

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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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

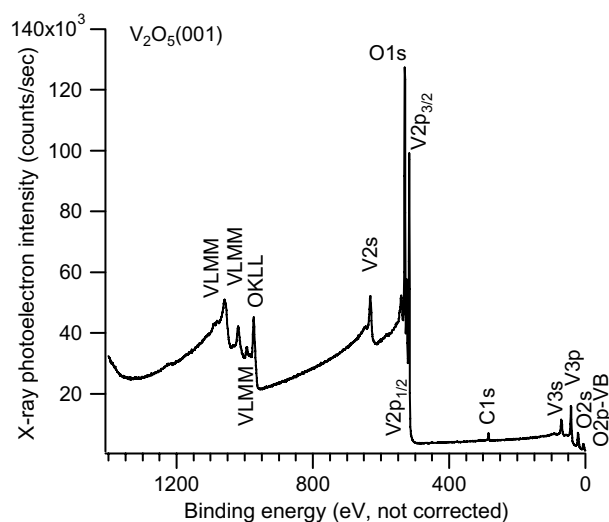


Fig. 1. Wide scan XPS spectrum of the in vacuum cleaved $V_2O_5(001)$.

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.

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