Contrast Reversal and Shape Changes of Atomic Adsorbates Measured with Scanning Tunneling Microscopy

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Systematic, quantitative comparisons between scanning tunneling microscopy (STM) experiments and first principles simulations of O(2×2)/Ru(0001) have been performed. The shape of the atomic adsorbates in the images depends strongly on the tunneling resistance and changes reversibly from circular (high resistance) to triangular (low resistance). In addition, after adsorption of oxygen on the STM tip we observe a contrast reversal on the surface, confirmed by extensive numerical simulations.

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In many exciting areas of research, e.g., catalysis, high T_c materials, and other complex transition metal oxides, it is important to identify metal and oxygen sites at surfaces in order to understand processes such as dissociation of molecules, spatial inhomogeneities in the superconducting gap, or the role of impurities in the formation of striped phases [1]. Although scanning tunneling microscopy (STM) topographs can be used to characterize surfaces at an atomic level, they do not always simply reflect the real position of surface atoms [2–6]. If we restrict ourselves to adsorbed oxygen layers or oxide surfaces, there are experimental reports [7–12] claiming that, depending on the system and the state of the tip, either the O or the metal atoms appear as bright features in the STM images. In the case of isolated oxygen atoms adsorbed on flat metal surfaces, their observed shape (a depression) is well understood [3,6,13,14]. However, in dense, ordered arrays of adsorbed oxygen the situation is still unclear. Because the geometric and electronic structures of the surface, as well as the chemical state of the tip, play a role in determining the corrugation, contrast, and shape of the image, it is necessary to perform *ab initio* calculations to properly interpret the STM images.

Here we report on a fundamentally new level of comparison between experiment and theory to clarify the role of the different parameters determining STM images like tip structure, sample voltage (V_s), tunneling current (I_t), and gap resistance (R_G). The measured series of STM images of the model system, (2×2) superstructure of O adsorbed on Ru(0001), is shown to be in quantitative agreement with first principles simulations. The geometric structure (adsorption site, interatomic distance, and relaxations) of the chosen system has been carefully characterized by low energy electron diffraction (LEED) [15]. The control parameters of the operation of the STM were systematically varied over a broad range ($10\ \text{mV} < V_s < 1\ \text{V}$, $0.03 < I_t < 50\ \text{nA}$, $300\ \text{k}\Omega < R_G < 2\ \text{G}\Omega$), and the ensuing changes were recorded and compared to simulated images. We find reversible changes in the apparent shape of the adsorbate as the gap resistance varies, as well as a reversal of contrast when the chemical termination of the tip is modified.

The experiments have been carried out in a UHV chamber with base pressure in the low 10^{-10} Torr regime. The chamber contains a variable temperature STM, a rear view LEED optics, an ion gun, and a mass spectrometer. The Ru(0001) crystal was cleaned by cycles of Ar^+ sputtering and annealing followed by oxygen exposure and heating to high temperature. The polycrystalline W tips were routinely cleaned by ion bombardment and field emission. All images were recorded in the constant current mode at 300 K. The exposure was carried out by flooding the UHV chamber with a partial oxygen pressure of 1×10^{-7} Torr. Although the STM tip could not be protected from oxygen exposure, we will show below that it was possible to certify when oxygen atoms were picked up by the tip.

The electronic structure of the tip and the sample surface were calculated using the density functional theory (DFT) package, VASP (Vienna *ab initio* simulation package) [16], which describes ion-electron interactions by ultrasoft pseudopotentials [17]. The exchange correlation potentials were calculated using a generalized gradient method [18]. The clean Ru(0001) surface was modeled with a three dimensional supercell consisting of seven atomic layers (separation distance $c/2$, with $c/a = 1.586$) with 2×2 hexagonal surface unit cells (lattice constant $a = 2.723$ Å) and a seven layer vacuum range. The Ru atomic positions of the surface layer were relaxed in three directions. For the O(2×2)/Ru(0001) surface we have used a 2×2 surface unit cell. The preferred adsorption site of O was found to be the hcp site directly above second layer Ru atoms, at a vertical distance of 1.16 Å, in agreement with LEED [15] and previous calculations [19].

The tip structure was modeled with the same DFT method with a pyramid of seven W(110) layers; the

apex atom was either W or O. In these simulations all ionic positions of the two top layers were also fully relaxed. From the calculation of surface and tip electronic structures we obtained the Kohn-Sham states of surface and tip electrons, which then were used as the input for the STM simulation. We calculated the tunneling current in the Bardeen approach [20,21]. This perturbative method limits the validity of the calculation to tip-sample distances larger than 4–5 Å, which is also the limit for the majority of experimental scans described here. The surface irreducible Brillouin zone was sampled with 20 k points. The energy cutoff in the plane wave expansion is typically 30 Ry (400 eV).

At low bias voltage and low tunneling resistance the clean Ru(0001) surface is imaged as a hexagonal array of round protrusions separated by 2.7 Å, as shown in Fig. 1(a). Scanning tunneling spectroscopy experiments and *ab initio* calculations [22] indicate that the states that dominate the current at standard distances are due to a surface resonance of p_z character, located close to the Fermi energy and spatially localized on top of the Ru atoms. Figure 1(b) shows an STM image of a compact O adlayer with 2×2 periodicity with respect to the substrate recorded at standard gap resistance. The O atoms are visualized as *circular* depressions. The bright regions in the image correspond to (mobile) oxygen vacancies in the 2×2 superstructure, i.e., clean Ru patches. Images taken at lower tunneling resistances (e.g., 0.3 MΩ), in which both the bare Ru(0001) surface and islands of the O(2×2) superstructure appear simultaneously with atomic resolution, allow us to determine the oxygen registry with respect to the Ru lattice. In these conditions of low gap resistance, however, the oxygen atoms are seen as *triangular* depressions.

In order to separate the influence of different tunneling parameters and to establish a sequence of shapes of STM images where tip changes can be excluded, we employed a method based on recording dual-mode STM images. To this end, a large number of a series of STM images have been recorded at increasing tunnel current (or voltages) on the forward channel, while in the backward channel the tunnel current (or voltage) was kept constant. Since the reference channel images were recorded simultaneously with the others and always in the same conditions, modifications in the former would alert one of unwanted tip changes. A representative selection of dual-mode STM images from one of these series recorded at increasing tunnel currents (and fixed voltage, −30 mV) is shown in Fig. 2. The lower panels display the reference channel. All reference images are identical, except for a minor drift. The upper panels display three images illustrating a reversible transition observed in the appearance of the ''atomic'' features. As mentioned before, a hexagonal array of circular depressions is seen at large gap resistances. Upon decreasing the gap resistance, the depressions progressively acquire a triangular appearance. The dark triangles have all identical orientation when in

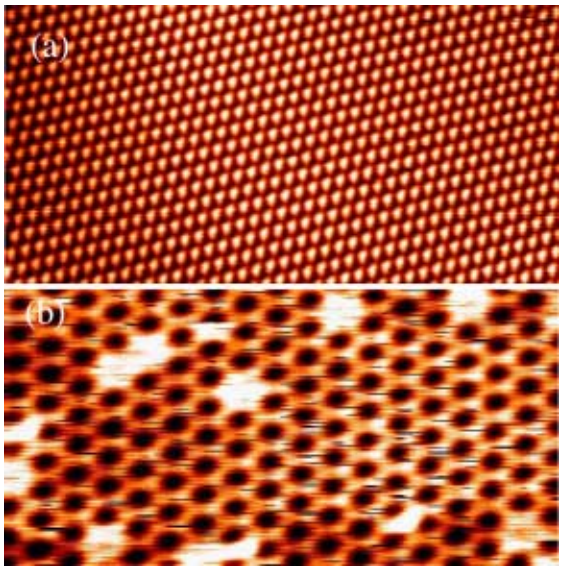

FIG. 1 (color online). (a) 10 nm × 5 nm STM image of a clean Ru(0001) surface recorded at a sample voltage of −23 mV with a gap resistance of 2 MΩ. (b) 10 nm × 5 nm STM image of the O(2×2) superstructure on Ru(0001) recorded with a sample voltage of −0.1 V and a gap resistance of 200 MΩ. The oxygen atoms appear as round holes in these conditions.

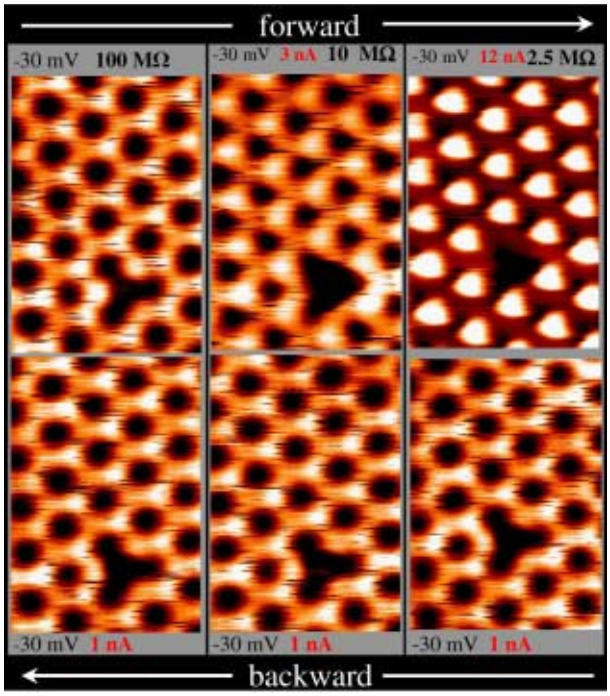

FIG. 2 (color online). A series of 2.2 nm × 3.2 nm dual-mode STM images. The upper panels show images recorded at a constant sample voltage of −30 mV and decreasing gap resistances (from left to right, 100, 10, and 2.5 MΩ). The reference images in the lower panels were all taken at a sample voltage of −30 mV and a constant gap resistance of 30 MΩ.

the same terrace, but they change orientation by 60° when crossing to the next terrace [13]. This observation excludes the triangular shape from being an imaging artifact caused by a particular atomic configuration of the tip. The center of the dark triangles corresponds to the center of the dark circles, i.e., the previously determined adsorption site of the oxygen atom. This reversible changing shape is also observed for a series of images recorded at constant current and varying voltages in the range -200 to 200 meV, i.e., while the surface resonance of Ru is the main contributor to the tunnel current. In fact, *images recorded with different voltage and current, but with the same gap resistance are found to be identical.* This indicates that the tip-sample distance is the main factor dictating the shape of the STM images in this voltage range.

In Fig. 3 we show measured (left panels) and simulated (right panels) STM images for two representative gap resistances. When imaged with a W tip, the O atoms appear as depressions, while Ru is seen bright. As gap resistance decreases by 1 order of magnitude, the changing shape of the features associated with O *and* Ru is nicely reproduced by the simulations. Their shape is circular when the tip is relatively far away from the surface and triangular at closer tip-surface distances. This change is mostly due to the different geometry of Ru p_z orbitals, with rotationally symmetric lobes pointing outwards, and hybridized s/p_{xy} orbitals, with threefold rotational symmetry with respect to the adsorption site. At large distances p_z orbitals contribute most of the current (circular shape), while closer to the surface the contribution from s/p_{xy} orbitals increases (triangular shape). It has to be mentioned, however, that cuts of the local density of states (LDOS) at different constant values reproduce accurately the measured STM images only at large gap resistances. The inclusion of a realistic tip structure and the use of the Bardeen approach in the calculations is essential to obtain quantitative agreement between simulated and measured images in the studied range. It should be noted that there are examples of ordered oxygen adlayers [$O(2 \times 1)/Cu(110)$ [7]] or oxide surfaces [$RuO_2(110)$ [11]] in which the bright atomic features in STM images taken with a clean W tip have been assigned to oxygen, contrary to the case described here. We have checked that the specific geometry and electronic structure of the different systems may result in reversed corrugations. Therefore, it is important to note that a precise knowledge of the geometrical structure of the sample *and* the tip and a specific calculation is required in each case before clear-cut assignments of the atomic size bumps seen in the STM images can be reached.

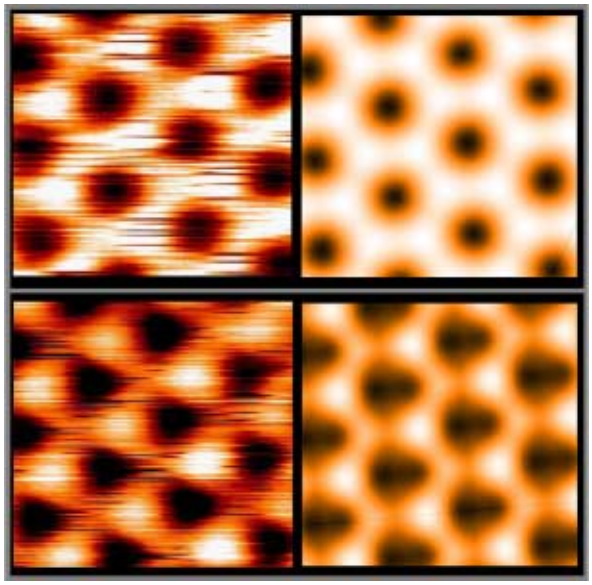

FIG. 3 (color online). Comparison of experimental (left panels) and simulated (right panels) STM images of $O(2 \times 2)/Ru(0001)$. In both cases the sample voltage was -30 mV. The simulations have been performed with tunneling currents of 0.03 nA (above) and 0.3 nA (below) and agree with the experimental ones for 300 MΩ (above) and 30 MΩ (below) gap resistances. The maximum corrugation is 0.5 Å in all cases.

In order to quantify the influence of the *tip* electronic structure in the images, we have simulated the effect of an O atom at the tip apex. Figure 4 shows that the calculated LDOS of the W tip is much sharper than that of the O tip. In fact, it is an order of magnitude larger at the same distance. As a result, the O tip is located around 1 Å closer to the surface than the W tip for the same nominal gap resistance. In addition, there is a relative minimum in the LDOS at the apex of the O tip. Because of this, when the O tip is located right above an O atom of the surface, the tunneling current from the neighboring Ru atoms is a maximum and the simulations predict a complete change of contrast, i.e., the oxygen depressions would turn into protrusions.

This prediction is confirmed by our experiments. In some cases a change in the contrast occurred suddenly in the middle of an image. It has been possible to trace this to the tip picking up a mobile oxygen atom from the surface [23]. The upper panel of Fig. 5 shows an image recorded in standard conditions with such an oxygen-terminated tip. It reveals the existence of vacancies (missing maxima) in a 2×2 hexagonal pattern of bright

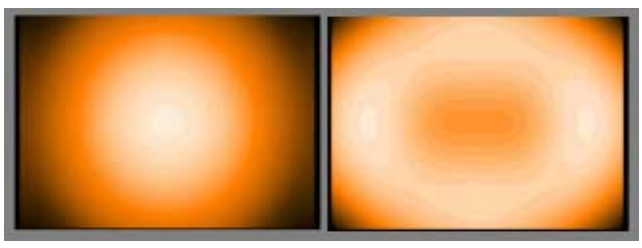

FIG. 4 (color online). Calculated LDOS for a W- (left panel) and an O- (right panel) terminated tip in an area of 6.8×4.8 Å. The apex atom is located in the center of the panels, but the color code differs by 1 order of magnitude in both panels.

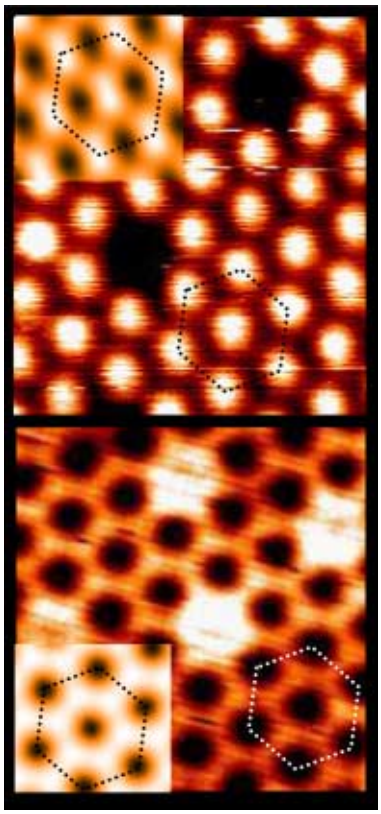

FIG. 5 (color online). Upper panel: 4 nm × 5.2 nm STM image recorded with an oxygen atom at the tip apex. The sample voltage was −0.35 V and the gap resistance 1.15 GΩ. The inset shows the image simulated with an O-terminated tip, calculated at −0.1 V and 1 GΩ and displaying the inversion of contrast. In both cases the maximum corrugation is 0.2 Å. Lower panel: 4 nm × 5.2 nm STM image taken with a W tip at −0.1 V and 200 MΩ. The experimental corrugation is 0.4 Å while it is 0.5 Å in the image calculated in the same conditions (see inset).

bumps. This indicates that the ''bumps'' now reflect the position of oxygen. The contrast has thus been inverted with respect to images obtained with a W-terminated tip, such as shown in the lower panel of Fig. 5. The inset in the upper panel of Fig. 5 shows the simulated image obtained with an O-terminated tip, which confirms that the O atoms are now imaged as maxima. As we move closer to the surface driven by the reduced LDOS of the O tip, the oxygen atoms appear in the surface LDOS as relative maxima with increasing intensity relative to the Ru atoms. This, combined with the spatial distribution and shape of the LDOS at the O-tip apex shown in Fig. 4, produces the predicted inversion in the contrast.

In summary, a series of STM images of O(2 × 2)/Ru(0001) show reversible changes in the shape of the atomic features from circular symmetry at larger gap resistances to triangular symmetry at low tunneling resistance. Our *ab initio* calculated images reproduce the experiments and confirm that the tip-sample distance is the main factor dictating the changing shape of the STM images in this voltage range. The subtle interplay of electron states with different symmetries as the gap resistance changes seems reproducible only with *ab initio* methods. Controlled changes in the tip composition produce a reversal of the contrast, also reproduced by the calculations. These results indicate that an unequivocal identification of O and metal ions in adsorbed oxygen layers and oxide surfaces requires both a large experimental data basis and an explicit calculation including a realistic tip structure.

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[23] A perfect O (2 × 2) structure is static at 300 K over many minutes. The mobility of oxygen atoms at the edge of the islands, however, is greatly enhanced when vacancies are present. The atoms are seen to perform jumps at a rate comparable with the scanning frequency. In many cases their disappearance from the image correlates with a reversal in the contrast.