Optical properties of amorphous tungsten oxide films: Effect of stoichiometry.

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Abstract. The optical properties of sputter deposited amorphous tungsten oxide films have been measured in-situ during slow electrochemical cycling in a lithium containing electrolyte. Amorphous films exhibit coloration under Li insertion and bleaching under Li extraction. Substoichiometric films show almost reversible optical changes already in the first electrochemical cycle and are completely reversible thereafter. Tungsten oxide films sputtered in a large excess of oxygen were found to be slightly overstoichiometric, as determined by Rutherford Backscattering Spectrometry. They exhibit irreversible charge transfer and coloration in the first cycle. Thereafter they cannot be completely bleached and exhibit transmittance contrast between coloured and partially bleached states. The irreversible colouration of the stoichiometric films is associated with a feature at 2.6 to 2.9 eV vs. Li in electrochemical measurements. Possible chemical reactions giving rise to this behaviour are discussed.

1. Introduction
Electrochromic materials are able to change their colour upon electrochemical intercalation of small ions, for example H⁺ or Li⁺, together with charge-balancing electrons [1]. There are a number of applications of electrochromic devices, for example in smart window technology [2]. Amorphous tungsten oxide is an excellent cathode material in electrochromic devices. There has been a great effort to understand the optical absorption in inorganic electrochromic materials and especially tungsten oxide since the middle of the last century [1-6]. When small (positive) ions are inserted by an applied potential, charge balancing electrons will also be incorporated in the material. These electrons will be localized at tungsten sites in the film. The optical absorption has been modeled as an intervalence charge transfer transition between states of localized electrons (W⁵⁺) and neighboring (W⁶⁺) states [5]. It has also been observed that near-stoichiometric tungsten oxide (WO₃) has a lower coloration efficiency than substoichiometric WO_y (y<3) [6]. In this work we investigate the effect of stoichiometry on electrochromism in tungsten oxide films further. We have found that overstoichiometric films exhibit a strikingly different electrochromic behaviour than films with lower O/W ratios.

2. Experiments
Tungsten oxide films were prepared by reactive dc magnetron sputtering in a Balzer UTT deposition system from a 5 cm radius tungsten target, with a purity of 99.99 %. The films were deposited on glass...
substrates covered with transparent and conductive \( \text{In}_2\text{O}_3\):\text{Sn} (ITO) with a resistance of 60 ohms per square and thickness 40 nm. For compositional determinations using Rutherford Backscattering Spectrometry (RBS) films on carbon and silicon substrates were also produced. The sputter parameters for overstoichiometric films were: a sputter power of 350 W, a pressure of 14.3 Torr and an \( \text{O}_2/\text{Ar} \) gas flow ratio of 80/50 (both in \([\text{ml/min}]\)). For comparison we produced substoichiometric films using a power of 200 W, gas pressure of 20.0 mTorr and an \( \text{O}_2/\text{Ar} \) gas flow ratio of 8/50 (both in \([\text{ml/min}]\)). Film thicknesses were measured by a Tencor Alpha-step stylus profilometer and were found to be 310 +/- 10 nm. X-ray diffraction measurements were performed with a Siemens D5000 diffractometer at diffraction angles between 10° and 80°, and showed that the films are amorphous.

Electrochemical measurements were carried out in an argon filled glove box containing less than 5 ppm of water. A standard three-electrode arrangement was used with the film as the working electrode, pure lithium foils as counter and reference electrodes and a solution of propylene carbonate (PC) dissolved in 1 M lithium perchlorate as the electrolyte. Measurements with cyclic voltammetry and the Galvanostatic Intermittent Titration Technique (GITT) were taken by a computer controlled ECO Chemie Autolab/GPES electrochemical interface. On both sides of the electrolyte container, optical fibers, connected to a lamp and an Ocean Optics spectrophotometer, were fastened. A transmittance spectrum, in the wavelength range from 300 to 800 nm, was recorded every 10 mV during cyclic voltammetry measurements from 4 to 2.2 V.

3. Results

3.1. Film composition

RBS measurements were carried out using alpha particles with energy 2 MeV, which were backscattered at an angle of 165 degrees. Figure 1 shows a RBS spectrum for a slightly overstoichiometric film. The signals from O and W atoms are clearly seen. Taking an average over four samples deposited under the same conditions, the composition was determined to be \( \text{WO}_{3.07} \). Compositional determination for substoichiometric films was reported previously [7] and the film considered in this paper was found to have the composition \( \text{WO}_{2.89} \).

![Figure 1](image_url)

**Figure 1.** Rutherford backscattering spectrum from a slightly overstoichiometric tungsten oxide film. Signals from O and W atoms are labelled. The low energy feature is due to the carbon substrate.
3.2. Electrochemical properties

Figure 2a shows cyclic voltammetry curves for the two first cycles for WO$_{3.07}$ and WO$_{2.89}$ thin films. The films are bleached at the potential U=4 V and colored at U=2.2 V, while the cycling direction is clockwise. The overstoichiometric film exhibits an irreversible behaviour on the coloring side at ~2.6 V. The first cycle shows a large “dip” while in the next cycle the “dip” is much smaller. It was found that the difference between the inserted and extracted Li ions in cycle 1 was 0.146 per formula unit, while in the second cycle the inserted and extracted charges were equal (0.35 per formula unit WO$_{3.07}$). Substoichiometric tungsten oxide films show only a very small irreversibility in the first cycle, and are completely reversible thereafter. The number of inserted/extracted charges was about 0.16 per formula unit.

Fig 2b shows the number of charges inserted per potential and formula unit, obtained from steady-state GITT measurements. It is seen that a pronounced peak (related to the dip in fig 2a) is seen only for the overstoichiometric film. For WO$_{2.89}$ thin films no peak is seen and it is known that these films can be cycled reversibly at least up to 0.5 Li ions per formula unit [4].

![Figure 2](image_url)

**Figure 2.** (a) Cyclic voltammetry curves for the first (thick lines) and second (thin lines) cycles and (b) steady-state GITT measurements of the number of charges inserted per potential and formula unit for WO$_y$ films with y=2.89 (dashed) and y=3.07 (full lines), are shown as a function of applied potential. In (a) the scan rate was 0.1 mV/s, while in (b) current pulses of magnitude 3.2 μA were applied for 100s and after each pulse the potential was allowed to relax for 1000s.

3.3. Optical properties

Figure 3 shows transmittance spectra during the first cycle for the overstoichiometric film. As the intercalation goes on the transmittance decreases and the film turns darker. At 2.2 V the transmittance is in its lowest state. Most of the coloration takes place during the dip in fig. 2a. After the bleaching process the coloration starts again from 4 V but now in a lower transmittance state than originally, as shown in figure 3b. The transmittance in the dark state at 2.2 V is the same as in the first cycle. In the second cycle the film shows optical reversibility but with a much lower transmittance in the bleached state than in the first cycle. Figure 3b shows also the transmittance spectra in the fully dark and bleached states for the substoichiometric film. The substoichiometric film shows almost total optical reversibility already in the first cycle.

Vink et al. (8) observed a voltammetric dip similar to the one seen by us in figure 2a. They found a dip at 2.8 V for an overstoichiometric film, which was ascribed to a reaction between the inserted Li and oxygen interstitials. The films of Vink remained transparent as the dip was traversed, and it was supposed that lithium oxide was formed:

\[ 2\text{Li}^+ + 2\text{e}^- + \text{O}_i \rightarrow (\text{Li}_2\text{O}_i). \]  

(1)
Figure 3. Transmittance as a function of wavelength for Li$_x$WO$_y$ films: (a) evolution of transmittance during the first coloration cycle for a film with $y=3.07$ and (b) transmittance in the fully bleached and coloured states in the second cycle for films with $y=2.89$ (dashed) and $y=3.07$ (full lines).

We think that a related lithium trapping reaction gives rise to the irreversibly colored state in our overstoichiometric W oxide films. We suggest that both oxygen interstitials and vacancies are present in our overstoichiometric films. Initially, the inserted Li$^+$ reacts with the interstitials, and the associated electrons are trapped deep in the band gap. The film is then colored by electron transitions to the conduction band. The deep band gap states cannot be depopulated at a potential of 4 V or less. Regions with an excess of vacancies and interstitials may be pictured as oxygen poor and oxygen rich. Inserted Li is then trapped in the oxygen-rich regions leading to coloration according to the reaction

$$2\text{Li}^+ + 2\text{e}^- + \text{WO}_3+z \rightarrow \text{Li}_2\text{O} + \text{WO}_2+z$$ (coloured) \hspace{1cm} (2)

4. Conclusions
We have observed a curious phenomenon in overstoichiometric WO$_3$ films, namely that they can be colored, but not completely bleached again. They show a large irreversibility in optical properties in the first cycle. Afterwards they are reversible in the sense that they can be cycled between less and more colored states. In conclusion, substoichiometric tungsten oxide films are to be preferred for electrochromic applications, because of the large reversible and stable transmittance contrast between the bleached and the colored states.

Acknowledgment
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