# Supporting Information: Point Defects and Related Excess Electrons in the Dielectric Profile of the Reduced TiO<sub>2</sub>(110) Surface

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## S1 Dielectric fits of loss spectra

Fits of the loss data (Figure 2 of the article) are performed by means of the following expression of the dielectric function<sup>1,2</sup> (see text):

$$\epsilon_{TiO_2}(\omega) = \epsilon_{Ph}(\omega) + \epsilon_{Ib}(\omega) + \epsilon_{gs}(\omega) + \epsilon_{Pl}(\omega).$$
(1)

While phonon  $[\epsilon_{Ph}(\omega)]$  and interband contributions  $[\epsilon_{Ib}(\omega)]$  are obtained from data of the literature, the BGS contribution is treated through an oscillator  $\epsilon_{gs}(\omega) = \frac{\Omega_{gs}^2}{\omega_{gs}^2 - \omega^2 - i\Gamma_{gs}\omega}$ and the transport properties through a Drude term  $\epsilon_{Pl}(\omega) = -\frac{\omega_P^2}{\omega^2 + i\omega\Gamma_P}$ . Fits neglect (i) the temperature-dependence of the absorption coefficient of polarons<sup>3,4</sup> and of phonons for which neglect is supported by the absence of shift of the  $A_{2u}$  and  $E_u$  bulk longitudinal modes (*i.e.*  $\omega_{sph,3}$  herein) between 300 and 740 K;<sup>5</sup> (ii) the decrease in phonon lifetime with defect den $sity^{6}$  since the reduction state of the crystal is low; (iii) the variations upon reduction of the interband transitions intensities (Figure 2 of the article); these are underestimated in simulations because the surface sensitivity of EELS in this energy-loss range (supporting information of Reference 7) overweights the  $O_b(vac)$ contribution.

Fits of loss spectra are shown in Figure S1 but also in Figure 1 of Reference 2. The dielectric parameters obtained from the fit in the two scattering geometries are gathered in Table S1. Their variations as a function of  $O_2$  exposure are plotted in the text (Figure 7). BGS characteristics are first extracted from EELS spectra (Figure S1-b,d) and then used to analyze the QEP/phonon region in HREELS (Figure S1a,b). Not included in the initial strategy to determine BGS characteristics, the use of Drude parameters fitted on HREELS data even improves *a posteriori* the agreement between simulations and EELS data in the phonon spectral range (not shown).

For spectra collected parallel to the c-axis, previously found values for bulk  $(\Omega_{qs,B,\perp})$ ,  $\omega_{gs,B,\perp}, \Gamma_{gs,B,\perp}, \omega_{P,B,\perp}, \Gamma_{P,B,\perp})$  and surface  $(\Omega_{gs,S,\perp}, \omega_{gs,S,\perp}, \Gamma_{gs,S,\perp}, \omega_{P,S,\perp}, \Gamma_{P,S,\perp})$  excitations along the normal direction were kept fixed to extract those relative to the parallel direction  $(\Omega_{qs,B,\parallel}, \omega_{qs,B,\parallel}, \Gamma_{qs,B,\parallel}, \omega_{P,B,\parallel})$  $\Gamma_{P,B,\parallel}$ ) and  $(\Omega_{gs,S,\parallel}, \omega_{gs,S,\parallel}, \Gamma_{gs,S,\parallel}, \omega_{P,S,\parallel})$  $\Gamma_{P,S,\parallel}$ ) by fitting the effective dielectric function  $\xi(\omega) = \sqrt{\epsilon_{\perp}(\omega)\epsilon_{\parallel}(\omega)}$  to data of Figure 2 of the article. In a way similar to the perpendicular direction, the bulk was analyzed first, before determining the surface parameters. Once corrected from the effective mass anisotropy, the plasmon damping  $\Gamma_P$  (Table S1) gives a lower bound for the anisotropy of the bulk carrier



Figure S1: Fit of loss spectra of R-TiO<sub>2</sub>(110), upon O<sub>2</sub> exposure, with the dielectric model developed in References 1,2: (a)(b) spectra recorded at 100 K with the beam perpendicular to c-axis and (c)(d) at 300 K with the beam parallel to c-axis. Experimental (circles) and fitted (lines) (a)(c) HREELS and (c)(d) EELS spectra. Complementary fits at 300 K with a beam perpendicular to c-axis can be found in Reference 2.

mobility  $\mu_{\perp}/\mu_{\parallel} > 3.5$  which is however larger than in Reference 8 ( $\mu_{\perp}/\mu_{\parallel} = 0.2$  at 300 K).

# S2 Calculation of bulk dielectric properties

Calculations of bulk transport characteristics are performed in the frame of a parabolic band model with a density of conduction states given by  $N_C = 2(2\pi m_e m^* k_b T/h^2)^{3/2}$ , in which  $m^*$  is the temperature-independent effective mass,<sup>9</sup>  $k_b$  the Boltzmann constant, T the temperature and h the Planck constant. Donor defects with a concentration  $N_D$  located and an energy level  $E_D$  are ionized to give rise to carriers at concentration  $n_B$ . Two extreme cases can be distinguished depending on temperature and the relative position of  $E_D$  from the bottom of the conduction band  $E_C$ .<sup>10</sup> In the freezing regime  $(kT < E_C - E_D)$  as assumed herein at 100 K, a partial ionization leads to  $n_B = (\frac{1}{2}N_D N_C)^{1/2} \exp\left[-(E_C - E_D)/2k_b T\right]$ . In the exhaustion regime as assumed herein at 300 K, all donors are ionized and  $n_B = N_D$ . From these assumptions, the carrier concentration  $n_B$  determined at 100 and 300 K by dielectric fit of (HR)EELS data (Table S1) allows to determine the position of the donor level  $E_C - E_D = 21 + 4.2 \ln(m^*) = 30 \pm 10 \text{ meV}$  and of the Fermi level  $E_C - E_F = k_b T \ln(N_D/N_C) \simeq$  $64 \pm 5$  meV assuming a given effective mass  $m^* = 10.^{6,8,9,11-13}$  The freezing assumption is based on an expansion to first order of the actual position of the Fermi level  $E_F = E_D +$  $kT \ln \left\{ \frac{1}{4} \left[ -1 + \sqrt{1 + \frac{8N_D}{N_C}} \exp\left[ (E_C - E_D)/k_b T \right] \right\}$ obtained by neglecting 1 in front of the exponential in the square-root and -1 in front of the latter. With the figures obtained in the article, this holds true within 10 % at 100 K. Note also that  $E_C - E_D$  and  $E_C - E_F$  are quite robust to uncertainties in  $m^*$  since for  $\Delta m^*/m^* = 100 \%$ ,  $E_C - E_D = 30 \pm 14$  meV and  $E_C - E_F = 64 \pm 18$  meV. Conversely, assuming a freezing regime at both 100 and 300 K, the measured values of  $n_B/m^*$  leads, besides  $E_C - E_D \simeq$ 20 meV, to  $N_D = 6.6 \, 10^{18} \sqrt{m^*} \text{ cm}^{-3}$ . Since  $N_D$ 

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should be larger than the room-temperature  $n_B$  value, this yields  $m^* < 1.1$ , a unreasonable value lower by one order of magnitude than commonly found values.<sup>6,8,9,11-13</sup> The values of  $E_C - E_D$  deduced herein compare nicely to data of the literature obtained indirectly from a combination of bulk resistivity and Hall coefficient measurements. Bulk resistivity is given by  $\rho_B = 1/en_B\mu_B$  where  $\mu_B$  is the drift mobility. From Hall coefficient  $R_H = (\mu_H/\mu_B/B)/n_Bec$  (*B* magnetic field and *c* speed of light), the density of carriers can be estimated under the assumption that drift  $\mu_B$  and Hall mobility  $\mu_H$  are of the same order which is not obvious in a tetragonal lattice.<sup>9,14</sup>

Finally, the bulk reduction state  $x \simeq 10^{-3}$  in  $\text{TiO}_{2-x}$  can be obtained from the donor concentration  $N_D = n_B(300K)$ . Since the writing  $\text{TiO}_{2-x}$  implies implicitly a concentration of bulk vacancy of  $[V_O(\text{bulk})] = \frac{x}{2}[O]$  where  $[O] = 6.4 \, 10^{22} \text{ cm}^{-3}$  is the oxygen density in  $\text{TiO}_2$  rutile and assuming the release of two electrons per bulk vacancy *i.e.*  $[V(\text{bulk})_O] = n_B/2$ , one finds  $x = n_B/[O] \simeq 0.001$ .

## S3 Photoemission analysis of band bending

In the discussion of the evolution of band bending upon O<sub>2</sub> exposure,<sup>15,16</sup> the shift of the valence band edge  $\Delta V_{XPS}$  seen in photoemission is assumed to correspond to the actual change in band bending *i.e.*,  $L_D \gg \lambda$ ,  $L_D$  and  $\lambda$  being the Debye length and the escape depth of photoelectrons. A basic exponential modeling of the depth dependence of the band position  $\Delta V(z) = V_{bb} \exp(-z/L_D)$  combined with the damping of photoemission signal over  $\lambda$ shows that the binding energy scale is shifted by  $\Delta V_{XPS} = \int_0^\infty 1/\lambda \exp(-z/\lambda)V_{bb} \exp(-z/L_D) =$  $V_{bb}L_D/(L_D + \lambda)$ . If  $L_D \gg \lambda$ ,  $\Delta V_{XPS} \simeq \Delta V_{bb}$ . The same reasoning holds true also for a more classical parabolic<sup>10</sup> band bending. Table S1: Effect of crystalline anisotropy on the dielectric behavior of bulk and surface excess electrons at T = 300 K. Bulk  $n_B/m^*$  and surface carrier density  $n_S/m^*$  are calculated from the plasma frequency  $\omega_P^2 = ne^2/m_e m^* \epsilon_0$  and surface layer thickness  $t_S = 6.5$  Å while electron mobility is obtained through  $\mu m^* = 2\pi e/m_e \Gamma$ . Surface values correspond to as-prepared R-TiO<sub>2</sub>(110) and bulk ones to strong O<sub>2</sub> exposure.

	Plasmon				Band gap states		
	$\hbar\omega_P$	$n/m^*$	$\hbar\Gamma_P$	$\mu.m^*$	$\hbar\Omega_{gs}$	$\hbar\omega_{gs}$	$\hbar\Gamma_{gs}$
	$(\mathrm{meV})$	$({ m cm^{-3}/cm^{-2}})$	$(\mathrm{meV})$	$(cm^2.V^{-1}.s^{-1})$	$(\mathrm{meV})$	$(\mathrm{meV})$	(meV)
Bulk $\perp$	$92 \pm 10$	$6.1 \pm 1.3 \ 10^{18}$	$\simeq 0 \pm 20$	> 60	$1270\pm100$	$1260\pm100$	$950\pm100$
Bulk $\parallel$	$170 \pm 40$	$2.1 \pm 1.0  10^{19}$	$230\pm100$	$5\pm 2$	$1100\pm250$	$1260\pm300$	$950\pm300$
Surface $\perp$	$650\pm150$	$2.0 \pm 1.0  10^{13}$	> 500	< 2.3	$1500\pm250$	$1100\pm200$	$970\pm200$
Surface $\parallel$	$440 \pm 150$	$0.9 \pm 0.6  10^{13}$	> 500	< 2.3	$1750\pm250$	$1100\pm300$	$970\pm300$

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