Transport in gold cluster structures defined by electron-beam lithography

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The near-room temperature current-voltage (I-V) characteristics of small structures made from the metal-cluster material $Au_{55}[P(C_6H_5)_3]_{12}Cl_6$ were studied. It is shown that these electron-beam defined structures have highly nonlinear characteristics with features, including a threshold voltage and scaling behavior, which are consistent with Coulomb charging of individual Au_{55} cores in a disordered array. Applied radio frequency signals introduce plateaus in the I-V characteristics, which demonstrates the presence of coherent tunneling in these cluster systems. © *1997 American Institute of Physics.* [S0003-6951(97)03331-7]

A well established technology to produce metal features is the exposure of organometallic gases or solid films by a reaction energy source. For example, focused ion-beams have induced the deposition of platinum structures from an organometallic gas,[1] and thin spin-coated films of palladium-acetate have been used with ion- and electron-beams to achieve palladium structures.[2,3] The use of metal-cluster compounds in conjuction with charged particle beams has also been reported. One metal-cluster compound that has been used for direct writing investigations is dodeca (triphenylphosphine)hexa(chloro)pentaconta gold, $Au_{55}[P(C_6H_5)_3]_{12}Cl_6$. Spin-coated thin films of this ligand-stabilized cluster have been exposed by ion- and electron-beams to produce organometallic features.[4,5] Usually, conducting gold structures are then formed by thermal treatment which removes the organic material.

Small, ligand-stabilized metal clusters are also of interest for nanoscale electronics based on the Coulomb charging energy.[6] The charging energy of clusters with metal core diameters below ~ 2 nm can be greater than kT at room temperature. Indeed, isolated clusters studied by scanning tunneling microscopy have shown room temperature blockade effects.[7] Arrangements of metal particles separated by organic material to provide an inter-core tunneling resistance, R_T, greater than the resistance quantum h/e^2 are expected to show Coulomb blockade phenomena similar to those observed in tunnel junction arrays. Several strategies have been reported for the fabrication of three-, two-, and one-dimensional arrays of metal clusters.[6,8,9] In this letter, we discuss the electrical transport properties of organometallic structures formed by the electron-beam irradiation of $Au_{55}[P(C_6H_5)_3]_{12}Cl_6$, in which the organic material has not been removed by thermal treatment. We show that the near-room temperature transport of these directly written structures has features including threshold behavior, current-voltage (I-V) scaling and coherent tunneling, which are consistent with the charging of the Au_{55} cores.

The gold cluster material was synthesized following the procedure of Schmid,[10] and was purified and prepared as a solid as previously described.[5] A solution of the gold cluster was made by dissolving 22 mg of the solid in 0.25 mL of CH_2Cl_2 and 0.25 mL of CH_2ClCH_2Cl. A supernatant solution was spin coated onto a Si_3N_4 coated Si wafer at 1500 rpm for 25 s immediately after preparation. The film was patterned by exposure to a 40 kV electron-beam at a line dosage of 100 nC/cm. The areas of the film exposed to the electron beam, adhered to the surface and a CH_2Cl_2 rinse removed the excess film. This procedure produced well defined structures, as shown in Fig. 1, that appeared to be smooth and continuous under inspection by scanning electron microscopy. Attempts were made to pattern the material using 254 nm ultraviolet lithography, but it was found to be insensitive to this wavelength. The defined structures had dimensions as small as 0.1 μm, and inspection by atomic force microscopy measured the film thickness to be 50 nm. The organometallic samples were spin coated with poly(methyl methacrylate), which was electron-beam exposed and developed to define contact regions. Contacts were fabricated using thermal evaporation of 100 nm of gold and conventional liftoff procedures.

I-V measurements of several samples were taken. A shielded chamber, submerged in an oil bath, contained the sample mounted on a clean Teflon stage. Rigid triaxial connections were used to connect the sample to a constant direct current (dc) voltage source and electrometer. The oil bath

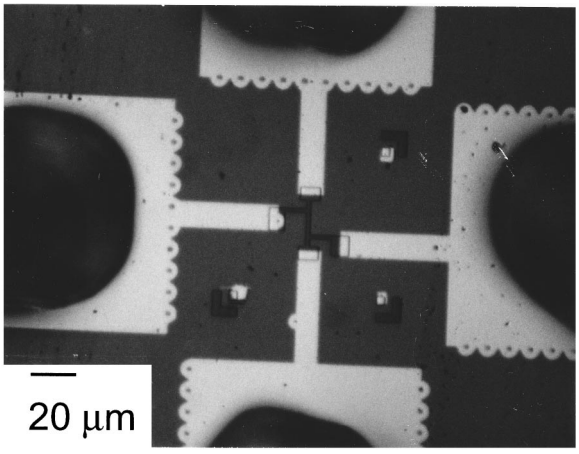

FIG. 1. Optical micrograph of a typical device.

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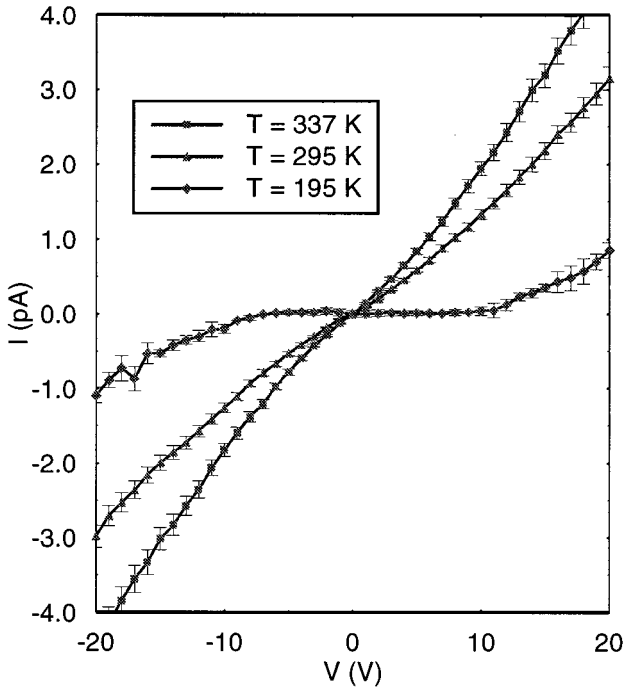

FIG. 2. The I-V characteristics at three temperatures.

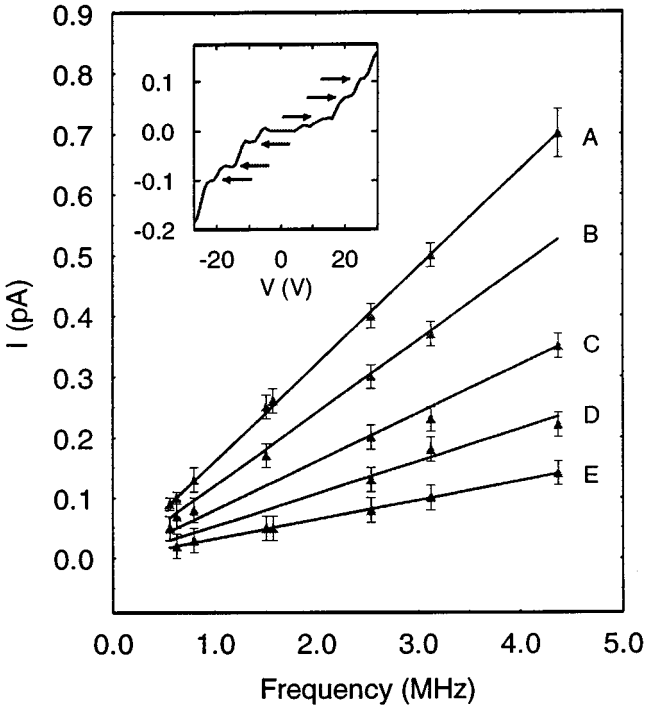

FIG. 3. Position of the observed current plateaus as a function applied frequency at 195 K. The solid lines have slopes, (A) e, (B) $3e/4$, (C) $e/2$, (D) $e/3$, and (E) $e/5$, where $e=1.6\times10^{-19}$ C. The inset shows the plateau structure at $f=0.626$ MHz.

temperature was controlled from 195 to 350 K. Thermal equilibrium was achieved with a 10 Torr partial pressure of He in the chamber. Before electrical measurements, the chamber was evacuated to a pressure $\sim10^{-5}$ Torr. The data showed little temperature drift over a typical 4 h measurement sweep. The intrinsic leakage current of the system was measured using a control sample which had the same substrate and contact pad arrangement as the actual samples, but did not have the organometallic between the pads. At room temperature, the leakage current was almost linearly dependent on bias over the range -100–100 V, and had a maximum value $\leqslant100$ fA. While the ultimate resolution of the current measurement was 10 fA, the leakage current set the minimum resolved conductance $\sim10^{-15}\ \Omega^{-1}$. Constant amplitude radio frequency (RF) signals with frequencies, f, from 0.5 to 5 MHz, were applied to the samples through a dipole antenna at 195 K. No attempt was made to optimize the coupling between the RF signal and the sample.

Without RF, the I-V characteristics for one sample at several temperatures are shown in Fig. 2. As the temperature was reduced, the low voltage portion of the curve flattened out, and the current became indistinguishable from the leakage current. Above an applied voltage magnitude of 6.7 ± 0.6 V, the current increased abruptly. The application of the RF signal introduced steps in the I-V characteristic, as shown in the inset to Fig. 3. The current at which these steps occured was found to be proportional to the applied signal frequency, as shown in Fig. 3. A least squares analysis of the linear current-frequency relationship for the highest current step shown, gives a slope $1.59\pm0.04\times10^{-19}$ C.

The nonlinear I-V characteristic is similar to that of either a forward biased diode or one-/two-dimensional arrays of ultrasmall metal islands or tunnel junctions.[11] However, the dependence of the I-V characteristic on the applied RF signal, is not consistent with straightforward diode behavior. Therefore, the data were analyzed in the context of an array of ultrasmall metal islands.

Several reports[12–14] have discussed the transport in ordered arrays of tunnel junctions that have tunneling resistances greater than the quantum resistance h/e^2 and a charging energy significantly above the thermal energy. In this case, Coulomb blockade effects introduce a threshold voltage below which the current through the array is suppressed. As the applied voltage is increased well beyond threshold, the I-V characteristic approaches a linear asymptote with a slope related to the tunnel resistance. With the same temperature and tunnel resistance constraints, Middleton and Wingreen (MW) have discussed one- and two-dimensional arrays of maximally disordered normal metal islands, where disorder is introduced as random offset charges on each dot.[15] MW predict current suppression below a threshold voltage and a high bias current $I\sim(V/V_T-1)^{\gamma}$. Here, the threshold voltage V_T scales with the number of junctions N along the current direction. Analytically, $\gamma=1$ for one-dimensional systems and 5/3 for infinite two-dimensional systems. Numerical simulations of a finite two-dimensional array gave $\gamma=2.0\pm0.2$.[15] While no effort was made to order our samples, the data were analyzed using both the ordered and the disordered models. The only consistent analysis was found to be given by the disordered model. In particular, the high bias data did not have the linear asymptote predicted for an ordered system, but did scale as expected for a disordered system, as shown in Fig. 4. The exponent γ is approximately 1.6, which is closest to the analytical prediction for an infinite, disordered two-dimensional array. From the analysis,

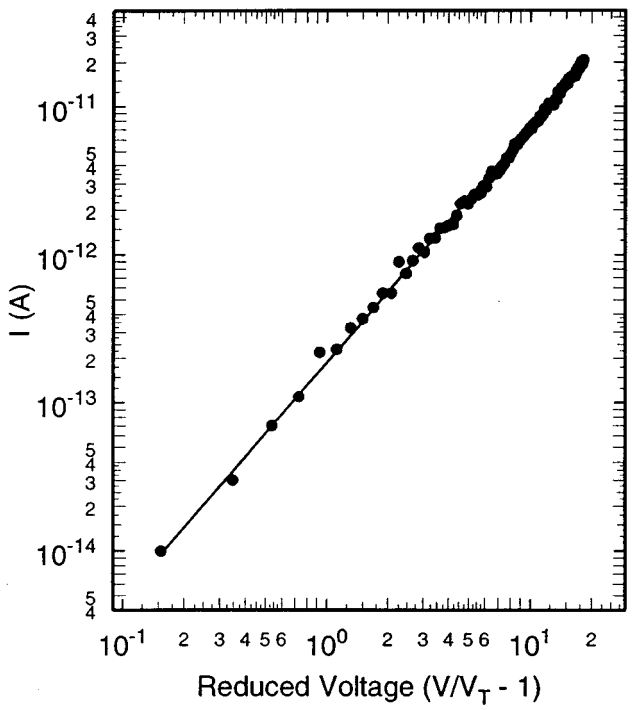

FIG. 4. Current vs reduced voltage at 195 K.

the magnitude of V_T is 6 ± 1 V which is in good agreement with that estimated directly from the I-V data.

The introduction of steps in the I-V characteristics by a RF field is similar to the RF response reported in other systems.[16,17] This effect has been attributed to phase locking of single electron tunneling events by the external RF signal.[11] If the applied frequency corresponds to a rational fraction multiple of the frequency of tunneling in the system, I/e, then the current is locked to a value $I=(n/m)ef$, where n and m are integers. Therefore, the linear relationships shown in Fig. 3 between f and I, suggests that correlated tunneling is present in the samples. The lowest slope observed is best described with $n/m=1/5$. For frequencies up to 3 MHz, the current resolution is insufficient to distinguish between the 1/5 and 1/4 harmonics. However, at higher frequencies where it should have been possible to distinguish between 1/5 and 1/4, the 1/4 step was not observed.

At temperatures above about 250 K, the I-V characteristic was almost linear up to V_T. In this regime the conductance was activated, with activation energies E_A in the range 30–70 meV for the samples studied. Similar activated behavior has been reported for tunnel junction systems.[18] It was argued that for an infinite two-dimensional array the charging energy for one island $E_C\approx4E_A$. Applying this argument to the present system, and assuming current supression requires $E_C\geqslant10kT$, the sample with the largest activation energy should develop a Coulomb gap below about 300 K. This estimate is within a factor of two of the measured temperature at which clear blockade behavior is seen. Thus, the temperature dependence of the observed current within the Coulomb gap is consistent with the observation of blockade behavior. From the threshold voltage, $V_T=\alpha Ne/C$,[15] and this estimate of E_C, αN is approximately 10. The energy E_C can also be estimated if the capacitance of an island is known. The capacitance of an isolated Au_{55} cluster is $C=4\pi\epsilon\epsilon_o r$, where r is the radius of the cluster and ϵ is the dielectric constant of the surrounding medium. The radius of a Au_{55} core is 0.7 nm and the ligand shell is expected to have $\epsilon\sim3$, which gives $C\approx2\times10^{-19}$ F. The Coulomb charging energy, $E_C=e^2/2C\approx340$ meV, which is within 20% of the maximum value of $4E_A$ found from the activation data. This result suggests that the current suppression is due to charging of individual Au_{55} clusters.

Given the constraint that steps in the I-V characteristics are only found when $f<0.1/(R_TC)$,[11] the fact that steps are seen up to $f=5$ MHz, gives the upper limit $R_T<1\times10^{11}\ \Omega$. The differential resistance obtained from the I-V characteristic well above threshold, is anticipated to be $R_{\rm diff}\approx(N/M)R_T$, where M is the number of parallel channels. This estimate yields $N/M\geqslant30$. From the sample dimensions and the size of an individual cluster, a close packed array would have $N/M\sim5$. The disparity between the expected and experimentally derived values of N/M suggests that the full width of the sample is not involved in transport. One explanation for the discrepancy in N/M may be that many of the gold cores coalesce during sample fabrication, so that the transport is dominated by individual clusters between larger regions of gold.

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