Small Clusters Hit the Big Time

New ways to create clusters of atoms on the nanometer scale are opening the door to quantum dot lasers, single electron transistors, and a host of other applications

Researchers are clustering around clusters. *Science* begins our special issue on the topic on this page, with a News story describing some reasons for this heightened interest: Advances in controlling the behavior of small clusters of atoms are paving the way for applications ranging from new thin films to vanishingly small lasers. Our second News story chronicles how clusters might determine the structure of atomic nuclei. A series of Articles, starting on page 925, discusses thermodynamics, kinetics, and magnetic and optical properties of a wide variety of clusters. And a related Report appears on page 963.

In the nanomaterial world—an expanding realm of shrinking features just billionths of a meter across—bigger advances come with smaller sizes. Grains of semiconductors a few nanometers across, for instance, emit different colors of light than do slightly larger chunks of the same material. And ceramic blocks made of nanosized grains can be molded into engine parts or other useful shapes without shattering during the process, as do ceramics made from larger particles.

Ever since the early 1980s, when scientists began discovering these and other advantageous properties of ultrasmall grains, there's been a stampede among researchers to create and control new types of particles. These small groups of atoms go by many names—nanoparticles, nanocrystals, quantum dots, and quantum boxes—but are commonly called "nanoclusters." Much of the recent research has gone into finding ways to make clusters of small and uniform size, which possess common optical, electrical, and mechanical properties. That effort has already kicked up a few commercial dividends, such as the ceramics and chemical catalysts with increased efficiency because they have a high surface-to-volume ratio. Recently, advances with semiconducting nanoclusters are bringing several new electronics and communications applications within view as well.

One with potentially far-reaching impact is the development of ultrasmall, highly efficient semiconductor lasers, known as quantum dot lasers, which could be used to transmit digital data between continents through fiber optic cables or between neighboring chips in high-speed computers. Another potentially lucrative scheme employs small particles in a different way: to make high-quality polycrystalline thin films, which conduct electrical charges in solar cells, computer displays, and other electronic devices. Still other burgeoning applications include nanocluster arrays that could lead to ultrasmall transistors (see box).

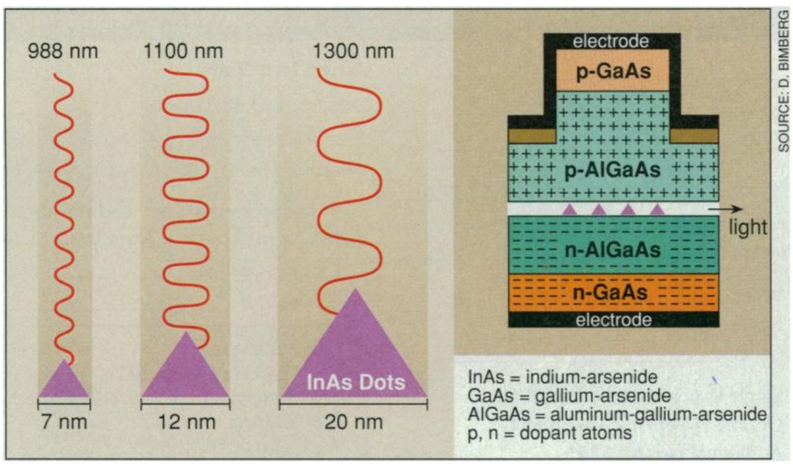
"The whole field is really exploding worldwide," says Richard Siegel, a nanocluster specialist at Rensselaer Polytechnic Institute in Troy, New York. While the technical hurdles between some of these advances and the marketplace are high—indeed, the technique for making quantum dot lasers that work at room temperature has just been identified, and is far from commercial production—Siegel notes that the pull of the market is moving developments along quickly.

Small bright hopes

By fabricating lasers from clusters of semiconductor atoms just a few nanometers in size, for example, researchers believe they can realize several advantages. For one, "by simply controlling the size of the cluster, you can change the color of light emitted by the materials," says Christopher Murray, a chemist at the IBM T. J. Watson Research Center in Yorktown Heights, New York. For another, says Pierre Petroff, a quantum dot expert at the University of California, Santa Barbara, "in principle you should get a device which is more efficient, will lase at a lower [electrical] threshold, will work at a higher frequency, and a device that you can make smaller."

Quantum dots can do all this because of the way they handle electrons. In all materials, electrons exist at discrete energy levels, known as bands. And in semiconductors the addition of energy can boost an electron from a lower "valence" band to a higher energy "conduction" band, leaving behind a positively charged electron vacancy, or "hole." An excited electron can then drop into a passing hole, giving up excess energy that corresponds to the "bandgap" between the conduction and valence bands. That energy is released as a photon whose frequency corresponds to the bandgap. In bulk semiconductors, the bandgap is unvarying, meaning they emit only one color of light. To make these materials emit beams of different colors, researchers must use laborious techniques to synthesize novel semiconductor alloys harboring different bandgaps, thereby allowing them to emit different colors of light.

Quantum dots could make this task of color tuning easier, as different-size dots of the same semiconductor material emit different colors. Such dots are so small that they tightly confine normally mobile electrons, so the charges spend less energy on their wanderings. This means that more energy is released when the electron and hole combine, resulting in a shorter wavelength—or blue-shifted—photon. The smaller the dot, the greater this frequency shift.



Tuning dots. A quantum dot laser *(right)* combines oppositely charged particles in tiny clusters of semiconductor atoms, and the collisions emit photons. By varying the sizes of the clusters *(left)*, researchers can alter the photons' frequencies.

A laser using quantum dots would have an array of dots at one particular size, surrounded by semiconductor alloys that require electrons to reside at higher energy levels. When electrons and holes are injected, they naturally flow into the lower energy levels in the dots. There they combine to produce equal-wavelength photons, which can then be amplified and focused into a coherent laser beam by a pair of mirrors.

Making a true quantum dot

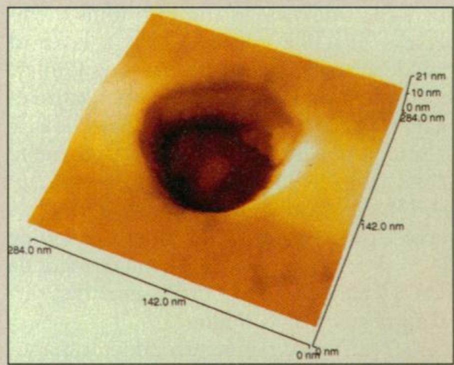
Ordering Nanoclusters Around

While controlling the size and makeup of individual nanoclusters is crucial in such applications as thin films, other uses add a third requirement: precise spatial arrangement. Uniform 2- and 3D arrays are critical, for example, for making batches of ultrasmall transistors and novel optical and electronic materials. Two recent advances in array creation have brought such applications a step closer.

One of those applications is a single electron transistor (SET). While conventional transistors require a stream of electrons to switch their electronic state, an SET needs just one. Such devices—consisting of a nanocluster framed by electric leads—would not only draw less power than conventional devices, but could pack more tightly on a computer chip. But researchers have had trouble creating arrays of these devices, because it is hard to deposit one and only one cluster in the center of each device.

Now James Heath and his colleagues at the University of California, Los Angeles, together with Shalom Wind and colleagues at IBM's T. J. Watson Research Center in Yorktown Heights, New York, report in an upcoming issue of the *Journal of Physical Chemistry* that they've created what amounts to a nanoscale egg carton that allows only one 6-nanometer-wide cluster to grow in each well. Heath and his colleagues use electron-beam lithography to carve parallel rows of 100-nanometer-wide wells in a silicon wafer. Next, the researchers evaporate a gas containing atoms of the semiconductor germanium over the surface of the wafer. A handful of these atoms settle into each well, binding to the base. Once such a nucleus takes root, says Heath, "it acts like a sponge," pulling in most nearby germanium atoms. This, he explains, ensures that only one cluster forms in each well.

The group has yet to add the metal wires needed to make actual working SETs. Still, what they've already accomplished is "a really big step forward," according to IBM nanocluster researcher Christopher Murray.



J. HEATH

Well arranged. After making rows of these nanosized wells in a silicon wafer, researchers can deposit one semiconductor cluster per well, forming an array.

The second advance comes from Moungi Bawendi of the Massachusetts Institute of Technology and his colleagues, who are developing arrays as the basis for novel materials whose electronic and optical behaviors depend on an internal nanocluster-size gradient. Such materials could ultimately be useful in creating displays and other electronic devices if researchers can find a way to systematically vary the size of their nanocluster components. In the 24 November 1995 issue of *Science*, they reported taking the first step by creating the first 3D arrays, or "superlattices," of semiconductor nanocrystals that each function as a quantum dot.

Oppositely charged electrical particles collide within these dots to produce photons (see main text), and the color of emitted light depends on the dot size. But the ordering of dots also affects their behavior. In disordered jumbles of dots, the electrical charges flowing into the dots and photons leaving them can fluctuate erratically. By contrast, the new evenly spaced arrays are "very exciting," says Pierre Petroff, a physicist at the University of California, Santa Barbara, because they don't have that problem.

To make their superlattices, the researchers start with near-uniform nanoclusters of cadmium-selenide in an octane-containing solution. They then turn up the heat. As the temperature rises and octane evaporates, the nanoclusters begin to precipitate out of solution and form a uniform, closely packed layer on a substrate, just as a single layer of oranges forms a uniform layer when dropped into a cardboard box. As this precipitation continues, additional layers of clusters stack on top like successive rows of oranges in a grocery store display.

The next step would be to arrange arrays of different-sized nanoclusters—which emit different colors of light—systematically across a display surface. If researchers manage this, that could put tunable nanocluster materials on display.

–R.F.S.

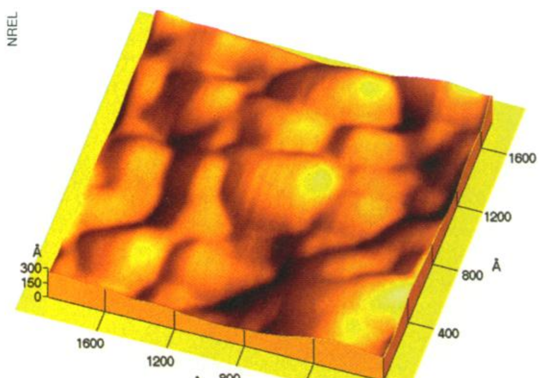
laser has proved difficult, however. It's been hard to make the dots the same size, and the result has been devices that still emit a range of light frequencies. These lasers have also had to be chilled, because added energy from heat can kick charges out of the dots before they combine and emit photons. Finally, researchers must prove that any lasing, or "gain," that does occur is coming from the dots and not the surrounding semiconductor alloy layers, which also harbor electron-hole collisions. A few teams have laid claim to making quantum dot lasers, but "often people don't believe the results," because the gain measurements are either absent or suspect, says Karl Eberl, a physicist and quantum dot maker at the Max Plank Institute for Solid State Research in Stuttgart, Germany.

Now, in unpublished work, two groups say they've seen more definitive fingerprints. The groups—one led by Dieter Bimberg at the Technical University of Berlin in Germany, the other by Anupam Madhukar at the University of Southern California—say they've been able to make electrically powered lasers that function at low temperatures. The latest results from Bimberg's group indicates their device works at room temperature.

To make their devices, both teams revised a technique developed by a number of groups in the mid-1980s. First, the researchers lay down ultrathin layers of semiconductor alloys, such as gallium-arsenide (GaAs), which channel electrons into the quantum dots. To make the dots themselves, the researchers use another alloy—indium-arsenide (InAs)—whose lattice of atoms has a different spacing than that of GaAs. The first InAs atoms settle at random places on the GaAs surface, forming tiny nucleation sites. Then, because of the lattice mismatch, other InAs atoms bind to these InAs nuclei more easily than to the GaAs layer. In this way the nuclei grow into clusters. Because the clusters all grow at about the same rate, the researchers end up with dots at a near uniform size. Finally, the researchers add additional hole-channeling GaAs layers above the dots, and a pair of charge-injecting electrodes.

The strategy seems to have worked. In a paper recently submitted to *Applied Physics Letters*, Bimberg and his colleagues report gain measurements for an electrically pumped array of InAs quantum dots. This laser had to be cooled to 77 kelvin to function. But in additional work, both groups say they've come up with similar gain measurements at higher temperatures by growing several layers of dots stacked on top of one another; quantum-mechanical interactions between the stacked dots make it harder for electrical charges to exit the dots once they fall inside. Madhukar says he and his colleagues are currently preparing a report that shows lasing measurements up to 200 K. And in another paper scheduled to be presented at the Conference on Lasers and Electro-Optics in Anaheim, California, in June, Bimberg's team reports lasing measurements up to room temperature (300 K). Researchers in the two teams say they are still unsure why these temperature differences occur. But they suspect it may have to do with subtle differences in growth conditions or vertical spacings between dots.

Amnon Yariv, a quantum dot laser expert at the California Institute of Technology in Pasadena, calls the new results "a very interesting development," as they bring commercial quantum dot lasers a step closer to reality. And Bimberg and Madhukar are now working to take additional steps. The lasers for both groups currently emit light at a wavelength near 1 micrometer. And down the road the researchers hope to grow larger dots that would produce light at wavelengths of 1.3 micrometers, which can be used to transmit data through fiber optic cables.



Just spray it on. Using a spray technique with nanoclusters, scientists can make smooth thin films.

Film stars

Laser-makers aren't the only ones benefiting from semiconducting nanoclusters. At the National Renewable Energy Laboratory in Golden, Colorado, David Ginley and his colleagues are using such atomic clumps to make polycrystalline thin films: sheets of semiconducting crystals used to conduct electrical charges over large areas in devices such as solar cells and computer displays, or that are patterned into wires on chips.

The cheapest way to produce thin films is to spray them on, but spraying usually produces defects and gaps that lower a film's ability to conduct electricity. As a result, this fabrication process has been restricted to thicker films, which are deep enough so that gaps typically don't go all the way through. But more material costs more money, so thick films are expensive. That's where nanoclusters come in. By smoothing out the spray process, "nanoclusters allow you to transition spray technology to the thin-film range," says Ginley.

Nanoclusters solve the basic problem of spray deposition: the large size of the grains in the starter solution, which measure about 1 to 2 micrometers in diameter, or roughly the same thickness as the thin films themselves. "It's like putting down a layer of boulders next to one another," says Ginley. Even when packed tightly together, gaps remain between neighboring particles. His lab's solution: smaller particles that pack more closely. In the 9 October 1995 issue of *Applied Physics Letters*, Ginley and his colleagues reported spray-painting solutions containing 2- to 3-nanometer-sized cadmium-telluride (CdTe) nanoclusters to make smoother, virtually defect-free thin films.

Just making semiconductor nanoclusters that small wasn't easy. To synthesize their tiny CdTe clusters, the researchers started by dissolving cadmium- and tellurium-containing compounds in two separate solutions of an organic solvent known as alkylphosphines. When they mixed these solutions, the cadmium and tellurium began agglomerating into clusters. By carefully controlling the temperature and the concentration of the reactants, the researchers ended up with 2- to 3-nanometer particles coated with a layer of alkylphosphine molecules, which prevent neighboring clusters from clumping together.

Next, they sprayed a thin layer of the cluster-filled solution onto a substrate heated to at least 250°C. The hot substrate burned off the particles' thin organic coating and fused neighboring particles into a thin, smooth layer. A first look at these layers with an atomic force microscope shows that the films have no gaps and are at least 250 times smoother than conventionally sprayed polycrystalline thin films.

The researchers have yet to measure the electrical performance of these films, but have used them to construct working solar cell prototypes. And Paul Alivisatos, a professor of chemistry at the University of California, Berkeley, calls the new film-making technique "a very good idea," because it makes it much easier to create high-quality polycrystalline films over large areas, which could lower the cost of any device that uses them.

Growing role

Nanoclusters are shaping other technologies as well. Researchers around the world are studying nanoclusters for use for environmentally friendly batteries, high-quality color copiers, and high-density magnetic data storage. Even these applications, Siegel suspects, are just the tip of the nanocluster iceberg: "We've started at the top and have discovered some very important applications already. But there are many more to come." This small world has big horizons.

–Robert F. Service

PHYSICS

Clusters Whip Light Atomic Nuclei Into Shape

Exactly one century ago, scientists knew nothing about the innards of atoms. But while experimenting with uranium in 1896, the French scientist Henri Becquerel discovered radioactivity, a phenomenon hinting that atoms were made of smaller particles. Some of the particles Becquerel detected, researchers learned later, were alpha particles: two protons and two neutrons glued together by one of the fundamental forces of nature, the strong force. And today, 100 years after Becquerel found clues to their existence, alpha particles are producing dramatic insights into the structure and behavior of atomic nuclei.

While many such models of nuclear architecture portray protons and neutrons—together known as nucleons—packed solidly together or stacked in concentric shells, researchers have theorized that the nuclei in the lightest elements, such as carbon or oxygen, look like alpha particles clustered in triangular shapes or tetrahedra. Now recent experimental and theoretical work by several groups of British and American physicists indicates that at high energies, the alpha particles in some of these atomic nuclei, such as carbon or magnesium, can form "nuclear molecules," where one cluster of alpha particles orbits around another, and even bizarre long chains.

And in the case of the carbon nucleus, the clustering has triggered a debate over the carbon state that plays a key role in the nuclear transformations that forge carbon and a whole chain of heavier elements in the interiors of stars. Says cluster theorist Brian Fulton of Birmingham University: "Without the existence of this cluster, carbon would not exist, and therefore we would not exist." But just what that cluster looks like is now open to question, as experiments point to both a chain and a triangle shape.

This emerging cluster of results has excited the research community. Says nuclear physicist Alan Shotter, head of physics and astronomy at the University of Edinburgh in Scotland, "While nuclear clustering in light nuclei at low energy has been known for some years, recent research shows that such clustering can also exist at higher energies. This clustering seems to be related to exotic nuclear shapes, which is not only fascinating in its own right but is also providing a valu-