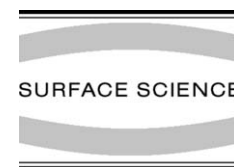


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An XPS study on the surface reduction of $V_2O_5(001)$ induced by Ar^+ ion bombardment

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Abstract

The effect of the irradiation with Al $K\alpha$ X-rays during an XPS measurement upon the surface vanadium oxidation state of a fresh in vacuum cleaved $V_2O_5(001)$ crystal was examined. Afterwards, the surface reduction of the $V_2O_5(001)$ surface under Ar^+ bombardment was studied. The degree of reduction of the vanadium oxide was determined by means of a combined analysis of the O1s and V2p photoelectron lines. Asymmetric line shapes were needed to fit the $V^{3+}2p$ photolines, due to the metallic character of V_2O_3 at ambient temperature. Under Ar^+ bombardment, the $V_2O_5(001)$ crystal surface reduces rather fast towards the V_2O_3 stoichiometry, after which a much slower reduction of the vanadium oxide occurs.

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Keywords: Vanadium oxide; $V_2O_5(001)$; X-ray photoelectron spectroscopy (XPS); V2p photoelectron core level; XPS analysis; Vanadium oxidation state

1. Introduction

Surface oxidation states are commonly studied with X-ray photoelectron spectroscopy (XPS), as the binding energy (BE) of core lines shifts to higher values with increasing oxidation state of the cation. For XPS on vanadium oxides, the V2p doublet is the most suited photoline. The chemical shift of the V2p binding energy (BE) in photoemission spectroscopy permits to determine the mean oxidation state after curve fitting of the V2p signal, if the BE values for the different V-oxidation states are known. Reported literature BE values for the different vanadium oxidation states show a considerable scatter which complicates an accurate determination ([1] + references therein). Different binding energy corrections, samples and sample preparations, measuring equipment and analysis procedures enhance the spread on the reported literature V2p binding energy values.

These effects can be minimised by studying one sample of which the mean oxidation state is varied by ion bombardment. Indeed, the surface composition of a solid can be altered by ion bombardment due to the preferential sputtering of atoms with the lowest mass. This effect has been shown for oxides like MoO_3 , Nb_2O_5 , TiO_2 , V_2O_5 and Ta_2O_5 for example, where the preferential sputtering of the oxygen atoms causes a surface reduction. A review on this topic is given in [2]. Recently we have shown that the V2p BE positions for the V^{5+} , V^{4+} and V^{3+} oxidation states can be determined by studying a pressed V_2O_3 pellet under an Ar^+ bombardment [1].

The interaction of the X-rays with the oxide surface during an XPS measurement can cause photoreduction. The reducing effect of the Al $K\alpha$ X-rays on the vanadium oxidation state of a fresh in vacuum cleaved $V_2O_5(001)$ crystal is therefore determined beforehand in Section 3.1. In order to test the transferability of the V2p fit parameters from [1], derived mostly on a V_2O_3 powder pellet, to other vanadium oxide systems, a $V_2O_5(001)$ single crystal sample was used in this work. Spectra with a different degree of reduction were obtained by Ar^+ bombardment of the $V_2O_5(001)$ surface

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due to the preferential sputtering of the oxygen atoms and are discussed in Section 3.2. Analysis of the set of XPS spectra confirms the transferability of the V2p fit parameters reported in [1]. However, asymmetric line shapes for the $V^{3+}2p$ core line proved necessary. Moreover, the asymmetric line shape for the $V^{3+}2p$ photoline is supported by re-analysis of representative $V^{3+}2p$ spectra from [1].

2. Experimental

All XPS measurements were performed on one V_2O_5 single crystal sample, grown in the laboratory [3]. The V_2O_5 crystal was cleaved in vacuum parallel to the (001) plane, the pressure in the preparation chamber during the cleavage was in the 10^{-6} Pa range.

The XPS measurements were recorded with a Perkin Elmer Phi ESCA 5500 system equipped with a monochromated 450 W Al $K\alpha$ source. Experiments were recorded with an angular acceptance of $\pm 7^\circ$ and a source power of 220 W. The angle between the specimen surface and the analyser axis was 45° . Wide scan spectra were measured over a binding energy range of 0–1400 eV with a pass energy of 187.85 eV. The O1s and V2p core levels were recorded with a step of 0.05 eV and a pass energy of 11.75 eV, unless otherwise stated. The O1s and V2p signals were measured simultaneously in one energy window. The Ar^+ bombardment on the V_2O_5 crystal was performed with an ion current of ~ 100 nA rastered over an area of 2×2 mm². The ion beam had an energy of 2.5 keV and made an angle of 60° with the sample surface. The total sputter time was 4500 s divided in 24 intervals, in between which the O1s and V2p XPS signals were recorded. The XPS spectra were taken without charge-up compensation. The base pressure of the ESCA system was below 1×10^{-6} Pa.

The procedure described in [1] was followed to analyse the O1s and V2p XPS photolines. In brief, the O1s region is included in the binding energy range used for determining the Shirley background underneath the V2p region. The O1s core level taken at 530.0 eV is used as an internal binding energy (BE) reference, the binding energy of the $V2p_{3/2}$ core level for each vanadium oxidation state is fixed relative to the O1s level and the $V2p_{3/2}$ and $V2p_{1/2}$ signal areas are restricted to a 2:1 ratio. The XPS data analysis was performed with the XPSPeak4.1 program [4]. This program uses an asymmetric Lorentzian–Gaussian sum function to fit the photolines, the L–G parameter indicates the Lorentzian character in percentage and the asymmetric tail is controlled by the so called TS and TL parameters [4, manual]. Symmetric line shapes were used, unless otherwise stated.

3. Results and discussion

3.1. Fresh in vacuum cleaved $V_2O_5(001)$

The wide scan spectrum taken on the $V_2O_5(001)$ surface after cleavage in vacuum and transfer to the main chamber

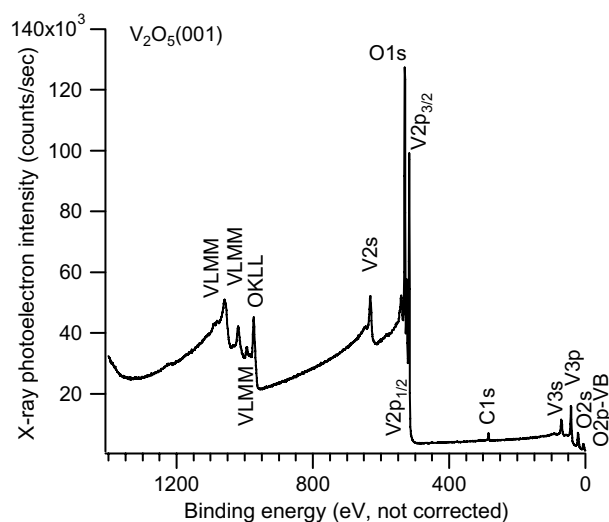


Fig. 1. Wide scan XPS spectrum of the in vacuum cleaved $V_2O_5(001)$.

is given in Fig. 1. The in vacuum cleavage resulted in a clean surface, although a small C1s signal is present with a corresponding atomic concentration of 6%. The C1s intensity is strongly reduced compared to a cleavage in air [1].

The irradiation of the $V_2O_5(001)$ surface with the Al $K\alpha$ X-rays during an XPS measurement can induce photoreduction. In order to study this effect 2 min XPS scans on the O1s and V2p region were taken as function of the irradiation time, up to a total time of 880 min. To enhance the signal to noise ratio, these spectra were taken with a higher pass energy of 23.5 eV for the electron analyzer. With increasing irradiation time, a small contribution grows at the base of the low energy side of the $V2p_{3/2}$ peak. The position of this contribution corresponds to the location of V^{4+} in the $V2p_{3/2}$ photoline. The peak decomposition of the O1s–V2p XPS region for the first (fresh surface) and the last spectrum (after 880 min irradiation time) is given in Fig. 2, the fit parameters were taken from [1]. The $V^{5+}2p_{3/2}$ peak has a small full width at half maximum (FWHM) of about 1.0–1.1 eV, the $V^{5+}2p_{1/2}$ peak has a larger FWHM, 2.6 eV, due to the Coster–Kronig effect. The first spectrum shows a single V^{5+} contribution for the V2p spectrum, while the spectrum after 880 min has about 5% V^{4+} . The evolution of the contribution of V^{4+} to the total V2p signal for a set of irradiation times is given in Fig. 3. The percentage of V^{4+} increases with increasing irradiation time, but seems to level off from 640 min on. For the study of the Ar^+ bombardment on the $V_2O_5(001)$ surface, the measuring time of the O1s and V2p XPS spectra was 120 min. From Fig. 3, the effect of the photoreduction is then only a few percent and is therefore further neglected in this study.

3.2. Ar^+ bombardment of the $V_2O_5(001)$ surface

The O1s and V2p XPS spectra on the $V_2O_5(001)$ as function of Ar^+ bombardment time are given in Fig. 4.

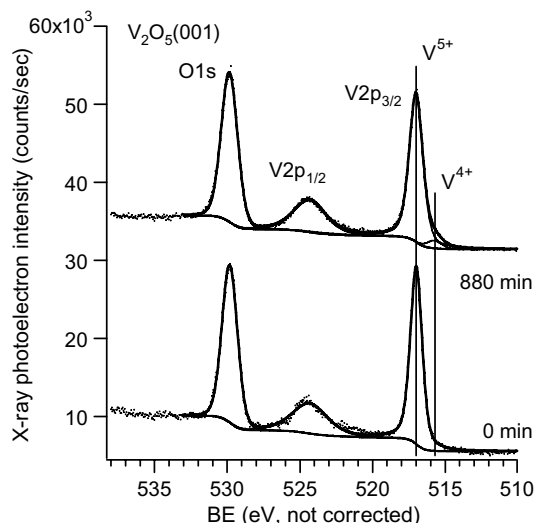


Fig. 2. Peak decomposition of the O1s and V2p XPS spectra (2 min scans), recorded after 0 and 880 min irradiation time with the monochromatic Al K α X-rays. Spectra are vertically shifted for clarity.

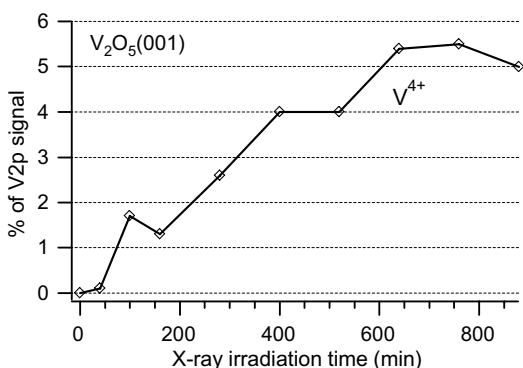


Fig. 3. Evolution of the V⁴⁺ contribution to the total V2p signal as function of the Al K α irradiation time.

With increasing bombardment time, the V2p doublet shifts to lower binding energies and becomes broader. As lower vanadium oxidation states have lower binding energies and broader V2p lines ([1] and references therein), this effect shows the reduction of the V₂O₅(001) surface by preferential sputtering of oxygen due to the Ar⁺ bombardment. From 174 s on metallic vanadium starts to appear. The photoelectron intensity in the energy region between the V2p_{1/2} and O1s increases with increasing sputter time accompanied by a growing asymmetry at the high BE side of the O1s peak. These contributions arise from V2p_{3/2} and V2p_{1/2} satellite peaks, respectively [1,5]. Because the spectra in between the ion bombardment cycles were recorded without charge-up compensation, the BE scale for each spectrum is referenced to the O1s (V–O) line taken at 530.0 eV [1,6]. The BE correction needed for each spectrum is given in Fig. 5 and varies monotonically with increasing bombardment time. From about 200 s on, the BE correction levels off to a value of about –0.6 eV.

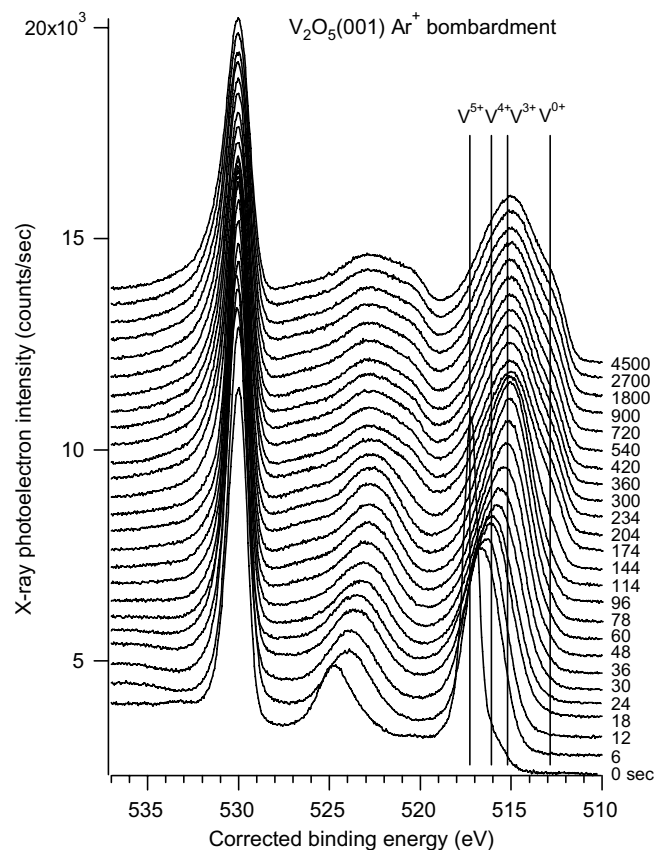


Fig. 4. O1s and V2p XPS spectra from the in vacuum cleaved V₂O₅(001) surface as function of Ar⁺ bombardment time. The numbers at the right are the total bombardment times in seconds when each spectrum was started. The vertical lines indicate the positions of the different vanadium oxidation states in the V2p_{3/2} signal. (The BE scale is referenced to the O1s (V–O) signal taken at 530.0 eV.) Spectra are vertically shifted for clarity.

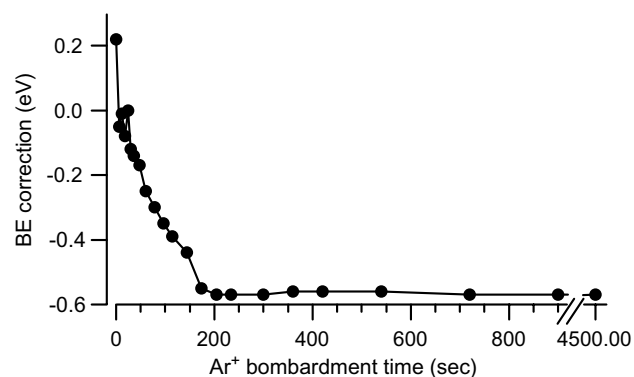


Fig. 5. Binding energy scale correction as function of the Ar⁺ bombardment time needed to align the O1s (V–O) signal to the value of 530.0 eV, used as internal energy reference.

In order to calculate the mean vanadium valence during the Ar⁺ bombardment, all XPS spectra were fitted to obtain the relative contributions for the different vanadium oxidation states present in the spectra. A selection of spectra with fit are presented in Fig. 6. Values for the V2p fit parameters for the different vanadium oxidation states

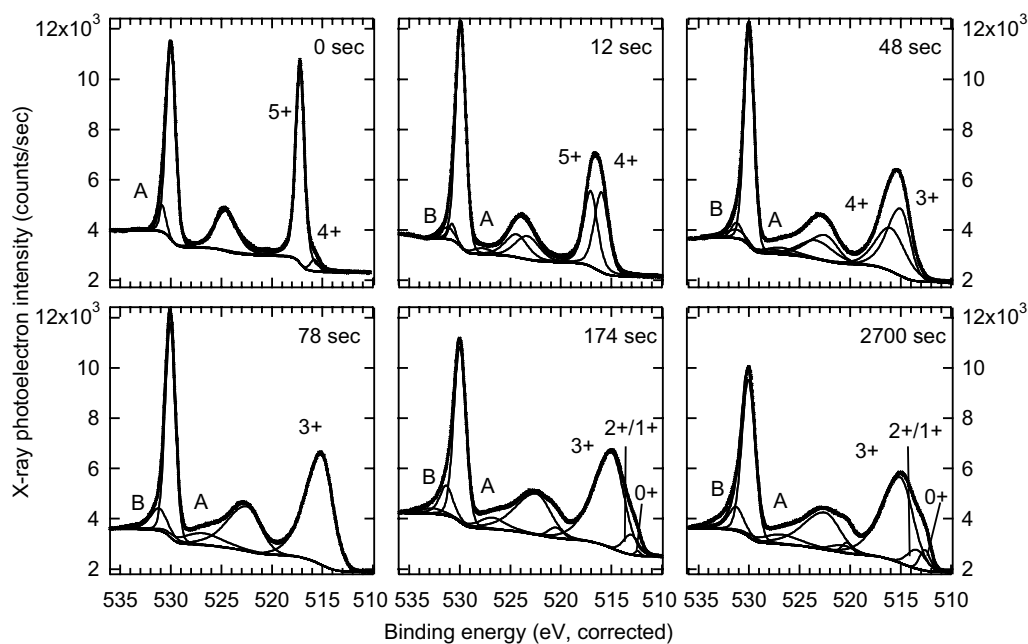


Fig. 6. Example fits on the O1s and V2p XPS spectra for the $V_2O_5(001)$ after different Ar^+ bombardment times. The corresponding oxidation states are indicated. The A and B components are the $V2p_{3/2}$ and $V2p_{1/2}$ satellite structures respectively (BE values are relative to the O1s (V–O) signal taken at 530.0 eV).

(V^{5+} – V^{0+}) were already determined in our previous work [1]. Nevertheless, from the set of spectra in Fig. 4 the fit parameters for the V^{5+} and V^{4+} vanadium oxidation states in the V2p doublet (V2p spin–orbit splitting, L–G character, BE position) were re-determined independently from the previous study [1]. The fit parameters for the V^{5+} and V^{4+} vanadium oxidation states in the V2p doublet are identical with our results previously reported in [1]. Example fits with the V^{5+} and V^{4+} components are given in Fig. 6 (0 and 12 s). The V^{5+} component vanishes from 30 s bombardment time on. The $V^{5+}2p_{3/2}$ photoline is a narrow peak, but the FWHM for the vanadium oxidation states lower than V^{5+} are larger, due to multiplet effects [5]. The FWHM for the $V^{5+}2p_{3/2}$ increases with increasing bombardment time, up to 2.6 eV for 24 s. The FWHM for the $V^{4+}2p_{3/2}$ line starts at 1.6 eV for the 12 and 24 s bombardment time and increases with bombardment time up to 3.8 eV for 60 s.

The spectra after 78 and 96 s bombardment time (Fig. 6, 78 s) are representative for the V^{3+} oxidation state. Although these spectra could be fitted with the V^{3+} parameters from [1], a better fit is obtained with an asymmetric $V^{3+}2p$ doublet. Moreover, the fit on the two spectra that served in [1] to determine the V^{3+} fit parameters are also better reproduced with an asymmetric peak shape for the $V^{3+}2p$ photoline. The fits with a symmetric and an asymmetric $V^{3+}2p$ line shape for the V_2O_3 -48 s spectrum from [1] and the $V_2O_5(001)$ -96 s are given in Fig. 7. The FWHM for the $V^{3+}2p_{3/2}$ photolines are 3.1 and 3.2 eV in the symmetric fits, 3.2 and 3.3 eV in the asymmetric fits for $V_2O_5(001)$ -96 s and V_2O_3 -48 s, respectively. The symmetric peaks do not reproduce well the top position and the sides

of the $V2p_{3/2}$. The fit models with an asymmetric line shape were statistically compared with the symmetric model using an *F*-test and are significantly better than the fits with symmetric peaks, with a significance level higher than 99%. Asymmetric peak shapes are commonly used in photoelectron spectroscopy for the core lines of metallic materials [7], due to electron–hole-pair shake-up events. At room temperature V_2O_3 is in its metallic phase [8], which supports the use of asymmetrical line shapes for the $V^{3+}2p$ photoline, as was also indicated by Zimmerman et al. (Ref. [28] in [5]). The asymmetric $V^{3+}2p$ fit parameters were determined from the 78 and 96 s bombardment time on the $V_2O_5(001)$ and the 48 and 60 s on the pressed V_2O_3 powder pellet reported in [1]. The resulting average fit parameter values from these four spectra for the $V^{3+}2p$ photoline are given in Table 1. The values for the TS and TL parameters in the XPSPeak program for the asymmetric $V^{3+}2p$ were 0.5 and 35, respectively. These average values were used for all final $V^{3+}2p$ fits in this work. With increasing bombardment time, the FWHM for the $V^{3+}2p_{3/2}$ line further increased up to 3.7 eV.

Based on the above results, we suggest that the method presented in [1] for the analysis of V2p photoelectron spectra should be extended with asymmetric $V^{3+}2p$ line shapes and the corresponding fit parameters from Table 1.

From 174 s on, metallic vanadium (V^{0+}) appears in the peak decomposition (Fig. 6, 174 s). As for the Ar^+ bombardment on a pressed V_2O_3 powder pellet in [1], an extra component in between the V^{3+} and V^{0+} is present for the spectra on the $V_2O_5(001)$ after an Ar^+ bombardment time of 114 s or higher (Fig. 6, 174 and 2700 s). The position of this component was allowed to vary in all the fits from 114

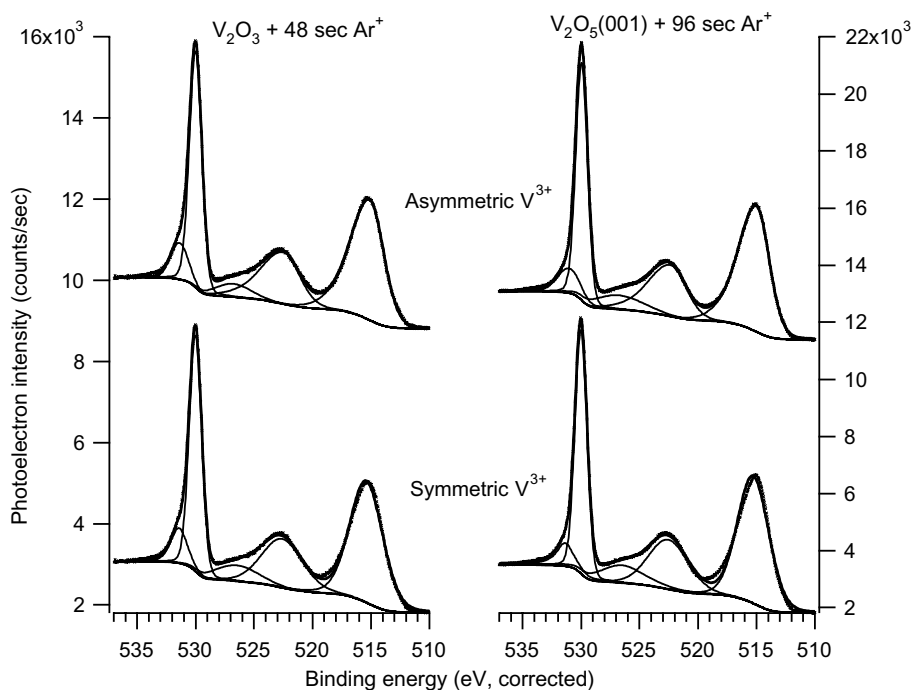


Fig. 7. O1s and V2p XPS spectra and fits with symmetric (lower panel) and asymmetric (upper panel) $V^{3+}2p$ line shapes of the V_2O_3 powder pellet (left) and the $V_2O_5(001)$ (right) after indicated Ar^+ bombardment times. Spectra are vertically shifted for clarity. (BE values are relative to the O1s (V–O) signal taken at 530.0 eV.)

Table 1

Average fit parameters for the asymmetric $V^{3+}2p$ photoline (numbers between brackets are the standard deviations)

Core line	Main peak			Satellite peak		
	BE (eV)	%L–G	Δ^{3+} (eV)	δE_{sat} (eV)	I_{sat}/I_{main}	%L–G
O1s	530.0	10	–	–	–	–
$V^{3+}2p_{3/2}$	515.0 ± 0.2	9 (3)	15.0 ± 0.2 (0.06)	11.8 (0.13)	0.14 (0.04)	60 (17)
$V^{3+}2p_{1/2}$	$V^{3+}2p_{3/2} + 7.44$	9 (3)	–	8.8 (0.14)	0.28 (0.03)	60 (17)

Δ represents the difference in BE between the O1s and $V^{3+}2p$ line, δ the separation between the V2p peak and its satellite peak and I_{sat}/I_{main} their intensity ratios [1,5].

to 4500 s and an average binding energy separation relative to the O1s of 16.7 eV (standard deviation of 0.14 eV) was found. In [1] a separation of 16.3 eV was found and this contribution arises from a vanadium oxidation state in between V^{3+} and V^{0+} and is referred to as $V^{2+/1+}$. As no pure vanadium oxide structures exist with a V^{1+} valence the V2p BE for V^{1+} is unknown and, as far as we know, no V2p BE values are reported in literature for the VO oxide. Therefore, the exact vanadium oxidation state of the $V^{2+/1+}$ component is not known.

3.3. Average vanadium valence of the $V_2O_5(001)$ surface under Ar^+ bombardment

The evolution of the concentration of the different vanadium oxidation states as function of Ar^+ bombardment time is shown in Fig. 8, expressed in percentage of the total $V2p_{3/2}$ signal. The V^{5+} component decreases fast and disappears within the first 30 s bombardment time. Meanwhile, the V^{4+} increases, reaches a maximum around 24–

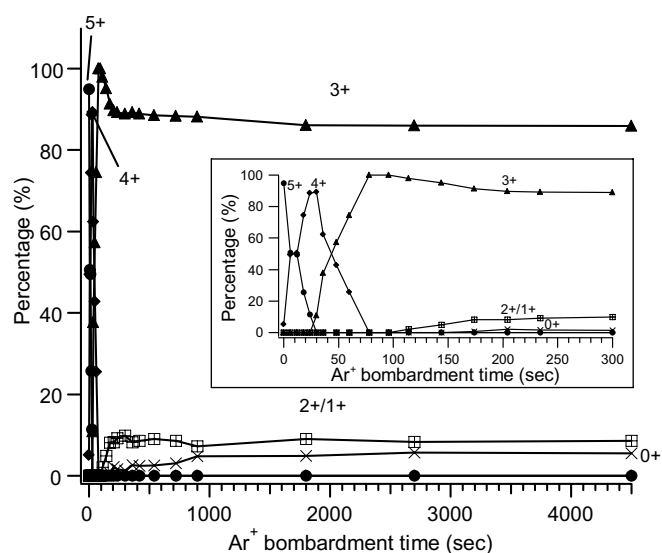


Fig. 8. Evolution of the different vanadium oxidation states as function of Ar^+ bombardment time. The inset shows the first 300 s in more detail.

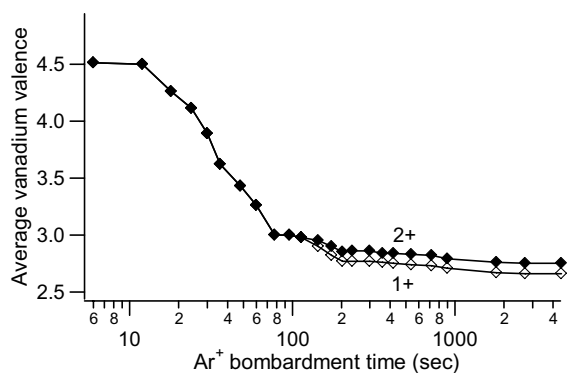


Fig. 9. Evolution of the mean vanadium oxidation state as function of Ar⁺ bombardment time (two valences for the V^{2+/1+} component are taken into account).

30 s and disappears after 78 s. The V³⁺ builds up from 30 s on and remains the most intense component even for the highest bombardment times. Its relative concentration becomes constant after about 1000 s Ar⁺ bombardment time. Compared to the Ar⁺ bombardment on the pressed V₂O₃ powder pellet from [1], the V₂O₅(001) is less reduced although the total bombardment time for the V₂O₅(001) is twice as long and the ion current about 40% higher.

From the relative contributions of the different vanadium oxidation states a mean vanadium valence can be calculated by multiplying each concentration with its formal oxidation state, the resulting valences are given in Fig. 9 on a semi-log scale, two possible valences (2 and 1) for the V^{2+/1+} component are presented. Due to the preferential sputtering of the oxygen atoms the O/V ratio will decrease with increasing sputtering time. The number of sputtered oxygen atoms in a homogeneous matrix is proportional to the amount still present at the surface, so a linear decrease of the O/V ratio, thus valence, with increasing ion bombardment time should be observed on a log time scale. The first two bombardment times yield a similar valence, but from 12 s on a linear decrease can indeed be observed until the V₂O₃ stoichiometry is reached, i.e. around 80–90 s. From about 100 s on, a new linear but much slower decrease is present extending until the longest bombardment times, further reducing the V₂O₅ surface until a mean oxidation state of about 2.7.

Naguib and Kelly [9] have studied the surface modification of V₂O₅ under Kr⁺ bombardment with reflection electron diffraction. They have found that after an initial amorphization of the V₂O₅ the final surface configuration is V₂O₃. As our analysis of the XPS spectra is in agreement with a transition from V₂O₅ to V₂O₃, which remains quite stable under further bombardment, this correspondence further supports the validity of our V2p XPS fit procedure.

4. Conclusions

The photoreduction and the Ar⁺ bombardment induced reduction of an in vacuum cleaved V₂O₅(001) crystal was studied with Al K α XPS. The freshly cleaved V₂O₅(001) surface has a fully oxidized V⁵⁺ 2p spectrum. The irradiation of the V₂O₅(001) surface with the Al K α X-rays induces a slight reduction from V⁵⁺ to V⁴⁺ cations. This photoreduction increases with irradiation time and reaches a maximum of 5% after an irradiation time of 640 min. No clear further increase was observed for longer irradiation times.

In order to test the transferability of our V2p XPS fit procedure, an Ar⁺ bombardment was performed on a V₂O₅(001) crystal to obtain a series of O1s–V2p spectra with varying mean vanadium oxidation state. The XPS spectra could be reproduced with the V2p fit parameters derived previously, but asymmetric line shapes should be used for the V³⁺ 2p photolines.

The Ar⁺ bombardment results in a drastic reduction of the V₂O₅(001) surface. The vanadium oxide rapidly reduces towards the V₂O₃ stoichiometry, but once this surface configuration is reached, a further but slower reduction of the vanadium oxide surface under of the Ar⁺ bombardment is observed.

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