# Tuning the Electronic Properties of γ-Al<sub>2</sub>O<sub>3</sub> Surface by Phosphorus Doping

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## S1. Morphology of the small cell surfaces doped with P atom:

O-sub (NS)	O-sub (S)	O-surf (NS)	O-surf (S)
AI5 AI7 P1 AI6 AI10 AI10	AIS AIT AIB AID AID	AITO AIZ	PT AIT AID AID AID AID
O-md (S)	O-md (NS)	O-bd (S)	O-bd (NS)
AIB AIB AIT AIZ	AIS AIS AIT AIT AIT AIT	AIT AIB AIT AIB	AIB AIB AIB AI AIP AIZ AITI AIZ IB AITI AIB

**Figure S1a:** The optimized surface morphology of the O terminated surfaces for small cell models with P atom. S: stoichiometric and NS: non-stoichiometric.



**Figure S1b:** The optimized surface morphology of the 100% hydroxylated surfaces (OH-terminated) for small cell models with P atom. S: stoichiometric and NS: non-stoichiometric.



# S2. The Computed PDOS of the small cell surface models doped with P atoms.

**Figure S2a:** The PDOSs of small cell surfaces of O terminated surface models for  $P-\gamma-Al_2O_3$ . The Fermi energy is set to zero. S: stoichiometric and NS: non-stoichiometric.



**Figure S2b:** The PDOSs of small cell surfaces of 100% hydroxylated surface models (OH-terminated) for  $P-\gamma-Al_2O_3$ . The Fermi energy is set to zero. S: stoichiometric and NS: non-stoichiometric.

# **S3. Morphology of the O terminated surface doped with two P atoms:** Upon their geometry optimization, the P atoms are 3 coordinated in a planar geometry. The surface structures of the models including two P at the three tetrahedral doping sites are shown in **Figure S3**.



### S4. The Computed PDOS of the O terminated surface doped with two P atoms: It

revealed that no states occur at the Fermi level which is located at the top of the VB. There are are two peaks at the bottom of the CB across the small band gap that are attributed to the P atoms.





**S6. Local minima surface geometries:** They were seen at each of the different doping sites. Also, water was removed from the model and re-optimized to see how the surface structure adjusts with water being eliminated.



**S7.** The Computed PDOS of the second doped P atom for hydroxylated model and that with water removed from the surface.



**S8. PF-KPFM measurement:** To understand the impact of phosphorus doping on the work function of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, we have conducted PeakForce Kelvin probe force microscopy (PF-KPFM<sup>TM</sup>). PF-KPFM<sup>TM</sup>, the combination of PeakForce Tapping mode and frequency modulated KPFM (FM-KPFM), integrates the benefits and capabilities of PeakForce Tapping and the superior spatial resolution and accuracy of FM-KPFM. PF-KPFM has the highest performance of KPFM working in a dual-pass fashion<sup>1</sup>. By utilizing KPFM method, one can obtain the local surface potential of materials in nanoscale level, while imaging their topography. Since KPFM measures the potential required to nullify the work function ( $\phi$ ) difference between the conductive tip and the sample or vice versa, (depending on whether the potential was applied to the sample or the probe), the contrast in the contact potential difference (CPD) window is equivalent to the local work function difference of the sample and the supporting substrate ( $\phi_{substrate} - \phi_{sample}$ =CPD). Therefore, the local surface potential can be used to calculate the work function of the sample, if the work function of the substrate is known.

PF-KPFM measurements on the alumina samples were conducted with a Dimension ICON AFM setup inside an Argon-filled glove box where both H<sub>2</sub>O and O<sub>2</sub> levels were below 0.1 ppm. The probes used were PFQNE-AL (Bruker AFM Probes), composed of a silicon nitride cantilever with a sharp silicon tip. The highly inert environment helped us to conduct more accurate measurements, since the dipole moment of any absorbed species can directly induce a difference in contact potential and, subsequently, a phase shift of our samples<sup>2</sup>. To measure the work function of P- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with PF-KPFM, we first disperse P- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> particles onto a boron-doped silicon substrate. Because the P- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> particles only partially cover the Si substrate, the measured work function value of doped Si substrate can be used as the reference to calculate the work functions of P- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> ( $\phi$  substrate -  $\phi$  sample=CPD). Knowing the work

function of the PFQNE-AL probe from previous experiments on a freshly cleaved HOPG (with a known work function of 4.68 eV), we calculated the work function of the doped-Si substrate to be 4.56 eV. The CPD for  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and P- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> were -312.6 mV and 397.3 mV, respectively, from which we calculated the work function of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as 4.88 eV, which is 720 mV higher than that of P- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (4.16 eV). Note that the dark contrast observed in the CPD image indicates their work function is higher than the Si substrate used in this work.

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PeakForce Kelvin Probe Force Microscopy, Application Note #140; Bruker Corporation: 2013.

Lägel, B.; Baikie, I.; Petermann, U. A Novel Detection System for Defects and Chemical
Contamination in Semiconductors Based upon the Scanning Kelvin Probe. *Surf. Sci.* 1999, 433, 249-253.

**S9. Surface-averaged electrostatic potentials:** We should point out that computing workfunctions for these surfaces is not a standard technique. We developed a methodology for plane averaging of the electrostatic potential to compute DFT energies and wavefunctions that allows to use very large vacuum lengths at little additional computational cost.

















Model	WF/GGA	WF/GGA+U	Dipole/GGA	Dipole/GGA+U
O-undoped	8.6750	9.0079	2.4812	2.7116
O-sub	8.0347	7.8122	1.8421	1.5432
O-surf	7.5214	7.8735	1.3193	1.5730
O-md	8.2451	8.5791	2.0435	2.2773
O-bd	8.2267	8.5660	2.0187	2.2652
OH-undoped	4.5387	5.2895	2.9613	3.0904
OH-sub	4.5004	4.3563	3.4322	3.5802
OH-surf	4.2995	4.4654	3.2991	3.5240
OH-md	4.7652	5.4663	3.1707	3.3080
OH-bd	6.0341	6.1390	4.0466	4.1272

**TableS1.** The computed WFs and surface dipoles (eV) of the surface models on the essential O-terminated and OH-terminated surfaces.

**S10. Work function and dipole correction values:** For all the surface structural models work functions ( $\phi$ ) and dipole correction ( $\phi_d$ ) are calculated using both GGA and GGA+U DFT calculations.



**Figure S10a.** Comparison of the determined work functions and dipole corrections for all non-doped, P-doped, and 2P-doped oxygen terminated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> subsurface models with 100% hydroxylated surface models.



**Figure S10b.** The change of work function ( $\phi$ ) (a) and dipole correction ( $\phi_d$ ) with respect to # of P dopant for the subsurface models (**O-sub** and **OH-sub**).



**Figure S11:** Plot of WF vs surface dipole  $\phi_d$  for supercell models of (a) O-terminated surfaces and (b) OH-terminated surfaces models. Those for small cell models are (c) and (d), respectively.

**S12.** Calculated vibrational frequencies of the P-doped  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> dentate models. The peaks around 3500-3700 cm<sup>-1</sup> can be assigned to the reaction of the phosphoric acid with the hydroxyl groups, as shown experimentally for phosphorous loading up to 1 wt%. <sup>40</sup>



**Figure S12a.** Calculated IR spectra for the undoped and dentate models (**O-md** and **O-bd**) on O-terminated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surfaces.



**Figure S12b.** Calculated IR spectra for the undoped and dentate models (**OH-md** and **OH-bd**) on the 100% hydroxylated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surfaces.