Molecular Interactions in Organic Ultra Thin films Studied by VUV Spectroscopic Ellipsometry

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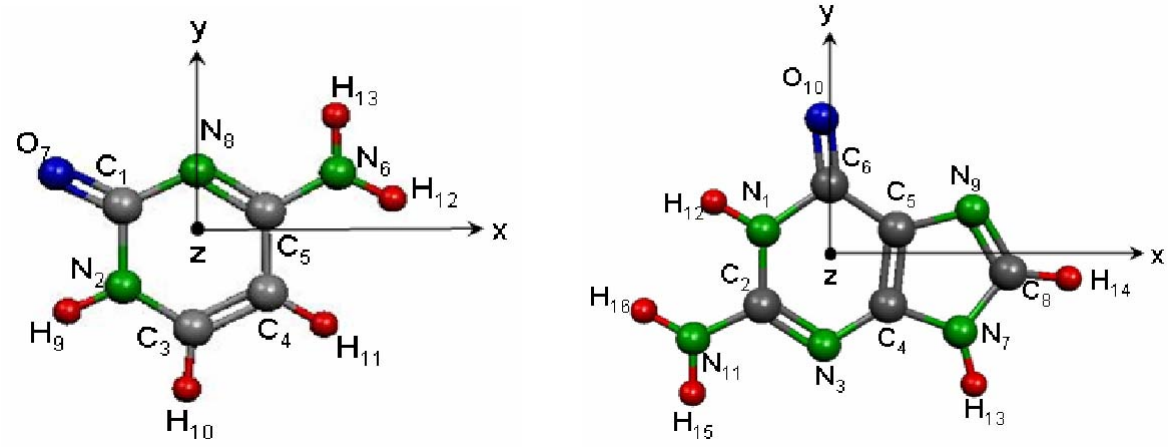
The ellipsometric studies at BESSY makes it possible to investigate the electronic transitions of organic layers in the Vacuum Ultra Violet (VUV) range. Especially for small molecules, like DNA base molecules which have the HOMO-LUMO transitions at energies higher than 4 eV [1], the access to the VUV range is essential. While the synchrotron radiation extends the range beyond the capabilities of commercial ellipsometers, we proved that the lower wavelength of the light allows the dielectric function of ultra-thin organic films to be investigated on the sub-nanometer scale [2]. Therefore in this work we report the changes in the Vacuum Ultra Violet (VUV) spectra upon increasing thickness for two DNA base molecules: cytosine and guanine. The molecular structure of these two molecules is presented in figure 1.



cytosine guanine

Figure 1. Molecular structures of cytosine (left) and guanine (right) projected in the (x, y) plane with z perpendicular on the molecular plane

Vacuum Ultra Violet (VUV) Spectroscopic Ellipsometry (SE) measurements were performed *in situ* for optical characterization of ultra-thin films of cytosine and guanine. The layers were prepared by organic molecular beam deposition (OMBD) on hydrogen passivated silicon H-Si(111). The measurements were performed at BESSY at the 3m-NIM 1A beam line using a rotating-analyser ellipsometer operating in the 4-9.5 eV range with an energy step of 0.025 eV. MgF_2 Rochon prisms were used as polarizers (for details see [3-5]).

Figure 2 shows the imaginary part of the measured effective dielectric function $\langle\varepsilon_2\rangle$ for H-Si(111) and for a 0.35 nm cytosine layer on H-Si(111). As can be seen in figure 2 clear changes in the ellipsometric data can be observed even for this coverage. While interpreting the ellipsometry data for very thin overlayers on a substrate (less than 10 nm) is rather difficult, the access to the VUV at BESSY makes it possible to achieve a higher separation in the experimental Δ values even for very small

changes in the refractive index [6]. In this case the dielectric function of the overlayer can be extracted using a first order approximation [6].

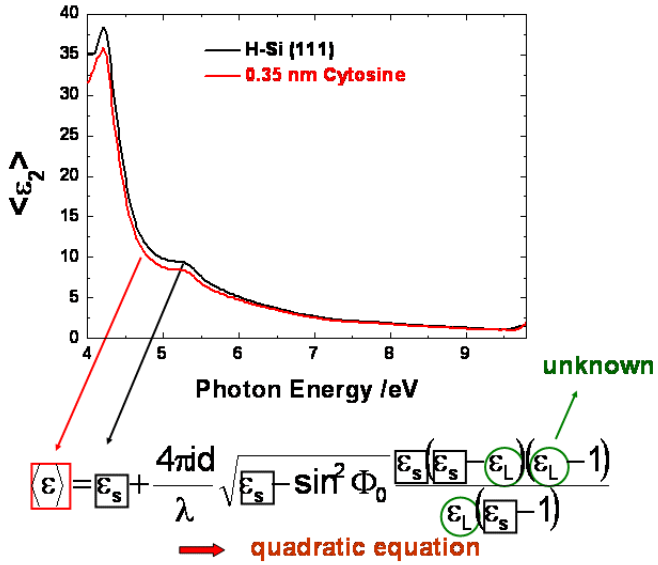


Figure 2. The measured effective $<\varepsilon_2>$ of the 0.35 cytosine sample compared with the $<\varepsilon_2>$ of the H-Si(111) substrate.

According to Aspnes [6], the measured effective dielectric function $<\varepsilon>$ can be approximated by the formula presented above. As ε_s is the measured dielectric function of the substrate and d is the layer thickness, the quadratic equation can be easily solved to find the dielectric function of the layer ε_L. The solution of the above equation for the 0.35 cytosine layer is presented on the left side of figure 3.

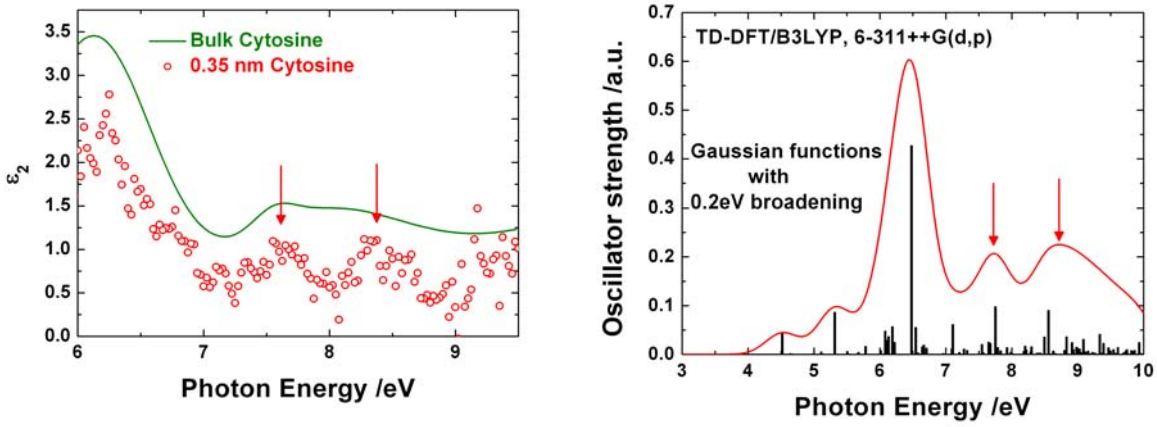


Figure 3. Left - Comparison between the imaginary part of the dielectric functions of the bulk cytosine and 0.35 nm cytosine layer. Right - TD-DFT calculation of the excited states for a single cytosine molecule.

For comparison the imaginary part of the dielectric function of the ultra-thin layer is plotted together with the imaginary part of the dielectric function of bulk cytosine. A detailed description of the experimental conditions and the ellipsometric model used to determine the bulk values can be found in ref. [7, 8]. While in the low energy range (below 7 eV) the dielectric function of the ultra-thin layer has similar shape like the bulk one, in the high energy range a clear splitting at the positions indicated by

arrows can be observed. The splitting can be attributed to the reduced intermolecular interactions between the cytosine molecules in the overlayer. This hypothesis is supported by theoretical calculations [8] of the excited states using time dependent density functional theory (TD-DFT). The computation was performed for an isolated molecule using Gaussian software [9]. The convolution of the excited states using Gaussian functions with 0.2 eV broadening is plotted on the right side of figure 3.

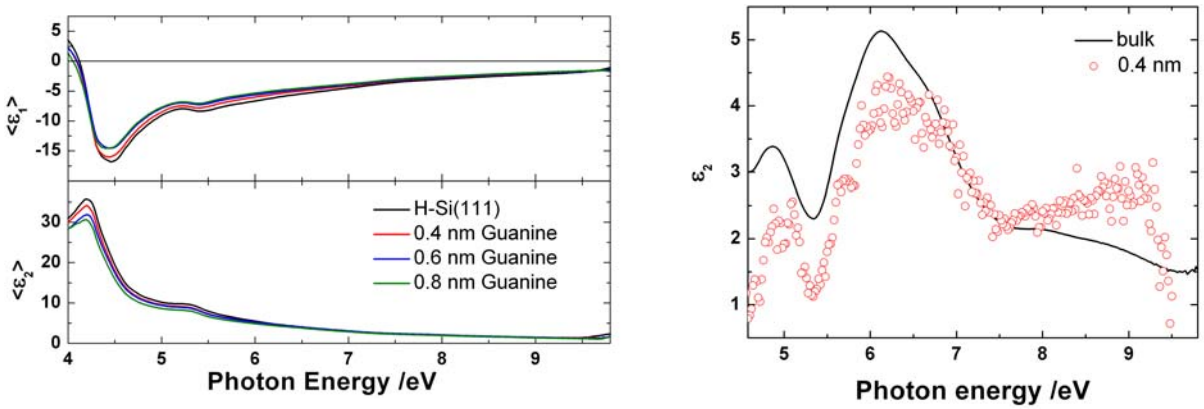


Figure 4. Left – the measured effective dielectric function of H-Si(111) and guanine layers of 0.4, 0.6 and 0.8 nm. Right - Comparison between the dielectric functions of bulk guanine and 0.4 nm guanine layer.

A similar study was performed for guanine layers. The solution of Aspnes formula presented in the right part of figure 4 yields in this case a dielectric function of a 0.4 nm guanine layer very similar to the bulk one. This is probably related to an island growth mode of the guanine.

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