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Room temperature negative differential resistance in DNA-based molecular devices

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A molecular device fabricated from metallic deoxyribonucleic acid (M-DNA) exhibits a negative differential resistance (NDR) behavior. When two gold electrodes were connected by Ni^{2+}-chelated DNA, which was converted from λ-DNA, not only was the conductivity of DNA improved, but a NDR device was formed as a full cyclic voltage sweep was applied to measure its current versus voltage characteristics at room temperature and in an ambient environment. Such electronic characteristics of a M-DNA device may have been caused by the redox reactions of Ni ions. This finding provides a simple way to construct electrical nanodevices from biological molecules.
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Negative differential resistance (NDR) refers to the electrical behavior of some semiconductors in which the electric current decreases with increasing applied voltage over a particular range. NDR is commonly employed in the fields of low-power memory or logic devices, such as Esaki diodes[1] and resonant tunneling diodes.[2] Recently, NDR characteristic have been observed not only in semiconductors but also in organic molecules.[3–5] Various mechanisms of NDR have been proposed for various molecular device systems. They include charging (reduction),[3] redox reaction,[5] structural change,[6] chemical reaction,[7] and the association-dissociation processes[8] of molecules. For example, molecules that contain a nitroamine redox center (2′-amino-4-ethynylphenyl-4′-ethynylphenyl-5′-nitro-1-benzenethiol) that is sandwiched between two metal electrodes exhibit NDR due to a two-step reduction process.[3] Metalloproteins (ferritin) that are embedded in the gap between two single-walled carbon nanotubes yield reproducible NDR peaks during cyclic voltage sweep measurements.[5] This NDR behavior originates in the redox reaction of the transition metal ions in ferritin. To exploit these molecules with NDR properties in nanodevices, detailed knowledge of the molecular electronic characteristics and reliable fabrication processes are both required.

The fact that aromatic heterocycles of DNAs are highly organized has been recently utilized in nanodevices.[9] In 1962, double-stranded DNA with π-electron cores of well stacked bases was suggested to be a pathway for charge transportation.[10] However, discrepancies exist among the measured values of DNA conductivity because of differences in the measuring methods, conditions, or DNA sequences.[11,12] Although the intrinsic conductivity of DNA has not been well characterized, metal-doped DNA, metallic DNA (M-DNA), has been demonstrated to behave as a conductive nanowire.[13] Lee and co-workers discovered M-DNA formed by the substitution of divalent metal ions (Zn^{2+}, Ni^{2+}, and Co^{2+}) with the imino protons of *G* and *T* of DNA, forming a stable tetrahedral geometry at $p\mathrm{H} > 8.5$. M-DNAs also have better conductivity than the corresponding native forms.[14–16]

In this study, NDR was observed in a M-DNA-based device. Simple lateral metal-molecule-metal (M-M-M) structures were fabricated after pairs of gold electrodes were formed with nanometer gaps on a silica substrate. Ni-DNA, which is derived from λ-DNA, was adopted to connect gold electrodes and act as the active molecule in molecular devices [Fig. 1(a)].

λ-DNA was purchased from TOYOBO CO., LTD. (Osaka, Japan). It is comprised of 23 130 base pairs (about

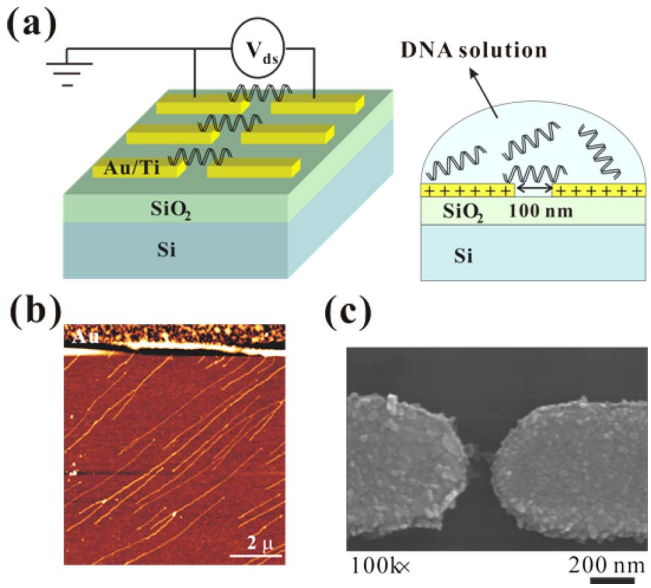

FIG. 1. (Color online) (a) Schematics of the DNA based NDR device (left) and electrostatic trapping (right). (b) AFM image of DNA molecules absorbed on silica oxide after electrostatic trapping process. (c) SEM image of DNA molecules, which are converted into silver wires and bridge on the gap between two gold electrodes.

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7.9 μm), with randomly distributed *A*, *G*, *C*, and *T* bases. λ-DNA was diluted in 10 mM tris-HCl buffer (pH=9.0) to yield a final concentration of 12.5 ng/μl. Ni-DNA was then converted from the diluted λ-DNA by adding 10 mM tris-HCl and 2.5 mM $NiCl_2$ at pH=9.0 and incubation for at least 8 h.

Standard e-beam lithography and lift-off processes were employed to pattern the nanometer scale electrodes.[17] First, 120 nm SiO_2 was grown on Si wafers by low-pressure chemical vapor deposition (LB45 Furnace system, ASM, Biltnoven, Netherlands). The nanoscale electrode pattern was then transferred to SiO_2 by evaporating 5-nm-thick titanium (as an adhesion layer) and 50-nm-thick gold using an e-gun evaporator (EBX-8C, ULVAC, Kanagawa, Japan). The resulting electrode gap was 100 nm (±10 nm, n=5). Electrical contacts between DNA and the gold electrodes were formed by electrostatic trapping.[18] Both λ-DNA and Ni-DNA solutions were dialyzed against with 2 L double-distilled water for 8 h at 4 °C, twice, to remove the salt and the excess Ni ions beforehand. Then a drop, around 5 μl, of λ-DNA (or M-DNA) solution was placed on the gap between the electrodes. A voltage of up to 1 V was applied to the electrodes to trap the DNA. (The mean electric field was approximately 7.85×10^2 V/m, parallel to the substrate.) After 20 min of incubation, the samples were dried slowly in nitrogen gas and their electronic characteristics were measured using a precision semiconductor parameter analyzer (HP 4156A, AVALON CA, USA).

After the electrostatic trapping process, λ-DNAs were observed under an atomic force microscope (AFM) (NanoWizard II, JPK, Berlin, Germany) in tapping mode. The DNA molecules were absorbed on the silicon oxide, stretched, and oriented toward the electrode [Fig. 1(b)]. A similar phenomenon was also observed in the case of Ni-DNA. According to our previous study,[16] the Ni-DNA molecules remained negatively charged on the backbone as well as native λ-DNA. These negative charges on the DNA molecules are attracted by the positive charges of the electrodes. As expected, more DNA molecules were trapped and some bridged the two electrodes. To confirm that λ-DNAs or Ni-DNAs bridged the two electrodes by electrostatic attraction, the DNA molecules were converted into silver wires by ion exchange,[19] and the SEM image [Fig. 1(c)] revealed the silver nanowire between the 100 nm spaced gold electrodes. Meanwhile, many of the silver nanoparticles were observed on the surfaces of the electrodes. DNA molecules were trapped between these surfaces, bridging the gap between them.

Electrical tests demonstrated that Ni-DNA molecular devices are very stable and their NDR characteristics are reproducible at room temperature in an ambient environment [Fig. 2(a)]. When the voltage applied to M-M-M devices constructed from both λ-DNA and Ni-DNA was swept from −10 to 10 V, λ-DNA [inset in Fig. 2(a)] exhibited a nonlinear *I-V* curve with a plateau at low voltage. This semiconductorlike energy gap, which was about 3 eV, has also been reported upon by Porath *et al.*,[11] who measured directly the electrical transport through individual short DNA molecules. This plateau indicates that a contact barrier is present between the junction of λ-DNA and the gold electrodes. When the applied bias voltage reaches a threshold, electrons (or holes) can be injected from the electrode to λ-DNA by tunneling through the contact barrier and passing through the

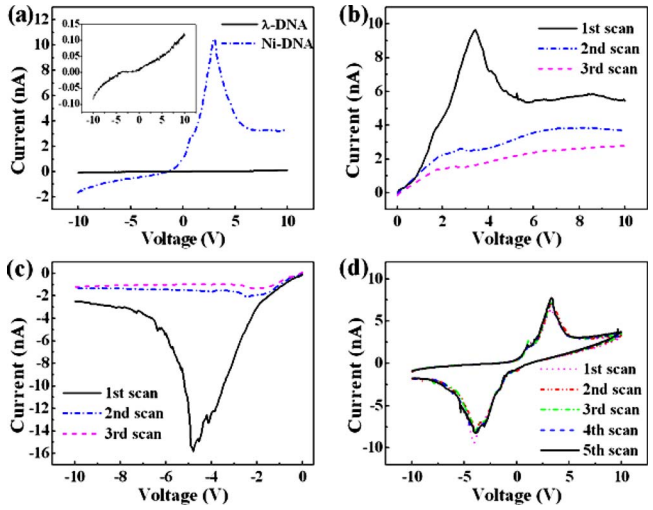

FIG. 2. (Color online) (a) Current-voltage (*I-V*) characteristics of λ-DNA and Ni-DNA, the sweep range from −10 to 10 V. (b) *I-V* characteristics of Ni-DNA with positive sweep (0–10 V). (c) *I-V* characteristics of Ni-DNA with negative sweep (0–−10 V). (d) *I-V* characteristics of Ni-DNA with repetitive full cyclic sweeps (−10 V→10 V→−10 V). The entire scan rate is 50 mV/s.

DNA molecule.[11] After the λ-DNA was replaced with Ni-DNA, the conductivity of the Ni-DNA device exceeded that of the native DNA device, such that the 3 eV conducting gap of the native DNA device disappeared [Fig. 2(a)]. The inserted metal ions may thus support the formation of a *d* band that is aligned with the Fermi level of the electrode.[14] Therefore, electrons (or holes) can be injected without a voltage threshold. The result is comparable with those of previous studies.[14] As well as the improvement in the conductivity of native DNA by Ni ions doped, an interesting NDR behavior was observed. Figure 2(b) plots the *I-V* curves of Ni-DNA for successive positive voltage sweeps (0–10 V) at room temperature. An NDR peak was positioned at around 3.50 V with a peak-to-valley ratio (PVR) of 1.78 for the first scan, and the peak disappeared during the subsequent sweep over the same voltage range in the same direction. A negative NDR peak was also observed at about −4.70 V with a PVR of 6.21 when the voltage on the device was swept from 0 to −10 V [Fig. 2(c)]. The negative NDR peak also disappeared upon successive negative sweeps. After the negative NDR peak had been observed, a positive NDR peak reappeared in a positive scan, confirming that both of the NDR peaks were observed when a full cyclic voltage sweep (−10 V→10 V →−10 V) was applied [Fig. 2(d)]. Besides the reproducible NDR behavior exhibited by the *I-V* curves, hysteresis was observed, possibly associated charge trapping.[20] These reproducible *I-V* curves are similar to the reversible redox behavior revealed by the cyclic voltammetry in electrochemical analyses.[16] The DNA-based devices can be reasonably suggested to act as a solid state electrochemical system. Two gold electrodes are the anode and cathode. The phosphate backbone of λ-DNA is the dielectric layer and the Ni ions that dope the λ-DNA act as the electroprobes. The Ni ions undergo redox reactions when the applied voltage approaches the redox potential in the cyclic voltage sweep process. The positive NDR peak corresponds to the oxidation peak of the Ni ions and the negative NDR peak corresponds to their reduction.[5] Namely, the mechanism of NDR in Ni-DNA involves the redox reactions of the Ni ions (oxidation

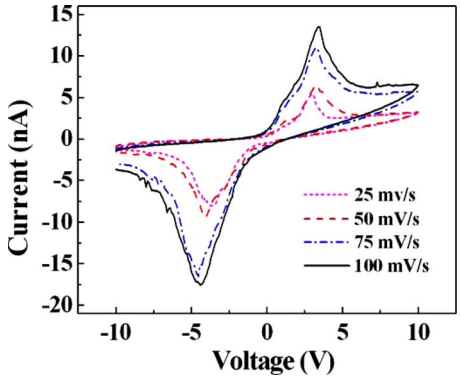

FIG. 3. (Color online) *I-V* characteristics of Ni-DNA with full cyclic sweep at a different scan rate.

of Ni^{2+} and reduction in Ni^{3+}). Additionally, according to previous studies, Ni-DNA is a decent charge conductor. These characteristics are responsible for the reproducible and stable electrochemical redox reactions of Ni ions during the *I-V* scan. Relatively stable *I-V* curves were measured during the repetitive full cyclic sweep [Fig. 2(d)].

Significant increases in peak currents with the scan rate were observed (Fig. 3), similar to those of the classical redox reaction parameters in the electrochemical system. The rate of the redox reaction increases with the scan rate increases, increasing the peak current. The *I-V* curves are asymmetric and the peak positions are slightly shifted, indicating that the redox reactions of Ni ions are quasireversible, because the charge transfer rate in Ni-DNA molecules varies during a cyclic voltage sweep. Previous investigations demonstrated that a DNA conformational change alters the conductivity.[21] Therefore, the conformational change in negatively charged Ni-DNA may occur during voltage sweep and contribute to the quasireversibility of the Ni redox reaction. Possible causes of such a DNA conformational change include applied bias, and the effect of the transformations between Ni^{2+} and Ni^{3+} (redox reaction) during the cyclic voltage scan.

In summary, a DNA-based NDR device is implemented using Ni-DNA molecules, which form a bridge between the two gold electrodes by electrostatic trapping. Not only does Ni-DNA serve as a pathway for transporting charges, but also the chelated Ni ions in Ni-DNA become redox centers. Reproducible and stable NDR behaviors are revealed by the *I-V* characteristics at room temperature and atmospheric pressure. This NDR behavior originates the active redox reactions of transition metal ions in DNA. Furthermore, the highest achievable PVR is about 6 in this work. Results of this study demonstrate the potential applications of the above aforementioned molecular devices.

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[1] L. Esaki, Phys. Rev. **109**, 603 (1958).
[2] T. C. L. G. Sollner, W. D. Goodhue, P. E. Tannenwald, C. D. Parker, and D. D. Peck, Appl. Phys. Lett. **43**, 588 (1983).
[3] J. Chen, M. A. Reed, A. M. Rawlett, and J. M. Tour, Science **286**, 1550 (1999).
[4] J. D. Le, Y. He, T. R. Hoye, C. C. Mead, and R. A. Kiehl, Appl. Phys. Lett. **83**, 5518 (2003).
[5] Q. Tang, H. K. Moon, Y. Lee, S. M. Yoon, H. J. Song, H. Lim, and H. C. Choi, J. Am. Chem. Soc. **129**, 11018 (2007).
[6] R. A. Kiehl, J. D. Le, P. Candra, R. C. Hoye, and T. R. Hoye, Appl. Phys. Lett. **88**, 172102 (2006).
[7] J. He and S. M. Lindsay, J. Am. Chem. Soc. **127**, 11932 (2005).
[8] J. L. Pitters and R. A. Wolkow, Nano Lett. **6**, 390 (2006).
[9] S. Nokhrin, M. Baru, and J. S. Lee, Nanotechnology **18**, 095205 (2007).
[10] D. D. Eley and D. I. Spivey, Trans. Faraday Soc. **58**, 411 (1962).
[11] D. Porath, A. Bezryadin, S. de Vries, and C. Dekker, Nature (London) **403**, 635 (2000).
[12] Y. Zhang, R. H. Austin, J. Kraeft, E. C. Cox, and N. P. Ong, Phys. Rev. Lett. **89**, 198102 (2002).
[13] P. Aich, S. L. Labiuk, L. W. Tari, L. J. T. Delbaere, W. J. Roesler, K. J. Falk, R. P. Steer, and J. S. Lee, J. Mol. Biol. **294**, 477 (1999).
[14] A. Rakitin, P. Aich, C. Papadopoulos, Y. Kobzar, A. S. Vedeneev, J. S. Lee, and J. M. Xu, Phys. Rev. Lett. **86**, 3670 (2001).
[15] Y. T. Long, C. Z. Li, H. B. Kraatz, and J. S. Lee, Biophys. J. **84**, 3218 (2003).
[16] P. C. Jangjian, T. F. Liu, C. M. Tsai, M. S. Tsai, and C. C. Chang, Nanotechnology **19**, 355703 (2008).
[17] B. Hartzell, B. McCord, D. Asare, H. Chen, J. J. Heremans, and V. Soghomonian, Appl. Phys. Lett. **82**, 4800 (2003).
[18] K. H. Yoo, D. H. Ha, J. O. Lee, J. W. Park, J. Kim, J. J. Kim, H. Y. Lee, T. Kawai, and H. Y. Choi, Phys. Rev. Lett. **87**, 198102 (2001).
[19] E. Braun, Y. Eichen, U. Sivan, and G. Ben-Yoseph, Nature (London) **391**, 775 (1998).
[20] H. Choi, S. Choi, T. W. Kim, T. Lee, and H. Hwang, Jpn. J. Appl. Phys., Part 2 **45**, L807 (2006).
[21] N. Kang, A. Erbe, and E. Scheer, N. J. Phys. **10**, 023030 (2008).