Quantum Dots

Nanotechnologists can now confine electrons to pointlike structures. Such "designer atoms" may lead to new electronic and optical devices

by Mark A. Reed

During the past few years, research in semiconductors has taken on, quite literally, new dimensions. Their numbers are two, one and zero. Electrons in recently developed devices can be confined to planes, lines or mathematical points—quantum dots.

Microchip manufacturers have developed a toolbox of nanofabrication technologies capable of creating structures almost atom by atom. These techniques have opened up a new realm of fundamental physics and chemistry as workers make and study artificial analogues of atoms, molecules and crystals. Experimenters are no longer limited by the atomic shapes, sizes and charge distributions available in nature.

In addition to the exciting science they portend, quantum dots promise properties that could be harnessed for a range of electronic and optical applications. Arrays of densely packed dots could form a substrate for computers of unprecedented power; indeed, Norman Margolus of the Massachusetts Institute of Technology has coined the term "crayonium." Dots could also constitute materials capable of absorbing and emitting light at whatever set of wavelengths their designers specify or could even serve as the basis of semiconductor lasers more efficient and precisely tuned than any now in existence.

Planes, lines and dots are mathematical constructs. They have no physical extent. How is it possible to make them in a real, three-dimensional material? The answer lies in quantum mechanics and Heisenberg's uncertainty principle. The position of an object (an electron, for instance) and its momentum cannot both be known to arbitrary precision. As an electron is more closely confined, its momentum must be more uncertain. This wider range of momenta translates to a higher average energy. If an electron were confined in an infinitely thin layer, its energy would also be infinite.

In general, the energy of electrons in a semiconductor is limited by their temperature and by the properties of the material. When the electrons are confined in a thin enough layer, however, the requirements of the uncertainty principle in effect override other considerations. As long as the electrons do not have enough energy to break out of confinement, they become effectively two-dimensional.

This locution is not just an approximation. Electrons confined in a plane have no freedom of motion in the third dimension. Those confined in a quantum wire are free in only one dimension, and those confined in a quantum dot are not free in any dimension. For common semiconductors, the length scale for a free conduction electron is about 100 angstroms. (One angstrom is 10^{-10} meter, approximately the radius of a hydrogen atom.) An electron inside a cube of semiconducting material 100 angstroms on a side is essentially confined to a point.

Engineering of less than three-dimensional semiconductors began in earnest during the early 1970s, when groups at AT&T Bell Laboratories and IBM made the first two-dimensional "quantum wells." These structures, made by thin-film epitaxial techniques that build up a semiconductor one atomic layer at a time, are thin regions of semiconducting material (usually gallium arsenide and related compounds) that attract electrons. The energy of electrons residing within the well is lower than the energy of those residing elsewhere, and so the electrons flow in, just as water runs downhill to fill up a deep well.

It is possible to create not only quantum wells but also quantum barriers—two-dimensional "hills" of material that repel electrons. In combination, the wells and barriers can be used to build complex structures that previously existed only as examples in quantum mechanics textbooks [see "Diminishing Dimensions," by Elizabeth Corcoran; SCIENTIFIC AMERICAN, November 1990].

Quantum wells have now become commonplace. They are the basis of the laser diodes found in compact-disc players and the sensitive microwave receivers that pull in signals from a satellite dish. In the meantime, researchers have learned how to confine electrons not simply in a plane but in a point.

The first hints that zero-dimensional quantum confinement was possible came in the early 1980s, when A. I. Ekimov and his colleagues at the Ioffe Physical-Technical Institute in St. Petersburg noticed unusual optical spectra from samples of glass containing the semiconductors cadmium sulfide or cadmium selenide. The samples had been subjected to high temperature; Ekimov suggested tentatively that the heating had caused nanocrystallites of the semiconductor to precipitate in the glass and that quantum confinement of electrons in these crystallites caused the unusual optical behavior.

To understand this chain of reasoning, imagine an electron trapped in a box. Quantum mechanics states that the electron has wave properties, like the ripples on water or the vibrations of a violin string. Just as a violin string is tied down at both ends, so the electron wave is bounded by the walls of the box. The wavelength of the string's vibrations (or the electron's) must fit within those confines [*see illustration on page 121*].

In the case of the violin string, the point at which it is tied down changes

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as the violinist's finger slides up the fingerboard. The length of the allowed waveform shortens, and the frequency of the string's vibrations increases, as does that of all its harmonic overtones. If the size of an electron's confining box is made smaller, the electron's lowest energy level (the analogue of the fundamental pitch of the violin) will increase. For semiconductor nanocrystallites, the fundamental "pitch" is the threshold energy for optical absorption, and the harmonic overtones correspond to new absorption features at higher energies.

How small must a nanocrystallite be for this phenomenon to be visible? In a vacuum the effects of confinement would begin to appear when the electron was trapped in a volume about 10 angstroms across. That size implies an electron wavelength of 20 angstroms and therefore an energy of about one fortieth of an electron volt.

Here semiconductor physics comes to the aid of the nanotechnologist. The wavelength of an electron depends on its energy and its mass. For a given wavelength, the smaller the mass, the larger the energy and the easier it is to observe the energy shift that confinement causes. The electrostatic potentials of the atoms in the crystalline lattice superimpose to provide a medium in which electron waves propagate with less inertia than they do in free space. The "effective mass" of the electron is thus less than its actual mass. In gallium arsenide the effective mass is about 7 percent of what it would be in a vacuum, and in silicon it is 14 percent. As a result, quantum confinement in semiconductors occurs in volumes roughly 100 angstroms across.

The optical absorption threshold for nanocrystallites of this size shifts to higher energies—away from the red end of the spectrum—as the crystallite becomes smaller. This effect appears most elegantly in cadmium selenide clusters; the progression from deep red to orange to yellow as the diameter of the

QUANTUM CONFINEMENT is responsible for the colors of cadmium selenide crystallites, each a few nanometers across, synthesized by Michael L. Steigerwald of AT&T Bell Laboratories. Electrons within the tiny specks of semiconductor scatter photons whose energy is less than a minimum determined by the size of the crystallite and absorb those whose energy is higher. The largest crystallites can absorb lower-energy photons and so appear red, whereas the smallest absorb only higher-energy quanta and so appear yellow.

cluster declines can be clearly seen by the naked eye. (An intriguing and as yet unresolved question is what happens when the crystallite is so small—less than 10 angstroms across—that the effective mass concept, derived from bulk solids, no longer makes sense. Quantum dots that small have yet to be made.)

Ekimov's hypothesis turned out to be true, but it took years of work by groups at Corning Glass, IBM, City College of New York and elsewhere to sort out the correct glass preparation techniques and convincingly demonstrate quantum confinement. Meanwhile Louis E. Brus and his co-workers at Bell Labs were making colloidal suspensions of nanocrystallites by precipitation from solutions containing the elements that make up semiconductors.

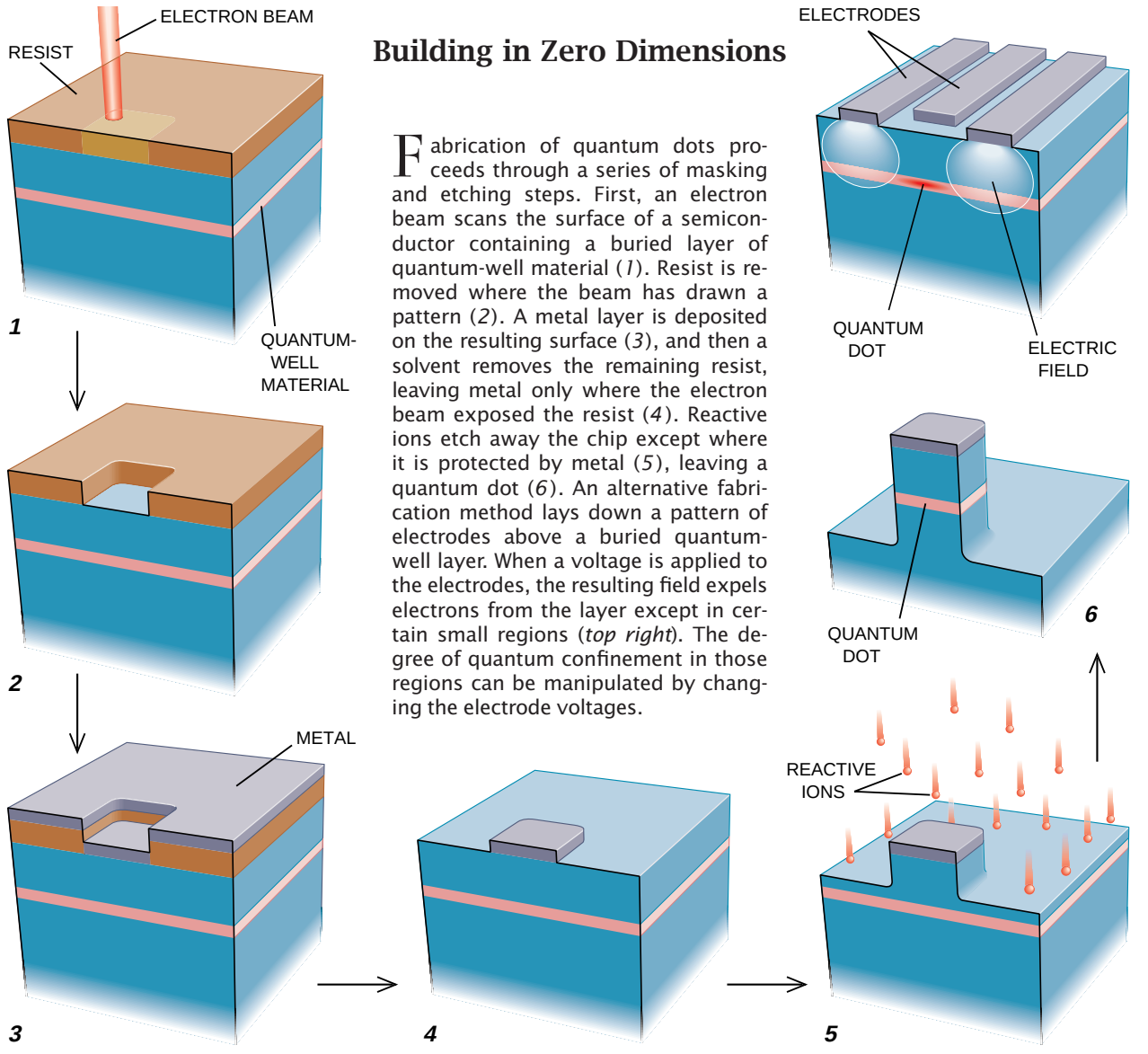
Such crystallites grow by the addition of individual ions until the supply is either depleted or removed. Consequently, by arresting the precipitation after a certain time, Brus and his colleagues could control the size of the precipitate in a range between 15 and about 500 angstroms. Sizes within a single batch varied by no more than 15 percent. Just as in the case of the glass-encased nanocrystallites, a dramatic shift of the fundamental absorption energy to higher energies suggested quantum confinement.

Workers in many laboratories worldwide have built on this approach. For example, A. Paul Alivisatos and his colleagues at the University of California at Berkeley have extended the range of elements from which crystallites can be made. In addition to the II-VI compounds (such as cadmium from the second column of the periodic table and selenium from the sixth), they have also precipitated III-V compounds such as gallium arsenide. Michael L. Steigerwald of Bell Labs and many others have employed an organic "soap bubble" wrapping known as a reverse micelle to stabilize the surface of the tiny semiconductor crystals. Groups at the University of California at Santa Barbara, the University of Toronto and elsewhere are stuffing clusters of atoms into the nanometer-scale cavities of zeolites, a technique that confers the advantage of precise dimensional control.

Encasing nanocrystals inside another material could significantly improve their quantum performance. The tiny specks of semiconductor have a very large surface-to-volume ratio, and sur-

Building in Zero Dimensions

Fabrication of quantum dots proceeds through a series of masking and etching steps. First, an electron beam scans the surface of a semiconductor containing a buried layer of quantum-well material (*1*). Resist is removed where the beam has drawn a pattern (*2*). A metal layer is deposited on the resulting surface (*3*), and then a solvent removes the remaining resist, leaving metal only where the electron beam exposed the resist (*4*). Reactive ions etch away the chip except where it is protected by metal (*5*), leaving a quantum dot (*6*). An alternative fabrication method lays down a pattern of electrodes above a buried quantum-well layer. When a voltage is applied to the electrodes, the resulting field expels electrons from the layer except in certain small regions (*top right*). The degree of quantum confinement in those regions can be manipulated by changing the electrode voltages.



faces in general are marked by atoms with dangling chemical bonds. These improperly terminated bonds can act as dampers, absorbing the energy of electrons vibrating in higher-energy (shorter-wavelength) modes. As a result, many nanocrystallites do not show the dramatic harmonic series of energy levels that would be expected from a quantum dot.

The inherent difficulties of making quantum dots from clusters of atoms led researchers in the mid-1980s to look for other fabrication schemes. My co-workers and I at Texas Instruments in Dallas made the first lithographic quantum dots in 1987. We cut slabs of quantum-well material into pillars by means of advanced etching techniques similar to those used in the fabrication of state-of-the-art integrated circuits.

Making pillars 100 angstroms wide requires electron-beam lithography instead of the optical techniques used to make most chips. An electron beam scans the semiconductor surface, which has been coated with a thin polymer layer called a resist. (Similar effects can also be achieved by means of x-rays or ion beams.) A series of process steps replaces the resist with a thin layer of metal in areas where the beam was scanned at high intensity. A shower of reactive gas then etches away the unprotected quantum-well material, leaving the pillars behind. Using this technique, pillars or other features as small as 1,000 angstroms across can be quite easily constructed. But the process becomes increasingly difficult as the scale falls to about 100 angstroms, the limit of the best-known resist.

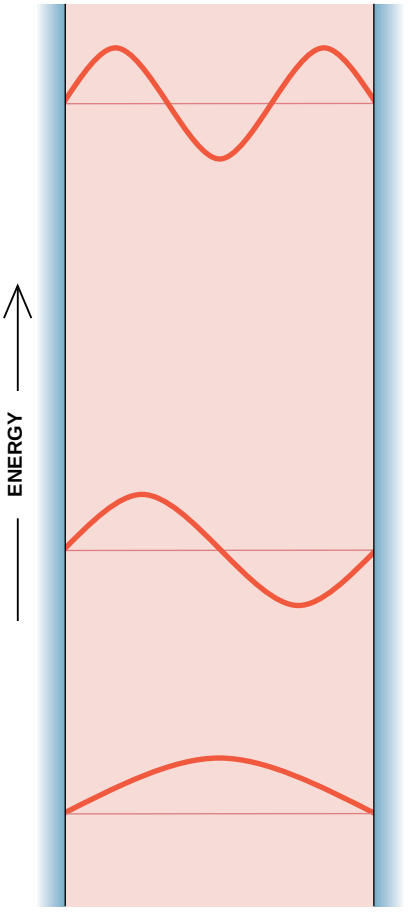
Above and below the quantum-well material in these pillars lie ultrathin insulating layers called tunnel barriers, followed by conductive contacts. The insulators confine electrons in the well for a very long time, but eventually the electrons can quantum-mechanically tunnel in and out, carrying a small current that can serve to probe the internal energy states of the well. Whenever the voltage across the well matches the energy of one of its resonant states, current flow increases. If the diameter of the pillar is very small, its current-voltage spectrum displays the harmonic series of peaks that marks quantum confinement. Indeed, by making only a single pillar that is isolated from its surroundings, one can calculate the properties of a single quantum dot, a task that is hard to imagine carrying out with nanocrystallites.

Moreover, the lithographic fabrication process naturally clads and protects the quantum dot from surface effects, at least on two faces. The top and bottom of the dot are single crystal interfaces made by advanced epitaxy and are essentially perfect. Because the pillar is electrically conductive, the surface bonds of the semiconductor we used create a positive charge with respect to the internal core of the pillar. This charge repels electrons from the surface into the quantum-confined interior; the region from which the electrons have departed forms an insulating sheath around the pillar, protecting the sides of the dot. A 1,000-angstrom pillar would thus contain a 100-angstrom dot.

The realization of a quantum dot depends on an insulating sheath of the correct thickness, which depends in turn on the size of the etched pillar. When we first tried to make quantum dots, no one knew what the correct sizes might be, and many attempts ended in failure. But early on the morning of August 20, 1987, as I was preparing to give a talk at a conference on quantum-well devices, my colleagues called to say they had successfully measured a quantum dot. I rushed to the hotel fax machine just in time to see the data print out, showing a rich harmonic series of electron energy levels. An hour later I had rewritten the finale of my talk, the hotel staff had transformed the fax into a viewgraph, and I delivered the news.

Subsequent measurements confirmed that dots of different sizes produced different harmonic spectra, a clear signature of quantum confinement. Since then, groups at CNET in France, NTT in Japan, the University of Cambridge, the State University of New York at Stony Brook and Princeton University have also employed this fabrication technique. Pierre Gueret and his co-workers at IBM Zürich have even made a "squeezable" dot by placing an electronic gate around the dot in a tour de force of fabrication technology. Increasing the electric potential on the gate reduces the size of the dot and increases the fundamental energy and harmonics in its spectrum.

The success of these electrical measurements on lithographically defined quantum dots, in contrast to the relative difficulty of optical measurements on dots made from atomic clusters, has underscored the importance of controlling damaging surface effects. Groups at IBM, AT&T, the universities of Hamburg and Munich, Delft University of Technology in the Netherlands, Philips, Cambridge, the Max Planck Institute for Solid State Physics in Stuttgart and M.I.T. have managed to eliminate surface effects entirely. They make quantum dots by placing tiny gate electrodes on top of a buried layer that confines electrons in two dimensions. The top electrodes squeeze the electrons into quantum-confined "islands."



ELECTRON IN A BOX is constrained to have a quantum wave function that fits evenly within its borders. The lowest energy level corresponds to a standing wave with a single antinode, the next lowest to a wave with two, and so on. Electron energy is inversely proportional to the square of the wavelength, and so the energy levels rise rapidly. This harmonic series of energy levels is the signature of a quantum dot.

One advantage of this approach is that it is possible to put as many or as few electrons in the dot as desired, simply by varying the squeezing voltage. The result is what might be called a designer atom: the confining potential acts as an attractive nucleus, and the valency (the number of electrons) is determined by the external gate voltage.

In natural atoms, confinement of electrons is caused by the radially directed electrostatic force of the nucleus, and the electron wave functions are radially

symmetric. In these quantum dots the shape of the gate electrodes controls the size, shape and symmetry of the confining potential, and so "wave-function engineers" may eventually be able to study atomic physics previously inaccessible in nature, such as the wave functions or electrons in square or rectangular atoms.

A group at the Stuttgart Max Planck Institute, as well as teams at IBM and AT&T, has made large, periodic arrays of dots by fabricating a gridlike gate electrode—the nanostructure equivalent of a window screen. Voltage applied to the grid forms a regular lattice of quantum confinement in the underlying material. The size and the number of electrons in each dot can be controlled, as can the height and thickness of the barrier between the dots. Regular peaks appear in the optical absorption spectra of these structures. This surprising phenomenon testifies to the precision with which the arrays—some containing more than a million dots—have been made, as any variation in size would smear out the harmonic spectra. Ray C. Ashoori and Horst L. Störmer of AT&T recently measured the capacitance of individual dots and demonstrated that it is possible to capture a single electron in each one. Electrons can then be added one at a time, in a digital fashion.

These results open up the possibility of making a planar artificial lattice in which virtually all the properties of the constituent "atoms" can be controlled. Just as individual quantum dots display energy levels analogous to those of atoms, an artificial lattice would possess an energy band structure analogous to that of a crystalline semiconductor. It could be used to study many questions in quantum physics and might also form the basis for a superfast electronic oscillator.

No one, however, has yet made a planar artificial lattice and unambiguously demonstrated its band structure. Success will require not only exacting precision in fabricating the electrode grid but also heroic control of defects in the underlying quantum-well material. In natural semiconductor lattices, engineers can rely on the fact that all silicon atoms, for instance, are identical, but in an artificial lattice, they will have to impose this uniformity by craft.

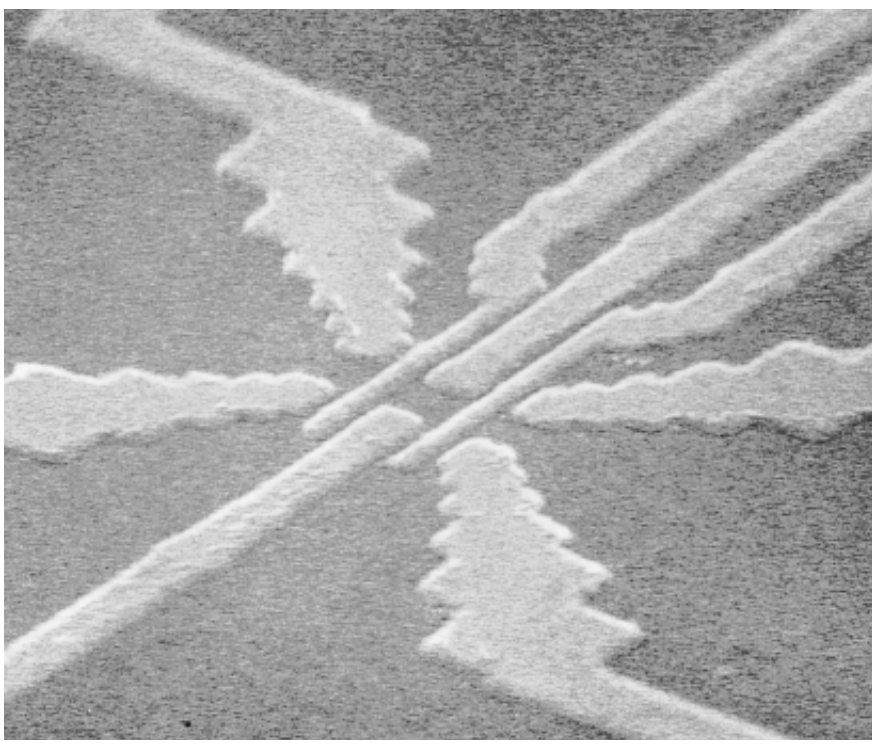
An intriguing twist in this genre is the "antidot" lattice. If the voltage on the grid is reversed, the islands that attracted electrons now repel them. Electrons are forced to reside in the intervening space, bouncing off the antidots as they move through the array in what is probably the smallest "pinball machine" ever made.

Another variant of the grid technique, demonstrated by Kathleen Kash and her co-workers at Bell Communications Research (Bellcore), uses compressive stress in place of electrodes to impose quantum confinement. The Bellcore team lays down a strained layer (a layer of material whose atomic lattice spacing differs from that of the substrate below it) on top of the quantum-well material, compressing it laterally. The workers then etch a pattern into the strained layer; wherever the layer is etched away, the compressive stress is relieved. The resulting tiny variations in atomic spacing within the quantum-well layer cause changes in electron energy levels that can form quantum dots.

Electrostatic squeezing produces dots whose quantum confinement can be controlled more easily than can that of dots produced by other methods. Until recently, it was impossible to make electrodes small enough for tunnel-barrier contacts to a single electrostatically squeezed dot. During the past three years, a number of groups have succeeded in this task, producing lateral contacts to the dot that consist of electrostatically controllable tunnel barriers.

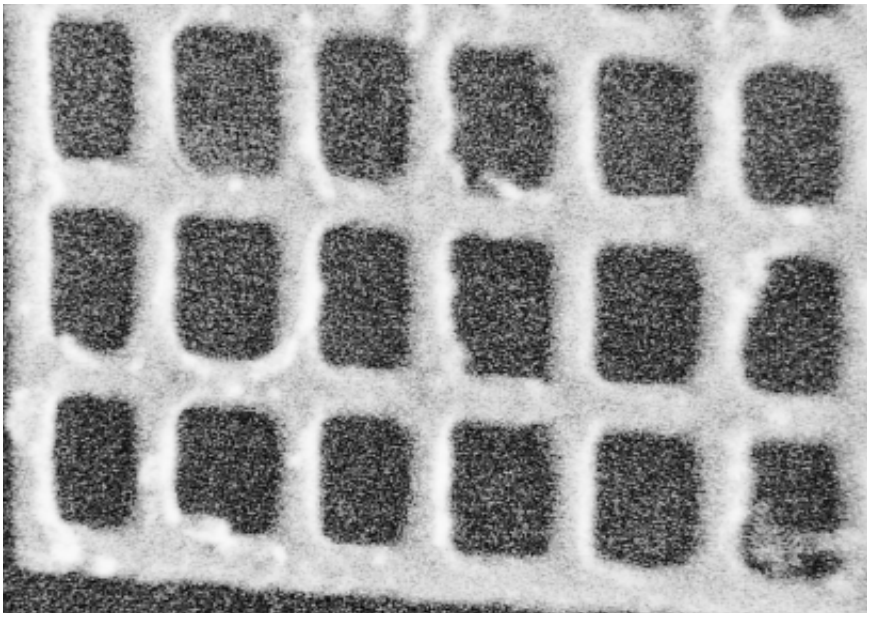
This structure gives the researcher control of many of the variables that define a dot, including size, number of electrons and transparency of the confining barriers. Such systems are ideal for testing textbook quantum mechanics problems, such as the properties of zero-dimensional states or the probability of electrons tunneling through barriers. By stringing two dots together to form an artificial molecule, one can investigate coupling between the states of adjoining quantum dots. And, as Leo P. Kouwenhoven of Delft University has demonstrated, it is even possible to string many dots together in a pearl-necklace fashion to generate an artificial one-dimensional crystal and to watch how the energy band structure of a crystal forms.

The Delft and M.I.T. groups have discovered that the energy levels of these small dots are determined not only by quantum mechanical rules based on size but also by the quantization of the electron charge [see "Single Electronics," by Konstantin K. Likharev and Tord Claeson; SCIENTIFIC AMERICAN, June 1992]. The energy level of a dot depends in part on its capacitance and the amount of charge contained within it, and the amount of charge must of course be a multiple of *e*.



ADJUSTABLE QUANTUM DOT lies buried at the intersection of electrodes in the above micrograph. The four interior electrodes "squeeze" electrons in the buried quantum-well layer into the dot. The outer electrodes serve as contacts for electrons to tunnel in or out of the dot; tunneling rates increase when the electron energies match the dot's energy levels. Those levels, in turn, can be controlled by changing the voltage on the inner electrodes.

The coexistence of these two kinds of quantization causes a complex interplay of effects. To understand which will be most important, one needs to know not just the wavelength and effective mass of the electron in the dot but also its electrical capacitance. If a dot is made from a metallic particle, it has many more conduction electrons than does a semiconductor; furthermore, the wavelength of the conduction electrons is only a few angstroms. As a result, in a 100-angstrom metallic dot, charge quantization exerts a much stronger effect, relatively speaking, than size quantization. The capacitance of the metal dot, however, is not so different from that of a semiconductor dot of the same size, and in the semiconductor the energies of the two effects may be approximately the same.



ELECTRODE GRID creates a lattice of quantum dots in the material underneath it. Such a lattice is, in effect, a crystalline layer made of artificial atoms whose energy levels can be controlled precisely. Arrays of quantum dots aid in the study of fundamental physics and also may eventually be made into novel electronic or optical devices.

The development of quantum dots is a culmination of 20 years of work, during which researchers have learned how to tailor electronic materials. Before the 1970s, research in solid-state science was confined to materials provided by nature. The refinement of ultrathin-layer epitaxy during that decade gave researchers the tools to fabricate the two-dimensional structures that dominate technology today. Extensions of that technology have now led to exploration of the one- and zero-dimensional domains. Before these discoveries can be applied on a commercial scale, however, a new generation of fabrication techniques must be developed.

The most challenging obstacle is to achieve essentially perfect control over the size and purity of these nanostructures. The "top-down" approach to fabrication—carving, dicing or squeezing semiconductors—may not be sufficient without revolutionary advances in materials and nanofabrication. Current prototype devices are large (although the active region of the device is quantum-sized, the electrodes and contact pads take up enormous space), and they operate only at very low temperature.

Moreover, these devices are made by electron-beam lithography, a fabrication technology that cannot be used to make large numbers of the complex circuits crucial for economic success. New lithographic tools that permit three-dimensional atomic-scale control, such as structured epitaxial growth or self-organizing molecular assembly, are needed. Indeed, it may be necessary to develop novel materials and synthesis techniques that blend conventional semiconductor technology with alternative approaches. Workers at the Fujitsu Laboratories in Japan, for example, have made quantum wires and dots from organic polymers. The location of conducting atoms within the polymer molecules is fixed, so this method offers much finer control than is possible with electron-beam lithography. If "bottom-up" assembly of quantum devices proves feasible, the methods now used to produce quantum dots will seem akin to making the books in the Library of Congress by whittling away at a large block of wood.

The most important challenge that researchers face, however, is not learning how to build quantum-confinement devices in quantity; instead it is to design useful circuits that exploit their potential. Although the technological size limits to quantum devices are in theory significantly smaller than those projected for silicon, the viability of quantum circuits will be determined by how well they compete in the marketplace against the coming decade's developments in conventional silicon technology.

Just as transistors found uses far beyond their initial role in radio receivers, so the ultimate application of quantum devices could be quite tangential to the tasks of digital computation and communications for which they have thus far been developed. If engineers can fabricate lattices containing millions or billions of quantum dots, specifying the shape and size of each one, they will be able to make any electronic or optical material of which they can conceive. Emission, absorption and lasing spectra could be precisely tailored, and a single slab of material could even be designed to contain a myriad tiny computers whose interconnections and internal architecture would change to match each new problem posed to them.

Even beyond the practical applications of quantum devices and the new intellectual territory they offer experimental physicists, quantum dots are exciting to researchers. The ability to manipulate matter on an atomic scale and create unique materials and devices with custom-designed properties has universal appeal. It marks a triumph of human ingenuity and imagination over the natural rules by which materials are formed.

FURTHER READING

TRENDS IN MATERIALS: DIMINISHING DIMENSIONS. Elizabeth Corcoran in *Scientific American,* Vol. 263, No. 5, pages 122–131; November 1990.

ENGINEERING A SMALL WORLD: FROM ATOMIC MANIPULATION TO MICROFABRICATION. Special Section in *Science,* Vol. 254, pages 1300–1342; November 29, 1991.

QUANTUM SEMICONDUCTOR STRUCTURES: FUNDAMENTALS AND APPLICATIONS. Claude Weisbuch and Borge Vinter. Academic Press, 1991.

NANOSTRUCTURES AND MESOSCOPIC SYSTEMS. Edited by Wiley P. Kirk and Mark A. Reed. Academic Press, 1992.