtering was necessary as little contamination or adsorbed water could reach the sample. Therefore, the surface of the sample was measured as prepared.

Tungsten trioxide is one of the most widely studied electrochromic material. Tungsten trioxide can undergo a reversible transition from WO_3 to M_xWO_3 tungsten bronzes which display a dark blue color (M can be any atom of the first column of the periodic table: H, Li, Na…) as shown in equation 1 [4].

$$\underset{\text{transparent}}{WO_3} + xM^+ + xe^- \longleftrightarrow \underset{\text{dark blue}}{M_xWO_3} \quad (1)$$

An electrochromic device is generally composed of five layers. A transparent conductive oxide serves as electrode, an electrochromic oxide acts as the color changing layer, and an electrolyte either liquid, gel or solid, is permeable for the ions but electrically insulating. A counter electrochromic layer and another transparent conductive oxide complete the device.

Tungsten oxide coatings were deposited by reactive magnetron sputtering varying different parameters. The effect of the total working pressure on the oxygen content was investigated. Then, the oxygen/argon mass flow ratio was adjusted to obtain a tungsten trioxide.

METHOD

Thin-film deposition and in-situ characterization of electronic properties

Reactive sputtering with sputter-up configuration was used as depicted in Figure 1 a). The base pressure in the deposition chamber was $4 \cdot 10^{-8}$ mbar or better. A metallic target of Tungsten (99.95% purity from Kurt J. Lesker) was used. Argon gas was used for the plasma (Ar 99.999% purity) and oxygen as the reactive gas to deposit oxides (O_2 99.995% purity). Deposition parameters of the studied samples can be found in table 1. Medium Frequency (MF) bipolar pulsed power supply from MKS was used.

The coatings to be analysed by XPS were deposited on Si wafer substrates. Electrochemical and optical properties were determined on samples deposited on ITO-coated glass.

Deposition chamber and XPS measurement chamber were connected; Figure 1 b) is a photograph of the two chambers. The base pressure in the measurement chamber was $6 \cdot 10^{-9}$ mbar or better. XPS measurements were performed with an EA11 energy analyser from SPECS with a photon energy of 1253.6 eV (Mg K_α). The survey scans were measured at a pass energy of 50.4 eV at the energy analyser. The high-resolution scans of the elements were measured at a pass energy of 29.9 eV.

As a reference, the Au 4f7/2 core level signal from a gold bulk element (99.99% purity) was measured. The concentrations of elements were obtained by integrating over the core level signal after subtracting a Shirley background.

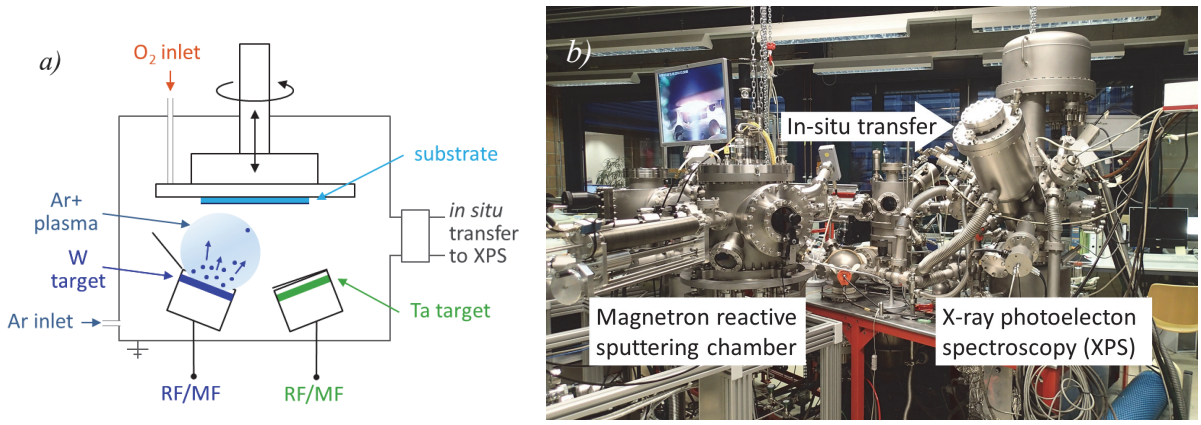

Figure 1: a) Diagram of the magnetron reactive sputtering chamber, b) Photograph of the deposition chamber, the transfer and the measurement chamber.

Optical and electrochemical characterizations

A Multispec 77400 spectrometer from ORIEL was used to determine the transmittance and reflectance of the sample in the visible wavelength range. Visible transmittance coefficients are calculated according to EN 410 standard using illuminant $D_{65}(\lambda)$ spectral power distribution and the photopic luminous efficiency function $V(\lambda)$. [5]

For electrochemical characterisation, tungsten trioxide was deposited on ITO coated glass (Delta Technologies, Ltd). Lithium perchlorate in polycarbonate (Li-PC) 1 M was used as the electrolyte. A graphite rod was used as a counter electrode. A constant voltage of 2.5 V was applied during charge, -2.5 V was applied for discharge.

RESULTS

The effects of deposition parameters on the properties of the films were studied. Particularly, the consequences of change in total pressure and oxygen:argon mass flow ratio (O_2/Ar) were investigated. Table 1 shows the deposition parameters used for the investigated tungsten oxide samples. Flow of argon and oxygen as well as the power applied on the target were maintained constant for sample A and B. Subsequently, a sample with higher O_2/Ar ratio was deposited (sample C).

	Sample A	**Sample B**	**Sample C**
Applied power	MF 150 W	MF 150 W	MF 150 W
Ratio O_2/Ar	0.48	0.48	0.61
Working pressure	$3{,}1.10^{-3}$ mbar (low working pressure)	$2{,}4.10^{-2}$ mbar (high working pressure)	$2{,}8.10^{-2}$ mbar (high working pressure)

Table 1: Deposition parameters

Right after deposition, the samples were transferred to the measurement chamber. Figure 2 displays the obtained XPS spectrum. Figure 2 a) represent the survey spectrum, it can be seen that only peaks from tungsten or oxygen can be observed. No carbon or traces of contaminants are detected, as expected for *in situ* XPS. Figure 2 b) shows the W 4f core-level spectra including the well-resolved doublet peaks belonging to W 4f 5/2 and W 4f 7/2 states

for sample B and C. However, the spectrum is more complex for sample A. Figure 2 c) shows the spectrum of O 1s core level peak.

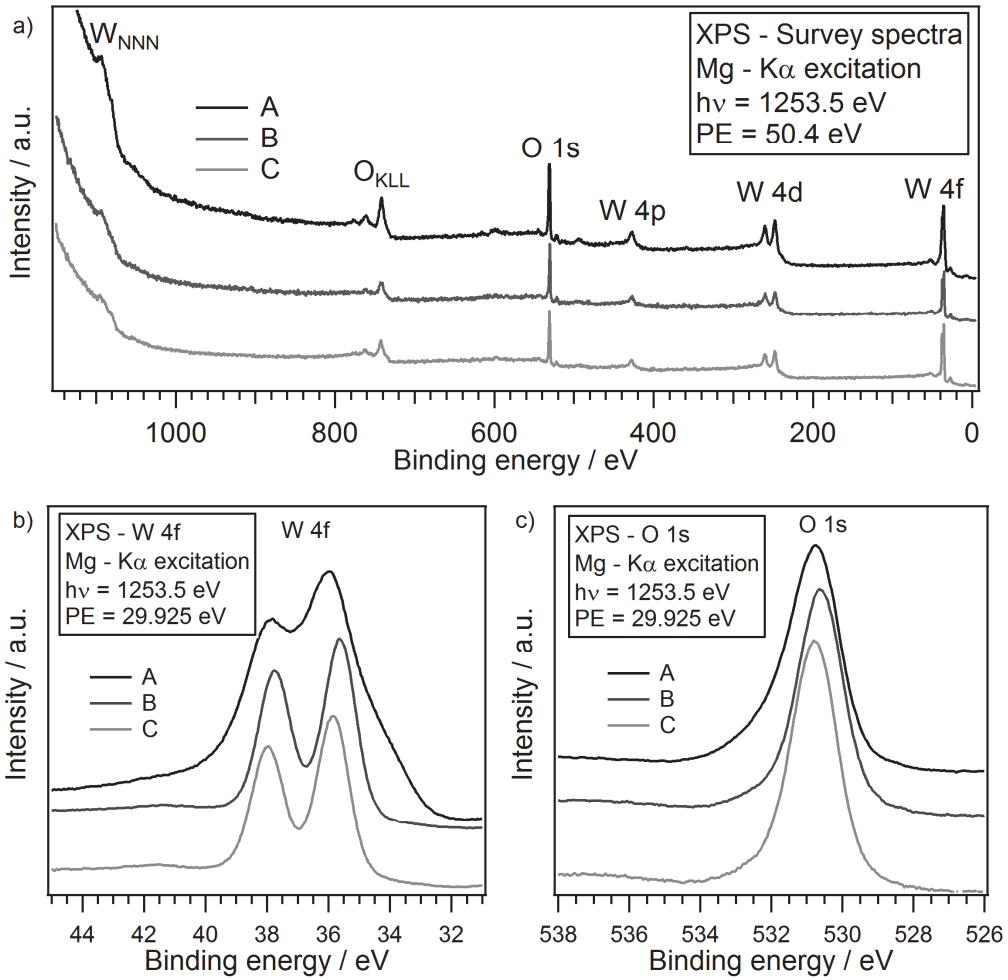

Figure 2: a) XPS survey spectrum of three samples of tungsten oxide. Sample A was made with a low working pressure (10^{-3} mbar range). Sample B and C were made with a high working pressure (10^{-2} mbar range). b) High resolution spectrum of the W 4f doublet peak. c) High resolution spectrum of the O 1s region.

Table 2 indicates the elemental composition of the samples determined by integration of peak area of W4f and O1s peaks. It can be observed that the oxygen amount is lower in the sample deposited at lower working pressure. Following the results obtained for samples A and B, the O_2/Ar ratio was increased to obtain a WO_3 thin film. According to XPS quantification, sample C has effectively a stoichiometry close to tungsten trioxide.

	O	**W**	**Corresponding formula**
Sample A	72.9	27.1	$WO_{2.69}$
Sample B	74.1	25.9	$WO_{2.86}$
Sample C	74.9	25.1	$WO_{2.98}$

Table 2: Quantification results obtained from integration of O 1s and W 4f core level peaks

In order to investigate the optical properties of these coatings, samples with same deposition parameters were deposited on ITO-coated glass. Sample A' was deposited, as sample A, at

low working pressure (WP) e.g. in the 10^{-3} mbar range. Sample B' was deposited as sample B at high WP (10^{-2} mbar range).

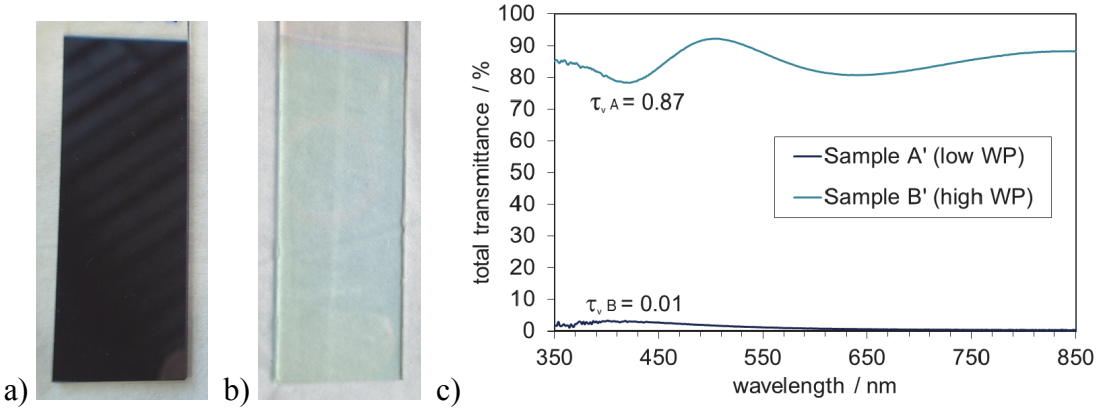

Figure 3: a) and b) Photograph of the samples A' and B' as deposited. c) Measured total transmittance of the two samples in the visible range. Visible transmittance τ_v determined according to EN410 is also indicated.

It can be observed that the sample deposited at low working pressure (sample A') at a very dark blue tint. Its visible transmittance is only 1 %. With the same mass flow of reactive gas, sample A' is transparent. Its visible transmittance reaches 87 %. As a comparison, the ITO-coated glass substrate alone has a visible transmittance of 88 %.

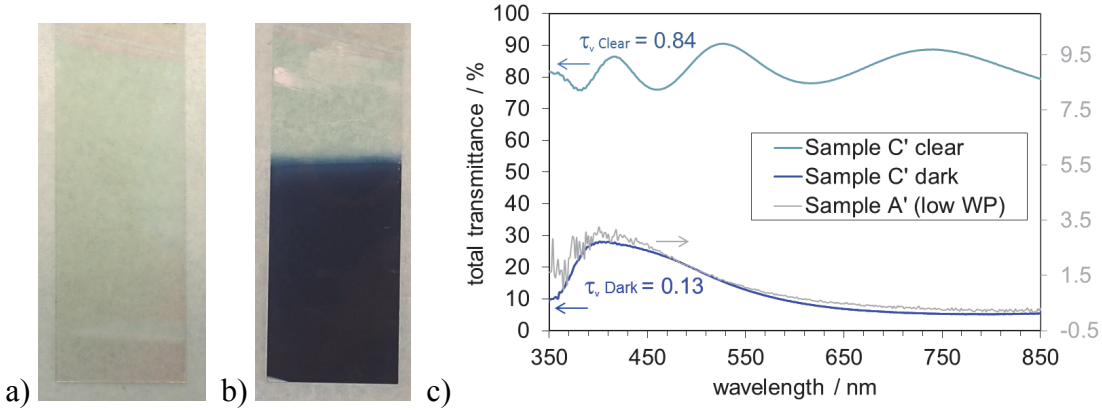

Figure 4: a) and b) Photograph of the sample C' in clear and dark states. c) Measured total transmittance and visible transmittance of the two states of sample C in the visible range. For comparison, sample A' with an adapted scale is also shown.

Sample C' was deposited, as sample C, with a higher O_2/Ar ratio and at a high working pressure. Figure 4 a) displays the clear as-deposited state. Figure 4 b) shows the dark state obtained after lithium intercalation in Li-PC with a voltage of 2.5 V. The visible transmittance in the clear state is similar to the one obtained for sample B'. The slight difference can be explained by a difference in thickness. A thicker sample was found to yield better results in terms of electrochromism. The visible transmittance in the dark state is reduced to 13 % and presents the distinctive blue color of tungsten trioxide.

DISCUSSION

Electrochromic oxides can be deposited by magnetron reactive sputtering from metallic tungsten and oxygen as a reactive gas. The different deposition parameters affect the stoichiometry and morphology of the film. The working pressure during deposition is known

to affect morphology of the film [1]; higher working pressures are commonly used in order to get a porous film. However, the working pressure also has an impact on the stoichiometry of the film for a given O_2/Ar mass flow ratio. At higher pressure, the mean free path of sputtered tungsten atoms is shorter. Therefore, the probability they get oxidised is higher. The XPS analysis allowed us to confirm the fact that the sample produced at lower working pressure (10^{-3} mbar range) contained less oxygen. These oxygen vacancies seem to affect the oxidation state of tungsten. As reported by Green at al., W4f 7/2 peak for tungsten shifts depending on the oxidation state [6]. The complex W4f spectra of the sample deposited at low working pressure (sample A) can therefore be explained by the presence of W^{4+}, W^{5+} and W^{6+}. A similar effect was demonstrated by Li et al [7]. By reducing the partial pressure of oxygen in the deposition chamber, dark samples were obtained.

Upon lithium intercalation, the clear tungsten trioxide becomes blue until reaching the dark blue final color depicted in this paper. The visible transmittance coefficient is higher for the electrochromic sample in the dark state (C') comparing to the sample with low oxygen content (A'). However, their visible transmittance spectrum is similar when normalised as shown in Figure 4 c). This observation suggests that lithium intercalation leads to a similar effect than low oxygen content in the film.

CONCLUSION

In this study, in-situ x-ray photoelectron spectroscopy was used for rapid determination of the elemental composition of the sample. Therefore, it allowed us to rapidly find the deposition parameters for electrochromic WO_3. The sample produced reached a modulation of the visible transmittance of 71 percentage point ($\Delta\tau_v$ = 71 pp). In addition, it enables us to identify the impact of working pressure on oxygen content. Furthermore, the observation of the W 4f core level peak gave us information on the oxidation state of tungsten. In the sample deposited at low working pressure, it could be found that tungsten is present at multiple oxidation states such as W^{4+}, W^{5+} and W^{6+} and that even in the absence of lithium or other intercalation cation, it affects the optical properties.

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HIGH PERFORMANCE THERMAL INSULATION - EXAMPLES FROM THE SWISS BUILT ENVIRONMENT

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ABSTRACT

Aerogel based solutions offer opportunities which combine aesthetics and cultural heritage criteria, often times in a unique way. In the field of energy efficient buildings, the search for improved envelope solutions has established Switzerland at the forefront of this type of applied research. Examples with granulate, aerogel sheets and aerogel render from 2002, 2008 and 2011 are presented [1, 2, 3]. For the development of the aerogel render [4], the speaker and his team received the Swiss environmental award for innovation in 2014. These are only a few selected examples of aerogel-based superinsulating solutions with many new ones being developed all over Europe. Experts and market analysts predict that aerogel materials will have a significant impact on the future built environment offering slim solutions, assuming that the high cost of production can be lowered to allow main markets penetration.

Vacuum Insulation Panels (VIPs) are a second class of high performance thermal insulation products with earlier market entry than aerogels, thus allowing us to look back on a full decade of experience with their applications and aging behaviour [5, 6, 7]. It was found that the aging behaviour of VIPs installed in 2004 is linear under the challenging conditions existing in flat roof terrace installations. This confirms that the prediction model [8] is applicable. Sufficient data exists to confirm that VIPs in Europe are of sufficient quality to be used in the building envelope..

In the context of a new project - the IEA EBC Annex 65 - the long term questions of aerogel and VIPs will be discussed on a top level. Having a team at Empa that synthesises a whole variety of aerogel is clearly helpful [10].

Keywords: Aerogel, Vacuum Insulation Panels (VIP), aging 10 years, aerogel granulate, aerogel sheets and render

INTRODUCTION

High performance thermal insulation as covered in this paper deals with aerogel and vacuum insulation panels. What aerogels are and how they are produced is the topic of two other contributions presented at CISBAT (oral presentations of Ana Stojanovic and of Lukas Huber).

Three pioneering projects with aerogel are revisited in this work in the context of a case study on applications motivated by the recently started IEA EBC project Annex 65 “Long Term Performance of Super-Insulating Materials in Building Components and Systems” [10]. Worldwide these three applications are the first of their kind and show the role of the Swiss market in building retrofit which is amongst the few trend-setting players which promote new solutions to reach energy efficiency under the stringent conditions of aesthetic and/or cultural heritage constraints.