

Band-offset engineering at organic/inorganic semiconductor heterointerfaces

S. Blumstengel, F. Henneberger, N. Koch
 Humboldt-Universität zu Berlin, Institut für Physik
 Newtonstr. 15, 12489 Berlin, Germany
 sylke.blumstengel@physik.hu-berlin.de

Abstract—To realize organic/inorganic semiconductor hybrid structures with advanced optoelectronic and photonic properties, control over the structure, morphology and electronic properties of the heterointerface is required. Here, we demonstrate that the assembly of conjugated organic molecules can be steered by the surface termination of a given semiconductor. In the case of α -sexiphenyl on ZnO, the orientation of the molecules can be changed from upright-standing to flat lying by varying the molecule-substrate interaction. The morphology change is accompanied by a change of the surface dipole and the molecule's ionization potential and provides thus an efficient means to engineer the band-offsets at the organic/inorganic heterointerface.

I. INTRODUCTION

Organic/inorganic semiconductor hybrid structures hold the promise to unite specific complementary properties of both material classes leading to optoelectronic and photonic devices with advanced functionalities. A simple combination of both materials will not improve the performance significantly, required are hybrid structures supporting efficient coupling of optoelectronic excitations across the heterointerface. Electronic coupling refers hereby to exchange of excitons or charges. To optimize the transfer, the organic/inorganic interface needs to be tailored structurally as well as electronically. This shall be illustrated in the following example: For light-emitting application, it would be beneficial to inject and transport charges in the “high-mobility” inorganic part of the hybrid structure while emission is generated in the organic layer taking advantage from the easy spectral tunability of organic materials. The excitation energy is thereby transferred via a Förster-type transfer process from the inorganic to the organic part given that the molecular transition dipole moments are properly aligned with respect to the heterointerface and the exciton energies are in resonance [1,2]. Furthermore, the energy offsets between frontier molecular orbitals, i.e. the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), and the valence band maximum (VBM) and conduction band minimum (CBM) of the semiconductor must be properly adjusted to prevent exciton dissociation. Preferably would be a type-I energy level alignment, or, in case of a type-II interface, the energy offsets must be smaller than the exciton binding energies, i.e. ca. 0.5 eV for organic Frenkel excitons. Photovoltaics, on the other hand, relies on efficient exciton dissociation at heterointerfaces,

therefore type-II interfaces with energy offsets larger than the exciton binding energy are required. Due to complex interface formation between organic and inorganic semiconductors which may involve redistribution of charges, interface dipole formation or even chemical bonding, it is impossible to predict the energy offsets for a given material couple on the basis of tabulated values of ionization potentials and electron affinities. On the other hand, if understood, these effects can be exploited to engineer the band offsets at organic/inorganic interfaces. We demonstrate that using the example α -sexiphenyl (6P) on ZnO and show that the energy offsets between HOMO and VBM for this fixed material couple can be tuned by as much as 0.7 eV.

II. RESULTS AND DISCUSSION

The hybrid structures are grown under ultra-high vacuum conditions by molecular beam epitaxy in a DCA double-chamber apparatus guaranteeing well-defined interfaces free of extrinsic defects. Details on ZnO growth are described elsewhere [3]. 6P is deposited at a rate of 0.1nm/min at 100°C on two differently terminated ZnO surfaces. Stark differences in the morphologies of the 6P layer are revealed in atomic force microscope (AFM) images depicted in Fig. 1.

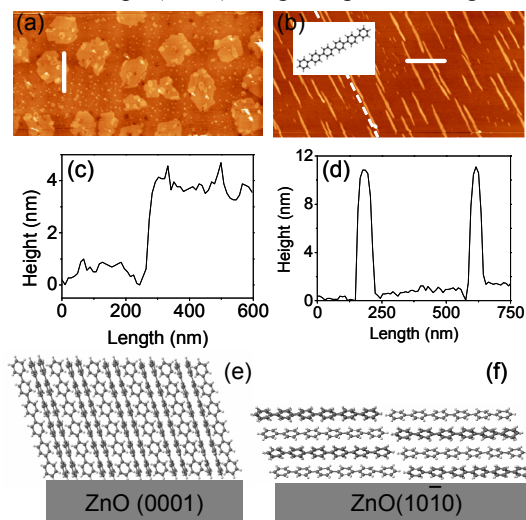


Figure 1. AFM images of 6P deposited on ZnO(0001) (a) and on ZnO(10-10) (b). The [0001] direction of the ZnO(10-10) surface is marked by the dashed line. The height profiles (c,d) are taken along the white lines in Figs. (a) and (b). Molecular orientation on ZnO(0001) (e) and ZnO(10-10) (f).

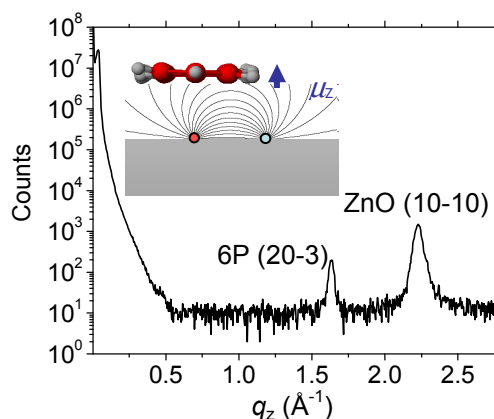


Figure 2. XRD of 6P grown on ZnO(10-10). The inset shows schematically the adsorption site of 6P on rows of positive Zn (red). The position of negatively charged O is marked blue.

On the polar Zn-terminated ZnO(0001) surface, 6P grows in flat extended islands whose height corresponds approximately to the length of the molecules, see Fig. 1c. The molecules assume thus an upright orientation as depicted in Fig. 1e. This morphology is typically found when molecule-molecule interactions outbalance molecule-substrate interactions. On the mixed-terminated, nonpolar ZnO(10-10) surface, 6P molecules aggregate in needle-shaped crystallites all oriented parallel to the *c*-axis of the ZnO wurtzite lattice. The contact plane is the (20-3) 6P crystal plane as revealed from X-ray diffraction (XRD), see Fig. 2. This means that the long axis of the molecules is exactly parallel to the ZnO surface and perpendicular to the needle axis, or in other words, the molecules assemble with their long axis parallel to the alternating rows of oxygen and zinc. The orientation and even the adsorption site can be derived from an electrostatic model. The alternating rows of negatively charged oxygen and positively charged zinc produce a dipolar field whose strength amounts to several V/nm above the ZnO surface in a distance where the molecules adsorb. 6P does not have a static dipole moment; however it possesses a quadrupole moment. The interaction energy is minimized if 6P adsorbs exactly on top of the rows of positively charged Zinc. It corresponds to the site where the induced dipole moment μ_z along the surface normal is maximized, as schematized in the inset of Fig. 2. The different orientations of the molecules with respect to the ZnO substrate as well as the formation of a dipole moment translate directly in a shift of 6P HOMO with respect to the ZnO VBM as outlined in the following.

The energy level diagrams of the two different 6P/ZnO hybrid structures derived from UPS measurements [4] are depicted in Fig. 3. The CBM and LUMO positions of ZnO and 6P, respectively, are estimated from band-gap energies based on the optical gap and the exciton binding energy. Firstly, one notices a lowering of the workfunction of pristine ZnO upon deposition of molecules. The effect is much more pronounced on the 6P/ZnO(10-10) interface as consequence of the induced 6P dipole moment in the “flat-lying” configuration. Secondly, the ionization potential of lying 6P molecules is larger by 0.4 eV as compared to standing molecules. This shift is due to collective electrostatics of intra-molecular polar bonds [5]. In

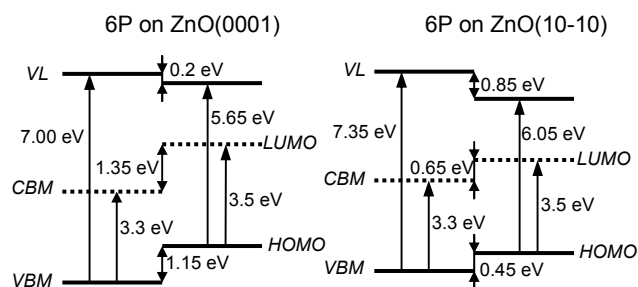


Figure 3. Energy level alignment at the 6P/ZnO(0001) and 6P/ZnO(10-10) interfaces as derived from UPS measurements. The LUMO positions are estimated from the optical gap adding the exciton binding energies.

the flat-lying orientation (see Fig. 1f), the π -electron system is oriented parallel to the surface forming a negatively charged plane which increases the barrier for electron release. Both effects add up resulting in a shift of the energy offsets between the frontier molecular orbitals of 6P and the ZnO VBM and CBM by 0.7 eV. When aiming, for instance, at electron injection from ZnO into the organic layer, the charge injection barrier can thus be significantly reduced selecting the proper interface. Still, both hybrid structures form interfaces of type II. By alloying ZnO with Mg, the bandgap can be enlarged up to 1 eV, therefore, by incorporation of Mg it should be possible to tune the energy offsets further to arrive eventually even at a type I interface.

In summary, we have demonstrated that the orientation of organic molecules can be switched from upright-standing to flat lying on a given semiconductor by changing its surface termination. The orientation of the molecules defines the direction of the transition dipole moment, and determines therefore critically the efficiency of Förster-type nonradiative energy transfer. Moreover, the energy offsets at an organic/inorganic interface can be tuned by molecular orientation which has direct consequences on the optoelectronic function of the hybrid structure.

ACKNOWLEDGMENT

The authors thank Stefan Kowarik (Humboldt-Universität zu Berlin) for XRD measurements.

REFERENCES

- [1] S. Blumstengel, S. Sadofev, C. Xü, J. Puls, and F. Henneberger, “Converting Wannier into Frenkel excitons in an inorganic-organic hybrid semiconductor nanostructure”, *Phys. Rev. Lett.* 97, 237401 (2006).
- [2] S. Blumstengel, S. Sadofev, and F. Henneberger, “Electronic coupling of optical excitations in organic/inorganic semiconductor hybrid structures”, *New J. Phys.* 10, 065010 (2008).
- [3] S. Sadofev, P. Schäfer, Y.-H. Fan, S. Blumstengel, and F. Henneberger, “Radical-source molecular beam epitaxy of ZnMgO and ZnCdO alloys on ZnO substrates”, *Appl. Phys. Lett.* 91, 201923 (2007).
- [4] S. Blumstengel et al., “Band-offset engineering in organic /inorganic semiconductor hybrid structures”, *Phys. Chem. Chem. Phys.* 12, 11642 (2010).
- [5] S. Duhm et al., “Orientation-dependent ionization energies and interface dipoles in ordered molecular assemblies”, *Nat. Mater.* 7, 326 (2008).