

obtained. They concluded that “the control of the Fermi level should be important in future applications of colloidal semiconductor nanocrystals and the electron transfer method may be the viable approach in the nanometer length scale with strong confinement.”

ROBERTSON ANSAH BILL

Semiconductor Quantum Dots Self-Assembled into 2D and 3D Ordered Lattices

Researchers in the Materials Department at the University of California—Santa Barbara have developed a technique for growing semiconductor self-assembled quantum dots (QDs) into ordered lattices. Typically, in self-assembled QD systems, the QDs are isolated or are arranged as ensembles that are randomly distributed within a structure. It is thought, however, that self-assembled QDs, when arranged in an ordered array or lattice, will exhibit attributes related to the electronic or photonic quantum dot coupling within the array. While a number of techniques for producing spontaneous long-range order in QDs have been employed, none have resulted in systems that demonstrate coupling effects between individual dots. In the January 1 issue of *Applied Physics Letters*, P.M. Petroff and co-workers describe a method for self-assembling QDs (InAs surrounded by GaAs) into two- and three-dimensional periodic lattices using a coherently strained layer of $\text{In}_{0.2}\text{Ga}_{0.8}\text{As}$ deposited by molecular beam epitaxy (MBE) over a semiconductor substrate.

Quantum dots are formed by the epitaxial deposition of coherently strained islands. When the area over which the QDs are deposited is large and uniform, the nucleation process is random. To reduce this randomness, the researchers nucleated the QDs on a limited surface area, or, specifically, a mesa top with nanometer dimensions. A square lattice of mesas was patterned on a {100} MBE-deposited GaAs film using optical holography. The surface mesas had a square base with ~170 nm sides and ~25 nm height, and the two-dimensional (2D) square mesa lattice had a periodicity of ~250 nm along the unit cell primitive vectors. The oxide layer on the GaAs was thermally desorbed and a 60-nm thick GaAs layer was deposited to remove the surface damage induced by the oxide. To obtain a periodic lattice of nucleation sites, the research team used a periodic strain pattern induced by a coherently strained subsurface stressor layer of $\text{In}_{0.2}\text{Ga}_{0.8}\text{As}$ re-grown on the GaAs patterned surface. InAs was then deposited and islands formed on the mesa tops.

Finally, a 10-nm thick capping layer of GaAs was deposited, transforming the islands into quantum dots.

The researchers' atomic force microscope (AFM) images illustrate three different island lattices formed on top of the mesas, each with a unit cell of a different in-plane orientation. Data show that over 90% of the InAs QDs are on top of the mesas and that the lattice periodicity of the QDs matches that of the mesa array. They also demonstrate that, by adjusting the mesa lattice, the lattice period and unit cell structure can be tuned. The number of QDs within the lattice can be adjusted by varying the indium flux during deposition. Furthermore, their AFM images show that, even for multiple islands that are closely packed on a mesa top, there is no coalescence between QDs. Cross-sectional TEM images indicate that, when stacks of QD lattices are grown, the strain coupling effects between layers preserve the regular order of QDs from one layer to the next, resulting in dislocation-free, three-dimensional (3D) QD lattices.

“We are now investigating how the optical properties of these QD lattices differ from random ensembles,” said the lead author, H. Lee. “And already we see that the photoluminescence efficiency for an ordered QD lattice is higher than for a random ensemble of approximately the same QD density ($\sim 5 \times 10^9 \text{ cm}^{-2}$).” This technique, which should be applicable to a variety of QD materials systems, opens the possibility of exploring the properties of 2D and 3D semiconductor QD lattices.

STEFFEN K. KALDOR

Gradient-Field Raman Effect Allows Measurement of Both Raman and Infrared Active Modes

A team of physicists at North Carolina State University has discovered a method for measuring the vibration properties of materials, which could assist in the development of nanostructure technologies. Their technique, using near-field scanning optical microscopy in conjunction with what they call the gradient-field Raman (GFR) effect, measures the behavior of molecules at the nanoscale—rather than Raman spectroscopy's microscopic scale—by reflecting light off of the studied material.

As assistant professor of physics Hans D. Hallen and his research team applied a near-field scanning optical microscope (NSOM) to study the vibrations of molecules, they discovered vibration patterns that could not be explained using the rules associated with normal Raman spectroscopy. In normal Raman spectroscopy, the coupling between the light and the

molecule is brought about by a change in polarizability as the molecule vibrates along a bond. They found that the coupling between the light and molecule in the NSOM was moderated by a strong electric field gradient that shifted the potential energy of the atoms as they moved during the vibration. In particular, the gradient causes the force on a polarized atom to vary as the atom moves during a vibration, allowing the vibration to gain energy from the optical field.

In the November 6 issue of *Physical Review Letters*, the researchers describe how the strong electric field gradient can cause forbidden vibration modes to appear in the Raman spectra. A KTP sample demonstrates vibration energies at 683 cm^{-1} —observed as a weak line in Raman studies—and 712 cm^{-1} —observed as a strong infrared (IR) line. Typically NSOM-Raman studies reveal low signal levels. In this study, the researchers report that “the 683 cm^{-1} mode was not observed, but the 712 cm^{-1} mode was enhanced in the near field.” The researchers attributed the strong 712 cm^{-1} mode in the IR absorption to the GFR effect.

They said that with the GFR effect, “the amplitude of the signal should be similar to that of the allowed Raman modes, and the relative strength of the modes should be similar to those in infrared spectroscopy, for IR allowed modes.” The researchers said that the selection rules for the GFR process depends on the bond orientation.

[001] HRTEM Image of Iron Nanoparticles Reveals 3-nm-Thick Passive Layer

Iron nanoparticles obtained by gas evaporation in vacuum have an external oxide layer formed by $\gamma\text{-Fe}_2\text{O}_3$ and Fe_3O_4 . However, this oxide shell does not protect iron nanoparticles from further oxidation. By means of gas condensation of plasma-evaporated vapor, a team of researchers from Tianjin University in China obtained iron nanoparticles with corrosion resistance at room temperature. The nanoparticles were condensed from argon plasma evaporation of an iron target. A group of scientists from the Hong Kong University of Science and Technology used high-resolution transmission electron microscopy (HRTEM) to study the characteristics of these iron nanoparticles. A compressive oxide layer epitaxially grown over the iron core causes this increase in corrosion resistance, according to the researchers findings published in the December 18 issue of *Applied Physics Letters*.

The selected area diffraction patterns (SAD) of the iron nanoparticles revealed the presence of bcc iron and a cubic spinel structure similar to γ -Fe₂O₃ and Fe₃O₄. Further examination with x-ray photoelectron spectroscopy showed that the oxidation state of iron was Fe³⁺, clearly identifying the oxide shell as γ -Fe₂O₃. With the use of convergent-beam electron diffraction, the scientists obtained single crystal electron diffraction patterns and identified the epitaxial relationship between the iron core and the oxide shell. When analyzing the thickness fringes observed in HRTEM images, the scientists estimated the thickness of the oxide layer as 4.2 nm.

The investigators observed a continuous change in the orientation of adjacent iron {100} and {110} facets, and bending of the {111} oxide fringes. As a result, they estimated a compressive strain of 3% due to the mismatch on the {100} facets. They suggest that this compression reduced the oxide lattice spacing in the iron surface and therefore improved the passive characteristics of the oxide layer.

The analysis of the images obtained also showed that γ -Fe₂O₃ layers grew epitaxially on the iron surface. The researchers quantified the growth rate by using the Cabrera-Mott theory of oxidation of metal. They report that the rate of oxidation is initially very fast but decreases considerably after the oxide shell is 3 nm thick, at room temperature conditions. For a 4-nm layer, the growth temperature is about 420 K, which the researchers considered consistent with their experimental estimations. Following the assumptions taken in the application of this theory, the researchers suggest that the small size of the particles contribute to the growth of an epitaxial layer.

SIARI S. SOSA

Silicon Analogue of Spiropentadiene is Isolated

Disilenes, Si=Si double bonded compounds, are commonly hard to isolate because they are unstable. As reported in the October 20 issue of *Science*, a group of researchers at Tohoku University, Japan,

has synthesized and isolated a stable disilene, tetrakis[tri(*tert*-butyldimethylsilyl)silyl]spiropentasiladiene (compound 2), which is a silicon analogue of spiropentadiene (compound 1). As an original Si cluster (Si²¹), compound 2 has very attractive features, according to the researchers. Electrons are delocalized over the whole cluster through spiroconjugation, which is very sensitive to the twisting of substituents at Si=Si bonds. Therefore, the spiroconjugation can be tuned by the substituents. The researchers projected these features can be used for optoelectronic devices.

In their research, chemistry professor Mitsuo Kira and his colleagues established that the reaction of [tris(*tert*-butyldimethylsilyl)silyl]dibromochlorosilane with potassium graphite at -78°C gives two products, one of which is compound 2. Crystallization from hexane gives compound 2, an oxygen- and moisture-sensitive dark red crystal, in 3.5% yield. Contrary to compound 1, which decomposes at -100°C, spiropentasiladiene does not evolve to decomposition/degradation before its melting point (216°C–218°C). As previously proposed, the four bulky tri(*t*-butyldimethylsilyl)silyl groups contribute to the thermal stability of compound 2, but are not the main reason for the isolation. The fairly small strain energy of the ring systems in compound 2 is the key point for this successful isolation.

In studying the structure of compound 2 in comparison to other carbon and silicon compounds, Kira's group used ¹H, ¹³C, and ²⁹Si nuclear magnetic resonance (NMR) spectroscopy; ultraviolet-visible spectroscopy; and x-ray crystallography. The spectroscopic data indicates significant interaction between two remote Si=Si double bonds in the molecule. The x-ray single-crystal analysis shows a substantial deviation from the perpendicular arrangement of the two rings in compound 2. The two rings in compound 2 are a little twisted with a dihedral angle of 78.26° and the two Si=Si double bonds in these two rings are not planar. In contrast to tetrakis(di-*tert*-butylmethylsilyl)cyclotrisilene, which only has one three-

membered ring, the length of Si=Si double bonds and the Si-Si single bonds in compound 2 is longer and shorter, respectively.

The researchers are currently investigating the formation mechanism for compound 2. They said that the syntheses of various unknown types of group-14 organometallic compounds including silicon analogues of triple-bond molecules present new challenges in this field.

YING LI

Transparent, Conductive Coatings Produced

Researchers at the Fraunhofer Institute for Surface Engineering and Thin Films IST in Brunswick have developed a process to produce transparent, electrically conductive oxide coatings. They combined mid-frequency magnetron sputtering with a chemical reaction. The glass substrate is heated in a reactor and coated. In the course of magnetron sputtering, accelerated ions of inert gas "shoot" atoms out of a zinc-aluminum plate. The metal atoms are deposited on the substrate in a vacuum. For this coating to become both electrically conductive and transparent, the zinc needs to be oxidized so that the aluminum and zinc atoms bond together.

The researchers are pursuing this project in order to coat windshields to melt snow and ice. Bernd Szyszka of the IST said, "A prerequisite for use of these coatings systems is to convert the operating voltage for cars from 12 to 24 or even 42 V—a conversion that is expected over the next two to four years to improve the configuration of electronic systems in motor vehicles. Technically, the coatings can also function at low power, but manufacturing costs are then extremely high. With a higher voltage, thinner coatings suffice—which can be produced at substantially lower cost." The researchers at IST are currently using an industrial-scale plant to coat glass substrates of up to 0.6 m by 1 m in size.

Szyszka said that transparent and electrically conductive coatings are also needed for flat monitor screens and electrically switchable window panes for buildings. □

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