An XPS study on the surface reduction of V_{2}O_{5}(001) induced by Ar^{+} ion bombardment

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Abstract

The effect of the irradiation with Al Kα X-rays during an XPS measurement upon the surface vanadium oxidation state of a fresh in vacuum cleaved V_{2}O_{5}(001) crystal was examined. Afterwards, the surface reduction of the V_{2}O_{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_{2}O_{3} at ambient temperature. Under Ar^{+} bombardment, the V_{2}O_{5}(001) crystal surface reduces rather fast towards the V_{2}O_{3} stoichiometry, after which a much slower reduction of the vanadium oxide occurs.

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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_{2}O_{5}, TiO_{2}, V_{2}O_{5} and Ta_{2}O_{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_{2}O_{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 Kα X-rays on the vanadium oxidation state of a fresh in vacuum cleaved V_{2}O_{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_{2}O_{3} powder pellet, to other vanadium oxide systems, a V_{2}O_{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_{2}O_{5}(001) surface.
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 V3+2p core line proved necessary. Moreover, the asymmetric line shape for the V3+2p photoline is supported by re-analysis of representative V3+2p spectra from [1].

2. Experimental

All XPS measurements were performed on one V2O5 single crystal sample, grown in the laboratory [3]. The V2O5 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 Kα source. Experiments were recorded with an angular acceptance of ±7° 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 V2O5 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 V2p3/2 core level for each vanadium oxidation state is fixed relative to the O1s level and the V2p3/2 and V2p1/2 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 V2O5(001)

The wide scan spectrum taken on the V2O5(001) surface after cleavage in vacuum and transfer to the main chamber 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 V2O5(001) surface with the Al Kα 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 V2p3/2 peak. The position of this contribution corresponds to the location of V⁴⁺ in the V2p3/2 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 V⁵⁺2p3/2 peak has a small full width at half maximum (FWHM) of about 1.0–1.1 eV, the V⁵⁺2p1/2 peak has a larger FWHM, 2.6 eV, due to the Coster–Kronig effect. The first spectrum shows a single V⁵⁺ contribution for the V2p spectrum, while the spectrum after 880 min has about 5% V⁴⁺. The evolution of the contribution of V⁴⁺ to the total V2p signal for a set of irradiation times is given in Fig. 3. The percentage of V⁴⁺ increases with increasing irradiation time, but seems to level off from 640 min on.

For the study of the Ar⁺ bombardment on the V2O5(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 V2O5(001) surface

The O1s and V2p XPS spectra on the V2O5(001) as function of Ar⁺ bombardment time are given in Fig. 4.
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 V2p1/2 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 V2p3/2 and V2p1/2 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) signal 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.

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
(V\textsuperscript{5+} – V\textsuperscript{0+}) were already determined in our previous work [1]. Nevertheless, from the set of spectra in Fig. 4 the fit parameters for the V\textsuperscript{5+} and V\textsuperscript{4+} vanadium oxidation states in the V\textsubscript{2p} doublet (V\textsubscript{2p} spin–orbit splitting, L–G character, BE position) were re-determined independently from the previous study [1]. The fit parameters for the V\textsuperscript{5+} and V\textsuperscript{4+} vanadium oxidation states in the V\textsubscript{2p} doublet are identical with our results previously reported in [1]. Example fits with the V\textsuperscript{5+} and V\textsuperscript{4+} components are given in Fig. 6 (0 and 12 s). The V\textsuperscript{5+} component vanishes from 30 s bombardment time on. The V\textsuperscript{5+}2p\textsubscript{3/2} photoline is a narrow peak, but the FWHM for the vanadium oxidation states lower than V\textsuperscript{5+} are larger, due to multiplet effects [5]. The FWHM for the V\textsuperscript{5+}2p\textsubscript{3/2} increases with increasing bombardment time, up to 2.6 eV for 24 s. The FWHM for the V\textsuperscript{4+}2p\textsubscript{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\textsuperscript{3+} oxidation state. Although these spectra could be fitted with the V\textsuperscript{3+} parameters from [1], a better fit is obtained with an asymmetric V\textsuperscript{3+}2p doublet. Moreover, the fit on the two spectra that served in [1] to determine the V\textsuperscript{3+} fit parameters are also better reproduced with an asymmetric peak shape for the V\textsuperscript{3+}2p photoline. The fits with a symmetric and an asymmetric V\textsuperscript{3+}2p line shape for the V\textsubscript{2O}_3\textsuperscript{-48 s} spectrum from [1] and the V\textsubscript{2O}_5(001)-96 s are given in Table 1. The values for the TS and TL parameters in the XPSPeak program for the asymmetric V\textsuperscript{3+}2p photoline were 0.5 and 35, respectively. These average values were used for all final V\textsuperscript{3+}2p fits in this work. With increasing bombardment time, the FWHM for the V\textsuperscript{3+}2p\textsubscript{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 V\textsubscript{2p} photoelectron spectra should be extended with asymmetric V\textsuperscript{3+}2p line shapes and the corresponding fit parameters from Table 1.

From 174 s on, metallic vanadium (V\textsuperscript{0+}) appears in the peak decomposition (Fig. 6, 174 s). As for the Ar\textsuperscript{+} bombardment on a pressed V\textsubscript{2O}_3 powder pellet in [1], an extra component in between the V\textsuperscript{3+} and V\textsuperscript{0+} is present for the spectra on the V\textsubscript{2O}_5(001) after an Ar\textsuperscript{+} 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 s and higher (Fig. 6, 174 and 2700 s).
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 V3+ and V0+ and is referred to as V2+/1+. As no pure vanadium oxide structures exist with a V1+ valence the V2p BE for V1+ is unknown and, as far as we know, no V2p BE values are reported in literature. Therefore, the exact vanadium oxidation state of the V2+/1+ component is not known.

3.3. Average vanadium valence of the V2O5(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 V2p3/2 signal. The V5+ component decreases fast and disappears within the first 30 s bombardment time. Meanwhile, the V4+ increases, reaches a maximum around 24–
30 s and disappears after 78 s. The V$^{3+}$ 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 V$_2$O$_3$ powder pellet from [1], the V$_2$O$_5$(001) is less reduced although the total bombardment time for the V$_2$O$_5$(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 V$_2$O$_3$ 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 V$_2$O$_5$ surface until a mean oxidation state of about 2.7.

Naguib and Kelly [9] have studied the surface modification of V$_2$O$_5$ under Kr$^+$ bombardment with reflection electron diffraction. They have found that after an initial amorphization of the V$_2$O$_5$ the final surface configuration is V$_2$O$_3$. As our analysis of the XPS spectra is in agreement with a transition from V$_2$O$_5$ to V$_2$O$_3$, 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 V$_2$O$_5$(001) crystal was studied with Al K$_a$ XPS. The freshly cleaved V$_2$O$_5$(001) surface has a fully oxidized V$^{5+}$2p spectrum. The irradiation of the V$_2$O$_5$(001) surface with the Al K$_a$ X-rays induces a slight reduction from V$^{5+}$ to V$^{4+}$ 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 V$_2$O$_5$(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 V$^{3+}2p$ photolines.

The Ar$^+$ bombardment results in a drastic reduction of the V$_2$O$_5$(001) surface. The vanadium oxide rapidly reduces towards the V$_2$O$_3$ 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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