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Band gap states in nanocrystalline WO₃ thin films studied by soft x-ray spectroscopy and optical spectrophotometry

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Abstract

Nanocrystalline tungsten trioxide (WO₃) thin films prepared by DC magnetron sputtering have been studied using soft x-ray spectroscopy and optical spectrophotometry. Resonant inelastic x-ray scattering (RIXS) measurements reveal band gap states in sub-stoichiometric γ -WO_{3-x} with $x = 0.001$ - 0.005 . The energy positions of these states are in good agreement with recently reported density functional calculations. The results were compared with optical absorption measurements in the near infrared spectral region. An optical absorption peak at 0.74 eV is assigned to intervalence transfer of polarons between W sites. A less prominent peak at energies between 0.96 and 1.16 eV is assigned to electron excitation of oxygen vacancies. The latter results are supported by RIXS measurements, where an energy loss in this energy range was observed, and this suggests that electron transfer processes involving transitions from oxygen vacancy states can be observed in RIXS. Our results have implications for the interpretation of optical properties of WO₃, and the optical transitions close to the band gap, which are important in photocatalytic and photoelectrochemical applications.

1. Introduction

The interest in nanoporous tungsten trioxide (WO_3) is based on its many important technological applications, including electrochromics, photocatalysis, light emitting devices and sensors [1, 2]. Of particular interest is the influence of oxygen vacancies on its electronic and optical properties. Sub-stoichiometric WO_{3-x} can exhibit localized states in the band gap and significantly different optical and electrical transport properties as compared to stoichiometric WO_3 [1]. Experimental evidence for the existence of band gap states has been observed from optical absorption due to polarons [3, 4], and photoluminescence [5, 6]. Hence the existence of band gap states in WO_{3-x} is known, but the origin and the implications of them for the optical properties are still not fully understood. Results from studies of light emission and the chemical activity of band gap states also highlight the necessity of a detailed characterization [7-9]. Various models for band gap states in WO_3 have been proposed, but even the position of the O vacancy levels is still controversial [10, 11].

WO_3 is composed of corner sharing octahedral units. Different WO_3 phases owe their properties to the tilt and distortion of the octahedral units [11, 12]. WO_3 exhibits a number of different phases close to room temperature at standard pressures, and variations in phase composition complicate experimental work. We have previously shown that DC magnetron sputtered films are composed of the monoclinic $\gamma\text{-WO}_3$ phase (space group $P2_1/n$) together with small amounts of the monoclinic $\epsilon\text{-WO}_3$ (space group Pc), both shown in Figure 1, with varying oxygen vacancy concentration depending on deposition conditions [9]. Recent density functional theory (DFT) calculations show that the electronic structure of the different WO_3 phases is a result of varying W-O bond lengths along the x , y , and z directions in the crystal, with resulting bonding-antibonding orbital interactions, which give rise to (mainly) hybridized $W5d$ and $O2p$ conduction and valence band states, respectively [10, 11, 13, 14]. It has been predicted that for the monoclinic Pc and $P2_1/n$ phases W-O bond splitting occurs in all directions, and gives rise to an increased band gap compared to other phases [11]. The character and positions of the hybridized $W5d$ and $O2p$ states, which have e_g , t_{2g} and $t_{1g} + t_{2u}$ symmetry, are critically dependent on the orbital overlaps, which are different for the x , y and z directions in the monoclinic phases, and determine the formal charge on the W and O atoms [10, 11]. These properties hence imply that WO_3 is not a d_0 material with purely ionic W^{6+} and O^{2-} ions.

Figure 1 Polyhedral ball-and-stick model [15] of the (a) low temperature monoclinic ϵ - WO_3 phase with unit cell volume $V = 208.7 \text{ \AA}^3$ (drawn with solid lines) where $a = 5.277 \text{ \AA}$, $b = 5.159 \text{ \AA}$, and $c = 7.669 \text{ \AA}$, $\alpha = \gamma = 90^\circ$ and $\beta = 91.7^\circ$ [16] and (b) room temperature monoclinic γ - WO_3 phase with unit cell volume $V = 423.2 \text{ \AA}^3$ where $a = 7.301 \text{ \AA}$, $b = 7.539 \text{ \AA}$, and $c = 7.689 \text{ \AA}$, $\alpha = \gamma = 90^\circ$ and $\beta = 90.9^\circ$ [12].

When an O atom is removed from the WO_3 structure it results in two excess electrons. They can be paired up in a singlet (closed shell) spin state, or an unpaired triplet spin state. In addition one or both of the electrons can be transferred to nearby W atoms, thereby creating W^{5+} and $\text{W}^{5+} - \text{W}^{5+}$ centres, respectively. Introduction of an O vacancy increases the W-W distance across the O vacancy site, and modifies the W-O bond splitting, as discussed above, and leads to a reduced band gap for γ - WO_3 . [10, 11] It has been predicted that the low vacancy formation energy found in the monoclinic phases should favour O vacancy formation in these crystal phases [11]. In particular, stabilization of polaron and bipolarons in γ - WO_3 , related to the W^{5+} and $\text{W}^{5+} - \text{W}^{5+}$ centers, respectively, has been inferred [17, 18], while W^{4+} is calculated to be energetically unfavorable [18]. Wang et al. [10] and Chatten et al. [11] studied the effect of oxygen vacancies in several crystal phase structures of WO_3 . In both these studies it was inferred that the electronic properties of WO_{3-x} , such as band gap and band width was anisotropic and sensitive to small concentrations of O vacancies. It is difficult to prepare perfectly stoichiometric WO_3 samples, and most fabricated WO_3 thin films have a slight sub-stoichiometry due to O vacancies. It is therefore expected that O vacancies play a crucial role when interpreting their physicochemical properties. For example, optical properties are sensitive to small amounts of O vacancies and lattice distortions, which may be induced with high energy electron or photon beams.

In a previous study we found that WO_3 thin films produced by sputtering at 30 mTorr were photocatalytically active when irradiated with light around ≈ 2.7 eV (458 nm), which is well below the energy for the direct optical band gap excitation at $E_g \sim 3.1$ eV [9]. However, reported values of E_g in WO_3 vary and are spread over a wide range from 2.6 to 3.3 eV, which is expected to depend on both materials synthesis method and experimental techniques used to assess E_g [19-23].

Photon interactions with localized electrons are often described in terms of low-energy *d-d* and charge transfer excitations [24, 25]. Several models have been introduced over the years to explain optical absorption due to sub-stoichiometry, or excess electrons introduced by doping, e.g. by intercalation with H and Li in WO_3 thin films. In the polaron absorption models one considers the transition of an electron from one W^{5+} to a neighboring W^{6+} site after absorption of a photon [4, 26]. Schirmer and Salje have in a series of papers, employing electron spin resonance measurements, reported on the formation of “intermediate” polarons with extension beyond nearest neighbor lattice sites [26] and bipolarons [27] in the low-temperature ε - phase of crystalline WO_{3-x} , and their light-induced dissociation. The “intermediate” polaron was shown to exhibit optical absorption at 0.71 eV, and the bipolaron at approximately 1.1 eV. The bipolaron model has recently received additional support from DFT calculations by Bondarenko et al. [18], which found bipolaronic states, associated with W^{5+} - W^{5+} centers, to be localized in the band gap about 1 eV below the conduction band. A different model for optical absorption in defective WO_3 has been proposed by Deb [28], who introduced the O vacancy model and optical transitions involving electrons localized at O vacancies. According to Deb, the associated defect levels are expected to be located in the valence band when they are occupied by two electrons, in the band gap when one electron is left at the vacancy, and in the conduction band when both electrons are removed from the vacancy. In Wang’s vacancy model [10], all optical and thermal transition energy levels involving oxygen vacancies are situated in the band gap. Wang et al [10] used hybrid functional DFT calculations to describe the electronic localization and lattice distortion due to O vacancies in sub-stoichiometric $\gamma\text{-WO}_3$. In qualitative agreement with Chatten et al. [11], they found O vacancy induced states below the Fermi level in $\gamma\text{-WO}_{3-x}$, which were strongly dependent on crystal direction and O vacancy concentration. At low defect concentrations ($x = 0.06$ in WO_{3-x}) the optical transition energies between different charge states of the vacancies were found to be between 0.7 and 1.0 eV. This model considers the transition of an electron from the oxygen vacancy (V_O^0) to a neighboring W^{6+} , thus forming a W^{5+} center, or a transition of two electrons to form a bipolaronic W^{5+} - W^{5+} center. In contrast to the optical transition levels, relevant in e.g. photoluminescence, thermally equilibrated excitation levels were found to be situated approximately between 0.1 and 0.25 eV below the conduction band minimum depending on choice of hybrid functional. There is a strong coupling between the polaron and oxygen vacancy models, and it may be very difficult to distinguish between

them. It is likely that the charge distribution associated with the O vacancy is spread over both the vacancy site and neighboring W site(s) [10].

X-ray spectroscopy techniques provide means to explore the valence and conduction band structure in detail. With tunable light sources available at synchrotron beam-lines they provide means to selectively probe symmetry and energy selected portions of the band structure [14, 29-31]. For example, in x-ray emission spectroscopy (XES) the total density of (filled) valence band states can be probed, and in x-ray absorption spectroscopy (XAS) the density of (empty) conduction band states is probed. With resonant inelastic x-ray scattering spectroscopy (RIXS) the optical allowed transitions subject to simultaneous momentum and energy conservation are probed, and can be employed for sensitive symmetry selective valence band mapping [14, 32, 33]. Previous studies show that combined x-ray absorption and emission spectroscopy offers means to extract information about the electronic bands in semiconductors, which favorably can be used to compare with theoretical calculations [14, 31, 34].

In this paper we present an experimental study of the electronic states in DC magnetron sputtered γ -WO₃ thin films with varying O vacancy concentrations ($x \approx 0.001$ and $x \approx 0.005$)[35], with the purpose of describing O vacancy induced band gap states and their optical properties. We have previously shown that the O vacancy concentration in γ -WO₃ thin films is manifested by absorption in the near infrared region, an optical band gap of ~ 3.1 eV [13], and a pronounced absorption tail characterized by a demarcation energy at ~ 2.8 eV [9]. Samples used in this study were sputtered with the same parameters as in our previous studies, and we refer to those for a detailed description of the physical properties of the films [9, 13]. The WO₃ films are here examined with RIXS, XES, and XAS.

2. Materials and methods

2.1. Sample preparation and characterization

Tungsten oxide (WO₃) thin films were deposited on CaF₂ substrates (Crystran Ltd, Pole, UK) by reactive DC magnetron sputtering using a versatile deposition system based on a Balzers UTT 400 unit. The CaF₂ substrates were cleaned with deionized water and ethanol before sputtering. The sputter target was a 5 cm diameter plate of tungsten with 99.95 % purity (Plasmaterials Inc., Livermore, USA). Sputtering was conducted in Ar and O₂ plasma employing a power of 200 W. The purity of the gases was 99.998 %. The O₂/Ar gas pressure ratio was kept constant at 0.43, and the samples were sputtered at a substrate temperature of $T_s = 553$ K, and post-annealed at $T_a = 673$ K for 1 h ex situ to further improve the crystallinity of the samples. Structural analysis with grazing incidence x-ray diffraction (XRD) showed a typical room temperature monoclinic γ - phase pattern [12] after post-annealing. Films were sputtered at working pressures of $P_{tot} = 10$ and 30 mTorr, respectively, and the

deposition rate varied as a function of the working pressure from 36 nm min⁻¹ at $P_{tot} = 10$ mTorr to 11 nm min⁻¹ at $P_{tot} = 30$ mTorr. The WO₃ films deposited on CaF₂ were highly transparent. Close inspection revealed that films prepared at $P_{tot} = 10$ mTorr (thickness $d = 800$ nm) exhibited a slight bluish color, indicating sub-stoichiometry, as confirmed by their near-infrared absorption [9]. The samples sputtered at $P_{tot} = 30$ mTorr (thickness $d = 800$ nm) were slightly yellowish and reddish, characteristic of stoichiometric, or at least close to stoichiometric, WO₃, since perfect stoichiometry is difficult to achieve. These films also showed very little near-infrared absorption [9]. The O vacancy concentrations have been estimated from cyclic voltammetry measurements of trap states in films prepared in identical manner [35]. The O vacancy concentration in the film prepared at $P_{tot} = 30$ mTorr was estimated to be $x \approx 0.001$ (determined by an average over four films). This film is here for simplicity denoted stoichiometric WO₃. The film, prepared at $P_{tot} = 10$ mTorr, had about five times higher concentration of O vacancies, $x \approx 0.005$ (determined by an average over three films), and is here denoted sub-stoichiometric WO_{3-x}.

2.2. Optical absorption spectroscopy

The optical properties of the films sputtered on CaF₂ substrates were measured by spectrophotometry. The measured transmittance T and reflectance R were used to calculate the absorption coefficient α from the special absorption:[36]

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

where d is the thickness of the film. In the near-infrared range 800-2300 nm T and R were fitted to an optical oscillator model using the software Scout in order to extract optical constants.[37] Two Gaussian functions were used to fit the imaginary part of the dielectric function $\varepsilon_2(\omega)$ in the near-infrared region to determine the peak positions, widths and amplitudes, according to:

$$\varepsilon_2(\omega) = \sum_{i=1}^2 a_i e^{\left(\frac{\omega - b_i}{2c_i} \right)^2} \quad (2)$$

where a is the amplitude, b the position of the center of the peak, and c the width of the peak. The real part of the dielectric function $\varepsilon_1(\omega)$ was computed by the Kramers-Kronig relation. The thickness d of the film and the low frequency limit dielectric constant $\varepsilon_0 \sim 3.6$ was used as initial values in the Scout calculations, and the dielectric function was obtained by iterative fitting to experimental data.

2.3. X-ray absorption and resonant inelastic emission spectroscopy

The X-ray absorption spectroscopy (XAS) and resonant inelastic x-ray emission spectroscopy (RIXS) measurements were performed at beamline U41-PGM at BESSY II, Berlin, Germany [38], which delivers a flux of $\sim 10^{12} - 10^{13}$ photons s^{-1} to the focus on the sample in the excitation energy interval 170 to 1500 eV. XAS spectra were acquired by means of a photodiode recording the total fluorescence yield (TFY). RIXS spectra were acquired with a home built grazing incidence Rowland spectrometer [39]. The beamline resolution for both the XAS and RIXS O K measurements was 0.17 eV. The photon energy of the XAS spectra was calibrated to the known peaks of rock salt NiO [30]. The RIXS detector consisted of a two-dimensional microchannel plate (v-stack) detector with optical readout from a phosphor screen (Scienta). The RIXS spectrometer resolution was set to either 0.32 eV or 0.18 eV by measuring the first or second order diffraction, respectively, using a 1200 lines mm^{-1} spherical grating with radius of 5 m [39]. The energy dispersion of the emission data was determined by calibration to the literature values [40] of the Zn $L_{III,II}$ emission lines excited at 1080 eV in second and fourth order, respectively [41], and rigidly shifted using the monochromator energy calibration of the elastic peak to obtain a common energy scale with the XAS spectra. No smoothing was performed on the XAS and RIXS data unless explicitly stated.

3. Results and discussion

3.1. X-ray absorption and resonant inelastic emission spectroscopy

Figure 2 shows the normalized XAS (total fluorescent yield, TFY) and resonant inelastic x-ray scattering (RIXS) spectra (incident energy $h\nu_{inc} = 529.1$ eV) at the O1s edge (recorded in second order of diffraction) of the stoichiometric WO_3 film, and the sub-stoichiometric WO_{3-x} film. The spectra in figure 2 reflect the occupied (RIXS) and unoccupied (XAS) DOS projected on the O2p states of the valence and conduction bands, respectively.

Figure 2 High resolution O K_{α} RIXS emission and O 1s XAS total fluorescence (TFY) spectra plotted on a common energy scale for a stoichiometric WO_3 film (30 mTorr, offset along the y-axis for clarity), and a sub-stoichiometric WO_{3-x} film (10 mTorr). The RIXS spectra have been excited with monochromatized synchrotron radiation of 529.1 eV. For convenience we have plotted arrows to indicate the corresponding elastic peaks.

The RIXS spectra have five salient features where E3 is the valence band peak of the O 2p-states. At an excitation energy of 529.1 eV E3 is centered at 525.5 eV, with a pronounced broad shoulder E2 at 524.0 eV, and a weaker broad shoulder E1 at approximately 521.0 eV, in qualitative agreement with earlier work [42]. Note that the RIXS cross section is extremely low when using pre-edge excitation and therefore apparent variations between the two spectra are statistically insignificant. Previous studies on similar materials have shown that E3 is mainly due to non-bonding O 2p states of local $t_{1g} + t_{2u}$ symmetry, E2 corresponds to the π -bonding states of t_{2g} symmetry, and E1 corresponds to O2p and W5d σ -bonding states of e_g symmetry [14]. It has previously been shown that the relative intensity of the π -bonding states (associated with the E2 peak) increases when going from WO_3 to WO_2 [42]. In our case only a small decrease of the E1 peak relative to the E2 peak was observed when going from $P_{\text{tot}} = 30$ mTorr to $P_{\text{tot}} = 10$ mTorr, confirming that the difference in stoichiometry of the films is small ($x = 0.001$ and 0.005 , respectively). The peak E5 is close to the respective incident energy from the monochromator, which here is chosen to be close to the absorption threshold, and involves transitions

into vacant O 2p states that are strongly hybridized with the W5d band. At an incident energy $h\nu = 529.1$ eV a small distinct peak E4 is observed, which is more intense in the sub-stoichiometric film.

The XAS spectrum in figure 2 shows four bands between 530 and 544 eV, showing ~ 14 eV spin-orbit splitting between the $W5d_{5/2}$ and $W5d_{3/2}$ bands. The additional structures in the absorption spectrum arise from crystal field and electronic interactions, which results in a splitting of the W5d orbitals into t_{2g} and e_g symmetries. The five O K -edge features are labeled A1 = 530.5 eV, A2 = 535.6 eV, A3 = 537.2 eV, A4 = 541.0 eV and A5 = 544.3 eV. The strong absorption peak A1 is due to hybridized W5d and O2p states with anti-bonding character and has $2t_{2g}^*$ symmetry (i.e. π^*). The A2 and A3 peaks are the corresponding anti-bonding $3e_g^*$ states (i.e. σ^*), while A4 and A5 originate from mixing of W6s and 6p with O 2p states, and have $3a_{1g}$ and $4t_{1u}$ symmetry, respectively [43].

Figure 3 displays a band picture of occupied and unoccupied states of WO_3 around the valence band maxima (VBM) and conduction band minima (CBM). The red and black traces in figure 3 are the RIXS and XAS spectra from figure 2, where the XAS spectrum has been shifted 0.7 eV towards higher energy to compensate for the core-hole effect in the XAS final state, assuming the same shift as derived by B. Chen et al. [14] for single crystal WO_3 . Additionally, we display in Figure 3 RIXS spectra excited at higher energies (blue traces marked with “ii”). It is seen that the VBM shifts down as the incident energy is lowered. We interpret this as a “resonance detuning” RIXS effect where the spectrum represents a convolution of occupied and unoccupied states, and shifts to lower energy at lower excitation energy. The width of the band gap determined by the combined RIXS and XAS results is found by measuring the energy difference (double arrows) between the linearly extrapolated slopes of the valence band (VB) and conduction band (CB) band edges, respectively, to zero intensity (dashed lines in figure 3). The result shows a VBM-CBM separation of about 3.2 eV, in good agreement with our previous findings based on optical data [13].

Figure 3 Left panel: Maximum-normalized RIXS and XAS spectra of the band gap region of (a) stoichiometric and (b) substoichiometric WO_3 films. RIXS excitation energy positions (i and ii) relative to the XAS spectrum are indicated by arrows. The low (high) energy excitation RIXS spectra are drawn with red (blue) solid lines; the XAS spectra are drawn with black solid lines. The XAS spectra have been shifted 0.7 eV towards higher energy to compensate for the core-hole effect in the XAS final state. The vertical lines indicate the valence band maximum and the conduction band minimum, respectively. Right panel: zoom-in of the excitonic band gap states (E4 and E5) on an energy loss scale relative to the monochromatic energy, 529.1 eV.

By tuning to lower incident energy (529.1 eV), i.e. below the main peak threshold, we observe a relative increase of the intensity of the E4 and E5 peaks in the maximum-normalized RIXS spectra (see traces (i) in figures 2 and 3). This enhancement may be explained by a small resonance for the band gap states that is not discernible in the ordinary spectra. The right panel of figure 3 shows a zoomed-in version of this region of the RIXS spectra. It is observed that the E4 feature is situated about 1 eV from the elastic peak. The RIXS signal E5 is the elastic peak due to electrons recombining with the core hole.

Figure 4 Excitonic band gap peaks at a series of incident energies close to the absorption threshold. The black and green vertical tick marks indicate the position of the inelastic and elastic energy peak location, respectively. (Sub-) stoichiometric WO_{3-x} film spectra are shown by (blue) red solid lines. The RIXS spectra have been 3-point smoothed for clarity. Right panel: incident energy dependence (relative to the first point) of the emission energy position of the elastic peak (blue squares), the VB peaks (black diamonds), and VBM (red and blue circles). The incident energy dependence of the band gap state E4 (magenta triangles) is plotted relative to the incident energy, i.e. energy loss.

Figure 4 (top panel) explicitly shows the dependence of the intensity of the band gap states on the incident excitation energy as obtained from a series of RIXS spectra acquired in 1st order of diffraction (with lower resolution but increased statistical accuracy). Note that the peaks E4 and E5 are not resolved individually in these spectra as in the high-resolution spectra in figure 3. Nevertheless, the spectral series shows that band gap states resonate at an excitation energy (~ 529.1 eV) below the main absorption peak. Moreover, although the broad combined E4/E5-peak disperses somewhat upwards in energy, it does not follow the change of incident energy exactly (marked by the green vertical tick marks in figure 4) which proves that it is not simply the recombination peak. In the right panel of figure 4 we plot the position of several spectral features relative to the incident energy. The band gap state E4 is seen to deviate strongly from fluorescence like behavior (which would leave it stationary in

emission energy), and we therefore conclude that the E4 excitation involves localized states. The energy dependence of the VB edges and VB peaks can be understood as a resonance detuning at the lowest excitation energy. Above 529.1 eV they reach a threshold consistent with the flat dispersion of the VB and CB bands predicted by calculations [11, 13].

To summarize this section, we attribute the E4 RIXS feature to localized band gap states situated about 1 eV below the conduction band. Most likely, these states originate from oxygen vacancy levels. Hybrid functional calculations by Wang et al. [10] predict an energy for the oxygen vacancy states that is very similar to our observation. However, this value is also close to the position of the bipolaronic $W^{5+}-W^{5+}$ localized levels found by Bondarenko et al. [18]. This will be discussed in more detail below in conjunction to our results from optical spectroscopy.

3.2. Optical spectroscopy

Figure 5a shows the optical absorption coefficient, α , for sub-stoichiometric WO_{3-x} and stoichiometric WO_3 films obtained from transmittance and reflectance spectrophotometry measurements. The optical absorption edge is located at approximately 450 nm, with a small absorption in the visible range, a so called Urbach tail [44], extending between 450 and 800 nm. However, it is difficult to observe differences in the strength of the band tail absorption between sub-stoichiometric and almost stoichiometric films, because of the presence of interference fringes, which are pronounced at low values of the absorption coefficient. A further complication is that the absorption strength in the visible range varies somewhat between different batches of samples, which are otherwise produced at the same experimental conditions, and thus makes inter-sample comparisons difficult. The absorption close to the band edge might be associated with the asymmetry of the elastic peak E5 in the RIXS measurement, as seen in the right panel of figure 3, but due to these experimental uncertainties we cannot unambiguously attribute it to a variation of band tail absorption originating from differences in O vacancy concentrations. We note, however, that in our previous photoluminescence spectroscopy experiments [6], an emission peak was observed ~ 0.25 eV below CBM.

The broad absorption band between 1000 and 1800 nm can be due to either polaron absorption [3, 17], or transitions involving oxygen vacancy states. Figure 5b shows the imaginary part of the dielectric function, ϵ_2 , which has been fitted to the measured absorption in the near infrared range using two Gaussian functions, see section IIB. The main peak, P1, stays at approximately the same energy (0.74 eV) regardless of sputtering pressure, whereas the P1 amplitude decreases by a factor of approximately 4 going from the sub-stoichiometric to the almost stoichiometric film. The position of P1 is close to the polaron absorption peak (optical transitions due to $W^{5+} \rightarrow W^{6+}$ intervalence transfer) observed in

previous work [17], and it is probable that it has a similar origin. However, in order to create a W^{5+} site, an electron has to be excited from an oxygen vacancy, leaving the vacancy in the triplet state. Hence we suggest that an electron is excited from an oxygen vacancy to a W site, which then becomes a W^{5+} site. Subsequently polaron absorption by intervalence transfer between tungsten sites can then take place. It appears that these two processes can occur at similar energies. The $V_O^0 \rightarrow V_O^+$ transition was found to be at 0.73 eV in the calculations by Wang et al. employing B3LYP functionals [10]. In the polaron picture the optical excitation takes place between states localized on W sites, “thermalized” by the electron-phonon interaction. On time scales longer than a lattice vibration they are to be found at about 0.18 eV ($= 0.74/4$ eV) below the CB minimum [3]. As noted above it may be difficult to distinguish the polaron and oxygen vacancy mechanisms, and the charge distribution may also be spread over the vacancy and tungsten atom sites.

Figure 5 a) Absorption coefficient, α , of WO_3 films sputtered at $P_{tot} = 10$ mTorr $d = 800$ nm and 30 mTorr, $d = 800$ nm on CaF_2 substrates b) Dielectric function ϵ_2 in the near-infrared energy range 0.5 - 1.5 eV obtained from experimental data. The dashed curves show the deconvoluted spectra using two Gaussian functions P1 and P2.

The high energy peak P2 in Figure 5b shifts from 0.96 eV to 1.16 eV as the sputter pressure increases from $P_{tot} = 10$ to 30 mTorr, while the P2 amplitude decreases as a function of P_{tot} . The P2 peak appears at approximately the same value as the E4 energy loss in figure 3 with an almost identical shift as a function of P_{tot} ($E = 0.92$ and 1.10 eV for the 10 and 30 mTorr films, respectively). The origin of the E4 peak and the P2 peak is thus probably the same. In a recent study by Wang et al. [10] the transition energy levels between different O vacancy charge states (V_O^0, V_O^{1+} , and V_O^{2+}) were calculated by hybrid functional DFT methods. The transition energy levels calculated with the B3LYP functional were found to be 0.73 eV ($V_O^0 \rightarrow V_O^{1+}$), 0.99 eV ($V_O^{1+} \rightarrow V_O^{2+}$) and 0.86 eV ($V_O^0 \rightarrow V_O^{2+}$) below the CBM, in which case the band gap was calculated to be $E_g = 3.1$ eV. With the HF15LYP functional, E_g

= 2.72 eV, and the transition levels were calculated to be located 0.52 to 0.76 eV below CBM. It should be noted that the computed energies for the $V_O^0 \rightarrow V_O^+$ transition were consistently found to occur at lower energies than transitions to the V_O^{2+} state. Thus with E_g in the range of experimental data, these results suggest that the emission peak E4 shown in figure 3, and the small absorption peak in the NIR range shown in figure 5b, can be attributed to optical excitation of an O vacancy level, most probably involving the V_O^{2+} one, situated approximately 1 eV below the CBM. It should also be noted that the bipolaronic states found in other DFT calculations [18] also fall in this energy range. The shift of the P2 peak may in this picture be attributed to a concentration dependent energy shift of O vacancy sites, as P_{tot} increases, i.e. as we go from a sub-stoichiometric to a more stoichiometric film.

4. Conclusion

Band gap states in sub-stoichiometric WO_{3-x} thin films have been studied by RIXS, XAS and optical spectroscopy. The RIXS spectra clearly show a gap state situated about 1 eV below the conduction band. This is interpreted as the ground state of oxygen vacancies, in agreement with recent DFT calculations [11, 18]. The optical absorption in the NIR range consists of two contributions, where one peak position is constant at 0.74 eV regardless of sputter pressure. The other peak is shifted as a function of pressure during deposition from 0.96 eV at 10 mTorr to 1.16 eV at 30 mTorr. The peak at 0.74 eV is assigned to intervalence transfer of polarons between neighboring W sites and/or excitation of the oxygen vacancy to a triplet state. The high energy peak at around 1 eV is very similar to the energy position of the peak in the RIXS spectra corresponding to oxygen vacancy states in the band gap, and is attributed to optical transitions to the singlet state of the oxygen vacancy, possibly combined with bipolaronic absorption due to transitions between $W^{5+} - W^{5+}$ centers. In these processes, an electron transfer occurs from an oxygen vacancy state to neighboring W atoms in the optical absorption experiment and to a core hole in the RIXS experiment. RIXS band mapping further indicates flat dispersion of the VB and CB bands in agreement with calculations. The electronic structure of γ - WO_3 is very sensitive to small additions of vacancies, which give rise to concomitant pronounced changes in optical properties. Localized states due to vacancies and polarons may act as recombination centres and seriously decrease photocatalytic efficiency. It is concluded that the WO_3 thin film has to be highly stoichiometric to avoid recombination centres, which is important knowledge for photocatalytic and photoelectrochemical applications.

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