

Application of Electrodeposition and Etching Forms Stable Metallic Nanogaps

As research heads toward the age of nanoelectronics, some applications require electrodes with gap sizes on the same order of magnitude as the size of an atom or molecule. Researchers from the Department of Physics at Florida International University have fabricated stable molecular-scale gaps with sub-angstrom precision. As reported in the December 18 issue of *Applied Physics Letters*, gaps a few nm or less can be fabricated with a 0.5 Å resolution. The gap sizes may be readily increased or decreased by the process of electrodeposition or etching. The researchers indirectly measured the gap widths by the amplitudes of the electron tunneling current.

The initial calibration setup was comprised of a Pt_{0.8}Ir_{0.2} scanning tunneling microscope (STM) tip coated with Apiezon wax and a 100-nm thick gold film on a mica substrate in an electrical feedback circuit. The researchers C.Z. Li, H.X. He, and N.J. Tao narrowed the initial gap, 50 nm wide, by bathing the STM tip in a CuSO₄ and H₂SO₄ electrolytic solution. This caused copper to deposit onto the STM tip. They measured the tunneling current continuously while the gap narrowed. In order to produce long-term stable nanogaps, the researchers fabricated a pair of gold electrodes on oxidized silicon. An expected increase in tunneling current as the gap narrowed was observed. The unexpected event, however, was the observation of step-wise changes during this climb. The researchers said that the discrete nature of atoms may have caused this quantization in tunneling current through a process known as structural relaxation. Relaxed structures supply stable energy wells, which provide a predictable means of gap construction. These discrete changes in currents correspond to 0.5 Å changes to the physical widths of the gap.

The researchers further controlled the gap width with a feedback loop through reversibility by electrochemical etching. This is similar to the deposition process except for the reversed electrochemical potential. This method of nanogap fabrication contributes toward the future of nanotechnology due to its precision, stability, and reversibility.

JUNE LAU

Atomic Force Microscope Aids Fabrication Control of Gold Nanowires

A group of scientists from the National Research Institute for Metals in Japan has developed a technique for controlled

growth of gold nanowires. The researchers explained their method as well as their results in measurements of electronic transport in the December 25 issue of *Applied Physics Letters*. Using an atomic force microscope (AFM) in contact mode with a piezoresistive cantilever coated with gold, they grew the nanowires on top of a Si(111) substrate in ultrahigh vacuum. Prior to Au deposition the silicon is flashed to 1200°C several times until a clear 7 × 7 surface reconstruction is observed. The surface is then checked for cleanliness by Auger spectroscopy and scanning tunneling microscopy. The nanowires are then drawn onto the surface with the tip in contact. The gold actually "flows from the tip to the surface, like a fountain pen," said the researchers, while the cantilever is moving on the Si(111) surface. The resultant wires can be observed under imaging with the AFM in noncontact mode. Depending on the bias voltage applied to the tip, the contrast of the image changes. This effect is due to a difference in the Fermi level that causes electrons to flow from the Si substrate to the gold wire, charging it negatively. Consequently, it is possible to establish the metallic nature of these gold wires.

The line width of the wires depends almost exclusively on the characteristics of the cantilever tip, given that its velocity is less than 50 nm/s. The researchers obtained wires with a line width of 4 nm and lengths of 7 μm.

The researchers used four joint evaporated Ag electrodes to measure the conductance in the gold wires at liquid helium temperatures. The *I-V* curve for an applied bias voltage of ±100 mV is linear, corroborating the metallic behavior of the nanowires, although for larger bias voltages the *I-V* curve is nonlinear. According to the researchers, this is probably caused by the instability of the wires fabricated over the Ag electrodes, or by effects of the Si substrate.

This method has the advantage of great control of the cantilever tip, which means a potential for fabrication of nanometer devices at industrial level, especially if an array of cantilevers is developed.

SIARI S. SOSA

Electron Transfer Produces *n*-Type Colloidal Semiconductor Nanocrystals

M. Shim and P. Guyot-Sionnest at the James Franck Institute, University of Chicago have produced *n*-type colloidal semiconductor nanocrystals of CdSe, CdS, and ZnO by using electron transfer techniques similar to those used with

conducting polymers. The *n*-type character of the nanocrystals is maintained for several hours (in CdS) and for several days (in ZnO) at room temperature. According to the researchers, this is the first time that electrons have been successfully placed in the lowest unoccupied quantum-confined orbital (LUQCO) of strongly confined colloidal semiconductor nanocrystals without optical creation of an electron hole pair.

As reported in their article published in the October 26 issue of *Nature*, the scientists added ~50mM sodium biphenyl into a ~0.1mM dried and degassed solution of CdSe nanocrystals in heptamethylnonane. Electron transfer from the sodium biphenyl to the nanocrystal produced *n*-CdSe nanocrystals. The researchers measured the absorption spectra of CdSe nanocrystals using infrared spectroscopy. Shim and Guyot-Sionnest observed a strong peak infrared absorption at 0.3eV. In these nearly spherical nanocrystals, the infrared transition indicates the presence of *n*-type nanocrystals and arises when the electron is excited from the lowest conduction band state 1S_e to the next state 1P_e, similar to a hydrogen atom. To determine the different features of electron transitions from the LUQCO to the next higher state, the researchers measured the absorption spectra of various sizes of *n*-type CdSe nanocrystals and compared their results to previous research. When CdSe is subjected to various capping groups, they said, electrons still moved to quantum-confined states producing *n*-type semiconductor nanocrystals.

The researchers further confirmed their results by measuring the infrared absorption spectra of *n*-type CdS and ZnO nanocrystals along with CdSe, and observed the time decay of each absorption spectrum at room temperature. They found that the infrared absorption in ZnO nanocrystals takes a much longer time to decay than the corresponding absorption in *n*-type CdSe and CdS nanocrystals. According to the report, the stability of the *n*-type semiconductor nanocrystals is largely dependent on the reduction potential of the nanocrystals and the temperature of the surroundings. Since the electron transfer approach requires the injection of electrons into the LUQCO, eliminating electron traps in the bandgap of the colloidal semiconductor nanocrystals could also enhance stability of electrons in the quantum-confined states.

In terms of future applications, the researchers proposed that as methods are devised to control the electron injection by an external potential or current, novel electrochromic materials would be

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*.