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**SPECTROSCOPIC ELLIPSOMETRY CHARACTERIZATION
OF ELECTROCHROMIC TUNGSTEN OXIDE AND NICKEL OXIDE THIN FILMS
MADE BY SPUTTER DEPOSITION**

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Abstract

Electrochromic films of tungsten oxide and nickel oxide were made by reactive dc magnetron sputtering and were characterized by X-ray diffraction, Rutherford backscattering spectrometry, scanning electron microscopy, and atomic force microscopy. The optical properties were investigated in detail by spectroscopic ellipsometry and spectrophotometry, using a multiple-sample approach. The W oxide film was modeled as a homogeneous isotropic layer, whereas the Ni oxide film was modeled as an anisotropic layer with the optical axis perpendicular to the surface. Parametric models of the two layers were then used to derive complex refractive index in the 300-1700-nm-range, film thickness, and surface roughness. A band gap of 3.15 eV was found for the W oxide film, using a Tauc-Lorentz parameterization. For the Ni oxide film, taken to have direct optical transitions, band gaps along the optical axis, perpendicular to it, and in an isotropic intermediate layer at the bottom of the film were found to be 3.95, 3.97, and 3.63 eV, respectively. Parameterization for the Ni oxide was made by use of the Lorentz model.

Keywords: ellipsometry, electrochromic, tungsten oxide, nickel oxide

1. Introduction

Electrochromic (EC) devices can be used to control the throughput of visible light and solar energy in architectural windows as well as for other applications [1-5]. A typical device comprises two EC films separated by a transparent ion conductor, and this three-layer stack is positioned between transparent electrical conductors. The optical absorption can be modulated—reversibly and persistently—by shuttling charge between the two EC films, which is effected by applying a voltage between the transparent electrodes. The ability to regulate the energy flows through windows by EC devices can lead to huge energy savings largely by cutting down on the demand for air conditioning [6], and this technology can also give benign working and living conditions [7].

Efficient EC devices can be constructed by combining a cathodically coloring EC film (darkening under ion and electron insertion) and an anodically coloring EC film (darkening under ion and electron extraction) in a device whose other components are fully transparent. A particularly convenient combination uses tungsten oxide and nickel oxide as the cathodic and anodic layers [4], respectively, and devices of this type have been implemented on flexible polyester-based EC foils [8]. The electrochromism of W oxide films has been known for many years [9], and it is clear that the absorption is dominated by intervalency transitions between W^{6+} and W^{5+} in structural units, based on linked WO_6 units, that allow intercalation of small ions [4,10]. Electrochromic Ni oxide also has been known for years [11,12]; here the optical absorption—at least in sputter deposited films—is dominated by transitions between Ni^{2+} and Ni^{3+} in hydrous surface layers on NiO-type nanoparticles forming nanoporous films [13,14].

Accurate optical data on EC films of W oxide and Ni oxide are of obvious interest both from a fundamental perspective and with regard to technical applications. A third reason is that the optical properties of the pure oxides serve as starting points for understanding the EC performance of mixed W-Ni oxides which, as shown recently [15], can exhibit superior optical properties. Spectroscopic ellipsometry (SE) is the technique *par préférence* to investigate the optical properties [16], and, not surprisingly, it has been used in the past for detailed studies on EC films of W oxide made by evaporation [17-21], sputter deposition [22-29], and sol-gel technology [30], as well as EC films of Ni oxide made by pulsed laser deposition [31], sputtering [23,25,32,33], atomic layer deposition [34], and sol-gel technology [35].

The present work is devoted to oxide films prepared by reactive dc magnetron sputtering under conditions leading to fully transparent layers. Our deposition technology is notable for its up-scaling capability and, hence, industrial viability. A multiple-sample analysis of SE data was used to extract optical data [36]. This analysis is based on simultaneously measuring on at least two identical films deposited onto different substrates. We report detailed data on spectrally dependent optical constants.

One significant result is that the films of W oxide and Ni oxide differ, qualitatively, in that they are characterized by homogeneous and inhomogeneous optical properties, respectively.

2. Sample preparation and characterization

2.1 Sputter deposition

Our thin films were prepared by reactive dc magnetron sputtering in a versatile deposition system based on a Balzers UTT 400 unit. Sputtering took place from 5-cm-diameter targets of 99.95% pure W and Ni in a plasma of Ar + O₂ at a total pressure of 30 mTorr. The discharge power was 230 W and 250 W for deposition of W oxide and Ni oxide, respectively. Maximum optical transmittance, desirable for EC device applications, was achieved by setting the O₂/Ar mass flow ratio to 13 % and 2 % for W oxide and Ni oxide, respectively. These depositions are consistent with those in earlier work of ours [37].

Silicon (111) and ultraviolet-transparent borosilicate glass were chosen as substrates for SE measurements, scanning electron microscopy (SEM) and atomic force microscopy (AFM), whereas Rutherford backscattering spectrometry (RBS) was performed on carbon-based substrates. The glass substrates have a root mean square (rms) roughness of ~10 nm, whereas the Si substrates, whose surfaces are covered with naturally grown SiO₂, can be regarded as atomically smooth. Films were deposited also onto glass substrates pre-coated with ~40-nm-thick films of transparent and electrically conducting In₂O₃:Sn (known as indium-tin-oxide or ITO) having a resistance/square of 60 Ω.

2.2 Composition, structure and morphology

Elemental composition and film density were determined by RBS using facilities of the Uppsala Tandem Laboratory. We used 2 MeV He ions backscattered at an angle of 167 degrees and analyzed the data using the SIMNRA simulation program [38]. The W oxide films could be represented by WO_x with $x = 3.1 \pm 0.1$ and a density γ of about 5.2 g/cm³, whereas the Ni oxide film could be represented by NiO_y with $y = 1.25 \pm 0.05$ and $\gamma \approx 3.8$ g/cm³. Corresponding bulk densities are 7.16 g/cm³ for monoclinic WO₃ and 6.67 g/cm³ for NiO single crystals, thus showing that the films have a large amount of porosity. The Ni oxide film, in particular, is expected to be strongly hydrous [14].

The structure and grain size of the films were determined by X-ray diffraction (XRD) using a Siemens D5000 diffractometer operating with CuK_α radiation at a wavelength of 1.54 Å. The Ni oxide film was found to be polycrystalline with a grain size of 26.5 nm, whereas the W oxide film was amorphous as judged from its featureless XRD spectra [37].

The surface roughness of films deposited onto glass and Si were measured by AFM using a Veeco Dimension 3100 instrument employed in tapping mode. Figure 1 illustrates characteristic topographies for the two types of films. The W oxide film is found to have a root mean square (rms) roughness of 3 to 4 nm, whereas the Ni oxide film has a rms roughness of ~5 nm.

Surface and cross-sectional film morphologies were investigated by SEM using a LEO Ultra 55 FEG instrument. Figure 2 shows surface structures of the two film types with features that are consistent with the AFM data in Fig. 1. Figure 3 displays corresponding cross-sectional views on fractured samples. The latter SEM micrographs give clear evidence for columnar structures and porosity on the nanometer scale; these features are conducive to ionic transport and are hence advantageous with regard to EC performance [1,14]. Film thicknesses for samples on Si were found to be in the approximate thickness range $350 < d < 370$ nm.

The Ni oxide film depicted in Fig. 3(b) has a conspicuous double-layer structure with a 20 to 30 nm thick, seemingly uniform, film closest to the substrate on top of which the thicker porous film has been formed. The uniform bottom layer existed irrespectively of the substrate being of glass or Si. We were unable to obtain reliable data on the structure of this film. Its significance for the ellipsometric analysis will become apparent in our later discussion.

2.3 Preliminary optical characterization

A preliminary characterization of the optical properties of the two types of films is important for giving inputs to the subsequent detailed analysis based on SE. To that end we used a Perkin-Elmer Lambda 9 spectrophotometer with an integrating sphere coated with BaSO₄ paint in order to record spectral transmittance T and reflectance R in the $300 < \lambda < 2500$ nm wavelength range for films of W oxide and Ni oxide backed by ITO-coated glass. The spectral absorption coefficient $\alpha(\lambda)$, multiplied by the film thickness, was then derived from the approximate expression [39]

$$\alpha(\lambda)d = \ln \frac{1 - R(\lambda)}{T(\lambda)} \quad . \quad (1)$$

Figure 4 shows data for films of W oxide and Ni oxide on ITO coated glass, as well as for substrates with only ITO on glass. It is evident that the ITO-coated glass has very low absorption for $\lambda > 350$ nm. The W oxide starts to absorb for wavelengths shorter than ~400 nm as a result of electrons being excited over the band gap. The Ni oxide film displays a similar absorption at the shortest wavelengths, but it is clearly seen that the band edge is smeared so that a band tail exists. This absorption onset is roughly exponential, *i.e.*, it can be described as an Urbach tail [32]. For fitting purposes—as will be apparent later—this low energy tail was instead represented by a Lorentzian model of the interband absorption.

3. Ellipsometric analysis: Equipment and procedures

3.1 Experimental

Thin films of W oxide and Ni oxide, backed by Si or borosilicate glass, were investigated by use of a variable-angle spectroscopic ellipsometer with rotating analyzer and equipped with autoretarder (J.A. Woollam Co., Inc.). Measurements were carried out with 10-nm-steps in the $300 < \lambda < 1700$ nm spectral range and for incidence angles between 50° and 80° . An optical fiber between the monochromator and the entrance polarizer is not effective for $1350 < \lambda < 1450$ nm, and this wavelength range was not used for analysis. The backs of the glass substrates were roughened in order to eliminate incoherent reflection.

In ellipsometry one measures changes of the polarization state of light due to its reflection at a surface. The experimentally recorded quantities are Δ and ψ , which are angles defining the ratio of the reflections R_p and R_s for the parallel (subscript p) and perpendicular (subscript s) components of the wave [16], *i.e.*,

$$\frac{R_p}{R_s} = \tan \psi \exp(i\Delta). \quad (2)$$

In order to achieve mean resolutions in Δ and ψ of 0.04° or better, the signal-to-noise ratio was improved by acquiring data during 100 analyzer rotations for each measurement. Films on glass substrates were analyzed by simultaneously fitting transmittance and SE data in the $300 < \lambda < 1700$ nm range. Non-uniformity in film thicknesses was taken into account in the calculations. The data analysis was performed using commercially available WVASE32 software [41].

The Levenberg-Marquardt regression algorithm was used for minimizing the mean-squared error (MSE) [33], defined as

$$MSE = \frac{1}{2N - M} \sum_{i=1}^N \left[\left(\frac{\psi_i^{\text{mod}} - \psi_i^{\text{exp}}}{\sigma_{\psi,i}^{\text{exp}}} \right)^2 + \left(\frac{\Delta_i^{\text{mod}} - \Delta_i^{\text{exp}}}{\sigma_{\Delta,i}^{\text{exp}}} \right)^2 + \left(\frac{T_i^{\text{mod}} - T_i^{\text{exp}}}{\sigma_{T,i}^{\text{exp}}} \right)^2 \right] \quad (3)$$

where N is the number of (ψ, Δ, T) triplets, M is the number of fitted parameters in the model and σ are standard deviations of the experimental data points. The MSE value is the basis for estimating the quality of the match between the data calculated from the model data $(\psi_i^{\text{mod}}, \Delta_i^{\text{mod}}, T_i^{\text{mod}})$ and experimental data $(\psi_i^{\text{exp}}, \Delta_i^{\text{exp}}, T_i^{\text{exp}})$ as well as for judging the validity of the model employed. The algorithm also provides 90 % confidence limits for the fitting parameters.

Multiple-sample analyses [28] were applied for the films of W oxide and Ni oxide. Measured data for two films of each oxide, on borosilicate glass and on silicon, were thus analyzed simultaneously thereby giving a solution for the dielectric function of the films and their thicknesses due to parameter decoupling.

3.2 Basic models

The optical properties of the materials under study can be described in terms of their spectrally dependent complex refractive index, $N = n + ik$, or, alternatively, in terms of their complex dielectric function, $\varepsilon = N^2 = \varepsilon_1 + i\varepsilon_2$. Structural and micro-structural information—such as film thickness, composition, porosity, *etc*—can be obtained via non-linear regression analysis using an appropriate optical model for the sample. The films can be modeled in a variety of ways, including as a uniform layer (Fig. 5a), a graded-index layer (Fig. 5b) or as a uniaxial anisotropic layer with the optical axis perpendicular to the sample surface (Fig. 5c). These three models were used to analyze our films of W oxide and Ni oxide, as we return to below.

A graded-index film is usually described as a stack of thin layers, each being uniform and possessing properties slightly different from those of the neighbouring layers. The properties of each of these layers can be calculated from a specified grading profile that, in the simplest case, can be linear but in general can be arbitrary. In the present case, each of the investigated oxide films was represented as two layers with different thicknesses. Two layers obviously is a minimum for a graded-index model, and we verified that an increase of the number of layers did not significantly improve the fitting quality.

Effective medium approximations (EMAs) can be used to represent inhomogeneous materials as well as interface roughness in terms of effective dielectric functions denoted ε_{eff} . In ellipsometry it is customary to employ the Bruggeman EMA [42], whose constitutive equations can be written

$$\sum_{i=1}^m f_i \frac{\varepsilon_i - \varepsilon_{eff}}{\varepsilon_i + 2\varepsilon_{eff}} = 0, \quad \sum_{i=1}^m f_i = 1, \quad (4)$$

where $m = 2$ is the number of components, and f_i and ε_i are the volume fraction and the complex dielectric function of component i , respectively. In the analysis to be discussed below, the volume fraction of each constituent of the interface layers was taken to be 0.5. We note, *en passant*, that the Bruggeman EMA of Eq. (4) presumes isotropy as well as topological equivalence of the constituents; these restrictions can be relieved through the use of alternative or generalized EMAs [43], but these aspects have not been pursued.

3.3 Models for W oxide films

Two separate three-layer models were used to represent W oxide films on glass and Si substrates, as illustrated in Fig. 6. In both cases there is surface roughness, accounted for by an EMA to represent the top layer. Considering glass, the surface roughness—albeit small—necessitates the use of an EMA to describe also the interface between the substrate and the film. The Si substrate, on the other hand, is very smooth but its surface is oxidized implying that the effect of an intermediate SiO₂ layer needs to be included.

We first analyzed the data for W oxide films on Si. This film is virtually non-absorbing for $400 < \lambda < 1700$ nm, as apparent from Fig. 4, and hence a Cauchy dispersion equation [16] could be applied to find the thicknesses of the W oxide film and of the EMA layer. Then substituting these thicknesses into expressions for Ψ and Δ [16], a wavelength-by-wavelength fit over the whole spectral range was performed to extract optical constants. The initial value for this fitting was taken as the refractive index at the largest wavelength (1700 nm) obtained from the Cauchy dispersion model.

The derived optical constants and the layer thicknesses were then used as inputs for the Tauc-Lorentz (TL) model [16]. This empirical parameterization is based on the Tauc expression for the imaginary part of the dielectric function near the band edge [44] and the Lorentz oscillator model. Considering only a single transition, the imaginary part of the dielectric function of the TL model is given by [41]

$$\varepsilon_2(E) = \frac{AE_c B(E - E_g)^2}{(E^2 - E_c^2)^2 + E^2 B^2} \frac{\Theta(E - E_g)}{E}, \quad (5)$$

where E is photon energy, A and B represent amplitude and broadening of the ε_2 peak, respectively, E_c is resonance energy for the Lorentz oscillator, E_g is the Tauc gap, and $\Theta(E - E_g)$ is the Heaviside function [$\Theta(E) = 1$ for $E \geq 0$ and $\Theta(E) = 0$ for $E < 0$]. The expression for ε_1 is obtained via a Kramers-Kronig integration of ε_2 [16, 33] according to

$$\varepsilon_1(E) = \varepsilon_\infty + \frac{2}{\pi} P \int_{E_g}^{\infty} \frac{\xi \varepsilon_2(\xi)}{\xi^2 - E^2} d\xi, \quad (6)$$

where ε_∞ is the high-frequency contribution to ε and P denotes the principal value of the integral.

It should be noted, that the real and imaginary parts of the TL dielectric function correctly satisfy the Kramers-Kronig transformation, a feature which is absent in the Cauchy and wavelength-by-wavelength approach above. This property allows the TL function to accurately represent experimental data over a wide spectral range. Moreover, the band gap parameter in this model is particularly useful since it can be correlated with other properties of the film.

Multiple-sample analysis was used to increase the accuracy of the determination of optical constants and thicknesses with the TL model. Thus the fitting was performed simultaneously for films on glass and Si. The interface layer between the glass and the W oxide film is important in order to account for substrate roughness, and attempts to carry out the analysis without this layer led to significantly lowered fitting quality. Film thickness variation of the order of 3 to 5 %, typical for films made by sputter deposition in our set-up, was accounted for in the analyses.

3.4 Models for Ni oxide films

Two four-layer models were used for Ni oxide films backed by glass and Si, as described in Fig. 7. They are analogous to those for W oxide with one important difference: the experimentally found compact Ni oxide layer at the boundary towards the substrate (*cf.* Fig. 3b) is taken to be a separate entity, with isotropic properties, for the modeling.

The model for the optical properties must be qualitatively different from the ones for W oxide films and must account for the fact that the films display some optical absorption in a wide wavelength interval, as found from the preliminary optical characterization based on spectrophotometry and shown in Fig. 4. For the analysis, we used a parameterized Lorentz oscillator represented by the expression [16]

$$\varepsilon(E) = \varepsilon_1 + i\varepsilon_2 = \varepsilon_\infty + \frac{ABE_c}{E_c^2 - E^2 - iBE}, \quad (7)$$

where A and B are amplitude and the half width of the ε_2 peak, respectively, and E_c is the resonance energy.

The use of a Lorentz oscillator to represent optical absorption reminiscent of an Urbach tail is not the only possibility, but the logarithmic nature of the band tail can be accounted for explicitly, as done in the past for optical data of amorphous semiconductors [45] and EC films [46]. We believe that the Lorentz oscillator representation is sufficient for our purposes and, furthermore, it can be implemented using standard software [41].

We used multi-sample analysis to improve the accuracy of the fitting and took care of film thickness variations, in full analogy with the procedures adopted for the W oxide films.

4. Ellipsometric analysis: Results and discussion

4.1 Substrates

The substrates must be accurately characterized prior to analyses of the W oxide and Ni oxide films. The borosilicate glass could be represented by the Cauchy dispersion model [16]. Literature

data [47] were used for the dielectric function of Si and for its naturally grown SiO₂ layer. SE was employed to show that the latter layer had a thickness of 1.9 nm.

4.2 Data on W oxide films

Figure 8 illustrates ellipsometric data on $\psi(\lambda)$ and $\Delta(\lambda)$ for the indicated incidence angles, as well as spectrophotometric normal $T(\lambda)$, for a film on glass. Pronounced oscillations in the data ensue from optical interference, which is strong since the films are non-absorbing in most of the shown spectral range.

The optical data were modelled by taking the films to be homogeneous, graded and anisotropic, as discussed in Sec. 3.2, and representing the material by a TL model according to Sec. 3.3. The quality of the fitting was accounted for by the MSE value introduced in Sec. 3.1. The different presumed nanostructures led to excellent, and more or less identical, fittings with MSE values being 7.7, 7.4 and 6.1 for homogeneous, graded and anisotropic nanostructures, respectively. Using a graded model, the difference in the refractive index between the top and bottom layer was only ~ 0.03 , and a similar difference was found between the ordinary and extraordinary refractive indices if the films were regarded as anisotropic. Hence the films can be accurately represented as being homogeneous.

The excellent agreement to the experimental data, evident from Fig. 8, was obtained for fitted values of the W oxide layer thicknesses equal to 385.9 nm, and for its surface roughness (represented by EMA in Fig. 6) equal to 3.5 nm, respectively, when the glass substrate was used; the corresponding numbers were 360.0 nm and 7.4 nm for the Si substrate. The roughness values are consistent with those recorded by AFM and SEM. The EMA layer at the interface between the W oxide film and the glass substrate had a thickness of 7.4 nm. The pertinent parameter values for the TL model (*cf.* Eqs. 5 and 6) were $\varepsilon_{\infty} = 1.10 \pm 0.01$, $E_c = 4.58 \pm 0.01$ eV, $E_g = 3.150 \pm 0.003$ eV, $A = 55.6 \pm 0.6$ and $B = 1.60 \pm 0.04$ eV, where the intervals represent 90 % confidence limits. The value of E_g is in good agreement with literature data for EC films of W oxide prepared by a variety of techniques [1].

Figure 9 reports spectral data on n and k .

4.3 Data on Ni oxide films

Figure 10 shows ellipsometric and spectrophotometric data for a Ni oxide film on glass in the same manner as for W oxide in Fig. 8. The oscillations in the optical data are not as pronounced as for the W oxide film, which is a consequence of optical absorption.

Modeling of the optical data was done as before, *i.e.*, taking the films to be homogeneous, graded and anisotropic, and representing the material in terms of a parameterized Lorentz oscillator, introduced in Sec. 3.4. MSE values for the homogeneous, graded and anisotropic films were 45.0,

29.0 and 5.3, respectively. Thus, in contrast to what we found for the W oxide films, the Ni oxide films are clearly uniaxially anisotropic.

The fit to the measured results was accomplished by use of a Lorentz oscillator specified by a value of E_c around 4.0 to 4.5 eV (*cf.* Eq. 7). As seen from Fig. 10, the fitting is excellent for $\psi(\lambda)$ and $\Delta(\lambda)$ but not equally good for $T(\lambda)$. The modeled transmittance is larger than the measured one, presumably due to the approximate nature of the model in the band gap region. The film thicknesses used in the modeling were as follows, where the first mentioned data refer to the film on glass and the accompanying data in parentheses pertain to the Si substrate: the main part of the Ni oxide film was 338 ± 2 (298 ± 1) nm, the EMA layer at the surface was 19.6 ± 0.1 (17.6 ± 0.2) nm, the seemingly compact and presumably isotropic layer in the bottom part of the Ni oxide film was 9.8 ± 0.7 (26.8 ± 0.7) nm, and the intermixed EMA layer at the glass interface was 20.4 ± 2.0 nm. The parameters of the Lorentz oscillator are shown in Table I.

Figure 11 shows spectral data on n and k . Optical band gaps were evaluated from k . We used the relationship $\alpha = 4\pi k/\lambda$ and obtained the direct band gap from [48]

$$E\alpha \sim (E - E_g)^{1/2} \quad (8)$$

Specifically, we obtained band gaps of 3.97 and 3.95 eV for the directions perpendicular and parallel to the optical axis in the anisotropic material, respectively. The band gap was 3.63 eV for the isotropic bottom part of the films. These results are generally consistent with literature data [1], and a detailed analysis is not meaningful.

5. Summary and concluding remarks

We made an in-depth analysis of the optical properties of thin films of W oxide and Ni oxide based, in particular, on variable-angle spectroscopic ellipsometry. These films are of particular significance for electrochromic device technology. The W oxide film was homogeneous and could be well represented by a Tauc-Lorentz parameterization. The Ni oxide film was qualitatively different, and its main part consisted of a uniaxial anisotropic material, whereas a thin portion of this film closest to the substrate seemed to be compact and optically isotropic. This lower layer showed up distinctly in scanning electron micrographs. Its significance, if any, for electrochromic device technology remains a challenge. The optical analysis of the ellipsometric data and of accompanying spectrophotometric information is demanding and requires a structural model with three (for W oxide) or four (for Ni oxide) superimposed layers. Some of these represent intermixing of adjacent media, and it was reassuring that the layer thicknesses that appeared from the optical analysis were

corroborated by structural information obtained by scanning electron microscopy and atomic force microscopy.

Detailed analyses of electrochromic materials are highly demanding, and many questions concerning them are yet unanswered. This paper has shown that advanced variable-angle spectroscopic ellipsometric analyses can provide some unique information, whose importance for device technology needs to be investigated further.

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References

- [1] C.G. Granqvist, Handbook of Inorganic Electrochromic Materials, Elsevier, Amsterdam, The Netherlands, 1995.
- [2] C.G. Granqvist, Electrochromic tungsten oxide films: Review of Progress 1993-1998, Solar Energy Mater. Solar Cells 60 (2000) 201-262.
- [3] C.G. Granqvist, E. Avendaño, A. Azens, Electrochromic coatings and devices: Survey of some recent advances, Thin Solid Films 442 (2003) 201-211.
- [4] G.A. Niklasson, C.G. Granqvist, Electrochromics for smart windows: Thin films of tungsten oxide and nickel oxide, and devices based on these, J. Mater. Chem. 17 (2007) 127-156.
- [5] C.G. Granqvist, Transparent conductors as solar energy materials: A panoramic review, Solar Energy Mater. Solar Cells 91 (2007) 1529-1598.
- [6] A. Azens, C.G. Granqvist, Electrochromic smart windows: Energy efficiency and device aspects, J. Solid State Electrochem. 7 (2003) 64-68.
- [7] R.D. Clear, V. Inkarojrit, E.S. Lee, Subject responses to electrochromic windows, Energy Buildings 38 (2006) 758-779.
- [8] A. Azens, G. Gustavsson, R. Karmhag, C.G. Granqvist, Electrochromic devices on polyester foil, Solid State Ionics 165 (2003) 1-3.
- [9] S.K. Deb, Optical and photoelectric properties and colour centres in thin films of tungsten oxide, Philos. Mag. 27 (1973) 801-822.
- [10] L. Berggren, J.C. Jonsson, G.A. Niklasson, Optical absorption in lithiated tungsten oxide thin films: Experiment and theory, J. Appl. Phys. 102 (2007) 083538 1-7.
- [11] J.S.E.M. Svensson, C.G. Granqvist, Electrochromic hydrated nickel oxide coatings for energy efficient windows: Optical properties and coloration mechanism, Appl. Phys. Lett. 49 (1986) 1566-1568.
- [12] W. Estrada, A.M. Andersson, C.G. Granqvist, Electrochromic nickel-oxide-based coatings made by reactive dc-magnetron sputtering: Preparation and optical properties, J. Appl. Phys. 64 (1988) 3678-3683.
- [13] E. Avendaño, A. Azens, G.A. Niklasson, C.G. Granqvist, Proton diffusion and electrochromism in hydrated NiO_y and $\text{Ni}_{1-x}\text{V}_x\text{O}_y$ thin films, J. Electrochem. Soc. 152 (2005) F203-F212.

- [14] E. Avendaño, H. Rensmo, A. Azens, A. Sandell, G. de M. Azevedo, H. Siegbahn, G.A. Niklasson, C.G. Granqvist, Coloration mechanism in proton-intercalated electrochromic hydrated NiO_y and $\text{Ni}_{1-x}\text{V}_x\text{O}_y$ thin films, *J. Electrochem. Soc.* 156 (2009) P132-P138.
- [15] S. Green, C.G. Granqvist, G.A. Niklasson, Electrochromism in mixed nickel tungsten oxide, in *Proceedings of the International Baltic Sea Region Conference on Functional Materials and Nanotechnologies*, Riga, Latvia, 31 March-3 April 2009; p.41.
- [16] H. Fujiwara, *Spectroscopic Ellipsometry: Principles and Applications*, Wiley, West Sussex, UK, 2007.
- [17] G. Bader, P.V. Ashrit, Vo-Van Truong, Transmission and reflection ellipsometry studies of electrochromic materials and devices, *Proc. Soc. Photo-Opt. Instrum. Engr.* 2531 (1995) 70-81.
- [18] H. Rafla-Yuan, J.G.H. Mathew, B.P. Hichwa, Characterization of proton-induced color transition in an amorphous tungsten oxide film, *J. Electrochem. Soc.* 143 (1996) 2341-2346.
- [19] K. von Rottkay, M. Rubin, S.-J. Wen, Optical indices of electrochromic tungsten oxide, *Thin Solid Films* 306 (1997) 10-16.
- [20] E. Pascual, J. Martí, E. Garcia, A. Canillas, E. Bertran, Infrared and UV-visible ellipsometry study of WO_3 electrochromic thin films, *Thin Solid Films* 313-314 (1998) 682-686.
- [21] I. Porqueras, E. Bertran, Optical properties of Li doped electrochromic WO_3 thin films, *Thin Solid Films* 377-378 (2000) 8-13.
- [22] H.S. Witham, P. Chindaudom, I. An, R.W. Collins, R. Messier, K. Vedam, Effect of preparation conditions on the morphology and electrochromic properties of amorphous tungsten oxide films, *J. Vac. Sci. Technol. A* 11 (1993) 1881-1887.
- [23] J.S. Hale, M. DeVries, B. Dworak, J.A. Woollam, Visible and infrared optical constants of electrochromic materials for emissivity modulation applications, *Thin Solid Films* 313-314 (1998) 205-209.
- [24] M.J. DeVries, C. Trimble, T.E. Tiwald, D.W. Thompson, J.A. Woollam, J.S. Hale, Optical constants of crystalline WO_3 deposited by magnetron sputtering, *J. Vac. Sci. Technol. A* 17 (1999) 2906-2910.
- [25] C. Trimble, M. DeVries, J.S. Hale, D.W. Thompson, T.E. Tiwald, J.A. Woollam, Infrared emittance modulation devices using electrochromic crystalline tungsten oxide, polymer conductor, and nickel oxide, *Thin Solid Films* 355-356 (1999) 26-34.

- [26] Y. Yamada, S. Kawaji, S. Bao, M. Okada, M. Tazawa, K. Yoshimura, A. Roos, Estimation of the amount of the proton injected into tungsten oxide thin films during deposition using spectroscopic ellipsometry, *Thin Solid Films* 515 (2007) 3825-3829.
- [27] Y. Yamada, K. Tajima, M. Okada, S. Bao, M. Tazawa, K. Yoshimura, A. Roos, Control of the concentration of protons intercalated into tungsten oxide thin films during deposition, *Phys. Stat. Sol. C* (2008) 1105-1108.
- [28] Y. Yamada, K. Tajima, S. Bao, M. Okada, K. Yoshimura, A. Roos, Optical properties of tungsten oxide thin films with protons intercalated during sputtering, *J. Appl. Phys.* 103 (2008) 063508 1-4.
- [29] Y. Yamada, K. Tajima, S. Bao, M. Okada, K. Yoshimura, Optical charge transfer absorption in proton injected tungsten oxide thin films analyzed with spectroscopic ellipsometry, *Solid State Ionics* 180 (2009) 659-661.
- [30] K. von Rottkay, N. Ozer, M. Rubin, T. Richardson, Analysis of binary electrochromic oxides with effective medium theory, *Thin Solid Films* 308-309 (1997) 50-55.
- [31] D. Franta, B. Negulescu, L. Thomas, P.R. Dahoo, M. Guyot, I. Ohlídal, J. Mistrik, T. Yamaguchi, Optical properties of NiO thin films prepared by pulsed laser deposition technique, *Appl. Surf. Sci.* 244 (2005) 426-430.
- [32] C. Kim, E. Cho, S. Yoon, D. Kim, R. Jung, J. Lee, S. Seo, H. Cheong, M. Bastjan, B. Schulz, M. Rübhausen, Structural and stoichiometry change in NiO with a thin IrO₂ layer, *J. Korean Phys. Soc.* 53 (2008) 3390-3393.
- [33] J.-W. Park, K.N. Choi, S.H. Baek, K.S. Chung, H. Lee, Optical properties of NiO thin films grown by using sputtering deposition and studied with spectroscopic ellipsometry, *J. Korean Phys. Soc.* 52 (2008) 1868-1876.
- [34] H.L. Lu, G. Scarel, M. Alia, M. Fanciulli, S.-J. Ding, D.W. Zhang, Spectroscopic ellipsometry study of thin NiO films grown on Si (100) by atomic layer deposition, *Appl. Phys. Lett.* 92 (2008) 222907 1-3.
- [35] Y.R. Park, K.J. Kim, Sol-gel preparation and optical characterization of NiO and Ni_{1-x}Zn_xO thin films, *J. Crystal Growth* 258 (2003) 380-384.
- [36] K. Järrendahl, H. Arwin, Multiple sample analysis of spectroscopic ellipsometry data of semi-transparent films, *Thin Solid Films* 313-314 (1998) 114-118.
- [37] S. Green, J. Backholm, P. Georén, C.G. Granqvist, G.A. Niklasson, Electrochromism in nickel oxide and tungsten oxide thin films: Ion intercalation from different electrolytes, *Solar Energy Mater. Solar Cells* (2009), doi:10.1016/j.solmat.2009.05.009.

- [38] M. Mayer, SIMNRA, a simulation program for the analysis of NRA, RBS and ERDA, AIP Conf. Proc. 475 (1999) 541-544.
- [39] W.Q. Hong, Extraction of extinction coefficient of weak absorbing thin films from special absorption, J. Phys. D: Appl. Phys. 22 (1989) 1384-1385.
- [40] F. Urbach, The long-wavelength edge of photographic sensitivity and of the electronic absorption of solids, Phys. Rev. 92 (1953) 1324.
- [41] J.A. Woollam Co., Inc, Guide to using WVASE32, WexTech Systems, Inc 310 Madison Avenue, Suite 905 New York, Ny 10017 (212) 949-9595.
- [42] D.A.G. Bruggeman, Berechnung verschiedener physikalischer Konstanten von heterogenen Substanzen I. Dielektrizitätskonstanten und Leitfähigkeiten der Mischkörper aus isotropen Substanzen, Ann. Phys., 5th series (Leipzig) 24 (1935) 636-679.
- [43] G.A. Niklasson, C.G. Granqvist, O. Hunderi, Effective medium models for the optical properties of inhomogeneous materials, Appl. Opt. 20 (1981) 26-30.
- [44] J. Tauc, R. Grigorovici, A. Vancu, Optical properties and electronic structure of amorphous germanium, Phys. Stat. Sol. B 15 (1966) 627-637.
- [45] A.S. Ferlauto, G.M. Ferreira, J.M. Pearce, C.R. Wronski, R.W. Collins, X. Deng, G. Ganguly, Analytical model for the optical functions of amorphous semiconductors from the near-infrared to ultraviolet: Applications in thin film photovoltaics, J. Appl. Phys. 92 (2002) 2424-2436.
- [46] D. Saygin-Hinczewski, M. Hinczewski, I. Sorar, F.Z. Tepehan, G.G. Tepehan, Modeling the optical properties of WO₃ and WO₃-SiO₂ thin films, Solar Energy Mater. Solar Cells 92 (2008) 821-829.
- [47] E.D. Palik, Handbook of Optical Constants of Solids, Academic, Orlando, FL, U.S.A., 1985; pp. 547-569 and 719-747.
- [48] F. Wooten, Optical Properties of Solids, Academic, New York, NY, U.S.A., 1972.

Table I. Parameters for Lorentz oscillators used to model the Ni oxide film, as defined in Eq. (7). First two rows refer to the main anisotropic material and third row to the bottom isotropic material (*cf.* Fig. 5).

	ϵ_{∞}	A	B (eV)	E_c (eV)
Ordinary	2.272 ± 0.004	8.2 ± 0.2	0.22 ± 0.01	4.46 ± 0.01
Extraordinary	2.541 ± 0.011	6.3 ± 0.2	0.28 ± 0.01	4.18 ± 0.01
Isotropic	3.463 ± 0.048	4.6 ± 0.3	0.15 ± 0.01	3.89 ± 0.01

Figure captions

Fig. 1. AFM images of films of W oxide (a) and Ni oxide (b) deposited onto Si substrates.

Fig. 2. SEM micrographs of surfaces of films of W oxide (a) and Ni oxide (b) deposited onto Si substrates.

Fig. 3. SEM micrographs of cross-sections through films of W oxide (a) and Ni oxide (b) deposited onto Si substrates. Note the double-layer structure of the Ni oxide film.

Fig. 4. Absorption coefficient multiplied by film thickness for a bare glass/ITO substrate and for this substrate coated with W oxide and Ni oxide films.

Fig. 5. Schematic representations of a thin film as a homogeneous layer (a), a graded index layer (b), and an anisotropic layer whose optical axis is perpendicular to the surface (c). N_i is the complex refractive index of the i^{th} layer, and N_e and N_o are extraordinary (e) and ordinary (o) refractive indices, respectively.

Fig. 6. Structural models for W oxide films on substrates of borosilicate glass (a) and Si (b).

Fig. 7. Structural models for Ni oxide films on substrates of borosilicate glass (a) and Si (b).

Fig. 8. Spectral ellipsometric data (Ψ and Δ) at the shown angles, and normal transmittance, for a W oxide film on glass. Experimental results are indicated by symbols and dashed curve, and data fitted to a model discussed in the main text are shown as solid curves.

Fig. 9. Spectral refractive index n and extinction coefficient k for W oxide films.

Fig. 10. Spectral ellipsometric data (Ψ and Δ) at the shown angles, and normal transmittance, for a Ni oxide film on glass. Experimental results are indicated by symbols and dashed curve, and data fitted to a model discussed in the main text are shown as solid curves.

Fig. 11. (a) Spectral refractive indices and extinction coefficients for Ni oxide films. Refractive index n and extinction coefficient k correspond to the isotropic Ni oxide films. Principal refractive indices n_e , n_o and extinction coefficients k_e , k_o correspond to anisotropic Ni oxide films. **(b)** Extinction coefficients for Ni oxide films in the shorter wavelength range.

(a)

(b)

Figure 1

(a)

(b)

Figure 2.

(a)

(b)

Figure 3

Figure 4

(a)

(b)

(c)

Figure 5

Figure 6

Figure 7

Figure 8.

Figure 9.

Figure 10.

(a)

(b)

Figure 11.