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Changes in the Local Structure of Nanocrystalline Electrochromic Films of Hydrated Nickel Vanadium Oxide upon Ozone-Induced Coloration

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Abstract

Hydrated thin films of nickel vanadium oxide ($\text{Ni}_{1-x}\text{V}_x\text{O}_y$), made by reactive DC magnetron sputtering, were studied by X-ray absorption spectroscopy at the Ni and V K-edges using synchrotron radiation. The XANES signals were analysed within the full-multiple-scattering formalism, whereas EXAFS data were modelled within the multi-shell multiple-scattering approach. We found that transparent films exhibit a nanocrystalline NiO-type structure with homogeneous distribution of V ions substituting Ni ions. Exposure of the films to ozone resulted in dark brown coloration associated with an appearance of Ni^{3+} ions and accompanied by a modification of the local electronic and atomic structures of the V and Ni ions. The largest changes occurred in the environment of the V ions, which presumably change their valence state from V^{4+} to V^{5+} and displace into off-centre positions by $\sim 0.4 \text{ \AA}$.

1. Introduction

Electrochromic (EC) materials are able to reversibly alter their optical properties upon charge insertion-extraction caused by the application of an external voltage [1]. These materials can be used for a variety of applications, such as in architectural “smart windows capable of changing their transmittance thereby providing improved visual and thermal comfort for the occupants in conjunction with energy efficiency for the building. An EC device is characterised by a number of features, such as optical modulation, physical size, durability, etc.

Thin films of hydrated nickel oxide and nickel based oxides are of much interest. One reason for this is their ability for coloration upon ozone exposure [2], which allows charge balancing in order to make the films ready for facile device assembly consistent with large-scale production. Recent reviews of EC devices are found in [3].

The present paper presents X-ray absorption spectroscopy data of $\text{Ni}_{1-x}\text{V}_x\text{O}_y$ thin films at the Ni and V K-edges. The emphasis is on changes of the local atomic and electronic structures of Ni and V ions in transparent and ozone-coloured states of the films.

2. Experimental details and data analysis

Transparent hydrated $\text{Ni}_{1-x}\text{V}_x\text{O}_y$ thin films were deposited onto quartz and Kapton foil substrates by reactive DC magnetron sputtering from a non-magnetic Ni_{93}V_7 (wt %) target with a diameter of 5 cm. A base pressure of $\sim 4 \cdot 10^{-5}$ mTorr was reached in the deposition unit, and sputtering was carried in a mixture of $\text{Ar}/\text{O}_2/\text{H}_2$ (99.998% pure) at 35 mTorr and 200 W. The gas flows ratios were 50/2/4. Coloured films were produced by exposure during 6 minutes to ozone using a UV lamp [2].

Optical measurements were carried out on a Perkin-Elmer double-beam spectrophotometer operating at 300 to 2500 nm in wavelength.

X-ray absorption spectra of transparent and coloured thin films, and of reference compounds (crystalline $c\text{-NiO}$ and $c\text{-V}_2\text{O}_5$), were recorded at the Ni and V K-edges using synchrotron radiation from the LURE DCI storage ring. A standard transmission setup at the D21 (XAS-2) beam-line, with a Si(311) double-crystal monochromator and two ion chambers containing N_2 gas, was used. All experiments were done at room temperature with an energy resolution of 1 to 2 eV.

The X-ray absorption spectra were analysed, following standard procedures, by the EDA software package [4, 5]. The EXAFS part of the spectra was singled out by the Fourier filtering procedure and best-fitted within the multi-shell Gaussian/cumulant models using the theoretical amplitudes and phase shift functions, calculated by the FEFF8 code [6], for the two reference compounds. The E_0 position, defining the zero-photoelectron wave-number ($k = 0$), was set to provide the best match of the experimental and calculated EXAFS signals for the reference compounds. The XANES signals were analysed qualitatively by comparison of experimental spectra with the ones calculated by the FEFF8 code [6] within the full-multiple-scattering (FMS) approach. In all calculations, the complex Hedin-Lundqvist exchange-correlation potential [7] was used to account for the inelastic losses of the photoelectron, and the cluster potential was calculated self-consistently.

3. Results and discussion

Figure 1 shows the optical response of a $\sim 650\text{-nm}$ -thick $\text{Ni}_{1-x}\text{V}_x\text{O}_y$ thin film upon ozone exposure. The spectral absorbance $A(\lambda)$ was calculated from measured transmittance $T(\lambda)$ and reflectance $R(\lambda)$ as $A(\lambda) = 1 - T(\lambda) - R(\lambda)$. A huge modulation of the optical properties is observed within the solar range; it corresponds to a change of the visible colour from transparent to dark brown.

X-ray absorption spectra, measured at the Ni and V K-edges, allowed us to follow the modifications in the local electronic and atomic structures as the films were coloured in ozone.

Experimental XANES signals are shown in Fig. 2(a). At the Ni K-edge, a difference between the $c\text{-NiO}$ reference and a $\text{Ni}_{1-x}\text{V}_x\text{O}_y$ film is present in the pre-edge peak intensity and in the fine structure located above the edge. The pre-edge peak is associated with a transition from the $1s(\text{Ni})$ state to the $3d(\text{Ni})$ states mixed with the $2p(\text{O})$ states. The pre-edge intensity is smaller in the films than in $c\text{-NiO}$, as was also observed previously in pure nanocrystalline NiO films [8]. This effect was interpreted

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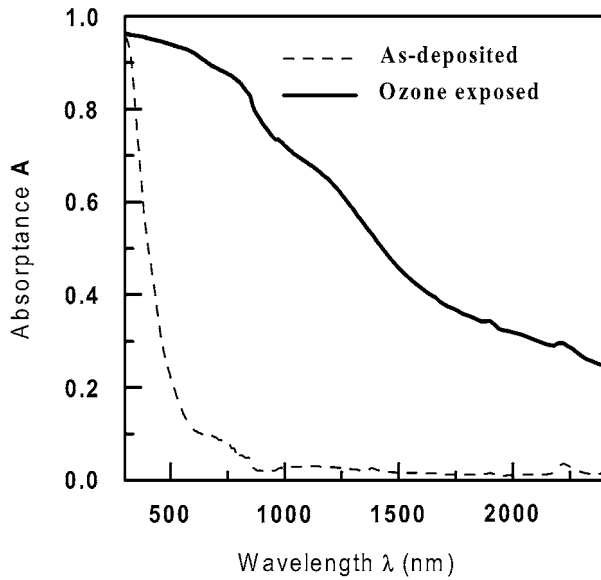


Fig. 1. Spectral absorbance within the solar range of $\text{Ni}_{1-x}\text{V}_x\text{O}_y$ thin films in the as-deposited (transparent) and ozone-exposed (coloured) states.

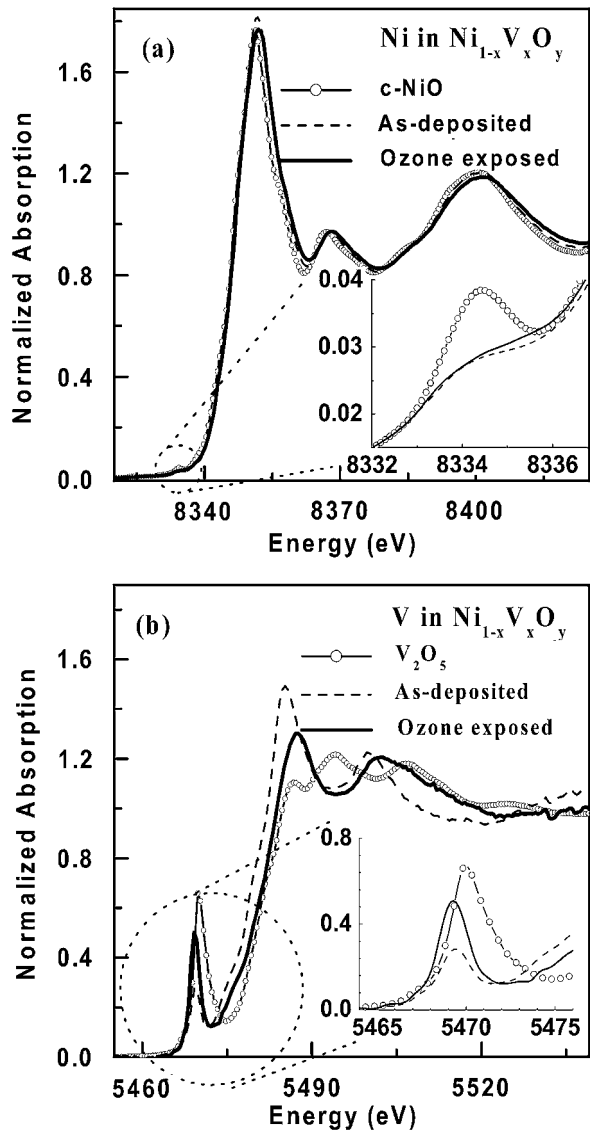


Fig. 2. Experimental XANES signals for the Ni (a) and V (b) K-edges in as-deposited (transparent) and ozone-exposed (coloured) $\text{Ni}_{1-x}\text{V}_x\text{O}_y$ thin films. XANES data for the reference compounds $c\text{-NiO}$ and $c\text{-V}_2\text{O}_5$ are shown in parts (a) and (b), respectively.

within the Zaanen-Sawatzky-Allen model [9] as being due to an increase of the oxygen-nickel charge transfer energy accompanied by a reduction of the amount of ground state configurations with holes in the $2p(\text{O})$ states. Thus a decrease of the pre-edge in the films can be associated with the fact that the Ni-O bonding becomes less covalent. It is noted that no significant change of the pre-edge peak occurs upon ozone exposure.

The V K-edge in the thin films is compared with data for $c\text{-V}_2\text{O}_5$ in Fig. 2(b). The pre-edge peak is related to the transition $1s(\text{V}) \rightarrow 3d(\text{V}) + 2p(\text{O})$. A comparison of two reference compounds, i.e. $c\text{-NiO}$ and $c\text{-V}_2\text{O}_5$, shows that the intensity of the pre-edge peak is much higher in vanadium oxide because the $3d(\text{V})$ states are more strongly mixed with $2p(\text{O})$ states due to shorter V-O bonds and lower local symmetry at the V sites. The pre-edge intensity is relatively small in a transparent film but increases strongly upon coloration. Such behaviour can be associated with the change of valence states from V^{4+} to V^{5+} [10]. Our preliminary FMS calculations suggest that this process is accompanied by an increase of the local distortion, responsible for a modification of fine structure located above the V edge.

Figure 3 shows Fourier transforms (FTs) of the EXAFS signals for the Ni and V K-edges. A comparison of the FT signals for the films and for $c\text{-NiO}$ allows to conclude that the films have a nanocrystalline structure; specifically, the peak amplitudes decrease more for the outer shell due to the

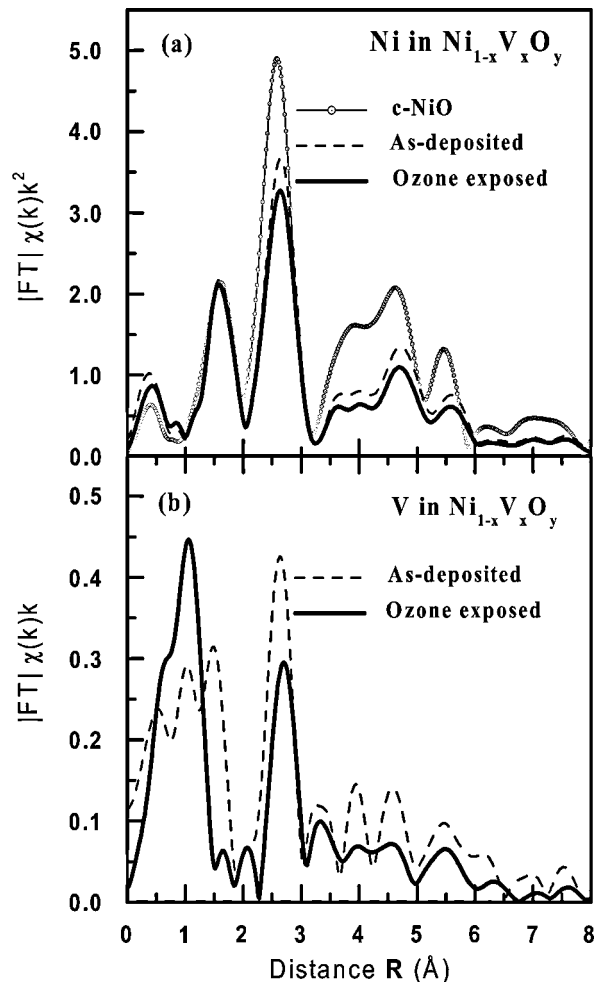


Fig. 3. Fourier transform (FT) moduli of EXAFS signals at the Ni (a) and V (b) K-edges in $c\text{-NiO}$ (part a) and $\text{Ni}_{1-x}\text{V}_x\text{O}_y$ thin films in the as-deposited (transparent) and ozone-exposed (coloured) states.

size effect [8, 11]. The first peak at 1–1.5 Å corresponds to the first coordination shell of Ni/V ions, composed of six oxygen atoms. The second peak at about 2.5–2.7 Å is due to three contributions: (i) nickel (Ni₂) atoms in the second shell; (ii) oxygen (O₃) atoms in the third shell; (iii) two double-scattering signals, generated within the 90°-triangular paths as $M_0 \rightarrow O_1 \rightarrow O_1 \rightarrow M_0$ and $M_0 \rightarrow O_1 \rightarrow Ni_2 \rightarrow M_0$ where M_0 is the Ni₀ or V₀ central/absorbing atom. Our multi-shell fitting procedure of the Ni K-edge EXAFS signals suggests that, on average, the film structure resembles that of *c*-NiO. However, some relaxation of the first coordination shell of the Ni ions, comprising six oxygen atoms, occurs in the films and leads to a decrease of the mean Ni-O distance by ~0.02 to 0.04 Å. At the same time, the second shell Ni-Ni distance increases by ~0.01 to 0.02 Å. The difference between the two films is mainly related to some increase of the disorder in the coloured film, which is probed by the Debye-Waller factor and resulted in a relative decrease of the peaks for the outer shells in the FT. The nanocrystallite size was estimated roughly by an approach proposed before [8]; it is based on the model of Ref. [11] and gave a nanocrystal diameter of ~10 Å.

The analysis of the V K-edge EXAFS signals suggests that V ions substitute Ni ions in the NiO-type structure and are distributed without any evidence for clustering. This conclusion is derived from the comparison of the experimental V K-edge EXAFS signals with the theoretical ones, calculated by the FEFF8 code for the V ion(s) placed at the Ni ions sites in NiO structure. Our best-fit modelling suggests no presence of vanadium ions in the second coordination shell of vanadium, but indicates clearly the vanadium first shell modification upon coloration. In transparent films, V ions are located at the centre of oxygen octahedra, whereas they shift to off-centre positions upon coloration. The displacement is ~0.4 Å in the [100] direction towards the nearest oxygen atom. Thus, V ions introduce a significant degree of disorder into the NiO-type structure of coloured thin films.

4. Conclusions

X-ray absorption spectroscopy at the Ni and V K-edges allowed us to reconstruct the local electronic and atomic structures of nickel vanadium oxide thin films in transparent and coloured states. We found that, while the main contribution to the optical properties of the films ensues from the Ni sublattice, the V ions are strongly affected by an ozone treatment.

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