Engineers are forever wanting to tune the optical properties of semiconductor materials, to change the output wavelength of a laser, for example, or get different colors from an LED. Quantum dots (QDs), tiny structures of semiconductor materials on the order of a few nanometers, render optical properties engineerable by quantizing the size of electronic wave functions (see *OE* magazine, January 2002, page 18).

When a particle (an electron in this case) is confined to a volume in space, it acquires kinetic energy (referred to as confinement energy), and its energy spectrum becomes discrete. In a bulk semiconductor, the conduction electrons are free to move around in the solid, so their energy spectrum is almost continuous, and the density of allowed electron states per unit energy increases as the square root of the energy (see figure 1). If one can synthesize a piece of the semiconductor that is so small the electron “feels” confined, the continuous spectrum will become discrete, and the energy gap will increase. The size of the crystallite must be comparable to the Bohr radius of the bound state of an electron and a hole. An electron-hole pair in a QD is usually referred to as an exciton, even when the charge carriers are bound by the confining potential rather than the Coulomb interaction.

Controlling the size allows us to engineer the optical properties of a semiconductor: Strong absorption occurs at certain photon energies, at the expense of reduced absorption at other energies. Ideally, the density of states becomes a series of delta functions (narrow spikes) in the QD. The emission of light via the lowest-energy transition is similarly wavelength-
Among the potential applications of such structures, exploitation of the discrete density of states to create a QD laser has been viewed as something of a Holy Grail in the field of quantized semiconductor structures. Researchers have demonstrated lasing in epitaxially grown III-V QDs, but the variable and relatively large (greater than 10 nm) dimensions of the QDs produce confinement energies comparable to room-temperature thermal energy and preclude control of the emission wavelength through quantum confinement.

When the confinement of electrons is strong, small variations in the size of the QDs in a sample translate into relatively large variations in the allowed energies, transition wavelengths, and absorption and emission linewidths. This inhomogeneous broadening counters the desired spectral concentration of transition strength and will degrade the performance of QD lasers. In addition, inhomogeneous broadening seriously hinders the determination of the intrinsic properties of single QDs, so it is a chronic problem in studies of the fundamental properties of the structures. An optically pumped amplifier, however, can benefit from inhomogeneous broadening: Broad, spectrally flat gain with independent saturation of each channel is desirable for telecommunications. Preliminary calculations show that such an amplifier can achieve temperature-insensitive, low-noise, and low-cross-talk amplification.1

**Quantum Confinement**

Quantum confinement generally shifts the optical transitions to higher energies (shorter wavelengths). QDs with size-quantized transitions at telecommunication wavelengths must be made from materials with bulk energy gaps further in the IR spectral region than the 1.3- to 1.55-µm telecom-wavelength range. In other words, they require narrow-gap semiconductors, such as indium arsenide (InAs), indium antimonide (InSb), and gallium antimonide (GaSb), among III-V materials. In addition, the semi-metal mercury chalcogenides—mercury sulfide (HgS), mercury selenide (HgSe), mercury telluride (HgTe), and alloys—exhibit IR transitions when synthesized as nanostructures. Finally, IV-VI compounds such as lead sulfide (PbS) and lead selenide (PbSe) can be synthesized as QDs with transitions at the desired wavelengths (see figure 2).

Researchers at Cornell University (Ithaca, NY) and Corning Inc. (Corning, NY) have collaborated on the development of lead-salt QDs since the early 1990s.2 These structures can be synthesized as colloids or in glass and offer a number of valuable properties. By varying the particle size, we can vary the emission wavelength from 600 nm to 2.2 µm. In the case of the smallest QDs, quantum size effects dominate the properties. For example, the electronic energies are approximately 85% confinement energy. One way to think of this is that the electrons have their energies determined by the surface of the QD, which defines the potential well that confines them. On the other hand, the electrons barely notice that the QD is a crystal made up of atoms. Another manifestation of the quantum nature of the smallest structures is the fact that their energy levels do not depend on temperature. QDs are sometimes referred to as "artificial atoms," and these structures actually have the sparse and temperature-independent energy spectra typical of atoms.

The absorption and emission spectra of 7-nm-diameter PbS QDs in a silicate glass host is one example (see figure 2 on page 26). The isolated transitions visible in the room-temperature absorption spectrum are evidence of the narrow distribution of QD sizes (∆R/R ~ 4%) in these samples. The emission spectrum shows the distribution of sizes because the sample was excited at high photon energy, at which all of the QD sizes in the sample absorb. It is worth mentioning that it is not practical to try to make QDs with an even narrower size distribution. The observed variation in sizes corresponds to a single layer of atoms, i.e., the size distribution is near the fundamental limit that arises from the fact that the structure is made of atoms.

**A New Telecom Window**

As a result of growth in the volume of telecommunications data, wavelength-division multiplexed (WDM) architectures will likely dominate future networks. The demand for high-volume communications will continue to pressure system designers to increase bandwidth. The bandwidth of existing telecommunication networks is determined, in part, by the spots in the spectrum where attenuation in the fiber peaks. The windows at 1310 and 1550 nm are currently used for...
long-haul routes, and these straddle the overtone absorption band of the hydroxyl vibrational mode around 1.4 μm. The recent development of “water-free” silica fiber by NTT (Tokyo, Japan) and Lucent Technologies (Murray Hill, NJ) opens up a new fiber transmission window that will expand the available bandwidth. To emphasize the ultimate potential that is possible thanks to water-free fiber, some researchers prefer to think of a single large band extending from roughly 1.2 to 1.6 μm.

Components capable of covering the extended wavelength region are required if WDM systems are to fully exploit the capacity of the new fibers. In particular, ultra-broadband optical amplifiers will be needed. Almost all new systems employ erbium-doped fiber amplifiers, which emit around 1.55 μm. In the past, erbium-doped fiber appeared to offer bandwidth to spare, but it will be inadequate, at least by itself, for future networks. The gain bandwidth of the erbium ion in silica is only about 30 nm, and the variation of the gain across the spectrum already makes it necessary to equalize or flatten the gain in commercial systems. Candidate approaches to broadband amplification include fibers doped with other rare-earth ions, Raman amplifiers, semiconductor optical amplifiers, and optical parametric amplifiers. Each of these has drawbacks, so there is ample motivation to develop new amplifier technologies.

The route to a broadband amplifier made with QDs is very simple: synthesize QDs of different nominal sizes (each with a distribution like that above) and combine their spectra. For example, if PbS QDs with diameters of 4.8, 5.5, and 6.0 nm can be combined (perhaps in distinct segments of fiber), the resulting emission spectrum will span the range from 1.2 to 1.6 μm. If 3-nm PbSe QDs can be added to the group, the emission would extend as low as 1 μm. The larger QDs will absorb some of the light emitted by the smaller structures, but this can be accommodated by varying the relative concentrations. All of these QDs could be pumped with the same laser because they all absorb at wavelengths below 1 μm, for example. The ability to pump several different structures with a single laser is a major advantage over standard active ions, each of which generally requires a unique wavelength.

Extremely broad-band emission spectra are possible, but the use of distinct sizes of QDs provides another important degree of freedom: the gain spectrum can be tailored simply by varying the relative concentrations of each set of QDs. Current system architectures make use of gain-flattening techniques, but with the approach described above, more general distributions of gain are naturally possible.

initial devices

It is clear that the properties of semiconductor QDs offer great potential for optical amplifiers at telecommunications wavelengths. The synthesis of QDs in glass hosts is naturally compatible with optical-fiber technology, and polymer hosts may even be acceptable. The expected scenario is to fabricate a fiber doped with QDs, but no one has accomplished this yet. One method of synthesizing semiconductor QDs in glass hosts would be to add the constituents of the semiconductor to a glass melt, forming the glass and then annealing it to form the QDs. Unfortunately, the thermal schedules for fiber pulling and QD synthesis do not necessarily coincide.

As a first step toward an amplifier device structure that is compatible with optical fiber, researchers at Corning have recently synthesized a glass waveguide that contains PbS quantum dots (see figure 4). Although the vision is that the waveguide will be pumped transversely, it may also be possible to pump it longitudinally. Such waveguides can be fabricated by silver-ion exchange (see figure 5). The absorption and emission spectra confirm the presence of high-quality PbS QDs. Detailed characterization of these structures has just begun.

Although semiconductor QDs offer great potential as broadband gain media, many issues will have to be resolved before they are close to competing with existing erbium-doped fiber amplifiers. Some of the issues are
fundamental; for example, the sparse electronic spectra of lead-salt QDs may lead to problems arising from a "phonon bottleneck." Electrons excited to a higher electronic state cannot relax efficiently to the lowest (emitting) state because the states in general will not be spaced by a phonon energy. (The phonon energies are also quantized in a nanocrystal.) Experiments are underway to address this issue. In this regard, an initial report of optical gain in PbS QDs is encouraging. To achieve large useful gain, it will be necessary to synthesize very-high densities of QDs. As mentioned above, it will also be highly desirable to develop optical fiber that is directly loaded or doped with semiconductor QDs.

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1. Professor J. Khurgin (of John Hopkins Univ.), unpublished results.

off the beaten path

Frank Wise describes himself as a "chief cook and bottle washer" at Cornell University (Ithaca, NY), teaching applied physics, advising first-year students, raising money, and performing administrative duties. In photonics, however, he's best known for his research on ultrafast optics and unique materials for semiconductor quantum dots (QDs).

“I’ve always been interested in electronic solid-state devices,” says Wise. But he’s especially interested in taking a slightly different tack than everyone else. “There is a huge effort in the world to work on cadmium salts and III-V semiconductors such as gallium arsenide. The material we choose to work on is pretty odd compared to most of these,” says Wise, who has focused his work on lead-salt QDs. “Lead salts allow us access to the limit of extreme quantum confinement of electrons.”

Wise also has an active program in ultrafast nonlinear optics. Recently, he has focused on new ways to generate ultrashort light pulses, including spatio-temporal solitons. Wise takes his teaching seriously, receiving awards for excellence and innovation in teaching in 1992, 1995, 1998, and 2001. He also recognizes the need for engineers to be able to write, as well as do math and science. “We used to constantly get feedback from recruiters that they were unhappy about how engineers communicated,” Wise says. In response, he began presenting his students with real-life scenarios in an applied physics lab, asking them to write proposals and reports for funding scenarios. “We try to show students that writing is not a dull, time-consuming thing that you do at the end when the fun is over,” Wise says. “Not only are the students writing better by the end, but they all seem to understand that this is important.”

Whether producing top engineering students for industry, characterizing new nanostructures, or spending time with his two children and wife on the weekends, Wise stays busy both professionally and personally. Says Wise of his work: “Our job is not to develop new products but to investigate new ideas. Who knows where that idea may lead 10 years down the road?”

—Laurie Ann Toupin