# Investigation of the electronic properties of bio-organic/inorganic semiconductor interfaces

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In recent years the possibility to use DNA bases in electronic devices such as organic field effect transistors[1] has attracted much attention. Also the transport properties of DNA strands (natural as well as artificial, e.g. poly(G)-poly(C) DNA) and whether or not these would be suitable molecular nano wires were subject of scientific discussions and a number of publications [2,3]. There is, however, little experimental work, addressing the electronic structure (i.e. the density of states) of the DNA bases in the condensed phase, which is of utmost importance for transport properties and device performance. Therefore a systematic photoelectron spectroscopy study of thin DNA base films was performed. The experiments were carried out at the Russian German Beam Line at BESSY employing the Multi User Stage for Angular Resolved Photoemission (MUSTANG) experimental station. This system is equipped with a Phoibos150 electron analyzer (SPECS) and consists of two main chambers for analysis and *in situ* sample preparation.

**Experimental:** The Si(111) substrates (n-type, resistivity 7.5Ω/cm) annealed under ultra high vacuum conditions (base pressure ≤ $3 \cdot 10^{-10}$mbar) by direct current heating at 800°C to desorb possible contaminants. Several DC flushes of 20s duration were applied to heat the samples up to 1100°C-1300°C in order to remove the natural oxide. After letting the sample cool down slowly enough to preserve the (7x7) reconstruction, the surface was passivated *in situ* by exposure to (2.0±0.5) Langmuir atomic hydrogen. This dose should be enough to passivate the dangling bonds without etching the surface. The DNA base layers were deposited onto the H-Si(111)(7x7) surface by organic molecular beam deposition (OMBD). The nominal layer thickness was monitored by a quartz microballance. The Valence band photoemission spectra (VB PES) of layers of the DNA bases adenine, cytosine and guanine were recorded for different thicknesses (1nm - 10nm) and with excitation energies of 55eV and 150eV. Exemplary valence band photoemission spectra (VB PES) are presented in Fig.1. The width of the spectra was determined by linear extrapolation of the onset of the VB PES at low binding energies and the cut-off at the vacuum level (i.e. low kinetic

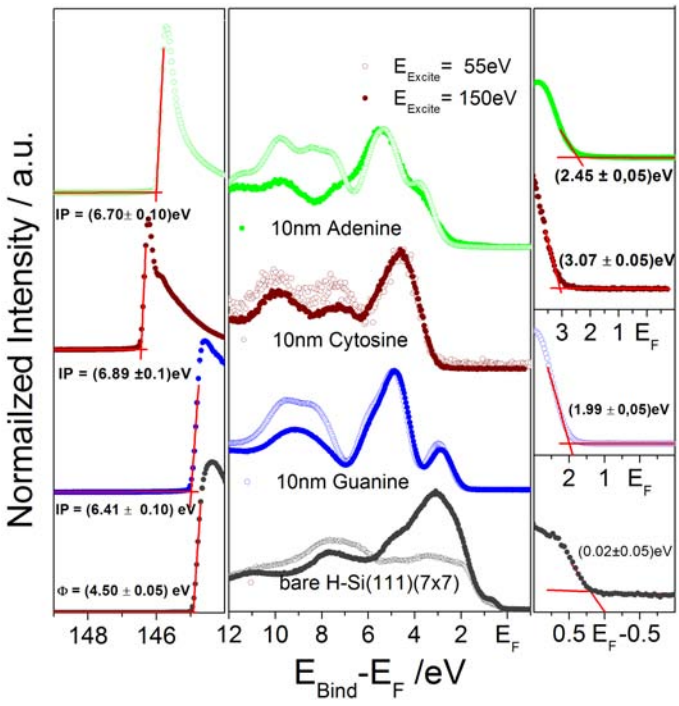


**Fig.1**: Valence band photoemisssion spectra of 10 nm layers of adenine (green), cytosine (brown) and guanine (blue) taken at $E_{excite}$=150eV(dots) and $E_{excite}$=55eV(circles)

energies). The ionization potential (IP) of the DNA base film can be derived by subtraction of the spectral width from the excitation energy. The IPs, determined by this procedure for bulk-like, thick DNA base layers are summarized in Tab.1. The experimentally determined IPs are significantly smaller than the values calculated by Preuss *et al.* for single molecules in [5], using a ΔSFC ansatz. This can be understood qualitatively as the result of the interaction between the molecules in the condensed phase which distributes the effect of the ionization over several molecules so that the individual molecular orbitals are less effected than in the single molecule case. The fact, that the experimental values are much closer to the calculated ground state eigen energies of the highest occupied molecular orbitals (HOMO's) (DFT/B3LYP functionals, 6-311G+(d,p) basis set [6]), suggests a strong interaction of the molecules. This is supported by the DFT/B3LYP calculation of the ionization potential of an infinite stack of guanine molecules published by Prat, Houk and Foote in [7], where they observe a similar shift in calculations including the neighbor interactions with respect to the calculation for single molecules.

| DNA base | Experimentally determined IP | IP(ΔSCF s.mol.) [2] | HOMO position (DFT/B3LYP; s. mol.) | IP(DFT/B3LYP;inf. stack)[3] |
|---|---|---|---|---|
| Cytosine | (6.89±0.10)eV | 8.66eV | 6.67eV | - |
| Adenine | (6.70±0.10)eV | 8.06eV | 6.34eV | - |
| Guanine | (6.41±0.10)eV | 7.63eV | 6.12eV | 6.64eV |

**Tab 1:** The ionization potentials determined from the valence band spectra follow the same trend as the values calculated for single molecules (s.mol.) with DFT/B3LYP(6-311+G(d,p)) and by a DSCF formalism. A better match in the absolute value can be achieved, if neighbor interactions are included, as performed by F. Prat and coworkers [3] for an infinite stack of guanine molecules.

By broadening the eigen energies calculated for single molecules with Gaussian functions, the density of occupied states (DOOS) displayed in Fig.3 is derived. The calculated curves compare very well to the measured VB PES after a shift towards higher binding energies is introduced. The full width at half maximum (FWHM) of the broadening functions is chosen to match the VB PES. It varies from *0.9eV* in the case of the adenine layers to *1.3eV* for cytosine and is considerably larger than the estimated overall experimental resolution of *0.07eV.* The experimentally observed FWHM is considerably larger than that observed in the case of molecules in the gas phase [8]. The broadening due to inelastic electron scattering should be very similar for all three investigated DNA bases and

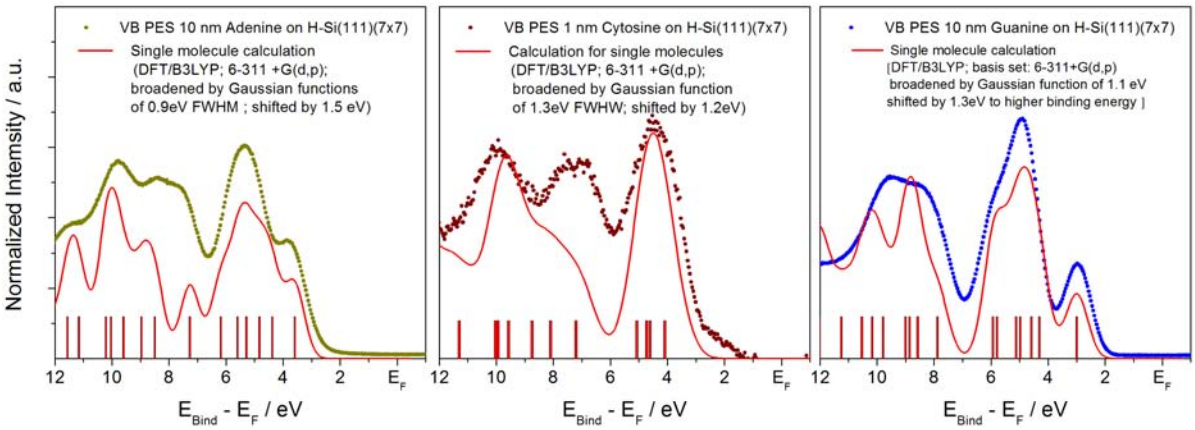


**Fig.3:** Comparison of the measured VB PES of 10nm thick layers of the DNA base on H-Si(111)(7x7) with the calculated DOOS (DFT/B3LYP; basis set: 6-311+G(d,p)). The molecular ground state eigen energies were broadened by Gaussian functions and shifted towards higher binding energies to fit the experimental data.

therefore one can conclude, that there is an additional, significant contribution to the broadening at least in the cases of cytosine and guanine. A possible broadening mechanism is the overlap of the molecular valence orbitals which could lead to delocalized, Bloch-type orbitals along the stacking direction and band-like behavior or at least to the lifting of the degeneration of the eigen energies of the molecular orbitals of neighboring molecules as proposed by Calzolari, Felice, and Molinari [9]. Since both possibilities would lead to the observed broadening and the spacing between the multiplet lines (0.02eV) described by Calzolari, Felice, and Molinari is smaller than $k_B T$ and well below our experimental resolution, we can not distinguish between the two. Yet an overlap in the valence orbitals that causes either of them, is in very good agreement with the above conclusion of strong molecular interaction.

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