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# $V_2O_3(0001)$ on Au(111) and W(110): growth, termination and electronic structure

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#### Abstract

We have prepared well-ordered  $V_2O_3(0001)$  films with thicknesses between 60 and 160 Å on W(110) and Au(111). These films have been studied with respect to the surface electronic and geometric structure and the interaction with oxygen. We find that after preparation with oxygen the surface is terminated by vanadyl groups. The surface may be reduced by electron bombardment. Oxygen adsorption with subsequent annealing restores the vanadyl groups. The vanadyl groups are thermally stable on the surface until at least 1000 K under UHV conditions.

In XPS spectra of the vanadyl terminated surface a V2p induced surface state becomes visible under surface sensitive conditions. The binding energy shift of this state is compatible with a higher oxidation state of the vanadium atoms on the surface as compared to the bulk atoms. The V2p surface state induces additional intensity also in NEXAFS spectra as concluded from a set of spectra recorded with two different methods.

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#### 1. Introduction

Physics and chemistry of metal oxide surfaces are of great interest since these materials find wide technological applications due to their multifaceted properties. Vanadium oxides are good examples to demonstrate the complexity of transition metal oxides. The V–O phase diagram shows the existence of many stoichiometric compounds like VO,  $V_2O_3$ ,  $VO_2$  and  $V_2O_5$ .  $VO_2$  and  $V_2O_5$  exhibit catalytic activity for oxidation reactions. It is often argued that lower oxidation states of vanadium play an important role in catalytic processes occurring on  $V_2O_5$  based catalysts (see [1,2] and references therein). Here we present results of studies on the surface properties of thin  $V_2O_3(0\ 0\ 0\ 1)$  films grown on W(1 1 0) and Au(1 1 1). This compound has been the subject of many theoretical and experimental studies over the last years due to its paramagnetic metallic to antiferromagnetic insulator phase transition at T = 150 K. Up to date this complex transition is still not completely understood.

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Since stoichiometric  $V_2O_3$  is an insulator at T = 150 K, application of electron spectroscopy may be difficult due to electrical charging of the surface. However, if films with sufficiently small thickness are used for the investigations, the conductivity may be high enough to avoid surface charging. Most of the studies on  $V_2O_3$  found in literature were performed on single crystals or powder materials, only a few on thin or ultra-thin films, grown for instance on Au(111) [3], Al<sub>2</sub>O<sub>3</sub> [4–7] and Pd(111) [8–11].

# 2. Experimental

X-ray photoemission spectroscopy (XPS) and near edge X-ray absorption spectroscopy (NEX-AFS) were performed at the BESSY II synchrotron radiation center in Berlin. For part of the XPS data a Scienta SES200 analyzer was used which was mounted at an angle of 55° with respect to the incident photon beam. The overall energy resolution was usually better than 100 meV. For another part of the data a chamber with a Omicron EA125 analyzer was employed. In this case the overall resolution was usually better than 150 meV. XPS spectra of the V2p and O1s levels were taken with a photon energy of 630 eV. At this photon energy the kinetic energy of the electrons is around 100 eV leading to high surface sensitivity. 120 eV photons were employed to excite valence band electrons. In all cases the energy scale was calibrated relative to the energy of the  $W4f_{7/2}$  level by taking spectra of the tungsten filament used for sample heating. NEXAFS spectra were taken by measuring the current flowing between ground potential and the sample and by a partial yield detector mounted below the sample. The energy resolution was usually better than 100 meV.

High resolution electron energy loss (HREELS) spectra were recorded in a chamber equipped with a Delta 0.5 HREELS spectrometer (VSI GmbH). Details of the experimental setup are discussed elsewhere [12,13]. All spectra presented here were recorded in specular geometry (angle<sub>in</sub> = angle<sub>out</sub> =  $65^{\circ}$  with respect to the surface normal). Infrared absorption spectra were obtained in the same chamber by use of a modified Mattson RS-1

FTIR spectrometer. The angle of incidence of the IR light relative to the sample normal is about 85°.

Au(111) was cleaned in UHV by cycles of Argon sputtering and annealing at 1150 K. To remove carbon from W(110) the usual cleaning cycle was performed. It consists of heating the sample to 1800 K in  $10^{-6}$  mbar of oxygen for a few minutes followed by annealing at 2300 K without oxygen.

The V<sub>2</sub>O<sub>3</sub>(0001) film on Au(111) was prepared by evaporation of metallic vanadium in an oxygen atmosphere ( $1 \times 10^{-7}$  mbar) followed by annealing at 700 K in  $5 \times 10^{-8}$  mbar of oxygen. In the case of the W(110) substrate vanadium was evaporated at a substrate temperature of 650 K in an oxygen atmosphere of  $2 \times 10^{-7}$  mbar followed by annealing at 800 K at an oxygen pressure of  $2 \times 10^{-7}$  mbar. For evaporation a Omicron EFM4 electron beam evaporator was used. Before vanadium evaporation the deposition rate was calibrated in situ with a quartz microbalance. Typical vanadium deposition rates used during were 1–2 Å/min.

The vanadium oxide so obtained is stable under UHV conditions up to  $T \approx 1000$  K for the tungsten substrate. Annealing at higher temperature leads to diffusion of tungsten to the surface. For the Au(111) substrate diffusion already occurs at  $T \approx 800$  K. Between 30 and 80 Å of vanadium were usually evaporated onto the substrates corresponding to oxide film thicknesses between approximately 60 and 160 Å.

For both substrates sample heating could be performed either by heat radiation from a glowing tungsten filament mounted behind the back of the sample or by electron bombardment using the same filament. With liquid nitrogen the samples could be cooled down to  $T \approx 90$  K.

### 3. Results and discussion

Gold is a face centered cubic metal and its (111) surface exhibits a hexagonal LEED pattern (see Fig. 1(A)). The atomic lattice of  $V_2O_3$  is isomorphic to that of corundum,  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. Perpendicular to the (0001) direction the oxygen atoms form quasi-hexagonal layers with the vanadium



Fig. 1. LEED patterns of (A) Au(111) at 175 eV, (B) 160 Å  $V_2O_3(0001)/Au(111)$  at 150 eV, (C) W(110) at 100 eV, and (D) 60 Å  $V_2O_3(0001)/W(110)$  at 100 eV.

atoms in a honeycomb-like arrangement between them. The gold–gold distance on the Au(111)surface (2.885 Å) and the average lateral oxygenoxygen distance on the  $V_2O_3(0001)$  surface (2.86) Å) are very close which is a good base for epitaxial growth. The LEED pattern of the  $V_2O_3(0001)$ film on Au(111) shown in Fig. 1(B) exhibits sharp reflexes, corresponding to a well-ordered structure. Tungsten is a body centered cubic metal with a quasi-hexagonal (110) face. The mismatch between the  $V_2O_3$  oxygen lattice and the tungsten lattice along the [001] direction of the W(110) surface is about 10%. In spite of the large mismatch the good quality of the LEED pattern film provides evidence for good crystallinity of the oxide film (see Fig. 1(D)).

The ideal bulk-terminated (0001) surface of V<sub>2</sub>O<sub>3</sub> may be terminated in three different ways as shown in Fig. 2. Cutting a V<sub>2</sub>O<sub>3</sub> single crystal

along the (0001) surface may lead to an oxygen terminated surface (Corundum(0001)-O in Fig. 2), a surface terminated by a single metal layer (Corundum(0001)-Me), and a surface terminated by a metal double layer (Corundum(0001)-2Me). Out of these structures only the one terminated with a single metal layer is stable according to Tasker [15]. The other ones are polar surfaces and exhibit Madelung energies which increase without limit with increasing film thickness. We note that surfaces which are unstable according to Tasker's criteria and thus should not exist may exist in reality: by changing the charge distribution in the surface region and by modifying the interlayer distances a polar surface may be stabilized [16]. Nevertheless, for  $Cr_2O_3$  which is iso-structural to V<sub>2</sub>O<sub>3</sub> it has been established that after annealing at 1000 K the termination of the (0001)surface corresponds to the one denoted by



Fig. 2. Different terminations of the  $V_2O_3(0001)$  surface and lattice parameter for different corundum type oxides as taken from Ref. [14].

Corundum(0001)–Me in Fig. 2 [17] which is the only non-polar bulk-terminated surface in this figure. The terminations shown in Fig. 2 are those where the structure of the surface layers is not different from that of the bulk layers. Of course, there are also other conceivable terminations. Therefore, one of the questions to deal with is: how is the  $V_2O_3(0001)$  surface terminated?

Directly after preparation of the  $V_2O_3(0001)$ thin film on W(110) a vibrational spectrum as shown in Fig. 3(b) is obtained. If the oxide is annealed by electron bombardment in UHV for a few seconds at 600 K the spectrum changes slightly and spectrum (a) is observed. Spectra (a) and (b) have been normalized to each other by adjusting the peak of the elastically reflected electrons to the same height. One obvious difference between the two spectra is that the loss intensities differ. A simple explanation for this may be that the electron reflection properties of the two surfaces are different; i.e. the angular distribution of reflected electrons may be more diffuse for the surface annealed in UHV. Another difference is that there is additional intensity in the peak at 127 meV in spectrum (b) as compared to spectrum (a). This additional intensity is more obvious in the infrared division spectrum displayed in Fig. 4. Identification of the origin of this feature is possible by comparison with the spectrum of the chromyl terminated  $Cr_2O_3(0001)$  surface (spectrum (c) in Fig. 3). The peak at 127 meV has also been observed for this oxide and there it could be assigned to chromyl groups [19,20]. These groups consist of oxygen atoms forming a double bond to the underlying chromium atoms. The loss peak is due to excitation of the Cr=O stretching vibration. For



Fig. 3. HREELS spectra of  $V_2O_3(0001)/W(110)$  taken after annealing in oxygen (b) and after annealing for a few seconds in UHV at 600 K by electron bombardment (a). At the top a HREELS spectrum of the chromyl terminated  $Cr_2O_3(0001)$ surface is shown for comparison (c) [18].



Fig. 4. IRAS spectrum of the surface corresponding to Fig. 3(b) divided by a spectrum of the surface corresponding to Fig. 3(a).

V<sub>2</sub>O<sub>3</sub>(0001)/Pd(111) Netzer and coworkers have found a peak at similar position and assigned it to vanadyl groups [11] which are equivalent to chromyl groups for the case of vanadium metal atoms. A loss peak at similar energy also shows up in vibrational spectra of  $V_2O_3(001)$  where vanadyl groups are a part of the bulk structure [2]. Combining the information we find that  $V_2O_3(0001)$  is terminated by vanadyl groups directly after preparation. The oxygen atoms of these groups may be removed by annealing with electron bombardment in UHV at 600 K for a few seconds. The vibrational spectrum of the so-obtained surface is shown in Fig. 3(a). There is still some intensity at about 127 meV which is to be attributed to a combination of the losses at 47 and 81 meV.

Tentative images of the two differently terminated  $V_2O_3(0001)$  surface are shown in Fig. 5 assuming that the vanadium terminated surface is terminated like the one denoted 'Corundum(0001)–Me' in Fig. 2 and that every surface vanadium atom binds one oxygen atom for the case of the vanadyl terminated surface.

Concerning the removal of the oxygen atoms of the vanadyl groups it is near at hand to ask whether they are removed thermally or whether the electrons used for heating play a decisive role. To answer this question a vanadyl terminated  $V_2O_3(0001)/W(110)$  surface has been annealed at different temperatures by thermal radiation from a glowing tungsten filament, i.e. without electron



Fig. 5. Tentative models of the vanadium terminated (A) and the vanadyl terminated  $V_2O_3(0001)$  surfaces (B).

bombardment. After each annealing step valence band and XPS spectra have been taken under surface sensitive conditions (electron kinetic energy near 100 eV and electron detection at grazing angle:  $\Theta = 70^{\circ}$ ). Under these conditions changes occurring in the surface region should be detectable. The spectra are displayed in Fig. 6. From this series it is obvious that not much happens on the surface until a temperature of about 1000 K is reached. Above 1000 K tungsten diffuses through the film from the substrate to the oxide surface as concluded from XPS spectra of the W3d region (not shown here). Fig. 6 demonstrates that the vanadyl groups are thermally stable on the surface until at least 1000 K. This means that the removal of the vanadyl groups by annealing at 600 K using electron bombardment is not a thermal process but induced by the electrons. The same conclusion may be drawn from adsorption experiments of CO (data not shown here). The vanadyl terminated surface does not adsorb CO in notable amounts at 90 K. The same result is obtained if the oxide is annealed by thermal radiation. However, if the sample is annealed by electron irradiation, significant amounts of CO adsorb.

A hint on the structure of the reduced  $V_2O_3(0001)$  surface may be obtained from CO



Fig. 6. Set of photoelectron spectra taken after annealing a vanadyl terminated  $V_2O_3(0001)/W(110)$  surface at different temperatures by thermal radiation from a glowing tungsten filament. The spectra have been recorded at an electron detection angle of 70° with respect to the surface normal in order to enhance surface sensitivity. (A) XPS spectra of the O1s and V2p region; (B) valence band spectra.

adsorption data. The valence band spectra of CO Cr<sub>2</sub>O<sub>3</sub>(0001) reveal extraordinarily high on binding energies of the CO valence levels  $(5\sigma + 1\pi)$ at about 11.8 eV and  $4\sigma$  at 14.4 eV) and there are also indications that one of the  $1\pi$  levels is shifted near to the  $4\sigma$  level [21,22]. The dependence of the CO valence level intensities on the experimental geometry (compare bottom and top spectrum in Fig. 7(A) is a strong indication that the molecules are lying more or less flat on the surface (for details see Refs. [21,22]). Fig. 7(B) shows that more or less identical properties of the CO valence levels are observed for the reduced  $V_2O_3(0001)$  surface which may be viewed as an indication that the surface structure of the reduced  $V_2O_3(0001)$  surface is similar to that of the chromium terminated  $Cr_2O_3(0001)$  surface. However, Fig. 7(C) demonstrates that the agreement between the spectra of CO on chromium terminated  $Cr_2O_3(0001)$  and reduced  $V_2O_3(0001)$  is sometimes less perfect. The spectra in Fig. 7(C) have been recorded for a another reduced surface and the different CO adsorption spectra strongly indicate that the two reduced surfaces are different. It may be assumed that the electron dose plays an important role for the quality of the reduced surface. Too high electron doses may remove too much oxygen leaving an inhomogeneous surface with a high number of defects behind. However, further experiments may be needed to verify this.

Surface sensitive O1s and V2p core level spectra of the vanadium- and the vanadyl terminated  $V_2O_3(0001)$  surface are compared with a spectrum of  $V_2O_3(001)$  in Fig. 8. For the O1s core level the peak position does not significantly depend on the vanadium oxidation state which is in agreement with literature data [2,23–25]. The O1s level of  $V_2O_3(0001)$  appears to be somewhat broader than that of  $V_2O_3(001)$  which may be traced back to the partial occupation of the V3d levels near to the Fermi level. This induces lowenergy excitations accompanying the O1s excita-



Fig. 7. Comparison of valence band spectra of CO on  $Cr_2O_3(0001)/Cr(110)$  (A) [21,22] and CO on reduced  $V_2O_3(0001)/W(110)$  recorded in different experimental geometries. (B) and (C) denote two different preparations of reduced  $V_2O_3(0001)$ . The spectra of the respective clean surfaces are drawn as dashed lines. For each set of spectra the experimental geometry is schematically drawn on the right-hand side.

tion which asymmetrically broaden it towards the high binding energy side (Doniach–Šunjić line shape [26]). Near to the O1s peak in the spectrum of the reduced surface a small feature at 531.7 eV is found. The origin of this state is not clear yet. Fig. 9(A) shows that sometimes this peak may be rather intense. Annealing at 800 K for 10 min reduces its intensity, but is does not disappear fully. The peak has been observed for reduced surfaces as well as for vanadyl terminated surfaces. Zimmermann et al. [27] identified a V2p satellite in this energy region. However, the feature in our data is



Fig. 8. XPS spectra of the V2p and O1s core levels for  $V_2O_3(0001)/W(110)$  (spectra (b)–(d)) in comparison with a spectrum of a  $V_2O_5(001)$  single crystal surface (spectrum (a)). The spectra of the  $V_2O_3(0001)$  surface have been fitted by asymmetrically broadened products of Gaussian and Lorentzian functions. A Tougard-type background has been subtracted from all spectra.

too intense for this assignment. The XPS binding energy of this state (531.7 eV) is also compatible with that of the O1s peak of hydroxyl groups. However, the valence band spectra displayed in Fig. 9(B) do not exhibit significant intensity at about 11 eV where the  $3\sigma$  state of the OH groups should appear. A carbon contamination can also be excluded since no C1s emission with detectable intensity could be found. Thus there are strong indications that the peak at 531.7 eV is not due to a surface contamination but to a vanadium–oxygen compound of yet unknown nature or to V<sub>2</sub>O<sub>3</sub> with different structural properties.

Significant differences are found in the range of the V2p states in the spectra in Fig. 8. First of all the peaks obtained for the  $V_2O_3(0001)$  surface are



Fig. 9. Photoelectron spectra obtained after reduction of  $V_2O_3(0001)/W(110)$  by electron bombardment. (A) O1s and V2p XPS spectra; (B) valence band spectra. (1) Directly after reduction; (2) after annealing at 820 K for 10 min.

significantly broader than those of the V<sub>2</sub>O<sub>5</sub>(001) surface. This effect may be traced to the same effect which led to the broader O1s peak for the V<sub>2</sub>O<sub>3</sub>(0001) case as compared to V<sub>2</sub>O<sub>5</sub>(001). However, for the V2p levels this effect is more pronounced since the coupling of the V2p ionization to accompanying V3d excitations is stronger because the V2p and V3d electrons reside on the same atom.

Another point to note is that the binding energy of the V2p levels depends significantly on the vanadium oxidation state as revealed by a comparison of the spectra of  $V_2O_3$  with the one of  $V_2O_5$  in Fig. 8. This is in agreement with literature data [23,27]. Thus the binding energy of the V2p level may be used as an indicator for the oxidation state in first approximation. In this context the low binding energy shoulder near to the V2p<sub>3/2</sub> level of  $V_2O_5(0\ 0\ 1)$  may be attributed to partial reduction of the surface.

The V2p<sub>3/2</sub> features in Fig. 8(b)–(d) have been fitted with two peaks and the V2p<sub>1/2</sub> features with three peaks. According to Zimmermann et al. [27]

the  $V2p_{1/2}$  state near to the O1s level may be attributed to a V2p satellite. The intensities of the remaining two  $V2p_{3/2}$  and  $V2p_{1/2}$  states (at 515.15, 517.15, 522.4, and 524.4 eV according to the fit) in the spectra of the vanadyl terminated surface depend on the emission angle with the states at higher binding energy getting more intense at higher emission angle. This means that the features at 517.15 and 524.4 eV are surface states, originating from the vanadium atoms of the vanadyl groups. Comparison with the spectrum of  $V_2O_5(001)$  at the bottom in Fig. 8 shows that the binding energy of the surface  $V2p_{3/2}$  state in spectrum (c) is near to the one of the  $V2p_{3/2}$  state of  $V_2O_5(001)$ . In a simple picture the vanadium atoms on a vanadium terminated surface would have a formal oxidation state of 2+. Adding a double oxygen-vanadium bond as in the vanadyl groups leads to a formal oxidation state of 4+. This may be the reason why the  $V2p_{3/2}$  binding energy of the vanadium atoms in the vanadyl groups is higher than that of the atoms in the bulk. We note that the oxidation states discussed in this paragraph are formal ones which means that they follow from a simple counting of charges assuming that the charges of the vanadium atoms in the bulk are 3+ and those of the oxygen bulk atoms are 2–. It may be expected that the real charges are different. Apart from the oxidation state there are also other parameters which influence the binding energy of core levels in XPS spectra such as screening effects. On the surface the screening energy is usually smaller since the number of neighbors is smaller which will shift the surface peak to higher binding energy. Therefore the shift of the surface state is a good indication that the oxidation state of the surface vanadium atoms is higher, but it is not really a proof in a mathematical sense.

Interestingly there are  $V2p_{3/2}$  and  $V2p_{1/2}$  states in the spectrum of the reduced surface (spectrum Fig. 8(b)) at the same energies as the surface states of the vanadyl terminated surface. It is obvious that the relative intensities of these states are smaller than the corresponding ones of the vanadyl terminated surface. This is a indication that not all vanadyl groups could be removed by electron bombardment.

Fig. 10 compares valence band spectra of the vanadyl terminated surface with spectra of the reduced one. The intensity near to the Fermi energy between 0 and 3 eV binding energy is due to V3d electrons not directly involved in the V-O bonding. Thus the occupation of these levels reflects the oxidation state. Since vanadium has five electrons and its formal oxidation state in  $V_2O_3$  is 3+, the levels near to the Fermi energy should contain two electrons in a simple ionic picture. Reduction of the vanadium atoms should lead to an increase of the occupation and, therefore, to increased intensity in photoelectron spectra. The spectra displayed in Fig. 10 show that the intensity is smaller for the vanadyl terminated surface than for the reduced one, indicating a higher oxidation state. This is in agreement with the above discussion where we concluded that the formal oxidation increases when going from the reduced surface to the vanadyl terminated surface.

Another effect is the shift of the intensity induced by the O2p + V3d levels to higher binding energy upon removal of the vanadyl oxygen atoms (see Fig. 10). This also reflects changes of the ox-



Fig. 10. Valence band photoelectron spectra of vanadyl terminated and reduced  $V_2O_3(0001)/W(110)$  recorded at different electron emission angles.

idation state. In Ref. [28], Hermann and Witko published calculated densities of states for  $V_2O_3$ ,  $VO_2$ , and  $V_2O_5$ . From these data it is obvious that the O2p + V3d hybrid states shift to smaller binding energy with increasing oxidation state which is the reason for the shift of the O2p + V2p states in Fig. 10 upon removal of the vanadyl groups. Another point to note is the additional intensity at a binding energy of about 5 eV in the spectra of the vanadyl terminated surface. This intensity has been observed in nearly all valence band spectra of the vanadyl terminated surface so that it is near at hand to assign this intensity to the vanadyl groups. A similar state has been observed for the chromyl terminated  $Cr_2O_3(0001)$  surface [29].

In order to check whether the removal of the vanadyl groups by electrons is reversible the interaction of the reduced surface with  $O_2$  was studied. Fig. 11 displays two sets of photoelectron spectra taken from a reduced surface annealed at different temperatures after exposure to  $O_2$ . Photon energy and electron detection angle have been set to values which grant high surface sensitivity. Spectrum (1) in panel (B) exhibits data obtained



Fig. 11. Photoelectron spectra obtained after annealing a reduced  $V_2O_3(0001)/W(110)$  surface at different temperatures after exposure to  $O_2$ . The electron detection angle was  $\Theta = 70^\circ$  with respect to the surface normal. Oxygen dosage (10 L  $O_2$ ) was performed at 80 K. (A) O1s and V2p XPS spectra; (B) valence band spectra. At the top a spectrum of the vanadyl terminated surface is shown in panel (B).

before oxygen dosage and spectrum (2) shows data recorded after the surface has been exposed to 10 L of O<sub>2</sub> at 80 K. Oxygen exposure immediately leads to a significant decrease of the V3d intensity which means that the oxidation state of the surface vanadium atoms increases. At about 5 eV a state appears which has also been found for vanadyl groups as discussed before. However, spectrum (2) is not yet the spectrum of the vanadyl terminated surface as demonstrated by a comparison with spectrum (7). Between 80 and 210 K the spectrum does not change significantly. Annealing at 610 K leads to a spectrum which is similar to the one of the vanadyl terminated surface. This is accompanied by a small increase of the V3d intensity which means that the surface vanadium atoms are slightly reduced. In panel (A) the initial oxidation of the surface vanadium atoms upon oxygen dosage at 80 K leads to a shift of the V2p levels to

higher binding energy which is compatible with an increasing oxidation state of the surface vanadium atoms. After annealing at 610 K (spectrum (6)) the  $V2p_{3/2}$  level exhibits the doublet structure characteristic for the vanadyl terminated surface. Thus it is obvious that vanadyl groups form upon annealing the oxygen-dosed surface at 610 K. However, the oxygen atoms or molecules which are transformed into vanadyl groups must also exist on the surface before vanadyl formation. Here we again refer to the case of chromium terminated  $Cr_2O_3(0001)$ . For this oxide it was shown that oxygen adsorption at low temperature leads to formation of a negatively charged molecular oxygen species which is transformed into chromyl at about 300 K [19,20], accompanied by desorption of part of the oxygen molecules. It may be that the same occurs on the reduced  $V_2O_3(0001)$  surface. In this context the small intensity change of the V3d states between 210 and 610 K could be correlated with desorption of part of the oxygen molecules, leading to a partial reduction of the surface vanadium atoms. However, additional studies will be needed to confirm this. There are also some small structures at about 535 eV in panel (A) and at about 11.5 and 13 eV in panel (B) in some spectra. These features are most likely related to a small water contamination which was hard to avoid at low sample temperature.

NEXAFS spectra of the vanadyl terminated and the reduced surface were recorded using two different methods. One method was measurement of the photoelectric current flowing between the sample and ground potential. This signal is not very surface sensitive due to the large number of low-energy secondary electrons which contribute to the signal. The second method was detection of electrons using a partial yield detector mounted below the sample. Since this device only detects electrons leaving the surface at grazing angle and since electrons with energies below 50 eV were eliminated from the signal by setting the mesh in front of the detector to a voltage of -50 eV, data obtained by this method are significantly more surface sensitive. In the difference of the spectra obtained with these two methods, emission from the surface should therefore be enhanced. A set of data and difference spectra are displayed in Fig. 12.

In a simple ionic picture no O1s $\rightarrow$ O2p NEX-AFS intensity is to be expected for  $V_2O_3$  since the O2p levels are fully occupied and cannot accommodate additional charge. However, if the oxygen-vanadium bond contains covalent parts, density of unoccupied V3d levels is mixed into the O2p levels and the O1s $\rightarrow$ O2p (actually  $O1s \rightarrow (O2p + V3d)$ ) transition becomes possible. This is the origin of the structure between 530 and 535 eV. Similarly the broad structure centered around 542 eV is attributed to a O2p + V4sp final state [27]. The structure of the O1s NEXAFS features reflects details of the hybridization and the intensity is governed by the degree of hybridization, by the occupation of the V3d levels, and, of course, by the dipole selection rules. The latter is responsible for the dependence of the spectral features on the light incidence angle. Strong effects

are observed for the O1s features whereas the effect of the light polarization onto the V2p induced states is somewhat weaker.

A general trend observed in the data is that the difference between the spectra obtained by the partial yield detector and by sample current measurement increases with increasing photon energy. One reason for this effect is that the partial vield detector was set to cut off electron kinetic energies below 50 eV. Thus it detects a smaller part of the total electron energy distribution and an increase of the upper limit of this distribution due to an increase of the photon energy leads to a higher relative increase of the measured signal. Another point is that this effect is stronger for a light incidence angle of  $\alpha = 70^{\circ}$  than for  $\alpha = 0^{\circ}$ . The reason for this is that the electron intensity is usually higher along the direction of the electric field vector than perpendicularly to it. Thus, the main electron emission intensity is directed parallel to the surface plane for  $\alpha = 0^{\circ}$  which means that most electrons cannot directly leave the sample and the relative part of inelastically scattered electrons is higher than for  $\alpha = 70^{\circ}$ . Therefore the relative increase of the NEXAFS signal due to the increasing photon energy is less pronounced for  $\alpha = 0^{\circ}$  than for  $\alpha = 70^{\circ}$ . It is obvious that this explanation is only rather crude. However, a more detailed one would be rather involved and is beyond the scope of this paper. Here also effects related to the angular dependence of electron emission would have to be discussed.

Fig. 12 shows that the NEXAFS spectra of the vanadyl terminated surface differ only slightly from those of the reduced surface, especially in the region of the V2p excitations. As explained before, in the NEXAFS difference spectra (spectra denoted by (3) in panels (A)-(D) of Fig. 12) structures due to the surface are enhanced. However, intensity from the bulk is most likely not fully suppressed. In order to achieve full suppression it would be needed to normalize the spectra such that they contain bulk intensity in equal amounts before calculating the difference spectrum which is not easily possible since the amount of intensity due to the bulk is not known. Nevertheless it may be assumed that the difference spectra of the vanadium- and the vanadyl terminated surfaces



Fig. 12. NEXAFS spectra of V<sub>2</sub>O<sub>3</sub>(0001)/W(110) recorded in sample current mode and with a partial yield detector (PYD). Spectra for the vanadyl terminated and the reduced surface are shown for two different light incidence angles ( $\alpha = 0^{\circ}$  and 70°) with respect to the surface normal.

contain bulk intensity in about equal amounts. Therefore in the difference of these spectra intensity from the bulk should vanish. These difference spectra are displayed in panels (E) and (F) of Fig. 12. Intensity due to the surface states of the vanadyl terminated oxide should lead to maxima and intensity due to the reduced surface should induce minima. One difference between the two surface terminations is that there is additional V2p induced intensity at the high-energy side of the two V2p peaks of the vanadyl terminated oxide (marked by lines). Since the shift of this intensity with respect to the bulk V2p intensity is about the same as the shift of the V2p surface XPS peak of the vanadyl terminated surface in Fig. 8 with respect to the XPS bulk peak (about 2 eV) we attribute the V2p induced NEXAFS peaks in the difference spectra to an excitation of the vanadium atoms of the vanadyl groups.

As already noted before, the oxidation state of the vanadium atoms on the vanadyl terminated surface is higher than on the reduced surface. This means that the number of unoccupied V3d states is higher on the vanadyl terminated surface. From this argument one would expect a higher  $O1s \rightarrow O2p$  NEXAFS intensity for the vanadyl terminated surface. It is clear from the difference spectra in Fig. 12 that this is really the case. The additional intensity for the vanadyl terminated surface is not uniformly distributed over the  $O1s \rightarrow O2p$  structure but concentrated on the lowenergy part. Part of this intensity should be due to the oxygen atoms of the vanadyl groups. Another part of the structure in the O1s regime will be related to the oxygen atoms beneath the surface vanadium atoms since their electronic structure will also be somewhat different from that of the bulk oxygen atoms.

# 4. Summary

Well-ordered  $V_2O_3(0001)$  film grown on W(110) and Au(111) with thicknesses between 60 and 160 Å have been studied with respect to their surface properties. After preparation these films are terminated by a layer of vanadyl groups. These groups are stable on the surface up to temperatures of more than 1000 K. They may be removed by electron bombardment leaving a more or less defective reduced surface behind. Oxygen adsorption onto the reduced surface followed by annealing restores the vanadyl terminated surface.

Under very surface sensitive conditions a V2p surface state is observed in XPS data of the vanadyl terminated surface. Its binding energy indicates that the oxidation state of the vanadium atoms on the vanadyl terminated surface is higher than the oxidation state of the bulk vanadium atoms (3+). This result is corroborated by ARUPS data which show that the V3d induced intensity is smaller for the vanadyl terminated surface than for the reduced one. NEXAFS difference data exhibit intensity due to the V2p surface state of the vanadyl terminated surface. In the O1s regime the oxygen atoms of the vanadyl groups and the oxygen atoms below the vanadium atoms of the vanadyl groups contribute to the intensity in the difference spectra.

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