Semiconductor Nanocrystals Perform as Fluorescent Probes

A team of researchers from Lawrence Berkeley National Laboratory and the University of California—Berkeley, led by Paul Alivisatos and Shimon Weiss, have developed nanometer-sized crystals of semiconductors, such as cadmium selenide and cadmium sulfide, that can be used as fluorescent probes for the study of biological materials. These semiconductor nanocrystals offer a distinct advantage over conventional dye-molecules in that they emit multiple colors of light, which means they can be used to label and measure several biological markers simultaneously.

As the team reported in the September 25 issue of *Science*, "Ideal probes for multicolor experiments should emit at spectrally resolvable energies; should have a narrow, symmetric emission spectrum; and the whole family should be excitable at a single wavelength." Semiconductor nanocrystals met these demands in a "dual emission from single excitation" labeling experiment on 3T3 mouse fibroblast cells. A core nanocrystal of cadmium selenide was enclosed within a shell of cadmium sulfide to boost the amount of fluorescence and reduce photochemical degradation. This core-shell combination was then enclosed within a shell of silica for water solubility and biocompatibility.

With earlier work by Alivisatos having shown that the color of light emitted by a semiconductor nanocrystal depends upon its size, the mouse cells were labeled with two different sizes of core-shell nanocrystals. It was also known that modifying the surface of the silica shell can be used to selectively control its attachment to components within a cell. In this case, the smaller nanocrystals (2 nm), which fluoresced green, were modified to penetrate the nucleus of each cell, and the larger nanocrystals (4 nm), which emitted red light, were modified so that they would attach themselves to actin filaments along the outer cell membrane. To modify the former, the researchers reported, "nanocrystals coated with trimethoxysilylpropyl urea and acetate groups were found to bind with high affinity in the cell nucleus." By incubating the nanocrystals in a 0.2% SDS [sodium dodecylsulfate] soap solution, the nuclear binding could be suppressed. To label the F-actin filaments with red nanocrystal probes, biotin was covalently bound to the nanocrystal surface and the biotinylated nanocrystals were used to label fibroblasts that have been incubated in phalloidin-biotin and streptavidin. In control experiments lacking phalloidin-biotin, these filaments were either not visible or only faintly so.

Using wide-field microscopy, the green and red labels were clearly visible and could be accurately photographed in color. Confocal microscopy images showed that cell nuclei had been penetrated with the green probes and the actin fibers had been stained red. After repeated scans, the nanocrystal labels showed far less photobleaching than would have occurred in the control sample labeled with conventional dye molecules.

The authors also assert that, compared with conventional fluorophores, semiconductor nanocrystals have a "narrow, tunable, symmetric emission spectrum, and are photochemically stable." These features, along with a relatively long fluorescence lifetime (hundreds of nanoseconds) indicate that, in addition to serving as direct probes, semiconductor nanocrystals could also be used as "sensitizers" for traditional dye-molecule probes, meaning they transfer their excitation energy to the dye-molecule. An earlier research team led by Weiss demonstrated that this energy sensitizing phenomenon, known as fluorescence resonance energy transfer (FRET), when it takes place between a single donor and a single receptor, could allow for the labeling and observation of dynamic events such as conformational changes in a protein.

Innovations in Materials Conference Presents Awards

At the Innovations in Materials Conference (IMC) held in July in Washington, DC, sponsored by the International Union of Materials Research Societies (IUMRS), **Kazuo Inamori**, founder and CEO of the Kyocera Corporation in Kyoto, received an award for a Lifetime of Innovation, and 12 Innovations in Real Materials Awards were presented. In his acceptance address, Inamori presented an array of sequential discoveries and products brought to the market over 40 years. He has also moved innovations beyond materials to digital technologies, and to philanthropy by establishing the Kyoto Prizes.

The Innovations in Real Materials Awards went to Materials Research Society members **Michel Bruel** (LETI-CEA, Grenoble) for "Separation of Silicon Wafers by the 'Smart-Cut Method'"; **Mark J. Cardillo** (Bell Labs), "Optical Fibers Prepared from Large Sol-Gel Silica Bodies"; **Shuji Nakamura** (Nichia Chemical Industries), "Synthesis of III-V Nitride-Based Materials and UV/Blue/Green Emitting Devices"; **C. Grant Willson** (University of Texas—Austin), "Revolutionary New Family of Ultrahigh Sensitivity Photo-Resist Materials"; **Richard P. Wool**, et al. (University of Delaware), "Affordable Composites from Renewable Resources"; and to **G. Dixon Chandley** (Metal Casting Technology, Inc.), "Use of Vacuum for Counter-Gravity Casting of Metals"; **Naoji Fujimori** (Sumitomo Electric Industries), "Surface Acoustic Wave Filter Made of Diamond"; **Joseph Robert Pickens** (Concurrent Technologies Corp.), "Ultrahigh Strength Weldalite™ Al-Li Alloys for Space and Other Applications"; **Edward Starke** (University of Virginia), "Development of Al-Li Alloy for Aircraft"; MRS member **Chang Xu Shi, Yaoxiao Zhu, Shunnan Zhang, Langhong Lou,** and **Kui Liu** (Chinese Academy of Sciences), "Superalloys with Low Segregation Controlled by Trace Elements"; **Kazuhito Hashimoto** (University of Tokyo), "Photocatalytic Titanium Dioxide Coatings Which Provide Self-Cleaning, Antifogging, Sterilizing or Deodorizing Properties"; **Dinesh Agrawal,** and MRS member **Jiping Cheng** and **Shalva Gedevanishvili** (The Pennsylvania State University), "Microwave Sintering to Full Density of Ceramics, Carbides, Powdered Metals, in 5–30 minutes"; MRS member **Per Just Andersen, Amitabha Kumar,** and **Simon K. Hodson** (E. Kashoggi Industries), "Inorganically Filled Starch Based Fiber Reinforced Composite Foam Materials for Food Packaging"; and **Pravin Mistry, Manuel C. Turchan, Shengzhong Liu, Gerolf O. Granse, Tom Baurmann,** and **Milad G. Shara** (QQC, Inc.), "Multiple Pulsed Lasers for Materials Processing."

Nanoshells Absorb Light in the Infrared

Rice University researchers, led by Naomi Halas, professor of electrical and computer engineering, have used a technique based on molecular self-assembly and colloid reduction chemistry to synthesize metal nanoshells, which are particles with an insulating core coated by a thin shell of gold. These nanoshells, which range in size from 50 to 1,000 nm in diameter, can absorb or scatter light at nearly any wavelength in the visible or infrared ranges depending upon the dimensions of the particle's core and shell.

In the May 22 issue of *Chemical Physics Letters,* the team describes the fabrication process of the nanoparticles, showing how the structure corresponds to the optical properties. The researchers grew monodisperse silica nanoparticles as their dielectric cores. They then adsorbed organosilane molecules (3-Aminopropyltriethoxysilane) onto the nanoparticles. These molecules bonded to the surface, extending their amine groups outward as a new termination of the nanoparticle surface. They added gold colloid, 1–2 nm in diameter, which bonded to the silica surfaces. The researchers observed 30% gold colloid coverage on the silica nanoshell surfaces. They reported that a "subsequent reduction of an aged mixture of chloroauric acid and potassium carbonate by a solution of sodium borohydride, where the gold-decorated silica nanoparticles are used as nucleation sites for the reduction, results in an increasing coverage of gold on the nanoparticle surface." The nanoshell growth, they said, is typically completed within a few seconds with a yield greater than 95%.

As the nanoshell growth progresses, the sequential uv-visible spectra increase in adsorbance. As the colloidal adsorbates grow, the peak adsorbance, reaching 550–800 nm, becomes red shifted. In addition to the core/shell ratio, the researchers observe that "the absolute size of the metal nanoshell provides additional control over the wavelength dependent optical response of the composite nanoparticles."

"The nanoshells act as an amazingly versatile optical component on the nanometer scale: They may provide a whole new approach to optical materials and components," Halas said. The particles can be made to absorb or scatter visible light and light in the infrared. The nanoshell resonances can be placed in spectral regions, such as the near infrared, where few strongly absorbing optical materials are available.

"We are pursuing strategies to get us out to the five micron range in the infrared," Halas said, "and we're pretty confident that we can do that by refining our current method. Using other techniques, I think we might be able to get out to 10 microns and beyond, into the far infrared."

Superconductivity Offered as Explanation for Conductivity Observed in 2D Electron Gas

Based on an analysis of theory and several experiments in which researchers have observed a conducting phase in dilute two-dimensional electron gases in zero magnetic field, physicists at the University of Illinois have determined the occurrence of superconductivity. Recent experiments were performed on a silicon metal-oxide semiconductor field-effect transistor (MOSFET). Philip Phillips, professor of physics at Illinois, said, "In such a device, electrons are confined to move at the interface between the metal oxide and the semiconductor. Because the electrons move only at the interface, they are said to be confined to two dimensions." According to theory, as the temperature is lowered, the resistivity is expected to continue to increase and the system will become an insulator; however, experimenters have reported a conducting phase.

Phillips, postdoctoral research associate Yi Wan, and graduate students Ivar Martin, Sergey Knysh, and Denis Dalidovich, in their report published in the September 17 issue of *Nature,* cite key observations to account for this novel superconductivity. First, features of the conducting transition, such as current-voltage characteristics and the scaling of the resistivity, resemble those of known insulator-superconductor phase transitions. Second, magnetoresistance measurements offer clear evidence for a critical magnetic field above which the conducting phase is destroyed.

"There are not many states of matter that are consistent with a critical magnetic field," Phillips said. "A critical parallel magnetic field indicates that the electrons are paired up in spin singlet states. The only conducting state that is compatible with this observation is a superconducting one."

Because the conductivity was independent of temperature at a particular electron density, that density marks the transition between the conducting and insulating phases, Phillips said.

He said, "In this density regime, the Coulomb interactions dominate. In the insulator, strong Coulomb interactions and disorder prevent the electrons from moving. But as the density is increased, these strong Coulomb interactions can lead to the formation of Cooper pairs, a prerequisite for superconductivity."

$NiCl_2$ Molecular Magnets Form as Fullerenes and Nanotubes

Weizmann Institute scientists have created a class of magnetic materials made of clusters of inorganic molecules. The molecules of nickel dichloride that make up the magnets are much smaller in size than the metalorganic compounds used previously to create most molecular magnets. As described in the September 24 issue of *Nature,* some of the molecules are shaped like fullerenes and others form nanotubes.

According to Reshef Tenne and colleagues, "$NiCl_2$ is the first of a family of halogen compounds with a layered structure to be shown to form new nanostructures." The researchers have produced a closed cage structure consisting of one closed atomic layer of $NiCl_2$ with a quasi-spherical or a polyhedral shape, and another structure with three and four layers. They have created a nanotube 6-μm long with a cross-sectional diameter of 70 nm. They have deduced a tube axis with [1$\bar{1}$00] direction (i.e., at 30° with respect to the *a* axis) and a chiral structure with an angle of 1.8°.

The scientists built the magnetic molecules from individual atoms. The molecules then self-assemble into a spherical layer one molecule thick. This method of creating a magnetic material gives scientists control over the size and structure of the magnet's molecules and the number of their layers. This, in turn, allows them to tailor the material to specific needs. According to the researchers, "Because Ni atoms in a layer are coupled ferromagnetically and the interlayer coupling is antiferromagnetic, these structures may show different magnetic behavior according to the parity of closed $NiCl_2$ layers in the nanoparticles."

The $NiCl_2$ structures are expected to be much less influenced by the magnetic fields of their neighbors and to be relatively indifferent to other environmental influences, such as temperature. Their seamless structure also suggests they should not be sensitive to hostile chemical effects of the environment, such as oxidation. And because these structures contain no impurities and because their spatial structure is well defined, their magnetic properties can be defined in a precise manner according to predetermined needs. These characteristics make these structures promising in the area of microelectronics industry.

Peak Current Density of $Si/Si_{0.5}Ge_{0.5}/Si$ Tunneling Diodes Engineered During Post-MBE Growth

Researchers at the University of Delaware, the Naval Research Laboratory, and Raytheon Systems have developed a tunnel diode that is compatible with a silicon integrated circuit process. Alan C. Seabaugh of Raytheon said, "Adding the diode to silicon circuits will increase circuit performance and could extend the life of existing production lines."

According to their report in the October 12 issue of *Applied Physics Letters*, the researchers used molecular beam epitaxy (MBE) to grow highly doped (delta-doped) silicon monolayers at 370°C. The materials were then cured or annealed at 700–800°C. The resulting diode has a 4-nm layer of pure silicon-germanium at the center, encased by delta-doped layers of boron and antimony. The boron and antimony layers are then encased by silicon with opposing electrical charges on a silicon substrate with positive charge carriers. According to the researchers, tunnel diodes have been inhibited by the difficulty in controlling peak current and the lack of an integrated circuit process. According to Paul R. Berger of Delaware, the five key points to the design of their $Si/Si_{0.5}Ge_{0.5}/Si$ resonant interband tunneling diodes (RITDs) are (1) an intrinsic tunneling barrier, (2) δ-doped injectors, (3) offset of the δ-doping planes from the heterojunction interfaces, (4) low-temperature MBE growth, and (5) postgrowth rapid thermal annealing (RTA) for dopant activation and/or point defect reduction.

In one RITD sample, the researchers employed a 4-nm undoped $Si_{0.5}Ge_{0.5}$ tunneling barrier and δ-doping planes at the Si/SiGe heterointerface, and in another sample the δ-doping planes were offset from the Si/SiGe heterointerface with 1 nm of undoped Si on either side of the tunneling barrier. As expected, the researchers found that the δ-doped layers offset from the $Si_{0.5}Ge_{0.5}$ spacer using undoped Si provided a higher quality tunneling barrier with reduced defects and higher peak-to-valley current ratio (PVCR) than the first sample. They reported that the peak current apparently occurs in the range of 0.30–0.34 V and that the lower PVCR and peak current density is observed for annealing temperatures up to 800°C. In the first sample, PVCRs ranged up to 1.21 with a peak current density of 2.1 kA/cm^2 and 1.35 with a peak current density of 470 A/cm^2 when annealed at 700°C and 800°C, respectively, while the second sample showed PVCRs up to 1.54 with a peak current density of 3.2 kA/cm^2 and 1.30 with a peak current density of 470 A/cm^2 when annealed at the same temperatures as the first sample. The researchers said that the peak current density can be engineered during postgrowth processing with a short high temperature anneal.

Nick Holonyak Jr., the John Bardeen Professor of Electrical and Computer Engineering and Physics at the University of Illinois at Urbana—Champaign and co-author of a landmark 1959 article on tunneling events in silicon and germanium materials and maker of the first practical, light-emitting diode, said the research is an exciting revival of some of his work. "I'm happy to see this work," he said, "It's very interesting to me because it all started with silicon and germanium."

Phillip E. Thompson of the Naval Research Laboratory said, "MBE wasn' t around when Holonyak was conducting those studies. It took us awhile to make it work at a lower temperature, which freezes atoms in place as you add them to the surface of materials."

To be useful in circuits, the researchers said, RITDs should offer a PVCR of about 4 at room temperature.

Electron Beam Irradiation Decreases Time to Clear Vision on Misted Dental Mirror

Researchers from Tokai University and Iwasaki Electric Group Co. in Japan have applied an electron beam (EB) treatment to dental mirrors to reduce the time required for steam to clear from the mirror. The purpose of this experiment is to aid dentists as they use a dental mirror during oral surgery. EB irradiation is performed by an electrocurtain processor. As reported in the December 1998 issue of the *Journal of Materials Research,* the scientists used several 0.38-s-long irradiation steps, with a current of 4 mA, under a protective nitrogen gas with atmospheric pressure in the apparatus. The temperature was below 323 K immediately after the irradiation. The success of the EB treatment is determined against the time needed to clear the mirror surface.

The scientists found that the time to clear the mist decreases with an increase in irradiation time and that the shortest time to clear the vision is 2.0 s at 36 Mrad. They said that the relation of the nucleation frequency and growth rate accounts for these results. According to the report, the interfacial energy of water between liquid and gas is evaluated by measuring the contact angle in a drop of water. EB treatment decreases both the total number of deposited drops and the mean size of the drops. According to the report, "Since the EB irradiation increases the interfacial energy and decreases the contact-angle of drop, the low contact-angle drop has a large specific surface area per volume for the evaporation. Thus, it is easy to evaporate the fine drops with the low contact angle."

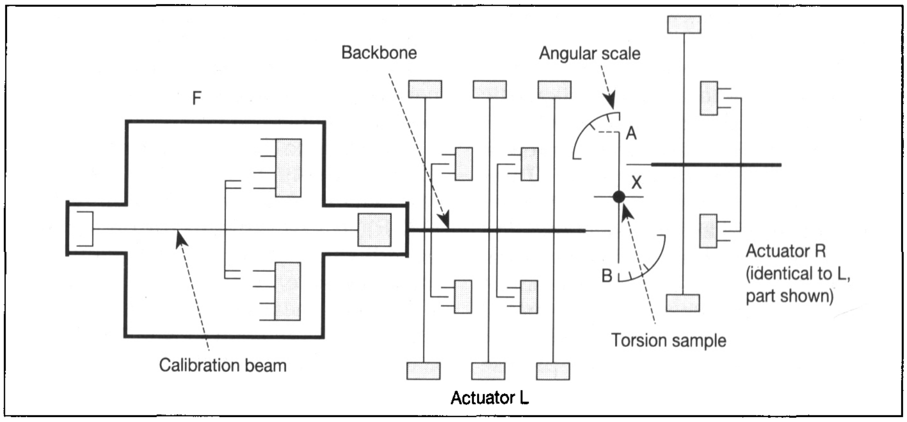
1998 IEEE/LEOS Awards Recognize Work on Laser and OLED Materials

Three of the awards to be presented at the 1998 meeting of the IEEE Lasers and Electro-Optics Society are for work on semiconductor lasers and organic light-emitting devices (OLEDs). The awards were presented at the Plenary Session of the Annual Meeting (LEOS '98) on December 1 in Orlando, FL. Frederico Capasso (Bell Laboratories, Lucent Technologies) and Jerome Faist (University of Neuchatel, Switzerland) received the IEEE/LEOS William Streifer Scientific Achievement Award "for the design, demonstration, and pioneering development of the quantum cascade laser which is revolutionizing the field of mid-infrared semiconductor lasers." David F. Welch (SDL, Inc.) received the IEEE/ LEOS Engineering Achievement Award "for the design, development, and commercialization of high power diffraction limited semiconductor lasers." Vladimir Bulovic (Princeton University) received the LEOS '97 Best Student Paper Award for his paper entitled "Surface-Emitting Vacuum-Deposited Organic Light Emitting Device."

Microinstruments Tested on Submicron Material Studies

In order to conduct submicron-scale material studies, M.T.A. Saif and N.C. MacDonald of Cornell University have developed microinstruments to replace macroinstruments that have posed limits on the minimum size scale of the samples. They tested the microinstruments with samples of single crystal silicon (SCS) bars with 1- and 2.25-μm^2 cross sections and an aluminum-silicon dioxide composite beam 1-μm wide and 1.5-μm thick. The microinstruments measure tension. With the aluminum-silicon dioxide composite beam, the scientists found a force to fracture of 220 μN. For the two SCS bars, the scientists measured maximum shear stress prior to fracture to be 5.6 and 2.6 Gpa.

The instrument consists of two actuators and the torsion test sample. Each actuator, spanning an area of 2 × 1 mm^2 and 10 μm deep, consists of a backbone supported by springs, called "beams," which originate from supports attached to the substrate. According to the scientists' report published in the December 1998 issue of the *Journal of Materials Research,* "The backbone supports cantilever beams from which originate the movable comb capacitors. The fixed combs are attached to the substrate. When a voltage is applied between them, the fixed combs attract the movable ones. The actuator thus moves toward the fixed combs by bending the supporting beams, and applies force on the sample" as shown in the figure.



Schematic (top view) showing the actuator, the torsion sample, and a calibrating buckling beam which calibrates the spring constants of and the force generated by the actuator.

According to the report, the microinstruments are successful because of their small size, low thermal mass, vacuum compatibility, and built-in vibration isolation all of which enable material characterization to be performed over a wide range of environmental conditions, including high humidity, high pressure, and high and low temperatures.