

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 Sr₂RuO₄ 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 Magnetics* 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 *IEE Proceedings—Optoelectronics* 150 (1) contains a special issue on physics and technology of dilute nitrides for optical communications.

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