Morphology-, Synthesis- and Doping-Independent Tuning of ZnO Work Function by Phenylphosphonates

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Supplementary information

Morphology of solution processed ZnO

Below we provide SEM and XRD information on film which show ZnO rods, ZnO pillars and ZnO sol-gel morphologies.



Figure 1SI Scanning Electron Microscopy images of ZnO rods (a, b) and ZnO pillars (c, d) in cross-section (a, c) and plan view (b, d).



Figure 2SI XRD of ZnO pillars and ZnO rods, normalized to (002) peak. The ZnO rods data are offset upwards for clarity. The lower relative intensity of the non (002) peaks at the pillars morphology indicates its higher ordering.



Figure 3SI ZnO sol-gel on FTO substrate; SEM image (left) and XRD data (right). The top XRD pattern is a 5 times magnification of the bottom pattern. Peaks marked in red arise from the ZnO, other peaks are from the FTO. The relative intensities of the ZnO peaks indicate the absence of preferred orientation in the film.

XPS analysis of persistent light induced WF shift

Further investigation of the persistent light effect origin was done using XPS. Figure 4SI shows a comparison of the Zn 2p and C 1s peaks of a PO₃-CN modified ZnO nanorod film, acquired at low and high X-ray intensities. The increase of x-ray intensity resulted in a shift of the Zn 2p and C 1s peaks by ca. 350 meV to higher BE. These shifts correspond very well to the ones seen in CPD using LED light. In addition, the Zn 2p peak full width at half maximum broadens by 270 meV, while the C1s one broadens only by 50 meV. The same trends were found for all the molecular films. The uniform peak shift and the fact that the energy of the C1s peak is measured from the substrate Fermi level suggests that the molecular core level shift arises from a shift in the ZnO vacuum level. Furthermore, the strong broadening of the Zn 2p peak, in contrast to the more modest broadening of the C1s, indicates that the chemical environment of the Zn has changed. This suggests that the change in WF is caused by formation of defects and not by photogenerated free carriers. The X-rays may form oxygen vacancies or Zn

interstitials (both contribute to n-doping) which can be annealed out by the heat treatment, either by bulk to surface oxygen diffusion or diffusion of interstitials back to their equilibrium position.

As the persistent light effect is correlated to defect formation under supra-bandgap illumination in the ZnO, it is an indication of the ability of the molecular film to tune the ZnO WF to the full extent, regardless of random starting conditions of the substrate.



Figure 4SI Zn 2p (on the left) and C 1s (on the right) position in low and high x-ray flux. The shift in the peak position is in excellent agreement with dark – light CPD results; initial widths (before high intensity-induced broadening) were 1.5 and 1.4 eV for the Zn and C peaks, respectively.

Molecular film thickness and coverage

The coverage and thickness can be obtained from AFM studies, which are not practical for most of the morphologies and for the very thin molecular films.

Instead, for all morphologies (except the nanorods, in which the photoelectrons takeoff angle is not well-defined) we deduce the thickness from XPS data, relying on standard signal attenuation considerations. By comparing the measured thickness with the molecule's theoretical length, we estimate the molecules density and tilt angle (w.r.t the surface normal). For example, in the simplest case where the two values coincide, high coverage and low molecular tilting are inferred.

The expression used for film thickness evaluation is:

$$d_{film} = \lambda_{eff} \cdot \ln\left(1 + \frac{I_{film}}{I_{substrate}}\right)$$

where ${}^{d}_{film}$ is the film thickness, ${}^{\lambda}_{eff}$ is the effective photoelectron attenuation length, taken here as 25 Å for the inorganic media and 33 Å for the organic layer, and I_{film} and $I_{substrate}$ are, respectively, the integrated signal intensities (in atomic %) of the film and substrate. Our data indicate the presence of a small amount of extra C-contamination (inferred from specific elemental ratios, C, P, N and also O), as compared to a discrete (atom by atom) calculation of the attenuation across the overlayer. The molecular layer thicknesses given in the table below are the result of this detailed analysis. The additional component of C-contamination is <4 Å in thickness. A comparison with the theoretical length of the molecules, as calculated using CambridgeSoft Chem3D software is presented at the final row. The excellent agreement between the molecular film thickness, as calculated from XPS data and the computer model strongly suggests a good coverage and a monomolecular layer. In this case, the tilt angle of the molecules in the film is expected to be close to 90°.

	PO ₃ -Phen	PO ₃ -CN	PO ₃ -OCH ₃
Film on top of ZnO (including contamination)	8.0	10.0	9.0
C contamination only	3.7	2.6	2.5
Molecular layer	4.3	7.4	6.5
Calculated (Chem3D)	4.6	7.0	6.5

Table 1SI Film thickness on ZnO pillars as calculated from XPS and computer model. All values are in Å, with an estimated experimental error up to $\pm 10\%$.

Charge transfer between the ZnO substrate and molecular monolayer

The HOMO-LUMO gap of the free molecules used in our case is 4.2 and 4.3 eV for CN and OCH₃ termination (fig. 5SI).

The position of the HOMO of the PO₃-OCH₃ is found to be ~0.45 eV above the ZnO VBM (fig. 6I), placing the LUMO at ~1.5eV above the ZnO CBM.

The HOMO of the PO₃-CN can not be determined by the onset position with such accuracy as it might be overlapping with the VBM of the ZnO, but according to the shape of the UPS spectra it seems to lay at up to 1 eV below that of OCH₃ (in analogy^{1,2,3,4} with other molecular layers in which an organic molecule with phenyl ring with either OCH₃ and CN substituent are used as surface modifiers) meaning the LUMO should be ~0.5 eV above the CBM of the ZnO. Under such conditions it is quite unlikely that significant charge transfer will occur between the ZnO and molecular layer.

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Figure 5SI absorption spectrum of PO₃-OCH₃ and PO₃-CN in THF solution.



Figure 6SI UPS spectra of modified ZnO valance band maximum using He I. E_f is at 0 binding energy.

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Regardless of deposition method and resulting morphology, ZnO work-function can be continuously modified over a 1.1 eV using mixed dipole baring phenylphosponates.