Scanning tunneling spectroscopy on clean and contaminated V(001)

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Abstract

Scanning tunneling spectroscopy measurements on clean V(001), carbon-covered V(001) and the oxygen-induced V(001)(1\text{\/\text{\(\sqrt{2}\)}}\text{\times0}) reconstruction are reported. The clean V(001) surface shows a strong surface state 0.03 eV below the Fermi level. Isolated impurities shift the surface state 0.05 eV upwards in energy and broaden the peak observed in \(dI/dV\). No significant influence of monoatomic steps on the surface state could be observed. For tunneling resistances down to about 1 M\(\Omega\) the surface state is unaffected by the tip of the scanning tunneling microscope. A surface state is detected around +0.75 eV in small \((2\times2)\) patches which are observed at higher carbon (and oxygen) coverages. The oxygen induced \((1\times5)\) reconstruction of V(001) shows a peak at similar energy (+0.63 eV) in the areas with O and C atoms in fourfold hollow sites and a peak around +0.91 eV above the rows of bridge-site oxygen. Ab initio band structure calculations confirm the existence of a surface state of \(d_{z^2}\) symmetry with an energy close to that observed experimentally on clean V(001). This agreement provides strong evidence that the V(001) surface is not magnetic (at least at room temperature) as predicted by the calculations. We also compare the experimentally observed peak shifts on the carbon and oxygen covered surfaces with calculational results for carbon-covered geometries.

Keywords: Carbon; Density functional calculations; Low index single crystal surfaces; Oxygen; Scanning tunneling microscopy; Surface electronic phenomena (work function, surface potential, surface states, etc.); Surface relaxation and reconstruction; Vanadium

1. Introduction

Many bcc(001) surfaces of the transition metals are known to have strong localized surface states of \(d_{z^2}\) symmetry around the Fermi level. Since these surface states make a large contribution to the local density of states (LDOS) at and above the surface, they may have a considerable influence on surface physics and chemistry [1]. With scanning tunneling microscopy (STM), these states are relatively easy to detect as their energies are close to the Fermi level and their position in \(k\)-space is near the center of the surface Brillouin zone \(\Gamma\) [2,3]. Recently, localized surface states have been observed as sharp features in \(dI/dV\) spectra...
on Fe(001) [4,5], Cr(001) [4–7] and V(001) [8]. These features could be used as chemical fingerprints to distinguish between Cr and Fe atoms on both Cr/Fe(001) [6] and Fe/Cr(001) [9] surface alloys.

Vanadium is an interesting material for a couple of reasons. It is able to solve enormous amounts of hydrogen in the bulk [10,11] and may therefore be an interesting material for hydrogen storage technology. It is also an interesting model system for the design of inverse “strong metal–support interaction” catalysts consisting of metal oxide islands (e.g. vanadium oxide) supported by a transition metal base (e.g. palladium, platinum, rhodium) [12].

Although bulk vanadium is paramagnetic, theoretical works are still conflicting regarding a possible non-vanishing magnetic moment on the V(001) surface ([13–16] and references therein). Recent studies report either relatively large magnetic moments [13–15] or vanishing magnetic moments on the V(001) surface [16]. The results seem to be very dependent on what approximation for the exchange–correlation interaction is used, whether theoretical or experimental lattice parameters are used, whether relaxed or unrelaxed geometries are used, whether an all-electron or a pseudopotential approach is followed, and even the $k$-point sampling seems to be very critical for this system. Therefore, it was argued that the magnetism of V(001) is very delicate [16] and may still exist at e.g. steps.

Experimental work on clean V(001) was hindered a long time by the extreme difficulties in cleaning of the surface [17]. Yet, Rau et al. found a spin-polarization of 34% at room temperature for this surface using electron-capture spectroscopy [18]. In contrast, Beckmann et al. concluded that their results for the magnetoresistance measurements and the anomalous Hall effect do not support a magnetic surface on vanadium [19]. It is evident that more experiments, preferably with local techniques to investigate the effects of defects and impurities, are needed to answer the question whether magnetic moments exist on the V(001) surface.

Knowledge of the electronic structure of the clean and contaminated V(001) surface, is essential for a thorough understanding of the above mentioned topics (i.e. gas adsorption, catalysis, magnetism, chemical identification in STM). Recent angular resolved photoelectron spectroscopy measurements by Pervan et al. reported a peak around the Fermi level which has largest intensity at the center of the surface Brillouin zone ($\Gamma$) and disperses away from the Fermi level with increasing polar angle [20–22]. Because this peak was very sensitive to surface disorder or contamination it was concluded that the peak is due to emission from a surface state. Momentum ($k$) resolved inverse photoemission spectroscopy (KRIPS) measurements by the same group did not reveal any surface resonances [22], while states of two-dimensional (surface state) character were reported by Ollonqvist et al. [23] at 0.4, 1.4, and 2.1 eV above the Fermi level using the same technique.

In this paper, we report on a scanning tunneling spectroscopy (STS) study of the clean V(001) surface, slightly contaminated V(001) and the oxygen-induced (1×5) reconstructed V(001) surface. The influence of a monoatomic step is studied. A possible modification of the surface electronic structure due to the presence of the STM tip is examined. Our results are compared to band structure calculations which have been performed for clean and carbon covered slabs. As the calculated geometries are only simplified models of the real experimentally studied geometries, the observed trends will be discussed in a qualitative way.

2. Experimental

STM and STS measurements were performed in ultra-high vacuum (pressure below $5 \times 10^{-11}$ mbar) at room temperature using an Omicron μ-STM with additional damping [24]. The electrochemically etched W-tips used were cleaned in vacuo by Ar ion sputtering and voltage pulses (up to 10 V) during tunneling.

STS measurements were performed by recording an $I(V)$ curve at each pixel. To avoid problems with thermal drift during the open feedback conditions of STS at room temperature, the measurement of each $I(V)$ curve was done as quickly...
as possible (typically 50 voltage steps of ~30 mV with acquisition and delay times of 470 and 150 μs, respectively, per step). Numerical $dI/dV$ curves were calculated using five point differentiation.

The amount of impurities was checked by Auger electron spectroscopy (AES) with a cylindrical mirror analyzer. Since the oxygen AES signal O(KLL) at 512 eV is too close to the vanadium signal V(LMM) at 509 eV, the oxygen signal near 492 eV was monitored instead. The detection limit for low amounts of carbon and oxygen impurities was below 0.5% of the Auger-peak-to-peak height (APPH) of the main V peak at 473 eV. Impurity signals at two positions on the sample were within a few percent of each other.

The APPH ratios are converted into real monolayer coverages by using earlier reported calibrations. It was found that 1 ML carbon corresponds to $C_{272\,eV}/V_{473\,eV} = 0.16$ [10,11], while 1 ML oxygen corresponds to $O_{492\,eV}/V_{473\,eV} = 0.045$ [25]. Of course, local carbon and oxygen contamination can also be inferred from atomically resolved STM images, since these electronegative atoms appear as depressed fourfold hollow sites [8,10,25,26]. However, the STM data indicate that the AES calibration used slightly overestimates the amount of impurities. Since the AES measurements were performed after the STM measurements possible adsorption from the residual gas can be one of the reasons for this overestimation. Consequently, the impurity concentrations obtained with AES are considered as upper limits.

The preparation of a clean V(001) surface on a bulk single crystalline sample is a difficult and lengthy process [10,11,17,25–27] and was discussed in more detail in Ref. [25]. Briefly, the first stage consisted of sputtering (2 keV Ar$^+$) at elevated temperatures (~850–950 °C) to remove sulphur. The second stage consisted of more than 1500 h of sputtering while the sample temperature was ramped up and down in the temperature range in which carbon and oxygen impurities preferentially segregate to the surface (typically 350 and 600 °C, respectively, as obtained by AES measurements as a function of sample temperature). In the later stage of the cleaning process, AES showed no contamination on heating the sample up to 900 °C. For the STM measurements, the sample was post-annealed at 650 °C after the sputter–annealing cycles which resulted in an atomically flat surface (typical terrace widths of ~100 nm). However, on cooling down to room temperature, the APPH ratio for $C_{272\,eV}/V_{473\,eV}$ started to rise near 500 °C. In order to minimize the segregation of carbon during the cooling process, the sample was cooled quickly to room temperature by bringing the molybdenum sample holder plate into contact with a copper block.

Although for the cleanest V(001) the carbon impurities on the surface are due to segregation out of the bulk, we exclude the possibility of high amounts of carbon in the subsurface layers. First, calculations indicate that the fourfold hollow site at the surface is the most favorable site for carbon impurities [26]. Furthermore, AES shows that carbon diffuses back into the bulk at temperatures above 400 °C indicating that the carbon concentration in the subsurface layers cannot exceed the solubility limit at this temperature, i.e. $\approx 10^{-6}$ [30,31].

### 3. Results and discussion

#### 3.1. V(001) contaminated with segregated impurities: low coverage regime

Fig. 1 shows STS measurements on V(001) contaminated with small amounts of segregated C. AES shows a C/V APPH ratio of 0.7% which corresponds to $\approx 0.05$ ML. The oxygen signal is below the detection limit ($\approx 0.1$ ML). In the constant current image of Fig. 1a, the areas covered with C (and possibly some O) impurities can be observed as 20–40 pm depressed areas. $dI/dV$ curves were measured at each pixel simultaneously with this constant current image. A clear difference is observed between $dI/dV$ spectra measured on dark (contaminated) and bright (clean) areas in

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3 Growth of 100 nm thick vanadium layers at small rates (0.2 nm/s) and high temperature (1100 K) on properly degassed MgO(001) substrates was shown to give clean (oxygen signal below detection limit of Auger and (1 × 1) pattern in RHEED) V(001) surfaces [28,29].
Fig. 1a. Fig. 1d shows two of these $dI/dV$ curves. Curve 1 is measured on a bright area of Fig. 1a (arrow marked 1) and shows a strong and sharp peak 0.03 eV below the Fermi level. Curve 2 is measured on a dark area of Fig. 1a (arrow 2). This curve shows a higher peak energy, lower amplitude and larger full width at half maximum (FWHM) compared to curve 1. Moreover, curve 2 has a higher $dI/dV$ at the high energy side of the Fermi level peak.

To determine the properties of the electronic state, we have fitted each $dI/dV$ curve between $-0.2$ and $+0.2$ V to a Gaussian function with a background. Due to the additional structure in $dI/dV$ at higher energies, it was not possible to obtain the background as an independent fitting parameter. Instead, a fixed value of 0.8 nA/V was used for this background. The peak energies and widths resulting from this fitting routine are shown in Fig. 1b and c. Comparing Fig. 1a with Fig. 1b and c shows that both the peak energy image and the peak width image are anti-correlated with the constant current image: at the clean V(001) areas the lowest peak energy and smallest peak width are measured.

Fig. 1e shows a line profile along the [1 1 0] direction over a small, almost spherical symmetric, depressed area. The FWHM of this depression is 0.7 nm. This is comparable to the resolution predicted by the Tersoff–Hamann theory at the relatively large tip–sample distance used during spectroscopy (~1nm) assuming an atomically
sharp tip [32]. Furthermore, due to the almost spherical symmetry of this depression (the extension in the slow scan direction might be due to drift which is not negligible during relatively slow STS measurements at room temperature), it is tempting to identify this depression with a single carbon (or, possibly, oxygen) impurity. The peak energy has reached a constant value of $-0.03$ eV at the clean areas. Since this value is always obtained on large clean areas (>1 nm), it is considered to be the surface state energy of clean V(001). The peak energy shifts to $+0.02$ eV at the feature attributed to a single impurity atom. The width of this feature in the peak energy line profile is the same as the FWHM of the topographic line profile (0.6 nm). Therefore, the width of the peak energy profile over the impurity atom is more likely to be determined by the resolution during the spectroscopy measurement than by the range of influence of the impurity atom on the V(001) surface state.

The FWHM of the surface state increases from 0.13 eV at clean V(001) to 0.35 eV at the single impurity atom. The value obtained on the clean area is of the same order as the FWHM found by Stroscio et al. [4] for the 3d$_z$ surface state of Fe(001) measured on extremely clean iron whiskers. Comparing the line profiles of the peak energy and the FWHM, one striking difference can be recognized: the peak energy reaches its constant value at a shorter distance from the impurity atom than the peak width. At a distance of 1 nm from the impurity, the peak energy has reached the saturation value of $-0.03$ eV while the peak width clearly has not obtained its lowest value yet as the arrows in Fig. 1e show. Only at a distance of about 2.5 nm the lowest value for the FWHM of 0.13 V is found. Since the FWHM of the surface state is related to its lifetime [33,34], these results imply that the influence of the impurities on the surface state lifetime is longer-ranged than the influence on the surface state energy. The lifetime of the surface state can be influenced by a few mechanisms. First, due to the peak shift away from the Fermi level, the phase-space for electron–electron scattering increases. We do not expect this to play much of a role for a state so close to $E_F$, however. Second, the local stress around the impurities (see also Section 3.5) may have an influence on the electron–phonon scattering. An electron–phonon coupling constant $\lambda$ of 1.45 is reported for the clean V(001) surface state which is one of the highest reported values so far and shows the importance of this scattering mechanism for this surface [35]. However, the mechanism we consider most important is coupling to bulk states via the impurity. Only recently, lifetimes of noble metal fcc(111) surface states measured by STS could be accurately predicted by theory [33]. For such states it is also known that scattering by adatoms leads to significant coupling between the surface state and bulk states, significantly reducing the amplitude of the outgoing wave of the surface state [36]. However, the effect of the lifetime and scattering by impurities of d$_z$ surface states on the peak widths observed in $dI/dV$ has not been discussed until now.

3.2. Influence of the tip on the Fermi level surface state

STS measurements on metal surfaces are usually performed at relatively high tunneling resistances. A typical setpoint of $V_s = -0.5$ V and $I = 1$ nA (tunneling resistance of 500 MΩ) corresponds to a tip–sample distance of about 0.9 nm (core–core), as determined by extrapolation of the $I(z)$ curve (see below). Under these conditions, the tip is not expected to have an influence on the electronic structure of the sample surface. Tersoff–Hamann theory which uses the Bardeen approximation for the tunneling matrix elements is valid and $dI/dV$ is predicted to be proportional to the sample LDOS [32]. However, at smaller tip–sample distances (i.e. smaller tunneling resistances), the presence of the tip might lead to distortions of the sample electronic structure. Hofer et al. [37] have shown that the Tersoff–Hamann model and simulations including realistic tip density of states but still based upon the Bardeen approach fail to describe the corrugation measured on a Fe(001) surface for tip–sample distances smaller than 0.4 nm. This problem was solved by assuming a $z$-dependent quenching of the surface state contribution in the LDOS. Nevertheless, a direct experimental confirmation of the influence of the tip on a surface state has not been reported until now.
To study a possible influence of the tip on the surface state, we have measured \( dI/dV \) around the Fermi level at clean V(001) areas as a function of tunneling resistance. To avoid overload of the tunneling current amplifier (50 nA range), \( dI/dV \) was only measured in a very small energy window of approximately \( \pm 0.1 \) V around the Fermi level. Unlike the case of Fe(001) where the surface state is at \(+0.17\) eV \([4,5]\), the V(001) surface state is very close to the Fermi level which allows measurements at lower tunneling resistances without current overload for standard STM current amplifiers.

The results are shown in Fig. 2a. The setpoint is changed from 1.3 to 47.3 nA at a bias voltage of \(-0.08\) V (from 62 to 1.7 M\( \Omega \), respectively) and back to 1.1 nA to exclude a tip change during the measurement and detect possible influences of drift. The curves have been normalized to the 62 M\( \Omega \) curve. Whereas we cannot determine from these curves whether the amplitude of the surface state depends on the tunneling distance (a reduced amplitude would equally affect the setpoint and the spectrum) one can immediately see that the surface state energy does not shift significantly down to a tunneling resistance of 1.7 M\( \Omega \). We only observe a slight drift of the peak position with time, presumably due to \( x \)- or \( y \)-drift of the STM tip towards an area with slightly higher surface state energy.

The vertical tip displacements during the STS measurements were also measured. Fig. 2b shows the tip displacement relative to the tip–sample distance at 1.7 M\( \Omega \) as a function of tunneling resistance (which is plotted on a log scale). In a simple one-dimensional tunneling model, the slope of this curve is determined by the effective barrier height (see e.g. \([38]\)) which can be approximated by the average of the sample and tip work function. In our case, a value of \( 3.1 \pm 0.4 \) eV is found for the effective barrier height. Kralj et al. reported a work function for clean V(001) of \( 4.1 \pm 0.1 \) eV \([39]\). In addition, it was shown that oxygen dosage can increase the work function by as much as 2.5 eV up to \( \sim 10 \) L \([40]\). The ab initio calculations described in Section 3.5 of the current work result in a work function of 3.7 eV for the clean surface and 4.4 eV for a full monolayer of carbon. The low work function measured can be an effect of the tip work function. In contrast to close-packed surfaces, rough open surfaces have rather low work functions, e.g. 3.7 eV for a W adatom on W(001) \([41]\) as compared to 4.4 eV for W(001) \([42]\). As it is likely that vanadium atoms have been transferred to the tip in our experiments, we can expect a tip work function significantly below that of V(001).

Whereas we cannot detect changes of the amplitude of the surface state from the spectra (Fig. 2a), any significant quenching of the surface state should lead to a reduction of the tunneling current.

![Fig. 2](image-url)
at the voltage of $-0.08$ V where the data of Fig. 2b were obtained. In such a case we would expect the curve in Fig. 2b to bend down at low tip–sample distance. As we do not observe this, we estimate that any possible quenching of the surface state is not more than 10% at a tunneling resistance of 1.7 MΩ.

The experimental tip–sample distances can be estimated by extrapolation of the tunneling resistance to the contact point [i.e. $\sim \hbar/(2e^2) = 12.9$ kΩ] where a tip–sample distance (core–core) of around 0.3 nm is assumed. Therefore, the lowest tunneling resistance studied in this work results in an absolute tip–sample distance (core–core) of around 0.5–0.6 nm. The absence of a tip influence on the sample electronic structure in this regime is therefore not in contradiction with the results of Hofer et al. [37].

### 3.3. V(001) contaminated with segregated impurities: high coverage regime

Fig. 3 shows STS measurements on a slightly more contaminated sample. The APPH ratio of C/V and O/V are 2.7% and 0.8% which corresponds to $\approx 0.17$ ML carbon and $\approx 0.18$ ML oxygen, respectively. A $dI/dV$ curve is measured at every pixel of the topographic image, i.e. Fig. 3a. Typical $dI/dV$ curves, which are taken at the points indicated in Fig. 3a–c are shown in Fig. 3d and e. A surface state is detected around $-0.03$ eV at the clean areas of Fig. 3, just as in the measurement of
Fig. 1, although its width is about three times larger (0.4–0.45 eV). This surface state has shifted to +0.1 eV at the contaminated area indicated by number 2. Furthermore, curve 2 shows a weak shoulder above +0.5 eV. In curves 3 and 4 which are measured at even more depressed (contaminated) areas in Fig. 3a this shoulder has evolved into a peak. The highest peak energy observed was ~+0.75 eV. For these curves, a shoulder is found around the Fermi level. The observation of shoulders in curves 2, 3 and 4 is attributed to the low spatial resolution during STS: at this setpoint a circle of about 0.7 nm diameter is estimated to contribute to the tunneling current (see Section 3.1).

Fig. 3b and c show \( \frac{dI}{dV} \) maps at +0.02 eV and +0.82 eV, respectively. These energies correspond roughly to the locations of the clean V(001) surface state and the high energy surface state. Comparison of Fig. 3a–c shows that the Fermi level peak is localized on the bright (i.e. clean) areas of the topographic image, while the high energy peak is localized on the most depressed (i.e. highly contaminated) areas.

In Fig. 3a, a monoatomic step along the [1 0 0] direction is visible. The grey scale has been used twice through the height range of the image to make the structure on both terraces visible (lower terrace is in the top-left of the image). The step has been marked by white dashed lines in Fig. 3a–c. The step cannot be clearly recognized in the \( \frac{dI}{dV} \) maps. Therefore, it seems likely that the step has only a small influence on the V(001) surface state. As an example, two single \( \frac{dI}{dV} \) curves measured on clean V(001) areas which are within 0.5 nm from the step edge are shown in Fig. 3e. Curve A and B are measured on the lower and higher terrace, respectively. C is measured on an obviously clean area of the upper terrace. The peak energies are 0.00 eV for A and B, and −0.02 eV for C. The step certainly does not have a large influence on the surface state, although a minor influence (peak shifts well below <0.05 eV) is difficult to disentangle from the influence of the impurities on the V(001) surface state.

Fig. 4a shows a topographic STM image of V(001) contaminated with the same amount of impurities as Fig. 3. The impurity atoms can be clearly resolved at this setpoint \( (V_s = -0.4 \text{ mV}, I = 1.4 \text{ nA}) \). Some small c(2 \times 2) patches can be recognized (distance between depressions along [1 1 0] direction is 0.43 nm). Recent calculations by Bergermayer et al. show that the c(2 \times 2) structure of pure carbon on V(001) is less stable than the p(1 \times 2) structure but that additional oxygen atoms stabilize the c(2 \times 2) structure [26]. This is in correspondence with an STM study which showed that the c(2 \times 2) ordering increased with increasing amount of oxygen contamination [26]. It is also in agreement with the Auger results obtained on the sample of Fig. 4a in which both oxygen and carbon impurities were detected.

Fig. 4b shows an STS measurement on the same area performed immediately after recording
Fig. 4a. The setpoint of \( V_s = -0.82 \) V, \( I = 0.98 \) nA used for STS does not allow atomic resolution. Fig. 4b clearly shows the blurring effect of topographic features at the STS setpoints. The \( dI/dV \) map at \( V_s = +0.7 \) V is shown in Fig. 4c. Comparing these three images shows convincingly that the high energy peak is localized on areas showing the local \( \text{c}(2 \times 2) \) structure.

3.4. Oxygen-induced \((1 \times 5)\)-reconstruction

Adsorption of \( \sim 1 \) L \((1 \text{ L} = 1.33 \times 10^{-6} \) mbar s\) oxygen on the oxygen-free V(001) sample at 200 °C leads to the formation of a \((1 \times 5)\) reconstruction which has been studied in detail by Koller et al. [25]. The driving force for this reconstruction was found to be increasing tensile stress with increasing oxygen coverage: the O–V bond length with oxygen in the fourfold hollow sites of an unreconstructed surface would be 0.216 nm, which is larger than the favorable length of \( \sim 0.20 \) nm. This stress can be reduced by large displacements of the vanadium atoms, decreasing the V–V in-plane bond lengths around the hollow-site O atoms. Due to this contraction the V–V distance increases elsewhere, leading to sufficiently large V–V distances for O adsorption on the twofold bridge-sites. A model for the reconstruction is given in Fig. 5 (from Ref. [25]).

Fig. 6 shows STM images taken after dosing of 0.9 L at 200 °C. The APPH ratios of 3% for O/V and 1.8% for C/V correspond to a coverage of \( \sim 0.67 \) ML oxygen and \( \approx 0.11 \) ML carbon. In Fig. 6b, the \((1 \times 5)\) reconstruction is clearly visible as dark lines at every fifth vanadium atom running along the [100] and [010] direction. Sometimes a spacing of six vanadium atoms is observed as indicated in Fig. 6b. In Fig. 6a a tip change causes a drastic change of the contrast. Note that there is no lateral shift after the tip change possibly indicating that the tip change is related to an exchange of the tip-apex atom. Fig. 6b is the image taken immediately after Fig. 6a. The white squares show the same area in Fig. 6a and b and are enlarged in Fig. 6c and d. Obviously, the bright protrusions in a and c are imaged as the most shallow fourfold hollow sites in b and d. Calculations [26] show that the bright protrusions in frames (a) and (c) are the empty (i.e. uncovered) fourfold hollow sites, while hollow sites occupied with C or O appear dark (low). Comparison of frames (c) and (d) demonstrates that these occupied hollow sites appear darker than unoccupied hollow sites also in atomically resolved images like (b) and (d). Furthermore, Fig. 6a clearly shows that the protrusions tend to order in a \( \text{c}(3\sqrt{2} \times \sqrt{2})R45^\circ \) structure which can be considered as a \( \text{c}(2 \times 2) \) structure with domain boundaries [7]. Its unit cell is also sketched in Fig. 5.

Fig. 7a shows an STM image of the oxygen-induced V(001) \((1 \times 5)\) superstructure taken at the setpoint of spectroscopy. A \( dI/dV \) curve was measured at each pixel \((100 \times 100 \) curves\). The average of all these curves reveals a strong peak at
with a FWHM of 0.45 eV (obtained from a Gaussian fit). However, the $dI/dV$ curves of Fig. 7b show that slightly different curves are obtained at the various local geometries of the (1\texttimes 5) reconstruction (i.e. bridge-site oxygen lines, occupied and unoccupied fourfold hollow sites). Curves 1 and 2 are the averages of four single $dI/dV$ curves obtained on the occupied (depressions) and unoccupied fourfold hollow sites (protrusions) which are marked by squares and circles in Fig. 7a, respectively. Strong peaks can be observed at $+0.66 \pm 0.01$ eV (curve 1) and $+0.63 \pm 0.01$ eV (curve 2). The FWHM of these peaks are $0.40 \pm 0.03$ and $0.39 \pm 0.03$ eV, respectively. To minimize the influence of the bridge-site oxygen line electronic structure (see below) only points exactly in between these lines were used for curves 1 and 2. The given errors indicate the scatter (standard deviation) of averages obtained on various equivalent surface areas within one STS measurement (excluding scatter among different tips).

Curve 3 is the average of four single $dI/dV$ curves obtained on the depressed area which is marked 3 in Fig. 7a. In this area without nearby unoccupied fourfold hollow sites (protrusions) the $dI/dV$ curves show a peak at $+0.57 \pm 0.01$ eV with a FWHM of $0.39 \pm 0.03$ eV. This peak energy is also found on highly contaminated V(001) surfaces showing the (1\texttimes 5) reconstruction (typically APPH ratios C/V = 3.5\%, O/V = 4.0\%) where the concentration of unoccupied fourfold hollow sites is much smaller.

Besides slight peak shifts, the major difference between curve 1 (occupied fourfold hollow sites in c(3\sqrt{2} \times \sqrt{2})-like structure), curve 2 (unoccupied fourfold hollow sites) and curve 3 (occupied fourfold hollow sites in p(1 \times 1)-like structure) is the peak amplitude. When the same background (1 nA/V) is subtracted, curve 2 has a 30\% (40\%)...
lower peak amplitude compared to curve 1 (3). In this context it should be realized that the peak amplitudes depend on the tip–sample distance. Therefore, at the position of the bright protrusion the tip–sample distance is increased by the apparent height of the protrusion (i.e. ~20 pm compared to depressions) if we assume that the protrusion is an electronic and not a geometric effect. The latter seems reasonable if we realize that the bright protrusion actually is an unoccupied fourfold hollow site. Using the exponential dependence of the tunneling current on the tip–sample distance ($I \sim \exp(-2k\Delta)$ with $k = 1 \times 10^{10} \text{ m}^{-1}$ [32]), it can be shown that a tip retraction of ~20 pm ($\Delta$) leads to a 33% lower tunneling conductance. The ~30 pm higher $z$ value of the protrusions marked 2 compared to the depressed area marked 3 leads to a ~45% reduction in the tunneling conductance.
These considerations show that the different peak amplitudes can be understood in terms of local variations in the tip–sample distance.

Curve 4 is the average of four single \( \frac{dI}{dV} \) curves measured at the bridge-site oxygen line of the reconstruction (position of pixels is roughly marked in Fig. 7a, c, and d by arrow). The \( \frac{dI}{dV} \) curve clearly shows a shoulder around +0.6 eV and a peak around +0.8 eV. Due to the limited resolution during STS, there is always a non-negligible contribution of the electronic structure of neighboring sites to the \( \frac{dI}{dV} \) curve measured on top of the lines. To find the energy of the bridge-site oxygen line state, we have scaled curve 3 to fit the rising slope of curve 4 and subtracted from curve 4. The result is curve 5 (Fig. 7b). This curve shows a peak at +0.90 eV. By performing the same analysis to various \( \frac{dI}{dV} \) curves measured at the oxygen lines, a peak energy of +0.91 ± 0.01 eV and a FWHM of 0.38 ± 0.04 eV are found.

To study the localization of these states, \( \frac{dI}{dV} \) maps at \( V_c = +0.62 \) V and \( V_c = +0.85 \) V are shown in Fig. 7c and d, respectively. Due to the tip-height effect explained above, the peak around +0.62 eV is highest at the occupied fourfold hollow sites in Fig. 7a and is reduced at the bright protrusions. The peak around +0.85 eV is localized at the bridge-site oxygen lines of the (1 \( \times \) 5) reconstruction as can be seen from Fig. 7c. The width of the lines in the +0.85 V \( \frac{dI}{dV} \) map can be obtained by fitting line profiles perpendicular to the bridge-site oxygen lines to Gaussian functions. The value obtained in this way (FWHM 0.5 nm) is again of the same order as expected from the resolution predicted by the Tersoff–Hamann theory at the tunneling resistance of the STS measurement.

### 3.5. Calculations

To understand the nature of the surface states observed, ab initio band structure calculations were performed for the clean V(001) and C covered surfaces: p(1 \( \times \) 4), p(1 \( \times \) 2), p(2 \( \times \) 2), c(2 \( \times \) 2), and p(1 \( \times \) 1) with C in fourfold hollow sites. A two step procedure was employed for efficiency. The systems were first fully relaxed with the Vienna ab initio simulation package (VASP [43]) using ultrasoft pseudopotentials [44,45]. A considerable first layer inward relaxation (−18%) was found for clean V(001), which is reversed by C adsorption and becomes +25% for a p(1 \( \times \) 1)C adlayer. A detailed discussion can be found in Ref. [26]. The position of the carbon atoms is 0.052, 0.042, 0.037 and 0.021 nm above the surface plane for the p(2 \( \times \) 2), c(2 \( \times \) 2), p(1 \( \times \) 2) and p(1 \( \times \) 1) structures, respectively. The in-plane lattice constant was fixed at the calculated bulk value of 0.299 nm. The relaxed geometry of the nine layer V(001) slabs served as the input for full-potential linearized augmented plane wave (FLAPW) [46] calculations (FLEUR code [47]). Using FLEUR, we have also calculated a p(1 \( \times \) 4) structure to simulate the boundary of carbon covered domains. This structure was created by taking the height of the C atoms and the geometry of their nearest V neighbors from the p(2 \( \times \) 2) structure. The positions of the first and second-layer V atoms in the center of the cell (uncovered area) were taken from the clean surface, leading to a small buckling of 0.005 nm in the V top-layer. In all calculations, exchange–correlation was treated within the generalized gradient approximation of Perdew (PW91) [48]. The number of basis functions per atom was \( \sim \)110 APWs. For clean V(001) and the p(1 \( \times \) 1)C coverage 36 \( k \)-points in the irreducible part of the Brillouin zone were used, for the p(1 \( \times \) 2)C and the c(2 \( \times \) 2)C coverage 16 \( k \)-points, and finally for the p(2 \( \times \) 2)C and the p(1 \( \times \) 4)C coverage 10 \( k \)-points.

No exchange splitting pointing towards a magnetic surface could be detected in our spin-polarized calculation. Complete carbon coverage increases the workfunction from 3.7 eV to 4.4 eV. Fig. 8 shows the calculated LDOS at \( \sim \)0.9 nm above the surface for V(001), V(001) p(1 \( \times \) 4)C, and V(001) p(1 \( \times \) 1)C. These calculations were restricted to \( |k|| < 1/6|I - X| \) for the (1 \( \times \) 1) cells, and an equivalent area for the (1 \( \times \) 4) cell, to mimic the \( I \)-dominated tunnel current for large (>1 nm) tip–sample distances [4]. The peak at +0.07 eV in the V(001) LDOS is due to a surface state in a bulk band gap at \( I \). Fig. 9a shows the

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\( ^2 \) As discussed in the experimental part, we do not expect a high carbon concentration in the subsurface layers.
charge density of this state. This state shows d$_{z^2}$ wave functions near the cores and has additional s and p$_z$-like contributions protruding far out into the vacuum, making this state easily detectable by STS. At C/C$_2$ this state shows little interaction with the layers below, but moving away from C/C$_2$ leads to an increased coupling to the subsurface layer which lowers the surface state energy. This results in a negative dispersion of the surface state band.

The LDOS above the V(001) p(1 x 1)C surface shows a peak around +0.75 eV (Fig. 8), which lies again in a bulk gap at $\Gamma$. This identifies it as a surface state, in spite of the relatively large charge density in the second layer (Fig. 9e). The influence of C can also be seen by examining the charge densities of the surface state in the other geometries (Fig. 9b–d), where only those second layer V atoms directly below a C atom have a high d$_{z^2}$ charge density. The calculations for perfect p(1 x 4), p(1 x 2), p(2 x 2) and c(2 x 2) carbon coverages find vacuum LDOS peaks at +0.16, +0.13, +0.46 and +1.52 eV, respectively (see Table 1). As a comparison of Fig. 9a–e shows, these states are derived from the same orbitals coupling in the same way as the surface states of the pure and p(1 x 1)C surfaces.

At first sight, it is puzzling why the energy calculated for the c(2 x 2) state is much higher than those of the similar surface states of the other structures studied. Especially the difference between p(1 x 1) and c(2 x 2) is remarkable as they are very similar in shape and symmetry as inferred from Fig. 9d and e. Having a look at their counterparts reflecting the C-p$_z$–V-d$_{z^2}$ interaction in the occupied region, one finds these states around -2.6 and -1.7 eV for p(1 x 1) and c(2 x 2) respectively. It is interesting to note that the splitting between these occupied states and our surface states is now ~3.4 eV and ~3.2 eV for p(1 x 1) and c(2 x 2), pinpointing the strong covalent interaction between C-p$_z$ and the V-d$_{z^2}$ below, which should be quite similar for both structures since the V–C distance is almost identical. In other words, the energetical position of the C-derived states is generally lower for p(1 x 1) than for c(2 x 2).

A simple tight-binding calculation including only nearest and next-nearest neighbor s–s, d–d and s–d hybridization [49] was performed to gain more insight into the properties of the V(001) surface state. Due to the next nearest neighbor s–d$_{z^2}$ hybridization a band gap opens along the bulk [001] direction. For a 80 layer slab (parameterized to give the correct bulk bands) the surface state of pure V(001) is shifted from the lower band edge if the next nearest neighbor vanadium s–d$_{z^2}$ hybridization in the surface layer is strongly reduced which is reasonable due to the charge spill-out to the vacuum at the surface.

Increasing (decreasing) the in-plane lattice constant decreases (increases) this hybridization also which moves the state up (down) in energy. This is in agreement with the FLAPW calculations where a 0.04 eV lower energy for the surface state of clean V(001) is found when a lattice constant of 0.298 nm is used (i.e. less than 1% smaller). On the other hand, FLAPW calculations in which the interlayer distance between the first and second vanadium layer was expanded by 25% did not have a strong effect on the surface state energy which shows that the huge relaxation of this system (i.e. -18%) has only a minor effect on the
surface state energy. As can be seen in Fig. 9b–e, when the V(001) surface is covered with carbon, the extended s,p$_z$-like contributions present in Fig. 9a, have been lost to the directional V–C d–p bonds. This will lead to a reduced in-plane s–d$^z_2$ hybridization between neighboring atoms and therefore to an increased energy of the surface state which explains the upward peak shifts at carbon contaminated areas observed in the STS measurements. Notice that the upward peak shifts cannot be explained by confinement effects since quantization of the parallel wave vector would lead to a downward shift due to the negative dispersion of the surface state.

To test the strong influence of the surface nearest neighbor s–d$^z_2$ hybridization on the surface state energy, FLAPW calculations were performed for V(001) with c(2 × 2) and p(1 × 1) hydrogen superstructures. It was found that hydrogen increases this hybridization and consequently, lower surface state energies are found. The c(2 × 2)H structure shows a surface state at −0.21 eV, the p(1 × 1)H structure at −0.53 eV. However, experiments where up to 1.8 L molecular hydrogen was dosed on a fairly clean V(001) surface (∼0.1 ML carbon) did not show any downward shift of the surface state. This could imply that the absorbed hydrogen immediately disappears into the

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**Fig. 9.** Charge density distribution of the (a) +0.07 eV V(001) surface state, (b) the +0.16 eV V(001) p(1 × 4)C surface state, (c) the +0.46 eV V(001) p(2 × 2)C surface state, (d) the +1.52 eV V(001) c(2 × 2)C surface state, and (e) the +0.75 eV V(001) p(1 × 1)C surface state. These states correspond to the strongest peaks in the LDOS. The position of the surface layer is given by the dashed line. The same logarithmic greyscale is used.
bulk in agreement with the results of Krenn et al. [10].

Having established now the strong impact of the in-plane vanadium–vanadium s–d\(_2\) hybridization on the surface state, the small influence of the monoatomic step on the surface state seems to be conflicting. At the step along the [1 0 0] direction, vanadium atoms are missing one surface nearest-neighbor and consequently, an effect on the s–d\(_2\) hybridization is expected. Calculations for a stepped geometry would be needed to solve this problem and might also be interesting from point of view of a possible existence of a magnetic moment [16].

The calculations find a surface state of d\(_z^2\) symmetry at +1.52 eV for the c(2\(\times\)2)C covered V(001) surface which is in contradiction with the experiments where a very strong peak in dI/dV is observed around +0.7 eV on the local c(2\(\times\)2) structures. However, as mentioned before, it is quite likely that the experimental c(2\(\times\)2) structure contains oxygen atoms [26]. Furthermore, since the c(2\(\times\)2) domains are quite small, relief of stress is possible at the domain edges. Therefore, the experimental configuration is not exactly comparable to an ideal c(2\(\times\)2) carbon coverage. The calculations for p(2\(\times\)2) and p(1\(\times\)4) carbon overlayers reveal surface states at +0.46 and +0.16 eV, respectively. These arrangements, in particular p(1\(\times\)4), are certainly much better suited to mimic domain edges. Now, the relaxed symmetry allows the d\(_z^2\)-like lobes to tilt away from the carbon atoms, which increases the overlap between them and counterbalances the loss of charge density to the V–C bond (Fig. 9b).

Due to the fact that the tensile stress is relieved in the (1\(\times\)5) reconstruction, the V–V in-plane nearest neighbor distances decrease between the oxygen lines by 6\% and 7\%, respectively, and increase over the twofold bridge sites by 27\% (see Fig. 5). In line with the discussion above, these large displacements are expected to have a large impact on the in-plane vanadium–vanadium s–d\(_z^2\) hybridization. In other words, the expected increased s–d\(_z^2\) hybridization on the terrace between the bridge-site oxygen lines, would be in agreement with a lower surface state energy compared to the value of +0.75 eV calculated for the p(1\(\times\)1) geometry. We therefore identify the peak at +0.57 eV observed on the protrusion-free areas of the (1\(\times\)5) reconstruction (curve 3 in Fig. 7) with the p(1\(\times\)1) surface state, shifted as a consequence of local relaxations. Although this qualitative discussion of the influence of the vanadium–vanadium s–d\(_z^2\) hybridization on the surface state energy is based upon quantitative calculations for carbon impurities, oxygen is not expected to have a complete different behavior on the V(001) surface state compared to carbon since both atoms are strongly electronegative.

### 4. Summary

STS results on differently prepared V(001) samples were presented. A sharp surface state near the Fermi level was detected on clean V(001) areas. Small amounts of segregated impurities (mostly carbon) shift this peak in dI/dV across the Fermi level towards higher energies. In particular, it was shown that a single impurity shifts the surface state upwards by 0.05 eV. It was verified that the presence of the tip has no significant influence on the energy or amplitude of the peak in the setpoint range usually available in STS measurements. The influence of [1 0 0]-oriented steps on the peak energy was found to be smaller than the effect of impurities. The surface state is observed around
+0.75 eV at c(2 \times 2) areas. By dosing the clean V(001) surface with oxygen, the (1 \times 5) reconstructed surface was obtained. Here, a strong peak in dI/dV is observed around +0.63 eV on the c(3\sqrt{2} \times \sqrt{2}) areas of the (1 \times 5) reconstruction. At areas with higher adsorbate concentrations (fully covered) this peak is observed at a slightly lower energy of +0.57 eV. At the bridge-site oxygen lines a peak is observed around +0.91 eV.

Band structure calculations show that the surface state observed on the clean V(001) surface has dz\(^2\) wave functions. The absence of any splitting of the experimental surface state together with the agreement between calculated and experimental peak positions leaves no room for a significant magnetic exchange splitting of the surface state of clean V(001). For the carbon and oxygen covered surfaces, the experimentally observed peak shifts can be qualitatively understood in terms of surface-plane vanadium–vanadium s–d\(_{z^2}\) hybridization. The experimentally and theoretically obtained peak energies for the various geometries are summarized in Table 1.

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