The Molecular Orientation of DNA Bases on H-passivated Si(111)(7x7) investigated by means of Near Edge X-ray Absorption Spectroscopy

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In recent years DNA bases have been discussed as promising candidates for electronic applications, such as (bio-)organic field effect transistors [1] or molecular nano-wires [2]. The strong anisotropy of charge transport within molecular crystals makes the knowledge of the molecular orientation of the DNA bases crucial for any device design. We therefore performed a systematic Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy study of layers of the DNA bases adenine, cytosine and guanine on H-passivated Si(111). The measurements were performed using the Multi User Stage for Angular Resolved Photoemission (MUSTANG) experimental station at the Russian German beam line at BESSY.

Experiment: The substrates were cut from a n-type, highly phosphor doped (resistivity 7.5 Ω/cm) silicon(111) wafer supplied by *SilChem GmbH*. The samples were annealed by direct current (DC) heating under ultra high vacuum (UHV) conditions (base pressure $\leq 3 \cdot 10^{-10}$ mbar) up to 750°C-800°C. The natural oxide was removed by several DC flushes of 20s duration up to 1100°C-1300°C. The substrates were then cooled down slowly to preserve the (7x7) reconstruction. In order to prevent a reaction of the DNA bases with the substrate, the surface was passivated *in situ* by exposure to (2.0±0.5) Langmuir atomic hydrogen. The dosis was chosen carefully and should be just enough to saturate the dangling bonds of the Si(111)(7x7) without etching the surface. This method of passivation leads to considerably lower surface roughness than achieved by a wet-chemical cleaning and passivation treatment of Si(111). The DNA base layers were deposited by organic molecular beam deposition (OMBD). The nominal layer thickness was monitored by a quartz micro balance.

The (NEXAFS) spectra were recorded in the partial electron yield mode in the region of the secondary electron background (at a kinetic energy of 10eV). The angle of incidence, Θ, between the incident light and the sample surface was varied between of 22°-115°. The measured data were corrected for the photon flux by division of the spectra by the electron yield of the clean H-Si(111)(7x7)
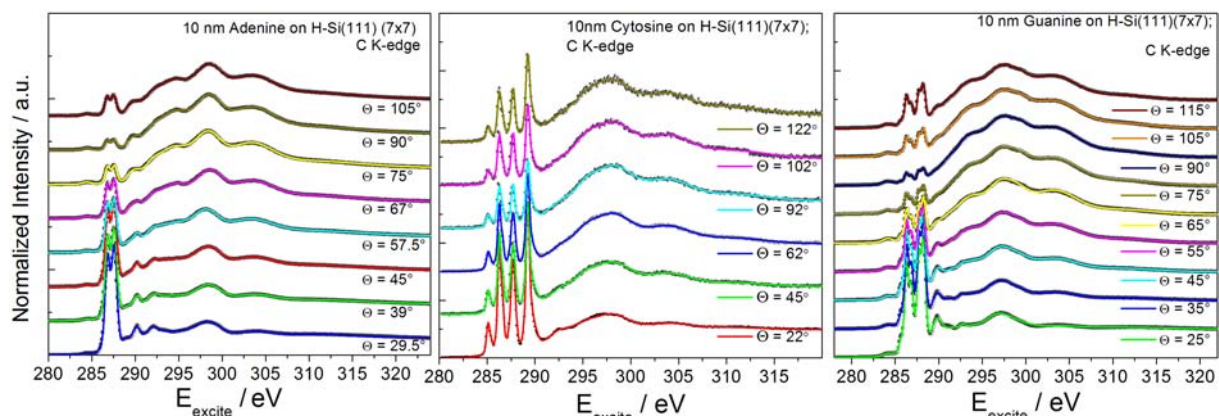

Fig.1: The carbon K-edge NEXAFS spectra of a 10nm adenine (left) cytosine (midle) and guanine (right) on H-Si(111)(7x7) as a function of the angle of incidence, Θ.

sample and the synchrotron ring current, the background was subtracted and the spectra were normalized to the absorption step edge at *320eV*. The angular dependent carbon K-edge NEXAFS spectra of 10nm thick layers of adenine, cytosine and guanine on H-Si(111)(7x7) are shown in Fig.1.

Peak assignment: The prominent features at the low excitation energies correspond to transitions from the carbon 1s core levels into the lowest unoccupied molecular orbitals (LUMO, LUMO+1 ...). The validity of this assignment can be checked by comparison the measured spectra with theoretical calculations employing density functional theory (DFT) for the single DNA base molecules (B3LYP functionals; 6-311G+(d,p) basis sets). For these calculations the commercial software package GAUSSIAN03 [3] was used. The contribution of different excitation sites (i.e. the carbon atoms) are treated separately. In molecules as small as the DNA bases the core hole created at the excitation site has a strong impact on the molecular orbitals and has to be considered in the calculation. This is done by the introduction of an extra charge to the core of the excited atom by replacing it with its Z+1 equivalent (i.e. nitrogen). The DFT calculation is then performed for the positively charged molecule, in order to keep the number of electrons constant. Afterwards, the calculated unoccupied molecular orbitals are decomposed into the contributing atomic orbitals[*]. The contribution of a single carbon atom to the π^*-resonances in the NEXAFS spectrum is mainly contained in the contribution of its antibonding $2p_z$ atomic orbital (were the z-axis is perpendicular to the molecular plane) to the unoccupied molecular orbitals. The excitation energy necessary for a transition into these states is calculated by subtracting the 1s core level binding energy of the particular carbon atom (measured by core level photoemission spectroscopy) from the calculated eigen energies. The contributions of all the carbon atoms within the molecule are averaged and broadened with Voigt functions of 0.3eV FWHM. In Fig.2 the calculated curves are compareed to the measured spectra. For adenine and cytosine, the Z+1 apporoach leads to very good agreement between the simulation and the measurement. The resemblance is not as good in the case of guanine, but still the π^*-nature of the peaks at the lowest excitation energies becomes obvious. The relatively large shift, which had to be introduced, to match the peaks with the highest intensities is due to the fact, that the extra positive charge on the molecule is overestimating the core hole effect on the molecular orbitals.
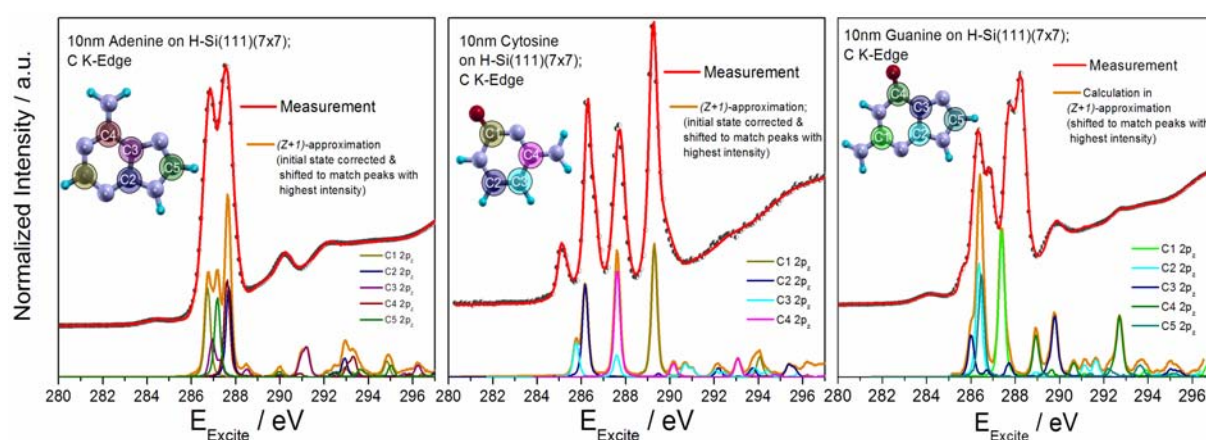

Fig.2: In the Z+1 approximation the DFT calculations are performed after substitution of a carbon (Z=6) atom by a nitrogen (Z=7) atom. The spectra are derived by assuming vertical transition between the atomic 1s and $2p_z$ orbitals. The spectra were shifted by ΔE_C = 4.36eV, ΔE_A = 2.86eV and ΔE_g = 2.54eV towards higher excitation energies.

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[*] The atomic orbitals were calculated from the Gaussian'03 output, using the AOMix program [5,6], which employs a Mulliken population analysis
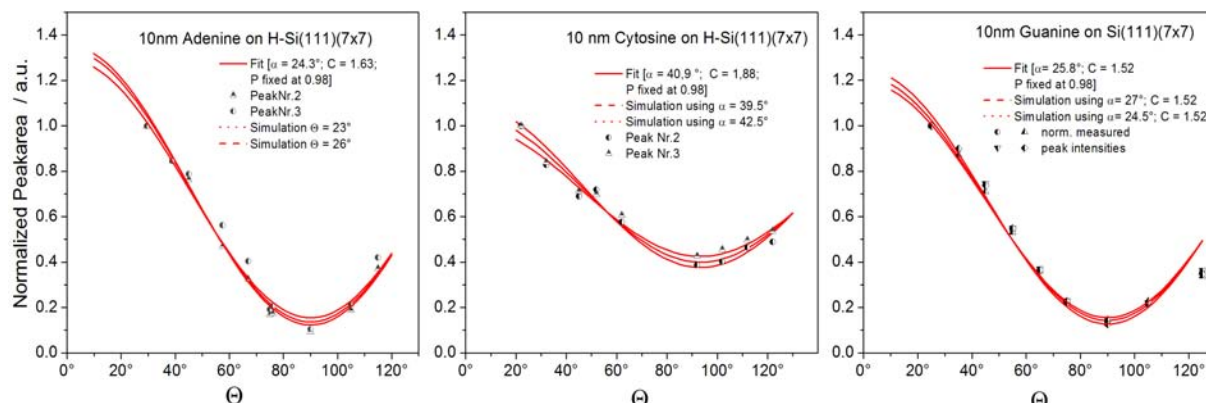
Fig.3: The dependence on the incidence angle (Θ) of selected π*-transition peaks in the NEXAFS spectra of adenine (left), cytosine (middle) and guanine (right). By variation of α and C to optimize the match between measurement and equation (1) the molecular orientation of each DNA base is obtained.

Molecular orientation: For the quantitative analysis of the angular dependence of the NEXAFS spectra at first the π*-transition peaks were fitted using Voigt functions. Because of the spherical symmetry of the initial state (a 1s orbital), the transition dipole moments of these resonances are oriented parallel to the final state, π*-orbitals, which are oriented perpendicular to the molecular plane. 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 [7]

$$I = C[P(\cos^2\Theta\cos^2\alpha + \frac{1}{2}\sin^2\Theta\sin^2\alpha) + \frac{(1-P)}{2}\sin^2\alpha] \qquad (1)$$

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

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

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