Supporting Information for

Energy level alignment at organic/inorganic semiconductor heterojunctions: Fermi level pinning at molecular interlayer with reduced energy gap

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Reorientation of 6P at an organic-organic interface



FIG. 1. C1s core level regions of incremental depositions of 6P onto ca. a monolayer HATCN on ZnO(000 1;). In full analogy to 6P on ZnO without the HATCN interlayer two distinct peaks are observed, which are indicative of different 6P orientations. Thus, also on the HATCN precovered ZnO(0001;) face the 6P monolayer is lying face-on (higher BE component) and subsequent 6P layers are standing upright (lower BE component).

Thick film NEXAFS of 6P on ZnO



FIG. 2.a) NEXAFS C K-edge spectra of a 32 Å thick 6P film on ZnO(0001). At ~286 eV a sharp feature related to π^* transitions arises. Its shape is slightly asymmetric and in agreement with previous NEXAFS investigations of 6P [1,2]. Additionally, one recognizes a shoulder at lower photon energies, which is an artifact related to low TEY currents. The angular dependence of the π^* intensities is shown in b). The molecular angle, α =74°, was determined according to [3].

Fig. 2 shows NEXAFS C K-edge spectra of a 32 Å thick layer of 6P on ZnO(0001). Around 286 eV a sharp feature arises related to π^* -transitions of 6P. A shoulder to lower photon energies is visible. The shoulder is an artifact due to offsets (e.g. dark currents or external jamming) on the TEY signals when measuring currents as low as pA. Upon closer inspection of the main feature at 286 eV one recognizes an asymmetry, which has also been observed within other NEXAFS investigations of 6P [1,2]. The pronounced angular dependence of the π^* intensities on the photon incident angle θ is shown in Fig. 2 b). The molecular orientation was calculated according to [3] for sixfold substrate symmetry, yielding an angle of 74° between the surface- and π -system's normal. Such angle is compatible with standing or edge-on 6P molecules. Note that also edge-on molecules, instead of standing ones, are consistent with the observed low BE peak in the C1s core levels. Nevertheless, AFM investigations of an equivalent system [4] have evidenced standing molecules.

Rationale for different absolute 6P C1s core level positions



FIG. 3. a) Differences of the work function (ϕ) at differently irradiated spots on the sample. At the neutral spot only SECOs were measured, ca. 30s each. At the UPS spot UV light exposure typically reached 30-60 min for each deposition. On the XPS spot X-ray light exposure was also ca. 30-60 min for each deposition. Yet, photon energy, flux and secondary electron yield are higher as for the UPS measurements. b) and c) Different energy level positions (in the adsorpted state with 6P; thicknesses indicated at the bottom of the panels) of the O1s and C1s core levels for the different ZnO faces used.

The thesis of an identical energy level alignment of 6P on the three different ZnO faces as discussed in the main paper, seems at first sight contradicted by the different observed final C1s core level positions [see Fig. 3 c)]. However, as we will rationalize in the following we attribute this finding to energy level degradation effects from the light used to perform the experiments. UV/X-ray light degradation or beam damage are a well documented phenomenon for organic semiconductors, possibly by the effects of the secondary hot electrons [5-8]. Yet, also for ZnO it was reported that the internal ZnO surface band bending, and to some extend also its electron affinity and ionization energy, reacts to UV/X-ray exposure [9]. Light induced changes of the ZnO surface are likely to have an impact on the bonding modalities with the first 6P layer adsorbed.

From Fig. 3 a) it is apparent, that the UV or X-ray light used for the measurements has an influence on the energy level alignment at the interface. One observes energy level differences of up to 0.4 eV between a minimally illuminated neutral spot (only exposed for ca. 30s for each incremental 6P deposition), the UPS spot (exposure ca. 30-60 min per coverage) and the XPS spot (exposure also ca. 30-60 min per coverage). However, note that photon energy, flux and secondary electron yield are higher on the XPS spot than on the UPS spot let alone the neutral one. Resultantly, at least for the XPS spot, X-ray light exposure seems to inhibit the pinning mechanism raising ϕ up to 4.0 eV on the ZnO(0001) face that is described in the main paper. Instead, for the XPS spot ϕ stays at 3.6 eV.

Since the upward energy level pinning on ZnO(0001) is realized by adsorption induced internal ZnO band bending, one would expect, in the case of its absence as on the XPS spot, also the ZnO related core levels to exhibit the same differences as visible in the C1s region of 6P. Indeed, this is the case, as the O1s core level positions [see Fig. 3 b)] of the three investigated ZnO faces vary in the same way as the C1s positions of the 6P layer on top [Fig. 3 c)]. Thus, we conclude that the differences of the absolute C1s core level positions by 0.5 eV are induced by the measurement light and do not contradict the main thesis of the paper of identical energy level alignment of 6P on all three ZnO faces.

Molecular gap narrowing in close contact to a dielectric medium

A charge q resides in a dielectric medium of ε_r at a distance z from a metal surface. Then the force F between the charge and its induced image charge can be written as [10]:

$$F(z) = \frac{1}{4\pi\varepsilon_r\varepsilon_0} \frac{q\cdot(-q)}{(2z)^2}$$

Leading to an energy level shift E [10]:

$$E(z) = -eV(z) = \frac{e}{4\pi\varepsilon_r\varepsilon_0 4z}$$

Where V is the potential. In the present case, since the substrate's dielectric constant is not infinity,

but rather ε_{ZnO} ca. 8 [11] the induced image charge is not equal to q, but only $\frac{(\varepsilon_{ZnO} - \varepsilon_r)}{(\varepsilon_{ZnO} + \varepsilon_r)}q$ [12]. Using reasonable assumptions of a distance z of 3.5 Å and an ε_r of 3 for 6P then the bandgap narrowing calculates to 0.3 eV.

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