Electrical Conduction through Poly(dA)-Poly(dT) and Poly(dG)-Poly(dC) DNA Molecules

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We report direct measurements of electrical transport through poly(dA)-poly(dT) and poly(dG)-poly(dC) DNA molecules containing identical base pairs. The observed experimental results suggest that electrical transport through DNA molecules occurs by polaron hopping. We have also investigated the effect of gate voltage on the current-voltage curve. It demonstrates the possibility of a DNA field-effect transistor operating at room temperature. Moreover, the gate-voltage dependent transport measurements show that poly(dA)-poly(dT) behaves as an *n*-type semiconductor, whereas poly(dG)-poly(dC) behaves as a *p*-type semiconductor.

Recently, electron transport through DNA molecules has received considerable attention because of possible applications ranging from electronic devices [1–4] to long-range detection of DNA damage [5,6]. However, the actual magnitude of DNA conductivity as well as its physical mechanism is under debate. A number of conflicting experimental results and a variety of theoretical models have been reported [1–12], but a consensus has not yet been reached. Until now, however, most experiments have been performed on λ-DNA with random base pair sequences, although two experiments [2,3] have been reported on poly(dG)-poly(dC). Here, we report direct measurements of electrical transport through poly(dA)-poly(dT) and poly(dG)-poly(dC) DNA molecules containing identical base pairs. The observed electrical transport properties of both DNA molecules are relatively well explained by the polaron hopping model. We have also investigated the gate-voltage effect on the current-voltage (I-V) curve. It demonstrates that poly(dA)-poly(dT) acts as an *n*-type semiconductor, while poly(dG)-poly(dC) behaves as a *p*-type one.

The specimens used in our experiments were poly(dG)-poly(dC) and poly(dA)-poly(dT) DNA molecules purchased from Amersham Pharmacia Biotech [13]. The average length of poly(dG)-poly(dC) is about 1.7−2.9 μm (5000−8600 base pairs) and that of poly(dA)-poly(dT) is about 0.5−1.5 μm. The Au/Ti electrodes as shown in Fig. 1(a) were fabricated by electron-beam lithography and a double-angle evaporation technique onto degenerately doped silicon substrate with a top layer of 0.5 μm SiO$_2$. Electrical contacts between DNA molecules and metal electrodes were made using the electrostatic trapping method [14]. A drop of DNA aqueous solution (2 μmol) was positioned on top of the gap between electrodes. A voltage of up to 5 V was then applied to the electrodes in series with a shunt resistor $R = 1$ MΩ. After trapping the DNA molecule between electrodes, the sample was dried

with nitrogen gas and characterized using a precision semiconductor parameter analyzer (HP4156A).

We have prepared more than 20 samples and carried out transport measurements at ambient conditions and in vacuum for every sample. Most samples exhibited almost identical results under both conditions, indicating that the effect of water on the conductance could be neglected. The scanning electron microscope images of these samples showed that a supercoiled DNA folded to the maximum size of 100 nm from the initial length of 0.5−2.9 μm was trapped between electrodes, as shown in Fig. 1(b). After
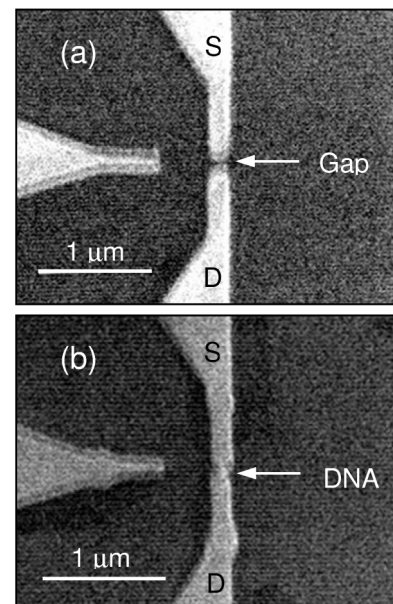

FIG. 1.   (a) Scanning electron microscope image of an Au/Ti nanoelectrode whose spacing is about 20 nm. Three electrodes are shown, but only two electrodes denoted by S (source) and D (drain) were utilized. (b) Scanning electron microscope image of a poly(dG)-poly(dC) DNA molecule trapped between two electrodes.

all transport measurements, to verify that the transport took place through the DNA molecule, a drop of buffer solution (1 mM $CaCl_2$ and 10 mM tris) containing a deoxyribonuclease (DNAse) enzyme was droped on the trapped DNA molecules. Then, the *I-V* curve was measured again at room temperature and the insulating behavior was observed. It confirms that the current flowed really through the DNA molecule.

Figure 2(a) displays the *I-V* curves measured at various temperatures on poly(dA)-poly(dT). The *I-V* curve is linear at room temperature and the room temperature resistance is about 100 MΩ. However, as the temperature decreases, the *I-V* curve becomes nonlinear and independent of the temperature below 50 K. In Fig. 2(b), we have plotted the *I-V* curve as a function of $\sinh(bV)$ ($b = 0.68$ V^{-1}). Surprisingly, the straight line is observed at all temperatures. As far as we know, the voltage dependence of $I \propto \sinh(bV)$ has been predicted by two theoretical models. One is the small polaron hopping model [15] and the other is the Korotkov and Nazarov (KN) model [16] for the tunnel junction in which single electron tunneling and barrier suppression coexist. However, the strong temperature dependence observed in poly(dA)-poly(dT) cannot be accounted for by the KN model.

According to the small polaron hopping model [15], the *I-V* characteristic takes the form

$$I \propto \sinh(eaV/2k_BTd)\exp(-E_a/k_BT), \qquad (1)$$

where a is the hopping distance, d the distance between two electrodes, and E_a the activation energy. The inset of Fig. 2(b) presents the plot of I versus $\sinh(0.68V) \times \exp(-E_a/k_BT)$, where E_a is assumed to be 0.18 eV, as determined from Fig. 2(c) (see below). For $T > 160$ K, all curves are nearly merged into a single straight line, indicating that our data are well described by Eq. (1). The fitting parameter $b = 0.68$ corresponds to $\beta = ea/2k_BTd$ in Eq. (1). If a is constant, β is expected to be inversely proportional to the temperature. However, as shown in Fig. 2(b), b is found to be independent of the temperature from the fit to the experimental data. With the assumption that $a = \alpha T$, α is estimated to be about 0.056 Å/K and the hopping distance a is calculated to be about 16.8 Å at 300 K.

Figure 2(c) presents the temperature dependence of the conductance at $V = 0$. The conductance is strongly temperature dependent around room temperature with a crossover to a weakly temperature dependent conductance at low temperatures. Similar temperature dependence has been also observed in λ-DNA by Tran *et al.* [7], who have measured the conductivity at microwave frequencies using the noncontact method. To explain their results, they suggested two transport mechanisms depending on the temperature ranges; that is, ionic conduction due to the counterions at low temperatures and carrier excitations across single particle gaps or temperature driven hopping transport processes at high temperatures. However, we consider that this temperature dependence is possibly
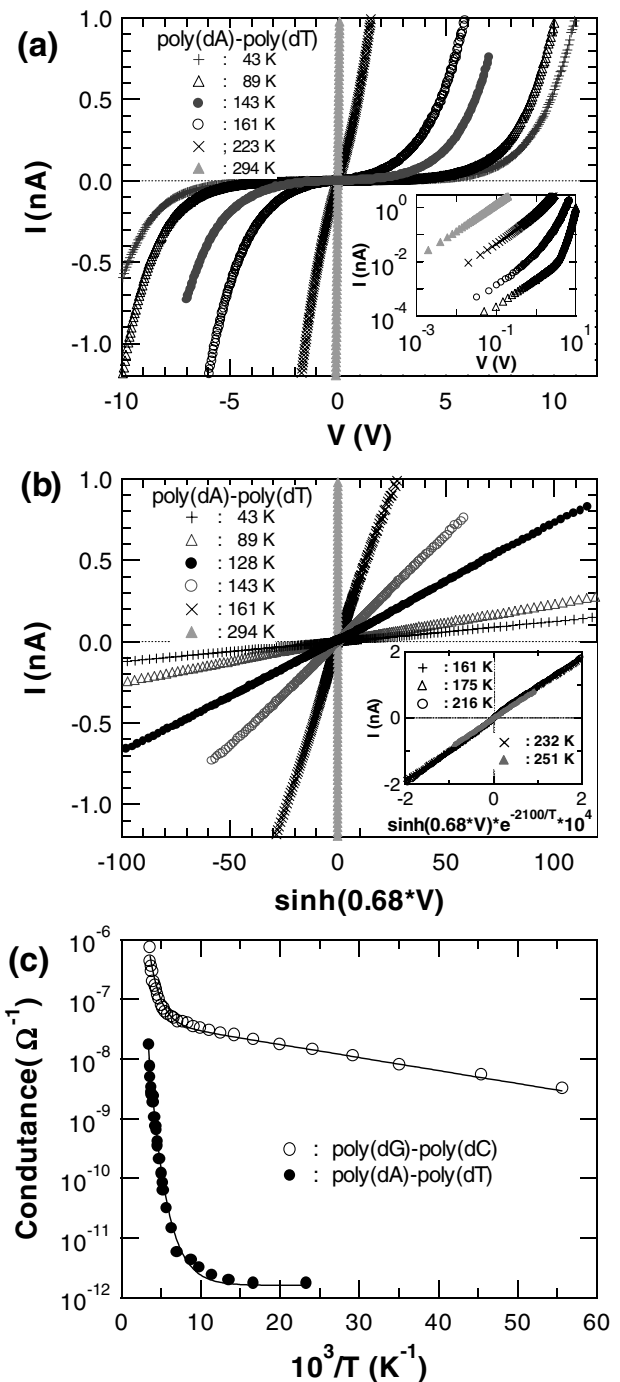

FIG. 2.   (a) The *I-V* curves measured at various temperatures on poly(dA)-poly(dT) trapped between two metal electrodes. In the inset, the *I-V* curves are plotted in the logarithm scales. (b) I versus $\sinh(0.68V)\exp(-E_a/k_BT)$ at various temperatures, where E_a is assumed to be 0.18 eV, as determined from (c). (c) Conductance versus inverse temperature for poly(dA)-poly(dT) (●) and poly(dG)-poly(dC) (○), where the conductance at $V = 0$ was numerically calculated from the *I-V* curve. The solid curves are the calculated ones using $\sigma = \sigma_o \exp(-E_a/k_BT)$ with $E_a(T)$ given by Eq. (2). See the text for details.

interpreted by polaron hopping over the whole temperature range. In the small polaron hopping model [15], the activation energy is described by
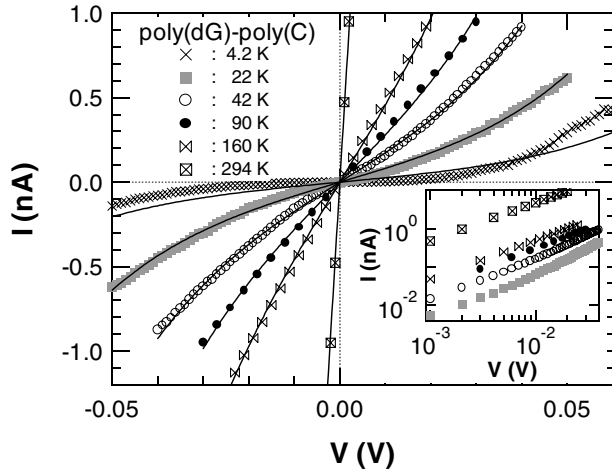
FIG. 3. The *I-V* curves measured at various temperatures on poly(dG)-poly(dC) trapped between two metal electrodes. The solid curves are the calculated ones using Eq. (1) with a fitting parameter of $b = 800/T$ and the values of E_a determined from Fig. 2(c). In the inset, the *I-V* curves are plotted in the logarithm scales.

$$E_a(T) = k_B T \sum_q C_q \tanh(\hbar \omega_q / 4 k_B T), \qquad (2)$$

where C_q is the coupling strength, and ω_q is the molecular vibrational frequency. The solid curve in Fig. 2(c) represents the conductances calculated using the relation $\sigma = \sigma_o \exp(-E_a / k_B T)$ with $E_a(T)$ given by Eq. (2), where $C_o = 29.4$ and $\omega_o = 1.3 \times 10^{14}$ Hz are assumed for poly(dA)-poly(dT). They are well fitted to the experimental data, supporting the polaron hopping model. However, since the temperature dependence of $a = \alpha T$ found in Fig. 2(b) is not explained by the polaron hopping model, the possibility of other mechanisms may not be excluded. In Fig. 2(c), E_a at high temperatures, E_{ah}, is approximated to the constant and estimated to be about 0.18 eV from the data above 160 K for poly(dA)-poly(dT).

In Fig. 3, the *I-V* curves measured at various temperatures are shown for poly(dG)-poly(dC). Although the behavior is similar to that observed with poly(dA)-poly(dT), the temperature dependence is much weaker than for poly(dA)-poly(dT). In further contrast to poly(dA)-poly(dT), whose *I-V* curve is independent of the temperature below 50 K, the *I-V* curve of poly(dG)-poly(dC) depends on the temperature down to 4.2 K. The room temperature resistance is about 1.3 MΩ, which is much smaller than that of poly(dA)-poly(dT). Assuming that the thickness of the trapped DNA molecule is about 10 nm estimated from the atomic force microscope investigation, the resistivity of poly(dG)-poly(dC) is calculated to be
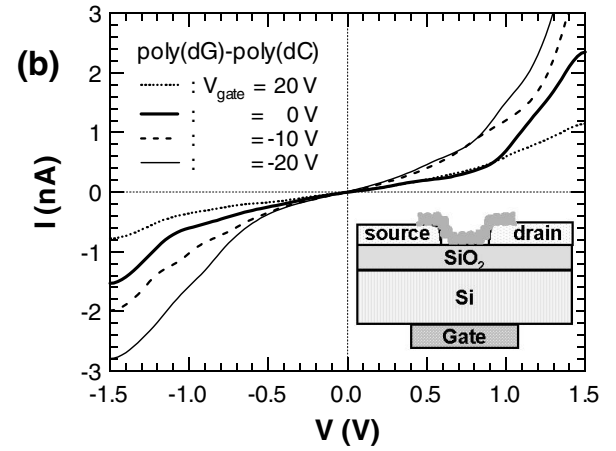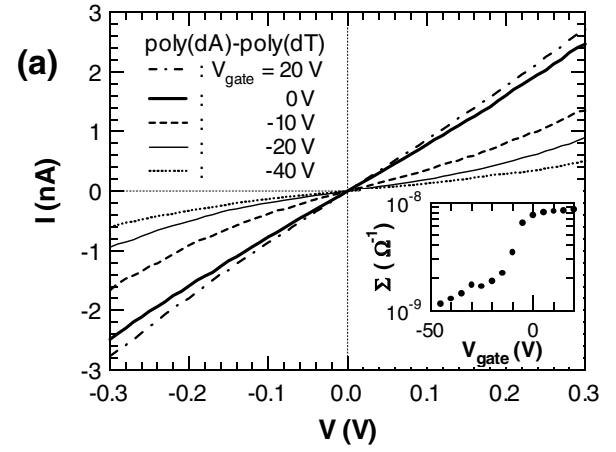

FIG. 4. The *I-V* curves measured at room temperature for various values of the gate voltage (V_{gate}) for poly(dA)-poly(dT) (a) and poly(dG)-poly(dC) (b). In the inset of (a), the conductance at $V = 0$ is plotted as a function of V_{gate} for poly(dA)-poly(dT). The inset of (b) is the schematic diagram of electrode arrangement for gate dependent transport experiments.

about 0.025 Ω cm. This value is smaller than the values previously reported such as 1 Ω cm for poly(dG)-poly(dC) [3] and 0.41 Ω cm for λ-DNA [7].

The conductance at $V = 0$ of poly(dG)-poly(dC) is represented by open circles in Fig. 2(c). Unlike poly(dA)-poly(dT), the best fit of the calculated conductance using Eq. (2) to the data leads to two frequencies with different coupling strengths, i.e., $\omega_1 = 1.8 \times 10^{14}$ Hz, $\omega_2 = 5.2 \times 10^{12}$ Hz, $C_1 = 19.2$ and $C_2 = 4.6$. Our results suggest that the coupling with the low frequency vibrational modes is negligible in poly(dA)-poly(dT), but it is not in poly(dG)-poly(dC). For poly(dG)-poly(dC), E_{ah} is estimated to be 0.12 eV, as summarized in Table I. It is

TABLE I. Parameters estimated from the experimental data. R_{RT} is the room temperature resistance, E_{ah} the activation energy at high temperatures, a the hopping distance, and ω_q the molecular vibrational frequency.

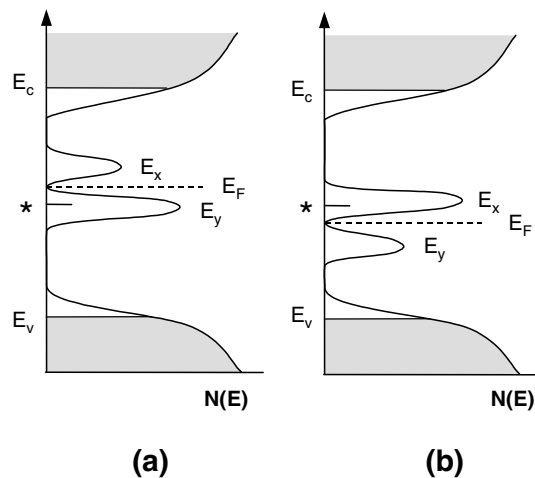|	R_{RT} (MΩ)	E_{ah} (eV)	a (Å)	ω_q (10^{14} Hz)
Poly(dA)-poly(dT)	100	0.18	$0.056T$	1.3
Poly(dG)-poly(dC)	1.3	0.12	25	1.8, 0.052

(a)   **(b)**

FIG. 5. Schematic representation of the density of states $N(E)$ for poly(dA)-poly(dT) (a) and poly(dG)-poly(dC) (b). E_c and E_v represent the conduction and the valence bands, whereas E_x and E_y the localized states. The Fermi level E_F lies above the middle of the band gap denoted by the asterisk (∗) for poly(dA)-poly(dT) (a), while E_F below the middle of the band gap for poly(dG)-poly(dC). The regions of extended states are shaded.

interesting to note that $E_a = 0.15$ eV of λ-DNA reported in Ref. [7] is very close to the average value of E_{ah} of poly(dA)-poly(dT) and poly(dG)-poly(dC).

The solid curves in Fig. 3 represent the I-V curves calculated using Eq. (1) with $b = 800/T$ and the values of E_a estimated from Fig. 2(c). They are in good agreement with experimental ones above 50 K, indicating the applicability of Eq. (1) to the I-V curves of poly(dG)-poly(dC). In contrast to poly(dA)-poly(dT), however, the fitting parameter b is observed to be proportional to $1/T$ and a is estimated to be about 25 Å, independently of the temperature for $T > 50$ K. Although the origin of different temperature dependences of b is not clear, it is guessed to be related to the bonding strength between base pairs.

Figure 4(a) shows the I-V curves measured at room temperature with various back-gate voltages V_{gate} for poly(dA)-poly(dT). When V_{gate} is increased to negative values, the current is suppressed and the gaplike nonlinearity develops around $V = 0$. On the contrary, upon the application of a positive V_{gate} the current is rather enhanced. The conductance at $V = 0$ is plotted against V_{gate} in the inset of Fig. 4(a). The conductance is changed by about 1 order of magnitude on a change of 20 V in V_{gate}. This asymmetric polarity dependence of the conductance on V_{gate} suggests that poly(dA)-poly(dT) behaves as an n-type semiconductor. In Fig. 4(b), the V_{gate} dependence of the I-V curves measured at room temperature is presented for poly(dG)-poly(dC) [17]. Unlike poly(dA)-poly(dT), the current is depleted by applying a positive V_{gate} and enhanced by a negative V_{gate}, implying that poly(dG)-poly(dC) acts as a p-type semiconductor.

Based on our experimental results, we propose the density of state $N(E)$ as depicted schematically in Figs. 5(a) and 5(b) for poly(dA)-poly(dT) and poly(dG)-poly(dC),

respectively. E_c and E_v denote the conductance and valence bands, and localized states E_x and E_y are located between them. Since poly(dA)-poly(dT) behaves similar to an n-type semiconductor, $N(E)$ of E_x is considered to be larger than that of E_y and the Fermi level to lie above the middle of the band gap denoted by the asterisk in Fig. 5(a). Conversely, for poly(dG)-poly(dC), $N(E)$ of E_y is assumed to be larger than that of E_x and the Fermi level to place below the middle of the band gap.

In summary, we have investigated the temperature dependence of I-V curves for poly(dA)-poly(dT) and poly(dG)-poly(dC) DNA molecules trapped between two metal electrodes. For both samples, most experimental results except the temperature dependence of the hopping distance for poly(dA)-poly(dT) can be interpreted within the polaron hopping model. We have also measured the gate-voltage effect on the I-V curve. Poly(dA)-poly(dT) exhibits n-type semiconducting behaviors, while poly(dG)-poly(dC) does p-type ones

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[17] The sample used in Fig. 4(b) is not the same one used in Fig. 3. The nonlinearity of the I-V curve observed at room temperature probably resulted from the contacts between DNA molecules and metal electrodes since these contacts are not expected to be metallic.