Atomic scale imaging and spectroscopy of the V$_2$O$_3$ (0001)-surface: bulk versus surface effects

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(Received January 9, 2022)

We present atomic scale images of a V$_2$O$_3$ (0001)-surface, which show that the surface is susceptible to reconstruction by dimerization of vanadium ions. The atomic order of the surface depends sensitively on the surface preparation. Scanning tunneling spectroscopy proves a dimerized surface has a gap in the electronic density of states at the Fermi energy, while a surface prepared by sputtering and successive annealing shows no dimerization and no gap. Photoemission spectra depend sensitively on the surface structure and are consistent with scanning tunneling spectroscopy data. The measurements explain inconsistencies in photoemission experiments performed on such oxides in the past.

PACS numbers: 68.37.Ef, 71.30+h, 73.20-r, 79.60.Bm

Despite intense efforts the field of electronically correlated materials still poses major challenges to a theoretical understanding. An excellent example for the richness of the problem is the transition metal oxide V$_2$O$_3$, which shows a complex phase diagram with paramagnetic metal (PM), paramagnetic insulator (PI) and antiferromagnetic insulator (AFI) regions as function of temperature and pressure. Recently, detailed predictions for the spectral functions in the PM and PI phase as measured by photoemission have been put forward. Numerous photoemission studies on V$_2$O$_3$ can be found in the literature, but only one study showed that the spectra were taken from an atomically ordered surface by utilizing low energy electron diffraction (LEED). Since the various published spectra differ with respect to their spectral weight at the Fermi energy, a comparison with theory is ambiguous. Moreover, surface states in photoemission spectra and surface reconstruction have been found in other oxides. To shed light on the inconsistencies of photoemission data on V$_2$O$_3$ and in view of the importance of reliable data to assess the validity of theoretical approaches, measurements on rigorously characterized surfaces are essential. Since V$_2$O$_3$ shows structural instabilities and is very sensitive to oxygen stoichiometry, the perturbation introduced to the lattice by a surface can be expected to render the surface electronic properties different to that of the bulk. To investigate a possible surface reconstruction in V$_2$O$_3$ and its effect on the photoemission spectra, we have performed scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS) and photoemission (PES) measurements on a V$_2$O$_3$ (0001)-surface at room temperature. We show that the V$_2$O$_3$ surface can be prepared in an atomically ordered state, but that two surface structures exist, depending on the surface preparation process. The STM images of the first structure show long range atomic order of dimerized vanadium ions with a domain structure of roughly hexagonally shaped domains. The surface density of states exhibits a gap at $\epsilon_F$, as evidenced from STS and is consistent with PES measurements. A second surface structure shows no dimerization, STS measurements show no gap and PES exhibits enhanced spectral weight at $\epsilon_F$.

The trigonal bulk lattice structure of V$_2$O$_3$ in the metallic phase, usually described in a hexagonal unit cell, possesses alternating vanadium and oxygen planes in the <0001> direction. Within the respective layers the vanadium ions form a corrugated honeycomb lattice with a lattice constant of 0.495 nm and a vanadium-vanadium distance of 0.287 nm (Fig. 1(a)), while the oxygen ions are arranged in a distorted hexagonal lattice with O-O distances ranging from 0.266 nm to 0.295 nm. The vanadium layer shown in Fig. 1(a) effectively exhibits two inequivalent sites, since only half of the surface vanadium ions form a vertical pair with a vanadium ion below. Dark spheres: Vanadium, light spheres: Oxygen.

FIG. 1. (a) Honeycomb structure of vanadium terminated (0001)-surface. (b) Vanadium terminated (0001)-surface showing only vanadium ions which form a vertical pair with a vanadium ion below. Dark spheres: Vanadium, light spheres: Oxygen.
tion. Crystals were introduced in an Omicron UHV system and a surface was prepared by either heating the as grown surfaces in situ up to 750 °C for several minutes, or by first sputtering with Argon in a grazing geometry followed by the same heating procedure. The respective procedures were repeated until a LEED pattern of good quality was observed. STM and STS measurements were performed using an Omicron variable temperature STM (VT SPM). All STM images were recorded in the constant current mode, using a W tip at a sample bias of −1 V or +1 V and a current of 0.1–0.2 nA. The topographic images show the height $z(x,y)$ of the tip over the sample after a plane and slope subtraction was performed. PES was carried out using a He-discharge lamp and an Omicron AR 65 electron analyzer. Spectra are shown after Shirley background subtraction and with the V 3d spectral weight normalized to one.

Fig. 2 shows a STM topographic image over an area of $60 \times 60$ nm of the $V_2O_3$ (0001)-surface prepared from an as grown crystal by heating under UHV. A maximum height variation of 0.6 nm is observed over the range displayed. The image shows a domain like structure of roughly hexagonal, atomically ordered regions with an average domain dimension of $7-9$ nm. The regions between adjacent domains are generally disordered and reminiscent of domain walls or grain boundaries, with notable exceptions (see upper panel of Fig. 3). The appearance of such a domain like structure already indicates that the surface termination does not correspond to that expected from the trigonal bulk structure. In the upper right corner of Fig. 2 steps of a height of $0.19 - 0.27$ nm are observed. This step size approximately corresponds to the distance between two vanadium or two oxygen layers along the $<0001>$ direction (0.233 nm) and suggests that the terminating layer consists solely of either oxygen or vanadium ions. The upper panel of Fig. 3 shows two adjacent domains. Within each domain lateral pairs of light spots are resolved, which are arranged in rows as indicated in the figure. Here a lateral pair is identified as the neighboring spots with shortest separation. Adjacent rows are displaced by about half the distance between the pairs along the direction of the rows, i.e. the pairs are arranged in a two dimensional hexagonal lattice. The periodicity is approximately 0.5 nm, which corresponds to the bulk in-plane lattice constant of the vanadium honeycomb lattice (0.495 nm). In fact, closer inspection of the single spots, which we identify as single atoms, show they are arranged in a distorted honeycomb lattice, as marked in Fig. 3 (upper panel). The observation of a distorted honeycomb lattice of single atoms together with the lateral periodicity suggests that the observed termination is a vanadium layer, in which the V ions are dimerized. At the boundary between two domains the orientation of the pair axis changes. The pairing axes in Fig. 3 (upper panel) form an angle of 113°, the angle measured for many domains varies between 110° and 130°. For an undistorted honeycomb lattice (bulk vanadium layer) three equivalent directions, differing by 120°, exist, along which dimerization can occur. We therefore attribute the observed domains to a dimerization along these directions resulting in a distortion reminiscent of that in the mono-
FIG. 4. (a) STS of dimerized (unsputtered) surface, exhibiting a gap in the surface DOS. (b) STS of mostly undimerized regions of sputtered surface, indicating metallic behavior of the surface.

FIG. 5. PES on unsputtered dimerized (a) and sputtered (mostly undimerized) surface (b) for various electron take off angles. The dimerized surface shows considerably less spectral weight at $\epsilon_F$, which decreases with increasing take off angle.
FIG. 6. STM image of boundary between dimerized (region I) and undimerized (region II) regions of a sputtered surface. Parameters: $I = 0.2$ nA, $U_{bias} = -1$ V.

tation we identify the bright spots of region II as single V ions, occupying only one of the two inequivalent sites mentioned above, most likely sites corresponding to a vertical vanadium pair (see Fig. 1(b)). A typical STS spectrum of region II (Fig. 4(b)) shows that, in contrast to region I, no gap exists and the structure observed at $-2.7$ V on the dimerized surface has vanished. Correspondingly, PES (Fig. 5(b)) shows an increased spectral weight at $\epsilon_F$ compared to Fig. 5(a). Still, with increasing take off angle the spectral weight at $\epsilon_F$ decreases somewhat and a structure at $E_R = -2.7$ eV, although much weaker than seen in Fig. 5(a), develops. The variation of spectral weight with take off angle probably reflects the fact that regions of dimerized vanadium ions still exist on the sputtered surface, although the majority (undimerized) surface phase does not exhibit a gap in the DOS.

The results presented here show the sensitivity of the V$_2$O$_3$ surface to reconstruction. The reconstructed surface displays a gap in the DOS resulting in a reduction of spectral weight in PES at $\epsilon_F$. This effect obscures the parameter set for a theoretical description of such spectra and shows the necessity for a thorough surface characterization to obtain a reliable comparison between experimental and calculated spectral function. In the case presented here, the spectra of the unreconstructed surface (Fig. 3(b)) correspond approximately to those taken with high photon incident energy ($> 500$ eV) [6] (we note that using an incident photon energy of 2000 eV further increases the spectral weight at $\epsilon_F$ [14] compared to Ref. [6]), while spectra taken from the reconstructed surface reflect measurements with incident energies $< 100$ eV. We attribute the slight reduction of spectral weight at $\epsilon_F$ in the spectrum taken from the unreconstructed surface compared to high incident energy measurements to the presence of a small amount of (reconstructed) minority phase. Although V$_2$O$_3$, and, more generally, the binary vanadium oxides, might be especially prone to surface reconstruction in view of structural transitions taking place as a function of temperature, the need for improved surface preparation and characterization for all the early transition metal oxides is clear. On the other hand, the results give hope that a carefully prepared surface can reflect the bulk properties and will allow to study the dispersion of the quasiparticle band in the near future.

ACKNOWLEDGMENTS

This work was supported by the Deutsche Forschungsgemeinschaft under Contract Nos. HO 522 and SFB 484.

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