Electrochromic Properties of Li$^+-$Intercalated Amorphous Tungsten ($a$WO$_3$$_{-x}$) and Titanium ($a$TiO$_2$$_{-x}$) Oxide Thin Films

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Abstract. We report on electrochromic properties of stoichiometric and oxygen-deficient amorphous films, denoted $a$WO$_3$$_{-x}$ and $a$TiO$_2$$_{-x}$, under Li$^+$-ion-electron inter/deintercalation. Optical characterization of the films in their as-deposited, fully intercalated (dark), and bleached states were performed by in-situ optical transmittance measurements. We explore electrochromism and optical absorption phenomena in the context of oxygen deficiency and nanostructure. Studies by cyclic voltammetry suggest good optical modulation and charge capacity upon Li$^+$-ion-electron inter/deintercalation for almost stoichiometric films.

1. Introduction

Switchable optical properties exhibited by electrochromic (EC) materials are of large importance for the development of intelligent multifunctional devices. Because of their applications in energy efficient “smart windows”, photocatalysis, displays, panels for emissivity modulation and gas sensors [1,2], this type of materials has been extensively studied in the last decades [3]. Reversible optical modulation (OM) from bleached to blue-colored states in EC thin films is obtained by applying a small electric field to produce intercalation (cathodic EC) or deintercalation (anodic EC) of charge, typically electrons $e^-$ together with small alkaline metallic ions (H$^+$, Li$^+$, Na$^+$, K$^+$) where the ion-$e^-$ inter/deintercalation processes can occur along with oxidation phenomena [4]. Cathodic EC properties in TiO$_2$ films produced by several deposition techniques have been studied previously; such analyses have shown that the EC behavior in TiO$_2$ differs considerably among different deposition methods [5-10]. Previous results of DC sputtered crystalline TiO$_2$ and amorphous $a$TiO$_2$ films have indicated that EC behavior is strongly dependent on the deposition processes, the morphology of the synthetized material, and on the synthesis parameters such as substrate temperature, $O_2$/Ar gas flow ratio, and sputter gas pressure [11]. Thus it was shown for DC sputtered films that high sputter gas pressure and low substrate temperature enhanced the EC properties in TiO$_2$ and $a$TiO$_2$ films. The EC effect in WO$_3$ thin films is well understood and widely studied both in the sixfold-coordinated crystalline structure $c$WO$_3$ and in amorphous $a$WO$_3$ [3]. In $c$WO$_3$, the ion-$e^-$ inter/deintercalation sites are located inside the empty spaces due to the octahedral arrangement of atoms. The inserted ion-$e^-$ pairs enter extended states, and reflective OM is described by Drude-like free electron absorption models [12]. In $a$WO$_3$, the OM upon ion-$e^-$ inter/deintercalation occurs in the visible and near-infrared spectral range and
leads to an absorption band centered at ~1.3 eV. It has been pointed out that such a behavior is due to variations in the valence states of W atoms. Thus the optical absorption band is modeled by hopping of small polarons between first-neighbor W sites exhibiting different W$^{4+}$-W$^{5+}$-W$^{6+}$ oxidation states [13,14]. It was found that aWO$_3$ displays superior OM and EC properties and inherent stability under extended inter/deintercalation of ions. Enhancements of the EC properties and durability have been displayed in DC sputter-deposited W-Ti oxide films [15].

Below we report on the OM and EC properties in stoichiometric and oxygen-deficient aWO$_{3-x}$ and aTiO$_{2-x}$ thin films under Li$^+$-ion-e$^-$ inter/deintercalation. We investigate the substoichiometry dependence on the optical absorption, the EC properties, and the OM for DC sputtered oxygen-deficient films in as-deposited aWO$_{3-x}$ and aTiO$_{2-x}$, and in fully Li$^+$-ion-e$^-$ intercalated aLi$_y$WO$_{3-x}$ and aLi$_y$TiO$_{2-x}$ states by in-situ optical transmittance.

2. Experimental
A number of aWO$_{3-x}$ and aTiO$_{2-x}$ films were prepared by reactive DC magnetron sputtering from 99.95%-pure metallic Ti and W targets, using a Balzers UTT-400 unit, in O$_2$/Ar reactive plasma of 99.99% purity at $\sim$1.5×10$^{-2}$ mbar. Stoichiometric and oxygen-deficient films were deposited onto unheated glass substrates pre-coated with In$_2$O$_3$:Sn. Depositions were done at the same pressure, power and Ar-flow-ratio but at different O$_2$-flow-ratios. X-ray diffraction analysis indicated amorphous structures. Atomic compositions and density were determined by use of 2MeV $^4$He-ions at $\sim$170$^\circ$ by Rutherford Backscattering Spectroscopy. The aWO$_3$-$x$ and aTiO$_{2-x}$ films had thicknesses of $\sim$300 nm, as verified by surface profilometry measurements (Bruker DektakXT step profilometer). Surface nanotopography and morphological features were investigated by Atomic Force Microscopy (AFM) employing a PSIA XE150 SPM/AFM instrument having an etched cantilever with a tip radius of $\sim$10 nm and $\sim$35$^\circ$ apex angle. Scans and evaluation of root-mean-square roughness were carried out over areas of $\sim$1000×1000 nm.

Li$^+$-ion-e$^-$ pairs inter/deintercalation was carried out in a glove box containing Ar gas (H$_2$O<4 ppm). Electrochemical measurements were performed in a three-electrode cell with the aWO$_{3-x}$ or aTiO$_{2-x}$ films as working electrode and metallic Li$^+$-foils as counter and reference electrodes immersed in 1M LiClO$_4$-C$_8$H$_8$O$_4$ electrolyte. Cyclic voltammetry (CV) measurements were conducted using an ECO Chemie Autolab/GPES Electrochemical Interface with voltage sweep rate of 10 mV/s in the voltage range 2.0-4.0 V vs. Li. The measurements were performed for 30 cycles in order to achieve reversibility of the inter/deintercalation process. Optical properties of aWO$_{3-x}$, aTiO$_{2-x}$, aLi$_y$WO$_{3-x}$ and aLi$_y$TiO$_{2-x}$ films during Li$^+$-ion-e$^-$ inter/deintercalation were measured as in-situ normal incidence transmittance $T(\lambda)$ spectra by using an Ocean Optics instrument.

3. Results and Discussion
Figure 1 shows a characteristic AFM image of an as-deposited aWO$_{3-x}$ thin film. The image exhibits a smooth surface characterized by a flat topography with granular traits and porous structure. Variations in particle sizes and granular/porous features were slightly dependent on the O$_2$/Ar ratio. Figure 2 reports $T(\lambda)$ for aWO$_{3.00}$ films obtained at O$_2$/Ar=44%, aWO$_{2.93}$ at O$_2$/Ar=36%, and aWO$_{2.84}$ at O$_2$/Ar=16%; data are shown at $380\leq\lambda\leq800$ nm for as-deposited, Li$^+$-ion-e$^-$ intercalated (dark-blue-colored), and bleached films. The stoichiometric aWO$_{3.00}$ films are transparent and exhibit a high value of $T(\lambda)$ of around $\sim$94%. Pronounced optical absorption can be observed as the oxygen deficiency is increased. As-deposited aWO$_{2.93}$ and aWO$_{2.84}$ films display a clear-blue color, and $T(\lambda)$ is reduced to $\sim$80% and $\sim$58% at $\lambda=500$ nm, respectively. Upon electrochemical Li$^+$-ion-e$^-$ intercalation, all films attain a dark-blue color. The transmittance is decreased in the whole spectral range and displays a strong and broad optical absorption. In particular, the aWO$_{3.00}$ and aWO$_{2.93}$ thin films display good coloration efficiency and good reversibility from dark-blue-colored to bleached states, which confirms their
suitable EC properties. However, the more oxygen-deficient films of aWO2.84 did not exhibit as good EC performance and OM behavior since the specimen did not bleach efficiently upon charge deintercalation. The variation in $T(\lambda)$, between dark-blue-colored and bleached states is highest for aWO3.00 (around $\sim$36 to 86% at $\lambda$=550 nm) but is lower for the substoichiometric films of aWO2.93 ($\sim$26 to 77% at $\lambda$=550 nm) and aWO2.84 ($\sim$8 to 48% at $\lambda$=550 nm). Charge capacity obtained from CV data was found to be in the range $\sim$16.8 to 18.2 mC/cm$^2$ (cf. figure 3) and was slightly influenced by the surface morphology of the films deposited at different O$_2$/Ar ratios. The fraction of intercalated Li$^+$-ions per formula unit of W-ions was found to be somewhat different among films of Li$_{0.72}$WO$_{3.00}$, Li$_{0.66}$WO$_{2.93}$ and Li$_{0.63}$WO$_{2.84}$; this could be due to small density variations which influence the ion diffusion processes.

A similar analysis was carried out for as-deposited aTiO$_2$-x thin films. Surface morphology reveals analogous smooth features with flat topography and granular-like porous structure, as shown in the AFM image in figure 4. Stoichiometric aTiO$_{2.00}$ thin films, obtained at a flow ratio for O$_2$/Ar of 4%, exhibit a $T(\lambda)$ of $\sim$90%, i.e., a transparent state. The oxygen-deficient aTiO$_{1.87}$
films, obtained at an O\textsubscript{2}/Ar flow ratio of 1.5\%, exhibit a transmittance of \(\sim78\%\) at \(\lambda=550\ nm\) and displayed a clear-blue colored state with slight optical absorption. Upon electrochemical Li\textsuperscript{+}-ion-\textsuperscript{e}\textsuperscript{−} pairs inter/deintercalation, it is found that the \(\alpha\)TiO\textsubscript{2.00} film displays suitable EC properties with good OM and reversibility. Variations in \(T(\lambda)\) spectra from dark-blue-colored to bleached state are observed in the range \(\sim40\) to \(90\%\) at \(\lambda=550\ nm\). For the oxygen-deficient \(\alpha\)TiO\textsubscript{1.87} films, EC properties, OM and reversibility are also present, but the specimen did not bleach efficiently upon charge deintercalation. Optical transmittance variations are displayed in the range \(\sim16\) to \(67\%\) at \(\lambda=550\ nm\), as indicated in figure 5. CV data yielded charge capacity in the range \(\sim28.3\) to \(32.6\) mC/cm\textsuperscript{2}, and the fraction of intercalated Li\textsuperscript{+}-ions per formula unit of Ti-ions was Li\textsubscript{0.65}TiO\textsubscript{2.00} and Li\textsubscript{0.60}TiO\textsubscript{1.87} (cf. figure 6); these values could be slightly influenced by the density increases in films at low O\textsubscript{2}/Ar deposition ratios.

Our results suggest that \(\alpha\)WO\textsubscript{3−\textsubscript{x}} and \(\alpha\)TiO\textsubscript{2−\textsubscript{x}} thin films display suitable OM and EC properties when deposited at high O\textsubscript{2}/Ar ratios. Increasing oxygen content results in nanoporous-like structures in as-deposited films in which pore orientation, homogeneity and
symmetry enable ion diffusion across the amorphous network of the films, hence improving their EC behavior. Increasing oxygen deficiency results in thin films exhibiting clear-blue or even dark-gray-colored appearances, which are not suitable for EC applications since the capability for Li\(^+\)-ion-e\(^-\) inter/deintercalation decreases considerably and the films display incomplete bleaching upon deintercalation of charge. The Li\(^+\)-ion diffusion and the fraction of intercalated ions can be strongly influenced by increases in density and variation in porosity. Since EC efficiency depends on the morphology of the amorphous network in the as-deposited \(a\)WO\(_{3-x}\) and \(a\)TiO\(_{2-x}\) thin films, it is of fundamental importance to ensure low deposition temperature, high O\(_2\)/Ar gas flow ratio and suitable deposition pressure in order to achieve the microstructural properties favoring the good optical and EC performance of these films.

Conclusions
We have carried out a study of EC properties in DC magnetron sputtered stoichiometric and oxygen-deficient \(a\)WO\(_{3-x}\) and \(a\)TiO\(_{2-x}\) thin films under Li\(^+\)-ion-e\(^-\) inter/deintercalation. Results show good EC behavior, which is strongly dependent on the oxygen content during the deposition process and slightly dependent on the surface morphology. We found good optical modulation and charge capacity upon Li\(^+\)-ion-e\(^-\) inter/deintercalation for almost stoichiometric films. However, strongly oxygen deficient \(a\)WO\(_{3-x}\) and \(a\)TiO\(_{2-x}\) films do not display good EC properties but show strong optical absorption also in the bleached state. Our results for stoichiometric films are comparable with those in previous studies carried out on amorphous EC thin films prepared by various deposition methods.

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