ADVANCED FUNCTIONAL MATERIALS

Supporting Information

for *Adv. Funct. Mater.,* DOI: 10.1002/adfm.201401493

Tuning the Work Function of Polar Zinc Oxide Surfaces using Modified Phosphonic Acid Self-Assembled Monolayers

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((Supporting Information can be included here using this template))

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Immersion time dependence of resulting WF. Figure S1 shows the relation between immersion time and resulting WF of BrBPA or 3FMBPA, respectively, on top of ZnO (000-1)-O single crystals. With increasing immersion time *t*, the WF increases as well according to an increasing density of dipoles. The highest WF value is reached after an immersion time of about 20 min. The subsequent decay at longer immersion times is caused by a disruption of the effective dipole moment. Because the SAMs appear to be rather robust, a destruction of the first monolayer is not likely. Therefore, the decay might be explained by inverted molecular overlayers. A rather textured topography of the AFM images supports this suggestion.

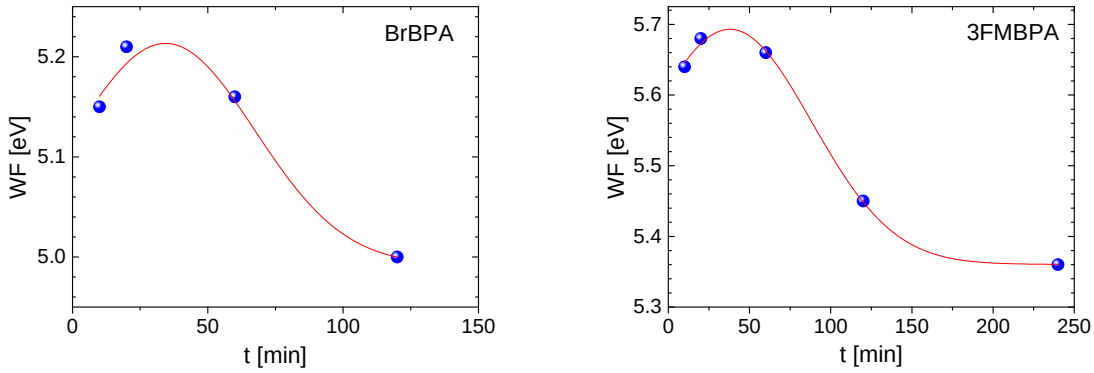

Figure S1. WF of the ZnO substrates after different immersion times to a BrBPA (a) or 3FMBPA (b) solution, respectively.

Etching Effect. Figure S2 displays the AFM height profile together with the corresponding phase image of a ZnO crystal surface after immersion to a 1 mM BPA solution in absolute ethanol (G CHROMASOLV®, Sigma Aldrich, 99.9%). A grainy structure is visible in both images. These grains are loosely bound to the surface and can easily be shifted away by an

AFM tip in contact mode (square in the middle). These grains do not appear if dried ethanol is used instead (see Figure 3 in the main part). Therefore, we attribute this effect to an etching of the ZnO surface caused by the residual water content of absolute ethanol with a concomitant stronger acidity of the PA´s.

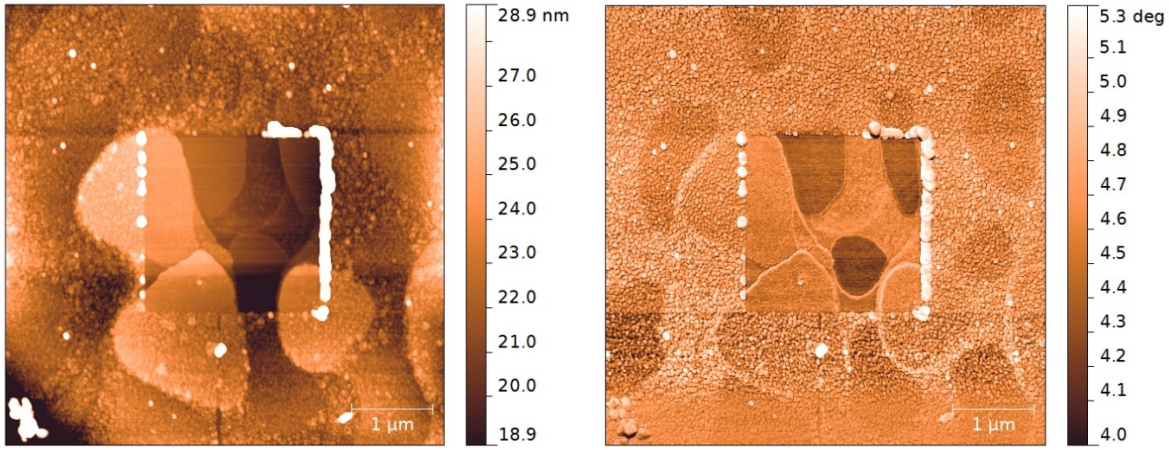

Figure S2. AFM height (a) and phase (b) image of a ZnO surface with etching effects.