

Charge Trapping at the Step Edges of TiO₂ Anatase (101)**

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Abstract: A combination of photoemission, atomic force, and scanning tunneling microscopy/spectroscopy measurements shows that excess electrons in the TiO₂ anatase (101) surface are trapped at step edges. Consequently, steps act as preferred adsorption sites for O₂. In density functional theory calculations electrons localize at clean step edges, this tendency is enhanced by O vacancies and hydroxylation. The results show the importance of defects for the wide-ranging applications of titania.

TiO₂ is used extensively in photocatalysis^[1,2] and photoelectrochemical (Grätzel) solar cells,^[3] and has promising properties for several other fields.^[4,5] The material exists in two technologically important forms, rutile and anatase. While the fundamental surface properties of the stable rutile phase are well-understood,^[6,7] less is known about the metastable anatase, which is used in most TiO₂ applications.

The behavior of excess electrons introduced into the material is a key issue in its applications. Electrons can be added by doping (oxygen vacancies (V_{OS}), Ti interstitials (Ti_{int}s), terminal hydroxy groups, impurities),^[6,8] or UV light. These electrons can be trapped in the crystal lattice, forming a quasiparticle called the small polaron,^[9] in essence a Ti³⁺ ion along with its surrounding lattice distortions. Transfer of electrons to adsorbed molecules is an elementary step in reduction and oxidation reactions. As a consequence, the charge-trapping centers, which accumulate excess electrons, often act as preferred sites for adsorption^[1,6,10] and chemical reactions. Electron trapping in a perfect anatase lattice is not favorable—neither in the bulk, nor on the (101) surface.^[11] This is in stark contrast to the rutile (110) surface, which allows self-trapping of electrons at any surface or subsurface Ti atom.^[12–14] In anatase, trapping can only occur at defects; herein we investigate the location of these trapped electrons.

Even though small polaron formation at the anatase (101) surface was previously excluded,^[11] photoemission data always show a significant gap state approximately 1 eV below the Fermi level (E_F),^[15] characteristic of a trapped electron.^[11] Anatase (101) surfaces prepared under ultra-high vacuum (UHV) conditions do not contain surface V_{OS}^[16] or other visible point defects, thus the origin of this state deserves a deeper analysis. We note that the (001) plane of anatase does not show the 1 eV gap state in photoemission^[15] and a delocalized, “large polaron” (manifested by a peak at ca. 40 meV below E_F in photoemission) was reported.^[17] Herein we use a combination of spatially resolved experimental techniques (STM, scanning tunneling spectroscopy (STS)) and theoretical calculations (DFT) to resolve this issue. We show that the trapped electrons are located exclusively at the step edges of the anatase (101) surface. Importantly, the steps activate the surface for O₂ adsorption.

Figure 1a shows photoemission (PE) spectra of the anatase (101) surface. No intensity is expected in the band-gap region (0–3 eV below E_F). Instead a gap state is observed at a binding energy of (-1.0 ± 0.2) eV, similar to previous data.^[15] The pronounced tail behind this peak is unusual; it is not observed in photoemission of rutile (110). We will show that this tail does not stem from a background of inelastically

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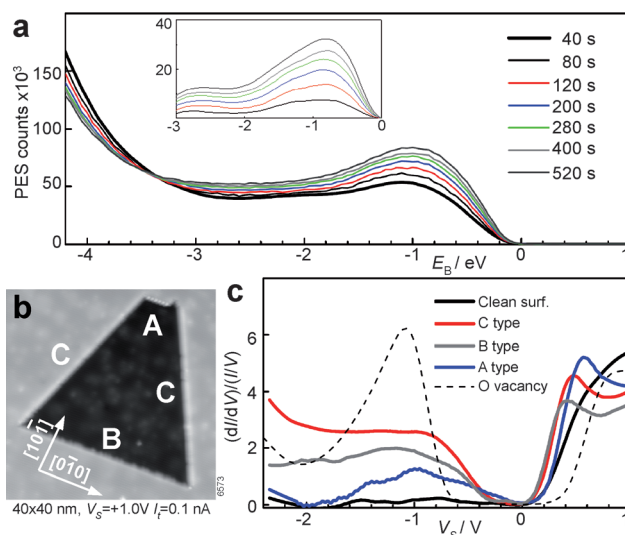


Figure 1. a) Photoemission spectra ($h\nu = 130$ eV, room temperature) of a TiO₂ anatase (101) surface taken after various exposures to the photon beam, measured at 300 K. Inset: same spectra after subtracting the first spectrum (40 s irradiation). b) STM image (empty states; $T = 78$ K) of anatase (101) with a typical step edge configuration, labeled A–C according to Ref. [18]. c) STS spectra measured at the steps and at the flat surface.

scattered photoelectrons, but is characteristic for electrons trapped at steps.

Even though as-prepared anatase (101) surfaces do not contain surface V_{Os} ,^[16,19] these can be created by the photon beam and thus the possibility of beam damage needs to be taken into account. Figure 1a displays PE spectra after various irradiation times, ranging from 40 to 520 s. The inset in Figure 1a shows the difference between the first curve (40 s irradiation) and the curves after longer irradiation times. The evolution of the state in the difference spectra represents the signal coming from the beam-induced defects (likely surface V_{Os}). Note that the tail at higher binding energies is suppressed in these spectra. From this analysis we conclude that the initial gap state in Figure 1a (40 s) is too intense to be solely due to the beam damage; it must have a different origin.

To determine the spatial distribution of the gap state we investigated the surface with STM and STS, see Figure 1b,c. At negative bias voltages (filled states), the clean anatase surface has a very small local density of states (LDOS), as expected.^[11] The situation is different when spectra are taken close to steps, however. Three different step types, termed A, B, and C as in a previous study,^[18] appear on the anatase (101) surface; the difference in their formation energies results in terraces with a characteristic, trapezoidal shape (Figure 1b). STS spectra (Figure 1c) taken close to these steps show a significant LDOS within the band gap. The peaks have a maximum at approximately 1 eV below E_F and a strong tail deeper in the band gap, very similar to the initial photoemission spectrum (Figure 1a, 40 s). STS shows the gap state directly at, as well as up to two lattice constants away from the step edge, at both, the upper and lower terrace. Spectra measured at various positions along the step edge are similar (see Figure S1 in the Supporting Information); the LDOS is homogeneous along the step. For comparison, we include an STS spectrum from an—artificially created^[11,19,20]—surface V_{O} on anatase (101), see the dashed line in Figure 1c. We note a much more pronounced peak, similar to the (V_{O} -derived) difference spectra in the inset of Figure 1a. The LDOS is highest at the C-type step. Step B, which can be viewed as a small stripe of a (100) plane shows an intermediate electron density.^[18] Step A shows a low intensity; this step is polar and possibly reconstructed.

In constant height STM mode it is possible to image the filled DOS on flat anatase (101) terraces,^[11] albeit not close to step edges where a feedback loop is needed to maintain the tip-sample distance. The tunneling-current-based feedback loop fails in filled states because the anatase (101) terraces have negligible LDOS in the band gap. Instead we resort to non-contact atomic force microscopy (nc-AFM), which allows the simultaneous measurement of force and tunneling current (Figure 2). The measured force (more precisely, the frequency shift) is used to maintain the tip-sample distance. The corresponding topography image is shown in the inset of Figure 2. The sample was biased negatively (−1.5 V), thus the tunneling current shows the distribution of filled states. The current is below the detection limit at the terraces, and, apart from a few defects, the LDOS is strictly localized at the steps. The STS spectra in Figure 1c are relevant for quantifying the

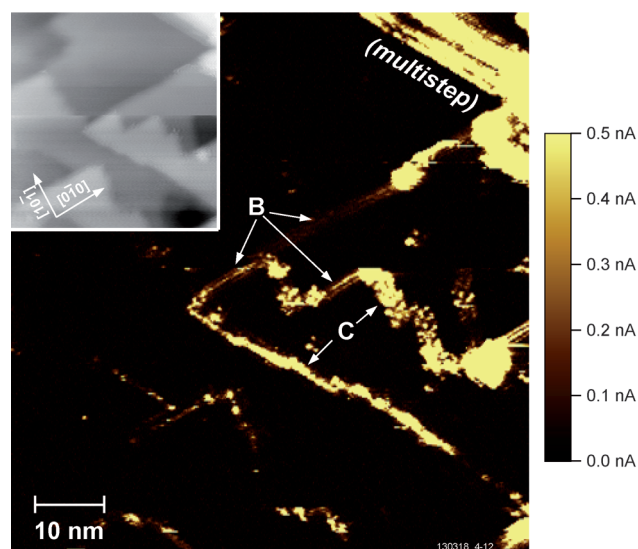


Figure 2. Spatial distribution of filled states on anatase (101). Inset: topographic nc-AFM image of the anatase (101) surface taken in constant frequency-shift mode ($V_{\text{sample}} = -1.5$ V, $f_0 = 59$ kHz, $A = 0.4$ nm, $Q = 1500$, 300 K). The large image shows the tunneling current recorded simultaneously with the topography. It shows filled states, localized at step edges.

intensity of the filled LDOS, while Figure 2 shows its spatial distribution.

We use O_2 adsorption to illustrate how the step edges affect the chemical reactivity of anatase. O_2 is an electron scavenger and can chemisorb on TiO_2 only after accepting an extra electron from the surface.^[1,21] Figure 3a,b show large-scale STM images of anatase (101) after O_2 exposure. The lighter features at the terraces are due to different forms of adsorbed O_2 .^[20] The STM contrast at step edges undergoes a significant change even after small O_2 exposure (Figure 3b). On the clean surface, the step edges always appear slightly brighter than the terraces, (Figure 1b). After dosing with O_2 , the steps become darker, which we attribute to upwards band bending caused by accumulation of negative charge.^[22]

To evaluate whether the charge trapping is an intrinsic property of the step (for example, whether a structurally perfect and clean step allows self-trapping of electrons excited by UV light) we employed DFT calculations. We took the C-type step as a model, as this step exhibits the strongest gap state in STS. When an excess electron was added to a (145)-oriented vicinal slab, electron localization at the step was slightly favored compared to a delocalized situation (polaronic energy^[11,12,23] ca. 46 meV, for details see the Supporting Information). This value seems rather low but it is well in-line with polaron formation energies calculated for rutile.^[11] One should further consider that the steps contain kinks and other defects (see Figure S3), which locally increase the lattice flexibility and, in turn, further support polaron formation.

In our calculations, we also considered the presence of oxygen vacancies (V_{Os}) and hydroxy groups at the steps. As detailed in the Supporting Information, both species are energetically possible at the steps and both provide electrons that trap at neighboring Ti sites. The presence of donors at the

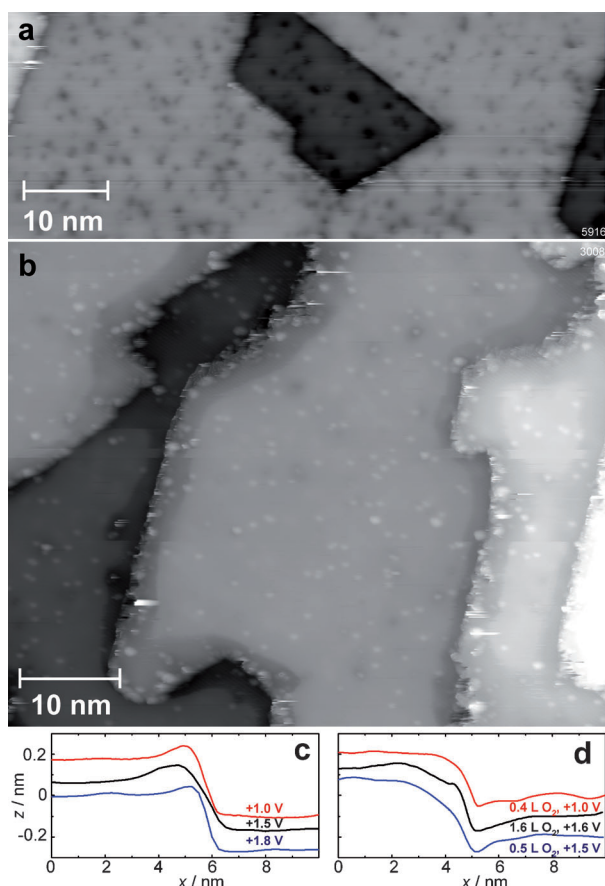


Figure 3. Influence of the step-edge states on the adsorption of O_2 a) STM image ($V_s = +2.3$ V, $I_t = 0.1$ nA) of anatase (101) after dosing 0.4 Langmuir (L) O_2 at $T = 40$ K. b) The surface after dosing 20 L O_2 at $T = 105$ K, scanned at 6 K. ($V_s = +1.5$ V, $I_t = 0.08$ nA). In both cases, the significant upwards band-bending results in a dark contrast at the step edges and indicates adsorbed oxygen. c,d) Line profiles across C-type step edges of clean and O_2 -exposed surfaces, respectively. Each profile is from a different experiment.

steps is further indicated by the experimental data: steps of a clean surface appear bright for empty-states in STM images (see Figure 1b). For n-type semiconductors, this observation indicates the presence of donors.^[22] For electrostatic reasons, it is likely that the electrons trapped at anatase steps originate mainly from the donors at the steps, although trapping of electrons from other sites, for example, donors in the bulk, is also energetically possible as discussed above.

In summary, we have shown that, on the (101) surface of anatase, step edges are donors. This situation makes the steps preferential adsorption sites for acceptor molecules and, possibly, reactive centers for (photo-)catalytic reactions. Our results point to the great importance of step edges for TiO_2 anatase. Steps and line defects of catalytic materials, such as rutile TiO_2 , CeO_2 , or MgO have been the focus of interest^[24–27] and increased activities have been reported for certain reactions. The importance of the anatase steps is special owing to the fact that charge trapping is not favorable on anatase (101) terraces and that the dominant (101) plane is relatively inert.

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- [1] M. A. Henderson, *Surf. Sci. Rep.* **2011**, 66, 185–297.
- [2] A. Linsebigler, G. Lu, J. R. Yates, *Chem. Rev.* **1995**, 95, 735–798.
- [3] M. Grätzel, *Nature* **2001**, 414, 338–344.
- [4] K. Szot, M. Rogala, W. Speier, Z. Klusek, A. Besmehn, R. Waser, *Nanotechnology* **2011**, 22, 254001.
- [5] Y. Furubayashi, T. Hitosugi, Y. Yamamoto, K. Inaba, G. Kinoda, Y. Hirose, T. Shimada, T. Hasegawa, *Appl. Phys. Lett.* **2005**, 86, 252101.
- [6] U. Diebold, *Surf. Sci. Rep.* **2003**, 48, 53–229.
- [7] H. Cheng, A. Selloni, *J. Chem. Phys.* **2009**, 131, 054703.
- [8] S. Wendt, T. S. Sprunger, E. Lira, G. K. H. Madsen, Z. Li, J. Hansen, J. Matthiesen, A. Blekinge-Rasmussen, E. Laegsgaard, B. Hammer, F. Besenbacher, *Science* **2008**, 320, 1755–1759.
- [9] I. G. Austin, N. F. Mott, *Adv. Phys.* **2001**, 50, 757–812.
- [10] Y. He, A. Tilocca, O. Dulub, A. Selloni, U. Diebold, *Nat. Mater.* **2009**, 8, 585–589.
- [11] M. Setvin, C. Franchini, X. Hao, M. Schmid, A. Janotti, M. Kaltak, C. Van de Walle, G. Kresse, U. Diebold, arXiv:1401.7817v1 (2014).
- [12] A. Janotti, C. Franchini, J. B. Varley, G. Kresse, C. G. V. d. Valle, *Phys. Status Solidi* **2013**, 7, 199–203.
- [13] P. Krüger, S. Bourgeois, B. Domenichini, H. Magnan, D. Chandesris, P. L. Fevre, A. M. Flank, J. Jupille, L. Floreano, A. Cossaro, A. Verdini, A. Morgante, *Phys. Rev. Lett.* **2008**, 100, 055501.
- [14] P. M. Kowalski, M. F. Camellone, N. N. Nair, B. Meyer, D. Marx, *Phys. Rev. Lett.* **2010**, 105, 146405.
- [15] A. G. Thomas, W. R. Flavell, A. K. Mallick, A. R. Kumarsinghe, D. Tsoutsou, N. Khan, C. Chatwin, S. Rayner, G. C. Smith, R. L. Stockbauer, S. Warren, T. K. Johal, S. Patel, D. Holland, A. Taleb, F. Wiame, *Phys. Rev. B* **2007**, 75, 035105.
- [16] Y. He, O. Dulub, H. Cheng, A. Selloni, U. Diebold, *Phys. Rev. Lett.* **2009**, 102, 106105.
- [17] S. Moser, L. Moreschini, J. Jacimovic, O. S. Barsic, H. Berger, A. Magrez, Y. J. Chang, K. S. Kim, A. Bostwick, E. Rotenberg, L. Forro, M. Grioni, *Phys. Rev. Lett.* **2013**, 110, 196403.
- [18] X.-Q. Gong, A. Selloni, M. Batzill, U. Diebold, *Nat. Mater.* **2006**, 5, 665–670.
- [19] P. Scheiber, M. Fidler, O. Dulub, M. Schmid, U. Diebold, W. Hou, U. Aschauer, A. Selloni, *Phys. Rev. Lett.* **2012**, 109, 136103.
- [20] M. Setvin, U. Aschauer, P. Scheiber, Y.-F. Li, W. Hou, M. Schmid, A. Selloni, U. Diebold, *Science* **2013**, 341, 988–991.
- [21] Y. Cui, X. Shao, M. Baldofski, J. Sauer, N. Nilius, H.-J. Freund, *Angew. Chem.* **2013**, 125, 11595–11598; *Angew. Chem. Int. Ed.* **2013**, 52, 11385–11387.
- [22] P. Ebert, *Surf. Sci. Rep.* **1999**, 33, 121–303.
- [23] I. G. Austin, N. F. Mott, *Adv. Phys.* **2001**, 50, 757–812.
- [24] U. Martinez, J. Hansen, E. Lira, H. H. Kristoffersen, P. Huo, R. Bechstein, E. Laegsgaard, F. Besenbacher, B. Hammer, S. Wendt, *Phys. Rev. Lett.* **2012**, 109, 155501.
- [25] H. Takahashi, R. Watanabe, Y. Miyauchi, G. Mizutani, *J. Chem. Phys.* **2011**, 134, 154704.
- [26] N. Nilius, S. M. Kozlov, J.-F. Jerratsch, M. Baron, X. Shao, F. Vines, S. Shaikhutdinov, K. M. Neyman, H.-J. Freund, *ACS Nano* **2012**, 6, 1126–1133.
- [27] G. Pacchioni, H. Freund, *Chem. Rev.* **2013**, 113, 4035–4072.