Metal Nanostructures

A New Class of Electronic Devices

by Walther Schwarzacher

Since the discovery of the transistor just over 50 years ago (see ***Interface*** Vol. 6, No. 1), the cost of electronic systems has been reduced and their performance dramatically improved. New technology has resulted in individual components becoming ever smaller and more highly integrated. Controlling the structure of semiconductor devices on a submicron scale has become routine. At the same time, the availability of structures with critical dimensions in the submicron range (nanostructures) has led to exciting developments in fields beyond semiconductor science. Research into metal and metal/oxide nanostructures has proved particularly fruitful, since their properties are not only of fundamental interest, but also extremely useful. Furthermore, in many cases they can be prepared simply and efficiently by electrodeposition.

Magnetic Nanostructures

Recently, the most intensively studied metal nanostructures have probably been those with a ferromagnetic component. This interest stems from the discovery, made almost simultaneously in France and Germany at the end of the 1980s,[1,2] that metal films consisting of alternating layers of a ferromagnetic metal and a non-magnetic metal can exhibit "giant magnetoresistance" (GMR) when the layer thicknesses are of the order of the appropriate electron mean free path, i.e. at most a few tens of nm. The magnetic configuration of a material exhibiting GMR can be changed from one in which the electrical resistance is high to one in which it is considerably lower simply by varying the applied magnetic field (see Fig. 1). This means that if their resistance is monitored, materials exhibiting GMR can be used to detect magnetic fields. Sensors using GMR can offer a better performance than earlier designs based on anisotropic magnetoresistance (a bulk effect, unlike GMR which is only observed for nanostructured materials), and are already being incorporated in hard disk drives for magnetic data storage.

The first films to show GMR were prepared by molecular beam epitaxy (MBE), a technique pioneered by semiconductor researchers and subsequently extended to metal deposition. MBE takes place at extremely low pressures (typically 10^{-8} Pa) and may be used to prepare very clean films, with good control over the structure. Shortly afterward, IBM researchers showed that GMR could be observed in ferromagnetic/non-magnetic metal multilayer films prepared by sputtering,[3] which, although it still requires a vacuum system, is cheaper and faster than MBE. Because electrodeposition, which takes place at atmospheric pressure and room temperature, is an even cheaper process, a number of research groups then took up the challenge of electrochemically making metal multilayer films exhibiting GMR.

In the early 1980s, a number of groups developed a method for electrodepositing metal multilayer films with individual layers as thin as a few Å from a single electrolyte.[4-6] It is, of course, also possible to deposit multilayers using separate electrolytes for each component,[7] but using a single electrolyte avoids such possible complications as cross-contamination of the electrolytes or oxidation during transfer between them. To illustrate the principle of deposition from a single electrolyte, consider two metals A and B, where A is the more noble. By

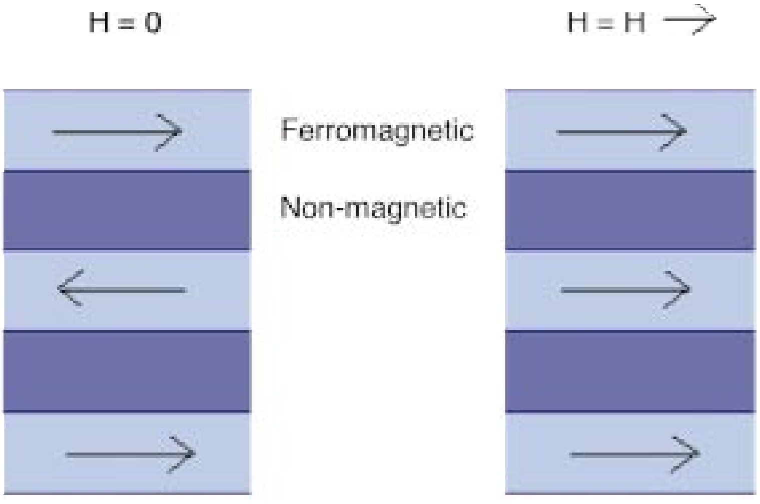

Fig. 1. To understand how giant magnetoresistance (GMR) can be caused by spin-dependent electron scattering, consider the multilayer shown, where the light blue blocks represent layers of a ferromagnetic metal, the dark blue blocks represent layers of a non-magnetic metal, and the arrows represent the magnetization direction. Assume that the electrons in the ferromagnetic metal are scattered weakly if their spin is parallel to the magnetization direction, but strongly if it is antiparallel. In the absence of an applied magnetic field, the multilayer can have the magnetic configuration shown on the left (either arising randomly or as a consequence of antiferromagnetic exchange coupling). All electrons will be strongly scattered in at least one of the layers: electrons with spin ← will be strongly scattered in the top and bottom layers, while electrons with opposite spin → will be strongly scattered in the middle layer. This means the electrical resistance will be high. If a sufficiently strong magnetic field H is applied in the → direction, then the magnetic configuration of the multilayer can change to the one shown on the right. Now, however, although the electrons with spin ← will be strongly scattered in all layers, the electrons with spin → will not be strongly scattered anywhere, and effectively "short-circuit" the ← electrons. This means the resistance will be much lower. Since switching between the two configurations is accomplished by applying a magnetic field, the associated change in resistance is a magnetoresistance (GMR).

switching between a deposition potential at which only A is deposited and one at which both metals are reduced, it is possible to grow a multilayer film consisting of alternating layers of pure A and a B-A alloy. In practice the process is often controlled through the current density (galvanostatic deposition) rather than the substrate potential (potentiostatic deposition). The trick used to ensure that the B-A alloy contains only a small amount of A is to keep the concentration of A in the electrolyte very low, so that its deposition is diffusion-limited.

Using this process, our group grew a series of Co-Ni-Cu/Cu multilayers from a sulphamate electrolyte, which exhibited GMR of up to ~20%, the largest GMR being obtained for the thinnest Cu layers (~7Å in our case).[8] This result showed that with regard to magnetotransport properties, metal nanostructures prepared by electrodeposition are competitive with those prepared by much costlier vacuum processes. The large GMR observed for very thin Cu layers was a particularly important indicator of structural quality, because defects ("pin-holes") in the Cu, or too much interfacial roughness, would couple the Co-Ni-Cu layers ferromagnetically and therefore suppress the GMR. Such suppression has been observed for the Co-Ni-Cu/Cu system at higher pH values[9] and for the Co-Cu system.[10]

In order to make it easier to integrate electrodeposited magnetic nanostructures and conventional semiconductor-based electronics, a number of groups have studied the electrodeposition of magnetic metals and multilayers on Si and GaAs.[11,12] For example, our group and André Pasa's group in Florianópolis, Brazil have shown that multilayers electrodeposited directly onto Si without any seed layer can show GMR of over 10%.[13] Magnetic films electrodeposited directly onto GaAs can be highly textured or even single-crystalline, and often exhibit in-plane magnetic anisotropies remarkably similar to those observed for MBE-grown films.[14,15]

Recently, Karen Attenborough and co-workers in Leuven, Belgium, used GaAs as the substrate for a magnetic multilayer which showed by far the greatest sensitivity (defined as the % change in resistance per unit change in applied field) of any electrodeposited GMR material to date.[16] This sensitivity is achieved partly by making use of a "spin-valve" design in which the magnetization direction in one ferromagnetic layer is free to move relative to the magnetization direction in a second "pinned" layer, and partly as a result of the magnetic anisotropies induced through electrodeposition on GaAs.

Other workers have concentrated on improving the quality of ultrathin magnetic films and multilayers electrodeposited on metal substrates. For example, Werner Schindler and Jürgen Kirschner in Halle, Germany have studied the electrodeposition of ultrathin Co films on single-crystal Cu(100) from 1mM $CoSO_4$.[17] The magnetic properties of the films were studied in situ using the magneto-optic Kerr effect, by which the polarization of light reflected from a material is affected by its magnetization. Since the Curie temperature of a Co film decreases with decreasing film thickness, and all measurements were made at room temperature, the saturation magnetization vanished for the thinnest films studied (Fig. 2). The onset of magnetization around 1.5 ML and the square magnetic hysteresis loops were compatible with a layer-by-layer growth mode in the initial stages of the deposition.

Multilayers are not the only nanostructured materials to exhibit GMR, as heterogeneous alloys consisting of ferromagnetic particles in a non-magnetic matrix can also show this effect (with the ferromagnetic particles corresponding to the ferromagnetic layers in a multilayer). The groups of Yuji Ueda in Muroran, Japan and Valery Fedosyuk in Minsk, Belarus have specialized in the electrodeposition of heterogeneous alloys, and have reported GMR in systems including Co-Cu and Co-Ag.[18, 19] An interesting difference between these systems is that annealing increases the GMR of electrodeposited Co-Cu films by increasing the segregation of Co and Cu, but for Co-Ag films it reduces the GMR, presumably because the Co particle size in the as-deposited films is already close to the optimum.[20] The sensitivity and magnitude of the GMR in these alloys is rather low, but they are extremely straightforward to prepare, and could find application in very low-cost sensor systems.

Nanowires

In addition to its low cost, electrodeposition has the great advantage of being area selective, in the sense that deposition will take place only where there is a conducting path to the external circuit. Hence, if a conducting substrate is partly covered with a patterned insulating layer, electrodeposition will take place only where the conductor is exposed. This makes electrodeposition an ideal method for filling high-aspect ratio templates, like the nanoporous membrane shown in Fig. 3a. Deposition will start at the ends of the pores where the conducting layer is exposed, and will continue until the pores are filled, creating wires of electrodeposited material. If,

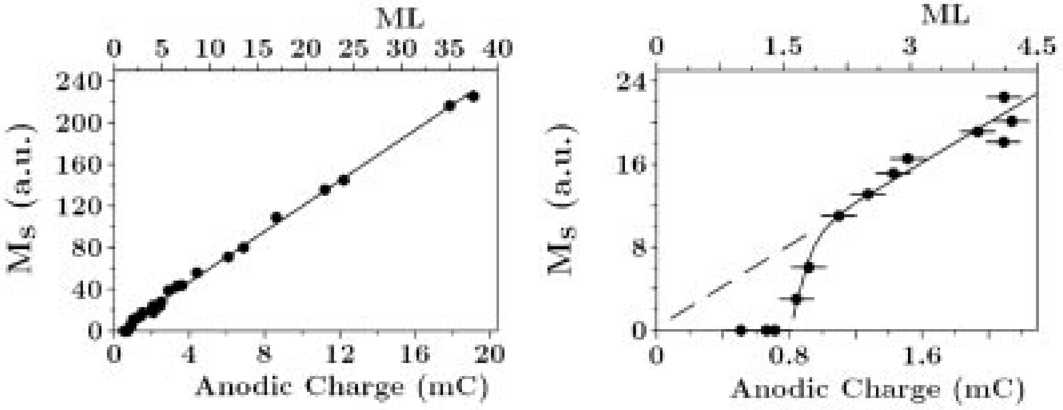

FIG. 2. Linear dependence of the magnetic moment (M_S) in arbitrary units (a.u.) on the film thickness for Co films electrodeposited from a deaerated 0.3M Na_2SO_4/1mM $CoSO_4$ electrolyte on a Cu(001) single-crystal substrate: (a) thickness range 0-40 ML; (b) expanded thickness range 0-4.5 ML. The disappearance of the magnetization below 2 ML is caused by the decrease of the Curie temperature with decreasing film thickness. (Courtesy of W. Schindler, Max-Planck-Institut für Mikrostrukturphysik, Halle).

by contrast, one were to try to use evaporation or sputtering to fill the pores, material accumulating on the surface of the membrane would soon block off their entrances.

Electrodeposition in nanoporous membranes may be used to prepare metal wires with diameters down to a few tens of nanometers and lengths of several µm or greater. The first such "nanowires" were electrodeposited in the pores formed by etching damage tracks produced in mica by high-energy charged particles,[21] but porous aluminum oxide and nuclear track-etched polycarbonate membranes have also proved highly successful as nanowire templates, and the materials deposited have been extended to include semiconductors and polymers as well as metals.[22, 23]

Electrodeposited nanowires can have extremely interesting electronic properties. For example, Peter Searson's group at Johns Hopkins University in Baltimore has recently measured a very large positive magnetoresistance (unlike GMR, which is generally negative) in nanowires of the semi-metal bismuth.[24] This positive magnetoresistance, which was previously observed in Bi single-crystals, has its origin in the curving of charge carrier trajectories under the influence of an applied magnetic field, but is much larger than the corresponding effect in metals because of the very low carrier densities in Bi. The magnitude of the observed effect indicates that these electrodeposited nanowires are of very high structural quality. Our group has also used electrodeposition to make nanowires with a very high degree of structural perfection, this time from lead,[25] which is a superconductor at low temperatures. Pulse deposition was used to electrodeposit selectively either polycrystalline or single-crystal Pb nanowires, and the superconducting transition temperature was found to be significantly lower for polycrystalline samples than single-crystal ones. This is actually quite a surprising result, and is probably a consequence of the one-dimensional nature of the nanowires. Another surprising aspect of this work was that the overpotentials necessary to obtain single-crystal nanowires were higher than those needed for polycrystalline wires. Overpotentials even higher than required for single-crystal nanowires gave nanocrystalline wires, as might be expected.

The groups of Luc Piraux in Louvain, Belgium and Jean-Philippe Ansermet in Lausanne, Switzerland have pioneered an elegant variation on the nanowire theme.[26,27] By using the same single electrolyte method previously used to prepare multilayer films, they were able to prepare multilayer nanowires consisting of a stack of disks of alternating composition (Fig. 3b). This is a good example of patterning an electrodeposited material with submicron precision in all three dimensions, laterally through the use of a template, and along the growth direc-

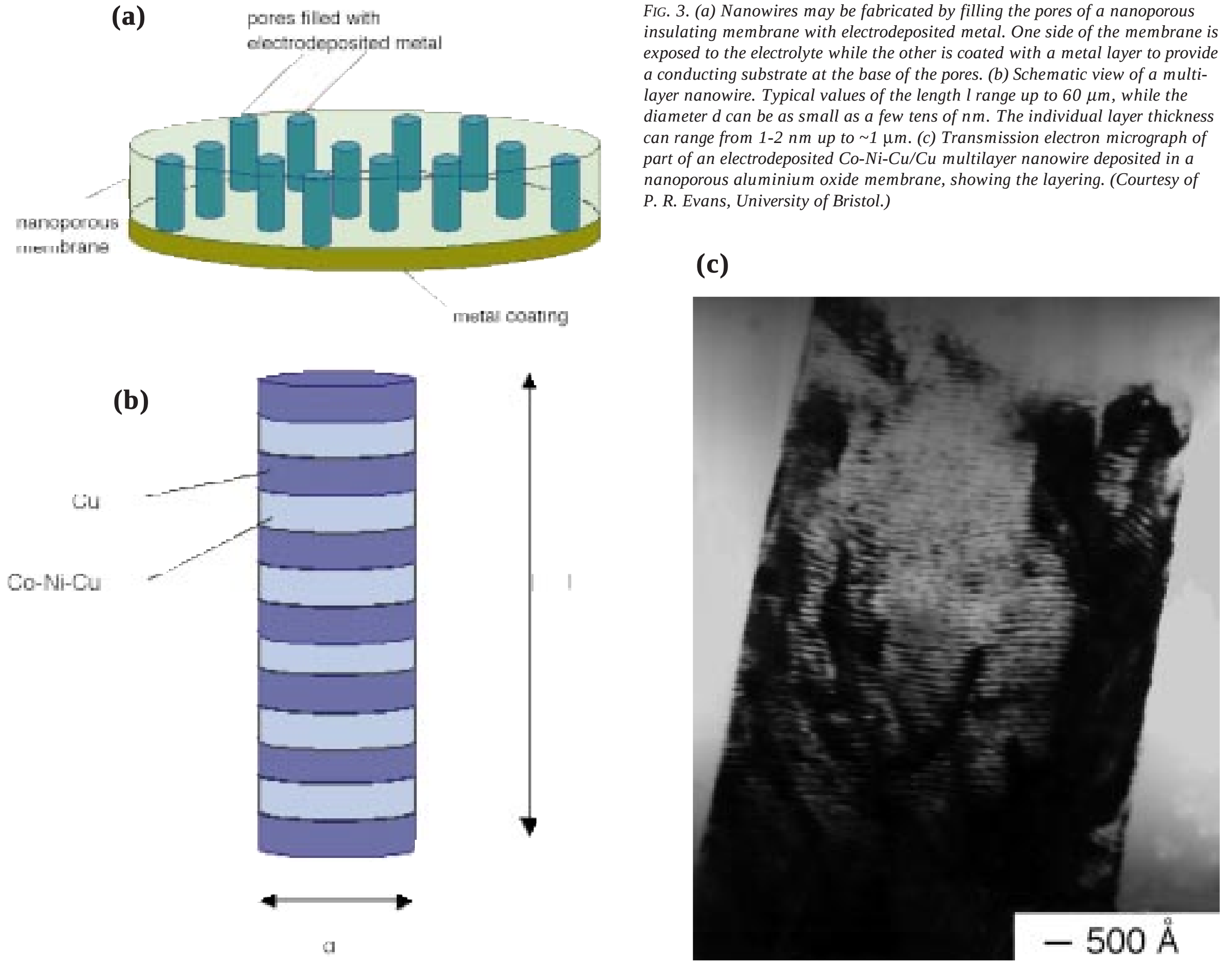

FIG. 3. (a) Nanowires may be fabricated by filling the pores of a nanoporous insulating membrane with electrodeposited metal. One side of the membrane is exposed to the electrolyte while the other is coated with a metal layer to provide a conducting substrate at the base of the pores. (b) Schematic view of a multilayer nanowire. Typical values of the length l range up to 60 µm, while the diameter d can be as small as a few tens of nm. The individual layer thickness can range from 1-2 nm up to ~1 µm. (c) Transmission electron micrograph of part of an electrodeposited Co-Ni-Cu/Cu multilayer nanowire deposited in a nanoporous aluminium oxide membrane, showing the layering. (Courtesy of P. R. Evans, University of Bristol.)

tion through the use of potential or current density modulation. Figure 3c shows a transmission electron micrograph of a Co-Ni-Cu/Cu multilayer nanowire, where the layering may be clearly seen.

Multilayer nanowires are very useful for studying electron transport across interfaces, because the resistance with the current flowing along the long axis of the wires and therefore, perpendicular to the plane of the interfaces is relatively easy to measure. This contrasts with the situation for conventional multilayer films, where resistance measurements in the current perpendicular to plane (CPP) geometry are extremely difficult because of the large surface area and small total thickness. The CPP geometry is, however, particularly appropriate for studying systems with GMR because it makes separating the effects of spin-dependent scattering at the interfaces and in the bulk reasonably straightforward.[28] CPP-GMR measurements of multilayer nanowires have already generated fundamental data on spin-dependent electron scattering in a number of metals.[29,30]

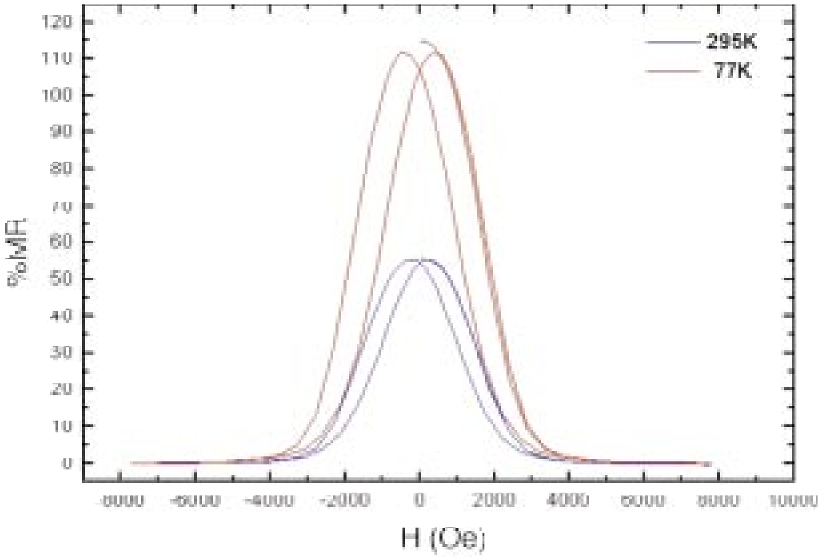

FIG. 4. Current perpendicular to plane giant magnetoresistance for 7.5 nm Co-Ni-Cu / 3 nm Cu electrodeposited multilayer nanowires with nominal diameter 20 nm. The magnetoresistance (%MR) is defined as 100 x (R_H-R_∞)/R_∞ where R_H is the resistance in an applied field H, and R_∞ is the high-field resistance. R_H has its maximum at H=0 before the applied field is cycled. (Courtesy of P. R. Evans, University of Bristol.)

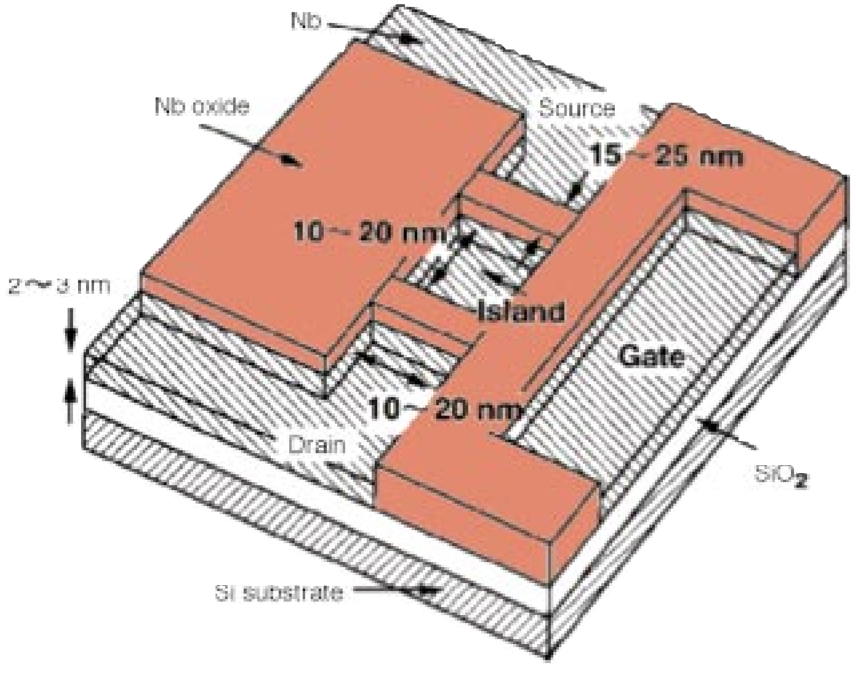

FIG. 5. Schematic of Nb-based side-gate single electron transistor (SET) with double junction structure (before thermal oxidation). (Courtesy of Jun-ichi Shirakashi, Electrotechnical Laboratory, Tsukuba.)

CPP-GMR in multilayer nanowires is also of interest for sensor applications, as the effect is often larger than the current in-plane GMR measured with multilayer films. For example, at room temperature our group has measured a maximum GMR of ~25% for Co-Ni-Cu/Cu films, but have observed up to ~60% GMR for Co-Ni-Cu/Cu multilayer nanowires.[31] At liquid nitrogen temperature we have measured a CPP-GMR of over 110% for these wires as shown in Fig. 4, which is a record for an electrodeposited sample.

A wide range of new electronic properties may be exhibited by metal nanostructures incorporating ultrathin oxide layers acting as insulating tunnel barriers, and this kind of nanostructure may also be made by electrodeposition. For example, Ansermet's group have prepared nanowires incorporating a metal-insulator-metal tunneling junction by partially filling the pores in nanoporous membranes with electrodeposited Ni, oxidizing the Ni anodically and then depositing Co from a non-aqueous electrolyte to avoid redissolution of the oxide.[32] Transport measurements below 100K showed that the oxide layer behaved as a tunneling barrier of thickness 2-3 nm and height 0.2-0.4 eV. Magnetoresistance measurements revealed abrupt resistance changes which could not be explained by changes from parallel-to-antiparallel alignment of the Co and Ni magnetizations (as in GMR), but rather appeared to be caused by changes in the spin-dependent trapping of single electrons by defects in the oxide layer.

Single Electron Transistor

As another example, if the capacitance C of a metal-insulator-metal tunnel junction can be made sufficiently small, the charging energy associated with a single electron tunneling across it, given by $E_C = e^2/2C$, may be much less than the energy k_BT of thermal fluctuations. This means that no current will flow until a bias voltage sufficient to overcome this charging energy is applied, which is a phenomenon known as "Coulomb blockade." The requirement that C be extremely small, while the tunneling resistance be not too great means that the area of the junction must also be extremely small; hence this is the relevance of nano-structures. In practice, Coulomb blockade is hard to observe with a single tunnel junction, because of the influence of the leads supplying the current.[33] However, Martin Moskovits's group in Toronto has presented some evidence for Coulomb blockade in junctions prepared by electrodepositing disordered Ni nanowires in anodically oxidized aluminum,[34] where the tunneling barrier is formed by the aluminum oxide layer between the Ni and the Al at the ends of the pores.

Coulomb blockade is much easier to observe in nanostructures containing more than one tunnel junction, such as the single electron transistor (SET). This consists of a conducting island connected to a current source and drain by tunnel junctions, and to a gate electrode by a capacitor. The potential applied to the gate electrode controls the charging energy of the island, which determines the rate at which single electron tunneling can take place and therefore controls the current between source and drain, rather as in a conventional field effect transistor such as a MOSFET. Like the MOSFET, the SET could in principle be used as the basis for digital electronic circuits. It is extremely sensitive, responding to tiny changes in the charge on the gate capacitor, but its fabrication requires the use of nanotechnology, since the dimensions of the conducting island need to be of the order of 10nm for the SET to work at room temperature. Of course, given the desirability of reducing the size of electronic components to facilitate large-scale integration, this could be considered an advantage!

Just this year Jun-ichi Shirakashi and co-workers in Tsukuba, Japan reported one of the very first SETs to operate at room temperature.[35] Remarkably, it was fabricated by an electrochemical method, namely the localized anodic oxidation of smooth ultrathin Nb films on insulating SiO_2/Si substrates. Localized oxidation was achieved by applying a positive bias to the Nb film relative to the conducting tip of an atomic force microscope (AFM) in a humidity of around 30% and was used to define source, drain, and gate as shown in Fig. 5. An additional thermal oxidation stage was used to reduce the size of the metal features still further, and the completed device showed clear SET behavior even at 298K.

Electrochemical methods can therefore be used to make metal and metal/oxide nanostructures with a wide variety of interesting and potentially useful electronic properties. They range from the SET which has features in common with conventional transistors, to nanowires and multilayers with novel magnetoresistive behavior. In some cases (e.g. ultrathin films) electrodeposition achieves similar results to costly techniques such as MBE, while in others (e.g. multilayer nanowires) there is no real alternative to electrodeposition. The study of electrodeposited metal nano-structures is still at a very early stage, but the combination of electrochemistry and patterning on the nanometer scale seems highly likely to lead to further exciting developments. ■

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