

Associated Content

Instability of Hydrogenated TiO₂

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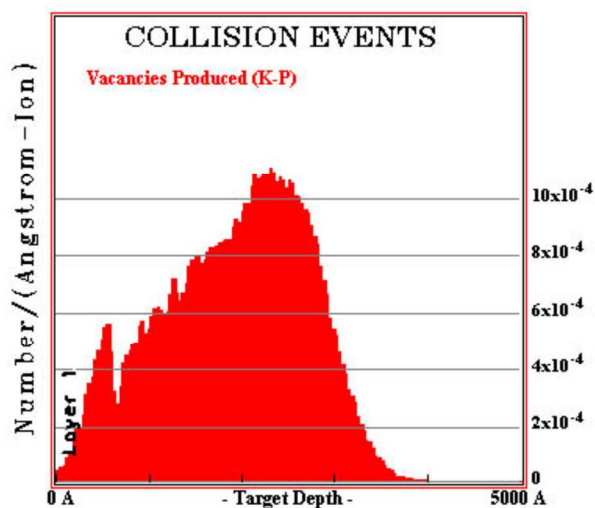


Figure S1: Oxygen vacancy profile obtained using the Kinchin-Pease (K-P) model. ¹ The profile corresponds to a peak defect generation probability of 1 in 1000 for every incident 45 KeV H⁺.

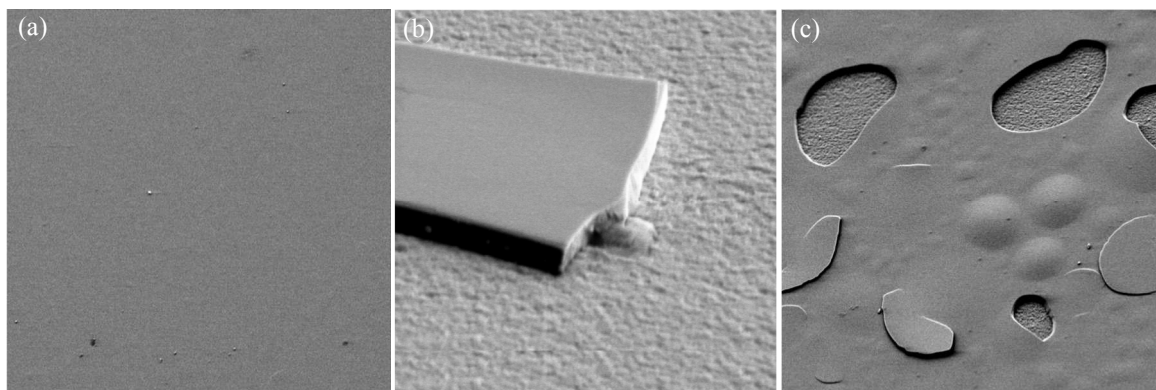


Figure S2: SEM images of H⁺-implanted surfaces (40 keV ion energy): (a) TiO₂(110) surface after annealing at 800 K, (b) SrTiO₃(100) after annealing at 870 K (image from ²), and (c) ZrO₂(100) after annealing at 770 K (image from ³). The H⁺ doses were 1.0x10¹⁷, 5.0x10¹⁶, and 1.0x10¹⁷ cm⁻², respectively.

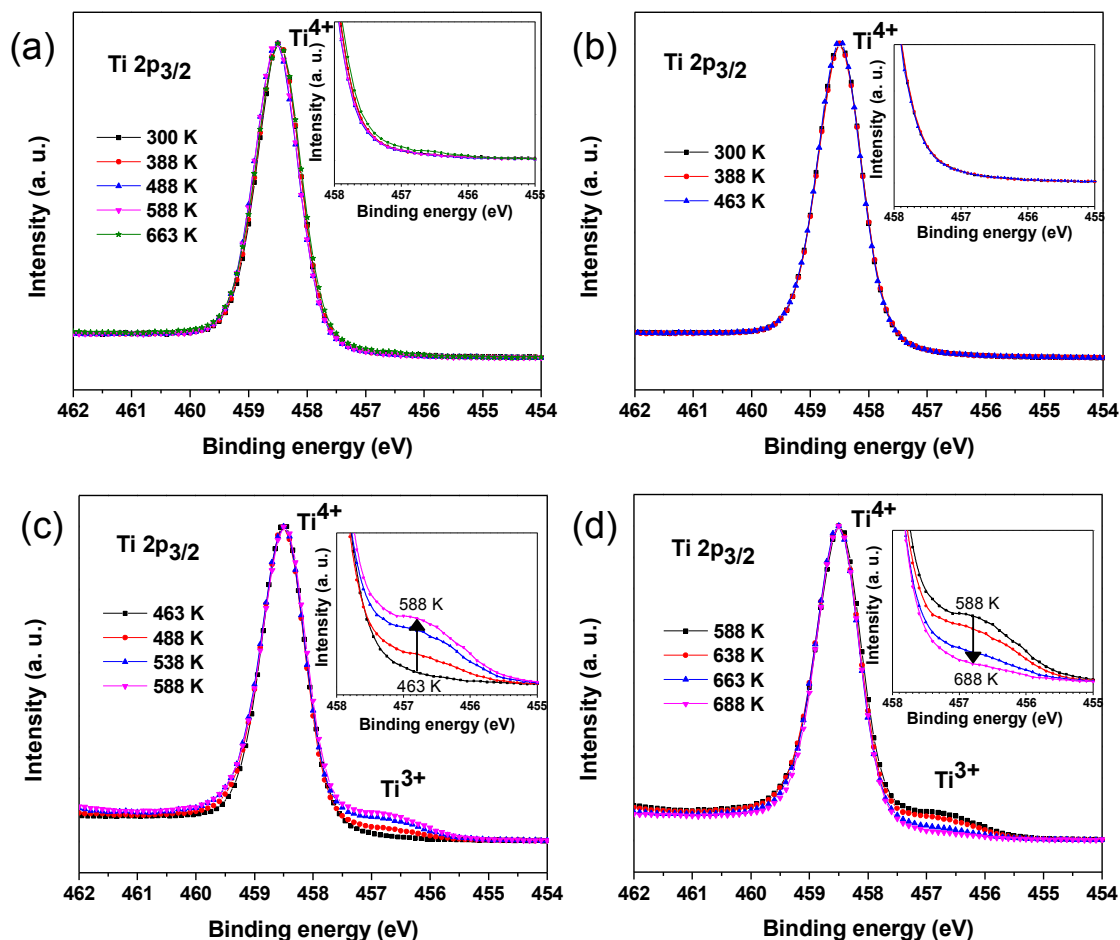


Figure S3. The XPS $Ti\ 2p_{3/2}$ high resolution spectra of the (a) pristine single crystal $TiO_2(110)$ sample in-situ annealed from room temperature to 663 K and H-implanted single crystal $TiO_2(110)$ sample in-situ annealed from (b) 300 to 463 K (c) 463 to 588 K, and (d) 588 to 688 K indicating the reduction of Ti^{4+} to Ti^{3+} from 463 to 588 K and re-oxidation of Ti^{3+} to Ti^{4+} from 588 to 688 K for H-implanted TiO_2 in contrast to pristine TiO_2 . The enlarged $Ti\ 2p$ regions associated with Ti^{3+} are shown in the inset of each spectrum.

The $Ti\ 2p_{3/2}$ peak of pristine $TiO_2(110)$ (Figure S3a) at 758.5 eV, ascribable to Ti^{4+} , was used as the reference point for all other spectra. This peak did not change in position or shape for the unimplanted sample after annealing up to ~ 700 K. (As noted in the experimental section, temperature readings in the XPS system erred toward higher values.) At most, the extent of thermally generated surface Ti^{3+} in pristine $TiO_2(110)$ was $\sim 3\%$, which did not change

significantly during the annealing sequence of Figure S3a. The H-implanted TiO₂(110) sample showed similar behavior to the pristine sample up to 463 K (Figure S3b and its inset), however Ti³⁺ peak appeared at 757.5 eV after annealing beyond 463 K (Figure S3c and its inset). This indicates that the H-implanted surface was readily reduced as the implanted H moved through the interface. Again, this is in sharp contrast to the behavior of pristine TiO₂(110) surface (Figure S3a). The near-surface Ti³⁺ concentration increased to, at most, ~12% with annealing from 463 to 588 K (see inset of Figure S3c), suggesting that most of the implanted H departed as H₂.

When the implanted sample was further annealed from 588 to 688 K (Figure S3d), the Ti³⁺ concentration decreased to ~4% almost reaching the amount of Ti³⁺ on the pristine TiO₂(110) surface. This result is consistent with the known thermal properties of reduced TiO₂ surfaces in vacuum, namely that excess surface reduction is transmitted at these temperatures into the bulk of rutile via diffusion of Ti³⁺ interstitials.^{4,5}

References

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