

# Tunneling resistance of double-barrier tunneling structures with an alkanethiol-protected Au nanoparticle

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(Received 22 November 2004; revised manuscript received 6 September 2005; published 29 November 2005)

Coulomb staircases in double-barrier tunneling junctions consisting of a scanning-probe–vacuum-gap–alkanethiol-protected Au nanoparticle/Au (111) electrode have been measured as a function of the set point current of scanning tunneling spectroscopy. The tunneling resistances of the scanning probe–Au core of a nanoparticle ( $R_1$ ) and the Au core–Au (111) electrode ( $R_2$ ) are evaluated by fitting a theoretical Coulomb staircase into the experimental tunneling current–voltage characteristics measured by scanning tunneling spectroscopy. When a vacuum gap exists between the scanning probe and alkanethiol Au nanoparticles,  $R_1$  is inversely proportional to the set point current. On the contrary, in the case of  $R_1 < R_2$ , the top of the tip of the scanning probe tends to penetrate the octanethiol-protecting molecule of an Au nanoparticle.  $R_2$  is found to be independent of the set point current, and  $R_2$  of octanethiol- and hexanethiol-protected Au nanoparticles are evaluated as  $7.6 \text{ G}\Omega \pm 10\%$  and  $460 \text{ M}\Omega \pm 10\%$ , respectively.

DOI: [10.1103/PhysRevB.72.205441](https://doi.org/10.1103/PhysRevB.72.205441)

PACS number(s): 73.23.Hk, 81.07.–b, 07.79.Cz

## I. INTRODUCTION

Over the last few years, nanomechanical single electron systems have attracted significant fundamental and technological interests for applications in nanoelectronic devices.<sup>1–8</sup> In 1998, Gorelik *et al.* proposed the electron shuttle model based on nanomechanical double-barrier tunneling junctions (DBTJs), in which the polarity of a number of electrons on the Coulomb island can be controlled by the two tunneling resistances between the Coulomb island and two reservoirs.<sup>4</sup> In the DBTJ structure, single electron shuttle phenomena based on the self-excitation process will be observed if the Coulomb island can be vibrated by the charges on the island and the tunneling resistance ratio  $R_1/R_2$  of the two junctions inverses due to the nanomechanical vibration. The design of the tunneling resistances in the nanomechanical single electron system is one of the most basic and important objectives to realize the single electron shuttle with self-excitation.

Only a few instances of electromechanical couplings have been experimentally reported in the studies of single electron systems.<sup>5,9,10</sup> Recently, we have demonstrated the electron shuttle motion by measuring the displacement and tunneling currents in nanomechanical DBTJs using a scanning vibrating probe.<sup>11–16</sup> However, it is still a challenge to fabricate a nanomechanical single electron system with self-excitation and to demonstrate the self-excited single electron shuttle motion experimentally.

Metallic nanoparticles protected by monolayer organic molecules have a wide range of applications as potential electronic components in nanoelectronic devices.<sup>17,18</sup>

Alkanethiol-protected Au nanoparticles are one of the most fundamental capped nanoparticles,<sup>19,20</sup> in which the alkanethiol-protecting molecule can behave as a part of the tunneling barrier having mechanical flexibility.

The transconductance of the alkanethiol molecule have been studied by several methods, such as a Hg junction, a solid metal–insulator–metal junction, conductive contact atomic force microscopy, an electrochemical method, and scanning tunneling microscopy (STM).<sup>21–27</sup> The tunneling resistance of a two-layer tunnel junction, consisting of a vacuum and an alkanethiol self-assembled monolayer (SAM), has been reported.<sup>23,28</sup> The tuning of tunneling resistances and capacitances of DBTJs consisting of a STM–probe–vacuum–alkanethiol-protected Au nanoparticle–SAM–Au (111) substrate has also been performed by adjusting the STM set point current.<sup>27</sup> It should be noted that the tunneling resistances between the Au (111) substrate and the Au core of the alkanethiol-protected Au nanoparticles can be controlled by changing the length of alkanethiol. However, more detailed experiments are required to design the structure in a subnanometer scale in order to realize the electron shuttle with self-excitation.

In this paper, we demonstrate Coulomb staircases in the current–voltage characteristics of the DBTJ structures consisting of a scanning-probe–vacuum–alkanethiol-protected Au nanoparticle–Au (111) substrate by changing the set point current of scanning tunneling spectroscopy (STS). Theoretical Coulomb staircase curves have been fitted into the experimental results by introducing the full “orthodox” theory.<sup>2,29,30</sup> Two parameters were mainly evaluated, namely,

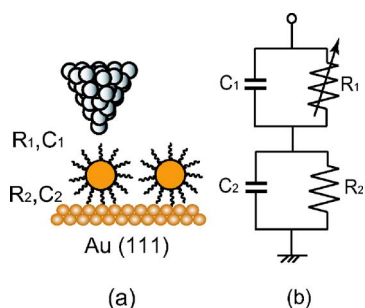


FIG. 1. (Color online) (a) Schematic drawing and (b) equivalent circuit of the nanomechanical double-barrier tunneling structure.

the tunneling resistance of the junctions  $R_1$  between the probe and the Au core of the nanoparticle and the resistance  $R_2$  between the Au core of the nanoparticle and the Au(111) substrate. The tunneling resistance ratios ( $R_1/R_2$ ) of octanethiol (C8S)-protected and hexanethiol (C6S)-protected Au nanoparticles are discussed on the basis of the set point current.

### II. EXPERIMENTAL

The synthesis of alkanethiol-protected Au nanoparticles is described elsewhere.<sup>19,31</sup> The diameters of C8S- and C6S-protected Au cores are controlled and estimated as approximately  $2.4 \pm 0.5$  nm and  $2.1 \pm 0.5$  nm, respectively, from a transmission electron microscopy (TEM) image. The lengths of protecting molecules are estimated as 1.44 and 1.18 nm for C8S and C6S, respectively.<sup>32</sup> As a result, the entire diameters of nanoparticles including the protecting alkanethiols and the Au core are estimated to be  $5.3 \pm 0.5$  and  $4.8 \pm 0.5$  nm for C8S- and C6S-protected Au nanoparticles, respectively. The dielectric constant of alkanethiol has been reported as 2.6.<sup>33,34</sup>

The Au substrate is prepared on cleaved mica by a vacuum evaporation method. After the evaporation, the Au substrate is heated at 450 °C for 6~7 h to form an atomically flat Au (111) surface. Droplets of toluene solution containing C8S- and C6S-protected Au nanoparticles are spread on the Au (111)/mica substrate, and the solution is allowed to evaporate at room temperature.

The tunneling current-voltage characteristics are measured by the ultrahigh vacuum (UHV) low-temperature STM (Unisoku, USM-501) at 68 K. Figure 1 illustrates the idealized geometry and equivalent circuit of the nanomechanical DBTJ described in our work, which consists of an STM-probe-vacuum-alkanethiol-Au nanoparticle-Au (111) substrate. When a vacuum gap exists between the top of the STM probe and alkanethiol-protected Au nanoparticle, the tunneling resistance  $R_1$  between the probe and the nanoparticle can be varied by adjusting the set point current, while the resistance  $R_2$  between the nanoparticle and the Au(111) substrate depends on the alkanethiol-protecting molecule. In this paper, the set point current  $I_{set}$  is defined as the tunneling current at a bias voltage of  $-2$  V and is varied from 1 to 800 pA.

### III. RESULTS

Figures 2(a) and 2(b) show the STM images of C8S- and C6S-protected Au nanoparticles on the Au (111) surface at a

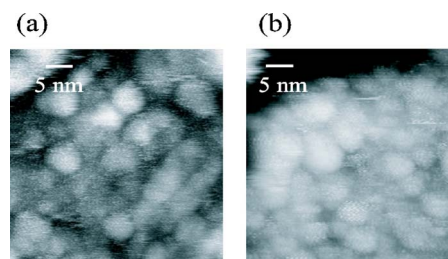


FIG. 2. (Color online) STM images of (a) C8S-protected and (b) C6S-protected Au nanoparticles on Au(111) substrates at a set point current of 3 pA and a probe bias voltage of  $-2$  V. Scan size is  $40$  nm  $\times$   $40$  nm.

set point current of 3 pA and a probe voltage of  $-2$  V. The packing structure of nanoparticles is observed in these images. In the case of both C8S-protected [Fig. 2(a)] and C6S-protected [Fig. 2(b)] Au nanoparticles, the typical diameter of a single nanoparticle in the STM images is approximately 4–5 nm, which corresponds to the entire size of a nanoparticle including the Au core and alkanethiol molecules. The diameters in the STM image are in good agreement with the estimated diameters of  $5.3 \pm 0.5$  and  $4.8 \pm 0.5$  nm for the C8S- and C6S-protected Au nanoparticles, respectively.

Figure 3 shows the normalized capacitance  $C/4\pi\epsilon r$  as a function of the normalized distance ( $x/r$ ) in a mirror image point-charge model of a charged sphere (radius  $r$ ) at the distance  $x$  below a conducting plate.<sup>12,35</sup> It should be noted that the capacitance  $C$  is proportional to  $4\pi\epsilon r$  that is equal to the capacitance of the sphere with the radius  $r$  in a free space.  $C$  decreases with increasing the distance  $x$ .

According to the full “orthodox” theory for the two junction system, the tunneling rate for the  $j$ th junction  $\Gamma_j^\pm(n)$ , where the  $\pm$  refers to the forward or reverse tunneling process across the junctions ( $n \rightarrow n \pm 1$ ), can be obtained from a basic golden-rule calculation.<sup>29,30</sup>

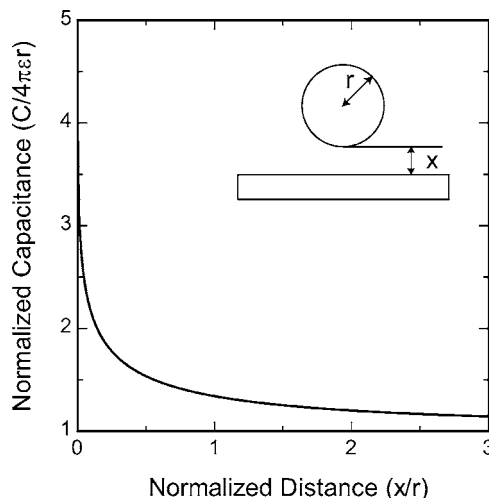


FIG. 3. Theoretical normalized capacitance  $C/4\pi\epsilon r$  as a function of the normalized distance ( $x/r$ ) in a mirror image point-charge model of a charged sphere (radius  $r$ ) at the distance  $x$  below a conducting plate.

$$\Gamma_j^\pm(n) = \frac{1}{R_j e^2} \left( \frac{-\Delta E_j^\pm}{1 - \exp(\Delta E_j^\pm/k_B T)} \right), \quad (1)$$

where  $\Delta E_j^\pm$  is the energy change of the system when the electron tunnels across the barrier.  $\Gamma_j^\pm(n)$  is inversely proportional to the tunneling resistance. The equations for  $\Delta E_j^\pm$  are obtained from electrostatic energy considerations ( $e > 0$ ).

$$\Delta E_1^\pm = \frac{e}{C_1 + C_2} \left( \frac{e}{2} \pm (ne - Q_0) \mp C_2 V \right), \quad (2)$$

$$\Delta E_2^\pm = \frac{e}{C_1 + C_2} \left( \frac{e}{2} \pm (ne - Q_0) \pm C_1 V \right),$$

where  $C_1$  is the capacitance between the probe and the Au core of the nanoparticle,  $C_2$  is the capacitance between the Au core of the nanoparticle and the Au(111) substrate, and  $Q_0$  is the fractional residual charge ( $|Q_0| \leq e/2$ ). Then the ensemble distribution of the number of electrons on the nanoparticle  $\sigma(n)$  is obtained by noting that the net probability for making a transition between any two adjacent states in steady state is zero as

$$\sigma(n)[\Gamma_1^+(n) + \Gamma_2^+(n)] = \sigma(n+1)[\Gamma_1^-(n+1) + \Gamma_2^-(n+1)]. \quad (3)$$

Since  $\Gamma_j^\pm$  are known from Eqs. (1) and (2),  $\sigma(n)$  can be solved by subjecting to the normalization condition  $\sum_{n=-\infty}^{\infty} \sigma(n) = 1$ . Tunneling current is then given by

$$\begin{aligned} I(V) &= e \sum_{n=-\infty}^{\infty} n \sigma(n) [\Gamma_2^-(n) - \Gamma_2^+(n)] \\ &= e \sum_{n=-\infty}^{\infty} n \sigma(n) [\Gamma_1^+(n) - \Gamma_1^-(n)]. \end{aligned} \quad (4)$$

As a consequence, the theoretical  $I(V)$ - $V$  curves can be numerically obtained.

Figure 4 shows typical theoretical normalized tunneling current  $[I(V)R_1]$ -probe bias voltage  $V$  dependence for various tunneling ratios  $R_1/R_2$  in the range from 1 to 1000 with  $R_2 = 10 \text{ G}\Omega$ ,  $C_1 = 0.18 \text{ aF}$ ,  $C_2 = 0.20 \text{ aF}$ , and  $Q_0 = 0.1e$  at 68 K. The theoretical  $I(V)R_1$  curves show the Coulomb staircase and the conductance quantization gradually disappears on decreasing the ratio  $R_1/R_2$ . The value of the tunneling resistances of  $R_1$  and  $R_2$  are explained as follows. In the case of  $1 < R_1/R_2 < 50$ , the shape of the theoretical normalized tunneling current  $I(V)R_1$  curves strongly depend on the ratio  $R_1/R_2$  especially in the probe voltage range between the onset of the first Coulomb step at the positive and the negative probe voltages. On the contrary, as the ratio  $R_1/R_2$  is larger than 50 ( $R_1 \gg R_2$ ),  $I(V)R_1$  curves show clear the Coulomb staircase and become independent of  $R_1/R_2$ . It should be noted that the slope of a tangential line of theoretical  $I(V)R_1 - V$  curve tends to be proportional to  $R_1/(R_1 + R_2)$  due to the Ohm's law. As a result, the total tunneling resistance of  $R_1 + R_2$  can be estimated by the reciprocal value of the tangential line. The ratio of  $R_1/R_2$  is discussed in detail in the next section.

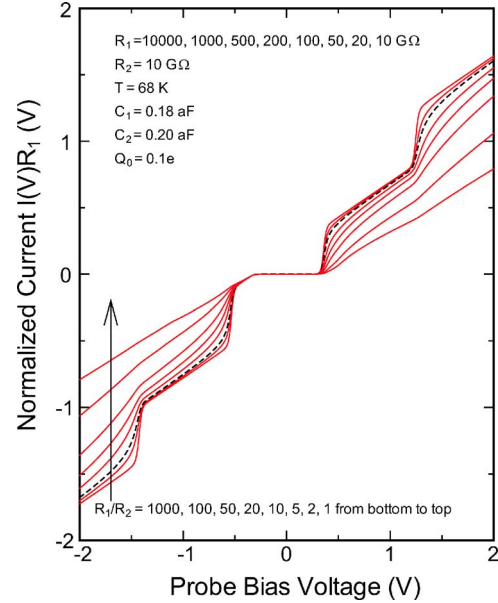


FIG. 4. (Color online) Theoretical normalized  $I(V)R_1$  curves as a function of the tunneling resistance ratio  $R_1/R_2$  where  $R_1/R_2$  are 1000, 100, 50, 20, 10, 5, 2, 1, assuming  $R_2 = 10 \text{ G}\Omega$ ,  $C_1 = 0.18 \text{ aF}$ ,  $C_2 = 0.20 \text{ aF}$ , and  $Q_0 = 0.1e$  at 68 K.

Figures 5 show typical experimental Coulomb staircases (solid lines) for C8S-protected Au nanoparticles [Figs. 5(a)–5(c)] at the set point currents of 6, 15, and 300 pA, and for C6S-protected Au nanoparticles [Figs. 5(d) and 5(e)] at the set point currents of 15 and 400 pA, respectively. Considering the small set point current such as 6 and 15 pA, clear Coulomb staircases have been observed for all the measurements. It should be noted that when the probe voltage becomes higher than  $\pm 1.5 \text{ V}$ , the tunneling currents tend to increase steeply and deviate from the theoretical curves, suggesting a change in the tunneling process from direct tunneling to Fowler-Nordheim (FN) tunneling.<sup>25</sup>

#### IV. DISCUSSIONS

In this section, we discuss the possibility of independently controlling the tunneling resistances  $R_1$  and  $R_2$  toward the design of the nanomechanical DBTJ on the basis of a decay constant and an effective contact area. As shown in Fig. 4, the total tunneling resistance of  $R_1 + R_2$  can be estimated from the tangential line of the experimental Coulomb staircase, however, the estimation of individual value of  $R_1$  and  $R_2$  should require the consideration of the values of  $C_1$ ,  $C_2$ , and  $Q_0$ . As the Au nanoparticles are protected by octanethiol C8S or hexanethiol C6S,  $C_1$  should become smaller than  $C_2$  when there exists a vacuum gap between the tip and the nanoparticle.

As a result, the distance of a vacuum gap between the tip and the nanoparticle ( $d_{\text{gap}}$ ) is important to decide  $C_1$  and  $C_2$ . Bumm *et al.* have estimated the transconductance of the alkanethiol molecule by the STM image of the mixed composition of SAM<sup>28</sup> and dodecanethiol on Au(111).<sup>23</sup> They introduced the two-layer tunnel junction model that composed of

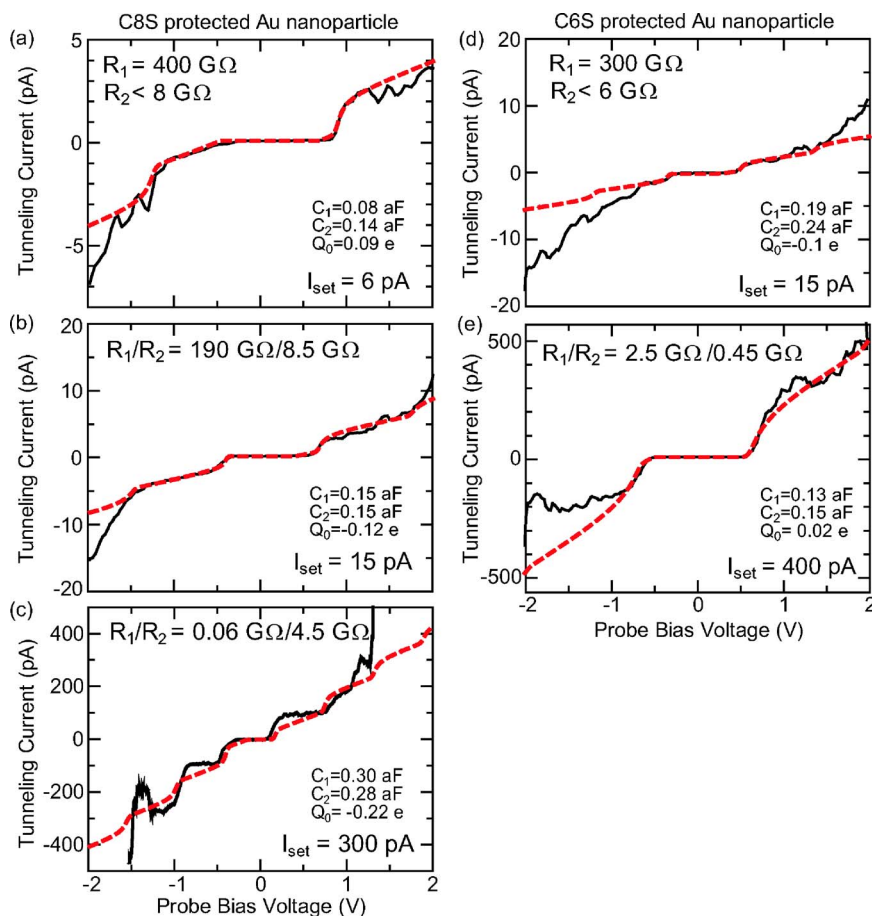


FIG. 5. (Color online) Typical Coulomb staircases of tunneling current versus voltage (solid line) at set point currents of (a) 6 pA, (b) 15 pA, and (c) 300 pA for C8S-protected Au nanoparticles; and (d) 15 pA and (e) 400 pA for C6S-protected Au nanoparticle, respectively. Dashed lines represent the theoretical curves. The  $I$ - $V$  curves of (a), (b), and (c) are obtained from different C8S-protected Au nanoparticles of the same sample, and those of (d) and (e) are obtained from different C6S-protected Au nanoparticles of the other sample.

two distinct layers of the alkanethiol SAM and a vacuum gap, and suggested the decay constant of the alkanethiol SAM as  $1.2 \text{ \AA}^{-1}$  which corresponds that the transconductance of the decanethiol SAM is one order higher than that of the dodecanethiol SAM. We have also reported the direct measurements of the tunneling resistances of octanethiol (C8S) and hexanethiol (C6S) SAMs on Au (111) substrate by the tunneling current ( $I$ ) distance ( $d$ ) dependence between the STM probe and alkanethiol SAMs on the Au (111) substrate. The decay constant of the alkanethiol SAMs ( $\alpha$ ) and a vacuum ( $\beta$ ) are estimated as  $1.2 \text{ \AA}^{-1}$  and  $2.0 \text{ \AA}^{-1}$ , respectively, at a probe voltage of  $-2 \text{ V}$ ,<sup>28</sup> suggesting good agreement with the hypothetical results of Bumm *et al.*

Assuming that the transresistance between the tip and the Au core of the nanoparticle is obtained based on the two-layer junction model of the tip/vacuum/alkanethiol SAM/Au(111) substrate, the transresistance between the tip and the Au (111) substrate is given by  $R = R_0 \exp(\beta d_{\text{gap}})$ , where the prefactor  $R_0$  is respective contact resistance. For example,  $R$  becomes  $1000R_0$ , when there exists a vacuum gap of  $d_{\text{gap}} = 0.35 \text{ nm}$  under the decay constant of  $\beta = 2.0 \text{ \AA}^{-1}$ .

Considering the radius  $r$  of Au cores ( $1.2 \pm 0.3 \text{ nm}$  and  $1.1 \pm 0.3 \text{ nm}$  for C8S and C6S), the lengths of protecting molecules (1.44 and 1.18 nm for C8S and C6S), and the dielectric constant of the alkanethiol (2.6), the change in  $C$  due to the vacuum gap should be small. For example, as shown in Fig. 3, the value of  $C$  decreases only 15% from  $x = 1$  to 3 nm under the diameter of 2 nm ( $r = 1 \text{ nm}$ ).

In the case of  $R_1/R_2 > 1$ , the capacitance  $C_1$  can be obtained by the Coulomb step in the current at equal voltage spacing of  $e/C_1$ . As discussed above, the value of  $C_2$  should become in the range between  $C_1$  and  $1.2C_1$ . The fractional residual charge  $Q_0$  may either vanish or offset the Coulomb blockade. It should be noted that  $Q_0$  is extremely sensitive to changes in the electrostatic environment such as electron tunneling to the neighboring Au nanoparticles.<sup>36</sup> As shown in Fig. 4, the zero-current region depends on  $C_1$ ,  $C_2$ , and  $Q_0$ , however, not on  $R_1/R_2$ . On the other hand, as the shape of the first Coulomb step directly depends on the ratio  $R_1/R_2$ , both  $R_1$  and  $R_2$  can be estimated individually. Consequently, the fitting procedure is applied to the probe voltage range between the onset of the first Coulomb step at the positive and the negative probe voltages to avoid the charging effect to the neighboring Au nanoparticles, and the fitting parameters of  $R_1$ ,  $R_2$ ,  $C_1$ ,  $C_2$ , and  $Q_0$  are obtained. In Figs. 5, the dashed lines represent the theoretical curves obtained by the fitting procedure. The theoretical curves are in good agreement with the experimental results of the probe voltage range of the onset of the first Coulomb steps. It should be noted that  $R_2$  cannot be estimated as a unique value in the case of  $R_1/R_2 \geq 50$ , since the shape of  $I(V)R_1$  curves are independent of the ratio  $R_1/R_2$  around the onset of the first Coulomb steps. In the case of  $R_1/R_2 < 1$ , the same fitting procedure can be applied by exchanging the subscripts 1 and 2 of the resistances and capacitances.

Figures 6(a) and 6(b) show the set point current ( $I_{\text{set}}$ ) dependence of  $R_1$  and  $R_2$ , respectively, which are evaluated by



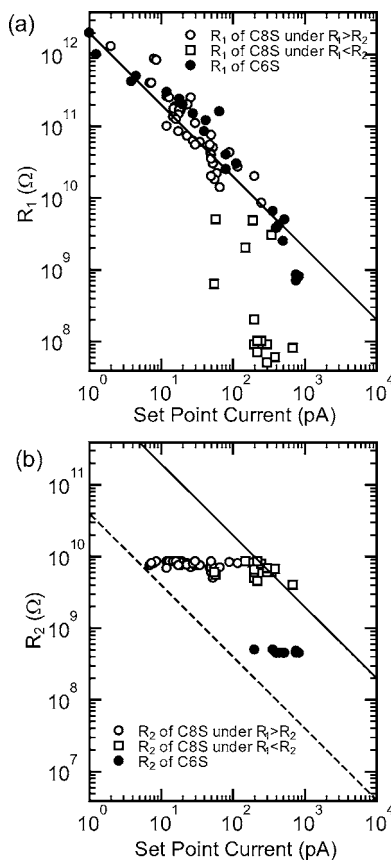


FIG. 6. Set point current dependence of tunneling resistances (a)  $R_1$  and (b)  $R_2$  for C8S- and C6S-protected Au nanoparticles. Open circles represent C8S-protected Au nanoparticle in the region of  $R_1 > R_2$ , open squares represent C8S-protected Au nanoparticles in the region of  $R_1 < R_2$ , and closed circles represent C6S-protected Au nanoparticles. (a) Solid lines indicate the power law of  $R_1 \propto I_{\text{set}}^{-1}$  under  $I_{\text{set}}R_1 = -2$  V as  $V_{\text{set}} = -2$  V. In (b), the solid and the dashed lines show the power law relationship of  $I_{\text{set}}R_1 = -2$  V and  $I_{\text{set}}R_2 = -0.04$  V ( $R_1/R_2 = 50$ ), respectively. The values of  $R_2$  estimated in the area above the dashed line are shown in (b). The average values of  $R_2$  for C8S- and C6-protected Au nanoparticles are  $7.6 \text{ G}\Omega \pm 10\%$  and  $460 \text{ M}\Omega \pm 10\%$  with the core sizes of  $\sim 2.4$  nm and  $\sim 2.1$  nm, respectively.

fitting the theoretical curves into the experimental Coulomb staircases. It should be noted that the fitting parameters of C8S and C6S data are estimated from the collections of  $I(V)$ - $V$  curves obtained from different nanoparticles on the same C8S and C6S samples, respectively. In Figs. 6(a) and 6(b),  $R_1$  of C8S-protected Au nanoparticles can be classified into two ranges  $R_1 > R_2$  and  $R_1 < R_2$ . On the other hand, the tunneling resistances of C6S-protected Au nanoparticles are always  $R_1 > R_2$  in the set point current range between 1 and 800 pA. When  $R_1$  dominates the total resistance,  $R_1$  should be inversely proportional to the set point current in the range of  $R_1 > R_2$ . The solid line in Fig. 6(a) shows the power law of  $R_1 \propto I_{\text{set}}^{-1}$  under the set point current measurement condition of  $I_{\text{set}}R_1 = -2$  V as the set point probe voltage  $V_{\text{set}}$  of  $-2$  V. It should be noted that the evaluated results of  $I_{\text{set}}$  dependence of  $R_1$  are in good agreement with the power law for both C8S- and C6S-protected Au nanoparticles. In Fig. 6(b), the

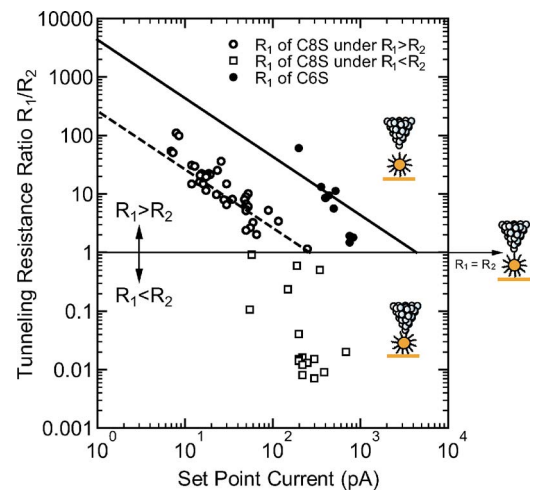


FIG. 7. (Color online) Set point current dependence of tunneling resistance ratio  $R_1/R_2$ . Open circles represent C8S-protected Au nanoparticles in the region of  $R_1 > R_2$ , open squares represent C8S-protected Au nanoparticle in the region of  $R_1 < R_2$ , and closed circle represent C6S-protected Au nanoparticle. The dashed and solid lines show the power law relationship of  $I_{\text{set}}R_1/R_2 = -260$  pA ( $=V_{\text{set}}/R_2 = -2$  V/ $7.6 \text{ G}\Omega$ ) and  $I_{\text{set}}R_1/R_2 = -4.3$  nA ( $=V_{\text{set}}/R_2 = -2$  V/ $460 \text{ M}\Omega$ ) for C8S- and C6S-protected Au nanoparticles, respectively. The insets provide the schematic DBTJ structures corresponding to the values of  $R_1/R_2$ .

solid and the dashed lines show the power law relationship of  $I_{\text{set}}R_1 = -2$  V [as the same in Fig. 6(a)] and  $I_{\text{set}}R_2 = -0.04$  V ( $R_1/R_2 = 50$ ), respectively. If the value of  $R_2$  is placed on the dashed line,  $R_1/R_2$  becomes 50. As shown in Fig. 4,  $I(V)$  curves are independent of  $R_1/R_2$  in the case of  $R_1/R_2 > 50$ . As a result,  $R_2$  can be obtained in the area above the dashed line in Fig. 6(b).  $R_2$  of C8S-protected and C6S-protected Au nanoparticles under the ratio range of  $1 < R_1/R_2 < 50$  are found to have constant values of  $7.6 \text{ G}\Omega \pm 10\%$  and  $460 \text{ M}\Omega \pm 10\%$ , respectively.

Figure 7 shows the set point current dependence of the tunneling resistance ratio ( $R_1/R_2$ ) for C8S- and C6S-protected Au nanoparticles. The dashed and solid lines show the power law relationship of  $I_{\text{set}}R_1/R_2 = -260$  pA ( $=V_{\text{set}}/R_2 = -2$  V/ $7.6 \text{ G}\Omega$ ) and  $I_{\text{set}}R_1/R_2 = -4.3$  nA ( $=V_{\text{set}}/R_2 = -2$  V/ $460 \text{ M}\Omega$ ) for C8S- and C6S-protected Au nanoparticles, respectively. As shown in Figs. 6(a) and 6(b), the tunneling resistance ratio ( $R_1/R_2$ ) is also separated into two regions by the boundary value of  $R_1/R_2 = 1$ . According to the DBTJ structure in Fig. 1, this boundary value suggests a symmetric structure, i.e., the probe is just in contact with the end group of the alkanethiol-protecting molecule.

As the resistance tends to depend on the area of the tunneling junction, it is important to take into account the effective contact area. Wang *et al.* have estimated a resistance between a heptanethiol-protected Au nanoparticle and Au(111) consisting of an Au-core-heptanethiol-protecting-molecule-decanethiol SAM/Au(111).<sup>27</sup> They suggested the resistance as  $69 \text{ M}\Omega$  with the core size of  $\sim 15$  nm. We find that  $R_2$  is independent of the set point current and nanoparticles in the region of  $R_1/R_2 > 1$ , and the average  $R_2$  values of C8S- and C6S-protected Au nanoparticles are estimated as

7.6 G $\Omega$  and 460 M $\Omega$  with the core sizes of  $\sim 2.4$  and  $\sim 2.1$  nm as shown in Fig. 6(b), respectively. The average  $R_2$  value of C8S is almost one order of magnitude higher than that of C6S, and the  $R_2$  errors of C8S and C6S are within  $\pm 10\%$ . It should be noted that the  $R_2$  values of the protecting molecules of C8S and C6S are the same orders with the tunneling resistances of C8S and C6S SAMs which values were measured by the tunneling current ( $I$ )-distance ( $d$ ) dependence.<sup>28</sup> Comparing the values of  $R_2$  in this paper with the resistance in Wang's paper,<sup>27</sup> the effective contact area should be found to strongly depend on the core size. As a consequence, in the case of the Au core diameter of approximately 2 nm, the tunneling resistance between the Au core and the Au(111) substrate tends to become almost same value of the individual alkanethiol molecules in SAM on Au(111) and can be controlled by the length of the alkanethiol-protecting group in the Au nanoparticle.

Since the tunneling resistance  $R_2$  between the Au core and Au (111) substrate is independent of the set point current, the tunneling resistance ratio  $R_1/R_2$  is also inversely proportional to the set point current  $I_{\text{set}}$  for both C6S-Au and C8S-Au nanoparticles in the region of  $R_1/R_2 > 1$ , as shown in Fig. 7. At the same value of  $I_{\text{set}}$ , it is found that the approximately one order of difference in  $R_1/R_2$  between the C8S- and C6S-protected Au nanoparticles is completely due to the difference in  $R_2$  between the octanethiol- and hexanethiol-protecting molecules.

As shown in Fig. 6(a), the value of  $R_1$  for C8S-protected Au nanoparticles tends to steeply decrease by several orders of magnitude within the set point current  $I_{\text{set}}$  range of 50  $\sim$  700 pA. On the contrary, the value of  $R_2$  tends to remain constant in the range of  $R_1 < R_2$  [Fig. 6(b)]. As a result, the top of the tip of the scanning probe should penetrate the C8S-protecting molecule of Au nanoparticles; however, the distance between the Au core and the Au(111) substrate is still maintained to a large extent by C8S-protecting molecules, as illustrated in Fig. 7. On the other hand, in the case of the C6S-protected Au nanoparticle, the tunneling resistance ratio  $R_1/R_2$  is always larger than 1;  $I_{\text{set}}$  is as high as 800 pA due to the small  $R_2$ .

In summary, the salient points for realizing the design of the nanomechanical DBTJ structures are as follows: the val-

ues of the tunneling resistances of the octanethiol- and hexanethiol-protecting molecules are 7.6 G $\Omega \pm 10\%$  and 460 M $\Omega \pm 10\%$  with the core sizes of  $\sim 2.4$  and  $\sim 2.1$  nm, respectively, which are of the same order as the individual octanethiol and hexanethiol molecules in SAMs on Au (111) substrates, respectively. The tunneling resistances of the alkanethiol-protecting molecule can increase by one order by using an alkanethiol having two extra methylene units in the case of the core diameter of approximately 2 nm. The top of the scanning probe tends to be in slight contact with the end group of the C8S- and C6S-protecting molecules at approximately 300 pA and 3 nA, respectively (Fig. 7). Considering the decay constants of a vacuum ( $2.0 \text{ \AA}^{-1}$ ) and alkanethiol ( $1.2 \text{ \AA}^{-1}$ ),<sup>28</sup> a vacuum gap between the probe and the alkanethiol-protecting molecule for the C6S-protected Au nanoparticle is only 0.1 nm longer than that for the C8S-protected Au nanoparticle at the same set point current. In the region of  $R_1/R_2 > 1$ ,  $R_1$  is inversely proportional to the set point current  $I_{\text{set}}$ . These results provide us with information that can be used to realize an electron shuttle with self-excitation.

## V. CONCLUSION

The tunneling resistances of the scanning probe-Au core of the nanoparticle ( $R_1$ ) and the Au core-Au (111) substrate ( $R_2$ ) have been investigated by fitting the theoretical Coulomb staircases into the experimental  $I$ - $V$  curves. The tunneling resistances of the octanethiol- and hexanethiol-protecting molecules have been evaluated as 7.6 G $\Omega \pm 10\%$  and 460 M $\Omega \pm 10\%$  with the core sizes of  $\sim 2.4$  and  $\sim 2.1$  nm, respectively, which indicates that  $R_2$  become the same order as the individual octanethiol and hexanethiol molecules in SAMs on Au(111) substrates and can be controlled by changing the length of the alkanethiol-protecting molecules. These results are significant for designing the nanomechanical DBTJ structure by using alkanethiol molecules.

## ACKNOWLEDGMENTS

This work is partially supported by the 21st Century COE Program, Photonics Nanodevice Integration Engineering by the Ministry of Education, Culture, Sports, Science and Technology (MEXT).

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