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Sputter deposited $W_{1-x-y}Ni_xTi_yO_3$ thin films: Electrochromic properties and durability

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Abstract. Previous research demonstrated that a small amount of nickel enhances the coloration efficiency of tungsten–nickel oxide electrochromic (EC) thin films with respect to that of pure tungsten oxide (WO$_3$) films. Furthermore the incorporation of titanium gives an improvement in the durability of tungsten–titanium oxide EC thin films. In this work we investigated the EC performance of tungsten–nickel–titanium oxide ($W_{1-x-y}Ni_xTi_yO_3$) EC thin films with emphasis on durability. The films were deposited on indium tin oxide covered glass by reactive dc sputtering from tungsten, tungsten–titanium alloy and nickel targets. Cyclic voltammetry was performed using 1 M LiClO$_4$ in propylene carbonate as electrolyte. The voltage window was chosen to induce fast degradation of the samples within 80 cycles. Elemental compositions were obtained by Rutherford Backscattering Spectroscopy.

1. Introduction

Global warming is a widely accepted phenomenon with many adverse effects for the earth’s ecosystems and for human activities. It is caused by excessive use of certain energy sources, such as fossil fuels, that lead to high carbon dioxide emissions. Hence research aimed at the generation of clean energy, as well as energy saving technologies, is essential. The built environment is particularly important since it accounts for 30–40% of the primary energy consumption. A lot of this energy is used to provide artificial illumination and for cooling or heating purposes. Windows are of great importance in this context since they are weak links in the buildings’ energy system and frequently let in or out too much energy [1]. There are numerous ways to improve windows; one of them is to go to the so called “smart window” which allows modulation of the transmittance of solar energy and visible light in order to create energy efficiency [1].

Smart windows can be made with electrochromic (EC) materials and allow transparency modulation upon the application of a small potential difference [2]. An EC device is composed of several parts and has a pure ion conductor (electrolyte) in the middle. This part is sandwiched between two layers, one of them being the main EC thin film and the other an ion storage film that could have EC properties or not. The layers are coated on transparent conductors to which the voltage source is connected, and the entire system can be laminated between transparent glass or PET sheets [3]. The most studied EC material is amorphous tungsten oxide, which allows high optical modulation. It is well known that tungsten oxide (WO$_3$) is a cathodic EC material (colors under charge insertion) with a perovskite-type structure based on corner-sharing WO$_6$ octahedra [3]. The ion storage film should be either transparent during charge insertion and extraction or possess EC properties opposite in nature with respect to the main EC film,
it should color anodically (under charge extraction) if the main EC film has cathodic properties, as for the case of WO₃.

Extensive color/bleach cycling of WO₃ films leads to a loss of the EC properties, and previous research has been focused on ways to improve their durability as EC films. A good option is the addition of a certain concentration of titanium oxide (TiO₂) into the WO₃ film, and a recent study of Ti doping of WO₃ films showed enhanced durability even when the voltage span was increased so as to subject the samples to stringent conditions [4].

Nickel oxide (NiO) is an excellent choice as ion storage film in EC devices. Several recent studies [5,6,7,8] have been devoted to its compatibility with electrolytes appropriate for WO₃, charge density exchange, durability and coloration efficiency. In particular, we note recent work on composites of WO₃ and NiO which produced interesting results regarding their optical, structural and electrochromic properties [9,10].

The principal objective of our present work is to investigate the effects of Ti addition to a Ni–W oxide matrix. The study is focused on the durability of EC films under harsh conditions obtained by applying a wide voltage window to accomplish electrochemical charge insertion/extraction, and we also study changes in the optical properties.

2. Film preparation and characterization

Thin films of W oxide, W–Ni oxide and W–Ni–Ti oxide were prepared by reactive DC magnetron sputtering in a deposition system based on a Balzers UTT 400 unit. Targets were 5-cm-diameter plates of W, Ni, W(95wt%) + Ti(5wt%) and W(90wt%) + Ti(10wt%) (Plasmaterials), all with 99.99% purity. The sputter system was first evacuated to 2 × 10⁻⁴ mTorr. Argon and oxygen, both of 99.997% purity, were then introduced through mass-flow controlled gas inlets. The O₂/Ar ratio was set to 0.15, and the pressure was 30 mTorr; these parameters were chosen based on previous studies [9]. To obtain different concentration of W–Ni–Ti oxide, the discharge power of the targets were maintained at \( P_W + P_{Ni} = 230 \) W; some more details on sample preparation are given elsewhere [4].

For studying electrochemical and optical properties, the films were deposited onto unheated 5 × 5 cm² glass plates coated with transparent and electrically conducting layers of In₂O₃:Sn (ITO) with an electrical sheet resistance of 40 ohms per square. Carbon substrates were used for films for Rutherford Backscattering Spectrometry (RBS) analysis, which was performed at the Tandem Laboratory of Uppsala University using 2 MeV ⁴He ions backscattered at an angle of 170°. RBS data were fitted to a model of a film–substrate system by the use of the SIMNRA program [11]. Optical transmittance was recorded in situ during electrochemical cycling in the 380–800-nm wavelength range using a fiber optical instrument from Ocean Optics. Film thicknesses were around 300 nm as measured by surface profilometry using a Bruker DektakXT instrument. X-ray diffraction analyses were made using a Siemens D5000 instrument and the diffractograms showed only peaks due to the ITO underlayer and no evidence of peaks associated to W, W–Ni or W–Ni–Ti oxides. Hence all of the as-deposited films were amorphous.

3. Electrochemical and optical data

Ternary Ni–Ti–W oxide EC films were investigated by cyclic voltammetry (CV) using a Solartron 1286 electrochemical interface in a three-electrode electrochemical cell with the sample as working electrode and Li foils serving as reference and counter electrodes. The electrolyte was 1M LiClO₄ in propylene carbonate (Li–PC). All measurements took place inside a glovebox with inert argon atmosphere. The voltage range and sweep rate were 1.7–4V vs. Li and 10 mV/s, respectively. Figure 1 shows voltammograms for EC films with various compositions at selected CV cycles. The films without titanium show poor stability within 80 CV cycles, the same behaviour is found for the W₀.₇₈Ni₀.₁₂Ti₀.₁O₃ film. However the W₀.₇₈Ni₀.₁₆Ti₀.₁₇O₃ sample is clearly more stable.
Figure 1. Cyclic voltammograms for (a) W oxide, (b) W–Ni oxide, and (c)–(d) W–Ni–Ti oxide films of the shown compositions immersed in 1M Li–PC. Data were taken after the indicated numbers of cycles for the voltage sweep range 1.7–4.0 V vs. Li. Arrows indicate the direction of insertion and extraction of charge.

It is important to study the extracted and inserted charge density $Q$ as a function of the number of voltammetry cycles to show the electrochemical activity of the films. Such evolution is illustrated in figure 2(a), where we confirm that only the $W_{0.67}Ni_{0.16}Ti_{0.17}O_3$ sample is able of maintain its charge capacity, whereas all of the other films show drastic drops of their charge capacity within the first 40 cycles. One way to emphasize the modifications in the charge capacity is to study the difference between the extracted and inserted charge density $\delta Q = \left| Q_{\text{inserted}} + Q_{\text{extracted}} \right|$, with $Q_{\text{inserted}} < 0$ and $Q_{\text{extracted}} > 0$, as shown in figure 2(b). Some samples seem to present a saturation of the amount of charge that could not be extracted, which is the case for films without titanium. The $W_{0.78}Ni_{0.12}Ti_{0.1}O_3$ sample, on the other hand, displays a high difference between the inserted and extracted charge in the first cycle, and then the difference tends to decrease. The $W_{0.67}Ni_{0.16}Ti_{0.17}O_3$ sample starts with a low difference and maintains this property during the 80 cycles.
Figure 2. (a) Extracted and inserted charge density during voltammetric cycling of films with the shown compositions, and (b) difference in charge density for successive charge extractions and insertions. Symbols indicate data and lines were drawn for convenience.

Figure 3. Evolution of transmittance at the wavelength 550 nm in the bleached and colored states for films with the shown compositions. The films were immersed in 1M Li–PC and studied as a function of cycle number.

4. Optical transmittance
Optical transmittance $T$ was recorded in situ during CV cycling, using an Ocean Optics fiber-optic instrument, at the wavelength 550 nm. Figure 3 shows transmittance in bleached and colored states for the same selected CV cycles as in figure 2. The pure tungsten oxide film lost its optical modulation during the charge insertion/extraction process. This is different from the case of films containing nickel and titanium that presented significant changes between the bleached and the colored states even after 40 cycles. An important aspect to highlight is the color of the films after cycling; we found it to be brownish–yellowish, which is typical for samples that have undergone several cycles using a large voltage window and a Li–PC electrolyte [4]. However, and in accordance with the electrochemical
results, this yellowish tint was much less marked for the W_{0.67}Ni_{0.16}Ti_{0.17}O_3 sample, indicating a lower degradation of the films.

As a complement to the optical and electrochemical characterization, we calculated the coloration efficiency (CE) by 

\[ CE = \ln\left(\frac{T_b}{T_c}\right)/\Delta Q, \]

where \( \Delta Q \) is the inserted charge density and b and c denote bleached and colored states, respectively. Data on CE as a function of cycle number are shown in figure 4, where it can be observed that W–Ni oxide shows the best response in CE, confirming results in previous research [10]. However the incorporation of titanium in W–Ni oxide produces a decrease in CE, as can be seen in figure 4. It is important to note here that the high values of CE for pure W oxide and for W–Ni oxide should not be overrated because of the mentioned yellowish coloration of these films.

![Figure 4. Evolution of coloration efficiency at the wavelength 550 nm for films with the shown compositions. The films were immersed in 1M Li–PC and studied as a function of cycle number.](image)

5. Conclusions

W oxide and W–Ni oxide films suffered clear deterioration in their electrochromic properties during less than 50 voltammetric cycles in a wide voltage range (1.7–4 V vs. Li) but an addition of ~17at.% of Ti improves the stability considerably. On the other hand the Ti content diminished the coloration efficiency. Future studies should investigate whether different concentrations of Ni could improve the coloration efficiency and eventually lead to electrochromic films with both good coloration and high durability.

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