

Observation of a Coulomb staircase in electron transport through a molecularly linked chain of gold colloidal particles

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Submonolayer gold colloidal particles were deposited by using aminosilane [3-(2-aminoethylamino)propyltrimethoxysilane] as an adhesion agent on the substrate. It was observed that these submonolayer particles transform themselves into short chains of a few gold colloidal particles after a subsequent dithiol (1,6-hexanedithiol) treatment and an additional gold colloidal particle deposition. These chains bridged a gap that was formed between source and drain metal electrodes defined by electron beam lithography; thus realizing a quasi one dimensional current path between the source and drain. The device exhibited a clear Coulomb staircase at both 4.2 and 77 K. © 1997 American Institute of Physics. [S0003-6951(97)01520-9]

Single electronics, among quantum functional device concepts, provides the strongest motive for advancing nanofabrication technologies since the operating temperature of single electron devices is directly determined by the geometrical size of the electron localization. The progress of lithography technology guided by the miniturization of conventional electronic circuits fails to satisfy the requirements arising from single electronics; a requirement which extends to a size range of a few nanometers or less.¹

Several attempts have been made to advance lithography technology in the sub 10 nm size range in the context of single electron device fabrication.²⁻⁴ The use of metal and/or semiconductor clusters surrounded by a shell of organic ligands has been proposed as a building block of nanoscale architecture.⁵⁻⁹ Graber *et al.*⁹ investigated the self-assembling nature of a gold colloidal particle monolayer, and also proposed a strategy for controlling the interparticle distance of deposits on a glass substrate.

The application of cluster chemistry to single electron device fabrication was first demonstrated by Klein *et al.*¹⁰ They were successful in capturing a single cluster particle in a 5 nm gap in metal electrodes formed by the combination of electron beam lithography and the shadow evaporation of metal electrodes. By this configuration, they demonstrated that alkane chain molecules act as electron tunneling barriers while the cluster particle acts as an electron localization site. This approach depends on elaborate electron-beam lithography techniques, and does not fully utilize the self-assembling nature of cluster chemistry.

We report the electrical characteristics measurement of a self-assembled chain of gold colloidal particles connected to metal electrodes formed by electron beam lithography, through organic molecules. In this device configuration, the self-assembling nature of the gold particle chain helps overcome the size limitations of lithography, and the electron transport characteristics through the chain exhibit Coulomb blockade effect at elevated temperatures.

Gold colloidal particles with an average diameter of 10 nm were deposited on a thermally grown SiO₂ (200 nm thick) surface on a Si substrate on which the source and drain electrodes, with a 30 nm gap between them, were formed using electron-beam lithography. A plan view of the metal electrode patterns in the vicinity of the 30 nm gap is shown in Fig. 1(a). The electrodes were connected to bonding pads defined by photolithography.

The sample with the electrode patterns was cleaned by a brief (~30 s) oxygen plasma ashing. Immediately afterwards, the sample was immersed in a 2.3 mM aqueous solution of amino silane [i.e., 3-(2-aminoethy-

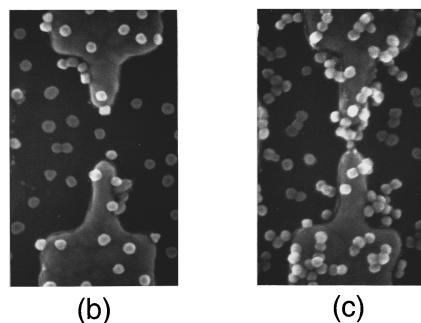
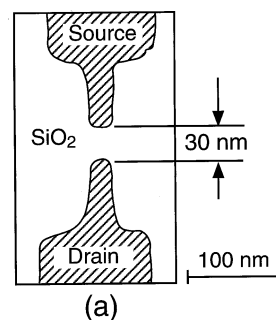


FIG. 1. (a) A plan view of the metal electrode patterns in the vicinity of a 30 nm gap formed by electron beam lithography and metal evaporation. (b) Submonolayer deposition of gold colloidal particles by aminosilane treatment. (c) The chaining of the gold colloidal particles by dithiol treatment.

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amino)propyltrimethoxysilane, APTMS,] for 5 min. After the APTMS immersion, the sample was rinsed in two distilled water baths, dried with a nitrogen gun, and placed in a 120 °C oven for 30 min to complete Si–O bond formation. The amino silane treatment replaces the hydroxyl groups (–OH) adsorbed on the SiO₂ substrate with APTMS molecules forming a siloxane bond between the Si on one end of the APTMS molecules and an oxygen atom on the SiO₂ surface. As a consequence, the amino group attached on the other end of the APTMS molecule is oriented away from the substrate. These amino groups on the APTMS molecules immobilize gold particles onto the substrate because of the affinity of the amino group to the gold.^{6,8,9} The silane coupler treated sample was then immersed in a gold colloidal particle (GCP) solution (viz., an aqueous solution of the GCPs with an average size of ~10 nm and a size variation of ~10% standard deviation) for 8–12 h, rinsed with two distilled water baths, and dried with a nitrogen gun. This procedure gave a submonolayer coating of the GCPs. The GCP solution used was a citrate sol prepared according to the recipe described in Ref. 11.

Figure 1(b) shows a scanning electron micrograph (SEM) of the submonolayer coated sample. The micrograph demonstrates that particles are separated; a commonly observed phenomenon in the gold particle immobilization process.^{6,8,9} Interparticle separation distances are explained by the presence of ionized adsorbates on the particle surfaces (viz., citrate ions for the citrate gold sols used in the present experiment),¹² which are created during the GCP synthesis process. Since immobilized particles on the substrate also retain their ionic charges due to the adsorbates having an electrostatic repulsive force between the particles, the GCP deposition automatically stops before it reaches to a close-packing density leaving interparticle distances of 10–50 nm. Only a few particle coagulations are observed in Fig. 1(b). Particle deposition with clear interparticle separation is one of the unique features of this method of introducing the particles on the substrate. As will be described in the following paragraphs, when a quasi one dimensional structure is needed, this feature is advantageous over other deposition methods such as spin coating,¹³ electrophoretics,¹⁴ etc., which end up with close-packed two-dimensional arrays.

After the submonolayer GCP coating, a dithiol treatment was carried out to induce the chaining of the gold colloidal particles. The sample was immersed in a 5 mM ethanolic solution of 1,6-hexanedithiol [SH–(CH₂)₆–SH] for ~24 h, and rinsed with two ethanol baths, and dried with the nitrogen gun. Immediately after the dithiol treatment, a second GCP immersion was carried out. The treatment replaces the ionic surface adsorbates with the dithiol molecules; more precisely, one of the two sulfur atoms on the dithiol forms a covalent bond with a gold atom on the surface of the immobilized GCPs deposited in the first GCP immersion, while the other sulfur atom on the other end of the alkane chain oriented away from the gold surface. Therefore, the immobilized GCP surfaces are terminated by the thiol groups prior to the second immersion in the GCP solution.

The effect of such dithiol replacement is twofold. First, the immobilized particles deposited in the previous GCP solution immersion do not hold ionic charges any more be-

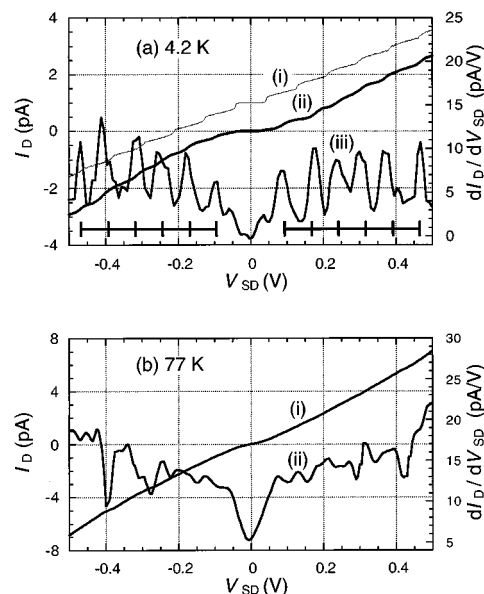


FIG. 2. (a) Results of an electrical measurement at 4.2 K. Curve (i): the orthodox theory; curve (ii): the drain current I_D vs the source-drain voltage V_{SD} ; curve (iii): dI_D/dV_{SD} . The bars in the bottom of the figure represents 70 mV intervals. (b) Results of the measurement at 77 K. Curve (i): drain current I_D ; curve (ii): dI_D/dV_{SD} .

cause the thiol groups attached to them do not ionize in the aqueous solution. Thus, this removes the accumulated ionic charges from the substrate and gives another chance of depositing more GCPs in the second GCP solution immersion, increasing the GCP coverage.⁹

Secondly, the thiol groups terminating the first layer of GCPs can immobilize incoming GCPs in the second GCP solution immersion forming covalent bonds with gold atoms on the incoming GCPs. As a consequence, the two GCPs can be bound together by alkyldithiol molecules, which causes the chaining of GCPs. However, since the incoming GCPs carry the ionic adsorbates, the second GCP deposition stops automatically keeping some distance between the particle chains. The result of the second GCP shows that, instead of filling the spaces between the first layer GCPs, the incoming GCPs tend to stick to one of the first layer GCPs forming linear chains of 2–4 particles [see Fig. 1(c)]. Even though the exact cause of this tendency is not clear at the moment, the chaining was observed over the entire submonolayer coated area with good reproducibility.

With these chains laid on the entire substrate, most of the metal gaps, three times as large as the particle size, were bridged by the GCP chains. For the particular sample shown in Fig. 1(c), the current path is converging on a single GCP dot forming a bottleneck. This situation may be approximated to as a double junction system: a single dot linked by molecular tunneling barriers to both the lower electrode directly and the upper electrode through an aggregate of GCPs.

Figures 2(a) and 2(b) show the results of electrical current measurement through a particle chain shown in Fig. 1(c) at 4.2 and 77 K, respectively. In Fig. 2(a), the middle curve (ii) is the result of the drain current (I_D) measurement as a function of the voltage (V_{SD}) applied between the source and drain electrodes. Curve (iii) is the numerical derivative

(dI_D/dV_{SD}) of the curve (ii). Curves (ii) and (iii) clearly exhibit a Coulomb staircase with an average onset separation of ~ 70 mV. The bars in the bottom of the figure designate 70 mV intervals.

The topmost curve (i) in Fig. 2(a) is calculated from the orthodox theory with the parameters $C_1=2.6$ aF, $C_2=1.8$ aF, $C_G=0.01$ aF, $R_1=185$ M Ω , $R_2=185$ G Ω , and $R_G=\infty$ assuming that the circuit is a double junction system.¹⁵ These values are chosen to approximate to the observed results. The sum of the capacitances $C_S=C_1+C_2+C_G=4.5$ aF gives a charging energy $E_c=e^2/2C_S\sim 18$ meV. A 10 nm metal sphere embedded in a dielectric medium with a dielectric constant value similar to that of an alkane chain monolayer (i.e., $\epsilon_r\sim 2.8$)¹⁶ gives a charging energy of ~ 27 meV with a self-capacitance value of ~ 3 aF; in reasonable agreement with the observed values. Assuming the simplified model, one can conclude that the current flow through the gold particle chain exhibits the Coulomb charging effect. The asymmetry in the pair of tunneling resistances is consistent with the clear Coulomb staircase observed in the $I_D - V_{SD}$ curve.

The tunneling resistance values, R_1 and R_2 , can be compared with a theoretical estimation based on the idea of a tunneling resistance assigned to a single organic molecule.¹⁷ Applying the concept to an alkane chain consisting of the 1,6-hexanedithiol, one can get a tunneling resistance value of ~ 30 G Ω as a crude estimate for the resistance of the single dithiol molecule; in this calculation, elastic tunneling through a barrier of an alkane chain (i.e., the barrier height for an alkane chain monolayer $E_g=2.8$ eV,¹⁶ the chain length=1.2 nm) was postulated. This value should be divided by the number of molecules involved in the tunnel junction in order to estimate a tunneling resistance of the barrier between the dot and the electrodes. According to the observed tunneling resistances, one of the barriers corresponding to $R_1=185$ M Ω may involve ~ 160 molecules connected in parallel, while the value $R_2=185$ G Ω may indicate that the other barrier has not been terminated perfectly by the dithiol molecules since it is about six times as large as the single molecule resistance value of ~ 30 G Ω .

In conclusion, it was observed that submonolayer gold colloidal particles deposited on a SiO₂ substrate by aminosi-

lane transform themselves into short chains of gold colloidal particles after the treatment with dithiol and an additional GCP deposition. These chains successfully bridged a gap of source and drain metal electrodes defined by electron beam lithography, forming a quasi one dimensional current path. The device exhibited a clear Coulomb staircase at both 4.2 and 77 K.

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