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Two-dimensional (2D) metallic states induced by oxygen vacancies (V$_{O_2}$) at oxide surfaces and interfaces provide opportunities for the development of advanced applications, but the ability to control the behavior of these states is still limited. We used Angle Resolved Photoelectron Spectroscopy (ARPES) combined with Density Functional Theory (DFT) to study the reactivity of V$_{O_2}$-induced states at the (001) surface of anatase TiO$_2$, where both 2D metallic and deeper lying in-gap states (IGs) are observed. The 2D and IG states exhibit remarkably different evolution when the surface is exposed to molecular O$_2$: while IGs are almost completely quenched, the metallic states are only weakly affected. DFT calculations indeed show that the IGs originate from surface V$_{O_2}$ and remain localized at the surface, where they can promptly react with O$_2$. In contrast, the metallic states originate from subsurface vacancies whose migration to the surface for recombination with O$_2$ is kinetically hindered on anatase TiO$_2$ (001), thus making them much less sensitive to oxygen dosing.

I. INTRODUCTION

Many functional properties of anatase TiO$_2$ of relevance, e.g., in photocatalysis, solar cells and sensors are critically affected by the presence of excess electrons induced by intrinsic defects, dopants or photoexcitation$^{1-7}$. Understanding and controlling the behaviour of excess electrons is thus essential for improving TiO$_2$’s performance in existing applications and for developing new applications as well. In particular, the chemical doping arising from oxygen vacancies (V$_{O_2}$) induces important changes in the electronic structure, such as the creation of in-gap defect states, the formation of depletion regions, and band bending$^{8,9}$. Another noteworthy feature connected with V$_{O_2}$ is the presence, under photoirradiation, of electronic states with metallic d-character (Ti 3d) at the anatase (101) and (001) surfaces, generally termed two-dimensional electron gas (2DEG) states$^{10-12}$. First observed at the LaAlO$_3$/SrTiO$_3$ (LAO/STO) interface$^{13}$, 2DEGs have been reported both in transition metal oxides (TMOs) parent compounds (e.g. bare surfaces of SrTiO$_3$ and KTaO$_3$) and in engineered heterostructures$^{14,15}$. Nevertheless, a number of important aspects are not yet settled, such as the depth distribution of the oxygen vacancies acting as electron donors. Another critical issue is the behaviour of 2DEG and localised in-gap (IG) defect states under reducing vs. oxidising conditions, notably to what extent and in what conditions it is possible to control the excess of V$_{O_2}$ created by photoirradiation or can be induced and tailored by means of controlled post-growth treatment (UHV annealing). ARPES measurements confirm the existence of both localised and delocalised electronic states, while Resonant-PES in the soft X-ray range identifies their character as Ti$^{3+}$ and Ti$^{4+}$, respectively. Spectral changes were monitored while molecular O$_2$ was steadily fluxed on the sample surface through a metallic capillary$^{21-23}$. Remarkably, the results reveal that 2DEG delocalized features are robust against oxygen exposure, whilst the localised IG states are suppressed. Comparison with DFT calculations provides evidence of a distinct depth-dependence of defect states. The 2DEG originates from subsurface V$_{O_2}$ and resides in sub-surface layers due to the attractive potential resulting from these V$_{O_2}$. In contrast, the deeper lying IG states that are suppressed by O$_2$ originate from the surface V$_{O_2}$. Our results also pro-

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provide a consistent explanation of previous contrasting findings and suggest possible strategies for controlling the carriers concentration and transport at the surface of anatase.

II. EXPERIMENTAL AND COMPUTATIONAL METHODS

II.1. Growth

Anatase TiO$_2$ thin films were grown by Pulsed Laser Deposition (PLD) at a dedicated chamber located at the APE-IOM laboratory (NFFA facility, Trieste, Italy)$^{21}$. Rutile TiO$_2$ single-crystal was ablated using a KrF excimer pulsed laser source kept at about 2 J/cm$^2$ energy density, with a typical laser repetition rate of 3 Hz. The substrate was kept at 700°C growth temperature, while oxygen background pressure was set to 10$^{-4}$ mbar. Annealed samples have been kept at the growth temperature for 10 minutes in UHV (PLD chamber base pressure is the range of 10$^{-7}$ mbar). Anatase TiO$_2$ thin films were grown on (001)-oriented LaAlO$_3$ (LAO) substrates. Epitaxial strain-less condition was verified for these films. All the samples presented in this work are $\sim 20$ nm thick.

II.2. Transmission and Scanning Transmission Electron Microscopy

Cs probe-corrected Jeol ARM 200 CF scanning transmission electron microscope with cold-FEG electron source, operated at 200 kV was used for high-resolution imaging of the samples. Electron Energy Loss Spectroscopy (EELS) was performed using Gatan dual-EELS Quantum ER system and elemental chemical analyses were performed with Cen- turio Jeol Energy Dispersive X-ray Spectroscopy (EDXS) system with 100 mm$^2$ SDD detector. Cross-sectional samples in the $[010]$ zone axis suitable for TEM/STEM analyses have been obtained by a conventional polishing technique followed by dimpling and ion milling.

II.3. Ultraviolet ARPES, Soft X-ray ARPES, RESPES

The as-grown samples were directly transferred in-situ to the Angle-Resolved Photoemission (ARPES) end-station installed on the Low-Energy branch of APE beamline (APE-LE) at Elettra synchrotron (Trieste, Italy). Such a chamber is equipped with a Scienta DA30 hemispherical electron energy and momentum analyser (30° angular acceptance), which allows to map the electronic bands over the extended areas of the Brillouin zone without rotating the sample. ARPES experiments were performed at a base pressure $\sim 10^{-10}$ mbar and with the samples kept at liquid Nitrogen. Photon energy of 46 eV was used with the light incidence angle of 45°. All the light polarisation available at the beamline have been exploited (linear vertical, linear horizontal, circular right and circular left). When not otherwise specified, the overall energy resolution was set to $\sim 40$ meV, and the angular resolution was set to $0.2°$ (corresponding to $\sim 0.01$ Å$^{-1}$ at 46 eV photon energy).

Soft x-ray ARPES, Resonant Photoemission (RESPES) and oxygen dosing were performed at 109 beamline at Diamond light source (Didcot, UK). The samples fabricated at the APE-IOM laboratory were transferred to the Soft X-Ray branch of 109 beamline 120 by means of a UHV suitcase. The surface’s contamination was thus prevented throughout the whole experiment. Sample temperature was 90 K. In order to reduce the effects of higher order components coming from the beamline optics in the resonant photoemission measurements, the monochromator has been tuned to obtain the best compromise between flux, resolution and higher order rejection. Furthermore, the residual second-order contribution was subtracted in all spectra. The energy position of the Fermi energy ($E_F$) and the energy resolution have been estimated by measuring the Fermi edge of poly-Au foil in thermal and electric contacts with the sample. The overall energy resolution (analyzer + beamline) was kept below 250 meV for the entire photon energy range. Molecular oxygen was injected through a metallic capillary placed close to the sample surface (i.e. $\sim 1-2$ cm). The amount of oxygen has been monitored by means of a Residual Gas Analyser (RGA) available in the experimental chamber. Base pressure in the experimental chamber was $1\cdot10^{-10}$ mbar, up to a maximum O$_2$ partial pressure of $4\cdot10^{-9}$ mbar.

II.4. Computational Details

DFT calculations for pristine and reduced anatase (001) were performed using the Vienna Ab Initio Simulation Package (VASP)$^{25,26}$. We used the projector augmented-wave (PAW) pseudopotentials to describe the electron-ion interactions and the PBE functional$^{27}$ within the generalized gradient approximation (GGA) to treat the exchange-correlation interaction between electrons. The energy cut-off for the expansion of the wave-functions was set to 500 eV. Since GGA is affected by the self-interaction error that favours de-localized electronic states, selected calculations using the PBE+U method with $U = 3.9$ eV$^{28}$ were also carried out in order to check the robustness of the PBE solutions (note that $U$ values in the range 2.5-4 eV are typically used to describe defect states in TiO$_2$$^{29,30}$). While predicting a more structured electronic charge distribution in comparison to pure PBE, these PBE+U calculations confirmed the delocalized character of the subsurface excess electron states at the anatase (001) surface$^{31}$, which was reported also in a previous PBE+U study$^{22}$.

We modeled the anatase TiO$_2$ (001)-(1×4) surface using a repeated slab geometry. We considered slabs of 8 TiO$_2$ layers with a (3×4) surface supercell for calculations of defect formation energies, in order to minimize interactions between defects in periodic replicas, and slabs of 12 TiO$_2$ layers with a (2×4) surface su-
Γ point of the second Brillouin zone (Γ point corresponds to the Fermi momenta (Fig. 1e and 1f) and a d_{xy} orbital character arising from Ti 3d states typical in TMOs\cite{9,11,15,35}. In addition, several replicas occur along both k_x and k_y directions, arising from the periodic lateral perturbation induced by the surface (1 x 4) – (4 x 1) reconstruction\cite{11,20}. Panels e) and f) compare the E vs. k dispersion of the 2DEG for UHV annealed and as-grown samples respectively. Both the as-grown and reduced samples were transferred in-situ in UHV (i.e. without exposure to air) for the ARPES experiments. Two dispersive parabolic-like states are evident in Fig. 1e: an outer parabola and a second (faint) parabolic-like state.

Oxygen vacancies were created by removing a neutral oxygen atom. The resulting neutral V\textsubscript{O} consists of a vacant site, effectively bearing a 2+ positive charge, and two compensating excess electrons. Their formation energies were calculated as $E_{\text{form}}(V\text{O}) = E_{\text{def}} - E_{\text{stoich}} + 1/2E_{\text{tot}}(O_2)$, where $E_{\text{def}}$ and $E_{\text{stoich}}$ are the total energies of the reduced (defective) and stoichiometric (defect-free) slabs, respectively, and $E_{\text{tot}}(O_2)$ is the total energy of the O\textsubscript{2} molecule.

III. EXPERIMENTAL RESULTS

III.1. Structural and Ultraviolet ARPES results

Epitaxial strainless anatase TiO\textsubscript{2} thin films were grown by PLD on LAO substrates. Details of the growth protocol and structural characterization by X-ray diffraction are given elsewhere\cite{9,10,24}. The results of our cross-sectional high-resolution Transmission Electron Microscopy (TEM) and high-angle annular dark-field scanning TEM (HAADF-STEM) measurements are shown in Fig. 1. In panel a), a representative high-resolution Z-contrast image shows an atomically sharp interface region. The typical dumbbell structure of Ti ions in TiO\textsubscript{2} anatase is clearly distinguishable in the film and occurs in the entire film region with no sign of presence of secondary phases. The crystal quality of the films extends up to the surface, as confirmed by the Low Energy Electron Diffraction (LEED) (1 x 4) – (4 x 1) surface reconstruction pattern in panel b)\cite{9,10,24}.

ARPES measurements were performed along the Γ-X direction of the surface projected Brillouin zone (Fig. 1c), obtained by superimposing the Fermi surfaces measured with different light polarisations (i.e. linear horizontal and vertical, circular right and left). With such a procedure we could compensate the lack of intensity due to symmetry-related selection rules typically occurring for bands of d_{xy} orbital character. The surface structural reconstruction is reflected in the Fermi surface measured in the first Brillouin zone, shown in Fig. 1d and the Supplemental Material\cite{31}. The bright circle centred at the Γ point corresponds to a 2DEG, characterised by a parabolic dispersion (Fig. 1e and 1f) and a d_{xy} orbital character arising from Ti 3d states typical in TMOs\cite{9,11,15,35}. In addition, several replicas occur along both k_x and k_y directions, arising from the periodic lateral perturbation induced by the surface (1 x 4) – (4 x 1) reconstruction\cite{11,20}. Panels e) and f) compare the E vs. k dispersion of the 2DEG for UHV annealed and as-grown samples respectively. Both the as-grown and reduced samples were transferred in-situ in UHV (i.e. without exposure to air) for the ARPES experiments. Two dispersive parabolic-like states are evident in Fig. 1e: an outer parabola and a second (faint) parabolic-like state.
Density values for the two samples are

as of free carriers in the sample of annealing, consistently with an increased number of the 2DEG peak of the as-grown sample weakens after the annealing, as observed elsewhere. The asymmetric shape of the peak in both curves of Fig. 2b indicates the presence of at least a second, distinct, in-gap state. Similar to changes observed upon annealing, photo-irradiation favours the formation of an IG located at shallower binding energies (i.e. ~1 eV BE). This may indicate that the localised states are related to two inequivalent oxygen vacancy sites and that the formation of the latter is more favourable under the beam.

III.2. Soft-X ray ARPES, Resonant Photoemission (RESPES) and dosing experiment

While some reports suggest that the metallic state has a 3D character a model linking the metallic state to the specific anatase surface arrangement has recently been shown to provide excellent agreement with the experimental data. The 2D nature of the metallic state is also supported by experiments studying both the effect of electron doping through alkaline adsorption and the influence of beam irradiation at the anatase surface. To gain further insight, we have performed soft X-ray ARPES and Resonant PES (RESPES) experiments, while simultaneously compensating the production of oxygen vacancies arising from photodissociation. This has been achieved during the measurements by in-operando fluxing molecular oxygen through a metal capillary positioned in the proximity of the sample surface. The ARPES spectra acquired in the second BZ for the pristine sample in UHV (i.e. base pressure 1·10^-10 mbar) measured with linearly polarised radiation of hν = 120 eV (panel a) and ARPES measured on the very same sample while dosing the surface with oxygen (i.e. base pressure 4·10^-10 mbar; partial O2 pressure 4·10^-10 mbar) (panel b). In Fig. 3c, the MDCs extracted at EF from panels a) and b) are compared. The value of kF is reduced from 0.19 Å⁻¹ to 0.15 Å⁻¹ (~20%) under oxygen dosing, i.e. it shows the opposite trend compared to that observed upon annealing in Fig. 1e and 1f, giving direct evidence of (partial) healing of VGS and consequent reduction of the number of free electron carriers at the surface, in agreement with previous reports. Such a decrease corresponds to a reduction in the carrier density of ~60%, qualitatively consistent with the theoretical picture for subsurface vacancies presented below. Fig. 3d compares the angle-integrated Density of States (DOS) extracted from panels 3a and 3b with a BE range covering also the IG states. Almost com-
The complete suppression of the IG states is observed as soon as oxygen is dosed; the residual IG intensity is little affected by further increase of the oxygen partial pressure (4 times the initial value), dropping below the background signal (it is visible only at resonance, see next section). Conversely, the 2DEG spectral weight is only slightly decreased and the reduction is mainly ascribable to the changes in the background signal. We also stress that the 2DEG maximum healing was already achieved at the lower oxygen partial pressure, as an increment of the oxygen pressure up to four times the initial dose (i.e. from $10^{-9}$ mbar to $4 \cdot 10^{-9}$ mbar recorded on RGA) did not further affect the 2DEG state. Such a distinct behaviour of IG and 2DEG has not been reported before in anatase TiO$_2$.

In contrast to our results, studies on SrTiO$_3$ have shown that both the IG and the 2DEG are completely suppressed under O$_2$ dosing, with the spectral weights of the two states reducing at the same pace$^{15,17,22,38-40}$. While incomplete compensation of the 2DEG was observed at the buried interface between a 4 u.c. epitaxial LaAlO$_3$ deposited on SrTiO$_3$,$^{22}$, in our study we are not sensitive to the film-substrate interface due to the short probing depth typical of photoemission spectroscopies. Therefore, our results should be compared to the bare SrTiO$_3$ rather than the LAO/STO buried interface.

The electronic character of the 2DEG and the localized IG states was investigated by means of resonant photoemission (RESPES) measurements at the Ti $L_2,3$ edges. As both IG and 2DEG arise from Ti 3d states,$^{11,12}$, RESPES provides additional information by exploiting the energy shift between the core levels of titanium atoms with different oxidation states. Fig. 4a shows the X-ray absorption spectra (XAS) measured in TEY across the Ti $L_3$ edge from an as-grown sample (red curve) and under oxygen dosing (dark blue curve).

The four main peaks (located at approximate excitation energies of 458.3 eV, 460.5 eV, 463.5 eV, and 465.5 eV excitation energies) can be ascribed to the combination of spin-orbit splitting of the initial states ($L_3-L_2$) and crystal field splitting of the d orbitals in the final state ($t_{2g}$-$e_g$) for Ti atoms in 4+ oxidation state. The additional splitting of the $L_3$-$e_g$ peak (∼460.5 eV) is the fingerprint of the anatase phase arising from distortion of the ideal octahedron around Ti atom and long-range effects.$^{42-44}$

Effects of O$_2$ dosing on the absorption spectrum (total yield) edges of anatase TiO$_2$ film were measured at 90 K. Pristine sample refers to base pressure in the chamber of $1 \cdot 10^{-10}$ mbar, while the dark blue curve corresponds to the highest oxygen partial pressure of the present work ($4 \cdot 10^{-9}$ mbar). Upon oxygen dosing, the spectral intensity is lowered in the pre-edge as well as in the valleys at ∼459 eV and ∼462.5 eV, which correspond to spectral lines of Ti$^{3+}$.$^{43}$ As found in similar systems, e.g., rutile TiO$_2$,$^{45}$ and SrTiO$_3$,$^{*}$ the observed changes can be directly linked to the number of vacancy sites inside the material. The suppression of the IG suggests that the relative oxygen vacancies are located either at the surface or at buried sites that can easily move to the surface and recombine with the adsorbed molecules, as observed in anatase (101)$^{11}$. Conversely, the 2DEG insensitivity against O$_2$ dosing indicates that the migration of the corresponding vacancies to the surface is unlikely, at least in the examined pressure and temperature range.

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of oxygen vacancies.

ResPES in the second BZ were acquired upon oxygen dosing (P = 1 × 10⁻⁹ mbar). The angle integrated photoemission EDCs, displayed as a color map in Fig. 4b, indicate that the IG and 2DEG states resonate at different photon energies. The IG is peaked at an energy corresponding to a Ti³⁺ oxidation states, i.e. the valley at ~459.3 eV (roughly 0.8 eV away from the resonance of the 2DEG states), in agreement with previous results. Conversely, the 2DEG follows the same trend of the XAS, with maximum intensity located around the L₂₋₃-e⁻ doublet at ~460.5 eV (characteristic of the stoichiometric Ti⁴⁺). Similarly, above 462 eV (i.e. in the valley before the L₂-edge) the IG intensity rises first.

To better decouple the IGs and the 2DEG signals, we further investigated the DOS evolution at E_F as a function of the photon energy before and during oxygen dosing (Fig. 5a and 5b). The IG states are strongly suppressed with oxygen dosing, yet both their BE and their resonating behavior are not affected. The signal of the 2DEG is much clearer in Fig. 4b, indicate that the IG and 2DEG states resonate at the lowest photon energy (i.e. at ~459.3 eV), whereas the electron pocket at Fermi is localized in the BZ centre, more intense in the middle of the valence band (458.5 eV), whereas the electron pocket at Fermi is localized in the BZ centre, more intense in the middle of the valence band (458.5 eV). Figs. 5d and 5e show the intensities of the IG and 2DEG states across the Ti L₃₋₂₄ absorption edge. Each square (dot) in panel 5d (panel 5e) corresponds to ARPES spectra acquired at different photon energies. The coloured rectangles in the top-left panel of Fig. 5c mark the binding energy/momentum region where the spectral intensity has been integrated. For both states two regions of momentum space were selected: the projected 2BZ across the Ti L₃₋₂₄ absorption edge while dosing oxygen at the surface, are shown in Fig. 5c. The IG state is well visible as non-dispersive red broad line which resonates at the lowest photon energy (i.e. at 458.5 eV), whereas the electron pocket at Fermi is localized in the BZ centre, more intense in the middle of the photon energy scan (459.7 eV). Figs. 5d and 5e show the intensities of the IG and 2DEG states across the Ti L₃₋₂₄ absorption edge. Each square (dot) in panel 5d (panel 5e) corresponds to ARPES spectra acquired at different photon energies. The coloured rectangles in the top-left panel of Fig. 5c mark the binding energy/momentum region where the spectral intensity has been integrated. For both states two regions of momentum space were selected: the projected 2BZ across the Ti L₃₋₂₄ absorption edge while dosing oxygen at the surface, are shown in Fig. 5c. The IG state is well visible as non-dispersive red broad line which resonates at the lowest photon energy (i.e. at 458.5 eV), whereas the electron pocket at Fermi is localized in the BZ centre, more intense in the middle of the photon energy scan (459.7 eV).
FIG. 5. (a), (b) DOS evolution at the Fermi level as a function of the photon energy before and during oxygen dosing; (c) Resonant angle-resolved-photoemission (ResARPES) spectra acquired while dosing oxygen; (d), (e) Intensity of the IG and 2DEG states across the Ti L3-edge absorption edge respectively.

FIG. 6. (a) Side view of the reconstructed anatase TiO2(001)-1 × 4 slab model; the investigated oxygen vacancy sites are indicated; Ti and O atoms are light blue and red, respectively. (b) VO formation energies (eV; blue bars) at different surface and subsurface oxygen sites computed using DFT-PBE; (c) Electrostatic potential profile in the surface region, computed from the shift of the Ti 3s peak in the different Ti layers of the pristine and reduced slabs with VO1, VO4 or VO7 defects. Here, layer 0 corresponds to the ridge Ti4c sites, layer 1 to the terrace Ti5c sites, and so forth. The yellow shading highlights the region of negative (attractive) potential; (d,e,f,g,h,i) Charge density contours of the excess electron states induced by VO1, VO3, VO4, VO5, VO6 and VO7, respectively; the vacancy positions are indicated by dashed red circles; dashed black lines show the unit cell used for the calculations. Additional density contours are shown in Supplemental Material.

adsorption on TiO2 is known to involve the transfer of excess electrons from the oxide to the molecule1,3,41,48. In the presence of a VO1, O2 undergoes a strongly exothermic and barrier-less adsorption at the vacancy site31, which results in the formation of a bridging peroxide (O2−) at the ridge, denoted (O2)0 in Fig. 7. The two excess electrons of VO1 are both transferred to the adsorbed species, so that no excess electron remains in TiO2, consistent with the strong reduction of the IG signal observed in ARPES when exposing the surface to O2.

A different picture holds for the adsorption of O2 on a surface with subsurface VO1. In this case, O2 adsorbs at a terrace Ti5c site and only one of the two excess electrons of the vacancy transfers to the molecule1,3,48, thus resulting in the formation of an adsorbed superoxide (O2−), denoted O2* in Fig. 7. As previously discussed for the reaction of O2 with the reduced anatase (101) surface41, the negatively charged adsorbate has an attractive interaction with the subsurface vacancy, so that migration of VO1 toward the surface would be energetically favourable (Fig. 7a). At variance with
FIG. 7. (a) $O_2$ adsorption energy as a function of the subsurface (VO4-VO7) or surface (VO3) oxygen vacancy location. Relevant structures with a subsurface VO, denoted VO$n+O^*$ ($n=4-7$), are shown in panels (c-f). For VO3, two nearly degenerate structures are present, as shown in panels (g-h), where O$^*$ indicates an oxygen adatom and $O_2^-$ a bridging peroxide replacing an $O_2^-$. The energy zero corresponds to the adsorption energy of VO7+O$^*$. (b) Energy barrier for the diffusion of an O-vacancy from VO4 to VO3 in the presence of adsorbed oxygen. (c-h) Atomic geometries of adsorbed $O_2$ on reduced anatase (001) with a subsurface (VO4-VO7) or surface (VO3) oxygen vacancy, as described in (a). Ti atoms are blue, O atoms are red, adsorbed $O_2$ is orange; dashed red circles indicate the positions of the vacant sites.

what found for anatase (101)$^{41}$, however, the energy barrier for subsurface $\rightarrow$ surface migration of the $V_O$ is quite high at the anatase (001) surface$^{19}$, at least for the $O_2$ concentration considered here, as shown by Fig. 7b for the case of the VO4$\rightarrow$VO3 migration step. It is thus quite likely that the $V_O$ remains subsurface at the low temperature of our experiment, so that the adsorbed $O_2$ remains a superoxide, i.e. one of the two excess electrons of the vacancy remains in TiO2. This explains the persistence of the 2DEG at the anatase-TiO2(001) as well as the decrease in the number of carriers observed under oxygen dosing without the necessity to include any interface effect with the substrate in the calculation.

IV. CONCLUSIONS

In summary, our results reveal distinct behaviors of localized and delocalized states induced by oxygen vacancies at the surface of anatase TiO2. Due to their different spatial locations and the kinetics of defect diffusion in anatase, the 2D delocalized states are much more robust than the localised in-gap states when exposed to molecular oxygen in a wide range of pressures. This robustness of the delocalized states is an important feature that could be exploited for different applications, e.g. to tune the electronic structure of TiO2 in engineered interfaces and heterostructures, or to precisely control the concentration of charge carriers in photo-sensitive devices.

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AUTHOR CONTRIBUTIONS

G.P., C.B., P.O. and G.M.P. conceived the experiment(s), A.S. planned the computational studies. G.P., C.B., P.O., G.M.P. and A.S. wrote the paper with contributions from J.F, I.V., Z.T. All authors discussed the results, commented manuscript and prepared written contributions. P.O. grew the films, G.D and R.C. characterized samples. Z. T. performed the calculations. C.B., G.M.P., A.V., T.L.L., A. R., P.D.C.K., G.R., A.T., T.P., D.B., P.K.D., performed synchrotron radiation experiments and analysed the data. C.B. and G.M.P. contributed equally to this
work.

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