

## RESEARCH/RESEARCHERS

### Hardness Measurements of Silicon Nanospheres Yield Values Four Times that for Bulk Silicon

Recently, a team of researchers from the University of Minnesota and Los Alamos National Laboratory directly determined the mechanical response of single nanospheres of silicon with hardness up to 50 GPa, which is 4× greater than that normally expected for bulk silicon (12 GPa).

As reported in the June issue of the *Journal of Mechanics and Physics in Solids*, W.W. Gerberich, M.I. Baskes, R. Mukherjee and colleagues first synthesized these monodispersed silicon particles by injecting vapor-phase silicon tetrachloride into an argon hydrogen plasma using a modified hypersonic plasma particle deposition technique. These particles were then transported to an aerodynamic lens system in a streamline under the influence of fluid drag and particle inertia. Lines of nanoparticles were deposited across a sapphire wafer mounted on a computer-controlled substrate translation system.

The researchers began their study by performing an atomistic simulation of a 12-nm-diameter silicon nanosphere and nanoindentation measurements of a 38.6-nm-diameter silicon nanosphere. The atomistic simulation of the 12-nm-diameter silicon nanosphere, which used a modified embedded atom method (MEAM) potential, showed that no apparent dislocation nucleation occurred when two stiff platens compressed it. The unloaded nanosphere had only a ~5% change in size in the direction of the surface contact, due to phase transformation and flow of Si atoms toward the outer regions of the nanosphere, in agreement with a geometric (perfectly plastic) contact. In contrast, the nanoindentation measurements on the larger silicon nanosphere showed staircase yielding events, which were attributed to the nucleation of contact loops at the contact edges that then move down or up a glide cylinder. The

researchers indicated that the differences between the simulation of the 12 nm nanosphere and the measurements on the 38.6 nm nanosphere may be due to the inability of dislocation loops to nucleate in small enough volumes.

Subsequently, spheres from 40 nm to 100 nm in diameter were repeatedly compressed. For these larger nanospheres, the researchers believe that plastic deformation is accomplished by dislocation nucleation. For these, it is shown that reverse plastic strain increases as the particle size decreases. For 38.6-nm-diameter silicon spheres, these particles showed as much as 48.6% strain reversal after they were loaded up to 70 μN and then unloaded. From these observations, the researchers proposed that this strain reversal is due to high dislocation densities within the particles and that these high densities also effectively work to harden the particle. For future studies, the researchers plan to verify this finding by transmission electron microscopy to confirm particle shape, size, and examine the residual dislocation array after indentation. The researchers indicated that superhard nanospheres may have potential applications in chemical-mechanical polishing or planarization of microelectronics and read-write heads of disk drives as well as for hardening surfaces of microelectromechanical systems devices.

KINSON C. KAM

### Biomimetic Strategy for Antifouling Materials Developed from Mussel Adhesive Protein Mimetic Polymers

The use of surface-modification techniques with poly(ethylene glycol) (PEG) has been shown to prevent protein, cell, and organism fouling at the interfaces with biological tissues. PEG is a biocompatible polymer and can be immobilized on the surfaces by the specific functional groups. However, these modifications can cause hydrolysis and thermal degradation of PEG coatings. A research group led by P.B.

Messersmith of Northwestern University has developed a biomimetic strategy to modify the biomaterial surfaces by incorporating 3,4-dihydroxyphenylalanine (DOPA) with PEG. DOPA, a catecholic amino acid formed by posttranslational modification of tyrosine, is a component of mussel adhesive proteins (MAPs). Known as one of the most notorious fouling organisms, mussels can adhere to wet surfaces by secreting this kind of protein glue. Messersmith's group used this idea and synthesized DOPA-containing peptide-PEG conjugates to prepare nonadhesive/nonfouling gold and titanium surfaces.

As reported in the April 9 issue of the *Journal of the American Chemical Society*, linear monomethoxy-terminated PEGs conjugated to a single DOPA residue (mPEG-DOPA) were synthesized as were PEGs conjugated to the N-terminus of Ala-Lys-Pro-Ser-Tyr-Hyp-Hyp-Thr-DOPA-Lys (mPEG-MAPD), a decapeptide analogue of a protein found in the foot of mussel (*Mytilus edulis*) adhesive plaques. Surface analysis and cell culture experiments were carried out on the modified gold and titanium surfaces—which are common implant materials—by absorbing mPEG-DOPA and mPEG-MPAD in the solution.

X-ray photoelectron spectroscopy showed a significant ether (C-O) peak increase in mPEG-DOPA-treated gold substrates, compared with the unmodified materials, which, the researchers said, is typical of a surface-bound PEG polymer. The positive-ion time-of-flight secondary-ion mass spectroscopy spectrum revealed an increase in the presence of fragments corresponding to PEG absorption, which further confirmed formation of Au-DOPA complexes. A cell culture experiment was performed by culturing 3T3 fibroblasts on the surfaces for up to 14 days, and the ability of modified surfaces to resist cell attachment was examined by quantitative image analysis. Fluorescence microscopy images revealed that cell adhesion to mPEG-DOPA and mPEG-MAPD modified surfaces

decreased by as much as 98%, compared with control surfaces, and the modified Ti surfaces exhibited low cell adhesion for up to two weeks in culture. Unlike Au, the bulk Ti substrate used in the experiment had a native oxide surface, and the interactions between the DOPA-containing PEG and Ti substrate are still under investigation.

The researchers said that many established and emerging technological systems in both medical and nonmedical applications rely on surface interactions. For example, the success of many cardiovascular implants hinges in part on the nature of the interaction of the implant with blood; implant surfaces that readily become fouled may increase the probability of implant failure and result in a

life-threatening condition. Similarly, in the burgeoning field of biochips and biosensors, strict control of the fluid/solid interface is relied upon for accurate device function. Additionally, due to the potential for DOPA-containing peptides to bind to a variety of surfaces, the non-fouling strategy described here may find use in anti-icing coatings in aerospace and may have the ability to inhibit the attachment to maritime vessels of the very mussels that inspired the strategy.

YUE HU

### Hybrid Electroactive Biomaterial Synthesized

The functionalization of electrodes with redox enzymes to create electroactive biomaterials for sensor applications is an

active area of research. The efficiency of electron transfer between the enzyme and the electrode is of vital importance in such materials. In the March 21 issue of *Science*, I. Willner and co-workers at the Hebrew University of Jerusalem and J.F. Hainfeld in the Department of Biology at Brookhaven National Laboratory described the use of a 1.4 nm gold nanoparticle (Au-NP) as the electron-collecting and -relaying system from a surface-reconstituted apoglucose oxidase (GOx) enzyme connected to a quinone-flavin adenine dinucleotide (FAD) on a gold electrode. The researchers show that this hybrid biomaterial exhibits a larger turnover rate than do biomaterials that use organic electron-relaying subunits. The researchers presented two synthetic strategies showing the flexibility of their approach. According to Willner, "In addition to possible biosensor applications, this study adds a new dimension to nano-bioelectronics."

The sensor material was prepared by two methods. In the first method, the Au-NP was attached to the FAD group and the GOx was then reconstituted with the FAD-functionalized Au-NP. The kinetics of the reconstitution was monitored by measuring the expected FAD fluorescence increase during this process and using scanning tunneling electron microscopy

### Review Articles and Special Issues

The May 15, 2003 issue of the *Journal of Applied Physics* 93 (10) contains the proceedings of the 47th Annual Conference on Magnetism and Magnetic Materials.

The May 2003 issue of *Reviews of Scientific Instruments* 74 (5) contains a review article by A.G. Drentje on "Techniques and Mechanisms Applied in Electron Cyclotron Resonance Sources for Highly Charged Ions," p. 2631.

The April 2003 issue of *Reviews of Modern Physics* 75 (2) contains A. Damascelli, Z. Hussain, and Z.-X. Shen, "Angle-Resolved Photoemission Studies of the Cuprate Superconductors," p. 473; and A.P. Mackenzie and Y. Maeno, "The Superconductivity of Sr<sub>2</sub>RuO<sub>4</sub> and the Physics of Spin-Triplet Pairing," p. 657.

The May 2003 issue of *Semiconductors* 37 (5) contains Yu. B. Bolkhovityanov, O.P. Pchelyakov, L.V. Sokolov, and S.I. Chikichev, "Artificial GeSi Substrates for Heteroepitaxy: Achievements and Problems," p. 493.

The April 2003 issue of *Optical Materials* 22 (2) pp. 81-176 contains the Proceedings of the Scientific Committee of the French Research Group—"GDR 1148 CNRS," LASMAT: Research Group on Laser Materials.

The July 2003 issue of *Solid State Electronics* 47 (7) pp. 1131-1248 contains the Proceedings of the 3rd International Workshop on Ultimate Integration of Silicon.

The March 3, 2003 issue of *Thin Solid Films* 427 (1-2) pp. 1-441 contains the Proceedings of Symposium K on Thin Film Materials for Large Area Electronics, of the 2002 European Materials Research Society (E-MRS) Spring Conference.

The March 20, 2003 issue of *Thin Solid Films* 428 (1-2) pp. 1-279 contains the Proceedings of Symposium J on Growth and Evolution of Ultrathin Films: Surface and Interface Geometric and Electronic Structure, of the 2002 European Materials Research Society (E-MRS) Spring Conference.

The May 9, 2003 issue of *Vacuum* 71 (1-2) pp. 1-346 contains the Proceedings of the 9th Joint Vacuum Conference (JVC-9), organized by the Austrian Vacuum Society, in cooperation with the Vacuum societies of Hungary, Croatia, Slovenia, Czech Republic, Slovakia, and Italy.

The May 19, 2003 issue of *Vacuum* 71 (3) pp. 347-436 contains the Proceedings of the Symposium on Plasma Surface Engineering at the Spring Meeting of the German Physical Society.

The March 2003 issue of the *Journal of Lightwave Technology* 21 (3) contains a special issue on Optical MEMS and Its Future Trends.

The May 2003 issue of *IEEE Transactions on Magnetism* 39 (3) contains selected papers from The Tenth Biennial Conference on Electromagnetic Field Computation (CEFC '02).

The May 2003 issue of *IEEE Transactions on Semiconductor Manufacturing* 16 (2) contains special sections on single-wafer manufacturing in the nanochip era and papers from the International Conference on Microelectronics Test Structures.

The February 2003 issue of *IEEE Proceedings—Optoelectronics* 150 (1) contains a special issue on physics and technology of dilute nitrides for optical communications.

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images to directly observe Au-NPs incorporated into the enzyme units. The reconstituted GOx was then assembled on a gold electrode. In the second method, the electrode was first decorated with FAD-functionalized Au-NPs, and this surface was then used to reconstitute the GOx enzyme. Microgravimetric quartz-crystal microbalance measurements indicate a 60% surface coverage for biomaterials prepared by both methods.

Cyclic voltammetry studies of the biomaterials prepared by both methods show the glucose electro-oxidation current increases with glucose concentration. Furthermore, the unimolecular electron transfer rate constant that is calculated from the anodic current-density plateau is seven times larger than that measured for native GOx when oxygen is used as the electron acceptor. This indicates an increase in the turnover number for the enzyme that can only be attributed to the use of the Au-NP as the electron-relaying functionality. Control experiments show that the functioning of the bioelectrocatalyst is not affected by the presence of oxygen (a potential electron scavenger) or citric acid (an oxidizable interferant).

GREG KHITROV

### "Scarring" Produced by Packing of Spherical Particles onto the Surface of a Sphere

Packing spherical particles onto the curved surface of a sphere produces "scars," distinctive high-angle grain boundaries, that are not observed in the packing of spherical particles onto planar surfaces. These scars are observed above a critical system size, and the number of additional defects in these scars increases linearly with the size of the sphere. These findings address a conundrum that has puzzled scientists for almost a century, dating back to theoretical work by J.J. Thomson, who attempted to explain the periodic table of the elements by modeling atoms in terms of rigid shells of electrons. Researchers A. Bausch (Department of Physics, Technische Universität München), M. Bowick (Department of Physics, Syracuse University), and colleagues from Fundamenteel Onderzoek der Materie, Institute for Atomic and Molecular Physics (Amsterdam); the University of Massachusetts; Harvard University; Iowa State University; and Ames National Laboratories reported their experimental studies of packing phenomena in the March 14 issue of *Science*.

Although scientists have theorized and used computational methods to predict minimum energy arrangements for dense packing of repulsive particles on spherical

surfaces, the researchers in the present study observed this packing experimentally. The "repulsive particles" were cross-linked polystyrene beads (1  $\mu\text{m}$  in diameter) packed by adsorption on the spherical surfaces of water droplets of various size (e.g., 12  $\mu\text{m}$  radius) formed in an oil bath. The arrangement of particles was imaged using an inverted microscope, and the lattice geometry was analyzed using Delaunay triangulation algorithms for spherical surfaces.

Whereas repulsive particles on a planar surface will form a simple lattice of triangles akin to the familiar billiard-ball packing, the distinctive scars observed by the researchers are necessary for translating dense packing onto a curved surface. The scientists also observed that these grain-boundary scars on the spherical surface terminate within the crystal lattice. A similar phenomenon of grain boundaries ending within the crystal is not typical on flat surfaces, due to the prohibitively high associated strain. Instead, flat surfaces display grain boundaries that terminate at the boundary of the sample. Theoretically, those planar grain boundaries can be considered "infinite" in length, since they extend across the periodic lattice.

The findings of this study may hold implications for such diverse fields as nanotechnology and drug design. Fullerenes, certain viruses and bacteria, and other naturally spherical surfaces are expected to display scars similar to those observed in the model polystyrene-bead spherical systems imaged by the researchers. The researchers see the next step as understanding how they can take advantage of these scars where they occur in nature.

According to Bowick, "Although dislocations are excited at finite temperature in flat crystals, our work shows that that spatial curvature can drive the proliferation of unusual dislocation arrays (scars) even at zero temperature. Such unavoidable irregularity in the ground state is a signature of curved geometries which we expect to encounter in many natural systems."

EMILY JARVIS

### Electric Field Drives Particles to Self-Assemble

With a combination of electric fields and fluid mixtures, researchers I. Aranson, M. Sapozhnikov, Y. Tolmachev, and W. Kwok of Argonne National Laboratory have caused tiny spheres of bronze and other metals to self-assemble into crystalline patterns, honeycombs, pulsating rings, and two-lobed structures that whirl like tiny propellers. Such self-assembling behavior could be exploited to create next-

generation nanostructures and micromechanical devices.

As reported in the March 21 issue of *Physical Review Letters*, Aranson and colleagues placed a quarter-teaspoon of 100  $\mu\text{m}$  bronze spheres between two transparent sheets coated with conducting material. Under high voltage, each bronze sphere acquires a charge from the bottom plate and is attracted to the upper sheet. The spheres reverse charge when they hit the upper sheet and are repelled back toward the lower sheet. As the process repeats 40 times per second, the bronze particles form a shimmering "gas" between the two plates. Groups of particles, responding to the electric field from the plates and from each other, tend to cluster together and coalesce into large, random groups.

Sapozhnikov, a postdoctoral researcher working under Aranson's supervision, then filled the electrostatic cell with various nonconducting fluids, including toluene and octane. The results were essentially random until he tried phenotole, a colorless, oily fluid used in medicines and dyes. At around 1000 V, the particles began to form regular patterns. By varying the voltage, the spacing between the plates and the amount of conductive fluid in the mix, the researchers found they could create a regularly spaced array of crystals, honeycombs, and other forms.

The results then were reproduced with other dielectric liquids mixed with a small amount of ethanol to control the electrical conductivity of the solution.

"Particles interact with each other and create hydrodynamic forces in the liquid. These interactions create the patterns," Aranson said. "You can actually 'tune' the patterns by adding impurities to the liquid."

The particles also form rings that grow, absorb other clusters of particles, and then burst open. "They grow, they rotate, they do all kinds of crazy things," Aranson said. "The rotation, especially, is still not understood."

Influencing nanometer-sized particles to self-assemble into useful structures is one of the field's most difficult challenges. Self-assembly techniques are usually driven by thermodynamic forces, which dictate the type of complex pattern formation.

"This electrostatic method provides an additional way to control the self-assembly process," Aranson said.

### AFM Adapted to Measure Adhesion between Carbon Nanotubes and Polymers

Researchers at the Georgia Institute of Technology and the National Aeronautics

and Space Administration (NASA) use chemical force microscopy to produce detailed information about adhesion between single-walled carbon nanotubes (SWNTs) and molecules of polymers with different functional groups. Their goal is to combine carbon nanotubes with lightweight polymers to produce composite materials with properties attractive for use on future space vehicles.

"Our hypothesis is that the stronger the adhesive interaction between molecules and nanotubes, the more likely it is that the polymer will fully wet the nanotubes, break up aggregations of nanotubes, and form a mechanically sound composite," said Larry Bottomley, a professor in the Georgia Tech School of Chemistry and Biochemistry. "The intent is to come up with two or three chemical groups that will give us the strongest interaction, and then incorporate these onto polymers for further studies."

Instead of using atomic force microscopy to map a surface, the researchers used the cantilever beam and deflection measurement to study the adhesion force between alkanethiol molecules on the microscope tip and nanotubes on the surface. As reported on March 23 at the 225th American Chemical Society National Meeting in New Orleans, the researchers raised a surface composed of nanotube bundles until it contacted the tip. When the nanotubes on the surface contacted

the alkanethiols on the tip, they adhered to it. When the surface was lowered, the adhesive force between nanotubes and polymer pulled the cantilever down.

"If there are no adhesive interactions between the tip and the sample surface, the cantilever tip just lets go cleanly when you lower the surface," Bottomley said. "If there is strong adhesive interaction, the adhesive interaction bends the cantilever down until the restoration force of the cantilever exceeds the adhesive force. That provides a direct measurement of the adhesion."

The adhesion forces they are measuring with this method are in the nano-Newton range. Instead of a three-dimensional map of the surface, the technique produces a force volume image showing adhesion force variations across a two-dimensional surface.

From that information, Bottomley and collaborators M.A. Poggi of Georgia Tech and P.T. Lillehei of NASA judge which polymers—and functional groups—provide the best adhesion to the nanotubes.

"We find dramatic differences in the adhesive interactions with subtle changes in the chemistry of the tip," Bottomley said. "You have the strongest interactions in the amine-terminated samples compared to the methyl-terminated, hydroxyl-terminated, and carboxyl-acid-terminated composites."

Carbon nanotubes tend to clump

together into bundles, which can pose problems in composite manufacture. If the polymer does not interact with or "wet" the nanotubes individually, the result is a mechanical defect that will weaken the resulting composite, the researchers said.

Bottomley said, "The real challenge is distributing the nanotubes throughout the polymer in a proper orientation."

### Silica-Reinforced Rubber Provides a Temperature-Resistant Mount

L. Reuvekamp from the University of Twente has mixed silica and rubber to produce a tire with a low rolling resistance, which will result in reduced fuel use for vehicles. Under a grant through the Netherlands Organization for Scientific Research, Reuvekamp mixed silica and rubber under the influence of organosilane. Tire manufacturers normally use carbon black instead of silica to strengthen the rubber of car tires. The organosilane used by Reuvekamp and colleagues acted as a coupling agent. It binds to the surface of silica and rubber, linking together two substances that can scarcely be coupled otherwise.

The ideal coupling temperature was determined experimentally. A temperature of at least 130°C is needed for the coupling agent to react with silica. The reaction temperature cannot go above 150°C or the rubber will vulcanize and become too hard for further processing.

The researchers discovered that zinc oxide, which is an essential part of the final tire, disrupts the coupling. However, they found that zinc oxide could be added after the coupling reaction without an adverse effect.

The researchers said that silica grain size influences the rolling resistance, and silica split into minute particles reduced this the most. The researchers have applied for a patent. □

## International Congress on Materials Science and Nanotechnologies (NANMAT 2003)

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