

gen atoms—mathematical entities that assign the surface atoms the same reactivity as that of a real nanoparticle in suspension. The positions of the interior atoms were calculated with the valence force field method, which models the strength, elasticity, and direction of bonds among atoms.

Then LDA was used to determine the charge “motifs” around a number of representative atoms, including the surface pseudohydrogens. Through charge patching, the calculation is extended to include the entire nanostructure. In a final step, a “folded spectrum” method that Wang developed 10 years ago is used to determine the material’s electronic states near the bandgap, including the highest energy state of the valence band and the lowest energy state of the conduction band (see Figure 1b).

Mapping the ways different compounds are assembled into different structures reveals the structures’ optical and electronic properties.

Wang said, “The charge-patching method allows us to model thousand-atom structures with *ab initio* accuracy in about one hour.”

High Purity and Controllable Growth of Mg₂B₂O₅ Nanowires Accomplished by CVD

Magnesium borate (Mg₂B₂O₅) is a remarkable ceramic material that has been shown to be a thermoluminescent phosphor, a friction-reducing additive, and a ferroelastic material that may find application in nanocomposites, nanomechanics, and nanoelectronics. Synthesis of MgB₄O₇ (another form of magnesium borate) nanowires has been previously attempted by heating mixed powders of MgO, B₂O₃, and B with catalysts, but the result was a mixture of precursors or fiberlike agglomerates, necessitating a further purification process. Furthermore, with this kind of process, it is difficult to control size and location of the nanowires. Recently, researchers Y. Li and R.P.H. Chang of Northwestern University, and Z. Fan and J.G. Lu of the University of California, Irvine, have attained controllable growth and pure fibers by using chemical vapor deposition (CVD) to grow Mg₂B₂O₅ nanowires on MgO substrates.

As reported in the June 29 issue of *Chemistry of Materials* (p. 2512), they first coated a polished MgO substrate with a 2–3 nm layer of Pt/Pd nanoparticles as catalysts. The substrate was then heated in a tube furnace to 750–1100°C under Ar flow. BI₃/H₃BO₃ vapor was carried by Ar to the substrate. Straight nanowires with

uniform diameters were grown on the substrate after several hours of reaction for substrate temperatures between 850–1050°C. The diameter of the nanowires is in the range of 30–150 nm and the length is 1–10 μm. The researchers said that the dimensions of the nanowires can be manipulated by growth time, substrate temperature, and BI₃/H₃BO₃ vapor concentration. Each nanowire usually has a Pt/Pd nanoparticle attached to its end, suggesting a vapor–liquid–solid growth mechanism. Electrical transport measurement on a single nanowire indicates that the Mg₂B₂O₅ is a semiconductor at room temperature, and its bandgap is 5.44 eV, according to theoretical calculation.

Based on the high purity and controllable growth of Mg₂B₂O₅ nanowires this experiment demonstrates, the researchers said, “Metal borate nanowires can be synthesized by introducing boron and boron oxide sources to a metal oxide substrate coated with a thin film of some catalyst.”

SHIMING WU

Models of Failure in Brittle Solids Supported by *In Situ* Observation of Crack Behavior in Plasma-Sprayed YSZ Tube

Plasma-sprayed yttria-stabilized zirconia (YSZ) is commonly used as a thermal barrier coating. It produces coatings with a microstructure containing high porosity and microcracks that will have an effect on the mechanical behavior of the material. As reported in the May issue of the *Journal of the American Ceramic Society* (p. 960), J.P. Levin, G.R. Dickinson, and R.W. Trice at Purdue University observed *in situ* the microstructure evolution of a plasma-sprayed YSZ stand-alone tube under incremental compressive load while simultaneously viewing it in a scanning electron microscope (SEM). They found that cracks oriented parallel to the loading direction have opened, while cracks oriented perpendicular to the applied stress have partially closed. They also observed that new cracks nucleated and then propagated parallel to the direction of the applied load.

Previous observations indicated that plasma spraying forms a microstructure dominated by lamellae with significant porosity and cracks both in and between the lamellae. The sample was prepared by plasma-spraying aluminum powder onto an alumina rod, followed by plasma-spraying a 280 μm YSZ layer. After dissolving the aluminum, the scientists obtained YSZ stand-alone tubes consisting of an yttrium-rich, nonequilibrium tetragonal zirconia phase with a bulk density of ~5.2 g/cm³ and a porosity of 15%. To measure the axial strain, two strain

gauges were attached to the outer surface of the YSZ tubes, which were then placed in a load frame located inside the SEM. The samples were compressed incrementally using stress increments of ~13 MPa and 8 MPa, until fracture; SEM images were taken after each stress increment.

The stress–strain curve showed variable slope, but the researchers reported the data as having two slopes, corresponding to the two main regions. The first slope, up to stresses of 46 ± 1 MPa, had a modulus of 30 GPa; at higher stresses, a modulus of 60 GPa was measured. The region of the outer tube that was investigated by SEM had cracks of various widths and orientations: parallel, perpendicular, and off-axis with respect to the applied load.

The scientists’ observation supports the hypothesis that the increase in modulus of the material under compression was caused by cracks oriented perpendicular to the applied load that close partially or completely, thus increasing the planar density of the sample. Cracks parallel to the applied load widen as the crack faces slide relative to one another under the shear stress. The formation of microcracks was observed at approximately half the failure stress of the tube. The researchers’ observations agree with previous research done on the failure of brittle solids.

MARIA CORTALEZZI

Charge Transfer across Nanocrystalline Metal Oxide/DNA Interfaces Enables DNA Recognition

Molecular recognition of biological molecules has become an active area of research, partly due to the increasing importance of the fields of molecular patterning, genome sequencing, and drug affinity studies and their applications in bioelectronics. A necessary step in molecular recognition is control of the spatial positioning of the biomolecules. T. Rajh and co-workers at Argonne National Laboratory and N.F. Scherer of the University of Chicago have reported the use of TiO₂ nanoparticles (5 nm diameter) in conjunction with DNA strands in the development of biosensing technology. As reported in the June 9 issue of *Nano Letters* (p. 1017), the researchers linked the metal oxide nanoparticles to DNA oligonucleotides by using bridging enediol ligands such as dopamine (DA). The researchers said that the oxygen-rich DA ligands bond readily to TiO₂ nanoparticles smaller than 20 nm because their coordination sphere is incomplete and exhibits high affinity for the oxygen-containing ligands. Dopamine repairs undercoordination of the Ti atoms at the surface, thus forming strongly coupled conjugated structures.

Electron paramagnetic resonance (EPR) spectroscopy was used to examine the photoexcited nanostructures. Photoexcitation of structures with single-stranded DNA attached to the TiO₂/DA nanostructure showed the same EPR signature as for photoexcitation of the TiO₂/DA nanostructure alone. According to the researchers, this indicates that the charge separation in the single-stranded DNA/DA/TiO₂ nanostructure is terminated at the dopamine and never reaches the DNA. Double-stranded DNA/DA/TiO₂ nanostructures were obtained by hybridizing the attached oligonucleotides with their complementary strands. EPR studies of the double-stranded DNA/DA/TiO₂ nanostructures showed that charge separation into the DNA occurs.

The researchers also used silver reduction studies to confirm these results. Silver ions act as receptors for photogenerated electrons, and silver metal precipitates preferentially on the TiO₂ if excess electrons are available. Deposition of silver onto the TiO₂ was monitored for double-stranded DNA/DA/TiO₂, single-stranded DNA/TiO₂, and DA/TiO₂ nanostructures. More silver was found to deposit on the double-stranded structures than the other two structures, consistent with the interpretation of the EPR studies.

The researchers said that by using the interface of a nanocrystalline metal oxide semiconductor linked to a DNA molecule to probe DNA recognition, they have shown that the binding of DNA molecules to nanocrystalline metal oxide parti-

cles yields a photoelectrochemical system that can be used to perform extended pair-charge separation, a technique that finds application in constructing sensors for DNA hybridization. An important aspect of the work is that, since the nanoparticles are photoresponsive and therefore serve as a source of photogenerated charges, they can act as reporters of the electronic properties of the biomolecules. The researchers conclude that similar approaches may be used to detect DNA binding due to the change of redox properties of DNA molecules, and that the method opens doors to a new class of site-specific biomolecule electronic sensors and electronically tunable site-specific metal oxide catalysts.

MARKUS J. BUEHLER

News of MRS Members/Materials Researchers

Ronald W. Armstrong, a senior scientist in the Munitions Directorate of the Air Force Research Laboratory at Wright-Patterson Air Force Base in Ohio and professor emeritus at the University of Maryland College Park, has been honored by the Minerals, Metals, and Materials Society and the American Institute of Mining and Metallurgical Engineers for his lifetime achievement by sponsoring a symposium in his honor at the TMS 132nd annual meeting and exhibition held in San Diego, Calif. Armstrong's main efforts involved energetic material technologies and promoting collaboration with non-U.S. governments and organizations, other services and agencies, universities,

and industry, as relevant to the directorate thrusts and long-range goals of involving energetic materials and their uses.

Steven Chu, professor in the Physics and Applied Physics Departments at Stanford University, has been named director of Lawrence Berkeley National Laboratory.

Gustavo A. Cragolino has been promoted to Institute Scientist in the Center for Nuclear Waste Regulatory Analyses at Southwest Research Institute (SwRI) by the U.S. Nuclear Regulatory Commission. The position is among the highest technical positions an SwRI staff member can attain.

Mary L. Good, dean of the Donaghey

College of Information Science and Systems Engineering at the University of Arkansas, Little Rock, received the 2004 Vannevar Bush Award from the National Science Board of the National Science Foundation for her lifelong contributions to science, engineering, and technology, and for leadership throughout her multifaceted career.

Donald Paul of the University of Texas at Austin has been named a fellow of the Society of Plastics Engineers.

Xie Sishen has been appointed principal investigator of China's National Center for Nanoscience and Nanotechnology.

The American Academy of Arts and Sciences has announced the election of 2004 fellows and foreign honorary members, including:

A. Paul Alivisatos, professor of chemistry at the University of California, Berkeley;

Moungi Gabriel Bawendi, professor of chemistry at the Massachusetts Institute of Technology;

Arden L. Bement Jr., director of the National Institute of Standards and Technology;

Murray S. Daw, R.A. Bowen Pro-

fessor of Physics at Clemson University;

Subra Suresh, Ford Professor of Engineering and department head, Massachusetts Institute of Technology; and

Herbert Gleiter, director of the Institute of Nanotechnology, Germany. □

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