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Structure and optical properties of electrochromic tungsten-containing nickel oxide films

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Electrochromic Ni_xW_{1-x} oxide thin films with $0.5 < x < 1$ were deposited by reactive DC magnetron co-sputtering from pure Ni and W metal targets. Films with different compositions were characterized structurally by X-ray diffraction, X-ray photoelectron spectroscopy and Rutherford backscattering spectrometry. The optical and electrochemical properties were investigated by spectrophotometry and cyclic voltammetry in $LiClO_4$ dissolved in propylene carbonate. Pure Ni oxide films were crystalline, but even small amounts of W led to amorphous structures. The Ni_xW_{1-x} oxide films probably consisted of hydrated Ni oxides and $NiWO_4$. Charge insertion/extraction and optical modulation were modest. Aging of the films led to strong bleaching. Concerning electrochromic properties, the W addition was beneficial and enhanced the bleached-state transmittance for all compositions at luminous and near-infrared wavelengths.

1. Introduction

Tungsten trioxide is the most popular material in electrochromic (EC) devices, which is a consequence of its stability and good optical contrast for visible wavelengths [1–3]. WO_3 is a cathodic EC material and colors when charge is inserted. A normal EC device also comprises a complementary anodic EC material which colors under charge extraction [4]. Both EC layers hence contribute to the functionality and should operate properly together both with regard to electrochemistry and optical appearance. NiO-based films work well in tandem with WO_3 [4], and the colors in the dark state complement each other and produce a neutral gray appearance when the device is in its colored state, WO_3 and NiO being blue and brown, respectively. This combination of materials could be difficult to work with in practice, however, since NiO corrodes in acidic solutions and WO_3 corrodes in basic solutions. Another drawback of using NiO as a complementary EC electrode is its yellowish tint in the bleached state [5]. In the present work we address these two issues.

NiO-based films doped with various metals can display improved bleached-state transmittance [5]. In this work we have co-sputtered W and Ni under reactive conditions to produce a variety of different Ni_xW_{1-x} oxides with $0.5 < x < 1$. The samples were electrochemically cycled in an electrolyte of lithium perchlorate in propylene carbonate (Li–PC). Previous work of ours showed that this is a suitable electrolyte for examining both W oxide and Ni oxide, notwithstanding the poor optical contrast between the dark and bleached states in Ni oxide [6]. The majority of studies on electrochromic Ni oxide have been done in aqueous electrolytes, mainly potassium hydroxide (KOH). However, WO_3 is unstable in those electrolytes. As far as we know, our earlier work [6] – together with investigations by Passerini et al. [7–10] – are the only prior studies on pure electrochromic Ni oxide in non-aqueous Li electrolytes. Passerini et al. [7–9] found an optical modulation of ~15% for ~60-nm-thick Ni oxide films upon Li intercalation. However, subsequent work demonstrated that the optical modulation of Ni oxide in Li electrolytes could be greatly improved if some Li was incorporated already when the thin film was manufactured [11–16].

To the best of our knowledge, only Penin et al. [17] and Lee et al. [18,19] have previously examined electrochromic Ni oxide with additions of W. Their samples were deposited by pulsed laser deposition and RF magnetron sputtering, respectively. Penin et al. [17] observed that the durability of NiO under electrochemical cycling in a KOH electrolyte could be improved by W addition. Lee et al. [18,19] studied Ni_xW_{1-x} oxide films with $0.65 < x < 1$ in non-aqueous Li–PC plus 1,2 dimethoxyethane, 50/50 by volume, and found very good optical modulation. The difference between dark and bleached-state transmittance was ~50% at a wavelength λ of 550 nm for a ~100-nm-thick film. Lee et al. [18,19] also noted that W addition led to an increase in Li diffusion coefficient and a decrease in charge transfer resistance and suggested that the mobility of ions and electrons was enhanced as a result of W opening up the Ni oxide structure; such a porous structure is well

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known to be beneficial for EC performance [20]. Gillaspie et al. [21,22] fabricated $Li_{1.2}NiW_{0.1}$ oxide films by RF magnetron sputtering and cycled them electrochemically in Li–PC; they found good optical contrast between dark and bleached states and that the W containing Li–Ni oxide film had a significantly larger bleached-state transmittance than a comparable Li–Ni oxide film.

The purpose of our present work is to shed more light on the EC properties of the Ni–W oxide system which, despite some earlier investigations [17–22], has not been researched in sufficient detail. Our goal is to study how physical properties — such as crystal structure and chemical bonding — depend on the composition in Ni_xW_{1-x} oxide films. Further, it is of significance to elucidate whether the bleached-state transmittance of Ni oxide was improved by W addition. Electrochemical and optical properties were investigated upon electrochemical cycling in Li–PC. This electrolyte is easy to use, and it is compatible with W oxide and hence allows studies of “liquid devices” comprising two EC films and an intermediate liquid electrolyte. By using Li–PC it is also possible to single out the effect of the Li ions and avoid possible interference from water, protons and hydroxides. Moreover the present results, and findings from previous studies of ours on Ni-containing W oxides [23–25], describe the whole Ni_xW_{1-x} system — ranging from cathodic WO_3 to anodic NiO — with regard to composition, crystal structure, phase composition, density, electrochemistry and optical properties.

2. Methods

2.1. Thin film deposition

Thin films were made by reactive DC magnetron co-sputtering from metallic targets of W and Ni, both with 99.99% purity, in a deposition system based on a Balzers UTT 400 unit. The total discharge power, $Power_{Ni}+Power_W$, was set to 230 W and the different compositions were accomplished by varying the power ratio between the two targets, i.e., $Power_{Ni}/\ Power_W$. Deposition took place in an argon/oxygen atmosphere with targets operating in the reactive mode. An O_2/Ar mass flow ratio of 0.15 was used at a working pressure of ~30 mTorr. The films were deposited onto unheated glass plates pre-coated with transparent and electrically conducting In_2O_3:Sn (known as ITO) with a resistivity of 60 Ω/square. Thin films were deposited simultaneously on small substrates of C and Si and were employed for Rutherford backscattering spectrometry (RBS) and X-ray diffraction (XRD) measurements, respectively.

2.2. Structural characterization

X-ray photoelectron spectroscopy (XPS) measurements were carried out to determine compositions and binding energies (BEs). A PHI Quantum 2000 Scanning ESCA Microprobe, operating with Al K_α radiation, was used, and data were analyzed with the MultiPak program [26]. We used a pass energy of 46.95 eV and a step size of 0.2 eV/s. Surface compositions were obtained from integrations over the W 4 f, Ni 2p, O 1 s and C 1 s peaks. The energy scale was calibrated by putting the C 1 s binding energy at 284.5 eV. Calibration offsets often vary among published XPS data, and in order to allow correct comparisons between our results and those in the literature we recalculated all BEs so that they are consistent with a calibration offset of 284.5 eV.

Atomic compositions of the films were inferred from RBS measurements taken at the Uppsala Tandem Laboratory. The incoming ions were 2 MeV ^{4}He, and data were fitted to a model of the film-substrate system by use of the SIMNRA program [27]. Apart from element type and composition, the film's thickness N_s was found in atoms/cm^2, which makes it possible to calculate the film density ρ by

$$\rho = \frac{MN_s}{n_{atoms}N_A d}, \tag{1}$$

where M is molar mass, n_{atoms} is number of atoms in a molecule, N_A is Avogadro's constant and d is film thickness in centimeters. In addition, some carbon was detected in the films, up to an atomic concentration of 15%. When calculating ρ, this amount of C atoms was subtracted from the value of N_s found by SIMNRA. Film thicknesses were found to be ~200 nm, as measured with an Alphastep surface profilometer.

XRD, using a Siemens D5000 diffractometer, was employed to determine the crystalline order of the samples. The instrument operated with CuK_α radiation at a wavelength of 1.54 Å, and data were taken with a parallel-plate collimator having an acceptance angle of 0.4°. The incoming beam was fixed at an angle of one degree, and the detector angle was scanned with two seconds per step for increments of 0.05°. Orientations of the crystal planes were inferred by comparing experimental spectra with the JCPDS database [28].

2.3. Electrochemical and optical characterization

EC properties of the Ni_xW_{1-x} oxide films were investigated by cyclic voltammetry (CV) and spectrophotometry. CV measurements were conducted inside an argon-filled glove box, using a three-electrode set-up controlled by an ECO Chemie Autolab/GPES interface. The reference and counter electrodes were Li foils, and the electrolyte was 1 M Li–PC. The sweep velocity was 10 mV/s, and CVs were recorded between 2 and 4 V vs. Li during 20 cycles. A few tests were extended to 150 cycles. The potential ranges were set in order to avoid (i) rapid ITO degradation (at < 1.0 V vs. Li) [29], (ii) risks for irreversible formation of Li_2O and LiOH (at < 2.0 V vs. Li), and (iii) oxidation of PC (at > 4.5 V vs. Li) [30,31]. Moreover it has been found that ITO can display an oxidation and reduction process at < 2 V vs. Li [29,32]. Hence, in order to assure that ITO was not affected by the electrolyte and to avoid confusing extraneous features in the CVs, we set the lower potential limit at 2 V vs. Li.

The CV recordings were followed by ex-situ spectral optical measurements in the $300 < \lambda < 2500$ nm range by use of a Lambda 9 spectrophotometer. Data were taken for the bleached and colored states at the 20th CV cycle. Optical density (OD) was used to calculate absorption coefficient (α) and coloration efficiency (CE) for the films from the formulas

$$OD = \alpha d = \ln\left(\frac{1-R}{T}\right), \tag{2}$$

$$\alpha_{film} = \frac{OD_{total} - OD_{substrate}}{d_{film}}, \tag{3}$$

$$CE = \frac{\Delta OD}{\Delta Q} = \frac{OD_{colored} - OD_{bleached}}{\Delta Q}, \tag{4}$$

where R and T are total reflectance and transmittance, respectively, of the whole sample; OD_{total} and $OD_{substrate}$ are optical densities of the whole sample and of the ITO coated glass, respectively; α_{film} and d_{film} are absorption coefficient and thickness of the EC thin film, respectively; and $OD_{colored}$ and $OD_{bleached}$ are optical densities of the whole sample in its colored and bleached states, respectively. Finally, ΔQ is the average of the inserted and extracted charge densities. Charge density is counted per surface area of electrolyte/electrode interface.

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