

Patterning of Narrow Au Nanocluster Lines Using V₂O₅ Nanowire Masks and Ion-Beam Milling

M. G. Ancona,* S. E. Kooi, W. Kruppa, A. W. Snow, E. E. Foos, L. J. Whitman, D. Park, and L. Shirey

Naval Research Laboratory, Washington, D.C. 20375

Received September 30, 2002; Revised Manuscript Received November 20, 2002

ABSTRACT

A shadow mask technique employing V₂O₅ nanowires and ion-beam milling is used to define narrow lines of monolayer-encapsulated Au nanoclusters. When positioned between electrodes these lines are shown to be conducting and to have nonlinear I–V characteristics with nonzero threshold voltages consistent with Coulomb blockade.

In recent years there has been considerable interest in metallic and semiconducting nanoclusters for a variety of reasons, not least of which is their potential for electronics and sensors.¹ Although there are worthwhile applications of these clusters in devices at the micron scale, e.g., in chemical vapor sensing,² the most intriguing possibilities arise when the numbers of clusters are reduced to a relative few and the inherent scalability associated with their nanoscale dimensions is fully exploited. One set of such possibilities involves metallic nanoclusters whose ultrasmall sizes (<2–3 nm in diameter) imply large charging energies and hence strong Coulomb blockade even at room temperature. For the blockade phenomenon to be manifested in an electrical signal one needs to minimize statistical averaging effects by having only small numbers of nanoclusters participate in the transport processes. The extreme example is the limit of a single cluster that has been studied extensively using scanning tunneling microscopy (STM).³ A more practical configuration involves “small” numbers of clusters arrayed between two nanoscale electrodes defined on the surface of an insulator with possibly a third terminal situated on the surface or on the backside. This arrangement has been explored in a number of experiments, and a variety of Coulomb blockade signatures have been observed. In the simplest case, the restriction on the numbers of clusters comes about merely by having small enough electrodes and relying on the Coulomb threshold to suppress fringing currents.⁴ More sophisticated efforts position the clusters between the electrodes using e-beam lithography,⁵ atomic force microscope (AFM) manipulation,⁶ or electrostatic trapping.⁷ Although these latter methods work, they have drawbacks including that they have not yet been successful

with ultrasmall clusters. In the present work, we report a simpler technique that uses nanowires to pattern the clusters (of any size) into narrow lines between electrodes.

The nanoclusters used in this study are composed of gold cores encapsulated by a monolayer shell of alkanethiol. They are prepared using a synthesis similar to that reported by Brust,⁸ where the core size and shell thickness can be varied by respective control of the Au/RSH stoichiometric ratio and selection of the alkanethiol chain length.⁹ The particular clusters used here had a core diameter of approximately 1.8 nm and a hexanethiol shell approximately 0.4 nm thick as inferred from density and TGA measurements and from Langmuir–Blodgett isotherms.

For the masks we use V₂O₅ nanowires that are prepared using the methods of refs 10 and 11. The V₂O₅ nanowire dimensions can be influenced by the growth conditions including the temperature and the possible presence of modification agents. Room-temperature synthesis produces rectangular V₂O₅ nanowires that are 10 nm wide and 1.5 nm thick by mixing 0.1 g ammonium (meta) vanadate and 1 g of DOWEX 50WX8-100 in 10 mL of H₂O. For this work, the growth conditions were modified so as to obtain larger nanowires by adding 0.02 g *N*-methylformamide and heating the solution to 60 °C for 2 h after mixing. As measured by AFM, the wires grown in this way were typically ~30 nm in width, ~5 nm in thickness, and many microns long as a result of being allowed to grow for at least 5 days. A key advantage of the V₂O₅ nanowires is that they are readily removed (by etching in dilute HCl) after ion beam milling without damaging the clusters. This contrasts with carbon nanotubes, which we and others¹² have found harder to remove.

Our approach to defining cluster lines employs a technique much like that of Sordan *et al.*¹³ In their work V₂O₅

* Corresponding author. E-mail: ancona@estd.nrl.navy.mil.

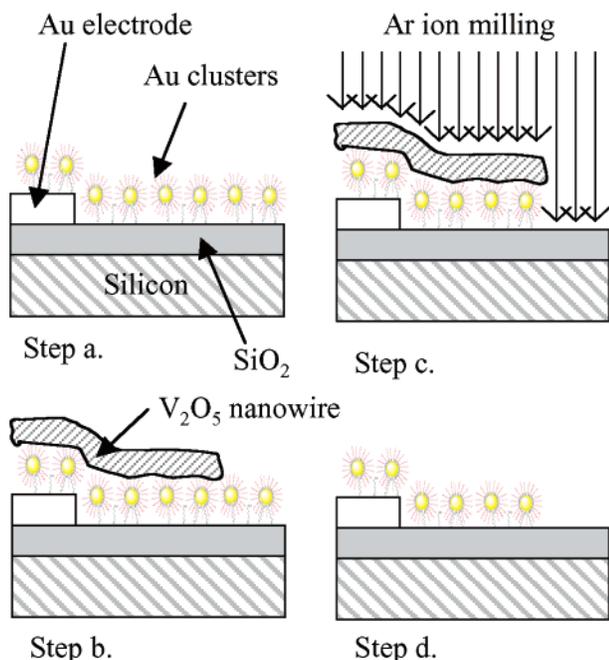


Figure 1. Process for making nanocluster lines using V_2O_5 nanowires and ion milling.

nanowires were deposited on a AuPd film and then used as a shadow mask for Ar ion milling. Here we use an identical procedure but applied to a film of Au nanoclusters as depicted in Figure 1. The process starts (Figure 1, step a) with a pre-patterned substrate in which Cr/Au electrodes have been defined on a Si/SiO₂ substrate. Clusters are then self-assembled on the substrate using an alkanedithiol linker molecule for attaching the clusters to the electrodes and (mercaptopropyl)tri-methoxysilane as a linker for attaching them to the SiO₂ substrate.¹⁴ Next the V_2O_5 wires are deposited (Figure 1, step b) by dipping the substrate in an aqueous V_2O_5 nanowire solution for five seconds, rinsing with water and blowing dry with nitrogen. By controlling the direction of rinsing and drying, the nanowires can be preferentially oriented so as to increase the likelihood of a nanowire bridging the gap between electrodes. Ar ion milling is then used to remove the clusters that are not protected by the V_2O_5 wires (Figure 1, step c). The milling rate for a single-layer cluster film as a function of milling time, as evaluated by XPS, is plotted in Figure 2; we typically use 200V Ar at 2.2W/cm² for 15 s. An important question regarding this step (which was not an issue in ref 12) is whether the ion milling damages the organic shells of the clusters under the wires and possibly fuses their gold cores or otherwise affects their transport characteristics. The evidence presented in this paper (see below) suggests that this does not happen and that ion milling is therefore a useful tool for defining cluster patterns. The final step in the fabrication process is removal of the V_2O_5 nanowires (Figure 1, step d). Their removal is desirable because they are semiconducting¹⁵ and if left in place they can obscure and even dominate the cluster conductivity at least at room temperature as discussed below.

To verify that the process of Figure 1 can indeed create cluster lines, we characterized our samples with AFM. The

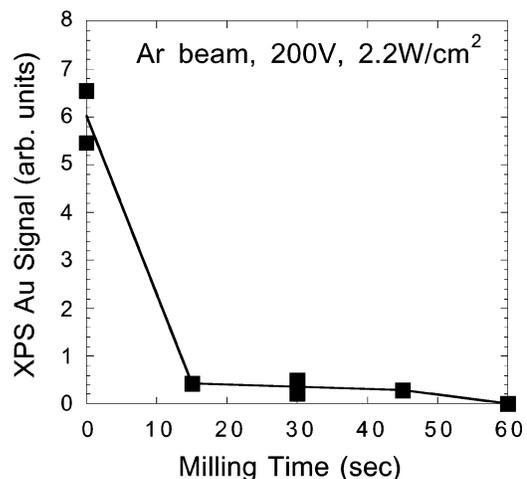


Figure 2. Milling rate of a single Au nanocluster layer as monitored by XPS.

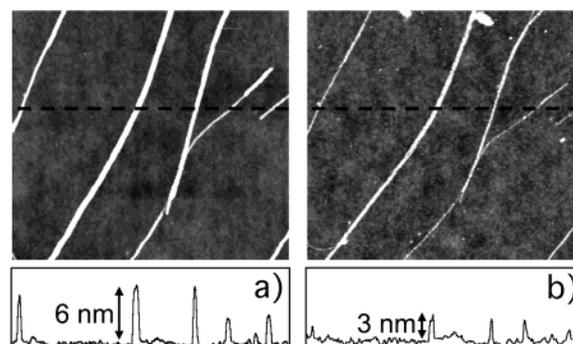


Figure 3. AFM images and profiles of cluster lines (a) before and (b) after V_2O_5 nanowire removal. The images are each $3 \times 3 \mu\text{m}$ and the cluster lines are $\sim 20\text{--}50$ nm (or roughly 10–25 clusters) wide.

images in Figure 3 show a test sample (with no electrodes) that had clusters assembled on the substrate and then V_2O_5 nanowires deposited on top. The image in Figure 3a is from after milling but before the V_2O_5 nanowires were removed (Figure 1, step c), and Figure 3b is from after their removal (Figure 1, step d). The measured profiles (also shown in Figure 3) confirm that the removal of the nanowires decreases the height of the lines by roughly the expected amount. The lines left behind (Figure 3b) are about 2–3 nm in height and are thus almost certainly formed of a single layer of Au nanoclusters. In a final AFM image in Figure 4, a device with a micron-size gap is shown with the V_2O_5 shadow mask in place.

Electrical testing of the cluster lines was performed using a micro-manipulated cryoprobe system (Janis CT-420) that allows measurements to be made on unbonded devices at temperatures down to 5 K. The devices tested had electrodes spaced approximately 30 nm apart and were usually connected with only a single line of clusters defined by a V_2O_5 wire. Typical current–voltage (I–V) characteristics for these devices are plotted in Figures 5 and 6 as a function of temperature. The curves are strongly nonlinear, nearly symmetrical about $V = 0$ (not shown), and have nonzero threshold voltages. For the particular device studied in Figure

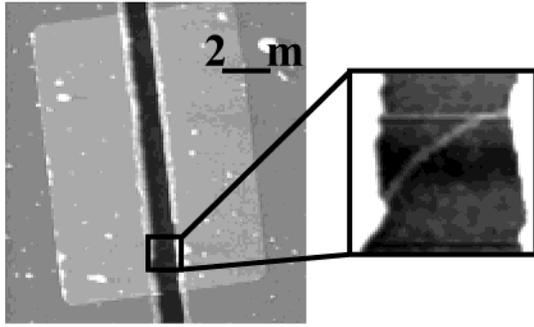


Figure 4. AFM image of electrodes with a micron-size gap and a V_2O_5 shadow mask.

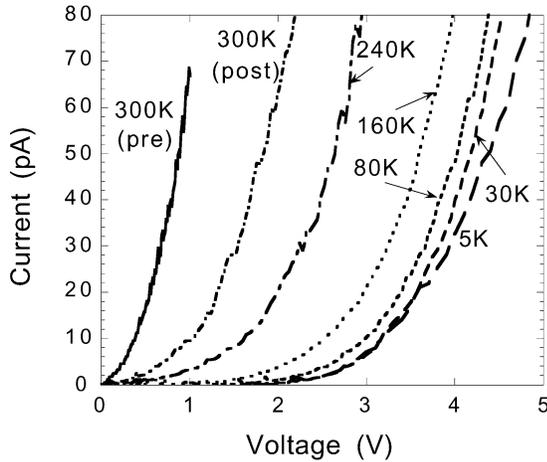


Figure 5. I–V characteristics with temperature as a parameter for a V_2O_5 -defined cluster line between two electrodes spaced ~ 30 nm apart.

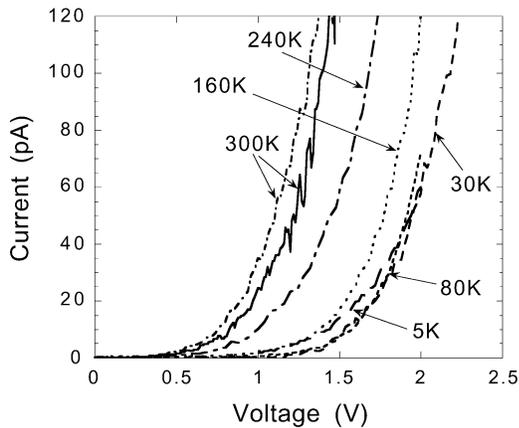


Figure 6. I–V characteristics with temperature as a parameter for a cluster line after the V_2O_5 nanowire has been removed by etching in HCl. The two curves at 300 K are from before and after the temperature cycling.

5, the V_2O_5 nanowire was still in place. That this wire conducts some current, at least initially, is shown by the difference in the I–V characteristics at 300 K before (pre) and after (post) thermal cycling down to 5 K. Apparently, differential thermal expansion moves, damages, or dislodges the nanowire, thereby raising its resistance and causing the current through the cluster line to become dominant. In addition, as the temperature is lowered below 300 K any

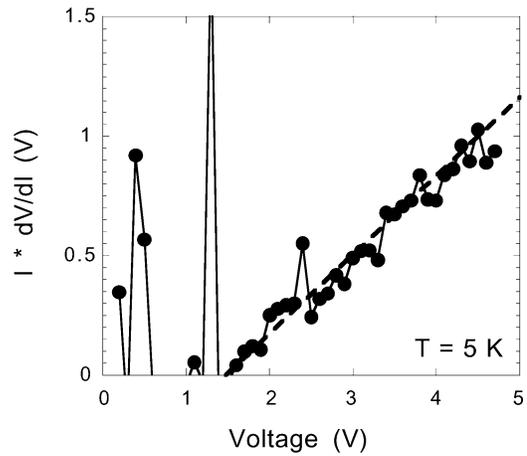


Figure 7. The data in Figure 5 for 5 K plotted as $I \, dV/dI$ versus V . The linearity shows that power law behavior is observed and allows an accurate determination of V_T .

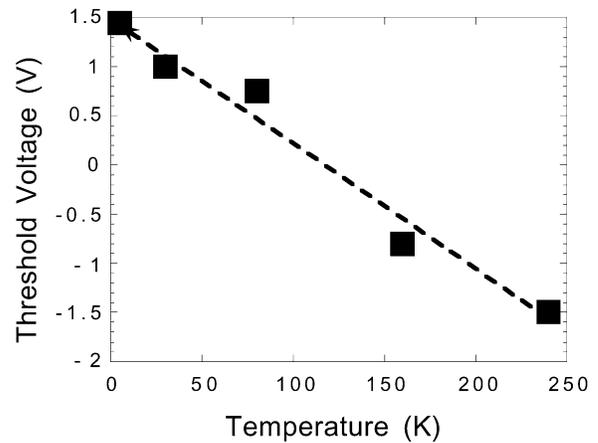


Figure 8. V_T values determined from plots such as Figure 7 as a function of temperature. The linearity observed is characteristic of cluster transport.

residual nanowire current would decline exponentially (as a result of the Schottky barrier contact between the electrode and nanowire) and would quickly become completely negligible.¹⁵ The minimal contribution of the V_2O_5 nanowire to the conduction observed in Figure 5 was further demonstrated by removing the nanowires by etching in dilute (5%) HCl. Sample I–V curves following nanowire removal are shown Figure 6; the nonlinear I–V characteristics associated with the cluster conduction are again seen.

Additional evidence that the currents seen in Figures 5 and 6 are associated with cluster conduction is obtained from a closer examination of the I–V curves themselves. These curves do not display temperature-activated characteristics (associated with current flow over a Schottky barrier) but rather show a power law dependence, i.e., $I \sim (V - V_T)^\zeta$ with an exponent (ζ) greater than one and a nonzero threshold voltage (V_T), that is commonly associated with cluster transport.⁴ This is best shown by the fact that, when the data is plotted as $I \, dV/dI$ versus V in Figure 7 (for the 5 K data of Figure 5), a straight line is obtained. From the slope and intercept of this line we infer that $\zeta \sim 3$ and $V_T \sim 1.5$ V (for this sample at 5 K). Plotting the data of Figure 5 at

other temperatures in the same way, we find that ζ is fairly constant but that the threshold voltage varies linearly with temperature as shown in Figure 8. This too, including the fact that V_T is found to go negative, is remarkably similar to the behaviors reported previously for single-layer cluster transport between nanoscale electrode fingers with a gap and width of similar dimensions.⁴ This is strong evidence that “normal” cluster transport is occurring and that the V_2O_5 process therefore represents a viable technique for creating narrow cluster lines.

To summarize, in this work we have demonstrated that narrow Au nanocluster lines can be fabricated using a process in which V_2O_5 nanowires are employed as a mask for ion-beam milling. These single-layer cluster lines are conducting and show nonzero threshold voltages and nonlinear I – V characteristics likely associated with Coulomb blockade. This electrical behavior is quite similar to that previously observed in unpatterned clusters assembled between nanofinger electrodes.⁴

Acknowledgment. The authors thank ONR for funding support, J. B. Boos for help in the fabrication, and D. Hsu, R. W. Rendell, and E. Snow for useful conversations. S.E.K. is supported by an NRC-NRL Postdoctoral Research Associateship.

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NL0258224