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Research Paper

Dielectric Response of Ultra-Thin Multilayer of Guanine and Cytosine DNA Bases

J SINDU[1], D LEHMANN[1], S SILAGHI[2], C COBET[2], N ESSER[2], M G V SANKARACHARYULU[3] M FRIEDRICH[1] and D R T ZAHN[1]

[1]*Chemnitz University of Technology, Semiconductor Physics, D-09107 Chemnitz, Germany*
[2]*Institute for Analytical Sciences, Department Berlin, Albert-Einstein-Str. 9, 12489 Berlin, Germany*
[3]*Arignar Anna Govt. Arts College, Karaikal 609 605, Puducherry, India*

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In recent years multilayered organic structures have attracted considerable attention. Compared to bulk materials multilayered hetero-structures can have unusual optical and physical properties which open new possibilities for optoelectronic devices. It is well known that a guanine and cytosine rich DNA molecule shows p type properties. It is thus interesting to study the optical response of multilayers of very thin layers of guanine ($C_5H_5N_5O$) and cytosine ($C_4H_5N_3O$) molecules. Multilayered hetero-structures of guanine and cytosine of six periods were prepared by organic molecular beam deposition under ultra high vacuum on ZnO (0001) substrates. Spectroscopic ellipsometry measurements were carried out *in situ* using a Variable Angle Spectroscopic Ellipsometer (VASE) in the NIR-Vis-UV range from 0.73 eV to 5 eV and the Vacuum Ultra Violet (VUV) Spectroscopic Ellipsometer in the range from 4 eV to 9 eV using synchrotron radiation at BESSY II, Berlin. Thicknesses and the offsets are determined from the low energy measurements and these are used as starting parameters to determine the dielectric function of the multilayers in the high energy range, where these DNA bases show strong absorption. It is observed that the line shape of the effective dielectric function is strongly dependent on the starting layer, either cytosine or guanine. This shows the possible existence of template effect. Guanine lay flat on ZnO whereas cytosine makes a large angle with respect to the substrate. This affects the orientation of the molecules grown on them thereby giving rise to different dielectric responses.

Key Words: Multilayers; Heterostructure; Guanine; Cytosine; Dielectric Functions

Introduction

The use of more complex structures than just an organic thin film on a substrate is needed in electronic applications of organic materials. Several organic layers of different materials are used in applications as OLEDs or solar cells where basically a p-n junction allows the effective transport of electrons and holes towards or away from the organic-organic interface. Compared to the individual bulk materials, multilayered heterostructures have unusual optical and physical properties. Construction of such heterostructures involves many organic-organic interfaces. The interface can influence the molecular orientation and the electronic transitions and thus change the optical properties of the multilayered heterostructures. The study of such interfaces is of interest in the technology of organic electronic devices.

DNA electronics is a newly developing field. Charge transport through DNA takes place through the overlapping of the π orbital of the adjacent DNA bases [1, 2], adenine (A), guanine (G), cytosine (C) and thiamine (T). In particular guanine is rich in π orbital [3,4]. G-C sequences show p type semiconducting properties whereas A-T sequence

*Author for Correspondence: E-mail: sinjai80@yahoo.co.in
[2]*ISAS-Leibniz-Institut für Analytische Wissenschaften*

shows n type properties [5]. In the present work, heterostrutures of guanine and cytosine bases are prepared. The main aim is to study the inter-molecular interaction at the interface, possible influence on the orientation of the molecules and the substrate interactions using the spectroscopic ellipsometric technique. This technique is very sensitive to the bulk as well as the surface properties.

Experimental Procedure

Thin films of guanine and cytosine and also the multilayers were grown by OMBD method on ZnO substrates. The guanine and cytosine source material with 99% purity was purchased from Aldrich Company and is used without further purification. The ZnO substrates were cleaned in acetone, iso-propanol and deionised water for 10 min in ultrasonic bath. The substrates were then immediately transferred into the deposition chamber. The ultra thin films of guanine and cytosine and their heterostructure were prepared in the UHV preparation chamber in BESSY. The base pressure was 6 x 10^{-10} mbar and during deposition, however the pressure was 1.1 x 10^{-8} mbar. The substrate was kept at room temperature while depositing the molecules. The layer thickness was monitored by a quartz crystal microbalance located in the vicinity of the substrate. The frequency shift of this microbalance is proportional to the film thickness. Throughout the deposition, the rate was maintained constant, (0.30±0.01) nm/min. *In situ* VUV-SE investigations were performed at the Berliner Elektronenspeicherring Gesellschaft für Synchrotron Strahlung m.b.H, BESSY II. The BESSY ellipsometer (Fig. 1) is also a rotating analyser type ellipsometer consisting of MgF_2 Rochon prisms as polariser and analyser, a silicon photodiode as detector and operates with synchrotron radiation as light source. The usage of synchrotron radiation in the current investigations of the DNA base films is extremely important because of the onset of the absorption for DNA molecular systems starting around 4 eV. The accessible photon energy ranges between 3 to 30 eV while the commercial ellipsometers are still limited to an operation photon energy range between 0.73 and 8.85 eV. The BESSY ellipsometer is placed in a UHV analysis chamber which is optically aligned with a 3 m normal incidence monochromator (NIM) via several mirrors. The analysis chamber is connected to a preparation chamber. The VUV-SE measurements were performed in the energy range of 4-9.5 eV under an angle of incidence of about 67.5.

The VUV Spectrososcpic Ellipsometer at BESSY II provides us means to monitor the dielectric responses of these multilayered heterostructures in the VUV range where these DNA bases show strong absorption. The smaller wavelength in the VUV region allows us to reach even sub monolayer resolution,

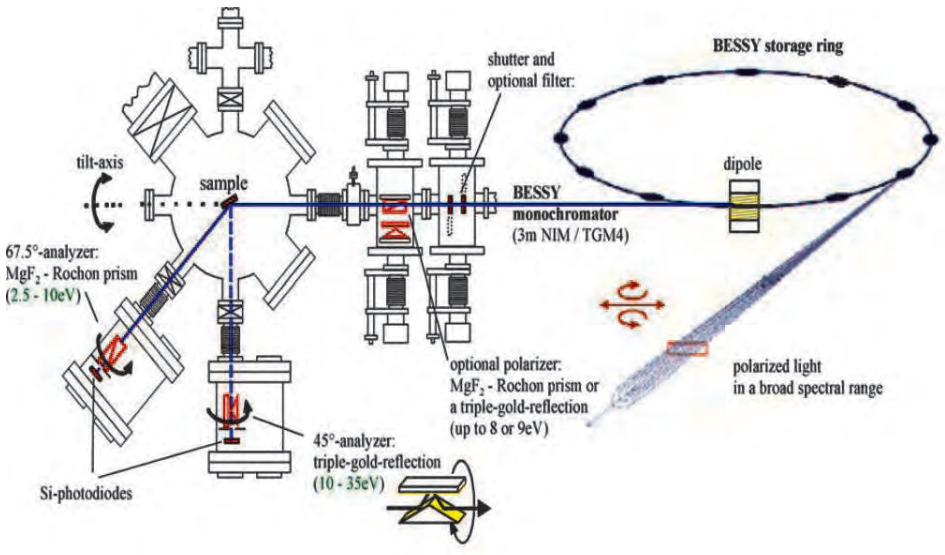

Fig. 1: VUV-XUV BESSYII ellipsometer

thereby allowing for direct inspection of intermolecular interactions.

In the ellipsometric technique, the changes in the polarization state of a polarized light beam after reflection from the sample under study are measured and expressed as the ellipsometric parameters ψ, the polarization angle and Δ, the phase delay, which are related to the ratios of Fresnel reflection coefficients r_{pp} and r_{ss} for p and s polarised light by,

$$\rho = \frac{r_{pp}}{r_{ss}} = \tan\psi \exp^{i\Delta}$$

To evaluate the spectra, a suitable model is used to describe the interaction of light with the material used. By fitting for the experimentally acquired Ψand Δ values, the best simulated spectra describing the model are obtained. The mean square error (MSE) value quantifies the differences between the experimental and simulated data.

$$MSE = \sqrt{\frac{1}{2N-M}\sum_{i=1}^{N}\left[\left(\frac{\Psi_i^{\mathrm{mod}} - \Psi_i^{\exp}}{\sigma_{\Psi,i}^{\exp}}\right)^2 + \left(\frac{\Delta_i^{\mathrm{mod}} - \Delta_i^{\exp}}{\sigma_{\Delta,i}^{\exp}}\right)^2\right]}$$

where N is the number of measured Ψ and Δ, M is the number of fit parameters and $\sigma_{\Psi i}^{\exp}$ and $\sigma_{\Delta i}^{\exp}$ the standard deviation of the experimental data points for Ψ and Δ.

Results and Discussion

The experimental data and the fit are shown for guanine bulk and cytosine bulk in Figs. 2 and 3. The thickness, roughness and dielectric functions (DF: $\langle\varepsilon\rangle = \langle\varepsilon_1\rangle + i\langle\varepsilon_2\rangle$) for thick (bulk-like) guanine and cytosine films on ZnO (0001) substrates were first determined in the UV range. A 300 nm thick guanine film revealed a low roughness of ~1 nm. Relatively higher roughness of ~2.5 nm was obtained for a 320 nm cytosine film. The determined dielectric functions of cytosine and guanine on ZnO (see Fig. 4) were in good agreement with those published before for thick films on H-Si(111) [6].

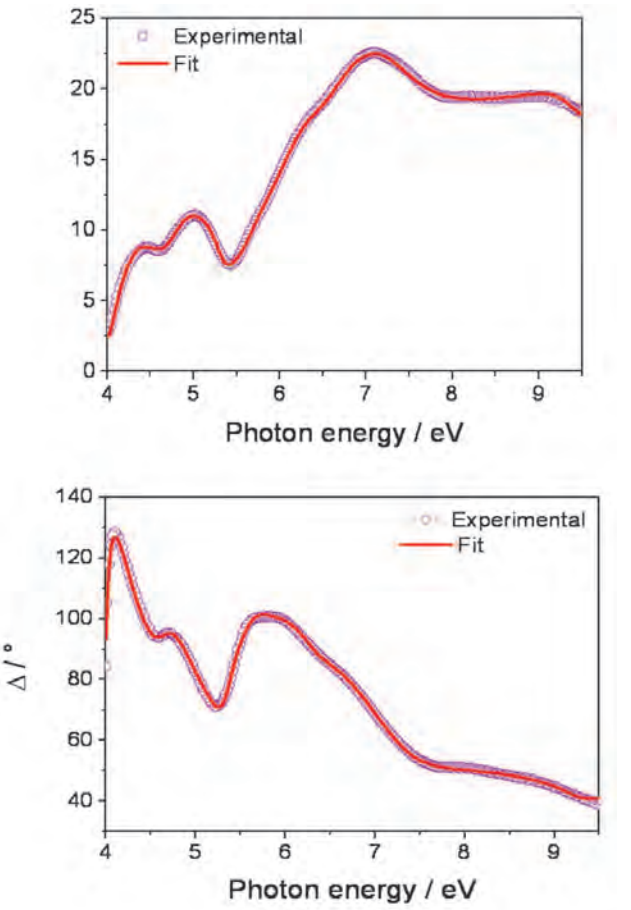

Fig. 2: Ellipsometric Ψ and Δ spectra for guanine bulk sample

The dielectric function of the uniaxial guanine film is perfectly matching, implying the average molecular orientation of guanine to be 18°±2°. Slightly higher values were observed for the isotropic dielectric function of cytosine on ZnO.

To understand the contribution of various electronic transitions in the the UV-Vis range for very thin films of guanine and cytosine the pseudo-dielectric function of these thin films were simulated using the bulk-like dielectric function obtained earlier using the WASE program. The only parameter changed during the simulation was the film thicknesses. All other parameters were kept constant. This as well implies that the orientation of the molecular plane is also fixed.

Multilayer Starting with Guanine

Fig. 5 represents the multilayered heterostructure starting with guanine. Three alternating layers of

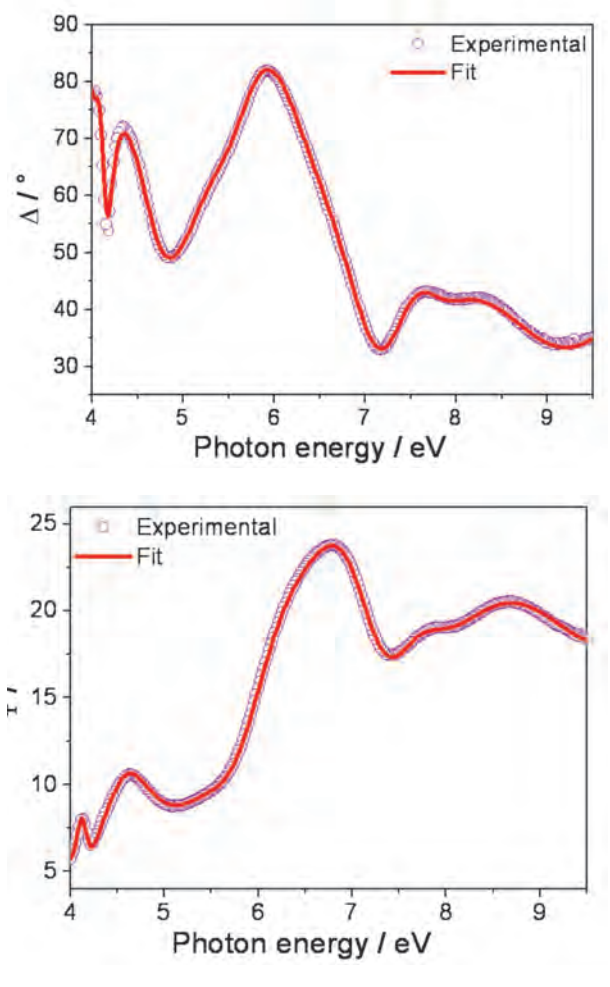

Fig. 3: Ellipsometric Ψ and Δ spectra for cytosine bulk sample

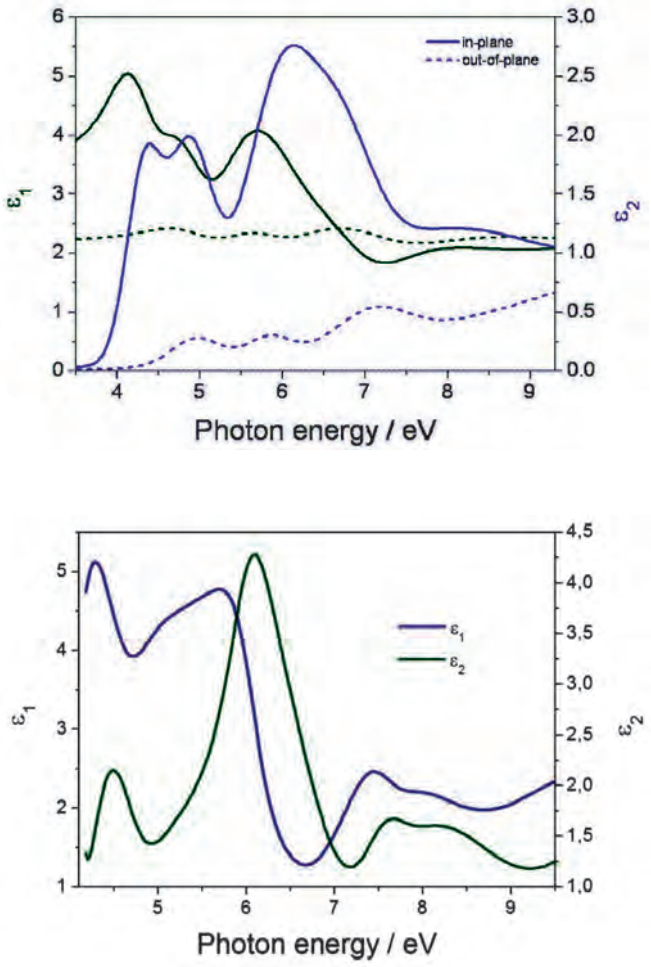

Fig. 4: Dielectric function of guanine and cytosine bulk sample

guanine and cytosine were prepared. The first two layers were ~0.3 nm each corresponding to ~1 monolayer of molecules and the next consecutive layers were 0.6 nm each. The total thickness of the heterostructure is 3 nm. The $<\varepsilon_2>$, measured (m) after each deposition and the simulated (s) $<\varepsilon_2>$ is shown in Fig. 6. The dielectric function determined from thick films was used for the simulation of these thin layers.

For the first layer of guanine, the anisotropic dielectric function was used and the simulation was perfect, implying that the guanine molecules show similar molecular orientation and anisotropy as in the bulk-like film. Upon addition of the second cytosine layer we observe some deviation in the range where cytosine has strong absorption (6.1 eV). The dielectric function of cytosine used in the simulation was the one obtained from the isotropic model and the differences in the spectra indicate that there is some ordering of the cytosine molecule over the guanine layer. The lower values of $<\varepsilon_2>$ observed in the measured spectra are an indication for a more upright orientation of cytosine molecules with respect to the substrate.

The guanine-cytosine bases are known to couple via the three hydrogen bonds between them [7]. This bonding is optimal when the molecules are paired along a straight line [8, 9, 10]. We suggest that cytosine couples with the guanine which is almost flat on the substrate trying to have its optimal position. From the first π-π* transitions in the in-plane and out-of-plane

Fig. 5: Guanine/Cytosine structure

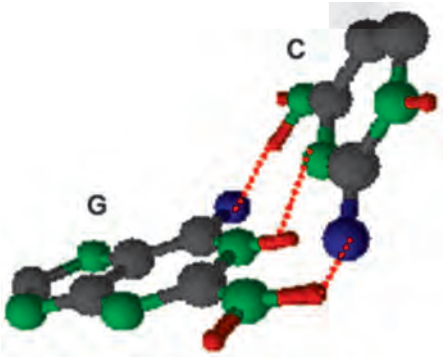

Fig. 7: Proposed positioning of G and C on ZnO

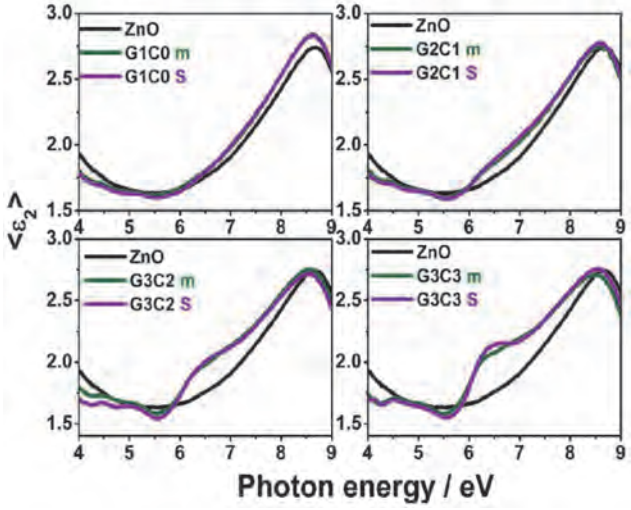

Fig. 6: Measured and simulated $\langle\varepsilon_2\rangle$ for G/C multilayer in comparison with the $\langle\varepsilon_2\rangle$ for ZnO substrate

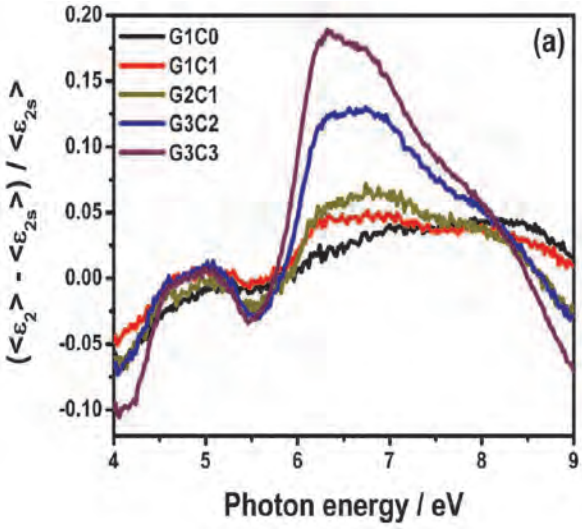

Fig. 8: Difference between $\langle\varepsilon_2\rangle$ of the thin film HS and the uncovered ZnO substrate divided by $\langle\varepsilon_2\rangle$ of the substrate G/C heterostructure

contribution to the dielectric function the molecular tilt angle of guanine is found to be ~18° ± 2°, which agrees well with the previous results [11-15]. So the cytosine is likely to grow in a fashion with a larger tilt angle with respect to the substrate trying to form straight bonds with the guanine (see Fig. 7). Above this cytosine layer again the guanine seems to have the same flat molecular orientation.

Multilayer Starting with Cytosine

Multilayered heterostructures were prepared as explained before with cytosine as the starting layer (Fig. 9). The total multilayer thickness now is 3.2 nm. The corresponding measured (m) and simulated (s) spectra are presented in Fig. 10. Even though the line shape for the simulated spectra is in good agreement with the measured spectra, we observe lower intensities at 6.4 eV (the position of cytosine absorption peak) in the measured spectra starting from the very first layer. This is a hint that the first cytosine layers tend to grow with a more upright molecular orientation on the ZnO substrate. The decrease in deviation between measured and simulated data with increasing number of layers indicates that the preferential orientation gets lost after several layers.

For the guanine layers more upright orientation of molecules would lead to a decrease in the measured data compared to the simulated data. Since this is not observed, we conclude that the molecules in the guanine layers on top of cytosine preferentially are lying flat.

In Fig. 6 the difference between the $<\varepsilon_2>$ of the thin film heterostructure and the uncovered ZnO substrate divided by the $<\varepsilon_2>$ of the substrate is presented. The relative change in the $<\varepsilon_2>$ is smaller for the guanine/cytosine, Fig. 8 compared to the cytosine/guanine heterostructure Fig. 11. This cannot be explained by the slightly higher thickness of the cytosine/guanine structure alone. The suppressed $<\varepsilon_2>$ for the guanine/cytosine heterostructre (Fig. 8) is mainly caused by the preferential upright orientation of cytosine on top of the first guanine layer which is preserved over several layers. As discussed before the ZnO substrate surface has a similar effect on the orientation of cytosine as on the guanine layer. The higher magnitude in the measured values (Fig. 11) together with the faster decreasing difference between measured and simulated values in Fig. 10 indicates that the bare substrate influence on cytosine orientation is weaker compared to the influence of the guanine layer. From the data no trend in change of guanine layer orientation with increasing layer number can be derived.

Fig. 9: Cytosine/Guanine structure

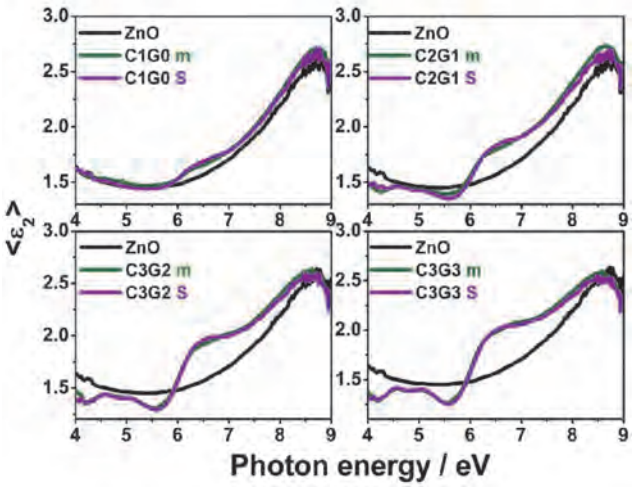

Fig. 10: Measured and simulated $<e_2>$ for C/G multilayer in comparison with the $<e_2>$ for ZnO substrate

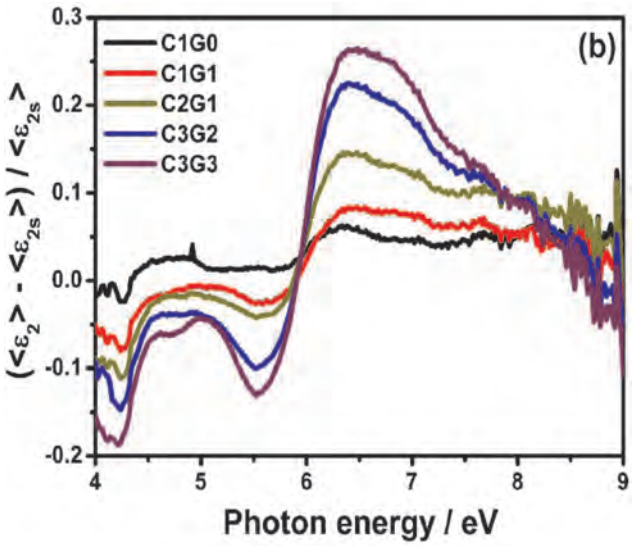

Fig. 11: Difference between $<e_2>$ of the thin film HS and the uncovered ZnO substrate divided by $<e_2>$ of the substrate C/G heterostructure

Summary

Thin layers and multilayer structures of the DNA bases guanine and cytosine on ZnO substrates were prepared by organic molecular beam deposition under ultra high vacuum conditions and measured *in situ* by means of vacuum ultraviolet spectroscopic ellipsometry at the synchrotron source BESSY. Using the dielectric function of the individual layers the optical

response of the guanine/cytosine and cytosine/guanine heterostructures are modelled. Deviations between simulated and experimental data are mainly attributed to the ordering of cytosine over guanine in the guanine/cytosine and cytosine/guanine structures and to the influence of the substrate.

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