

Science at the atomic scale

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On the evidence of *Nature's* recent conference in Tokyo, technologies at the nanometre scale are now within reach. But how are they to be realized, and what form will they take?

"I CHALLENGE the notion that nanotechnology exists," said Don Eigler at *Nature's* conference* convened to discuss that topic. Coming from someone whose atom-manipulating feats serve in some eyes to define the field, this may seem ironic; indeed, each talk at the conference gave concrete evidence of our ability to observe and control matter at the atomic and molecular scale. But Eigler's point was a subtler one: he suggested that no technologies had yet come from the basic science.

This, of course, begs the question of when science becomes technology. But what was made abundantly clear by speakers ranging from solid-state physicists and electronics engineers to organic chemists and materials scientists, is that science at the nanometre scale is full of potential for practical exploitation.

For a start, there is already evidence (or what John Hopfield (Caltech) calls an "existence theorem") for a working molecular technology, in the form of biology. Mechanical, electronic and computational operations can, it seems, be conducted efficiently by relying on molecular interactions; moreover, the machinery for such processes can to some extent assemble itself from the basic components. What remains for chemists is to identify which are the guiding principles that one might usefully mimic in making artificial molecular assemblies. In materials science, too, there is much to be learned from the way that biology contrives to engineer superior properties by control of microstructure and growth.

For more conventional electronics technology, based on semiconductors such as silicon or gallium arsenide, the challenge of the nanometre scale is not so much that of constructing small enough devices, as of coping with the new physics that becomes manifest on entering the domain of quantum mechanics. But this new physics has also been turned to advantage, not only in providing the basis for novel devices but as a fascinating field for basic research.

Novel devices

Not surprisingly, much of the impetus towards nanotechnology has come from the electronics industry. In the past 40

years, the characteristic size of a transistor has decreased from 1 cm to less than 1 μm ; there are now commercial integrated-circuit chips containing more than a million devices. At this scale, macroscopic principles of electronic circuit design are still valid, but a further 10–100-fold reduction, which could be achieved in one or two decades, will bring individual devices to a size at which the quantum-mechanical, wave-like nature of the electron can no longer be ignored.

This 'mesoscopic' realm, in which an electron's behaviour is dictated as much by the structure through which it travels as by bulk material properties, has been explored by means of engineered structures that confine electrons to progressively fewer dimensions. As Hiroyuki Sakaki (Univ. Tokyo) pointed out, quantum confinement in two dimensions has existed for 20 years in the form of ultra-thin semiconductor films deposited by molecular-beam epitaxy or chemical vapour deposition. As the thickness of such a film is reduced, the electron energy for motion normal to the layer is quantized into discrete sub-bands — just as only certain frequencies of sound are allowed to resonate in a wind instrument. For a layer as thin as ~ 10 nm, the energy spacing between bands is large compared to the characteristic thermal energy $k_B T$, even at room temperature, so that almost all electrons are in the ground-state sub-band. This quantization already forms the basis for practical devices, such as the resonant tunnelling diode and quantum-well laser.

Beyond the quantum well lies the one-dimensional quantum wire. The further reduction in dimensionality brings with it markedly higher electron mobilities, because elastic scattering of electrons by impurities is limited to nearly exact backward scattering, which has very small probability. Inelastic scattering by optical phonons, the dominant process at high temperatures, can also be suppressed if the ground-state bandwidth is narrower, and the first energy gap wider, than the phonon energy, so that absorption or emission of phonons is prevented. In practice, this means that quantum coherence effects can be observed at room temperature, provided that the wire width is less than ~ 20 nm. This has allowed the fabrication of 'quantum interference devices', in which

external signals control the interference of coherent electron waves, to increase or reduce electron transmission. Quantum wires can also support high electron velocities, making an array of quantum wires an attractive option for more conventional high-speed devices.

New physics

The same high electron mobility that makes mesoscopic conductors attractive for device applications has made them a veritable playground for those interested in the basic physics of electron transport. When the dimensions of the conductor are smaller than the electron mean free path, the electrons travel 'ballistically', undisturbed by interactions with phonons or impurities. When these dimensions are also comparable to the electron wavelength (strictly speaking, the Fermi wavelength), quantization effects are observed.

Bart van Wees (Univ. Groningen) described the completely unexpected discovery of conductance quantization in a quantum point contact (B. J. van Wees *et al. Phys. Rev. Lett.* **60**, 848–850; 1988). The quantum point contact creates a constriction of variable width through which electrons confined to a two-dimensional semiconductor layer can pass; the unexpected finding was that the conductance of this constriction exhibits plateaux as a function of its width. This behaviour is now understood to arise from the quantization of transverse momentum in the constriction: each increase in width by half the electron wavelength allows an additional one-dimensional sub-band, or 'channel', to be added to the conductance, increasing it by $2e^2/h$. (Those familiar with the quantum Hall effect will recognize $2e^2/h$ as the spacing of plateaux in the Hall conductance (ignoring spin splitting); van Wees explained that the two effects are indeed related, as the variation of conductance with magnetic field can also be explained in terms of the occupation of quantized channels.) The surprise was that this behaviour, which had been predicted to occur in an ideal quantum wire in which scattering is absent, can be observed in a real experimental system.

A different type of quantization — that of electric charge — also rears its head as circuits shrink. Michel Devoret (Centre d'Etudes Nucléaires de Saclay) described how, at low temperatures and

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in sub-micrometre-scale metallic circuits, it is possible not only to detect single electrons but to manipulate them. The phenomenon of single-electron tunnelling (SET) arises from the interplay of electron delocalization and the Coulomb interaction: an electron is allowed to tunnel across a narrow insulating barrier to a region of low capacitance, C , only if it can supply the requisite electrostatic charging energy $e^2/2C$. At low temperatures and/or very low capacitances, this energy can be made large compared with thermal fluctuations, so that passage through the barrier (lifting of the 'Coulomb blockade') can be controlled reliably by an external gate voltage. This is the basis for the 'electron turnstile' (L. J. Geerligs *et al.* *Phys. Rev. Lett.* **64**, 1861–1864; 1989), in which a radio-frequency gate voltage 'clocks' electrons one by one around a circuit, with an accuracy of 10^{-3} . With sub-micrometre circuit elements, the characteristic capacitance is about 10^{-15} farad and single-electron tunnelling can be seen at temperatures below about 0.3 K; if the dimensions could be reduced to the sub-nanometre scale, with capacitances of about 10^{-18} farad, then SET could be observed at room temperature.

Just as two Josephson junctions can be arranged in parallel to make an exquisitely sensitive device for measuring magnetic flux (the superconducting quantum interference device, or SQUID), two normal-metal tunnel junctions can be combined in an exactly analogous circuit to yield a charge-measuring device termed the 'SET transistor'. With this device, one can observe single tunnelling events, and monitor the charge on an electrode with sub-single-electron accuracy. In principle, SET (in the shape of the electron turnstile) provides an exact relationship between frequency and current, just as the Josephson effect ties together frequency and voltage, and the quantum Hall effect links voltage to current. Devoret hopes that SET may someday "close the metrological triangle" by providing a very accurate current standard, but notes that this would require a turnstile accuracy of 10^{-8} , instead of the present value of 10^{-3} .

At first sight, the SET transistor might seem to be the fulfilment of a nanoelectronic dream, with only one electron needed for each bit of information. But Devoret points out that as the transistor has no voltage gain, it is unlikely to be of interest to engineers. The same can certainly not be said of its analogue, the SQUID. In a presentation that showed just how quickly new science can be turned into commercially viable technology, John Clarke (Univ. California, Berkeley) demonstrated that high-transition-temperature oxide superconductors, the

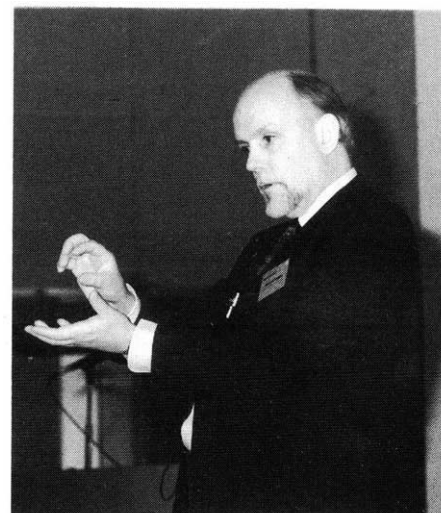
first of which was discovered only in 1986, already provide the essential components for an electronics technology. As with semiconductor electronics, the fabrication of superconducting devices relies on the controlled epitaxial growth of thin films, followed by photolithographic patterning. Individual Josephson junctions have been patterned with widths as small as 0.2 μm , so that device sizes of a few hundred nanometres seem within reach. Closer to the market, Clarke described an 'integrated magnetometer' comprising a SQUID and a flux transformer (for increased sensitivity), made by depositing eight epitaxial layers on the same substrate; as yet it works only at 75 K and below, but there is no reason why this should not be increased to ~ 90 K.

Another lesson that would-be nanotechnologists might learn from the high- T_c superconductor experience is that any emerging technology will have to compete with whatever technology exists already — in the case of digital electronics, this means silicon chips. It looks likely to be a long time before a Josephson computer will be able to compete with silicon, but high- T_c superconductors have nevertheless already found several niches outside computing, notably in far-infrared detectors, microwave components and magnetometers

Making nanostructures

The wealth of new devices and new physics discussed above suggests that we are not yet limited, either in technology or basic science, by our ability to fabricate small structures. Defining 'nanostructures' as structures with dimensions less than 0.1 μm , Alec Broers (Univ. Cambridge) inferred from past trends that the mainstream electronics industries would not be needing nanostructures for more than 10 years, yet present-day electron-beam lithography can already be used to fabricate useful devices measuring ~ 20 nm. (The resolution of this apparent paradox lies in the fact that electronics technology comprises not just individual devices, but literally integrated circuits; it is the need of each successive generation of chips for new circuits, new materials and new design concepts that seems to limit the speed of progress.) But even if electronics companies are not forcing the pace, there is surely a demand from research physicists for ever-smaller structures. So what are the limits on nanolithography?

Electron optics can produce beams of about 0.2 nm in diameter, but the smallest practical structure made so far is 100 times larger than this. As Broers explained, this limit arises from the use of polymers as 'resists' in the electron-beam lithographic process: where the polymer has been exposed to the beam, it can be



Richard Smalley encapsulating fullerene research.

preferentially etched away, leaving a pattern for subsequent deposition of circuit elements on the substrate. But although it is possible to write a line as thin as ~ 1 nm on the resist, it will not be etched successfully; the thinnest lines that can be developed properly are ~ 10 nm wide. This behaviour is not completely understood, but it seems that inelastic interactions between electrons in the beam and resist molecules — for example, secondary electron excitation and subsequent straggling of the secondaries — give rise to a smearing-out of the electron dose with a characteristic width of 12 nm. This behaviour seems to characterize all spin-on polymer resists, irrespective of molecular size.

Two techniques have been used to overcome the 10-nm resist limit, but each has its problems. In direct structuring sublimation, the electron beam is used not to expose a resist, but to sublime a metal halide or oxide substrate. This technique has been used to drill holes 2 nm in diameter and 4 nm apart, but has not yet created any useful structures. In direct-exposure lithography, the beam is used to write a pattern on SiO_2 , with the effect of enhancing the etch rate in hydrofluoric acid. This technique has been used to create slots 10 nm wide and 15 nm apart, which can then be replicated in silicon by reactive ion etching, using the patterned SiO_2 as a mask. The difficulty here, however, is the rather small difference in etch rate (about a factor of three) between exposed and unexposed regions of the SiO_2 , giving rise to slots with sloping sidewalls.

The higher resolution achieved with these two techniques lends support to the idea that what is needed is an image-forming process that is activated only by the high-energy primary electrons, rather than by the low-energy (20 eV) secondaries. Breaking a bond in a

polymer such as polymethylmethacrylate requires only 5 eV; defect formation in SiO₂ requires about 30 eV. "If we had something that requires 100 eV", said Broers, "we would have better resolution." This plea prompted Richard Smalley (Rice Univ.) to make the first of several suggestions of novel uses for the buckminsterfullerene molecule: why not use the electron beam to crosslink molecules in a thin film of C₆₀? This might well take a lot of energy, and the unpolymerized C₆₀ could be dissolved away with benzene.

Carving versus constructing

The struggle to extend lithographic techniques to smaller scales raises the question of how far it is worth pursuing a 'top-down' approach to nanofabrication. As Hopfield put it, "Using molecular-beam epitaxy or lithography for nanoelectronics seems increasingly like making a suspension bridge by carving it out of a large block of steel." The opposite approach is to build nanostructures atom by atom, a capacity that is now available courtesy of the scanning tunnelling microscope (STM).

The sheer joy of being able to move single atoms pervaded Don Eigler's (IBM Almaden Research Center) presentation. He told how a problem — is the STM tip perturbing the system? — was converted by some handy lateral thinking into a new capability. It turned out that the force exerted by the STM tip on a xenon atom adsorbed on a metal surface could have a surface-parallel component large enough to pull the xenon atom across the surface, while having a surface-normal component small enough to leave the atom bound to the surface. Eigler's first feat was to construct a linear chain of seven xenon atoms on a nickel (110) surface; his colleague C. P. Lutz then did the same with platinum atoms on platinum — a trickier task than for weakly bound xenon. Eigler looks forward to the day when we will be able to use the atomic force microscope to do similar things with metal atoms on an insulating surface — building circuits atom by atom to study electron transport in exceedingly small structures.

Not content with a flatlander's approach to atomic manipulation, Eigler and others have since learned to pick up atoms with the STM: this allows atoms to be carried over step edges, and provides in principle for the fabrication of three-dimensional structures. Eigler's two-terminal "atom switch", in which the reversible transfer of a xenon atom from the STM tip to a nickel surface modulates the conductance between tip and surface, can be thought of as the prototype for an atomic-scale electronic device. But Eigler is the first to point out

that this 'atomic-scale' device has a roomful of equipment attached to it. In fact, it is not clear whether the atom switch would work with nanoscopic leads, which might not provide a sufficient heat sink to prevent the device from destroying itself.

Eigler stressed that the mechanism that causes the xenon atom to move back and forth from tip to surface is not yet understood; such general questions of mechanism are being addressed systematically by Masakazu Aono (RIKEN) in the ERATO "Atomcraft Project". Perhaps as an incentive to solve the difficult problems standing in the way of reliable fabrication, Aono poses the question, "If you have a monolayer of silver atoms on silicon, and remove one out of three silver atoms, will you get a SET transistor working at room temperature?" Even if not, it is clear that the rewards will be enormous. In fact, Aono's colleague H. Nejh (Nature 353, 640–642; 1991) has claimed to have seen single-electron tunnelling from an STM tip to a liquid-crystal molecule at room temperature. This prompted Devoret to suggest that the ubiquitous C₆₀ might be an even better molecule to use, as it would be a nearly ideal spherical capacitor.

Aono described a systematic set of experiments from which he concluded that field evaporation of ions from both tip and sample is the cause of the atomic-scale ditches and bumps created by scanning an STM tip over the reconstructed surface of silicon known as 7×7. The hope is that such experiments will ultimately provide the bedrock of fundamental understanding that will have to underlie a successful manipulation technology.

Another essential requirement for any type of nanofabrication system is the ability to position a tool (whether it be an STM tip, an electron beam, or even a molecule) with nanometre accuracy. Shoichiro Yoshida (Nikon Corp.) demonstrated that, even if there is as yet no technology based on nanostructures, we already have a technology with nanometre precision. In particular, Yoshida's ERATO "Nano-mechanism Project" has developed a fine position control for 1-nm positioning, using a rolling ball guide, and a laser interferometer for measuring nanometre displacements, which by using two different wavelengths reduces errors of 30–40 nm caused by atmospheric turbulence to a few nanometres.

From self-assembly to devices

Building molecular devices and assemblies by manipulation of individual molecules is, with the STM's new-found versatility, not beyond our means, but it is likely to be prohibitively slow. At the

nanometre scale, it will be much more efficient to let chemistry do the job — that is, to design molecules that will assemble spontaneously into useful structures. Mutsuyoshi Matsumoto (National Chemical Lab., Tsukuba) and George Gokel (Univ. Miami) provided elegant examples of the extent to which self-assembly can now be controlled. In neither case were the basic structures hot off the drawing board: the ordered, lamellar arrays of amphiphiles described by Matsumoto were studied by Irving Langmuir and Katharine Blodgett in the 1910s, while Gokel's bilayer vesicles have a history as old as the cell. But clever chemistry has allowed functionalities to be built into these structures of the sort that could generate many new applications.

Matsumoto described Langmuir-Blodgett (LB) films whose electrical conductivity, potentially substantial by virtue of the TCNQ-based charge-transfer complexes incorporated in the amphiphile head groups, is photochemically switchable (H. Tachibana *et al.* J. Am. chem. Soc. 111, 3080–3081; 1989). This immediately invites speculative applications for energy conversion and signal transduction. The amphiphiles are designed on a modular basis: as well as the charge-transfer 'working' unit, they contain a switching unit in the 'tail', linked to the head-group working unit by a linear alkyl 'transmission' unit. The switch is an azobenzene group, in which the -N=N- double bond may adopt either a *cis* or a *trans* conformation. The *trans* form is favoured at room temperature, yielding a more or less linear molecule which will form an ordered two-dimensional array when a monolayer on the surface of water is compressed in an LB trough. Multilayer, lamellar stacks can be deposited from this apparatus onto a solid substrate by a simple dipping procedure. As the head groups lie side by side in a periodic fashion, these deposited LB films show an appreciable in-plane conductivity. But irradiation with ultraviolet light switches the conformation to *cis*, leaving the molecules kinked and altering the arrangement of head groups; the conductivity drops as a result. Matsumoto showed that a similar photoinduced switch in a monolayer film can cause reorientation of molecules in a smectic liquid-crystal film above it; this might form the basis of a new method for switching liquid-crystal displays.

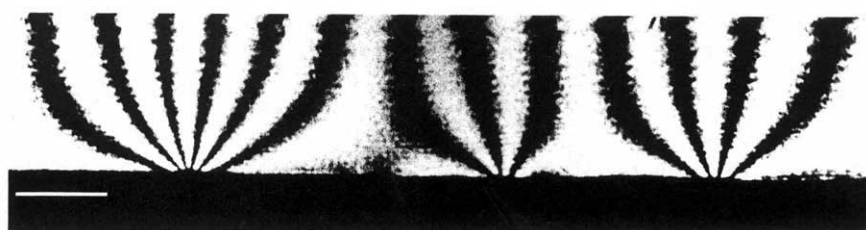
Switching behaviour also lies at the heart of Gokel's self-assembling structures. A reduced cholesterol (nature's own membrane stiffener) attached to ferrocene (an Fe²⁺ ion sandwiched between two cyclopentadienyl rings) constitutes a somewhat unusual kind of amphiphile, but these molecules will

Seeing the unseeable

The ability to move atoms and molecules with the STM has perhaps diverted attention from the equally wonderful possibilities for 'seeing', and more broadly, sensing, offered by this microscope and its relations. Heinrich Rohrer (IBM Zürich Research Laboratory) surveyed the broad sweep of these possibilities, pointing out that the range of possible interactions between tip and sample (van der Waals, adhesive, magnetic and electrostatic, to name a few) offers both opportunities and potential problems. In principle, one can isolate any property of interest and measure it locally: under the broad heading of magnetism, for example, one can use the magnetic valve effect (in which the tunnelling current is sensitive to the electron polarization), magnetic force microscopy (with a magnetized tip), or magnetic resonance microscopy. Any of these techniques can also be combined with spectroscopy — for example, one might inject polarized electrons from the tip, and measure the emission of polarized photons. But Rohrer cautioned that the sheer number of interactions makes it hard to be sure that one is really looking at the interaction of interest, and one must also ensure that the probe itself doesn't interfere with the experiment one is trying to perform.

Akira Tonomura (Hitachi Advanced Research Laboratory) reminded the

audience that the STM is not the only way to create atomic-scale images. The availability of coherent electron beams, produced by field emission from a pointed tungsten tip, has led to the technique of electron holography, for both high-resolution imaging and electron interferometry. Tonomura illustrated the use of reflection interferometry to measure surface topography with a resolution of less than 0.01 nm. Like the STM, however, the technique can do far more than simply sense topography. Thanks to the Aharonov–Bohm effect, the phase of an electron wave is sensitive to the presence of an electromagnet field: the fringes in an interference micrograph appear along magnetic lines of force, with a separation of one flux quantum between adjacent fringes. Following the use of electron holography to demonstrate definitively the existence of the Aharonov–Bohm effect, Tonomura has used the technique to image flux lines in superconductors — providing direct evidence for flux-line pinning, and other aspects of flux-line dynamics induced by thermal excitations or interactions with the supercurrent. Having seen Tonomura's videotape of flux lines dancing across the surface of a superconductor (see figure), one is inclined to believe him when he says, "with this technology, even thought experiments will be possible". □



Electron interference micrograph showing bundles of flux-lines emerging from the surface of a superconducting lead film. Scale bar, 2 μm .

nevertheless form bilayer vesicles in just the same way as phospholipids. This propensity is, however, determined by the redox state of the iron — electrochemical oxidation of the Fe^{2+} to Fe^{3+} causes vesicles to form, while reduction breaks them down again (J. C. Medina *et al.* *J. Am. chem. Soc.* **113**, 365–366; 1991). Gokel has also demonstrated redox-switchable binding of metal ions in a ferrocene derivative in which the two cyclopentadienyl rings are bridged by several tertiary diamine loops (nitrogens joined by aliphatic chains), leaving a rigid cavity between the nitrogen donor atoms. The bound metal ion sits next to ferrocene's Fe^{2+} , and is therefore expelled when the iron is oxidized to give a positively charged

ferrocenium species.

One might also regard as a kind of mechanical switching the structural changes that binding of substrate to receptor can initiate. Particularly suggestive of this mechanical response was Gokel's 'cleft-like' receptor in which the rotational freedom of ferrocene's aromatic five-carbon rings around the iron 'ball bearing' is exploited to build receptors with arms that swing around to lock their substrates in place. Of an entirely different nature is the mechanical switching of toroidal molecules threaded on a linear chain — the so-called rotaxanes. Fraser Stoddart's group in Sheffield has proposed that their rotaxanes, comprising cyclic bipyridinium units threaded on linear hydroquinols or vice versa, might

be assembled into a 'molecular abacus'; a variant presented by Gokel was a cyclodextrin on a hydrocarbon chain capped with ferrocene and a sulphonate group.

Masuo Aizawa (Tokyo Inst. of Technology) suggested that mechanical switching also lay behind the transfer of conformational change between two proteins covalently linked by a kind of molecular transmission shaft. Binding of a calcium ion to calmodulin converted from an inert to an active form the phosphodiesterase enzyme to which it had been attached by a covalent bond.

To some extent one might regard these molecular-based switches as components in search of a device. But as an example of a practical device that relies on engineering and interactions at the molecular scale, the biosensor provides arguably the best example currently on the scene. The earliest glucose sensors, developed in the 1960s, were little more than electrochemical oxygen sensors that depended on the immobilization of the enzyme glucose oxidase at the electrode surface. But Aizawa discussed possibilities for improving signal transmission at the molecular level. He showed that the electrical connection between the enzyme and the electrode can be enhanced by attaching to the electrode surface molecular wires (in this case conjugated polypyrrole molecules), the free ends of which may find access to the redox site on the enzyme.

Materials design

Fullerenes, inevitably, surfaced in many contexts: C_{60} is perhaps the perfect nanoscale construction material, a structural unit itself only marginally smaller than a nanometre. But Richard Smalley considers the graphitic microtubules reported recently (S. Iijima, *Nature* **354**, 56–58; 1991) to be of potentially equal importance; calculations indicate that some may be semiconducting and that their perfect crystallinity will make them the strongest fibres known. It is far from nanotechnological oversell to imagine welding these girders into rigid superstructures with an electron beam (perhaps having first arranged them with the STM?). The hierarchical structure of these frameworks, the basic elements of which are themselves built from the graphite 'chicken-wire' mesh, should imbue them with some of the advantages that hierarchy bestows on natural substances such as bone, an issue addressed by Paul Calvert (Univ. Arizona).

Among these superior properties, said Calvert, are toughness, damage tolerance (local failure need not lead to global breakdown), repairability and ease of further growth. Bone provides perhaps the classic example: the porous

ity, extending over several length scales, not only allows transport of fluids but also gives flexibility and high strength-to-mass ratios. Growth of bone and similar biomineral materials such as tooth enamel and shell is generally a template-directed process that allows for structural control at the micrometre level (if not finer still). Biomineralization takes place typically either in a polymer matrix (as is the case with bone) or through the guidance of a membrane, and can lead to the rapid and efficient production of extraordinarily complex shapes such as the delicate platelets of calcium carbonate found in coccoliths or the fullerene-like silica cages of diatoms.

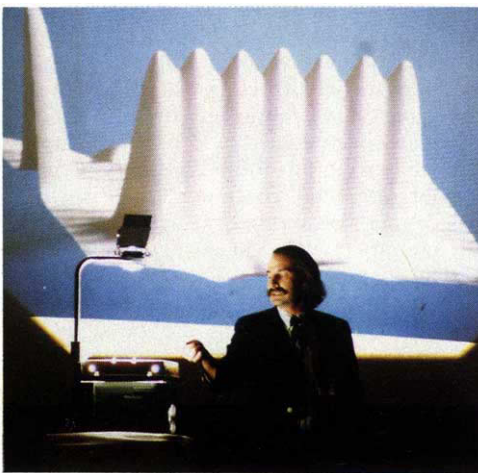
To mimic these growth processes requires an *in situ* precipitation technique in which particle size, shape and crystallographic orientation can be controlled. In biological systems, acidic proteins act as crystal growth modifiers that can, according to the conditions, either inhibit or promote growth. Calvert suggested that treating surfaces using, for example, photolithographic methods might provide a route to localized and patterned precipitation, while drawn or brushed polymer films have already been shown to be efficient at controlling the orientation of crystallization (J. C. Wittman & P. Smith, *Nature* 352, 414–417; 1991). But to achieve anything remotely like true mimicry of biomineralization, Calvert pointed to the need for new synthetic polymers that can rival proteins in their ability to provide a guiding matrix.

That nature's composite materials can achieve what monolithic ones cannot is no recent revelation. The essential attraction of composites lies with their potential to combine the strength of homogeneous, dense monolithic materials with the toughness of coarse-grained, inhomogeneous solids, in which weak links can absorb energy without catastrophic failure. Past attempts at making composites that combine these attributes have centred around the use of fibres and whiskers of micrometre dimensions embedded in a matrix. But Koichi Niihara (Osaka Univ.) showed how the fabrication of composites from elements of nanometre size is leading to far superior properties.

One variant of this approach incorporates nanometre-sized clusters either within or between larger grains of another phase. Intra-grain nanocomposites in which silicon carbide or nitride nanograins are dispersed in oxide matrices such as MgO and Al₂O₃, for example, can be prepared from powdered starting materials using standard metallurgical techniques — ball milling, hot-pressing and sintering. The improvements in properties relative to corresponding microcomposites are striking:

both toughness and strength can be increased by up to a factor of four, while the maximum operating temperatures are increased by 400 to 800 °C. These micro/nano composites provide another illustration of how a hierarchical structure can make for improved materials.

An alternative type of nanocomposite, consisting entirely of nanoscale grains, may exhibit entirely new mechanical properties compared with monolithic materials. A nano/nano-composite of this kind formed from silicon carbide (SiC) and silicon nitride (Si₃N₄) grains less than 500 nm in size will become ductile, or 'superplastic', at temperatures above ~1,600 °C, and can therefore be



Don Eigler, with a row of xenon atoms in the background.

readily moulded into components that retain both hardness and toughness at lower temperatures. These non-oxide composites are formed by hot-pressing of powders in which the grains have been put together atom by atom via chemical vapour deposition. It appears that the morphology and size of the silicon nitride grains can be controlled by the volume fraction of nanoscale silicon carbide particles in a manner that recalls inhibition or promotion of crystallite growth in biomineralization: at low SiC fractions, the SiC particles act as nucleation sites for the formation of large, elongated Si₃N₄ grains, leading to high toughness, while larger SiC fractions promote the growth of the equiaxed, nanoscale Si₃N₄ grains necessary for superplasticity.

Optical effects

Rather than considering the behaviour of nanoscale clusters *en masse*, Louis Brus (AT&T Bell Labs) described how their finite size affects the properties — electronic and optical — of individual clusters. When they contain only a few hundreds or thousands of atoms, one might expect the electronic structure not yet to have acquired the truly band-like character of the bulk solid, so that a description in terms of molecular orbitals

may remain valid. In semiconductors, it is the separation between the highest occupied molecular orbital (HOMO) and the lowest unoccupied orbital (LUMO) (which in a dimer translates as the splitting between bonding and antibonding orbitals) that ultimately metamorphoses into the bulk band gap. For clusters in the intermediate size regime, one might expect still to find discrete HOMO and LUMO levels, with an energy gap greater than that between the fully broadened bulk bands and therefore a blueshift of the absorption spectrum.

To study these effects, a highly monodisperse range of cluster sizes is needed.

The various ways in which this might be achieved include the precipitation of clusters in zeolites, porous glasses, vesicles and gels; but Brus showed that the use of inverse micelles as self-assembling 'cluster moulds' is particularly effective and convenient. In non-aqueous phases, these spherical assemblies of amphiphiles can encapsulate in their hydrophilic interiors small pools of water within which clusters of the semiconductor cadmium selenide can be precipitated with diameters of typically 30–40 Å. These particles can be stabilized against flocculation by giving them an organic coat of phenyl groups attached to selenium.

The hope is that these clusters may constitute 'quantum dots' — zero-dimensional systems for which the electronic levels are quantized. Spectroscopic studies do show the expected blueshift of absorption peaks relative to the bulk material, but the peaks are broadened, in part by the size distribution. Hole-burning spectroscopy can be used to eliminate this 'inhomogeneous' broadening, allowing the spectra of clusters of a single size to be measured.

But even these individual spectra fail to show ideal 'quantum dot' behaviour. The reason for this is that an appreciable proportion of the atoms in the particles are at or near the surface, so surface electronic states exert a strong influence. In particular, they can act to localize and trap charge carriers, leading to bleaching of the absorption. Brus suggested that chemical tailoring of the cluster surfaces might provide a way to suppress this influence of surface states.

Conjugated polymers in the bulk state provide semiconducting materials whose electronic and optical properties can be exquisitely tuned by chemical modification. Variation of the band gap of poly(*p*-phenylene vinylene) (PPV) by attaching appropriate side groups to the polymer chain, for example, can provide a means for moving the absorption maximum across the optical spectrum. Richard Friend (Univ. Cam-

bridge) described how this chemical handle on the electronic properties can be exploited to create polymer-based light-emitting diodes with a range of colours. Injection of electrons into the conduction band, and holes into the valence band, of a PPV film leads to the formation of mobile radical ions (polarons) on the polymer backbone. Oppositely charged polarons can combine to form excited states (polaron excitons) in the energy gap, providing the potential for new optical transitions. Radiative recombination of these excitons leads to luminescence from the polymer films.

Friend has now extended the efficiency and processibility of these electro-luminescent systems through a *tour de force* of nanoscale band-gap engineering which makes use of block copolymers. These incorporate stretches of different monomer chains (generally methoxy derivatives of *p*-phenylene units) along the polymer backbone, which can be made either conjugated (semiconducting) or non-conjugated (insulating) by chemical modification. Trapping the excitons in one-dimensional quantum wells bordered at each end by insulating sections of the chain prevents their migration to quenching sites such as defects, which otherwise causes a reduction in the luminescence efficiency; enhancements by factors of up to 30 are possible (see next week's issue of *Nature*). Moreover, patterning of these copolymer films is possible by lithographic means: masking regions of a conjugated/non-conjugated (orange) film with aluminium and treating exposed areas with acid to eliminate methoxy groups will, for example, write yellow (fully conjugated) patterns into the unmasked portions.

Molecular computing

Molecular biologists might shrink from suggestions that they too are engaged in a form of nanotechnology, but there is no question that the process of translation from the four-symbol nucleic acid code to the twenty-symbol protein alphabet is a computational operation at the molecular level (John Hopfield). Often praised for its fidelity, this process actually tolerates an appreciable error rate — a mistake every 10,000 or so operations — by virtue of massive redundancy: so many protein molecules are synthesized that a wrong one here and there (which will generally be non-functional) does not matter.

This example of a biological symbol-conversion process serves to provide Hopfield's "existence theorem" for molecular-scale computing — a demonstration that in principle it can be done. But most computational problems require more complex logical operations, such as those found in neurobiological processing. The behaviour of neural net-

works, both real and artificial, is of a more collective and ultimately macroscopic character than anything in molecular biology. A collective response, made possible by a high degree of parallelism, lowers the accuracy requirements for individual processing steps.

Can one contemplate an artificial, molecular-scale computer that could compete with the complexity of the brain (roughly 10^{11} neurons linked by 10^{14} synapses)? Aizawa demonstrated that the growth of nerve cells on an indium tin oxide substrate can be directed by applied electric fields, raising the intriguing prospect of synthetic, biologically based networks; but it is hard to see how a third dimension could be added or interfacing to VLSI technology achieved. More immediate was Hopfield's suggestion for constructing parallel networks using wires fabricated by conventional VLSI techniques to connect 'synapses' made from novel (and in the fashionable jargon, intelligent) materials such as copper salts of the organic acceptor compound TCNQ, chalcogenide glasses or tungsten bronzes. The conductivity of these materials is field dependent and hysteretic, providing the possibility of read, write and erase operations.

Although they would rely on molecular-scale engineering, such systems are nevertheless essentially macroscopic. In the way of truly molecular devices Hopfield envisages substantial hurdles. The 'molecular shift register' (J. J. Hopfield *et al. Science* **241**, 817–820; 1989), for example, exhibits behaviour that might reasonably be characterized as device-like. In this four-component molecular assembly, absorption of light by the first component, a chromophore, sends an electron tumbling down an energy-level cascade on the successive components. One could imagine the simultaneous shift of a whole bank of electrons if the four-part units could be linked into a polymeric chain. But Hopfield cautioned against considering this to be a real device. How one might process and interface such a polymer is not clear, and it lacks the essential ingredient of an error-correction mechanism. The latter requires some form of collective behaviour. The occurrence of cooperative two- and four-electron oxidations in biology, however (for example, in the action of haemoglobin), shows that ultimately this may not be too much to ask.

Does nanotechnology exist?

Hopfield characterized the field of molecular nanocomputing as suffering from "an excess of imagination and a deficiency of accomplishment"; can the same harsh assessment be made of nanotechnology more generally? Paul Horn (IBM Thomas J. Watson Research

Center), whose duties for IBM include "research, technology definition and early development of advanced logic and memory products", echoed Eigler in saying that, while the technical capabilities described at the conference provide "wonderful tools for science", he did not expect any of these to make a real impact on mainstream electronics technology ("the electronics you have in your home") in the next 25 years. As Eigler emphasized, and those working in high- T_c superconductors have learned, it is important to distinguish between what is physically possible, what is technologically realizable and (in the face of competition from well established technologies) what is economically advantageous. For example, Eigler admitted that although he could store the equivalent of a year's worth of IBM's information storage products on a one-inch wafer, it would take him the age of the Universe to write the information.

Part of the problem is that a working device, of any kind, is only the first tentative step towards a 'technology'. Supposing one has a molecular solar-cell, for example, how does one then go about collecting the electricity that it generates? If a molecule signals its recognition of another molecule by changing its shape, how can this signal be processed? Even in the more conventional world of semiconductor electronics, how does one get a useful amount of current out of a few-electron quantum device? The problem of providing interfaces between the nanoscopic and macroscopic worlds is clearly not trivial.

But as Hopfield reminded the audience, electronics isn't everything: a molecular device that behaved like a chloroplast (for carbon fixation) might be very useful, and would not require any 'leads' to connect it to the outside world. Far from an excess of imagination, our problem may be that we have not yet learned to think in the new ways that will be required to make the best use of these novel (proto)-technologies. In this sense, the lessons of nanotechnology extend beyond the very small, to encompass the general process of learning from biology and chemistry, and then going beyond what is observed in the natural world, to deliberate engineering.

It has been said of technological progress that we always overestimate what we can do in two years and underestimate what we can do in twenty. Horn's high-school science teacher taught the class that they would never see an atom. In the face of these lessons, it would seem foolish to deny that our dreams may come true sooner than we think. □

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