A photoresponsive single electron transistor prepared from oligothiophene molecules and gold nanoparticles in a nanogap electrode

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Gold nanoparticle-oligothiophene pentamer networks were prepared in a nanogap electrode and their photoresponsive and conductive properties were measured. Coulomb diamond appeared in the differential conductance map of the device at cryogenic temperatures, indicating that the device worked as a single electron transistor. Upon irradiation with UV light, the current showed discontinuous changes. The I-V_{SD} curve and differential conductance mapping before and after irradiation showed that the abrupt changes in current can be explained by a shift in the potential of the Coulomb island. © *2010 American Institute of Physics*. [doi:10.1063/1.3359424]

The conductive properties of mesoscopic materials make them an attractive research target for future electronic devices.[1] Among them, single electron tunneling devices are expected to surpass the limits of conventional silicon devices and are candidates for future nanoelectronic circuits.[2] Single electron transistor (SET) using a metal nanoparticle,[3] a metal semiconductor,[4] a carbon nanotube,[5] or an organic molecule[6] as a Coulomb island is reported. Meanwhile, photoresponsive molecules can bestow photoresponsive properties on electronic devices. Although single electron tunneling devices consisting of metal nanoparticles and organic molecules are attracting interest because of the versatility of their structure and function, devices containing photoresponsive systems are almost unexplored.[7] In this letter, we report the photoinduced digital changes in current achieved in a nanostructured junction consisting of oligothiophene molecules and gold nanoparticles.

As a linker between the gold nanoparticle and the electrode, oligothiophene pentamer **1** was synthesized [Fig. 1(a)]. A mixed solution of compound **1** and gold nanoparticles[8] was placed onto a nanogap electrode that was prepared by an electromigration process [Fig. 1(b)].[9] A scanning electron microscopy (SEM) image of the fabricated junction showed that the gap width is approximately 10 nm and approximately 5 nm of nanostructure is bridging the gap [Fig. 1(c)].[10]

The devices were transferred to a vacuum probe station and I-V_{SD} curves were measured at 12 K. The I-V_{SD} curves showed the Coulomb blockade effect with the threshold of the low conductive region V_{Th}, which is obtained to be 40 mV at no gate voltage. A gate voltage V_G was applied to the nanogap electrode using a Si back gate technique and the gate voltage dependence of the conductive characteristic was examined. Four diamondlike structures in the dI/dV_{SD} mapping suggest the formation of a SET [Fig. 1(d)]. The consistency of the diamond size implies uniformity of the energy levels of the Coulomb island. The uniformity indicates that the gold nanoparticle functions as a Coulomb island because when an organic compound behaves as a Coulomb island, the diamonds are not of uniform size,[11] but when a gold nanoparticle acts as the island, the diamonds are uniform.[3] The charging energy (E_C) of the Coulomb island was estimated to be 40 meV from the peak tops of the diamonds (V_C). E_C is described by

$$E_C = eV_C = e^2/C_\Sigma, \tag{1}$$

where C_Σ is the total capacitance of the SET ($C_\Sigma = C_D + C_S + C_G$, where C_D, C_S, and C_G are the capacitance between the

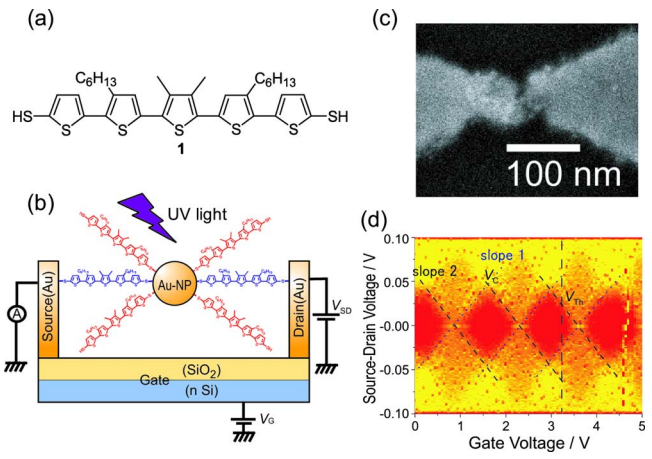

FIG. 1. (Color online) (a) Molecular structure of compound **1**. (b) Schematic illustration of the nanogap electrode. The SiO_2 layer is 50 nm thick. (c) SEM image of the nanogap electrode. The size of the gap and gold nanoparticle is approximately 10 nm and approximately 5 nm, respectively. (d) dI/dV_{SD} mapping as a function of both V_{SD} and V_G of the junction. The differential conductance is shown by the color scale increasing from dark (red) (0 nS) to bright (yellow) (100 nS).

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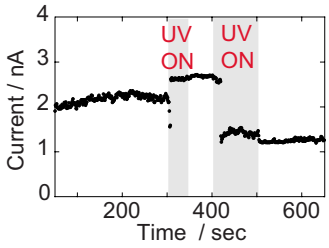

FIG. 2. (Color online) Real-time profile of the change in current under irradiation with UV light: V_{SD}=50 mV; V_G=0 V. The gray areas indicate periods of UV irradiation.

Coulomb island and the drain, source, or gate electrode, respectively). Because the slopes of the Coulomb diamond are expressed as (slope 1)$=C_G/(C_G+C_S)=0.056$ and (slope 2) $=-C_G/C_D=-0.055$, each capacitance is obtained as C_Σ =4.00 aF, C_S=1.86 aF, C_D=2.03 aF, and C_G=0.11 aF.

A real-time profile of the current at the junction was measured under irradiation with UV light ($\lambda<450$ nm) [Fig. 2]. No change in current was observed in the dark. Interestingly, when the sample was irradiated with UV light, the current value immediately jumped from 2.0 to 2.7 nA. This high current state was maintained in the dark. When the light was turned on again, the current value stayed at 2.7 nA for 10 s and then suddenly dropped to 1.5 nA. After the light was turned off, the current value remained at 1.5 nA. This phenomenon was also observed in other junctions prepared by the same method. When the UV light was irradiated for several thousands of seconds, tens of abrupt current jumps were observed at all times. This discontinuous change in current is attributed to a change at a single molecule level because if many molecules were involved the change would be continuous.

Using several intensities of UV light, the dependence of the photoresponsive behavior on the light intensity was studied. No photoresponsive behavior was observed under irradiation with weak (0.032 mW/cm^2) light, but the frequency of the changes in current was dramatically increased when strong (1.3 mW/cm^2) light was used. The wavelength dependence of the abrupt changes in current was also studied. Under irradiation with monochromatic 520 nm light, no digital-type changes in current were observed. Because oligothiophene **1** does not absorb 520 nm light and gold nanoparticles exhibit strong plasmon absorption, the abrupt change in current observed for UV irradiation is considered to be due to the electronic excitation of the oligothiophenes.

To clarify the mechanism of the digital-type change in current, I-V_{SD} curves before and after irradiation were measured at different gate voltages [Figs. 3(a) and 3(b)]. The shape of the I-V_{SD} curves significantly changes after photoirradiation. The slope of the I-V_{SD} curves, which is dependent on the conductance of the oligothiophene molecule between the electrode and the nanoparticle, showed almost no change upon photoirradiation. However, the threshold voltage of Coulomb blockade effect V_{Th} was found to change significantly. This phenomenon suggests that the abrupt change in current is not associated with changes of the interconnecting molecules, but is a result of changes in the energy level of the Coulomb island, which is controlled by the gate voltage.

For quantitative evaluation of the effect of photoirradiation on the gate dependence of the I-V_{SD} curve, the differential conductance mappings as a function of both V_{SD} and V_G

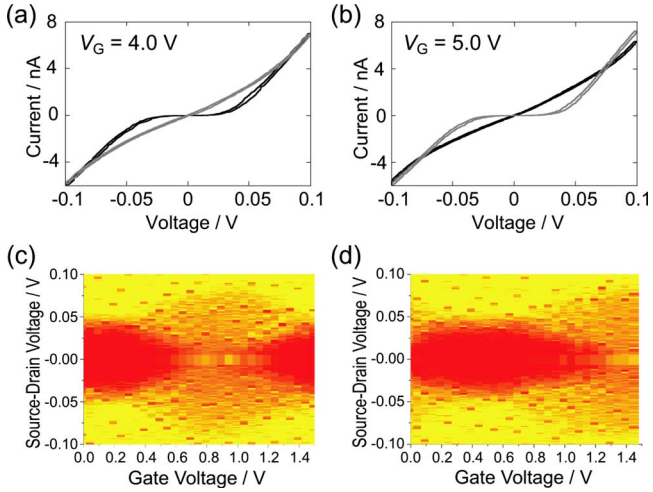

FIG. 3. (Color online) I-V_{SD} curves of a junction at different gate voltages. Black line, before irradiation; gray line, after irradiation with UV light: (a) V_G=4.0 V; (b) 5.0 V. dI/dV_{SD} mapping before and after UV irradiation: (c) before irradiation; (d) after irradiation. The differential conductance is shown by the color scale increasing from dark (red) (0 nS) to bright (yellow) (100 nS). (c) is an expanded image of Fig. 1(d).

were compared before and after photoirradiation [Figs. 3(c) and 3(d)]. While two diamond structures were observed in the V_G region from 0 to 1.5 V before irradiation, only one diamond structure was observed after light irradiation. The charging energy and the capacitance of the junction before and after irradiation were almost identical. This result suggests that the primary structure of the SET device, characterized by the conductance and the capacitance of the tunnel barrier, is not changed by photoirradiation. Instead it suggests that photoirradiation changes the position of the Coulomb diamond, that is, the potential of the Coulomb island.

Figure 4 shows a schematic illustration of the mechanism of the observed abrupt change in current. The electron can tunnel from the source electrode to the drain electrode when the potential of the Coulomb island is between the Fermi energies of the source (μ_S) and drain (μ_D) electrodes [Fig. 4(a)]. When the applied source-drain voltage V_{SD} is lower than the threshold voltage of Coulomb blockade effect V_{Th}, no current is observed. When the potential of the Coulomb island is changed by photoirradiation, V_{Th} is also

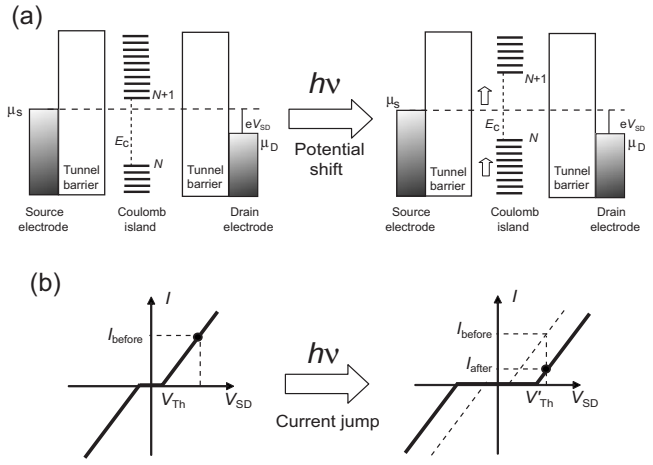

FIG. 4. Schematic illustration of the shift in potential of the Coulomb island. (a) The energy diagram before and after irradiation. (b) The I-V curve before and after irradiation.

shifted. When the V_{Th} is shifted to higher voltage, the downward current change should be observed in the real-time current profile. In the case of the shift of V_{Th} to lower voltage, the current change should be upward. Both cases were observed in this experiment [Fig. 4(b)].

The same experiment was performed for the junctions that did not show significant dependence on the gate voltage, that is, did not show the SET property, for example, because of larger sizes of the nanostructure in the gap. The amplitude and frequency of the abrupt change in current were much smaller than observed for the junction exhibiting significant dependence on the gate voltage. The electrode which shows strong dependence on the gate voltage exhibits photoresponsive behavior.

The experiment investigating the dependence of the abrupt change in current on the wavelength of irradiation revealed that the phenomenon originates not from the plasmon excitation of gold nanoparticles but from a change in the oligothiophene molecule. The discontinuity of the change in current means that the possibility that the photoexcitation of the SiO_2/Si structure causes the change in current can be excluded.[12] It was also found that the conductance and the capacitance of the tunnel barrier were not changed upon photoirradiation. This suggests that the "bridging" molecules [Fig. 1(b)] that exist between the electrode and the gold nanoparticle remain unchanged by UV light. In fact, significant quenching of the excited state is anticipated for the "bridging" molecules because of the surface plasmon resonance of the gold surface.[13]

In this experiment there were also "open-ended" molecules [Fig. 1(b)], which are connected to the gold nanoparticle by a single thiol group. The conductance of the "open-ended" molecule has little direct effect on the conductance of the junction, but structural changes of the "open-ended" molecule can perturb the potential of the gold nanoparticle. Because the conductance of the junction showed almost no change under photoirradiation, a structural change of the "open-ended" molecule should be the origin of the abrupt change in current. We believe that the abrupt current change was attributed to some reversible change of an individual molecule because the change was observed continuously for a long period. One plausible candidate is the change of the polarization originating from the conformational change.[14]

In summary, we studied the photoresponsive conductive properties of a gold nanoparticle-oligothiophene network in the nanogap electrode. The nanostructured junctions showed Coulomb blockade-type I-V_{SD} curves at cryogenic temperatures. These junctions showed clear dependence on the gate voltage and exhibited SET behavior. When a junction was irradiated with UV light, it showed digital-type changes in current under a constant applied voltage. The I-V_{SD} curves and the differential conductance mapping before and after irradiation showed that the mechanism of the abrupt change in current can be explained by a shift in potential of the Coulomb island. The change in potential of the Coulomb island was attributed to the photoinduced change of an "open-ended" oligothiophene molecule on the gold nanoparticle at a single molecule level.

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