



XAS, XRD, AFM and Raman studies of nickel tungstate electrochromic thin films

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Abstract

Systematic studies of nanocrystalline nickel tungstate, NiWO₄, thin films were performed by several experimental techniques such as Ni K- and W L_{1,3}-edges X-ray absorption spectroscopy, X-ray diffraction, Raman spectroscopy, atomic force microscopy and cyclic voltammetry measurements. We found that the NiWO₄ thin films exhibit electrochromic properties similar to that of amorphous tungsten trioxide films, but show better structural stability upon multiple colouring/bleaching cycling. It was observed that a nanocrystallinity of the thin films results in strong modifications of the Ni–O and W–O interactions, which affect both local atomic and vibrational structures. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Amorphous tungsten trioxide (a-WO₃) thin films are well-known materials for the use in electrochromic devices [1,2]. They belong to a class of cathodically colouring substances, which possess a reduced coloured state, i.e. tungsten ions change their formal valence state from 6+ to 5+ upon colouration. From the point of view of commercial applications, long-term stability and performance of electrochromic devices based on a-WO₃ present the main problem. The degradation of thin films is related to their transformation from metastable amorphous state into crystalline state upon multiple colouring/bleaching cycling [3], accompanied by injection/extraction of small cations, such as H⁺ and Li⁺ and electrons. Therefore, many attempts

were performed to improve the stability of a-WO₃ thin films [2].

In this work, we present a systematic study of a new promising material, nanocrystalline nickel tungstate NiWO₄ thin films, having electrochromic properties similar to a-WO₃, but better long-lasting structural stability.

2. Experimental

Tungsten oxide, WO₃, nickel oxide, NiO, and NiWO₄ thin films (t.f.) were produced from metallic tungsten and nickel targets by separate and simultaneous reactive magnetron sputtering in a plasma-focusing DC magnetic field. A gas mixture of argon (80%) and oxygen (20%) was used as the sputter atmosphere. The sputter deposition was performed during 60–90 min at a total gas pressure 6–6.7 Pa. Pure glass substrates and the ones covered with ITO (In₂O₃/SnO₂) were mounted

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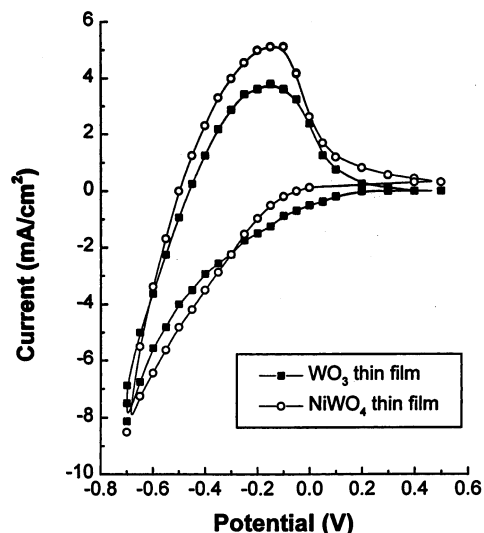


Fig. 1. Cyclic voltammograms for NiWO₄ and WO₃ thin films taken in 0.1 N H₂SO₄ acid electrolyte. The film thickness was about 0.5 μm. The curves shown were measured after several tens cycles, when the shape of the voltammogram become nearly unchanged.

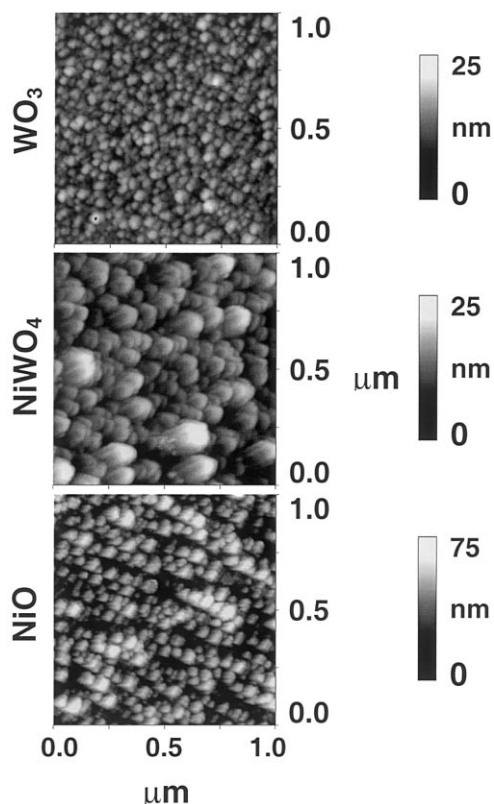


Fig. 2. AFM 1 × 1 μm images of WO₃, NiWO₄ and NiO thin films, obtained in tapping mode [5]. Note larger grain size in NiWO₄ compared to WO₃ and NiO.

about 8 cm above the target and were not intentionally heated. The films had a thickness of 0.5–1.2 μm. The as-deposited NiWO₄ films were nearly transparent, but the WO₃ films were bluish-grey, and the NiO films were brownish. For comparison, we used a-NiWO₄ and polycrystalline (c-) NiWO₄ powders [4], and commercial polycrystalline CaWO₄ and WO₃.

The electrochemical properties of t.f.-NiWO₄ were studied by cyclic voltammetric measurements. They were performed in 0.1 N H₂SO₄ acid electrolyte at a scan rate of 50 mV/s, and the potential was measured using the three-electrodes scheme with platinum counter electrode and Ag/AgCl reference electrode. The surface topography of all films was examined at micrometer scale by tapping mode atomic force microscopy (TM-AFM) [5].

The local environment around nickel and tungsten ions in thin films and two NiWO₄ compounds was probed by the Ni K-edge and W L_{1,3}-edges X-ray absorption spectroscopy (XAS). The details of the experiments and data analysis can be found in Ref. [4]. The conventional macro-Raman measurements were also done in 90°-geometry to investigate the vibrational dynamics of the tungsten–oxygen bonds [4].

3. Results and discussion

Voltammograms for NiWO₄ and WO₃ thin films are shown in Fig. 1 and suggest similar response for both films on charge insertion/extraction. The surface topography of the prepared films can be evidenced from the AFM images presented in Fig. 2. Both WO₃ and NiO thin films exhibit similar size of grains of the order of 20–60 nm. The grain size increases several times for t.f.-NiWO₄, being about 60–120 nm. These results are in good agreement with our XRD studies [4]. The as-prepared NiWO₄ films have nanocrystalline structure with <111> preferential orientation, and the crystallites size is larger than in the other two oxides. No change in the XRD patterns was observed for tungstate films after annealing at 450°C, which suggests good structural stability [4].

Crystalline NiWO₄ has wolframite-type structure, which is built up of hexagonally close-packed oxygens with certain octahedral sites filled by Ni²⁺ and W⁶⁺ cations in an ordered way [6]. The [NiO₆] octahedra possess small tetragonal distortion, whereas [WO₆] octahedra are strongly distorted with tungsten ions being off-centre. The octahedra of the same type are connected via edges, but of the opposite type by corner sharing. An interaction between neighbouring Ni²⁺ [3d⁸] (*S* = 1) ions is of superexchange-type and is expected to be strong enough, because NiWO₄ orders antiferromagnetically below 67 K [6].

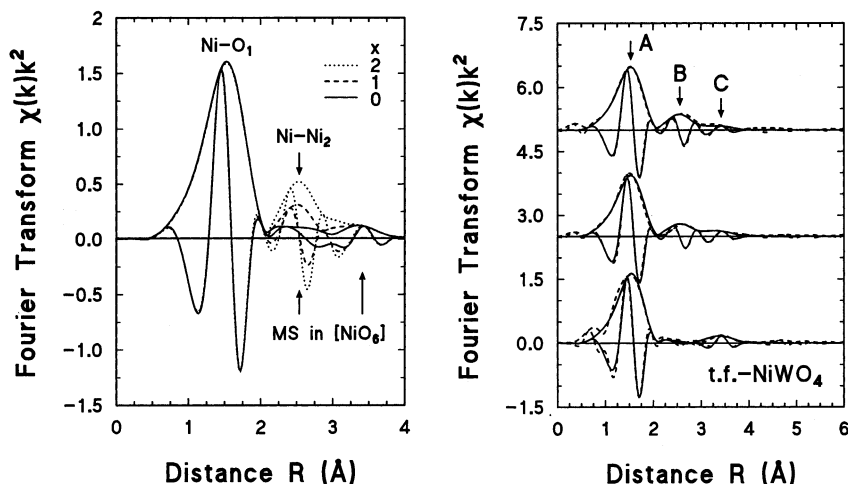


Fig. 3. Left panel: Fourier transforms (FTs) of the calculated Ni K-edge EXAFS $\chi(k)k^2$ signals for NiO_6Ni_x ($x=0,1,2$) clusters. The six oxygen atoms are responsible for the main peak at 1.5 Å, and one/two nickel atoms contribute at 2.5 Å. The peaks due to multiple-scattering contribution from the first oxygen shell are also indicated. Right panel: FTs (dashed line — experiment; solid line — calculation, based on the model from left panel) of the Ni K-edge EXAFS signals in three typical NiWO_4 thin films. The origin of peaks A, B and C is as in left panel.

The local structure around nickel and tungsten ions was probed directly by XAS. Apart from the grain size effect [7], it resembles, in general, that of polycrystalline NiWO_4 . A comparison of the intensity of the pre-edge peak at the W L_1 -edge, related to the dipole-forbidden transition $2s(\text{W}) \rightarrow 5d(\text{W})$ [8] in t.f.- NiWO_4 with a- NiWO_4 and WO_3 suggests that a degree of the $[\text{WO}_6]$ octahedra distortion in t.f.- NiWO_4 and a- NiWO_4 is similar, being larger than in WO_3 . However, in spite of large $[\text{WO}_6]$ octahedra distortion, tungsten ions in tungstates are still octahedrally coordinated that is supported by a comparison with the W L_1 -edge in CaWO_4 [4]. In the latter case, the tetrahedral coordination of tungsten ions results in the pre-edge peak of larger intensity. This conclusion also agrees with the results for the W L_3 -edge. Thus, the coordination of tungsten in t.f.- NiWO_4 can be described as $[\text{WO}_4\text{O}_2]$, meaning four short and two long W–O bonds [4].

The Ni K-edge spectra allowed us to obtain complementary information on the Ni–O bonding. The Fourier transforms (FTs) of the experimental EXAFS signals are shown in Fig. 3 (dashed lines in left panel). They are dominated by peak A, being due to six oxygen atoms of the first shell, whereas the peaks above 4 Å are smeared out due to large static disorder. To understand the origin of the two peaks B and C, we performed the model calculations within the multiple-scattering (MS) approach [9] for the small NiO_6Ni_x ($x=0,1,2$) clusters, which represent a fragment of the local structure around nickel ions in crystalline NiWO_4 . Six oxygen atoms, forming a regular

octahedron, surround the central nickel atom. The remaining two nickel ions are connected to the central nickel via oxygens of the two opposite octahedron edges. Thus, the in-plane Ni–O–Ni angles are equal to 90° . The FTs of the calculated EXAFS signals are shown in Fig. 3 (left panel). For $x=1$ (solid line), the two peaks at 2.5 and 3.5 Å correspond to the MS contributions from the first shell octahedron [10]. For $x=1$ (dashed line) and $x=2$ (dotted line), an additional contribution from one and two nickel atoms, respectively, appears at 2.5 Å. This model is able to fit perfectly the experimental signals (Fig. 3, right panel). However, more precise analysis shows that six oxygen atoms surrounding the central nickel ion can be additionally separated into two groups: four strongly bound in the plane with square-like arrangement and two weakly bound at the remaining vertices of an octahedron above and below the plane. The latter two oxygens are strongly bound to tungsten ions. Note also that no significant Ni–W contributions are observed in the Ni K-edge EXAFS signal, which suggests weak interaction between the tungsten and the nickel sublattices.

The Ni K-edge XANES signals (not shown) allow to obtain complementary information on the character of the Ni–O bonding by studying the variation of the pre-edge peak, which corresponds to $|1s3d^8 + {}^i\bar{L}^i\rangle \rightarrow |1s3d^8 + {}^i\bar{L}^{i-1}\rangle$ ($i=1,2$) transition [7,11]. Here \bar{L}^i denotes the oxygen 2p-orbitals having i -holes in the place of i -electrons back donated to the nickel 3d orbitals, and $\bar{1s}$ stands for a Ni 1s core hole. The change of the

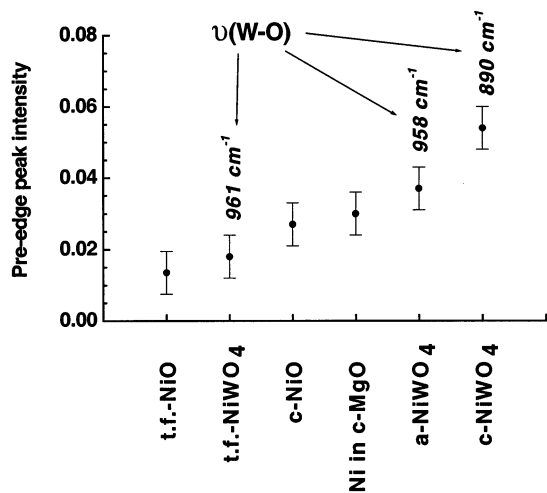


Fig. 4. Pre-edge peak intensity $I_{\text{pre-peak}}$ at the Ni K-edge in several compounds. The frequencies $\nu(\text{W-O})$ of the highest stretching W–O mode, obtained from Raman spectra, are also given for the tungstates. Note a negative correlation between $I_{\text{pre-peak}}$ and $\nu(\text{W-O})$.

pre-edge peak intensity for several compounds is shown in Fig. 4 (the data for c-NiO and c-MgO/Ni were taken from Ref. [12] and for t.f.-NiO from Ref. [7]): it is related to the variation in the covalency of the Ni–O bonding or more precisely to the change in the oxygen-to-nickel back charge transfer [11]. The higher intensity of the pre-edge peak indicates stronger covalency or larger charge transfer. One can compare (Fig. 4) the pre-edge peak intensities with the values of the stretching mode frequency $\nu(\text{W-O})$, provided by Raman spectroscopy. The negative correlation is observed indicating a concurrence for electron charge in Ni–O–W atomic chains: the Ni–O bonds become stronger at the expense of the W–O bonds.

The Raman spectra of tungstate are sensitive mainly to the tungsten sublattice, since the nickel environment shows relatively weak Raman activity. A peculiarity of the Raman spectra is the presence of a gap, which divides the external ($< 600 \text{ cm}^{-1}$) and internal ($> 600 \text{ cm}^{-1}$) modes of tungsten coordination polyhedra. The interesting result is observed for the lattice modes at low frequencies ($< 200 \text{ cm}^{-1}$) [4]: in t.f.-NiWO₄ and a-NiWO₄ they are closer to those of CaWO₄ with tetrahedral tungsten coordination but not to those of c-NiWO₄, where tungsten ions have distorted octahedral environment. This result is in agreement with that discussed before for the W L_{1,3}-edges: the tungsten ions are strongly coordinated to four oxygen atoms of the [WO₄] octahedra.

4. Conclusions

In this work, we propose a new electrochromic material — nanocrystalline NiWO₄ thin films. A systematic study of the thin film structure and vibrational properties using X-ray absorption spectroscopy, X-ray diffraction and Raman spectroscopy suggests that the local Ni–O and W–O chemical bonding depends strongly on the size of the NiWO₄ grains. The obtained results show that the interaction between nickel–oxygen and tungsten–oxygen polyhedra in thin films is weak, and the local environment around nickel and tungsten ions can be described as tetrahedral-like [WO₄]O₂ or plane-square-like [NiO₄]O₂. Note that in this model both tungsten and nickel ions are coordinated by six oxygen atoms but are strongly bound with only four of them. Such a situation for tungsten ions represents an intermediate case between WO₃ and CaWO₄ compounds.

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