Supplementary Information

Evidence for Intrinsic Nature of Band-Gap States Electrochemically Observed on Atomically Flat TiO$_2$(110) Surfaces

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Supplementary S1:

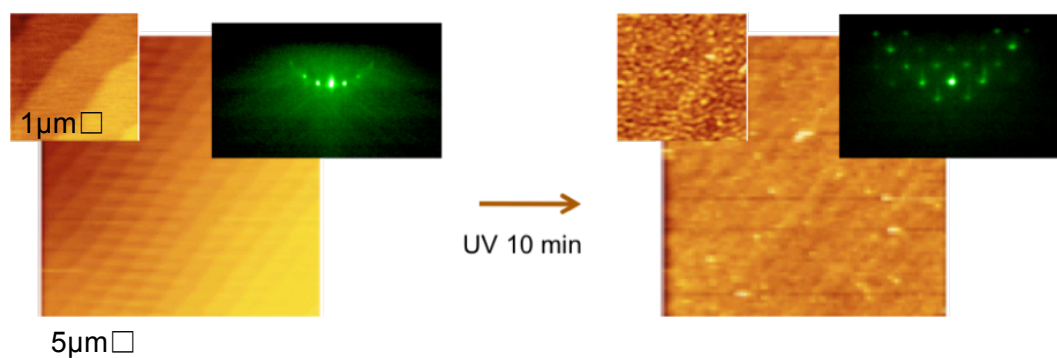**A set of AFM images and RHEED patterns before and after UV illumination.**

Figure S1 shows a set of AFM images and RHEED patterns for a different, but similar sample before and after UV illumination. After UV illumination, a spotty RHEED pattern that appears different from spots along a Laue circle characteristic to the $TiO_2(110)$-(1×1) surface before UV illumination, resulted from transmission of the primary beam through asperities rising above the plane of a rough surface, was observed and consequently the surface morphology, which had been atomically flat before UV illumination, became rough, but still can be seen the original steps-and-terraces structure. This result is a direct evidence for the photoetching that has been inferred to occur during UV illumination, but it is very limited to near the surface region.

Supplementary S2:

Estimation of the defect density by a simple analytical model
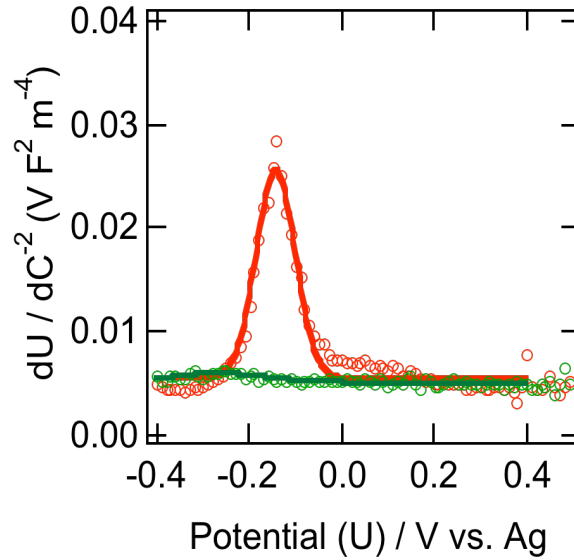
The defect density was estimated using the analytical model proposed by Tomkiewicz in 1979(1). In this model, the following equations can be derived:

$$\frac{dU}{d\left(1/C^2\right)} = \frac{\varepsilon\varepsilon_0 e N_D}{2} + \frac{\varepsilon\varepsilon_0 e^2 N_D}{2 C_H}\left(\frac{dN_{SS}^+}{d\Delta\phi_s}\right) \quad (1)$$

$$\Delta\phi_S = U - U_{fb} \quad (2)$$

$$\frac{dN_{SS}^+}{d\Delta\phi_s} = \frac{e N_t}{\sqrt{4\pi\lambda kT}}\exp\left(-\frac{e^2\left(U - U_t\right)^2}{4\lambda kT}\right) \quad (3)$$

U: the electrode potential

U_{fb}: the flat band potential

U_t: the most probable potential

N_D: the donor density

N_{SS}^+ the area concentration of ionized surface states

N_t: the defect density of the surface states

ε_0: the vacuum permittivity

ε: the relative permittivity of TiO_2 (=89) (2)

C_H: the capacitance of the Helmholtz layer

λ: the reorganization energy

k : the Boltzmann constant

Figure S2 is a plot of the values taken from the derivative of the nonlinear Mott-Schottky plot as a function of U. It was fitted by Gaussian line shape to compare with the following theoretical function obtained by combining Eqs. (1)~(3).

$$\frac{dU}{d\left(1/C^2\right)} = y_0 + A\exp\left(-\frac{\left(U-x_0\right)^2}{width}\right) \tag{4}$$

Then each quantity can be obtained using the value of the Helmholtz layer capacitance C_H $63\mu C/cm^2$ (1) as follows:

$$N_D = \frac{2y_0}{\varepsilon\varepsilon_0 e}$$

$$U_t = x_0$$

$$N_t = \frac{C_H A\sqrt{width}}{ey_0}\sqrt{\pi}$$

$$\lambda = width/4kT$$

Note that the values of reorganization energy ranged from 0.48 to 1.55eV, which is within a typical range of λ for semiconductors (3).

Supplementary S3:

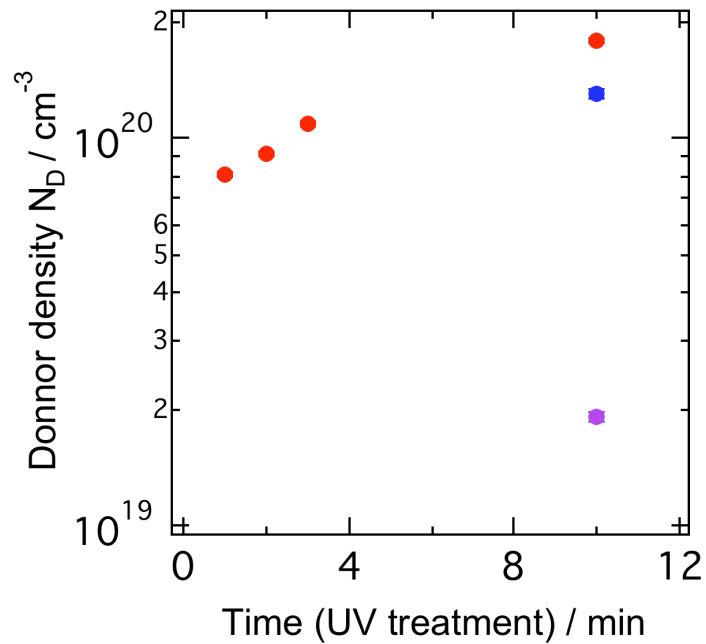**Behavior of the donor density N_D near the surface region**

Figure S3 is a plot of the values of N_D as a function of UV illumination time (●), together with those after the subsequent reduction (●) and growing the TiO_2 film (●). With increasing the UV illumination time, the donor density increases, approaching to the nominal value of the Nb dopant concentration of 1.4×10^{20} cm^{-3} (i.e. 0.5wt%). This indicates that the as-supplied Nb-doped $TiO_2(110)$ is likely to have a kind of dead layer near the surface region in which some of Nb dopants may become inactive. The photoetching process removes the dead layer, resulting in a fresh TiO_2 surface exposed. The donor density changed little or sometimes rather decreased even after the reduction, while the grown TiO_2 film had a small donor density of 1.9×10^{19} cm^{-3} near the surface region. The origin of the donors is bulk oxygen vacancies and they can be easily re-oxidized near the film surface region during cooling the sample in O_2 (4).

References

1.   Tomkiewicz, M. The Potential Distribution at the TiO_2 Aqueous Electrolyte Interface. Tomkiewicz, M. *J. Electrochem. Soc.* **1979**, 126 (9), 1505-1510.

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3   Nozik, A. J. and Memming, R. Physical Chemistry of Semiconductor–Liquid Interfaces. *J. Phys. Chem.* **1996**, 100, 13061-13078.

4   Takata, S.; Tanaka, R.; Hachiya, A. and Matsumoto, Y. Nanoscale Oxygen Nonstoichiometry in Epitaxial TiO_2 Films Grown by Pulsed Laser Deposition. *J. Appl. Phys.* 2011, 110, 103513-1-5.