Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information for Hole diffusion across leaky amorphous TiO_2 coating layers for catalytic water splitting at photoanodes

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Effect of the cooling rate on the structural and electronic properties of atomistic models of am-TiO_2

We here compare the structural and electronic properties of atomistic models of am-TiO_2 achieved through the melt-and-quench technique (cf. main text for details) using different cooling rates: (i) 75 K/ps (Model 1), (ii) 300 K/ps (Model 2), and (iii) 600 K/ps (Model 3). In Fig. 1, we compare the radial distribution functions (RDFs) calculated for these three models. The RDFS generally differ negligibly among the generated models. Nevertheless, we note that the double-peak structure observed in the experimental Ti-Ti RDF is slightly better reproduced with the faster cooling rates. The calculated mass density of the three models is found to increase by only 2% when going from Model 1 to Model 3 (cf. Table 1).

Similarly, the electronic properties are barely affected by the adopted cooling rate, with band gap differences amounting to at most 0.05 eV (cf. Table 1). Overall, our analysis indicates that melt-and-quench procedures with cooling rates varying between 75 and 600 K/ps lead to equivalent atomistic models of the amorphous oxide.

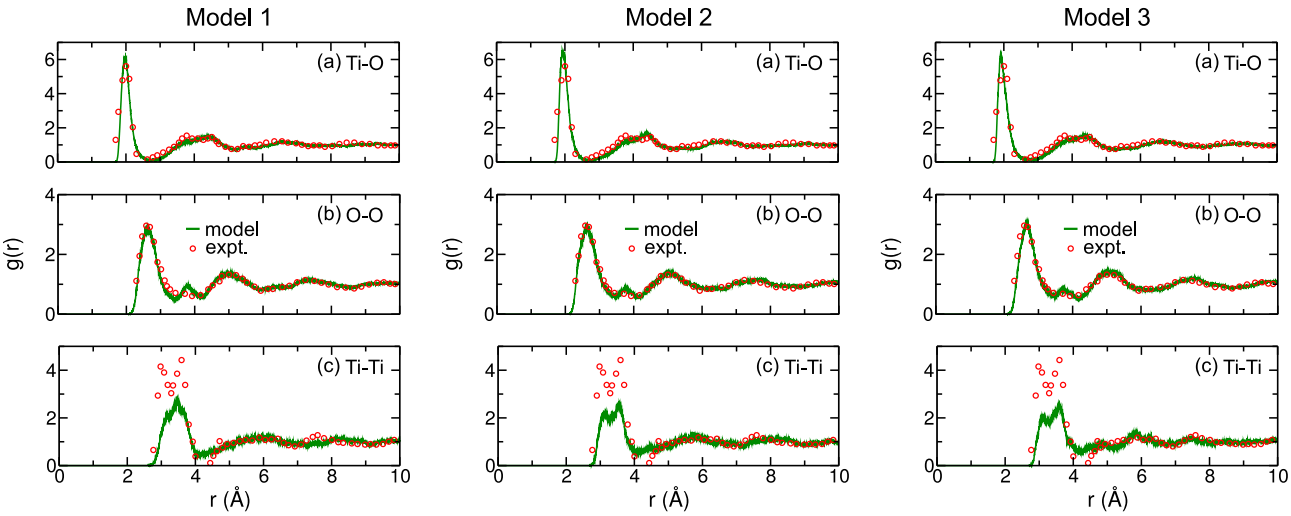

Figure 1: Comparison of the radial distribution functions $g(r)$ achieved for three models of am-TiO_2. Models 1, 2, and 3 have been generated with cooling rates of 75, 300, and 600 K/ps, respectively. RDFs as achieved from X-ray diffraction for sputtered TiO_2 amorphous layers[1] are shown for comparison.

Table 1: Calculated lattice parameters and mass density ρ at the PBE level for various am-TiO_2 models generated with cooling rates of 75 K/ps (Model 1), 300 K/ps (Model 2), and 600 K/ps (Model 3). The band gaps E_g are calculated at the PBE0 level with $\alpha = 0.15$, on structural configurations relaxed at the PBE level. Experimental values for both structural and electronic properties are reported for comparison.

	a (Å)	b (Å)	c (Å)	ρ (g/cm^3)	E_g (eV)
Model 1	14.31	14.23	12.17	3.85	3.42
Model 2	14.07	14.73	12.20	3.78	3.47
Model 3	14.40	14.26	12.32	3.77	3.48
Expt.				3.80-3.85[a–d]	3.20-3.40[e–f]

[a] Ref. 2. [b] Ref. 3. [c] Ref. 4. [d] Ref. 5. [e] Ref. 6. [f] Ref. 7.

Charge transition levels and bond lengths of O-O peroxy linkages

In Fig. 2, we give the calculated (+2/0) charge transition levels vs. O-O bond length for the 30 different peroxy configurations investigated in the present work. The distribution of the calculated energy levels shows an average value of 1.25 eV referred to the valence band edge and a standard deviation of 0.15 eV. The bond length distribution has an average of 1.46 Å and a standard deviation of 0.014 Å.

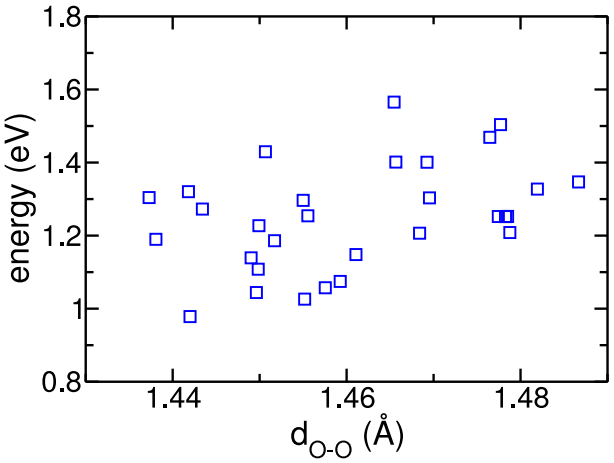

Figure 2: (+2/0) charge transition levels vs. O-O bond length for 30 different peroxy configurations.

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