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DNA BASE MOLECULES ON SILICON SURFACES STUDIED BY OPTICAL SPECTROSCOPY WITH HIGH SURFACE SENSITIVITY

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ABSTRACT. Amongst biomolecules the DNA base molecules adenine, cytosine, guanine, and thymine may also find interesting applications in organic electronics. They have optical gaps in the near ultra-violet and have already been considered as charge transport molecules in organic field effect transistors. Still there is very little knowledge on their electronic and optical properties when deposited as layers on inorganic substrates. Here the growth of the DNA bases deposited on vicinal, hydrogen passivated Si(111) substrates is studied using reflectance anisotropy spectroscopy (RAS). The RAS response of the DNA bases is monitored as a function of thickness. Ordering in the layers is induced by the step and terrace structure of the vicinal Si substrates. Even though the molecular structure is not dramatically different the RAS response is very distinct and allows an unambiguous identification of the base molecules.

1 Introduction

The usage of DNA base molecules as charge transport molecules in biomolecular electronic and optoelectronic devices is still a challenge. Recently, field effect transistor studies based on a modified DNA base revealed that the prototype bio-transistor gives rise to a better voltage gain compared to carbon nanotubes (CNTs) [1]. Silicon can be patterned in many ways and it is possible to use it as a versatile template and combine biomolecules with silicon electronics. 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 the nucleation along the step edges, thus being potential substrates in controlling the ordering of molecules in so-called molecular nano-wires. In this sense, *in situ* reflectance anisotropy spectroscopy (RAS) is employed in ultra-high vacuum (UHV) conditions for monitoring the ordering of DNA base molecules on vicinal hydrogen passivated Si(111).

2 Experimental

Vicinal p-type (B-doped) Si (111) surfaces with resistivity in the range of 1-30 Ωcm were used as substrates for the DNA base films. Prior to biomolecular deposition, the substrates were wet-chemically hydrogen terminated [2]. The vicinal Si(111) surfaces were off cut oriented by 3° and 6°, respectively, towards the $[\bar{1}\bar{1}2]$ direction. The surface reconstruction (1x1) was checked by low energy electron diffraction (LEED). In the case of the vicinal surfaces the LEED pattern shows 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 Sigma-Aldrich were evaporated under UHV conditions (base pressure ~ 10^{-8}Pa) from Knudsen cells. Molecules of thymine and cytosine were evaporated at temperatures of 365 and 410 K with corresponding evaporation rates of 0.8 and 0.3 nm/ min, respectively, while adenine and guanine molecules were evaporated at temperatures of 400 and 510 K with evaporation rates of 1.5 and 2 nm/min, respectively. The thicknesses were *in situ* monitored via a quartz crystal microbalance and then *ex situ* calibrated via both ellipsometry and atomic force microscopy film thickness measurements.

The molecular ordering of DNA base molecules on both vicinal and "flat" H:Si(111) surfaces was monitored *in situ* during the growth by reflectance anisotropy spectroscopy (RAS) in the energy range of 1.5-5.5 eV. RAS measures the difference in normal incidence in reflection for light linearly polarized along two orthogonal directions in the sample surface. In the case of a vicinal Si(111) surface the RAS signal can be expressed as follows:

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

Due to the fact that RAS is performed in normal incidence the technique is very sensitive to surface changes and capable of measuring very small optical anisotropies of 10^{-3} or even smaller.

3 Results

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) substrates 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) [3, 4]. The RAS signal of vicinal Si(111) surfaces is similar with the response of Si(110) surface as shown in fig.1. The fractional contribution of the $[110]$ direction to the vicinality of (111) surface can be determined from the ratio between the magnitude of the E_2 peak for the vicinal surface and that for the (110) surface [2]. The values determined experimentally from the spectra are about 0.08 and 0.17 corresponding to 3° and 6° off cut angles which are quite close to the expected theoretical values of 0.09 and 0.18.

Figure 2 depicts the *in situ* RAS monitoring of DNA base layers on vicinal H:Si(111)-6° surfaces. During the RAS measurements the substrate geometry was always kept identical with the one sketched in fig.1. All four molecules behave optically different when deposited onto the vicinal surface. Very small anisotropies are observed in the case of guanine and cytosine in comparison with the large RAS signals arising from adenine and thymine layers. When increasing the guanine coverage the RAS signal reaches a saturation level for thicknesses above 30 nm. The amplitude of the silicon features increases with thickness. Larger changes can be observed around the silicon E_2 gap which overlaps with the absorption of guanine since the onset is around 3.5 eV. Moreover, the HOMO-LUMO gap of guanine at 4.31 eV is extremely close to the 4.25 eV energy gap of silicon. The lineshape of the

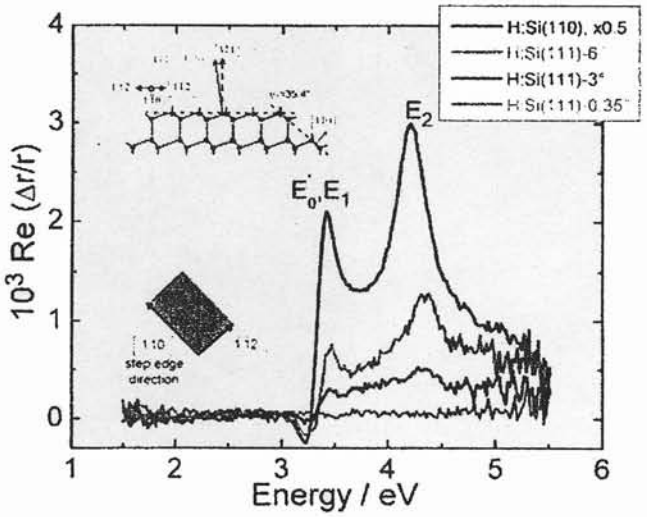

Fig. 1 RAS spectra of various silicon surfaces.

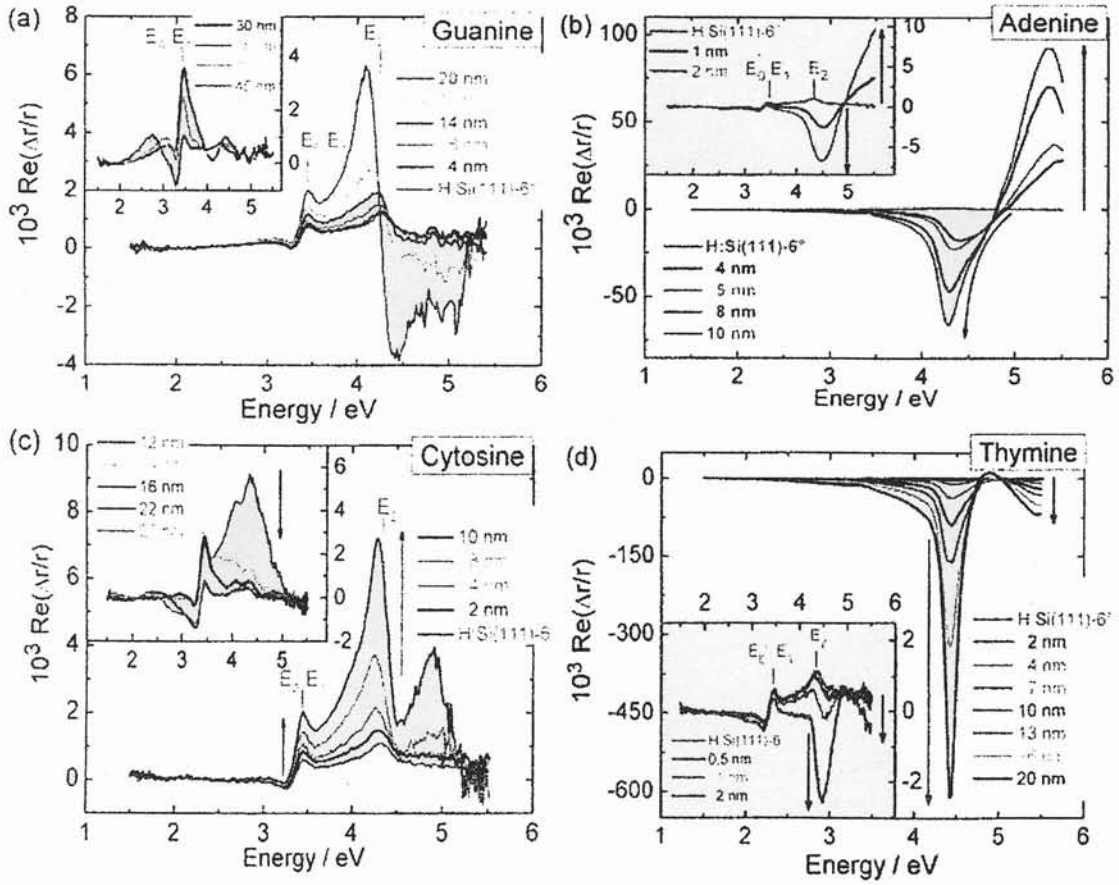

Fig. 2 *In situ* RAS spectra of monitoring: (a) guanine, (b) adenine, (c) cytosine, and thymine layers on H:Si(111)-6° surface.

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 for thicknesses around 30 nm as shown in the inset of fig. 2 (a). This can be related to the fact that the molecules form an isotropic layer and consequently the signal vanishes due to equal absorption in orthogonal directions. In order to distinguish between the anisotropy of the substrate and the anisotropy of the guanine films, RAS measurements of guanine deposition on almost flat H:Si(111)-0.35° were carried out (see fig. 3(a)). The observed features are attributed to thickness artifacts. The weak anisotropy of guanine films on vicinal substrates seems to be caused by the vicinality which induces ordering of the guanine molecules up to critical thickness of about 20 nm.

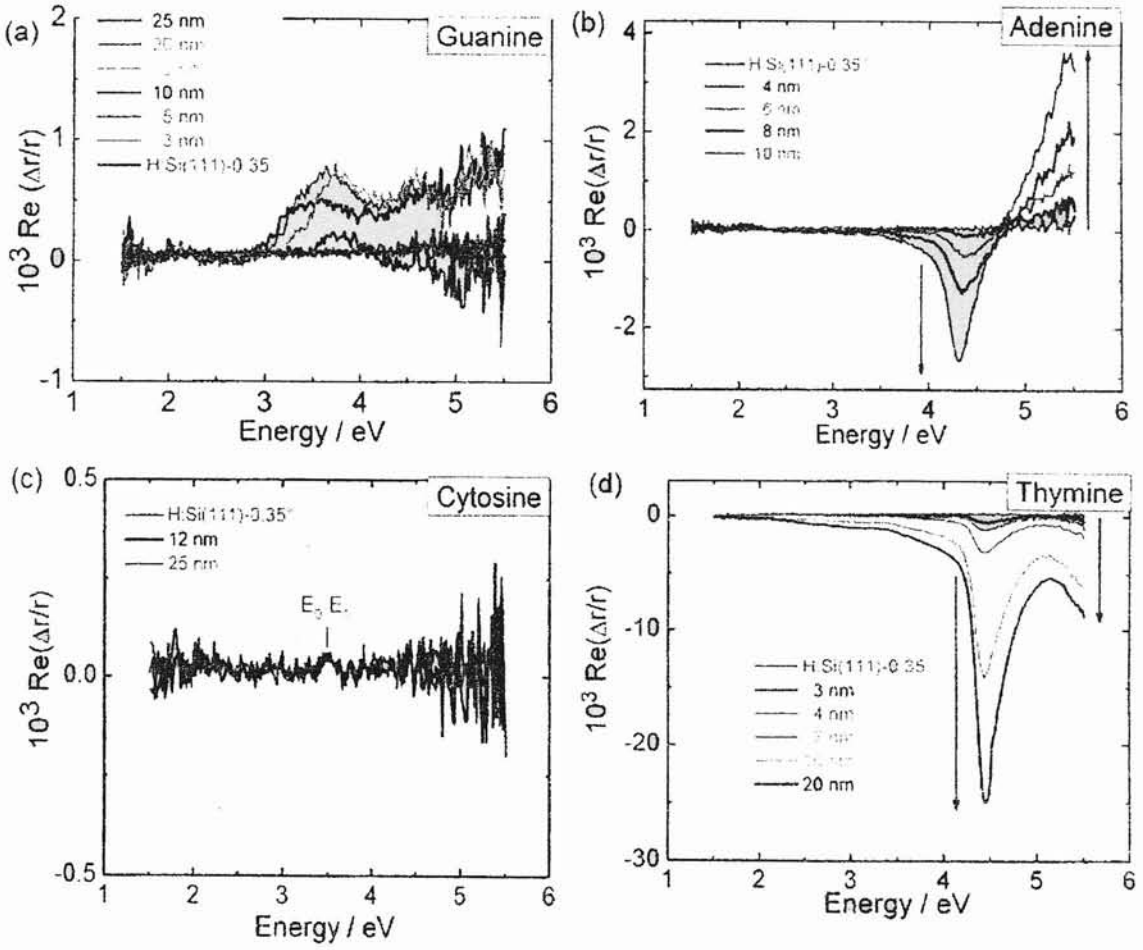

Fig. 3 *In situ* RAS spectra of monitoring: (a) guanine, (b) adenine, (c) cytosine, and thymine layers on "flat" H:Si(111)-0.35° surface.

On the contrary to guanine, adenine exhibits large anisotropy signals. By increasing the adenine coverage the RAS signal evolves in a derivative-like lineshape in the absorption range of adenine while the silicon features gradually vanish. The asymmetric evolution in the lineshape of the derivative-like RAS signals indicates

the contribution of at least two oscillators above 4 eV. Following the surface dielectric anisotropy model [5] it is found that the dominant absorption takes place mainly along $[\bar{1}\bar{1}2]$ direction suggesting furthermore strong ordering of adenine molecules with respect to this direction. Weak anisotropy can be observed with a similar derivative-like lineshape also on the almost flat silicon surface (fig. 3 (b)). Such small anisotropies were not observed by ellipsometry. The RAS monitoring of cytosine deposition on H:Si(111)-6° shows that the lineshape of the signal is strongly thickness-dependent as in the case of guanine. Larger changes can be observed around the E_2 gap of silicon at 4.25 eV which overlaps with the absorption of cytosine with the onset at 3 eV. At certain cytosine coverage a new feature around 4.90 eV appears which is closed to the second electronic transition at 4.95 eV as obtained from ellipsometry results. For very thin cytosine coverages, the molecules seem to preferentially align on vicinal surfaces with respect to the $[1\bar{1}0]$ direction. Already for higher coverage larger than 12 nm the signal starts to decrease and finally saturates for thicknesses around 20 nm as shown in inset fig. 2(c). There is no anisotropy of the cytosine layers on H:Si(111)-0.35° meaning that the anisotropy of cytosine on vicinal substrates is caused by the vicinality which induces ordering of the cytosine molecules up to critical thickness of ~ 10 nm.

The strongest RAS signals were observed in the case of thymine layers on H:Si(111)-6° as reproduced in fig. 2 (d). By increasing the thymine coverage the RAS signal of the substrate completely vanishes while large anisotropy signals appear in the absorption range of the molecule. The lineshape of the RAS signal of thymine is very much like ε derived from ellipsometry results not discussed here. The negative sign of the signal suggests high absorption along $[\bar{1}\bar{1}2]$ direction and hence a preferential alignment of the transition dipole moments of the molecule parallel to the same direction. Smaller anisotropies were also observed on "flat" silicon substrates but still larger signal amplitudes compared to the case of adenine layers on the same type of substrate (see fig. 3 (d)).

4 Summary

The RAS technique was employed for the first time in monitoring the growth of DNA base molecules on both flat and vicinal H:Si(111) surfaces. The RAS measurements revealed information about the molecular ordering of DNA bases induced by the density of steps on silicon surfaces.

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