

## Gold Clusters and Colloids in Alumina Nanotubes

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*Dedicated to Professor Achim Müller on the occasion of his 60th birthday*

**Abstract:** The fabrication of a supported and insulated quantum wire would be of great interest, especially if electronic information could be accessed to determine charging and conductivity profiles. The feasibility of forming one-dimensional configurations of  $\approx 15$  nm gold colloids and 1.4 nm gold clusters via template methods of synthesis has now been demonstrated. The template host material consisted of porous alumina membranes formed by an electrochemical anodic process. The pores of the membrane, and hence the parallel pore channels, were packed in a hexagonal array. Alumina membranes are excellent template materials because of their high degree of order,

thermal and chemical stability, and optical clarity. Pore diameter was controlled by regulation of the applied anodic potential (ca.  $1.4 \text{ nm V}^{-1}$ ). The pore channels were filled by one of three methods: vacuum induction (colloids only), electrophoresis (clusters only), or immersion (clusters, which were then converted into colloids by heating). Rudimentary wires consisting of colloids and clusters were successfully formed. In both cases, the diameter of the pore channel exceeded that

of the clusters or colloids. The wires thus formed conformed to the pore channel by forming helical secondary structures. It was not possible to form contiguous wires of clusters by immersion, or of colloids formed from clusters after heating. Composites (consisting of the gold–alumina system) were a bright scarlet color with an absorption maximum ( $\lambda_{\text{max}}$ ) at 519.5 nm. This is an unexpected result for spherical and small-diameter (10 nm) gold colloids, which normally absorb at  $\lambda_{\text{max}}$  525–530 nm, a ruby-red color. Possible causes of this small but remarkable blue shift are discussed below. A new  $\text{Au}_{55}$  cluster ligand system consisting of a silsesquioxane-derivatized thiol is also described.

### Keywords

clusters · colloids · gold · nanostructures · quantum wires

### Introduction

Metal particles in the nanosize region can show quantum properties.<sup>[1]</sup> These quantum size effects are not merely of theoretical interest but have potential for future applications in nanoelectronics. Quantum dots are able to communicate via single elec-

trons, and will play a decisive role as building blocks in materials with completely novel physical and chemical properties. However, the use of such ultimately miniaturized materials will only be possible if we are able to organize them in a proper configuration, that is, into three-, two-, or one-dimensional arrays. The study of the electronic interactions between the single quantum dots is easiest if they are arranged one-dimensionally as in a wire. The wire can be composed of ligand-stabilized metal clusters or of colloids. Both are available in preparative amounts and have been investigated extensively.<sup>[2]</sup> For example, it is known that ligand-stabilized gold clusters  $[\text{Au}_{55}(\text{PPh}_3)_{12}\text{Cl}_6]$ , of 1.4 nm diameter and stabilized by  $\text{PPh}_3$  ligands, exhibit semiconductor behavior in a three-dimensional dense-packed ensemble.<sup>[2, 3]</sup> Therefore, the tunneling behavior of 20–100  $\text{Au}_{55}$  clusters formed in a one-dimensional configuration would be of great interest. Comparison with the conductive nature of wires made of 10–15 nm colloids would also be interesting, as the diameters of the colloids are ten times those of the clusters.

The generation of one-dimensional cluster and colloid arrays can be accomplished with the appropriate substrates by a self-assembly process. We decided to try a template material consisting of porous aluminum oxide formed by anodic oxidation of

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high-purity aluminum plates or foils.<sup>[4, 5]</sup> A schematic illustration of the structure of a porous film is shown in Figure 1. The pore channels are parallel throughout the membrane and are packed in a hexagonal configuration. The interfacial oxide layer between the porous layer and the aluminum metal substrate (the barrier layer) can be removed so that the pore channels are open on both faces of the membrane. The porosity of such membranes is between 20 and 30%.

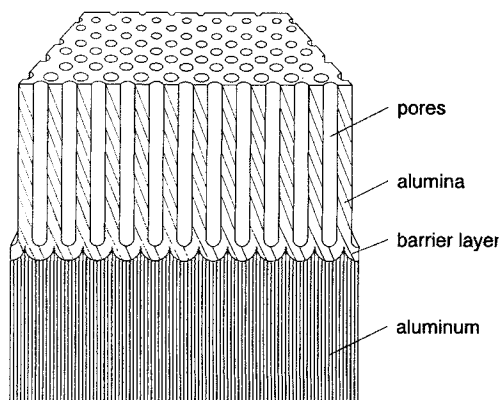


Figure 1. Schematic illustration of an idealized nanoporous alumina membrane. The pores are hexagonally arranged and are still fixed to the aluminum, but separated by a barrier layer.

The diameter of the pores is regulated by the applied anodic potential. The relationship between pore diameter and anodic voltage is approximately 1.2–1.4 nm per anodic volt applied.<sup>[6]</sup> Membranes with a very high degree of order have been formed by Masuda and co-workers<sup>[7]</sup> but membranes with a good degree of order can be produced routinely. Template-based fabrication strategies based on porous alumina films have been developed extensively in the laboratories of Martin,<sup>[8]</sup> Masuda,<sup>[9]</sup> and Moskovits.<sup>[10]</sup> Porous alumina membranes possess excellent thermal, chemical, and optical properties. They can be im-

mersed in solutions over a wide range of pH values. The membranes may be exposed to both inorganic and organic solutions without great danger. The membranes possess high optical transparency in the visible range of the spectrum.<sup>[11]</sup> Films thicker than 10  $\mu\text{m}$  have excellent mechanical properties, but thinner films require support. This is not problematic, since the porous oxide can be left on the aluminum metal during filling and other steps which require handling.

Formation of one-dimensional wires on the nanoscale is technologically challenging. In order to form a useful quantum wire, one that may be included in nanodevices of the future, the wire has to be supported, isolated, and insulated. The template method offers possible solutions to this challenge by providing the means by which nanoparticles can be assembled, supported, and insulated. The final form of the wire would depend on the dimensions of the pore channel. Ideally, a one-dimensional wire consisting of a chain of clusters or colloids is possible if the diameter of the pore channel coincides with the diameter of the ligand-stabilized cluster or colloid. The clusters or colloids have to be packed tightly into the pore channel so that contact between them is maintained throughout the thickness of the membrane. Linking of the spherical particles in situ by chemical means is also possible once they have been introduced into the pore channel. Electrical contacts can then be applied on both surfaces of the filled alumina membrane by sputtering silver or gold on both faces of the membrane. For STM analysis, only one side needs to provide an ohmic contact. The length of the nanowire would depend on the thickness of the porous film; it is possible to vary the thickness of the film from 10 nm to greater than 100  $\mu\text{m}$ .

## Results and Discussion

Three methods were employed for pore filling: vacuum induction, electrophoretically based, and capillary-dipping procedures. Other methods are also being investigated, including the formation of nanoparticle assemblies by electrodeposition<sup>[12]</sup> and electroless<sup>[10]</sup> strategies. For clusters, the electrophoretic method gave the best results; for colloids, the pores were better filled by the vacuum induction method. The dipping technique served to saturate the alumina surfaces (both inside the pore channels and on the faces of the membrane) with clusters but without forming contiguous wires. The formation of colloids during heat treatment of a cluster-saturated membrane following immersion in cluster solution is also described here.

Two analytical methods were employed to determine the pore size and structure of a generic alumina membrane: atomic force microscopy (AFM) and transmission electron microscopy (TEM). The results of the measurements are compared below. In Figure 2a, an AFM image of the surface of a porous membrane is shown. This membrane was formed under 20 V anodizing conditions. Ion milling of the surface of this membrane improved the smoothness of the surface significantly. The degree of order of the pore distribution was quite high. The pore diameter determined by AFM was 25 nm. When determined by TEM (Figure 2b), the pore diameter of the same membrane was 30 nm, about 1.2 times that determined by AFM. It is well known that objects imaged by AFM or STM appear larger than

**Abstract in German:** Die Möglichkeit zur Herstellung eindimensionaler Anordnungen von  $\approx 15$  nm großen Goldkolloiden und 1,4 nm großen Goldclustern über Templatsynthesen wird gezeigt. Das Templatmaterial besteht aus porösen Aluminiumoxidmembranen, welche durch anodische Oxidation von Aluminium gewonnen werden. Die parallelen Poren sind überwiegend hexagonal angeordnet. Dank der hohen Ordnung der Poren, der thermischen und chemischen Stabilität sowie der optischen Transparenz stellen solche Membranen ausgezeichnete Template dar. Die Porendurchmesser werden über das anodische Potential gesteuert. Die Kanäle können auf dreierlei Arten gefüllt werden: Durch Vakuuminduktion (Kolloide), Elektrophorese (Cluster) oder durch einfaches Eintauchen (Cluster). So konnten, allerdings noch unvollkommene, Kolloid- und Clusterdrähte erhalten werden. Helikal angeordnete Goldclusteranordnungen werden in Poren beobachtet, die geringfügig größer sind als der Clusterdurchmesser. Die Thermolyse cluster-haltiger Membranen führt zu intensiv rot gefärbten transparenten Materialien, deren Absorptionsmaxima vom Porendurchmesser abhängen.

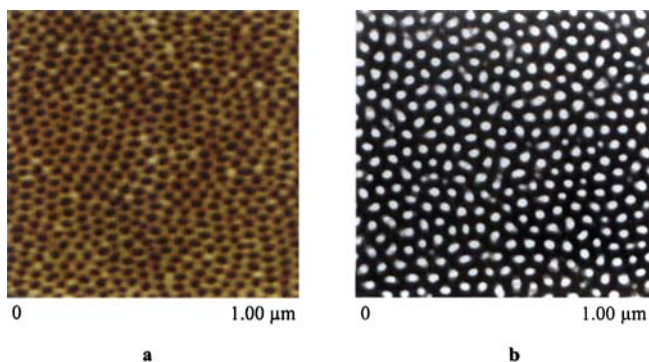


Figure 2. a) AFM image of an ion-milled alumina membrane. The average diameter is measured as 25 nm. b) TEM image of the same ion-milled membrane. The pore diameter is measured as 30 nm. The reason for the difference is explained in the text.

they are,<sup>[13]</sup> because of the interactions between the tip and the object. Consequently, the diameter of a pore seems to be smaller when measured by AFM than TEM measurements suggest.

A TEM micrograph of rudimentary nanowires formed in an alumina membrane anodized at 40 V is shown in Figure 3. The pore diameter of this film was 50 nm, and it was filled with gold

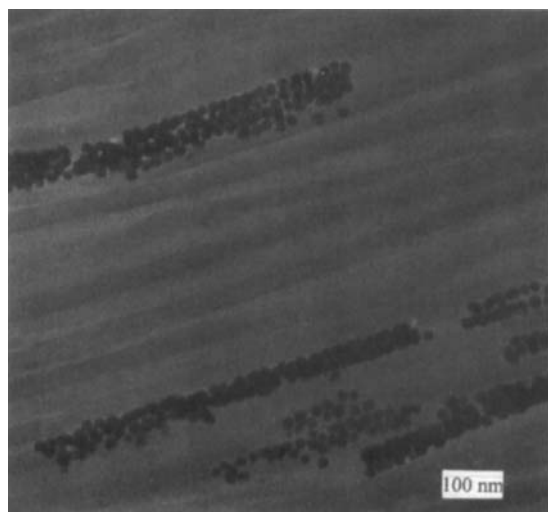


Figure 3. TEM image of rudimentary wire structures made of ligand-stabilized Au colloids (diameter 15 nm) in pore channels of 50 nm diameter. The colloids were forced into the pore channels of the alumina by vacuum induction.

colloids of 15 nm diameter by the vacuum induction method described in the Experimental section. Since the pore channel diameter was larger than that of the gold colloids, up to four colloids could be packed along the diameter of the pore. Another difficulty with this method was that not all the pore channels were filled uniformly. This was partially attributable to the differential flow resistance of individual pore channels within the matrix.

Vacuum induction of 15 nm gold colloids was also performed with specially prepared membranes in which the pore diameter was reduced systematically. Because voltage reduction occurred before anodization was finished, the pore size decreased while the number of pores increased. Essentially, the colloids were tunneled into smaller and smaller pore channels. This method

was an improvement over the previous one, as steric surface and static charge exclusion problems were overcome. From Figure 4 it can be seen that the colloids have achieved a one-dimensional configuration in several of the narrow channels.

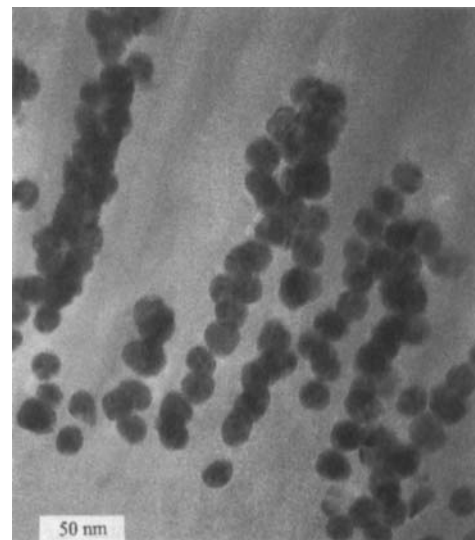


Figure 4. TEM images of rudimentary one-dimensional wires made of 15 nm diameter ligand-stabilized Au colloids. The pore channel diameter in this case was ca. 20 nm.

Electrophoretic filling of pores as small as 6–8 nm with Au<sub>55</sub> stabilized with the T<sub>8</sub>-OSS-type ligand (Figure 5) has been accomplished.<sup>[14]</sup> This newly synthesized Au<sub>55</sub> ligand system possesses several advantages over the standard PPh<sub>3</sub> ligands used previously. The diameter of the cluster is 4.2 nm (the Au<sub>55</sub> cluster stabilized with PPh<sub>3</sub> ligands was only 2.1 nm in diameter).

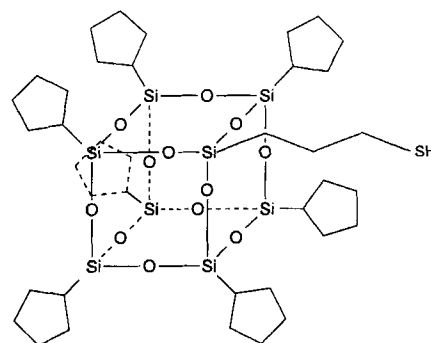


Figure 5. The T<sub>8</sub>-OSS ligand (T = RSiO<sub>3/2</sub>, OSS = oligosilsesquioxane).

This is a highly desirable characteristic in that extremely small pores of about 2 nm in diameter, which are more difficult to fabricate, are not needed. Another advantage of the new ligands is that agglomeration among clusters is effectively prevented. The clusters are soluble in pentane as well as in CH<sub>2</sub>Cl<sub>2</sub>, and solutions of clusters are stable over extended periods of time.

A TEM micrograph of a single pore electrophoretically filled with T<sub>8</sub>-OSS-stabilized Au<sub>55</sub> clusters is shown in Figure 6a. Along the distance of 70 nm indicated, 20 or 21 clusters are arranged, not exactly in a straight line but rather in a helical

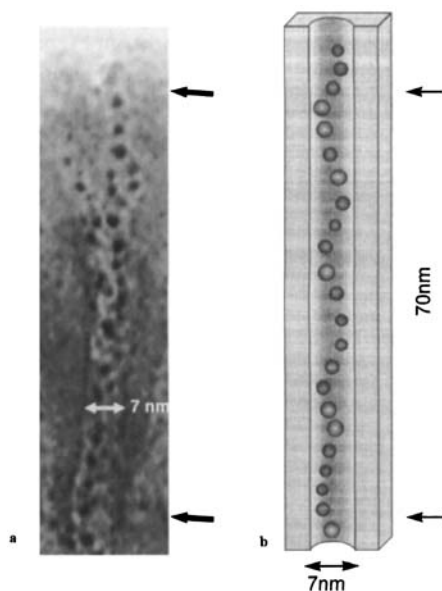


Figure 6. a) TEM image of one-dimensional wire composed of  $T_8$ -OSS-stabilized  $Au_{55}$  clusters. The clusters were introduced into the pore channels by electrophoresis. Because the diameter of the pore channel was ca. 7 nm and that of the clusters 4.2 nm, a helical structure consisting of clusters was formed. b) Schematic representation of the possible helically structured quantum wire in the pore channel.

structure. A sketch of the possible structure is shown in Figure 6b. As the diameter of the pore is about 7 nm, whereas that of a cluster, including the ligand shell, is only 4.2 nm, the helical arrangement is understandable. Only 16 or 17 clusters could be arranged in a straight line in a pore 70 nm long.

For the dipping method, membranes of different pore sizes were immersed in dichloromethane solutions containing  $Au_{55}$  clusters. The amount of cluster material absorbed (adsorbed) by the membranes depended on the size of the pores. Membranes with smaller pores absorbed substantially more clusters than did membranes with larger pores. This can be attributed to a surface effect, as smaller-pore membranes possess more inner surface area per membrane than those with larger pores, assuming that the porosity and membrane thickness were the same for both. Membranes filled in this way were subsequently heated to 300 °C for a few hours. This procedure converted the  $Au_{55}$  clusters into colloids. A TEM micrograph of a transverse sample of a 20 V membrane ( $\approx 30$  nm pore diameter), formed in 10% w/w  $H_2SO_4$  and subsequently filled with  $Au_{55}$  clusters and heated, is shown in Figure 7.

As indicated in Figure 7, the density of the gold colloids increased towards the solution side of the membrane. This density gradient was formed by thermal movement of smaller gold clusters and colloids inside the membrane during heat treatment; these metal particles moved towards the open side of the membrane while aggregating, and formed larger particles. Finally they reached a certain size and became trapped in a region close to the solution side (occupying approximately 350 nm of the overall thickness of 18  $\mu m$ ). By means of this mechanism, a heavily filled region is formed which seems to be responsible for the unexpected bright scarlet transmission color (the membranes were back-lit with a tungsten light source). The color is shown in Figure 8, which was obtained with a binocular microscope at low power.

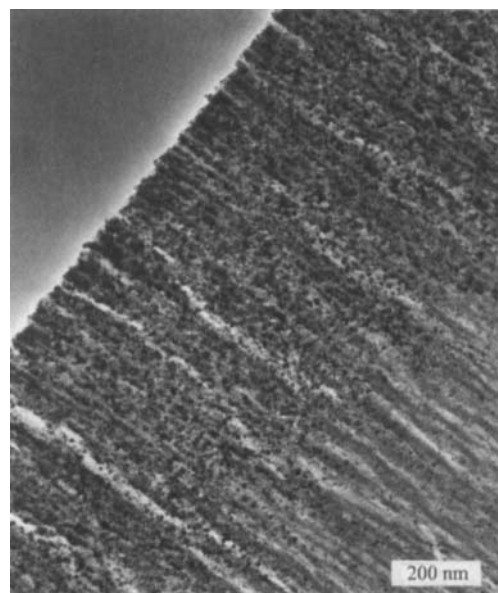


Figure 7. TEM image of a transverse section of an alumina membrane formed at 20 V with a pore diameter of ca. 30 nm, showing gold colloids formed in situ. The membrane was dipped into a solution of  $CH_2Cl_2$  which contained  $Au_{55}$  clusters, and then heated at 300 °C to form the colloids.



Figure 8. Photographic representation of the color of transmission of the colloidal alumina composite in Figure 7, seen through a binocular microscope under low magnification. A tungsten bulb provided the means of back-lighting.

A UV–visible spectrum of the red gold–alumina composite film is shown in Figure 9. The absorption maximum is at  $519.5 \pm 0.5$  nm. The broadness of the peak is due in part to the distribution in particle size ( $10 \pm 5$  nm). As stated earlier, the particular shade of red of this composite was unexpected. If suspended in water, gold colloids of this particle size are known to absorb at  $\approx 525$  nm, corresponding to a ruby-red color. Larger colloid suspensions are purplish to blue in color. There are several explanations for the apparent blue shift in absorption. For example, the refractive index of the “effective medium” surrounding the gold nanoparticles can induce shifts in the position of maximum absorption. From Figure 10 (a higher-magnification image of Figure 7) it can be seen that the gold nanospheres are not surrounded completely by alumina. The net effect of such an environment is that the effective medium is also partly composed of air and has a refractive index somewhat

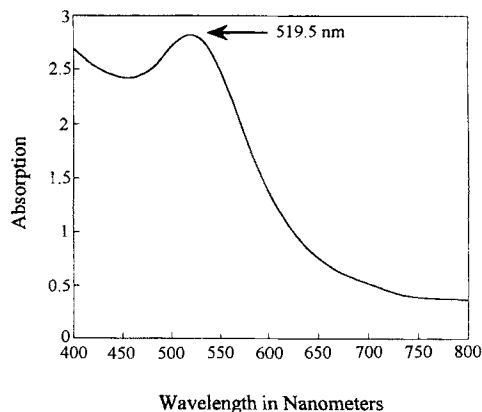


Figure 9. Visible spectrum of the gold colloid–alumina composite. The position of maximum absorption is at 519 nm. The broadness of the band is due to the distribution in particle size ( $10 \pm 5$  nm).

less than that of pure alumina, causing a blue shift in absorption. Secondly, from Figure 10 it can also be observed that several gold nanospheres are stacked on top of one another in the pore channel. Spheres arranged in a line in this fashion resemble a cylinder in terms of optical properties, and present a spectrum that is shifted relative to that of independent spheres. This is the Kappa shape and orientation effect.<sup>[11]</sup> Both factors will be discussed more fully in a future paper.

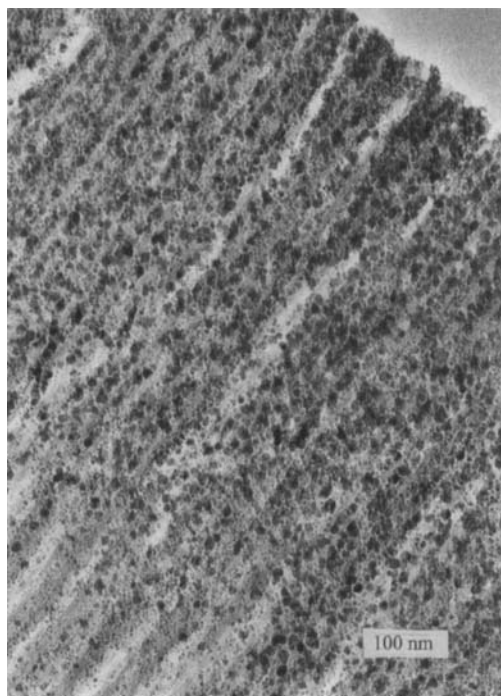


Figure 10. Higher-magnification TEM of the image in Figure 7. It can be seen that the colloids are spherical and are not completely surrounded by alumina. The polydisperse distribution in particle size can also be observed.

Depending on the experimental procedure, it is also possible to form uniformly sized colloids within pore channels. There appeared to be a correlation between pore diameter and eventual colloid size. A TEM micrograph of colloids formed in membranes with larger pore diameters is shown in Figure 11. The diameter of the pores is 30 nm. The diameter of the colloids

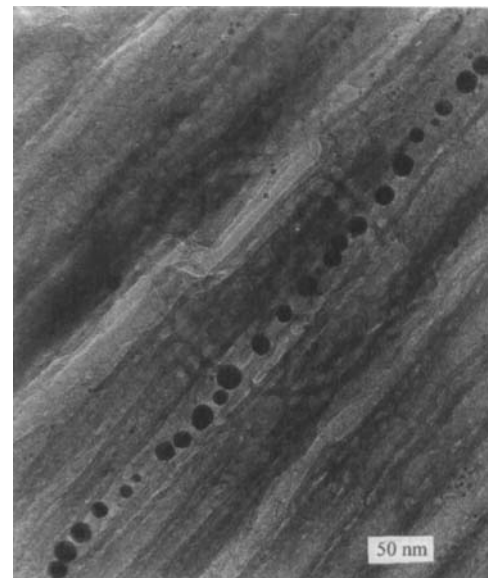


Figure 11. TEM image of colloids formed in situ in pore channels. Variation of the pore size and the conditions of formation permits colloids with a specific size distribution to be formed.

formed within the pores is  $16 \pm 2$  nm. Although some evidence of groupings of colloids resembling wires was seen, the formation of wires by this method is not likely. However, formation of colloids of a specific size that are impossible to generate in aqueous media by standard chemical reduction processes is a likely prospect.

## Conclusions and Outlook

Pore filling by electrophoresis shows promise as a means of fabricating a one-dimensional arrangement of  $\text{Au}_{55}$  clusters, a quantum wire. Application of the template method of synthesis makes possible the realization of a quantum wire that is supported (and therefore useful). The porous alumina, besides being an excellent inorganic insulator, is optically transparent and provides the necessary framework within which useful quantum wires can be fabricated. Since the template oxide is formed as a two-dimensional structure with nominal thickness, two-dimensional arrays of quantum wires are possible. However, perfect pore filling of the major part of a membrane requires a thickness in the range of only 100–200 nm. Pores of that length could be filled with chains of 25–50 4 nm clusters, in contrast to the present case of pores that are microns long, in which thousands of clusters can be arranged without disturbances only with great difficulty. To be handled, membranes of 100–200 nm thickness need a support. Current experiments indicate that 100–200 nm aluminum films on conductive supports can be transformed into 100–200 nm alumina membranes fixed to the support. Such devices promise a solution to the problem and should be available in the near future. Development of the new ligand-stabilized species of  $\text{Au}_{55}$  has alleviated the problems associated with agglomeration and stability. Conductivity measurements and electronic tunneling processes for quantum wires can now be planned. As an interesting “by-product” the special conditions in the nanopores make gold colloids into novel sources of temperature-stable color centers in ceramics.

## Experimental Procedure

**Porous membranes:** Porous alumina films were formed according to well-established procedures.<sup>[4–6, 11, 12]</sup> Plates of aluminum (ca. 99.5%) and aluminum foil of higher purity (>99.99%) were used as the anode material. Lead served as the cathode. The aluminum plate stock was electropolished in a solution consisting of 60% H<sub>3</sub>PO<sub>4</sub> and 40% v/v H<sub>2</sub>SO<sub>4</sub>. Approximately 1% glycerol was added to the solution. Polishing took place at a temperature of ca. 80 °C for 10 min until a mirror finish was achieved. The potential applied during polishing was 10 V. The high-purity foil was used as received. Two types of electrolytes were used for the anodization, depending on the desired pore size. For pores larger than 30 nm in diameter, a 4% w/w oxalic acid solution was used. If smaller pores were needed, 10–15% w/w sulfuric acid was used as the anodizing electrolyte.

Anodization of plate stock took place in a 10 L tank cooled to 0–10 °C. Membranes were formed at anodic potentials of 5–80 V. Anodization proceeded for several hours; the time depended on the desired film thickness. After the conclusion of anodization, the plates with the newly formed alumina films were subjected to the process of voltage reduction so that the anodic film can eventually be detached from the parent aluminum metal substrate.<sup>[15]</sup> The voltage was reduced incrementally to ca. 1.0 V. Each step lasted approximately 4 min, to allow for current recovery. The plates were then removed from the anodizing solution and placed in a room-temperature acid detachment bath, which consisted of 25% H<sub>3</sub>PO<sub>4</sub> w/w. After approximately 1–2 h the interfacial oxide layer formed during the voltage reduction step was dissolved. A membrane which possessed open and larger pores on one side (the solution side) and a network of small pores on the opposite face (the barrier side) was obtained.

Foils were anodized at 5–10 V in an inverted cell ca. 2 cm in diameter in 10% w/w sulfuric acid chilled to 0 °C. The cell was cooled by means of a glass jacket through which coolant consisting of ethylene glycol–water (1:1 v/v) was circulated. Only one side of the foil was anodized in this configuration. Anodization was performed for 10 min (creating a film of 100 nm thickness) or longer. No voltage reduction was needed for these films because they remained intact on the aluminum surface.

**Pore filling by vacuum induction:** Membranes were placed barrier side down on the top of a thin tube with an opening of ca. 5 mm. A vacuum was applied through the tube by an aspirator or a vacuum pump. This induced unidirectional flow of air or fluid through the pore channels of the alumina. A solution of ligand-stabilized gold colloids (diameter 15 nm) was added dropwise to the surface of the alumina membrane. Upon application of the aspirator, fluid in which the gold colloids were suspended was forced down the channels of the alumina. Because the barrier side contained pores with diameters smaller than 5 nm, the colloids were prevented from leaving the membrane; they would then accumulate in the pore channel and form a wire. Larger sections could be filled in a specially made fritted glass apparatus.

**Pore filling by electrophoresis:** Electrophoretic pore filling was performed under an electric field strength ranging from 5 to 20 Vcm<sup>-1</sup>. From past experience, it was determined that Au<sub>55</sub> clusters in CH<sub>2</sub>Cl<sub>2</sub> stabilized with PPh<sub>3</sub> or T<sub>8</sub>-OSS ligands acquired a positive charge. The aluminum foil was therefore made to act as the cathode during the pore-filling process. Although the barrier layer remained intact, it was no problem to direct an electric field through the very thin oxide layer (a film formed at 5 V, for example, has a barrier layer of ca. 5 nm). An inverted cell similar to the one used during anodization was employed.

**Pore filling by immersion and capillary action:** This method was applied to pore filling with clusters. For light distributions of clusters in pores, membranes were floated on top of solutions containing clusters, which crept into the pore channels by capillary action. Heavy ingress of clusters could be attained by immersing the membrane in an appropriate cluster solution. Ligand-stabilized Au<sub>55</sub> clusters in CH<sub>2</sub>Cl<sub>2</sub> adhere strongly to the walls of the porous alumina. Depending on the initial concentration of clusters in solution, solutions would eventually become depleted of clusters and become lighter upon transmission. Membranes have been left in cluster solutions for short durations (a few hours) or for extended periods of time (two months).

**TEM and AFM sample preparation and analysis:** Specimens for TEM analysis were prepared by one of two methods. In the first, specimens were embedded in Spurr's resin and sectioned with an ultramicrotome (Leica Ultracut). Transverse sections of cluster- and colloid-filled membranes were obtained in this way. Sections ranged in thickness from 5 nm to 150 nm. In another technique, planar sections of the porous alumina film were thinned by ion milling (GATAN Duo Mill 600). The gun voltage and gun current were 5 kV and 1 mA respectively. The sample was held at 13° and rotated at 10 rpm. Ion milling and TEM analysis of the ion-milled samples were accomplished with a JEM 100C instrument operated at 100 kV. Images of sections were acquired by JEM 2000 FX, Philips CM120 BioTWIN Cryo, and Philips FEG CM200 microscopes. In addition, surface analysis by AFM used a Dimension 5000 microscope (Digital Instruments). The samples were imaged with a silicon tip in tapping mode.

**Acknowledgments:** G. S. is grateful to the Deutsche Forschungsgemeinschaft and the Bundesminister für Bildung, Wissenschaft, Forschung und Technologie, Bonn (Germany), for funding this project. The Fonds der Chemischen Industrie, Robert Bosch GmbH, Stuttgart, and Cerdec AG, Hanau (Germany), are also gratefully acknowledged for financial support. J.-O. B. is grateful to the Swedish Natural Science Research Council (NFR).

Received: June 12, 1997 [F 723]

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