the floating gate makes the structure more tolerant to defects in the tunnel oxide and therefore reduces leakage. This permits the use of thinner tunnel oxides, which in turn reduces the operating voltage, improves endurance and retention, and increases the write/erase rate.

To fabricate their devices, the researchers took advantage of the fact that tungsten silicide on SiO_2 forms elemental tungsten when thermally oxidized. As described in the March issue of *Electrochemical and Solid-State Letters* (p. G71), the team began by growing a 4.5 nm tunnel oxide on silicon substrates, followed by sputter deposition of 8 nm of W_5Si_3 for the floating gate and 10 nm of amorphous silicon. A thermal oxidation step formed the control oxide and the elemental W in the SiO_2 matrix. The W particles had an average diameter of 4.5 nm and an areal density of 3.7×10^{11} cm^{-2}. Fourier transform infrared spectroscopy analysis showed that elemental tungsten was clearly present, with little or no tungsten oxide formation.

The researchers used capacitance–voltage measurements to demonstrate the electron charging effect of their W particles. A bidirectional voltage sweep from 3 V to –4 V and back to 3 V yielded a shift in the threshold voltage ΔV_t of 0.95 V, which is sufficient for binary switching. The researchers found that there was no appreciable decrease in ΔV_t until after 10^6 cycles and in fact, after 10^9 cycles, ΔV_t had only dropped to 0.71 V.

The operating characteristics of the W nanoparticle EEPROMs represent an improvement over both the high 7 V operating voltage of conventional floating gate devices and the rapid drop-off seen in the endurance of other nanoparticle devices. In addition, this silicide technique is easily integrated with existing semiconductor technology, making the W nanocrystal devices viable competitors to conventional EEPROMs.

AMANDA GIERMANN

Transparent Hydroxyapatite with High Crystal Orientation Produced by Pulsed Electric Current Sintering

Hydroxyapatite [$Ca_{10}(PO_4)_6(OH)$, HAp] is a major mineral component found in bones and teeth. As a biomaterial, it aids the growth and development of bones and teeth by providing attachment sites for new cells. HAp has a hexagonal crystal structure and there is a large difference in cell attachment between the *a* plane and the *c* plane. Sintered dense HAp bodies with a high degree of crystal orientation are useful for culturing cells and as scaffolds for the regeneration of bones and teeth.

In the January issue of the *Journal of American Ceramic Society* (p. 243; DOI: 10.1111/j.1551-2916.2004.00041.x), researchers Yujiro Watanabe of Hosei University, Japan, and Toshiyuki Ikoma of the National Institute for Materials Science, Japan, and colleagues reported a sintering process for producing dense, transparent, and highly oriented crystalline HAp bodies.

The researchers first prepared the HAp powder by reacting $Ca(OH)_2$ with H_3PO_4 solution, followed by spray drying and then calcining at 800°C for 3 h. Sintering of the HAp sample was carried out by pulsed electric current sintering (PECS) in a spark plasma sintering (SPS) system. In the PECS process, powder particles are charged with electrical energy and a high pressure is applied on the sample.

During the sintering of HAp, the sample was pressed uniaxially at 50 MPa in vacuum. The sintering temperature was elevated at a rate of 50°C/min to 1200°C. After maintaining the temperature for 10 min, the sample was slowly cooled to 600°C at a rate of 5°C/min. The electric current was then stopped, the pressure was released, and the sample was cooled to room temperature.

The resulting bulk sample has high optical transmittance at wavelengths above 700 nm to at least 1100 nm (i.e., >70% for a 1-mm-thick sample), and a density >99.7% of the theoretical value. As for the crystal orientation, the researchers concluded from x-ray diffraction measurements taken perpendicular and parallel to the direction of the pressure that there is a very significant crystal orientation on the *a*, *b*, and *c* planes. The *c* plane is aligned parallel to the pressure direction, while the *a* and *b* planes are aligned perpendicular to the pressure direction. Orientation indexes of the *a* and *b* planes are much higher than those of samples obtained with other processes.

SHIMING WU

$LaPO_4:Eu^{3+}$ Nanowires Luminesce More Efficiently than Dots

One-dimensional $LaPO_4:Eu^{3+}$ nanowires luminesce more efficiently than zero-dimensional, spherical $LaPO_4:Eu^{3+}$ nanoparticles, said Hongwei Song and co-workers from the Chinese Academy of Sciences. As reported in the March 1 issue of *Optics Letters* (p. 483), the researchers studied the luminescent properties of low-dimensional $LaPO_4$ doped with rare-earth Eu in order to better understand the fundamental physics of this new condensed-matter system. With the technological drive toward smaller and novel devices, $LaPO_4$ is appropriately studied as it is used in fluorescent lamps, cathode ray tubes, and plasma display panels.

The research team reported that the Eu atoms partially filled *f* orbitals, which carry magnetic moments. In addition, Eu^{3+} ions are sensitive activators for use in the study of local symmetry. The researchers used this property of Eu^{3+} to study the structural differences between nanowires, nanoparticles, micron-sized powders, and micron-sized rods.

The $LaPO_4$:Eu nanowires, nanoparticles, micropowders, and microrods were prepared by a wet chemical method. The colloidal nanoparticles and micropowders were basic and the nanowires and microrods were acid. The diameter of the nanoparticles and nanowires ranged from 10–20 nm, whereas the length of nanowires ranged by several hundred nanometers. The diameters of micropowders ranged over 1–2 μm. The diameters and lengths of the microrods were ~200 nm and 1–2 μm, respectively. X-ray diffraction patterns revealed that the crystal structures of all of the samples belong to the monoclinic monazite type. Time-resolved emission spectra and high-resolution transmission electron micrograph images show that the Eu^{3+} ions occupy two sites in the nanowires as well as the microrods, but not in the nanoparticles or the micropowders. The researchers attributed this result to a degeneration of the crystal field in the micropowders. They also concluded that the observed higher radiative rate for nanowires, as compared with the nanoparticles, micropowders, and microrods, was due to the "variation of the electronic–magnetic dipole field caused by shape anisotropy."

VIVEK RANJAN

Raman Measurements in Silicon Nanowires Reveal the Diameter Dependence of Phonon Confinement

Phonon confinement in a small nanosystem leads to an asymmetric broadening of the Raman bands. Recently, P.C. Eklund from the Pennsylvania State University, G.U. Sumanasekera from the University of Louisville, and their co-workers determined the evolution of phonon confinement with wire diameter of long, crystalline Si nanowires using the Raman microprobe method.

As reported in the March 1 issue of *Nano-Letters* (p. 409; DOI: 10.1021/nl0486259), the researchers prepared Si nanowires by pulsed Nd:YAG laser vaporization of a Si target containing ~10 at.% Fe. The wire growth process occurs through the vapor–liquid–solid mechanism in which a

Fe/Si nanoparticle acts as a "seed" and the Si filaments grow from the Fe/Si nanoparticle surface. This approach produced wires with a distribution of diameters ranging from 8–40 nm. In order to produce smaller-diameter wires, the researchers developed a post-synthesis approach. They used oxidation at elevated temperature to diffuse oxygen radially inward and shrink the Si crystalline core. Fractions were then separated according to the wire diameter using centrifugal separation. Using this method, the researchers produced a series of four crystalline Si nanowire samples whose most probable diameters were 4.5 ± 0.2 nm, 6.5 ± 0.3 nm, 9.5 ± 0.3 nm, and 23.1 ± 0.7 nm. The researchers probed the phonon bands in these nanowires using Raman spectroscopy at low enough laser intensity that temperature broadening was not a factor. Comparison of the Raman spectra of these Si nanowires showed that with decreasing diameter, the first-order Raman band at ~520 cm^{-1} develops a noticeable asymmetry to lower frequency, and the peak position downshifts.

The researchers analyzed their results based on an asymmetric line-shape model developed by Richter with an adjustable parameter (α) added to the theory that defines the width of the Gaussian phonon-confinement function. The researchers found that this parameter is not sensitive to diameter over the 4–25 nm range if they took into account the measured diameter distribution. This result is contradictory to the large range of reported α values. While attributing the difference to a variety of unknown conditions, the researchers said that the thickness and nature of the oxide coating on the wire might also impact the phonon confinement. That is, they said, the phonon in the crystalline core of the nanowire has to decay into phonons in the oxide shell. Therefore, the researchers suggested future experiments on hydrogen-terminated Si nanowires to see how hydrogen termination affects the value of the confinement parameter.

TAO XU

Bulk Metallic Glass Foam Achieves High Ductility

Metallic foams are currently used as ultralight structural materials. Bulk metallic glasses (BMGs) show exceptional strength and elasticity, in addition to other favorable properties, rendering them also useful for structural applications and potentially for biocompatible implants. A.H. Brothers and D.C. Dunand of Northwestern University considered, then, whether BMG foams offer unique opportunities in engineering structures or biomedical implants. They have found that Vit106 ($Zr_{57}Nb_5Cu_{15.4}Ni_{12.6}Al_{10}$) foam shows compressive properties not unlike ductile aluminum foam, despite a lack of ductility in monolithic Vit106. Furthermore, Vit106 contains neither precious metals nor toxic beryllium, and shows biocompatibility.

As reported in the February 18 issue of *Advanced Materials* (p. 484, DOI: 10.1002/adma.200400897), the researchers produced samples by crushing optical-grade BaF_2 and sieving it to produce and select 215–220 µm particles. These were then packed into graphite crucibles and sintered at 1250°C for 10 h under high vacuum. The 7-mm-diameter patterns were then placed in stainless steel crucibles and vacuum-dried at 300°C for 30 min. Vit106 charges were then combined with the BaF_2 patterns in preheated crucibles and melted. High-pressure argon gas was applied to the Vit106 surface to drive it into the BaF_2 pattern. After cooling, the Vit106/BaF_2 composite was ground to a desired size and the BaF_2 was leached out using nitric acid. Scanning electron microscope images of Vit106 foams of 4.5 mm diameter and 8.7 mm height show 78% open porosity with pore sizes of 212–250 µm. The thickness of all Vit106 struts is well below 1 mm, where high bending ductility is expected. X-ray diffraction shows that no crystalline phases were present in the foam. The researchers concluded that BMG foams can achieve high compressive ductility through strut bending, in sharp contrast to the brittle compressive behavior of BMG in monolithic form.

VIVEK RANJAN

Corrections

MRS Bulletin misprinted the sponsors of Symposium LL in the report on the 2004 Materials Research Society Fall Meeting (*MRS Bulletin* **30** [3] [March 2005] p. 239). Support to Symposium LL was given by the Army Research Office (United States of America) and the Engineering and Physical Sciences Research Council (United Kingdom). Following is the corrected report.

Materials Issues in Solid Free-Forming

Symposium LL brought together discussions addressing important issues related to free-forming and other parallel processing methods for advanced materials. The symposium opened with a special address titled "Electrospraying Wings of Molecular Elephants" by John Fenn (Virginia Commonwealth Univ.), 2002 Nobel Laureate in Chemistry. The presentation elucidated the electrospray technique and the significant advantage in the use for weighing large biomolecules. Several sessions followed, with invited papers from a host of eminent scientists from around the world. The first session covered the broad field of solid free-forming, with M. Edirisinghe (Queen Mary, Univ. of London), B. Derby (Univ. of Manchester and UMIST), A. Safari (Rutgers), and L. Iuliano (Politecnico di Torino) presenting talks on jet-based and other advanced materials-forming methods at both the nano- and micrometer scales. The following session covered 3D fabrication and applications (J. Beaman, Univ. of Texas; E. Sachs, MIT; Y. Gogotsi et al., Drexel). The second day started with a session on processing and fabrication of advanced materials (G. Babini and L. Settineri, Politecnico di Torino). The final session addressed electrohydrodynamic atomization and applications (J. De la Mora, Yale; K.L. Choy, Univ. of Nottingham; M. Brenner, Harvard, and I. Loscertales, Univ. of Malaga).

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Nobel Laureate John Fenn (left) with Suwan Jayasinghe, lead symposium organizer.