Monitoring the Ordering in Biomolecular Films on Vicinal Silicon Surfaces by Reflectance Difference/Anisotropy Spectroscopy

Simona D. Silaghi and Dietrich R. T. Zahn

Institut für Physik, TU Chemnitz, D-09107, Germany

Abstract. DNA base molecules, adenine, thymine, guanine, and cytosine may be employed as charge transport molecules in biomolecular electronic devices. Their electronic properties are comparable with those of inorganic wide bandgap materials, *e.g.* GaN with the absorption onset in the near ultra-violet (UV) range. A recent field effect transistor study based on a modified DNA base revealed that the prototype bio-transistor gives rise to a better voltage gain compared to one based on carbon nanotubes (CNTs) [1]. Here, *in situ* reflectance difference/anisotropy spectroscopy (RDS/RAS) is employed under ultra-high vacuum (UHV) conditions for monitoring the growth of DNA base molecules on vicinal hydrogen passivated Si(111) surfaces. Such vicinal substrates consisting of steps and terraces may serves as suitable templates for molecular ordering. Indeed, RDS/RAS measurements reveal information about molecular ordering of DNA bases induced by the density of steps on silicon surfaces. All four molecules, however, behave differently on the vicinal substrates. The first transition dipole moments corresponding to adenine and thymine molecules align mainly perpendicular to the step edge direction while for guanine and cytosine they align parallel to this direction, however, only in very thin layers. The RDS/RAS signal of the guanine and cytosine layers with thicknesses above 20 nm saturates due to a loss of ordering at higher coverages. Additionally, time-resolved RDS/RAS measurements at the silicon E_2 (4.25 eV) critical point (CP) demonstrate the sensitivity to the biomolecular/inorganic interface formation.

Introduction

The adsorption of DNA base molecules particularly on semiconductor surfaces is motivated by biosensing and nanotechnology applications [2]. Their contribution as charge transport molecules in biomolecular electronic and optoelectronic devices is promising but still a challenge. An enormously important issue for future applications in nanoelectronics is the capability to fabricate well-ordered structures with characteristic dimensions of a few nanometers. Silicon can be patterned in many ways and it is thus possible to use it as a versatile template. Flat Si(111) has a 3-fold symmetry inducing the growth of three equivalent superstructure domains by symmetry but vicinal Si(111) surfaces can limit overlayer growth to a single domain. Moreover, vicinal surfaces should favour nucleation along the step edges, thus being potential substrates in controlling the ordering of molecules in so-called molecular nano-wires.

Reflectance difference/anisotropy spectroscopy (RDS/RAS) is one of the few optical techniques that can probe bulk, surfaces and interfaces of ordered materials [3-5]. It has been initially applied to semiconductor and metal surfaces [3-7], metal-semiconductor interfaces [8, 9], and recently used to investigate organic layers on various surfaces [10-18]. Here, *in situ* RDS/RAS is employed under UHV conditions for monitoring the ordering of DNA base molecules on vicinal hydrogen passivated Si(111) surfaces.

Experimental Details

Vicinal p-type (B-doped) Si (111) wafers with resistivity in the range of 1-30 Ωcm were used as substrates for the DNA base films. Double-side polished substrates off cut oriented by 3° and 6°, respectively, towards the $[\bar{1}\bar{1}2]$ direction were supplied by Silchem. Prior to biomolecular deposition, the substrates were wet-chemically hydrogen terminated [19]. The surface reconstruction (1x1) was checked by low energy electron diffraction (LEED) showing a double splitting of the diffraction points in the $[\bar{1}\bar{1}2]$ direction typical for the formation of steps and terraces. The source materials of high-purity DNA base powders purchased from Across Organics were evaporated under UHV conditions (base pressure ~ 10^{-8} Pa) from Knudsen cells. Molecules of

thymine (99%) and cytosine (99+%) were evaporated at temperatures of 365 and 410 K while adenine (99.5%) and guanine (99+%) molecules were evaporated at temperatures of 400 and 510 K.

The molecular ordering of DNA base molecules on vicinal H:Si(111) surfaces was monitored *in situ* during the organic molecular beam deposition (OMBD) growth by RDS/RAS in the energy range of 1.5-5.5 eV. RDS/RAS measures the difference in reflection for light normally incident and linearly polarized along two orthogonal directions in the sample surface. In the case of a vicinal Si(111) surface the RDS/RAS signal can be expressed as follows:

$$\frac{\Delta r}{r} = \mathrm{Re}\left(\frac{\Delta r}{r}\right) + i\,\mathrm{Im}\left(\frac{\Delta r}{r}\right) = 2\,\frac{r_{[1\bar{1}0]} - r_{[\bar{1}\bar{1}2]}}{r_{[1\bar{1}0]} + r_{[\bar{1}\bar{1}2]}} \qquad (1)$$

Results and Discussion

The anisotropy of cubic materials, *e.g.* silicon, arises at the surface due to a broken symmetry as in the case of vicinal Si(111) where the surface anisotropy is induced by the formation of steps and terraces. Such anisotropy is often referred to as surface induced optical anisotropy (SIOA) [4, 20]. The RDS/RAS signal of vicinal Si(111) surfaces is similar to the response of the Si(110) surface (see fig.1).

Figure 1: RDS/RAS spectra of various silicon surfaces.

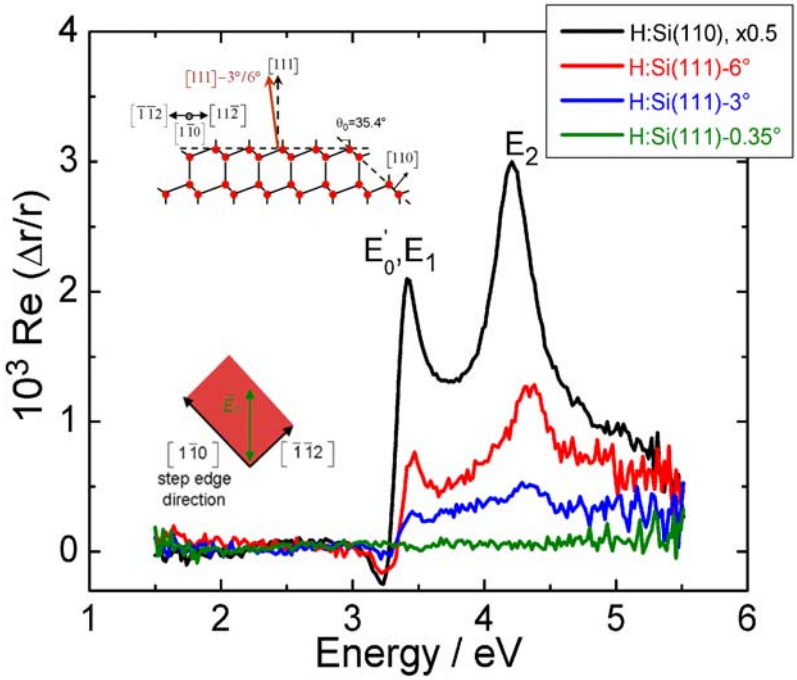
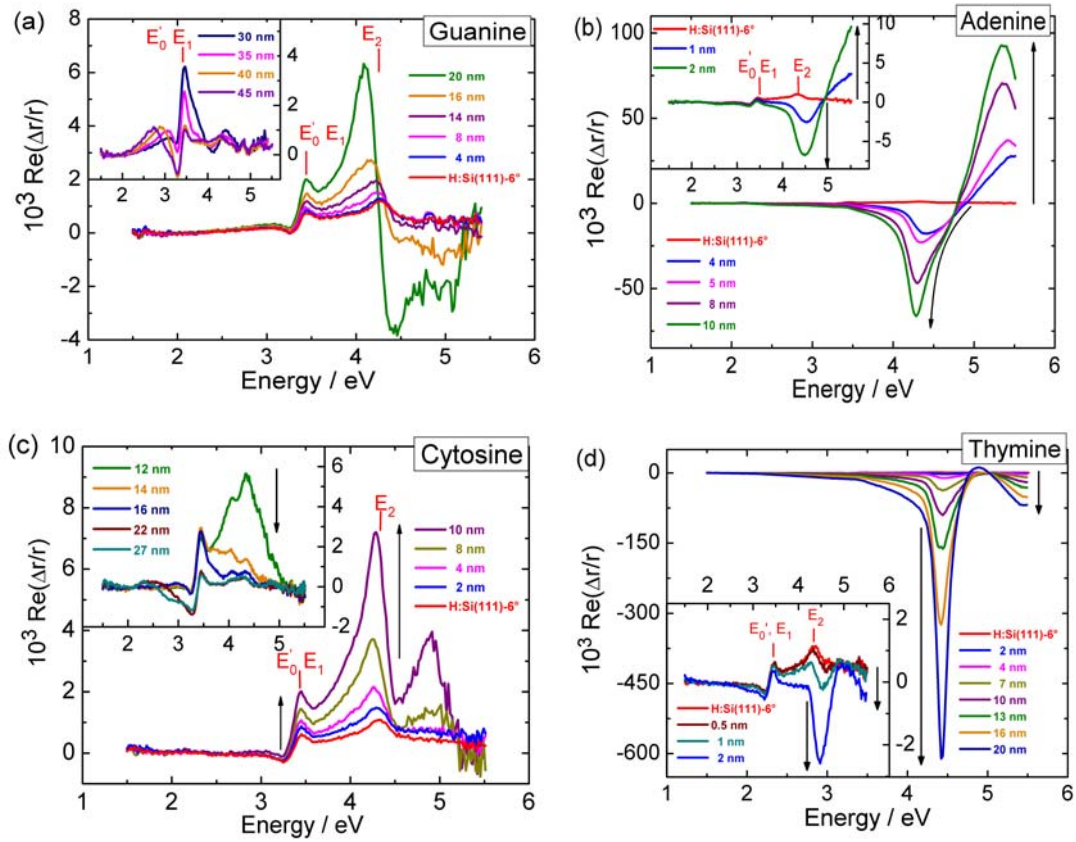


Figure 2 summarizes the RDS/RAS monitoring of DNA bases on H:Si(111)-6° surfaces. All four molecules behave optically different on the vicinal surfaces. Small changes in anisotropy are observed in the case of guanine and cytosine deposition in comparison with the large signals arising from adenine and thymine layers. Considering guanine the RDS/RAS signal reaches a saturation level for thicknesses above 30 nm. Changes can be observed around the silicon critical points which overlap with the absorption of guanine. The highest occupied molecular orbital (HOMO)→lowest unoccupied molecular orbital (LUMO) transition of guanine at 4.31 eV is close to the E_2 CP (4.25 eV) of silicon [21]. The lineshape of the signal evolves in a derivative-like lineshape with increasing guanine coverage above 14 nm. For coverage above 20 nm the signal starts to decrease and finally saturates (fig. 2a). This is likely to be related to the loss of ordering of molecules. Besides, the

RDS/RAS measurements of guanine deposition on "flat" H:Si(111)-0.35° revealed only features related to thickness artefacts [21]. Therefore, one may conclude that the weak anisotropy of guanine films on vicinal substrates is caused by vicinality which induces ordering of the molecules up to thickness of ~ 20 nm along $[1\bar{1}0]$.

Figure 2: *In situ* RDS/RAS spectra of: (a) guanine, (b) adenine, (c) cytosine, and (d) thymine layers on H:Si(111)-6°.



Contrary to guanine, adenine exhibits very strong anisotropy signals (fig. 2b). By increasing the adenine coverage the RDS/RAS signal evolves in a derivative-like lineshape in the absorption range of adenine (HOMO→LUMO transition~4.47 eV) [21]. Following the surface dielectric anisotropy model [22] it is found that the dominant absorption takes place mainly along the $[\bar{1}\bar{1}2]$ direction suggesting furthermore strong ordering of adenine molecules with the first transition dipole moment mainly parallel to this direction. Weaker signals with similar derivative-like lineshape were also observed on H:Si(111)-0.35° [21].

The RDS/RAS monitoring of cytosine (HOMO→LUMO transition~4.46 eV) deposition on H:Si(111)-6° shows that the lineshape of the signal is strongly thickness-dependent as in the case of guanine (fig. 2c). At a certain cytosine coverage a new feature around 4.90 eV appears which is close to the second electronic transition in cytosine at 4.95 eV [21]. The presence of the new feature may be inferred to a change in molecular arrangement which seems to be thickness-dependent. However, for very thin cytosine coverages, the molecules seem to preferentially align with the first transition dipole moment along $[1\bar{1}0]$. For coverages larger than 10nm the signal starts to decrease

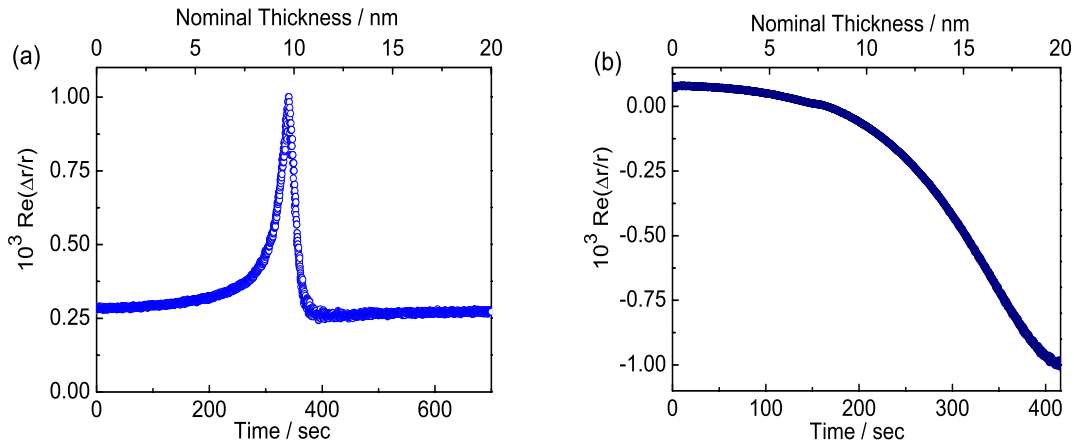
and finally saturates for thicknesses above 20 nm, an indication of the loss of molecular ordering (fig. 2c).

Strong RDS/RAS signals were again observed in the case of thymine layers on H:Si(111)-6° as reproduced in fig. 2d. Such large anisotropies suggest an average order of both thymine and adenine layers, which preserves with increasing coverage and may indicate the crystalline nature. The lineshape of the RDS/RAS signal is very much like that of dielectric function ε of thymine [21]. The sign of the RDS/RAS signal suggests a preferential alignment of the transition dipole moment (HOMO→LUMO transition~4.44 eV) parallel to the $[\bar{1}\bar{1}2]$ direction. Smaller anisotropies but with ε-like lineshape were also observed on H:Si(111)-0.35° [21].

Generally, slight red-shifts of the characteristic peak positions of the biomolecular overlayers occur with increasing coverage. Besides, the change in the broadening of the spectral features is also coverage dependent. Similar effects were previously observed in the case of α-sexithiophene (6T) layers on (010)-oriented single crystals of potassium acid phthalate (KAP) [18]. These were attributed to structural or morphological rearrangements of the 6T layers.

The anisotropy is additionally probed by time-resolved RDS/RAS measurements of the DNA bases/silicon interface formation at the E_2 CP of silicon. As an example the situation for cytosine and thymine deposition is presented in fig. 3.

Figure 3: Time-resolved RDS/RAS measurements at E_2 (4.25 eV) critical point of Si during the adsorption of (a) cytosine and (b) thymine layers on H:Si(111)-3°. The signals were normalized with respect to their maximum absolute value.



Since the penetration depth of light in silicon at this energy position is around 5 nm and beyond 50 nm for the DNA base layers, the contribution to anisotropy of both substrate and overlayer is expected. However, with increasing the coverage the contribution of the overlayers should prevail. The evolution of the anisotropy signal upon cytosine deposition must be related with a rearrangement of the molecules in agreement with the RDS/RAS spectra. With increasing the cytosine coverage the anisotropy signal increases up to a maximum value corresponding to a nominal thickness of ~ 10nm, as previously observed in RDS/RAS spectra. Afterwards the signal decreases for larger coverages and finally saturates indicating the loss of molecular ordering. In the case of thymine the evolution of the anisotropy signal at E_2 CP of silicon is different than that observed for cytosine. However, with increasing coverage the sign of the signal gets negative suggesting again the preferential alignment of the first transition dipole moment along $[\bar{1}\bar{1}2]$ direction.

Summary

The RDS/RAS technique was successfully employed for monitoring the growth of DNA bases on vicinal H:Si(111). The measurements reveal information about the molecular ordering of DNA bases induced by the density of steps on vicinal surfaces. Moreover, time-resolved RDS/RAS measurements performed at the E_2 critical point of silicon support the molecular ordering and demonstrate the sensitivity to monitor the formation of the biomolecular/inorganic interface.

Acknowledgements

The authors thank Dr. U. Rossow and Dr. K. Hinrichs for fruitful discussions. The financial support by Sächsisches Staatsministerium für Wissenschaft und Kunst (SMWK) and Deutsche Forschungsgemeinschaft Graduiertenkolleg GRK 829/1 "Accumulation of Single Molecules to Nanostructures" is acknowledged.

References

[1] G. Mauricio, P. Visconti, V. Arima, S. D'Amico, A. Biasco, E. D'Amone, R. Cingolani, R. Rinaldi, *Nanoletters* **3** (2003) 479
[2] K. Meeker and A. B. Ellis, *J. Phys. Chem*. **B 104** (2000) 2500
[3] D. E. Aspnes and A. A. Studna, *Phys. Rev. Lett*. **54** (1985) 1956
[4] D. E. Aspnes, *J. Vac. Sci. Technol.* **B 3** (1985) 1498
[5] D. E. Aspnes, J. P. Harbison, A. A. Studna, L. T. Florez, *J. Vac. Sci. Technol.* **A 6** (1988) 1327
[6] V. I. Berkovits, V. A. Kiselev, V. I. Safarov, *Surf. Sci.* **211/212** (1989) 489
[7] Ph. Hofmann, K. C. Rose, V. Fernandez, A. M. Bradshaw, W. Richter, *Phys. Rev. Lett.* **75** (1995) 2039
[8] C. Goletti, C. Springer, U. Resch-Esser, N. Esser, W. Richter, B. O. Fimland, *Phys. Rev*. **B 61** (2000) 1681
[9] K. Fleischer, S. Chandola, N. Esser, W. Richter, J. F. Gilp, *Phys. Rev*. **B 67** (2003) 235318
[10] M. E. Pemble, A. R. Turner, N. Shukla, T. Bitzer, B. G. Frederick, K. J. Kitching, N. V. Richardson, *J. Chem. Soc. Faraday Trans.* **91** (1995) 3627
[11] B. G. Frederick, J. R. Power, R. J. Cole, C. C. Perry, Q. Chen, S. Haq, Th. Bertrams, N. V. Richardson, P. Weightman, *Phys. Rev. Lett.* **80** (1998) 4470
[12] B. G. Frederick, R. J. Cole, J. R. Power, C. C. Perry, Q. Chen, N. V. Richardson, P. Weightman, C. Verdozzi, D. R. Jennison, P. A. Schultz, M. P. Sears, *Phys. Rev*. **B 58** (1998) 10883
[13] P. Weightman, *Phys. Stat. Sol*. **(a) 188** (2001) 1443
[14] E. K. Miller, K. Hingerl, C. J. Brabec, A. J. Heeger, N. S. Sariciftci, *J. Chem. Phys.* **113** (2000) 789
[15] T. U. Kampen, U. Rossow, M. Schumann, S. Park, D. R. T. Zahn, *J. Vac. Sci. Technol*. **B 18** (2000) 2077
[16] C. Di Natale, C. Goletti, F. Della Sala, M. Drago, P. Chiaradia, R. Paolesse, P. Lugli, A. D'Amico, *Appl. Phys. Lett.* **77** (2000) 3164
[17] C. Goletti, R. Paolesse, C. Di Natale, G. Bussetti, P. Chiaradia, A. Froiio, L. Valli, A D'Amico, *Surf. Sci.* **501** (2002) 31
[18] C. Goletti, G. Bussetti, P. Chiaradia, A. Sassella, A. Borghesi, *Org. Electron*. **5** (2004) 73
[19] T. Yasuda, D. E. Aspnes, D. R. Lee, C. H. Bjorkman, G. Lucovsky, *J. Vac. Sci. Technol*. **A 12** (1994) 1152
[20] D. E. Aspnes, A. A. Studna, *J. Vac. Sci. Technol*. **A 5** (1987) 546
[21] D. R. T. Zahn, S. D. Silaghi, *Adv. Sol. State Phys*. **45** (2005) accepted
[22] R. J. Cole, B. G. Frederick, P. Weightman, *J. Vac. Sci. Technol*. **A 16** (1998) 3088