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Photoemission study of poly(dA)–poly(dT) DNA: Experimental and theoretical approach to the electronic density of states

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We present results of an ultraviolet photoemission spectroscopy study of artificially synthesized poly(dA)–poly(dT) DNA molecules on *p*-type Si substrates. For comparison, we also present the electronic density of states calculated using an *ab initio* tight-binding method based on density-functional theory (DFT). Good agreement was obtained between experiment and theory. The spectra of DNA networks on the Si substrate showed that the Fermi level of the substrate is located in the middle of the band gap of DNA. The spectra of thick (~70 nm) DNA films showed a downward shift of ~2 eV compared to the network samples. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1850187]

There have been many proposals that DNA molecule is a promising material for the fabrication of molecular electronic devices. The most striking application is to make excellent one-dimensional wires. This proposal is especially attractive, since advanced synthetic methods exist that produce, on-demand, a wide variety of complex DNA sequences and structures. However, it has been controversial whether or not DNA exhibits good conductivity. Also, it remains to be established whether the carriers are electrons or holes. Eventually it is very important for device applications to realize both *n*-type and *p*-type doping and desirable interfacial properties.

The mechanisms of electron or hole transport in a DNA molecule have been intensively examined within the last few years. Pioneering experiments have produced different interpretations and lively discussions.[1–15] For example, Fink *et al.*[2] observed a resistance on the order of 1 MΩ for a 1-μm-long molecule (making DNA a good conductor). In contrast, Porath *et al.*[3] observed a nonlinear $I-V$ curve with an insulating gap which makes DNA a wide-gap semiconductor. Cai *et al.*[4] found that the resistance exponentially increases with the length of the DNA molecule in the atmospheric condition. Zhang *et al.*[5] reported a high resistivity exceeding 10^6 Ω cm. To address the above-memtioned issues, photoemission spectroscopy is expected to provide unique and useful information. Also, the position of the Fermi level with respect to the band gap can be studied by photoemission spectroscopy. Recently, resonant photoemission spectroscopy near the Fermi level has been reported, indicating the localized unoccupied states of the bases.[16] In the present work, we report on a photoemission study of artificially synthesized poly(dA)–poly(dT) in the film and network forms.

Poly(dA)–poly(dT) was synthesized by self-hybridization of poly(dA) of 50 mer (base pairs) and poly(dT) of 50 mer (purchased from Amersharm Biosciences Co., Ltd). The poly(dA)–poly(dT) samples were prepared as solutions with a concentration of 1.25 mg/ml. In a previous study, we found that the DNA 50 mers are assembled naturally and form a widely spread network structure on SiO_2 surfaces with the concentration of 1.25–0.25 mg/ml.[17] It is known that isolated DNA molecules yield deformed structures such as the relaxation of the pitch of the double helix. In the case of the network, on the other hand, the original molecule structure of the DNA molecules is maintained, that is, the pitch of the helix remains about 3.4 nm, which corresponds to the pitch of the ideal B-type form.

To guarantee the structure of the DNA molecules with atomic level accuracy, the molecules should be fixed on an atomically flat substrate. To obtain the flat surface, we treated a Si(111) wafer with an H_2O_2–HCl solution, an H_2O_2–NH_3 solution, an HF solution, and a NH_4F solution sequentially as in the RCA method.[18] Furthermore, we treated the H-terminated *p*-type Si(111) substrate with concentrated HNO_3 to obtain the SiO_2 surface.

Both DNA network structures and DNA films (polycrystals covering the substrate) were then deposited on the SiO_2 surface. To form the DNA network, the DNA solutions in quantities of 20 μl were dropped on the SiO_2 surface and blown off after 10 min fixation. To form the DNA film, the DNA solutions (also in quantities of 20 μl) were dropped on the SiO_2 surface and placed in vacuum for 3 or 4 h until they dried completely. The thickness of the film thus prepared was ~70 nm. The samples were characterized using an atomic force microscope (AFM) in the tapping mode. A typical AFM image of the network structure is shown in Fig. 1. A DNA network structure was observed with a height of 2.0–3.0 nm, which suggests that the network was composed of bundled DNA molecules.

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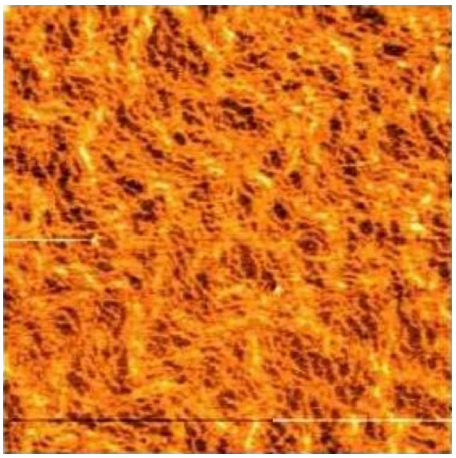

FIG. 1. (Color online) Typical AFM image of the DNA network structure of poly(dA)–poly(dT). The scan area is 5 μm$\times$5 μm.

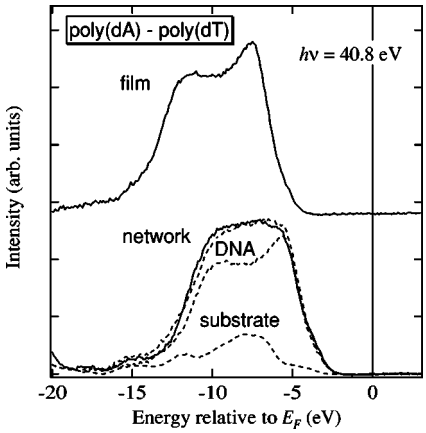

FIG. 2. Photoemission spectra of poly(dA)–poly(dT). Top: film sample. Bottom: network sample. The dashed curves are the film (shifted) and substrate spectra and their superposition. The solid curves are raw data.

Photoemission measurements were performed using a VSW hemispherical analyzer and the He II resonance line ($h\nu$=40.8 eV) of a VG helium discharge lamp. The samples were introduced into the spectrometer through a fast-entry airlock. The energy resolution was set at about 100 meV. The Fermi level (E_F) position was determined using the spectra of gold which has electrical contact with the substrate. In order to remove absorbed water, we heated the samples to 350 K in the vacuum of the spectrometer, but no appreciable change was observed in the spectra. This suggests that there was negligible amount of absorbed water in our DNA samples. We also measured spectra of the Si substrate for background subtraction.

For comparison with the photoemission experimental results, the density of states (DOS) for 10 base pairs of poly(dA)–poly(dT) DNA sequences were calculated using first-principles methods. We obtained a series of 100 snapshots from nanosecond classical molecular-dynamics simulations, separated by 0.5 ps (see Ref. 19 for details). A single-point calculation of the DNA structure of each snapshot was performed using a local-orbital method (called FIREBALL) based on density-functional theory (DFT) and separable pseudopotentials.[20] For the purposes of these calculations, we choose a gradient corrected exchange-correlation functional with Becke exchange and Lee–Yang–Parr correlation, which is necessary for a hydrogen-bonded system such as DNA. A double numerical basis set was used for H, C, N, O, and P. Further details of these calculations are described in Refs. 19 and 20. The DOS for these 100 snapshots were averaged together to obtain the average DOS; this averaging yields contributions which include thermal and structural disorder to the electronic structure.

Figure 2 shows photoemission spectra of the poly(dA)–poly(dT) film and network. The spectra have been normalized to the area after the secondary electron background subtraction using the procedure of Ref. 21. The spectrum shows a prominent emission band in the binding energy range 5–15 eV for the film and 3–13 eV for the network. The spectrum of the film consists of two distinct peaks with the lower binding energy peak being more pronounced. In the case of the network, the spectrum starts at about 2.5 eV below E_F whereas in the film it starts at about 5 eV below E_F. One can see that the line shape of the spectrum of the network is different from that of the film and is shifted toward a lower binding energy compared to that of the film.

In order to see whether there was charging effect in the film sample, we took the spectra by changing the photon flux, and could not find any energy shift. However, we cannot completely rule out the possibility of a charging effect, and more careful studies are necessary to establish the E_F position in the film sample. As for the line shape, we consider that the spectrum of the film represents the intrinsic spectrum and that the spectrum of the network is a superposition of the intrinsic spectra of DNA and the spectrum of the substrate without the DNA deposition.

As shown in Fig. 2, we could indeed reproduce the spectrum of the network from that of the film and that of the substrate by shifting the film spectrum by $\sim$2 eV and superimposing the substrate spectrum. In the visible ultraviolet absorption spectra, the absorption edge occurs at 4.7 eV for poly(dA)–poly(dT).[22] Therefore, in the networks, where little charging effect is expected, the Fermi level is located in the middle of the band gap. In fact, the spectrum of the Si/SiO_2 substrate is considered to be free from charging effect, in comparison with the previously reported spectra.[23] From these results, we obtained the schematic band diagram of poly(dA)–poly(dT) DNA on the Si/SiO_2 substrate as shown in Fig. 3. (Possible band bending in the Si substrate is not taken into account.)

Figure 4 shows comparison of the spectrum of the poly(dA)–poly(dT) film with the calculation. The calculated DOS has been broadened with a Gaussian of full width at half maximum 250 meV. The hatched area corresponds to the unoccupied part of the calculated DOS. Agreement between experiment and calculation is quite good. In comparison with the results of the calculation,[19] the first peak ($\sim$−7.5 eV from E_F) is considered to be dominated by adenine and thymine and the second peak ($\sim$−12 eV from E_F) by ribose and phosphate. The magnitude of the calculated band gap [$\sim$2.5 eV for poly(dA)–poly(dT)] is much smaller than the experimental one of $\sim$4.7 eV, due to the well-known drawback of DFT to underestimate the band gap.

Finally, we point out that the E_F position of the Si substrate, which is located in the middle of the band gap of DNA, means that a bias of $\sim$2 eV must be applied for the injection of carriers into the DNA networks on the *p*-type Si substrate. On the other hand, carriers created in the DNA molecules can be easily injected into the Si substrate. Since

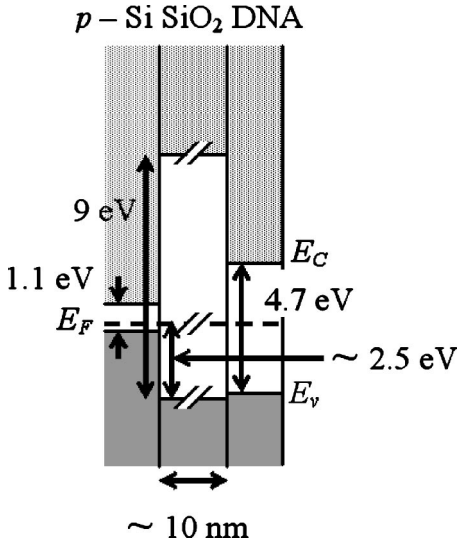

FIG. 3. Schematic band diagram of poly(dA)–poly(dT) DNA on the Si/SiO_2 substrate.

the spectra are shifted between the film and the network samples, it would be interesting to see how the E_F position is shifted as the thickness of the film increases.

In conclusion, we have measured the photoemission spectra of poly(dA)–(dT) film and network. The spectrum of the film sample is considered to represent the intrinsic DOS of DNA. The position of the Fermi level in the network sample is located in the middle of the band gap. Overall, we obtain nice agreement between the experimental DOS and the DOS from DFT calculation except for the magnitude of the band gap.

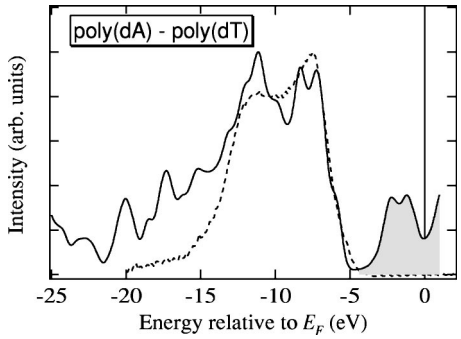

FIG. 4. Comparison of the theoretical DOS (solid curves) and the photoemission spectra (dashed curves) of poly(dA)–poly(dT). The hatched area corresponds to the unoccupied part of the calculated DOS.

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