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Invited Lecture

Investigation of bio-organic/inorganic semiconductor interfaces

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Layers of the DNA bases adenine, cytosine, and guanine of 1 nm and 10 nm thickness were deposited onto hydrogen passivated Si(111)7x7 surfaces. Valence band photoemission spectra (VB PES) of these layers were recorded at excitation energies of 55 eV and 150 eV. The VB PES offer access to the alignment of energy levels at the interface between the DNA base layers and the Si substrates. Additionally, quantitative conclusions about the structural properties (i.e. the growth mode) can be drawn. The average tilt angle of the DNA base molecules with respect to the substrate surface were determined by angular depended near edge x-ray absorption fine structure (NEXAFS) spectroscopy.

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1. Introduction

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 [2-5]. One important factor for transport properties and device performance is the electronic structure (i.e. the density of states) of the DNA bases. A number of theoretical calculations on the electronic properties of the DNA bases was published in the last decade [6-9]. The results of these calculations, however, are highly contradictory and there is little to none experimental data on this matter. Therefore a systematic photoelectron spectroscopy study of thin DNA base films was required. Due to the strong anisotropy of the transport properties of molecular crystals, a second, very important factor for the performance of possible devices is the orientation of the molecules. A technique that has been most successful in the determination of the orientation of molecules on different substrates is the angular depended NEXAFS spectroscopy.

2. Experimental details

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 station is equipped with a Phoibos150 electron analyzer (SPECS GmBH) and consists of two main chambers for analysis and *in situ* sample preparation. The Si(111) substrates (n-type, resistivity 7.5 Ωcm) were annealed under ultra high vacuum conditions (base pressure $\leq 3\times10^{-10}$mbar) by direct current (DC) 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. The samples were then allowed to cool down slowly in order to preserve the 7x7 reconstruction. The quality of the surfaces prepared by this method is illustrated in the STM image displayed in Fig. 1. a). The corresponding Si2p core level photoemission spectrum (CL PES) is displayed in Fig. 1. c). The individual components which were used to fit the 2p CL of the Si(111) 7×7 surfaces correspond very well to literature data [10,11] and are described in the Fig. 1. b) by the Dimer Atom Stacking Fault model [12]. Next to the bulk component (B) the most important surface contributions are assigned to the adatoms (A), the restatoms (R), the Si atoms that compose the underlying pedestal (P), and the dimer atoms (D). The CL PES data were fitted using a Levenberg-Marquardt nonlinear least square optimization algorithm. In order to avoid a strong chemical interaction between the substrate and the organic molecules the surface was passivated *in situ* by exposure to (2.0±0.5) Langmuir atomic hydrogen. STM studies proved that such a dose is sufficient to passivate the dangling bonds and preserve the surface quality (e.g no roughening of the surface). The passivation of the dangling bonds can be observed in the Si2p CL PES spectra after the hydrogen exposure (right side of the Fig. 1.b), where the contribution of the adatoms (A) and the restatoms (R) is attenuated. At the same time the relative intensity and the full width at half maximum of the pedestal component (P) increases. This suggests that after passivation more atoms with similar chemical environment will contribute to this component.

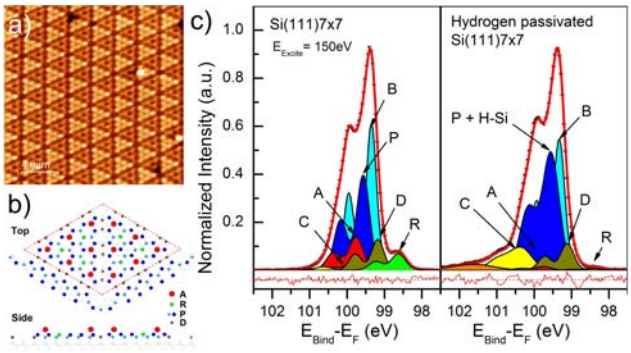

Fig. 1. a) STM immage of the Si(111) substrate after DC flush heating (Sample bias -2.0V Set point current: 1.8nA) b) Dimer Atom Stacking Fault model of the Si(111)7x7 unit cell [12] with A = Adatoms; R = Restatoms; D = Dimer atoms; and P = Pedestal atoms c) Si2p CL PES of the Si(111)7x7 surface before (left) and after (right) in situ hydrogen passivation both taken at E_{excite} = 150 eV.

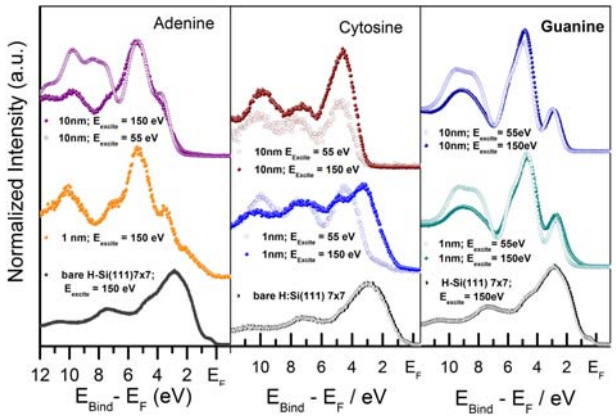

Fig. 2. VB PES of adenine (left), cytosine (middle), and guanine (right) layers on H:Si(111)7×7.

The DNA base layers were deposited onto the H:Si(111)7×7 surface by organic molecular beam deposition. The nominal layer thickness was monitored by a quartz microbalance. The VB PES of layers of the DNA bases adenine, cytosine, and guanine were recorded for different thicknesses (1 nm – 10 nm) using selected excitation energies of 55 eV and 150 eV. The NEXAFS measurements were performed by sweeping the excitation energy between 280 eV and 320 eV and recording electrons having a selected kinetic energy of 10eV.

3. Results and discussion

VB PES:

The VB PE spectra for two different thicknesses (i.e. 1nm and 10 nm) of the three DNA base layers (i.e. adenine, cytosine, guanine) are displayed in Fig. 2. For the 10nm thick cytosine layer no significant difference in the VB PES can be observed upon changing the excitation energy from most surface sensitive conditions (55eV) to less surface sensitive conditions (150eV). In the case of the other two bases (i.e. adenine and guanine) an analogous change in the excitation energy leads to a significant change in the region between 8eV -12eV while the highest occupied molecular orbitals (HOMO's) remain unchanged. This is different in the case of the VB PES of the thinner layers. Especially in the case of cytosine a pronounced difference in the VB PES can be observed for the HOMO region of the spectrum. This behavior can be explained with a Stranski-Krastanow like growth of cytosine on the silicon substrate, where the molecules adapt a columnar growth after the completion of the first mono layer. The strong contribution of the substrate signal at the less surface sensitive excitation energy (150eV) then originates from areas of thinner coverage. At 55eV the inelastic mean free path (IMFP) of the photoelectrons is too small (4Å - 5Å) to allow for a significant substrate contribution. At larger layer thickness, the columns percolate and the substrate signal vanishes also in the VB PES spectra taken with 150eV. In the case of guanine the effect of changing the excitation energy is much smaller. At 150 eV the contribution of the substrate only leads to a slight broadening of the HOMO feature in the VB PES of the 1 nm thick layer. This suggests that the guanine film is much denser in comparison to the other two DNA bases and that at the initial stages the film grows in a layer by layer fashion.

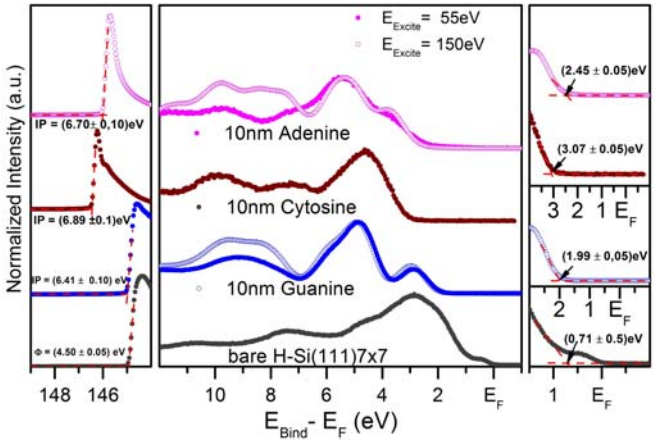

Fig. 3. VB PES of the DNA base layers of 10nm thickness. The panels to the left and the right show how the vacuum level cut-off (left) and the HOMO position (right) are determined by the interception between the linear extrapolations of the background and the edges of the spectrum.

The difference that can be observed between the VB PES of the adenine layers of 1nm and 10nm nominal thickness are also related to a significant contribution of the substrate to the spectrum of the thinner layer. A simple subtraction of the substrate signal multiplied by a scaling factor from the VB PES of the thin film leads to a very good reproduction of the spectrum of the 10 nm thick layer. Following the above argumentation for cytosine, this suggest a Stranski-Krastanow like growth of the adenine layers on the H:Si(111)7×7 substrates.

The energetic position of the highest occupied

molecular orbital (HOMO) was determined from the interception of the linear extrapolations of the background and the low energy edge of the VB PES. In combination with the position of the low kinetic energy cut-off at the vacuum level, the width of the spectra can be determined (see Fig. 3). The ionization potential (IP) of adenine, cytosine, and guanine films was obtained by subtracting the width of the VB PES from the excitation energy. The energy level alignment between the substrate and the DNA base layers is summarized in Fig. 4. The indicated positions of the lowest unoccupied molecular orbitals (LUMOs) were derived by adding the values for the optical gaps (previously published in [13]) to the HOMO positions. These values therefore represent a lower energetic limit to the LUMO. Generally, the the optical excitation of molecules leads to the formation of strongly bound Frenkel-excitons. This leads to a lower energy gap determined by optical absorption (or optical gap) with respect to the band gap measured for example by the combination of PES and inverse PES [14]. The energy level diagrams in Fig. 4 nicely illustrate the formation of interface dipoles in the case of the adenine (0.3eV ± 0.1eV) and cytosine (1.0eV ± 0.1eV) layers on H:Si(111)7x7.

The IPs for bulk-like, thick DNA base layers are summarized in Table 1. The experimentally determined IPs are significantly smaller than the values calculated by Preuss *et al.* for single molecules in [9], using a ΔSFC ansatz. They are in fact much closer to the eigen energies of the HOMOs calculated for the singe molecules in the ground state (DFT/B3LYP functionals, 6-311G+(d,p) basis set [15]). This suggests a strong influence of the surrounding matrix on the measured final state. This is supported by the DFT/B3LYP calculation of the ionization potential of an infinite stack of guanine molecules published by Prat *et al.* in [7], which takes the interaction of neighboring molecules into account. It fits the measured data remarkably well.

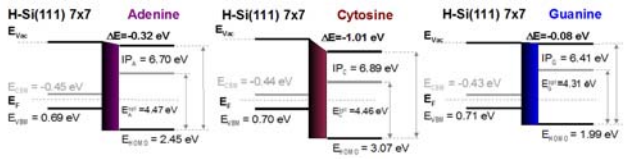

Fig. 4. Energy level alignment at the interface between adenine (left), cytosine (middle), and guanine (right) layers and the Si(111)7×7 substrates.

By broadening the eigenenergies calculated for single molecules with Gaussian functions, the density of occupied states (DOOS) displayed in Fig. 5 is obtained. 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. The experimentally observed FWHM is considerably larger than that observed in the case of molecules in the gas phase [16].

Table 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 ΔSCF 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.

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

4. Near edge X-ray absorption spectroscopy

The carbon K-edge NEXAFS spectra of adenine, cytosine, and guanine layers were recorded by sweeping the excitation energy from 280 eV up to 320 eV. The angle of incidence, Θ, between the incident light and the sample surface was varied between 22° and 115°. The measured data were corrected for the photon flux by division of the spectra to the electron yield of the clean H-Si(111)7x7 sample and to the synchrotron ring current. Afterwards, a constant background was subtracted and the spectra were normalized to the absorption step edge at 320 eV.

Fig. 6 shows the carbon K-edge NEXAFS spectra of the 10nm thick adenine, cytosine and guanine layers as a function of the angle of incidence. The solid lines in the graphs are fits to the measured data. Voigt functions were used to reproduce the π*-resonance peaks at low excitation energies. The vacuum step edge was modeled by an error function (i.e. a convolution of a Gaussian and a step function). For the σ*-transitions at higher excitation energies Gaussian functions were introduced. Fig. 6 shows the carbon K-edge NEXAFS spectra of the 10 nm thick adenine, cytosine and guanine layers as a function of the angle of incidence. The solid lines in the graphs are fits to the measured data. Voigt functions were used to reproduce the π*-resonance peaks at low excitation energies. The vacuum step edge was modeled by an error function (i.e. a convolution of a Gaussian and a step function). For the σ*-transitions at higher excitation energies Gaussian functions were introduced.

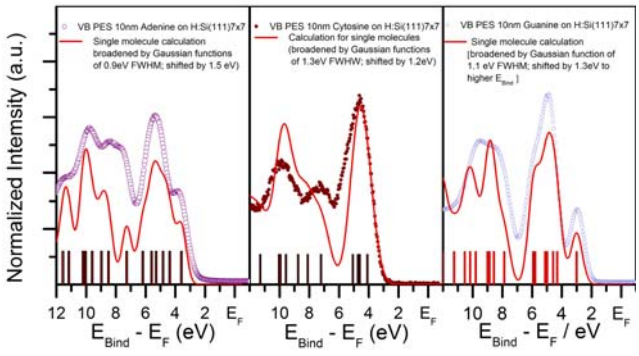

Fig. 5. Comparison of the measured VB PES of 10nm thick layers of the DNA base on H-Si(111)(7x7) with the calculated DOOS (DFT/B3LYP; basis set: 6-311+G(d,p)). The molecular ground state eigen energies were broadened by Gaussian functions and shifted towards higher binding energies to fit the experimental data.

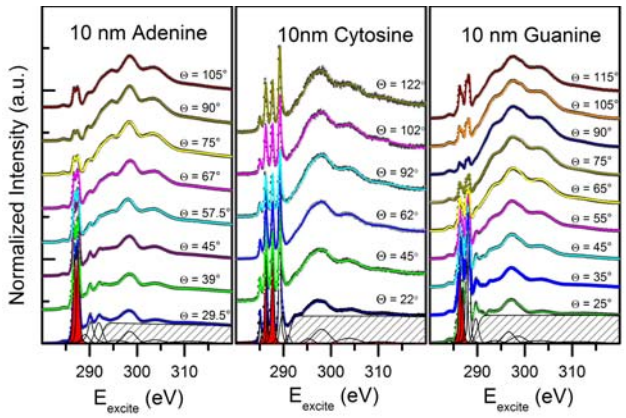

Fig. 6. Carbon K-edge NEXAFS spectra of 10nm of adenine (left), cytosine (middle), and guanine (right) on H:Si(111)7x7 as a function of the angle of incidence Θ. For the fits to the measurements at grazing incidence the individual components are displayed.

At first the fits were performed for the measurements at an incidence angle of 45°. The obtained peak positions and the values for the FWHM were kept constant and only the intensities were varied to fit the experimental data recorded at the remaining incidence angles. The individual contributions are displayed exemplary for the measurements at grazing incidence in Fig. 6.

The areas of the π*-transition peaks which are marked with the solid filling in figure 6 were used to determine the molecular orientation of the DNA bases. Because of the spherical symmetry of the initial state (a 1s orbital), the transition dipole moments of the π*-resonances are oriented parallel to the final state π*-orbitals. These are oriented perpendicular to the molecular plane [17]. In this case, the dependence of the resonance intensity on the angle of incidence, under the condition of threefold (or higher) substrate symmetry, is given by [17]:

$$I = C\,[P\,(\cos^2\Theta\cos^2\alpha + \tfrac{1}{2}\cdot\sin^2\Theta\sin^2\alpha) + (1\text{-}P)/2\,\sin^2\alpha] \quad (1)$$

where P is the degree of polarization and C a normalization factor. Θ is the angle of incidence and α the angle between the transition dipole moments and the surface normal (or the molecular tilt angle). The angle Θ and the polarization factor are known quantities, which only leaves the molecular orientation and the normalization constant C unknown. These parameters can be determined by curve fitting the above equation to the relative intensities of the π*-resonances in the NEXAFS spectra of adenine, cytosine and guanine. The fitted curves are presented in Fig. 7.

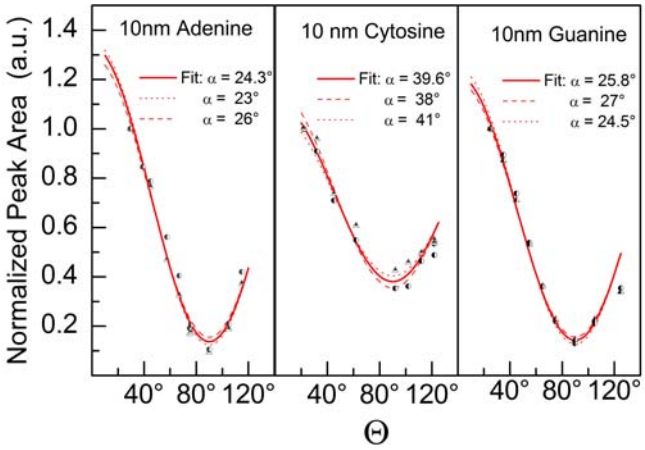

Fig. 7. The dependence on the incidence angle (Θ) of selected π-transition peaks in the NEXAFS spectra of adenine (left), cytosine (middle) and guanine (right). The solid lines By variation of α and C to optimize the match between measurement and equation (1) the average molecular orientation of each DNA base is obtained.*

The average molecular tilt angles of the DNA base molecules with respect to the substrate surface are determined to be:

$\alpha_A = (24°\pm3°)$; $\alpha_c = (40.5°\pm1.5°)$; $\alpha_G = (25.8°\pm1.3°)$

5. Summary

The interfaces between H-passivated Si(111)7x7 surfaces and layers of the DNA bases adenine, cytosine, and guanine were investigated by valence band photoemission and near edge x-ray absorption spectroscopy. The analysis of the VB PES showed that adenine and cytosine layers grow in islands on the substrate while guanine grows either layer by layer or in very close pact crystallites. By a extrapolation of the edges of the VB PES to the background the alignment of the energy levels at the interfaces was determined. Interface dipoles are observed in the case of adenine and cytosine layers on H:Si(111)7×7, whereas the vacuum levels of the guanine layer the substrate align. The orientation of the

molecules with respect to the substrate surface was determined from the angular dependence of the π*-resonances in the NEXAFS spectra.

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