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# Analogy for the maximum obtainable colouration between electrochromic, gasochromic, and electrocolouration in DC-sputtered thin $WO_{3-y}$ films

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## Abstract

Tungsten oxide films with varied substoichiometry were deposited by reactive DC-sputtering from a W target at different oxygen partial pressures. The inherent maximum achievable electrochemical colouration and electrocolouration were found to be dependent on the oxygen content and consequently on the film substoichiometry. These results were related to those obtained in a previous study by colouration with hydrogen spillover from a catalyst (gasochromic colouration) of films fabricated in the same way. A clear analogy among the colouration by the three different techniques appeared.

*Keywords:* Optical coatings; Optical properties; Tungsten oxide; Chromogenic materials

## 1. Introduction

The colouration properties of tungsten trioxide with varying stoichiometry ($WO_{3-y}$, $0 \leq y < 1$) have been subjected to intensive investigations for several decades starting with the initial paper by Deb [1].

The scientific as well as technological interest in studying tungsten oxide is persistently growing because of its high potential in different device applications, such as "smart windows," antidazzling mirrors, displays, hydrogen sensors, etc. [2–6].

In spite of the great number of published papers and comprehensive reviews on tungsten oxide films (see [2–5] and the references therein), many experimental results are still not very well understood, and, often, some of them are even not consistent. The reason for that could be the pronounced correlation between deposition conditions, which vary considerably depending on the preparation method employed and thin film properties. Moreover, there is not one common concept describing the mechanism of colouration in tungsten oxide films.

Essentially, three different models have been proposed to explain the optical absorption in the coloured state: by an intervalence charge transfer of electrons alternatively between valence states $W^{6+}/W^{5+}$ [7] (model 1), $W^{5+}/W^{4+}$ [8] (model 2), or between $W^{6+}/W^{5+}$ and $W^{5+}/W^{4+}$ simultaneously (model 3) [9]. These models have been discussed in detail in a recent paper by Stolze et al. [10].

For RF-sputtered $WO_{3-y}$ thin films and electrochemical or photochromic colouration, Zhang et al. [8] and Bechinger et al. [11] gave experimental evidence for the $W^{5+}/W^{4+}$ concept although merely based upon the colouration efficiency, which will also be discussed within this publication. For the case of DC-sputtered $WO_{3-y}$ thin films and gasochromic colouration (i.e., spillover from a Pt catalyst) using $H_2$ gas, Ref. [10] has reported experimental data of the optical density that point to a validity of the $W^{5+}/W^{4+}$ concept.

The present paper aims at bridging the gap of experimental evidence for a possible analogy between the thoroughly investigated case of electrochromic colouration

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and both that of gasochromic colouration and electrocolouration in thin films of tungsten oxide produced by the DC-sputtering method. To our knowledge, for this deposition method, it is the first published comparison between the three colouration techniques with regard to the relationship between stoichiometry (and related W valence fractions) in as-deposited state and the maximum obtainable colouration. The driving force behind our fundamental interest is the need for a better understanding of the mechanism of colouration in DC-sputtered $WO_{3-y}$ thin films.

## 2. Experimental details

### 2.1. Sample preparation

For the electrochromic measurements, the $WO_{3-y}$ thin films were deposited on $In_2O_3/SnO_2$ (ITO)-coated float glass (Flachglas, Fürth/Germany, $R_{sqr} = 10-20\ \Omega/sqr$). The glass substrates were prepared for deposition according to the following procedure: cleaning several minutes in ethanol and methanol (both 99%), drying with hot air, and preheating at 300 °C in air for $\geq 1$ h. Deposition was done by reactive DC-sputtering using a commercial sputter equipment in the diode arrangement (Balzers SCD 040) with a W target (Alfa Aesar, 99.9 wt.%) and in defined $Ar/O_2$ mixture. The parameters of deposition were kept the same as those reported in Ref. [10] to provide a reliable basis for comparison. The sputtering conditions were as follows: a target-substrate distance of 60 mm, an $O_2/Ar$ gas mixture with different $O_2$ percentage ranging from 0 to 20 vol.%, a base pressure of less than 0.03 mbar ($3.0\times10^0$ Pa), a working pressure of 0.15 mbar ($1.5\times10^1$ Pa), and a sputter current of 35–40 mA. Heating of the substrates was not applied during the deposition. For the long run (up to 1 h), the estimated substrate temperature was well below 70 °C, thus ensuring fully amorphous structure of the sputtered films, as proved additionally by X-ray diffraction measurements, which are beyond the scope of that paper. The thickness of the samples was varied from 30 to 300 nm, depending on the sputtering time and the growth rate. It was verified with a DEKTAK 3030 profilometer. The growth rate varied from ~0.6 A/s for nominally 0 vol.% $O_2$ through ~1.4 A/s for 1.0–1.5 to 0.33 A/s for>2.5 vol.% $O_2$. The mentioned growth rate maximum position 1.5–$2.25\times10^{-3}$ mbar (1.5–$2.25\times10^{-1}$ Pa) $O_2$ absolute partial pressure compares well to 1.3–$1.95\times10^{-3}$ mbar (1.3–$1.95\times10^{-1}$ Pa) reported by Kaneko et al. [12] for a working pressure of $6.5\times10^{-2}$ mbar ($6.5\times10^0$ Pa).

The film stoichiometry, i.e., the ratio $W/O_{total}$, was determined by Wavelength Dispersive X-ray analysis (WDX), as in Ref. [10], for samples grown at the same conditions and with nominally same composition as the films studied here. A relatively high H content was found by Nuclear Reaction Analysis (NRA) with $^{15}N$, and part of the $O_{total}$ from WDX could be attributed in Ref. [10] to built-in water and reflects the reported high base pressure prior to deposition.

For studies of the gasochromic effect, the W oxide films were prepared on glass substrates, covered with a disperse Pt coverage as in Ref. [10]. The role of the nobel metal is to catalyse the dissociation of hydrogen and its incorporation into the film. The sputtering of the Pt was carried out in the same sputtering unit as for the $WO_{3-y}$ films. The preparation conditions were chosen after a process optimisation as follows: Pt target with 99.99 wt.% purity, a target-substrate distance of 35 mm, presputtering time of 60 s, and sputtering for 30 s with 5-mA sputter current. This Pt coverage is known from own transmission electron microscopy (TEM) observations to have a thickness of 4 nm, that is, it is in the transitional range from isolated Pt islands to agglomeration. On one hand, this is enough to fullfill its catalysing role. On the other hand, separate optical measurements of glass/(uncoloured) $WO_{3-y}$/Pt at 632.8 nm from the Pt side as a function of the Pt coverage (not reported here) gave evidence for an unaffected reflectance and only a small reduction of the transmittance as a consequence of the Pt coverage for the uncoloured system. Furthermore, for the Pt coverage used, there were no significant changes in the measured reflectance during colouration of the whole system. Thus, the $\Delta$OD derived from the transmittance measurements was representative for the optical changes under investigation.

For the electrocolouration experiments on some of the tungsten oxide samples grown on bare float glass substrates, additional large area Au contacts at a distance of 25 mm from each other were deposited by DC-sputtering in the same sputtering equipment.

It is well known from literature that the tungsten oxide films adsorb water vapours and OH radicals from the air [4]. To avoid this, all samples were purged and then stored at well-defined conditions in dry Ar (99.995 vol.%) atmosphere in vacuum-sealed stainless-steel metal vessels. Additionally, the transfer time prior to the measurements was kept very short.

### 2.2. Measurements

The setup for the electrochemical colouration and its measurement consisted of an optical glass cuvette filled with 0.1 M orthophosphoric acid $H_3PO_4$ (99% puriss. p.a., company Fluka) in propylene carbonate (puriss. anhydros., $H_2O<0.01\%$, company Fluka). As a working electrode acted the Glass/ITO/$WO_{3-y}$ sample with an active area of ~3 cm$^2$. The counter electrode was a Pt grid placed at a distance of 10 mm. As reference electrode, we used a standard saturated calomel ($Hg/Hg_2Cl_2$) electrode with 4.2 M KCl solution and Pt diaphragm (Type B2910, Schott Glass Works Mainz/Germany).

Optical transmission measurements were performed in normal incidence with a beam from a laser diode with a wavelength of 780 nm. The voltage applied to the cell and the induced current were measured simultaneously.