

## Supplementary Material for:

### On the dielectric constant of titanium dioxide

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#### Hydrogen implantation and hydrogen concentration profile

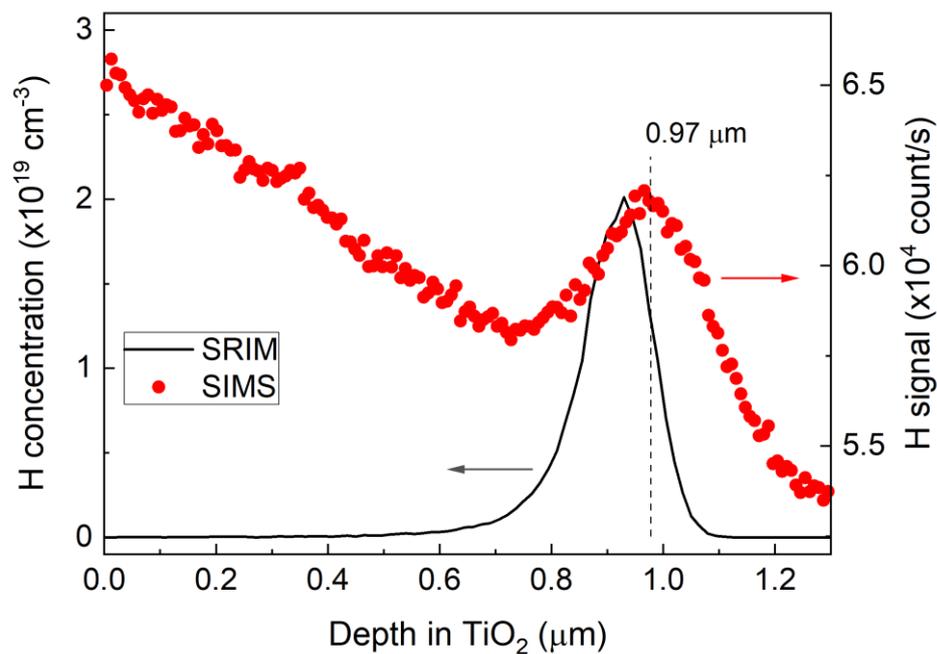


Fig. S1. Hydrogen distribution predicted by SRIM simulations for 200-keV H<sup>+</sup> implantation with a dose of  $3 \times 10^{14} \text{ cm}^{-2}$  and the hydrogen signal (counts/s) in SIMS measurements as a function of depth in TiO<sub>2</sub>.

Heat treatments were performed in forming gas (FG) flow (N<sub>2</sub> + H<sub>2</sub> with [H<sub>2</sub>]/[N<sub>2</sub>] ≈ 1/9) at 600°C for 90 min, labeled as TiO<sub>2</sub>-FG, or in N<sub>2</sub> flow at 1100°C for 60 min, labeled as TiO<sub>2</sub>-N<sub>2</sub>. After the heat treatments and deposition of 150-nm thick Pd contacts, the samples were implanted at room temperature with 200-keV H<sup>+</sup> ions to different doses in the range  $6 \times 10^{12}$  -  $3 \times 10^{14} \text{ cm}^{-2}$ . The implantation depth in TiO<sub>2</sub> was predicted to be 0.93 μm by Stopping and Range of Ions in Matter (SRIM) simulations [1].

Hydrogen distribution was then measured by secondary ion mass spectrometry (SIMS). Since SIMS is a destructive method, only one sample (TiO<sub>2</sub>-FG) was selected. The measurements

show a significant presence of hydrogen (Fig. S1) due to the treatment in FG and implantation. It should be noted, however, that hydrogen in  $\text{TiO}_2$  can exist in different atomic configuration, forming complexes with other defects. Thus the total hydrogen concentration, determined by SIMS, may not be equal to the net donor concentration. The implantation results in a pronounced peak in the hydrogen concentration at  $d_{peak}=0.97 \mu\text{m}$ , as can be seen from the SIMS data in Fig. S1. This implantation depth is within 4% accuracy of the depth predicted by SRIM ( $0.93 \mu\text{m}$ ).

### Frequency dependence of the dielectric constant

Frequency dependence of  $\epsilon$  was investigated in the range 1 kHz–1 MHz. The measurements were performed in two modes: (1) so-called parallel mode ( $C_p$ - $G_p$ ) and (2) so-called series mode ( $C_s$ - $R_s$ ), where the series resistance is significant.

Fig. S2 shows the frequency dependence of capacitance-voltage (CV) measurements recorded at  $T_{\text{meas}} = 150 \text{ K}$  for the  $\text{TiO}_2$ - $\text{N}_2$  sample after  $\text{H}^+$  implantation.  $T_{\text{meas}} = 150 \text{ K}$  is chosen as being about the middle of the studied temperature range (20 – 300 K), and it is representative for other temperatures. Measurements in the  $C_p$ - $G_p$  mode do not reveal any dispersion for frequencies in the range 1–60 kHz (Fig. S2a). The product  $N\epsilon_0\epsilon$  exhibits a maximum at the same voltage ( $-5.0 \text{ V}$ ) for all the frequencies (Fig. S2b). An indication of dispersion can be observed for a frequency of 0.25 MHz, and a strong dispersion is revealed for 1 MHz (Fig. S2a). We, however, attribute this dispersion to a measurement artifact due to limitations of the  $C_p$ - $G_p$  model, rather than frequency dependence of  $\epsilon$ .

The impedance of the depletion region depends on the probing frequency,  $f$ , as  $(2\pi fC)^{-1}$ . With increasing  $f$ , the impedance of the depletion region decreases and can become comparable to or less than the serial resistance of the sample. In this case, the  $C_p$ - $G_p$  model is no longer applicable, and the  $C_s$ - $R_s$  model should become valid. The measurements in the  $C_s$ - $R_s$  mode at 1 MHz (symbols in Fig. S2a) indeed remove the frequency dispersion. We conclude, thus, that  $\epsilon$  has no frequency dependence in the range 1 kHz – 1 MHz, and the results reported for  $f= 60 \text{ kHz}$  in the main text are valid for all frequencies.

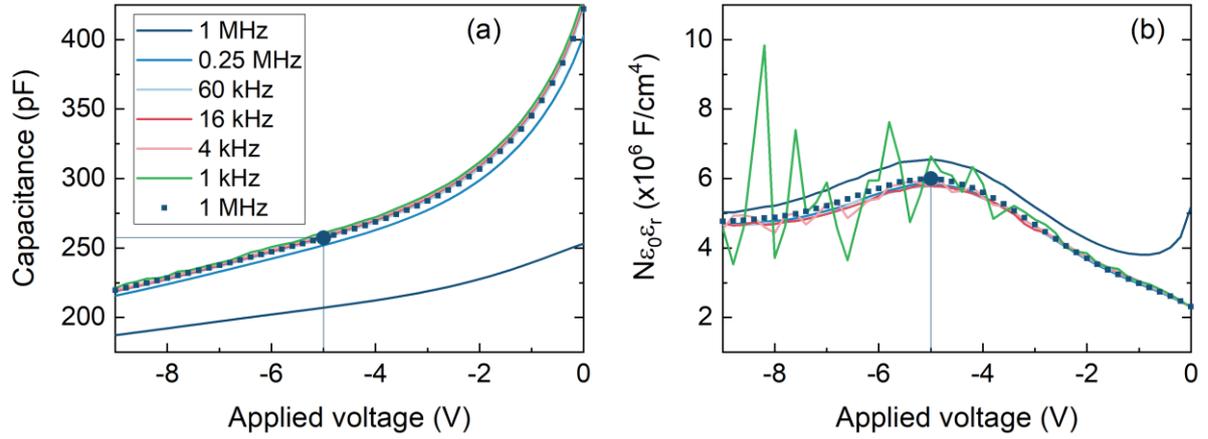


Fig. S2. Capacitance (a) and the product  $N\epsilon_0\epsilon_r$  (b) for different frequencies as functions of voltage for a hydrogen-implanted  $\text{TiO}_2\text{-N}_2$  sample. The solid curves are data from measurements recorded assuming a  $C_p - G_p$  circuit, while squares represent data measured assuming a  $C_s - R_s$  circuit. The voltage,  $V_{peak}$ , corresponding to the peak in  $N\epsilon_0\epsilon_r$  is indicated by a drop-down line in (b). The corresponding value of capacitance, obtained for the given  $V_{peak}$ , is also marked in (a).

## References

<sup>1</sup> J. F. Ziegler, M. D. Ziegler, and J. P. Biersack, Nuclear Instruments and Methods in Physics Research B **268**, 1818 (2010).