1. Introduction

Formation of a functional structure of a desired texture on the subnanometer scale is a primary concern in the design of nanodevices such as single-electron and molecular devices.\(^1\)\(^-\)\(^4\) A molecule-based chemical assembly technique is one of the candidate methods for realizing subnanometer-scale formation, as molecules have unique structures and can be used as building blocks.\(^4\)\(^-\)\(^5\) Despite their simple structures, alkane-thiols and alkanedithiols consisting of alkyl chains and thiols groups have been extensively studied in both electronics and photonics fields.\(^6\)\(^-\)\(^8\) It is well known that the thiol groups in these molecules can be chemically bonded onto the surfaces of metal electrodes. Further, their tunneling resistance depends on the chain lengths of the alkyl units; therefore, they are strong candidates for use as building blocks in nanodevices.\(^5\)\(^-\)\(^9\)\(^-\)\(^11\)

Single-electron transistors (SETs) have been studied extensively as prospective nanodevices because of their potential for low power consumption and high charge sensitivity.\(^12\)\(^-\)\(^18\) In SETs, a quantum dot is electrically connected to the two reservoirs of the source (S) and drain (D) electrodes as a Coulomb island, to form double-barrier tunneling junctions (DBTJs). The gate electrode is located near the Coulomb island to control the offset charge of the quantum dot using the gate voltage \(V_G\). The drain current \(I_D\) flows between the S and D electrodes by way of the Coulomb island. The drain current–drain voltage \((I_D-V_D)\) characteristics of the SETs involve the Coulomb blockade region, where the current flow is restricted even under the application of \(V_D\), and exhibit a Coulomb staircase profile. These characteristics are described by the orthodox model, that is governed by tunneling rates and master equations for DBTJs.\(^10\)\(^-\)\(^14\)\(^-\)\(^19\) The \(I_D-V_D\) characteristics can be calculated by considering the following five parameters: the capacitance between the source and the Coulomb island \(C_1\) and that between the Coulomb island and the drain \(C_2\), the tunneling resistance between the S electrode and the Coulomb island \(R_1\), and that between the Coulomb island and the D electrode \(R_2\), and the offset charge \(Q_0\).\(^10\)\(^-\)\(^19\)\(^-\)\(^21\) These five parameters can be evaluated by fitting the theoretical curves
obtained from the orthodox model to the experimental $I_D-V_D$ characteristics.$^{10,19}$ Over the past two decades, many SET structures have been realized, based on top-down silicon techniques and two-dimensional electron gases of GaAs-based materials, for example.$^{22-29}$ SETs have also been fabricated by combining top-down and bottom-up technologies.$^{30-39}$

Recently, we have demonstrated the fabrication processes for chemically assembled SETs consisting of electroless-Au-plated nanogap electrodes$^{40-42}$ covered by alkanethiol- and alkanedithiol-mixed self-assembled monolayers (SAMs),$^{8,10,43,44}$ with chemically anchored Au nanoparticles,$^{20,45-47}$ positioned between the nanogap electrodes. Chemically assembled SETs exhibit ideal and reproducible Coulomb diamonds,$^{48-50}$ uniform and controllable charging energy $E_C$,$^{48,51-53}$ discrete Au nanoparticle energy levels,$^{54}$ adoption of SiNx passivation,$^{55}$ and all the two-input logic operations.$^{56}$ The robustness of the chemically assembled SETs is extremely high, for instance, the gate voltage of $\pm 12$ V is available.$^{48}$ The structures of these SETs have been discussed in terms of the values of the five parameters determined from the experimental Coulomb diamonds. In particular, $C_1$ and $C_2$ have been found to be dependent on the diameter of the Coulomb island and to agree with a concentric sphere model.$^{51}$

On the other hand, $R_1$ and $R_2$ have been analyzed in a step-by-step manner as follows: in the case of a physisorbed Au nanoparticle on an Au electrode surface, the tunneling resistance between the Au core and the Au electrodes was found to be identical to that of a chemically bonded alkanethiol protecting molecule on an Au core surface using scanning tunneling spectroscopy (STS) measurements. These tunneling resistances were evaluated as 460 MΩ and 7.6 GΩ on hexanethiol (C6S) and octanethiol (C8S), respectively. This indicates an increase of one order of magnitude in the tunneling resistance with increasing alkyl chain length in a two-methylene group.$^{4,8,10,20,57,58}$ In the case of our SETs consisting of a decanethiol (C10S)-protected Au nanoparticle and electroless-Au-plated nanogap electrodes, the C10S-protected Au nanoparticles were chemisorbed by the use of the decanethiol (C10S2) anchor molecule in a C10S2/S8S mixed SAM on the surfaces of electroless-Au-plated nanogap electrodes. In the case of an Au nanoparticle single-side chemisorbed by a C10S2 anchor molecule, the typical resistance of the chemisorbed nanoparticles between the Au core and the Au(111) substrate was measured at 1.2 GΩ.$^{45}$ As reduction in the tunneling resistance is key to improving the SET signal-to-noise, it is important to attempt to shorten the chain length of the anchor molecule.

In this study, we demonstrate rhombic Coulomb diamonds on a chemically assembled SET consisting of a C10S-protected Au nanoparticle anchored by octanethiol (C8S2) between the electroless-Au-plated nanogap electrodes. The adsorption of the Au nanoparticle is discussed in terms of the values of resistances and capacitances of the DBTJs between the Au core and the S/D electrodes. The tunneling resistance ratio ($R_1/R_2$) dependence of the Coulomb diamond shapes is also discussed.

2. Results and discussion

Fig. 1(a) shows the equivalent circuit of a fabricated SET with two side-gate (G1 and G2) electrodes, while Fig. 1(b) is a scanning electron microscopy (SEM) image of the SET. A single

![Fig. 1](image-url)
bright spot can be confirmed between the S and D electrodes in the SEM image. Fig. 1(c) shows the candidate schematic diagram of the SET with the top view perspective. Chemical anchoring of the core of the Au nanoparticle between the electroless-Au-plated nanogap electrodes is discussed as follows. Fig. 2(a) shows the experimental \(I_D-V_D\) characteristics under the application of \(V_{G1}\) voltage \(V_{G1} = 0\) and 3.2 V, which correspond to the on and off states \((Q_0 = 0.5e \text{ and } 0)\) of the SET, respectively. The experimental \(I_D-V_D\) characteristics were fitted against theoretical curves,\(^{10,19}\) and agree with the theoretical curve obtained for the parameters \(R_1 = 4.5 \ \Omega, R_2 = 4.8 \ \Omega, C_1 = 1.4 \ \text{aF}, \text{ and } C_2 = 1.3 \ \text{aF}\). Note that \(R_1\) and \(R_2\), and \(C_1\) and \(C_2\), were almost equivalent.

Fig. 2(b) shows the experimental \(I_D-V_{G1}\) characteristics under the application of \(V_{D} = 14, 28, 42\) and 50 mV. Clear and stable Coulomb oscillations were observed. Theoretical curves were calculated using the same \(R_1, R_2, C_1,\) and \(C_2\) parameters as above, with the \(G1\) capacitance (\(C_{G1}\)) being 0.025 aF. The theoretical curves in Fig. 2(a) (dashed lines) also agree with the experimental results. In Fig. 2(b), the experimental \(I_D-V_{G1}\) characteristics were symmetric at the axis of \(V_{G1} = 0\). These symmetric Coulomb oscillations originated from the same \(R_1\) and \(R_2\).\(^{24}\)

Fig. 2  (a) Experimental \(I_D-V_D\) characteristics under applied \(V_{G1} = 0\) and 3.2 V at \(T = 9\) K. Theoretical \(I_D-V_D\) characteristics (dashed lines) are also shown. Here, \(Q_0 = 0.5e\) for \(V_{G1} = 0\) and \(Q_0 = 0\) for \(V_{G1} = 3.2\) V. (b) Experimental \(I_D-V_{G1}\) characteristics under applied \(V_{D} = 14, 28, 42,\) and 50 mV. The theoretical characteristics calculated for \(Q_0 = 0.5e\) are also shown. In (a) and (b), the common parameters for the theoretical calculation are: \(R_1 = 4.5 \ \Omega, R_2 = 4.8 \ \Omega, C_1 = 1.4 \ \text{aF}, \text{ and } C_2 = 1.3 \ \text{aF}, \text{ and } T = 9\) K.

Next, we consider the Coulomb oscillation dependence on \(R_1/R_2\). Fig. 3(a) shows the \(R_1/R_2\) ratio dependence of the theoretical \(I_D-V_{G1}\) curves under the application of \(V_{D} = 28\) mV, which was almost half the Coulomb-diamond peak voltage. The value of \(R_2\) was adjusted to yield \(R_1/R_2\) ratios within the 0.001-1000 range, with \(R_1 = 4.5 \ \Omega, C_1 = 1.4 \ \text{aF}, \text{ and } C_2 = 1.3 \ \text{aF}, \text{ and } C_{G1} = 0.025 \ \text{aF}\). \(I_D\) was normalized by the maximum current \(I_{\text{peak}}\). At \(R_1/R_2 = 1\), the symmetric Coulomb oscillation at the \(V_{G1} = 0\) axis was observed. In contrast, the \(I_D/I_{\text{peak}}\) peak voltages negatively and positively shifted under \(R_1 < R_2\) and \(R_1 > R_2\) conditions, respectively, however, the current rising and falling \(V_{G1}\) voltages did not change, as the Coulomb blockade break voltages are defined by \(C_1\) and \(C_2\).\(^{10,19}\) Fig. 3(b) shows the \(V_{G1}\) peak shift (\(\Delta V_{G1}\) illustrated in Fig. 3(a)) dependence on the \(R_1/R_2\) ratio under various \(V_{D}\). From this calculation, the large difference between \(R_1\) and \(R_2\) as well as the large \(V_{D}\) resulted in large \(\Delta V_{G1}\). The difference between \(R_1\) and \(R_2\) means that the adsorption condition of the Au nanoparticle between the S and D electrodes was asymmetric. Therefore, chemical anchoring of Au nanoparticles onto both the S and D electrodes resulted in symmetric \(I_D-V_{G1}\) characteristics.

Fig. 4(a) and (b) show the experimental stability diagrams obtained by plotting the color maps of \(dI_D/dV_D\) for the SET as functions of \(V_D\) and \(V_{G1}\) and \(V_D\) and \(V_{G2}\), respectively. In both the stability diagrams, clear and reproducible Coulomb diamonds can be observed. As indicated above, \(C_1, C_2, \text{ and } C_{G1}\) are also shown.
can be evaluated from the shape of the Coulomb diamonds.\textsuperscript{12}

From the boundary slopes of the diamonds and the gate voltage difference between neighboring diamonds, $C_1$, $C_2$, $C_{G1}$, and $C_{G2}$ were evaluated as 1.4, 1.3, 0.025 and 0.015 aF, respectively. The $C_1$ and $C_2$ values obtained from Fig. 4(a) and (b) agree with the values obtained from the theoretical fitting shown in Fig. 2(a). Note that the Coulomb diamond shapes are primarily determined by $C_1$, $C_2$, $C_{G1}$, and $C_{G2}$, as reported in a previous study.\textsuperscript{12} For the majority of the experimentally reported Coulomb diamonds, including those in our previous reports, the diamonds were parallelograms rather than rhombuses, because of differences between $C_1$ and $C_2$.\textsuperscript{48,49,54–56} In contrast, comparable $C_1$ and $C_2$ result in the almost rhombic diamond shapes apparent in Fig. 4(a) and (b).

Compared with the diamond shapes, the external regions of the Coulomb diamonds are also noteworthy. In our previous reports, the conductance peak lines along the edges of the Coulomb diamonds were extrapolated outside the diamonds.\textsuperscript{48,51,54,56} In contrast, the experimental Coulomb diamonds in Fig. 4(a) and (b) did not exhibit such extrapolated conductance peak lines. Besides the conductance peak lines, higher conduction regions were observed near the Coulomb diamond vertexes, such as $V_D = 0.07$ V and $V_{G1} = 3.2$ V in Fig. 4(a). This difference cannot be explained by consideration of the capacitance values.

Previously, we have measured the Coulomb staircases in DBTJs consisting of a scanning-probe/vacuum-gap/alkanethiol-protected Au nanoparticle/Au(111) electrode as a function of the set point current using scanning tunneling spectroscopy,\textsuperscript{10} demonstrating that the Coulomb staircase profiles depend on $R_1/R_2$. This result indicates that not only the Coulomb staircase profiles, but also those of the stability diagrams depend on the $R_1/R_2$ ratio. Fig. 5(a) shows the stability diagrams ($dI_d/dV_D$ plots) calculated for $R_1 = 4.5$ M$\Omega$, $R_2 = 4.8$ M$\Omega$, $C_1 = 1.4$ aF, $C_2 = 1.3$ aF, $C_{G1} = 0.025$ aF, and $Q_0 = 0.5$ e at a temperature ($T$) of 9 K. The theoretical stability diagram agrees with the experimental stability diagram shown in Fig. 4(a). Fig. 5(b) shows the...
distance, the comparable electrode. Due to these two di-equal to that between the Au core and the surface of the drain
seen. In contrast, here we used a C8S2/C6S mixed SAM to
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C10S2/C8S mixed SAM was used to anchor a C10S-protected
anchor a C10S-protected Au nanoparticle to reduce the tunnel-

Fig. 6 SEM images of Au nanoparticles anchored by C8S2 on the
C8S2/C6S mixed SAM/Au substrate. The Au nanoparticle solution immersion time was 12 h and the Au nanoparticle density was 88 per 100 × 100 nm².

3. Experimental
We used electron beam lithography and a lift-off process to fabricate the initial Ti (2 nm)/Au (10 nm) electrode patterns, comprising S, D, G1 and G2 electrodes on a SiO₂ (50 nm)/Si substrate. Prior to the electroless Au plating, the initial Au electrodes were cleaned using O₂ plasma treatment. Probing electrodes of 150 × 150 µm² area were then added via photolithography, and electroless plating in an Au iodine solution reduced the nanogap sizes via a self-termination reaction. The nanogap electrodes were immersed in a 1 mM hexanethiol [CH₃(CH₂)₅SH, C6S] solution in ethanol for 12 h to allow the formation of the C6S self-assembled monolayers (SAMs); the electrodes were then rinsed with ethanol twice. Subsequently, the sample was immersed in a 1 mM octanedithiol [HS(CH₂)₈SH, C8S2] solution in ethanol for 12 h to yield C8S2/C6S mixed SAMs. It was then rinsed with ethanol twice. After the substitution, the sample was immersed in a solution of decanethiol [CH₃(CH₂)₁₀SH, C10S]-protected Au nanoparticles with a core diameter of 6.2 ± 0.8 nm in toluene for 12 h. It was then rinsed with toluene twice. The electrical measurements were conducted using a semiconductor parameter analyzer (Agilent B1500, USA) in a vacuum (∼10⁻⁵ Pa) at 9 K (in a helium refrigerator, Nagase GRAIL10-LOGOS01S, Japan). The experimental differential conductances dI/dVₚ were numerically calculated based on the experimental Iₓ-Vₓ characteristics.
4. Conclusions

We have demonstrated rhombic Coulomb diamonds in a chemically anchored Au-nanoparticle SET consisting of a C10S-protected Au nanoparticle anchored by C8S2 molecules at both ends of an electroless-Au-plated nanogap. The $I_D$-$V_D$ characteristics showed Coulomb blockade phenomena and agree with the theoretical fitting curve calculated using the orthodox model. The evaluated $R_1$ and $R_2$ were almost identical, at 4.5 and 4.8 MΩ, respectively, and are attributed to the tunneling resistance of the chemisorbed octanethiol at both ends. The experimental stability diagram agreed with the theoretical calculation with $R_1$, $R_2$, $C_1$, and $C_2$ being evaluated from the $I_D$-$V_D$ characteristics. The changes in the stability diagrams for $R_1 \approx R_2$ (double-anchored Au nanoparticle), $R_1 > R_2$, and $R_1 > R_2$ (single-anchored Au nanoparticle) were discussed. In the stability diagrams, identical $R_1$ and $R_2$ did not yield extrapolated conductance peak lines. In contrast, different $R_1$ and $R_2$ corresponded to asymmetric adsorption, as indicated by the extrapolated conductance peak lines. The realization of a symmetric chemically anchored Au nanoparticle between S and D electrodes is significant, as it yields rhombic Coulomb diamonds.

Acknowledgements

We thank Ms M. Miyakawa for technical support regarding SEM. This study was partially supported by the MEXT Elements Strategy Initiative to Form Core Research Center of the Ministry of Education, Culture, Sports, Science, and Technology (MEXT) of Japan; JSPS KAKENHI (15K17483) [Y. Ariga], the Collaborative Research Project of the Materials and Structures Laboratory, Tokyo Institute of Technology; the Collaborative Research Project of the Institute of Chemical Research, Kyoto University (Grant 2015-72); and the BK Plus program, the Ministry of Education of Korea through the Basic Research Science Program (NRF-2014R1A6A1030419).

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