Structure and composition of sputter-deposited nickel-tungsten oxide films

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Article history:
Received 6 May 2010
Received in revised form 8 October 2010
Accepted 12 October 2010
Available online 21 October 2010

Keywords:
Tungsten oxide
Nickel oxide
X-ray photoelectron spectroscopy
Rutherford backscattering
X-ray diffraction
Raman spectroscopy

ABSTRACT
Films of mixed nickel-tungsten oxide, denoted Ni x W 1−x O 4 , were prepared by reactive DC magnetron co-sputtering from metallic targets and were characterized by Rutherford backscattering spectroscopy, X-ray photoelectron spectroscopy, X-ray diffractometry and Raman spectroscopy. A consistent picture of the structure and composition emerged, and at x<0.50 the films comprised a mixture of amorphous WO 3 and nanosized NiWO 4 at x=0.50 the nanosized NiWO 4 phase was dominating, and at x>0.50 the films contained nanosized NiO and NiWO 4 .

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1. Introduction
Films of tungsten oxide and nickel oxide have many applications, such as in electrochromic devices, gas sensors and photocatalytic surfaces [1,2]. Mixed nickel-tungsten oxide films, denoted Ni x W 1−x O 4 oxide, may have properties that are superior to those of the two components. In this work Ni x W 1−x O 4 oxide films were investigated with the main objective to elucidate the structural evolution of the phases that emerge for 0<x<1.

Our specific interest is connected with the electrochromic properties of the Ni x W 1−x O 4 system. Electrochromic materials change their optical properties when a potential is applied so that electrical charge is inserted or extracted. Both tungsten oxide and nickel oxide are widely used materials with excellent and complementary electrochromic properties [1–3]. The electrochromic effect ensues from electron transitions between different atomic states. For tungsten oxide, electron transitions between W 5+ and W 6+ cause absorption which sets in progressively as the W 6+ content is increased. Nickel oxides with Ni 2+ are transparent, which is the case for NiO and/or Ni(OH) 2 , whereas oxides with Ni 3+ are absorbing and this is so for NiOOH and/or Ni 2 O 3.

Mixed oxide thin films can have improved electrochromic properties, as has been known for many years [2,4–7], and at least one study has been made on thin film electrochromic tungsten oxide containing nickel, showing that the additive had beneficial effects that led to faster response times for the optical modulation, lower power consumption and good stability [8]. There is also some prior work by Kuzmin et al. on thin films of nickel tungstate, NiWO 4 , with foci on local atomic structure and electrochromic properties [9,10].

The phase diagram for the bulk NiO–WO 3 system forms a suitable point of departure for discussing thin films of this material. The system does not form solid solutions and the only compound NiWO 4 melts incongruently at 1420 °C and forms a eutectic with WO 3 at 73 mol % WO 3 and 1245 °C [11]. The crystalline phases present after solidification of melts are comprised of NiO + NiWO 4 and NiWO 4 + WO 3 in the composition range below and above 50 mol % WO 3 , respectively. These results may provide guidelines for structural evolutions, but films of Ni x W 1−x O 4 oxide can sustain metastable phases so that structural and compositional characterizations are essential in order to develop a fundamental understanding of their properties, notably for the electrochromic performance. To that end we studied sputter-deposited Ni x W 1−x O 4 oxide films with several different techniques, specifically being Rutherford backscattering spectroscopy (RBS), X-ray photoelectron spectroscopy (XPS), X-ray diffractometry (XRD), and Raman spectroscopy (RS).

The present work forms part of a larger investigation of the electrochromic films of Ni x W 1−x O 4 oxide. As a starting point for this investigation, we reported recently on the electrochromism of pure tungsten oxide and nickel oxide in various electrolytes [12].

2. Sample preparation and characterization techniques
Mixed nickel-tungsten oxide thin films were made by reactive DC magnetron co-sputtering from separate 5-cm-diameter metallic targets of pure tungsten and pure nickel in a versatile deposition system based on a Balzer UT 400 unit. Depositions took place in a gas mixture with an O 2 /Ar mass flow ratio of 0.15 and a working pressure...
of −4 Pa. A comparison with the voltages for sputtering from pure Ni and W targets indicates that the co-sputtering was carried out in the reactive mode. The target–substrate separation was ~13 cm. The total discharge power, $P_{\text{Ni}} + P_{\text{W}}$, was set to 230 W. The power to the targets was varied in order to obtain Ni$_x$W$_{1-x}$ oxide thin films with different magnitudes of $x$. Some samples were deposited onto unheated 5 × 5 cm$^2$ glass plates precoated with transparent and electron conductive In$_2$O$_3$:Sn in order to allow electrochemical measurements for subsequent investigation of the electrochromic properties. The XPS measurements used small pieces of such films. XRD, RBS and RS measurements were made on films deposited onto Si, C and pure glass, respectively. Some samples on silicon substrates were post-treated at 800 °C for 6.5 h in air in order to induce crystallization. Film thicknesses, as measured by an Alpha step profilometer, were 200 to 300 nm except for some RS samples that were as thick as 1 μm in order to ensure good Raman signals.

RBS gave information on composition and density for the whole film–substrate system when data were fitted to a model by use of the SIMNRA code [13]. The spectra reveal what kind of atom is detected (by peak position), atomic concentration (by relative peak height), and thickness in atoms/cm$^2$ (by peak width). These measurements were carried out at the Uppsala Tandem Laboratory using 2 MeV $^4$He ions backscattered at an angle of 172°.

XPS measurements were performed with a PHI Quantum 2000 Scanning ESCA Microprobe operating with monochromated AlK$_\alpha$ radiation (1486 eV), a pass energy of 46.95 eV and a step size of 0.2 eV/σ. Energy calibration was done by setting the binding energy of C 1s to 284.5 eV. Spectra were analysed using the Multipak program [14] and the magnitude of $x$ was obtained from integration over the W 4f and Ni 2p peaks.

XRD information was recorded on a Siemens D5000 diffractometer operating with CuK$_\alpha$ radiation at a wavelength of 1.54 Å. The detector was a parallel plate collimator with an acceptance angle of 0.4°. During measurements the incoming beam was fixed at an angle of 1°, and the detector angle was scanned with 2°/step for increments of 0.05°. Structure, phase composition and orientation of the planes were inferred by comparing experimental spectra with the JCPDS database.

RS data were taken at room temperature (20 °C) by use of a confocal microscope with a “Nanofinder-S” (SOLAR TII, Ltd.) spectrometer [15]. The measurements were performed through a Nikon CF Plan Apo 100× (NA = 0.95) optical objective. The Raman spectra were excited with a He–Cd laser (441.6 nm, 50 mW cw power) and dispersed by a 600 grooves/mm diffraction grating mounted in a 520 mm focal length monochromator. To exclude possible sample heating, the laser power at the sample was regulated by a variable neutral-density filter (optical density from zero to 3.1). A Peltier-cooled back-thinned CCD camera (ProScan HS-101H, 1024 × 58 pixels) was used as the detector. The elastic laser light component was eliminated by an edge filter (Omega, 441.6 AELP-GP).

3. Results and discussion

3.1. Composition found by RBS and XPS

The composition dependence of the Ni$_x$W$_{1-x}$ oxide thin films on the sputter power ratio $P_{\text{Ni}}/P_{\text{W}}$ was readily inferred from RBS and XPS as shown in Fig. 1. The RBS and XPS values from the two sets of measurements were in good agreement. The figure also illustrates whether the samples were visually transparent or not. The colour of the dark films was brownish. The reason for the sudden increase in $x$ when $P_{\text{Ni}}/P_{\text{W}}$ is 1.9 is not known, but it seems that whether films deposited in this range are transparent or absorbing is very sensitively dependent on the detailed sputtering conditions [16]. The density, found by RBS, lay close to that of W oxide films, i.e. in the 5 to 6 g/cm$^3$ range [2,12].

### Fig. 1. Composition of Ni$_x$W$_{1-x}$ oxide thin films as determined by two techniques vs ratio of sputter powers, and visual impression.

#### Fig. 2. W 4f XPS spectra for pure W oxide and mixed Ni$_x$W$_{1-x}$ oxide films. The small peak at 41 to 42 eV is due to W 5p$_{3/2}$.
to \( x \approx 0.20 \). Upon addition of up to \( x = 0.5 \), the binding energies of \( W^{4f_{7/2}} \) and \( W^{4f_{5/2}} \) states decreased slightly and some peak broadening was observed. As even more Ni was added, a film with \( x = 0.75 \) became dark in colour and the double peak changed to lower binding energies, as shown in Fig. 2. This peak shift is due to the presence of reduced tungsten ions \( W^{5+} \) [2,19]. For \( x = 0.50 \) the peak is displaced to a binding energy close to that of NiWO4, but the shift for the dark \( \text{Ni}_{0.75} \text{WO}_{0.25} \) oxide could also be due to the presence of \( W^{5+} \). Also the broadening of the peak for \( \text{Ni}_{0.50} \text{WO}_{0.50} \) oxide could be associated with \( W^{5+} \).

### 3.2.2. Ni 2p

For nickel oxides the Ni 2p spectra contain multiple peaks at binding energies between about 852 and 870 eV, including the main peak and satellites [21–23]. According to theory for the XPS technique [24–26], these peaks have been interpreted as due to final state effects caused by charge transfer from oxygen to nickel. The Ni 2p\textsubscript{3/2} XPS spectra in Ni(OH)\textsubscript{2} and NiOOH [22] have more broadened shapes than in NiO, and the first peak for NiOOH is shifted to larger binding energies thereby reflecting the presence of Ni\textsuperscript{3+}. As mentioned, the Ni 2p spectra are often complex and contain multiple peaks, and it is difficult to assign specific binding energies to the Ni\textsuperscript{2+} and Ni\textsuperscript{3+} states. For example, a recent work put the main peaks for NiO, Ni(OH)\textsubscript{2} and NiOOH at 854.7, 855.3 and 855.8 eV, respectively [22].

Fig. 2 shows XPS spectra for the Ni 2p\textsubscript{3/2} peak. These consist of two broad bands located at 853 to 858 eV and 860 to 866 eV. For \( x \leq 0.5 \) the positions of the main peak and of the satellite are found at about 856.5 and 863 eV, respectively: these values are close to the binding energy of nickel in NiWO4. The main peak is progressively shifted to lower binding energies for higher nickel content, i.e. for \( x \approx 0.5 \). At \( x = 0.75 \) the binding energy of the main peak is decreased by about 1 eV, down to \( \approx 855.5 \) eV. This decrease can be explained by the appearance of a NiO phase in films with \( x = 0.5 \). However one cannot exclude the presence of NiOOH, since the sample has a darkish brown colour that indicates the presence of some Ni\textsuperscript{3+}, which possibly is responsible for the asymmetry of the XPS peaks.

### 3.2.3. O 1s

The O 1s binding energy of NiOOH is 531.7 eV [28], while the corresponding energies are 529.6, 531.3 and 531.8 eV for NiO, Ni(OH)\textsubscript{2} and NiOOH, respectively [18]. The O 1s binding energy for crystalline NiWO4 lies at 531.5 eV [20] and for WO3 at 530.6 eV [18].

Fig. 3 shows the O 1s peak for pure W oxide and mixed Ni\textsubscript{1-x}W\textsubscript{x} oxide films with different amounts of Ni. The peak at 530.8 eV for pure WO3 is in close agreement with literature data [18,20,29,30]. An addition of Ni makes the peak widen and shift. It has been shown [31] that the O 1s peak in W oxide is not affected by stoichiometry, i.e. the observed changes of the peak should be solely the result of the presence of another phase, caused by nickel ions. For \( x = 0.5 \) the 1s peak shifts to 530.4 eV, indicating the presence of nanosized NiWO4. It is expected that a local structure relaxation in nano-NiWO4 will slightly decrease the O 1s binding energy compared to that of crystalline NiWO4. Moreover the phases with larger O 1s binding energies, such as Ni(OH)\textsubscript{2}, NiOOH and NiO\textsubscript{2}, could contribute to the high-energy tail. The larger shift towards lower binding energies, seen for Ni-rich films with \( x \geq 0.50 \), can be related to the appearance of a nickel oxide phase in which oxygen atoms have lower binding energy. The colour of the film with \( x = 0.75 \) and the broadening of the peak towards higher binding energies could also indicate that some Ni\textsuperscript{3+}- containing phase is present.

### 3.3. Structures determined by XRD

As-deposited pure W oxide and mixed Ni\textsubscript{1-x}W\textsubscript{x} oxide films were found to be X-ray amorphous up to \( x = 0.75 \). They become crystalline upon high-temperature treatment at 800 °C.

Fig. 4 shows results for annealed pure W oxide and a mixed Ni\textsubscript{1-x}W\textsubscript{x} oxide film with \( x = 0.5 \). Both samples have a monoclinic structure and the peaks agree with literature data for WO3 [32] and NiWO4 [33], respectively. Fig. 6 shows results for an as-deposited polycrystalline Ni oxide film and for annealed mixed Ni\textsubscript{1-x}W\textsubscript{x} oxide with \( x = 0.75 \). The latter film consists primarily of a cubic rock-salt NiO phase [34], but there is some evidence, shown by the peaks marked with asterisks, that NiWO4 is present: this assignment can be made by comparison with the data in Fig. 5. Our XRD results on annealed thin films are in full agreement with the phase diagram of the bulk NiO–WO3 system [11].
Upon an increase of the nickel content, the intensity of the band at pure tungsten oxide corresponds to that of an amorphous bond stretching and to terminal W=O modes. The Raman signal of the main bands at about 790 and 970 cm$^{-1}$, compositions. The spectra are dominated by two bands, located at amorphous/nanocrystalline phases of WO$_3$, NiWO$_4$ and NiO. modes observed by RS, can resemble those of corresponding amorphous: however their local structure, and thus the local phonon order Raman bands with the highest one at ~1100 cm$^{-1}$ structure has weak Raman scattering and normally shows a defect-induced broad band at about 500 cm$^{-1}$.

Room temperature Raman spectra of pure W oxide and mixed Ni oxide Fig. 7. shows typical Raman spectra for thin films of several compositions. The spectra are dominated by two bands, located at about 790 and at 950 to 970 cm$^{-1}$, whose ratio changes with composition. These two bands are commonly assigned to O–W–O bond stretching and to terminal W=O modes. The Raman signal of the pure tungsten oxide corresponds to that of an amorphous film [35–37]. Upon an increase of the nickel content, the intensity of the band at 950 cm$^{-1}$ grew and became dominant for $x=0.2$.

An addition of nickel makes it possible to form local environments similar to those in NiWO$_4$ and NiO. Nickel oxide with a rock-salt structure has weak Raman scattering and normally shows a first-order defect-induced broad band at about 500 cm$^{-1}$ [37] or a set of second-order Raman bands with the highest one at ~1100 cm$^{-1}$ [38] neither of which were observed in the spectra in Fig. 7. Therefore we can exclude the presence of a NiO phase in the mixed films with $x\leq0.45$. On the other hand NiWO$_4$ has a very strong Raman signal and is easily detected in thin films [15]. This signal is dominated by the 891 cm$^{-1}$ mode, which is typical for tungstates and corresponds to stretching vibration of the W–O pair in the WO$_6$ group, a so-called “internal” mode [39]. This band is also not present in the spectra in Fig. 7; this excludes the presence of a crystalline NiWO$_4$ phase, which is consistent with our XRD results.

However, it was found recently [40] that nanosized tungstates, with crystallite sizes below 2 nm, are X-ray amorphous and have a Raman signal very close to that observed in Fig. 7 for $x=0.45$, i.e. a dominating band located at 970 cm$^{-1}$ and a broad low-intensity band at 790 cm$^{-1}$. Therefore we conclude that the Ni$_{1−x}$W$_x$ oxide film with $x=0.45$ has a nanosized NiWO$_4$ phase, which transfers into crystalline NiWO$_4$ upon annealing at a high temperature.

Finally, Raman signals for intermediate compositions with $0<x<0.45$ were found to correspond well to a weighted sum of pure amorphous W oxide and nanosized NiWO$_4$ phases, as shown in Fig. 8. One can utilize this result to estimate the film composition and to compare it with the nominal nickel content. At a nominal $x=0.12$, for example, the nickel content in the film, estimated from the decomposition of the Raman signal, is about $0.24 \times 0.45 = 0.11$.

### 4. Conclusion

Films of mixed Ni$_{1−x}$W$_x$ oxide were characterized by four different techniques, specifically being RBS, XPS, XRD and RS. From RBS analysis we inferred that the density was close to that of pure W oxide films, i.e. 5 to 6 g/cm$^3$. RBS together with XPS gave consistent results for the magnitude of $x$.

For films with $x<0.5$, XPS and RS showed clear evidence for a thin film structure of nanosized NiWO$_4$ and WO$_3$ with $y$ close to 3. The two phases are X-ray amorphous. For $x=0.5$, both XPS and RS show that the main constituent is nanosized NiWO$_4$.

In films with $x>0.5$, XPS gave evidence for NiO and reduced tungsten ions (W$^{3+}$). The tail in the O 1s spectrum at energies above 532 eV also indicated the existence of hydrated phases for $x\geq0.5$ which, however, are difficult to identify. No clear evidence was found for NiOOH and Ni(OH)$_2$, although they are often present in sputter-deposited films together with NiO [23]. In addition, the dark brownish colour of films with $x>0.5$ indicated the presence of Ni$^{3+}$. No clear evidence was found for NiWO$_4$ by XPS, but the broadening of both the Ni 2p and O 1s peaks, in addition to the shift in the W 4f peak, could be signs of its presence.
Table 1
Summary of structural phases found in sputter-deposited Ni0.75W0.25 oxide films and of the experimental techniques used to obtain this information. XPS, RS and XRD denote X-ray photoelectron spectroscopy, Raman spectroscopy and X-ray diffraction, respectively.

<table>
<thead>
<tr>
<th>x in Ni0.75W0.25 oxide</th>
<th>Phase</th>
<th>Experimental technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>x = 0.50</td>
<td>Amorphous WOx</td>
<td>XPS (W 4f, O 1s), RS</td>
</tr>
<tr>
<td></td>
<td>Nanosized NiWOx</td>
<td>XPS (Ni 2p, O 1s), RS</td>
</tr>
<tr>
<td>x = 0.50</td>
<td>Nanosized NiWOx</td>
<td>XPS (W 4f, Ni 2p), RS, XRD</td>
</tr>
<tr>
<td></td>
<td>other</td>
<td>XPS (O 1s)</td>
</tr>
<tr>
<td></td>
<td>NIO</td>
<td>XPS (O 1s, Ni 2p), XRD</td>
</tr>
<tr>
<td></td>
<td>W+–phase</td>
<td>XPS (W 4f)</td>
</tr>
<tr>
<td></td>
<td>Nanosized NiWOx</td>
<td>XRD</td>
</tr>
</tbody>
</table>

The as-deposited films were X-ray amorphous for x ≤ 0.75, but XRD on annealed samples showed that the Ni0.5W0.5 oxide film forms NiWOx and that the Ni0.75W0.25 oxide film forms a mixture of NiO and NiWOx. These results are in agreement with the phase diagram for NiO–WO3 [11].

Finally, our analysis has given a consistent picture for the structure of the notoriously difficult Ni0.75W0.25 oxide thin films, as summarised in Table 1. This information is useful for a number of applications including electrochromics (as will be elaborated in a later paper), conductometric gas sensors, photocatalysts, and others.

Acknowledgments
This work was supported by Clear-up (Clean and Resource Efficient Buildings for Real Life) which is an Integrated Project funded by the European Community’s Seventh Framework Programme (FP7/2007–2013) under grant agreement number 211948. Additional support was received from the Swedish Research Council for Environment, Agriculture Sciences and Spatial Planning (FORMAS) and by a scholarship from the Anna-Maria Lundin foundation. We are grateful to Jens Jensen for valuable input regarding RBS measurements. A. Kuzmin acknowledges the funding support from ESF Project 2009/0202/1DP/1.1.1.2.0/09/APIA/VIAA/141.

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