SUPPLEMENTAL MATERIALS Electronic structures and current conductivities by B, C, N and F defects in amorphous titanium dioxide

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Computational details on test procedures of constructing the amorphous model

The amorphousness was produced using the "melt-and-quench" technique. First, the TiO₂ crystals were heated up to high temperatures (4000K, which is far above the melting point 2116 K of TiO₂ crystals) until the crystals completely lose their structural memory. This was then followed by slowly cooling to room temperature that allows the formation of the amorphous phase. In this work, various structures (rutile, anatase, brookite) were considered as the input configurations for the production of the amorphous polymorph. The heating and cooling processes were computationally conducted with a temperature increasing/decreasing step of 200K. The time step for the MD simulations is 1 fs. At each temperature step (during the heating, as well as the cooling), the sample is equilibrated for 100 ps using the isothermal-isobaric ensemble (NPT). The obtained structures (amorphous) were then used for further atomic relaxation by means of first-principles calculations.



Figure 1. Potential energy shown for last steps of the cooling process



Figure 2. Temperature as a function of time (ps), during the last steps of the cooling process

Different starting crystals were initially used for the "melt-and-quench" process, including rutile, anatase and brookite supercells (containing 216, 216 and 192 atoms, respectively). Besides, the "melt-and-quench" was also tested on an arbitrary structure of 192 atoms with Ti:O stoichiometric ratio of 1:2, in which the initial atomic positions are randomly distributed. It showed that final amorphous structures, obtained from different initial TiO₂ configurations, have identical structural characteristics. This confirmed that the melting process has completely eliminated the structural memory and the amorphous model is independent of its input structures. The RDF and peaks shown are comparable with the experimental measurements on sputtered TiO₂ amorphous layers from reference 13 (V. Petkov, G. Holzhuter, U. Troge, T. Gerber and B. Himmel, *J Non-Cryst Solids*, 1998, 231, 17-30)



Figure 3. Radial distribution functions g(r) for a) O-O, b) Ti-O and c) Ti-Ti pairs of the amorphous model (a-TiO₂) at 300K, using the Matsui-Akaogi force field in comparison with experimental data

Schematic illustration for calculations of hole-transfer reorganization energy λ is presented below. The number of electrons before and after the hole transfer are N and N-1, respectively.

a) Both final configurations before and after charge transfer are the ground states. ΔR is the structural relaxation due to the presence of one hole. This scheme corresponds to cases of fully relaxed structures for a given energy functional, as used in the regular DFT+U calculations.

b) All configurations before and after charge transfer are shifted from the ground states by a value δ . This scheme corresponds to cases of DFT* and HSE06*, in which the preoptimized structures from DFT+U are used for the energy calculations

