Electronic structures of DNA molecules and their alignment control on Si(1 0 0) substrates with one-dimensional lattices

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Received 14 April 2006; received in revised form 23 June 2006; accepted 16 July 2006
Available online 27 October 2006

Abstract

We have carried out molecular-orbital calculations of the four bases of DNA, adenine (A), thymine (T), guanine (G), and cytosine (C), and the dimer dApA formed from a deoxyadenosine by using a phosphate and terminating at the sites of 5' and 3'. The calculated results for A, T, G, and C are compared with the UPS spectra obtained by using a He II lamp with irradiation at 40.8 eV, and the experimental spectra are found to be generally reproduced by the calculations. We have also examined the alignment of 1.5-μm-length ring-shaped pBR322DNA composed of 4361 bp on Si(1 0 0) substrates with one-dimensional lattices. It is found that pBR322DNA can be observed only in the bottom parts of the one-dimensional lattice, while no appreciable DNA can be observed on the top parts of the lattice. These results suggest that DNA alignment can be controlled by one-dimensional lattices on Si(1 0 0) substrates through capillary action.

Keywords: DNA; MO calculations; UPS; Si nanofabrication

1. Introduction

A single molecule is considered to be a basic element of ultimate nanoscale devices for electronics. Recently, extensive studies [1] have been carried out to theoretically and experimentally analyze electron transport through molecular junctions composed of rather simple molecules such as phenyldithiolates and alkanethiols. One of the main challenges is to understand electronic structures of more complicated molecules such as DNA for various applications to microelectronic devices. In order to realize practical molecular devices, it is also crucial to control the alignment of molecules for integration with macroscopic electrodes on most typically Si substrates in which large-scale-integrated (LSI) microelectronic circuits are fabricated.

In this paper, we have investigated optimized structures, energy levels, and wave functions of DNA molecules by using a computer software package for ab initio molecular-orbital calculations, Gaussian 03 [2], as a first step for the detailed analysis of more complicated systems including electrodes. The expected advantages of applying DNA molecules for electronic devices are: (1) possibility to synthesize any DNA oligomers with various sizes (~nm–μm) and sequences of four bases, adenine (A), thymine (T), guanine (G), and cytosine (C), to create nanoscale shapes and patterns [3], (2) flexible design of electronic structures by controlling the size and sequence to obtain useful electronic properties such as one-dimensional electron transports and superlattice structures as can be seen in the semiconductor microelectronic devices obtained by band engineering technologies, and (3) possibility to develop a new microscopic technique for the determination of the sequence in DNA strands. The calculated energy levels of the four bases A, T, G, and C [4,5] are compared with the experimental spectra obtained by ultraviolet photoelectron spectroscopy (UPS) measurements. We also show the preliminary results of controlling the alignment of relatively large DNA molecules by using one-dimensional lattices formed on Si(1 0 0) substrates.

2. Electronic structure

The molecular-orbital energies of the four bases A, T, G, and C were calculated by using the 6-31G(d) Gaussian
basis functions and Becke’s three-parameter formulation (B3LYP) [2] based on hybrid density functionals composed of Hartree–Fock, local, and gradient-corrected exchange terms for exchange-correlation energies. Fig. 1 shows the calculated molecular orbital energies of A, T, G, and C. Each highest occupied molecular orbital (HOMO) is located around 6 eV below the corresponding lowest unoccupied molecular orbital (LUMO). It is also found that each HOMO (LUMO) is bonding $\pi$ (antibonding $\pi^*$) composed of the 2p orbitals belonging to the central three carbon atoms in each base.

The UPS measurements were carried out using a He II lamp with irradiation at 40.8 eV and the sample was prepared by dropping four droplets of water solution including A, T, G, and C at each corner on a 3 $\times$ 3 cm$^2$ Si(100) substrate as illustrated in Fig. 2. Typical UPS spectra obtained from naturally-dried droplets are shown by the dots in Fig. 3. In these spectra, inelastic electron backgrounds were subtracted using the scheme proposed by Li et al. [6]. The energy origin of these spectra was taken at the top of the Si valence band determined by the UPS spectrum from the Si(100) surface without these droplets.

In order to compare the UPS spectra with the calculated MO energy levels, each MO level was broadened by using a Gaussian function with a standard deviation of 0.5 eV. The calculated results shown by the solid lines in Fig. 3 indicate that the experimental spectra can be generally reproduced, but the details cannot be well described by the calculations. One of the possible reasons is that the observed samples are not isolated bases as was assumed in the MO calculations, but rather complex systems composed of multiple bases and water molecules. Based on the wave functions and population analysis, the two main peaks observed in the energy regions 15–20 and 20–25 eV can be assigned to be primarily $\pi$ and $\sigma$ orbitals of the C, N, and O atoms, respectively.

Fig. 4 shows, as an example, how the MO energy levels change due to the formation of dimer from a deoxyadenosine by using a phosphate and terminating at the sites of 5$'$ and 3$'$. The dimer dApA has odd-number electrons and thus spin-polarized calculations were carried out. There exist two kinds of molecular orbitals: i.e., $\alpha$ or up-spin and $\beta$ or down-spin orbitals. It should be noted that the HOMO–LUMO gap becomes much smaller, which is important for device applications. For these relatively large molecules, the geometry optimization was at first performed by using the Hartree–Fock method with the 3-21G* base set. Then, the MO energy levels were calculated by using B3LYP for the optimized structure.

3. Alignment of DNA

For controlling the alignment of DNA molecules, we used the 1 $\times$ 1 cm$^2$ Si(100) substrate in which 111 nm-high one-dimensional periodic lattices with 8 lattice constants $d =$ 100, 132, 160, 200, 252, 300, 400, and 500 nm were formed in the central 200 $\times$ 200 $\mu$m$^2$ region as described in Fig. 5. The substrate surface was cleaned and slightly oxidized in chemical solutions before the introduction of DNA. We used 1.5-μm-length ring-shaped pBR322DNA composed of 4361 bp diluted by water including Tris–HCl, EDTA, and MgCl$_2$ as illustrated in Fig. 6. The DNA
Fig. 3. UPS spectra obtained from dried droplets shown in Fig. 2. The solid lines are obtained according to the procedure described in the text.

Fig. 4. Change in MO by dimerization.
Fig. 5. One-dimensional lattice structure formed in the central area of a Si(1 0 0) substrate. The SEM photograph for each lattice with different $d$ are also shown.

Fig. 6. DNA solution used in the experiments.
solution was put onto the Si(1 0 0) surface through a microsyringe by using a micropump, and it was introduced into the one-dimensional lattices primarily through capillary action as shown in Fig. 7. It is noted that capillary action becomes stronger as \( d \) becomes smaller.

Fig. 8 shows a typical example of AFM measurements for the alignment of DNA molecules on the flat Si(1 0 0) surface. It can be seen that pBR322DNA tends to make a neuron-like pattern with the maximum height \( \approx 4 \text{ nm} \). On the other hand, as shown in Figs. 9 and 10, it is found that pBR322DNA can be observed only in the bottom parts of the one-dimensional lattice with \( d = 0.5 \text{ \( \mu \)m} \) whose size just fits the ring-shaped pBR322DNA. No appreciable pBR322DNA can be observed on the top parts of the lattice. These results suggest that DNA alignment can be controlled by one-dimensional lattices on Si substrates through capillary action. Further experiments and analysis are currently under way to fully understand the alignment effects on DNA strands including the dependence on the lattice constant \( d \).

4. Concluding remarks

In summary, we have investigated the electronic structures and alignment of DNA molecules on Si(1 0 0) substrates for integration of Si technologies and molecular devices. Although DNA itself is of potential interest for microelectronic applications such as switches and memories, the electronic properties of DNA molecules are still controversial [7,8] and further investigations including large-scale computer calculations [9] should be necessary. DNA is also very attractive for patterning nanoscale metallization of microelectronic circuits through its remarkable molecular recognition and self-organization properties [10,11]. By combining these DNA characteristics and our alignment technique using one-dimensional lattices on Si(1 0 0), we believe that a new technology can be developed to integrate DNA molecular devices into LSI microelectronic circuits fabricated on Si(1 0 0).
Acknowledgements

This work was supported by JSPS Research for the 21st Century COE Program in the field of chemistry and material sciences under the project of “Molecular Informatics.” One of the authors (HU) would like to thank Kyushu University Venture Business Laboratory and Saga University Venture Business Laboratory for their kind support.

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Fig. 10. AFM line-scans of Fig. 9 in the vertical direction to the lattice (a) before and (b) after DNA introduction, and in the parallel direction to the lattice (c) before and (d) after DNA introduction.