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**ABSTRACTS****RAPID COMMUNICATIONS****Shock synthesis of nanocrystalline Si by thermal spraying**

R. Goswami, J.B. Parise, S. Sampath, H. Herman  
(State University of New York-Stony Brook)

Shock synthesis of nanocrystalline Si was accomplished for the first time using thermal spray, in which Si powder is injected into a high-energy flame where the particles melt and accelerate to impact on the substrate. A stream of molten Si particles impacted onto Si wafers of two orientations, (100) and (111). The shock wave generated by the sudden impact of the droplets propagated through the underlying Si layer, which experienced a phase transition to a high pressure form of Si due to propagation of the shock wave. The metastable high pressure form of Si then transforms to metastable Si-IX, Si-IV (hexagonal diamond-Si), R-8, and BC-8 phases as evidenced by transmission electron microscopy and x-ray diffraction studies. Back-transformed metastable Si grains, with a size range from 2 to 5 nm, were found to be dispersed within Si-I (cubic diamond-Si). The metastable phases form mostly in deposits on

the (100) substrate compared to those of the (111) substrate orientations. This behavior can be correlated with the anisotropic nature of the pressure-induced transformation of Si-I.

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**Diffusion of water in crystalline and glassy oxides: Diffusion-reaction model**

R.H. Doremus  
(Rensselaer Polytechnic Institute)

Diffusion of water in oxides is modeled as resulting from the solution and diffusion of molecular water in the oxide. This dissolved water can react and exchange with the oxide network to form immobile OH groups and different hydrogen and oxygen isotopes in the oxide. The model agrees with many experiments on water diffusion in oxides. The activation energy for diffusion of water in oxides correlates with the structural openness of the oxide, suggesting that molecular water is the diffusing species.

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**Can stress-strain relationships be obtained from indentation curves using conical and pyramidal indenters?**Y-T. Cheng,<sup>1</sup> C-M. Cheng<sup>2</sup><sup>(1)General Motors Research and Development Center,</sup><sup>(2)Chinese Academy of Sciences)</sup>

Applying the scaling relationships developed recently for conical indentation in elastic-plastic solids with work-hardening, we examine the question of whether stress-strain relationships of such solids can be uniquely determined by matching the calculated loading and unloading curves with that measured experimentally. We show that there can be multiple stress-strain curves for a given set of loading and unloading curves. Consequently, stress-strain relationships may not be uniquely determined from loading and unloading curves alone using a conical or pyramidal indenter.

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**ARTICLES****The formation of Bi-Sr-Ca-Cu-O superconducting films by electrodeposition**

M.S. Martín-Gonzalez, J. García-Jaca, E. Morán, M.Á. Alario-Franco

<sup>(Universidad Complutense de Madrid)</sup>

Superconducting films of the Bi-Sr-Ca-Cu-O family of oxides were prepared by electrodeposition of the constituent metals followed by an oxidative thermal treatment. The influence of water, stirring of the electrolyte, cleaning of the substrate, and deposition time on the quality of the films were studied. Before the thermal treatment, the electrodeposited films consisted of a mixture of different metals and carbonates of the constituent elements. The oxidation of the metallic phases and the decomposition of the carbonates occurred in the ranges 260–280 °C and 400–470 °C, respectively. The final oxides were obtained after an oxidative thermal treatment of 800 °C. Lower temperatures were not sufficient for the preparation of the superconducting oxide films. The prepared Bi-2201 films consisted of a mixture of two phases with different strontium, bismuth, and oxygen content. The Bi-2212 films were composed of platelike particles with a preference to orientate along the (001) direction. These films showed critical temperatures up to 92 K and critical current densities up to 15,000 A/cm<sup>2</sup> (at 77 K and zero field) when the films were pressed before the thermal treatment.

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**The mechanisms of structural anomaly and orthorhombic-tetragonal transition of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub>**

M-S. Wu, T-T. Fang

<sup>(National Cheng Kung University)</sup>

Powdered samples of oxygen-deficient YBa<sub>2</sub>Cu<sub>3</sub>O<sub>y</sub> were annealed in various atmospheres at 880 and 300 °C to study the relations of structural anomaly, phase transition, and oxygen content. It was found that the structural anomaly in the *c* axis is reversible during oxygenation and deoxygenation. The change of the *c* axis arose from the electrical repulsion among Ba and Cu cations as oxygen was removed or refilled. The anomaly in the *c* axis occurred when the oxygen was further removed or refilled to a critical value, at which structural relaxation and electrical repulsion changed greatly. The phase transition is attributed to the anomalous change in the *c* axis, and the mechanism is proposed and discussed in this paper.

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**Phase equilibria among the superconductors in the Y<sub>2</sub>O<sub>3</sub>-BaO-Cu-O system**

Z. Zhou, A. Navrotsky

<sup>(Princeton University)</sup>

The enthalpy of formation of Y<sub>2</sub>Ba<sub>4</sub>Cu<sub>7</sub>O<sub>14.864</sub> at room temperature was determined using high-temperature reaction calorimetry. The standard enthalpy of formation of the 247 phase is  $\Delta H_f^\circ = -5463 \pm 18$  kJ mol<sup>-1</sup>. Phase relationships among the superconductors, namely, the 123, 124, and 247, were assessed. It is intrinsic that impurity phases, such as Y<sub>2</sub>Cu<sub>2</sub>O<sub>5</sub>, BaCuO<sub>2</sub>, CuO, etc., coexist with the superconductors at equilibrium. Equilibria among the superconductor phases in the Y<sub>2</sub>O<sub>3</sub>-BaO-Cu-O system were determined. The results show that, at the 124 bulk composition, the 247 phase coexists with the excess CuO in a narrow area of  $p_{O_2}$  ~ *T* space confined by the stability fields of

the 124 phase, and a mixture of the 123 + CuO. The standard free energies of carbonation and hydration of the 247 phase were also determined, which are  $-629 \pm 13$  kJ mol<sup>-1</sup> and  $-873 \pm 45$  kJ mol<sup>-1</sup>, respectively. Like the 123 and 124 phases, the 247 phase is thermodynamically unstable with respect to corrosion by water vapor and carbon dioxide in ambient atmosphere.

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**Homoeptaxial (111) diamond grown by temperature-controlled chemical vapor deposition**M. Nishitani-Gamo,<sup>1</sup> I. Sakaguchi,<sup>1</sup> T. Takami,<sup>2</sup> K. Suzuki,<sup>2</sup> I. Kusunoki,<sup>2</sup>T. Ando<sup>1</sup><sup>(1)National Institute for Research in Inorganic Materials, 2Tohoku University)</sup>

We investigated the growth of high-quality homoeptaxial diamond on (111) face in a microwave-assisted plasma chemical-vapor-deposition system incorporating an individual substrate heating/cooling device. The grown diamond films were characterized by scanning electron microscopy, reflection high-energy electron diffraction, atomic force microscopy, confocal micro-Raman spectroscopy, and secondary ion mass spectrometry. The (111) diamond films show a tendency to incorporate a significant amount of hydrogen during chemical-vapor-deposition growth. Hydrogen incorporation degrades the crystal quality and surface smoothness. The amount of incorporated hydrogen decreases with the decrease in deposition temperature. We have shown that the crystal quality and surface smoothness of homoeptaxial diamond strongly depend on the substrate temperature. Independent control of the substrate temperature and incident microwave power is essential for high-quality diamond homoeptaxy.

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**Characteristics of dielectric layers formed by low-temperature vacuum ultraviolet-assisted oxidation of SiGe layers**V. Craciun,<sup>1</sup> I.W. Boyd,<sup>1</sup> J. Perriere,<sup>2</sup> B. Hutton,<sup>3</sup> E.J. Nicholls<sup>1</sup><sup>(1)University College London, 2Universities Paris, 3University of Hull)</sup>

Thin Si<sub>0.8</sub>Ge<sub>0.2</sub> layers epitaxially grown on (100) Si substrates were oxidized at temperatures from 150 to 450 °C under vacuum ultraviolet (VUV) radiation emitted by an excimer lamp working with Xe ( $\lambda = 172$  nm). The structure and composition of the grown dielectric layers were investigated by Rutherford backscattering spectrometry, nuclear reactions analysis, ellipsometry, Fourier transform infrared spectroscopy, and x-ray photoelectron spectroscopy. These investigations have shown that during the VUV-assisted oxidation process, Ge atoms were initially rejected from the grown SiO<sub>2</sub> layer, even at temperatures as low as those employed here. After a certain quantity of Ge accumulated at the interface, nanocrystalline Ge regions were directly excised from the remaining SiGe layer becoming embedded within the advancing SiO<sub>2</sub> layer. The layers containing these nanocrystalline Ge particles exhibited the same visible photoluminescence spectra as those recorded from layers already known to contain nanocrystalline Ge or GeO<sub>2</sub> particles, porous Ge, or nanocrystalline Ge particles exhibiting a different crystalline structure. This seems to indicate that the shell region of the nc-particle, and not its crystalline core, is the source of the photoluminescence.

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**Interfacial microstructure formed by reactive metal penetration of Al into mullite**P. Lu,<sup>1</sup> T.B. Du,<sup>1</sup> R.E. Loehman,<sup>2</sup> K.G. Ewsuk,<sup>2</sup> W.G. Fahrenholtz<sup>2</sup><sup>(1)New Mexico Institute of Mining and Technology,</sup><sup>(2)Sandia National Laboratories)</sup>

Microstructures in the reaction interface between molten Al and dense mullite have been studied by transmission electron microscopy to provide insight into mechanisms for forming ceramic-metal composites by reactive metal penetration. The reactions, which have the overall stoichiometry  $3Al_6Si_2O_{13} + (8+x)Al \rightarrow 13Al_2O_3 + xAl + 6Si$ , were carried out at temperatures of 900, 1100, and 1200 °C for 5 and 60 min, and 1400 °C for 15 min. Observed phases generally were those given in the above reaction; their proportions and interfacial microstructures, however, were strongly dependent on the reaction temperature. Using previously measured reaction kinetics data, the observed temperature dependence of the interfacial microstructure has been modeled as three sequential steps, each of which is rate limiting in a different temperature range.

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### Interface structure and formation between gold and trimethylcyclohexane polycarbonate

C.V. Bechtolsheim, V. Zaporojtchenko, F. Faupel  
(Universität Kiel)

This paper presents the results of a systematic investigation of structure and formation of the interface between gold and trimethylcyclohexane polycarbonate, particularly concerning interface evolution during gold evaporation and the influence of evaporation rate, substrate temperature, and subsequent annealing. The means of investigation were cross-sectional transmission electron microscopy, atomic force microscopy, and x-ray photoelectron spectroscopy. Extensive metal diffusion into the polymer and cluster formation near the interface were observed at deposition rates on the order of one monolayer per minute and below. The penetration depth is strongly temperature dependent. At high evaporation rates metal aggregation at the surface prevents cluster formation inside the polymer. No diffusion into the polymer was observed from metal films deposited at room temperature after extensive annealing at elevated temperatures.

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### The mechanical behavior of ceramic/metal laminate under thermal shock

D. Sherman, D. Schlumm  
(Technion-Israel Institute of Technology)

A new material system for applications involving thermal shock is proposed. The system consists of thin layers of ceramics and thinner metallic interlayers. In this study, a ceramic/metal laminate was constructed from Coor's ADS96R thin plates alternating with thinner Wesgo Cusil ABA interlayer foils and joined in active brazing. The maximum brazing temperature was 845 °C. Square shaped laminated plates were quenched in room-temperature distilled water, where very large heat transfer coefficient exists, and therefore, severe conditions of thermal shock occur. The laminated plates, initially at temperatures of 600 and 800 °C, were quenched at their bottom surface only in a specially designed apparatus. The temperatures at the top and the bottom surfaces of the specimens were measured by means of two thermocouples during quenching. The basic features of this architecture are described. The dominant behavior was the absence of interaction between the biaxial cracking mechanisms in a ceramic layer with those in an adjacent ceramic layer, and localization of the damage to those layers that experienced sufficient tensile stresses. The result was a dramatic increase of the residual strength after thermal shock. In addition, R-curve behavior upon mechanical loading due to plastic deformation of the metallic interlayer was observed.

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### Oxidation of nanocrystalline Mo-Si-N and nanolayered Mo-Si-N/SiC coatings

P. Torri  
(University of Helsinki)

Oxidation of sputter-deposited nanocrystalline Mo-Si-N ( $\text{MoSi}_{2.2}\text{N}_{2.5}$ ) coatings in oxygen-water vapor atmosphere was studied in the temperature range 400–850 °C. In addition, the oxidation properties of nanolayered Mo-Si-N/SiC coatings at 700 °C were studied and compared to those of single-layer coatings of both components. No pest disintegration was observed in Mo-Si-N up to 200 h of oxidation. A pre-exponential rate constant of  $(3.7 \pm 0.5) \times 10^9$  ( $10^{15}$  atoms/cm<sup>2</sup>)<sup>2</sup>/h and activation energy  $1.03 \pm 0.02$  eV were determined from an Arrhenius plot for parabolic oxygen buildup on Mo-Si-N. Up to 20% less oxygen was detected in the oxidized nanolayered coatings compared to either of the components as a single layer, indicating an improvement in oxidation resistance.

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### Microwave dielectric properties of $\text{Ca}[(\text{Li}_{1/3}\text{Nb}_{2/3})_{(1-x)}\text{M}_x]\text{O}_{3-\delta}$ (M = Sn, Ti) ceramics

J-W. Choi,<sup>1</sup> C-Y. Kang,<sup>1</sup> S-J. Yoon,<sup>1</sup> H-J. Kim,<sup>1</sup> H-J. Jung,<sup>1</sup> K.H. Yoon<sup>2</sup>  
(<sup>1</sup>Korea Institute of Science and Technology, <sup>2</sup>Yonsei University)

The microwave dielectric properties of  $\text{Ca}[(\text{Li}_{1/3}\text{Nb}_{2/3})_{(1-x)}\text{M}_x]\text{O}_{3-\delta}$  (M = Sn, Ti,  $0 \leq x \leq 0.5$ ) ceramics were investigated. In general, the ceramics prepared were multiphase materials. However, single-phase specimens having orthorhombic perovskite structure similar to  $\text{CaTiO}_3$  could be obtained in the vicinity of Sn = 0.2 to 0.3, and Ti = 0.2. As Sn concentration increased, the dielectric constant ( $\epsilon_r$ ) decreased and the quality factor (Q) significantly increased with the limited Sn concentration. As Ti concentration increased,

the dielectric constant ( $\epsilon_r$ ) increased, the quality factor (Q) decreased, and the temperature coefficient of resonant frequency ( $\tau_f$ ) changed from a negative to a positive value. The temperature coefficient of resonant frequency of 0 ppm/°C was realized at Ti = 0.2. The  $Q \cdot f_0$  value and  $\epsilon_r$  for this composition were found to be 26,100 GHz and 38.6, respectively.

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### Auto ignition synthesis of nanocrystalline $\text{MgAl}_2\text{O}_4$ and related nanocomposites

S. Bhaduri, S.B. Bhaduri, K.A. Prisbrey  
(University of Idaho)

Nanocrystalline powders of various compositions in the  $\text{Al}_2\text{O}_3$ -MgO binary system were synthesized using a novel "auto ignition" process. The respective nitrates were used as starting materials and urea as fuel. Thermodynamic calculations of the adiabatic temperatures were performed for various compositions from the  $\text{Al}_2\text{O}_3$ -rich to the MgO-rich side of the phase diagram. The combustion temperatures of the different compositions were also determined experimentally. The as-synthesized powders were characterized by x-ray diffraction (XRD) and transmission electron microscopy (TEM). As a result of processing, spinel, alumina, magnesia, and solid solutions/nanocomposites thereof formed. Grain sizes and the lattice parameter were calculated based on XRD results. Where appropriate, the lattice parameters versus the composition of these solid solutions satisfied Vegard's law. Spinel grains were in the 13–20 nm range, alumina grains were 30–40 nm, and MgO grains were 2–28 nm. The grain sizes calculated from XRD results were in good agreement with the TEM results.

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### Effect of divalent cations on the synthesis of citrate-gel-derived lanthanum hexaluminate powders and films

M.K. Cinibulk  
(Air Force Research Laboratory)

Citrate-gel-derived lanthanum hexaluminate was synthesized using divalent transition-metal cations to stabilize the magnetoplumbite structure. Pure, undoped  $\text{LaAl}_{11}\text{O}_{18}$  was obtained in 1 h only at temperatures  $\geq 1500$  °C after the formation and subsequent consumption of the intermediate perovskite,  $\text{LaAlO}_3$ , which first appeared at  $\sim 1150$  °C. Powders of  $\text{LaMAl}_{11}\text{O}_{19}$ , where M = Mg, Mn, Fe, Co, Ni, Cu, and Zn, were prepared at much lower temperatures. Highly crystalline, phase-pure powders of  $\text{LaMnAl}_{11}\text{O}_{19}$  and  $\text{LaCuAl}_{11}\text{O}_{19}$  were obtained at 1000 °C in 1 h directly from the amorphous powder without the formation of the intermediate perovskite. All other compositions could be obtained at 1100 °C in 1 h except for the nominal  $\text{LaNiAl}_{11}\text{O}_{19}$ , which formed primarily  $\text{LaAlO}_3$ ,  $\text{NiAl}_2\text{O}_4$ , and  $\text{Al}_2\text{O}_3$ . Powders containing dopants all had similar grain sizes and morphologies at 1200 and 1500 °C, which was significantly greater than that of pure  $\text{LaAl}_{11}\text{O}_{18}$ . The introduction of a second charge-compensating quadrivalent dopant for excess divalent cation did not greatly influence synthesis or grain growth below the eutectic temperature but did seem to enhance the 0001 texture of films on single-crystal yttrium-aluminum garnet substrates compared with singly doped films.

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### Effect of nickel on sintering of self-propagating high-temperature synthesis produced titanium carbide

S.K. Mishra (Pathak), S.K. Das, A.K. Ray, P. Ramchandrarao  
(National Metallurgical Laboratory)

A detailed study of the sintering behavior of titanium carbide (TiC) powder synthesized by the self-propagating high-temperature synthesis (SHS) route was carried out with varying percentages of nickel. With an increase in the nickel content, porosity was found to increase along with  $\text{Ni}_{2.67}\text{Ti}_{1.33}$  secondary phase at grain boundary. A 90–92% dense sintered body of TiC was produced from SHS-produced powder at 1800 °C with 10 wt% of nickel.

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### Preparation and characterization of alumina membranes and alumina-titania composite membranes

L. Shi, N-B. Wong  
(City University of Hong Kong)

Supported and unsupported  $\gamma$ -alumina membranes and alumina-titania composite membranes were prepared using the sol-gel method. In the course of preparation, effects of acid concentration, type of acid, alkoxide and binder on the particle size of the sols, and pore size of the membranes were investigated by thermogravimetry and differential thermal analysis,  $N_2$

physisorption, and light scattering. It was observed that the particle sizes of all the sols had only a small effect on the pore size of the membranes. Qualities of the membranes were improved by addition of polyvinyl alcohol as binder to the boehmite precursor. This resulted in less critical but more controllable drying and calcining procedures. Composite membranes with different pore sizes from 3.2 to 4.8 nm and surface areas retained about 100 m<sup>2</sup>/g could be regulated by different alumina-to-titania ratios.

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**Carbon-silicon alloy fibers:****Optimizing tensile properties by control of the stabilization stage**

S. Lu, B. Rand, K.D. Bartle

(University of Leeds)

The stabilization stage in the processing of carbon-silicon alloy (CSA) precursor fibers is investigated in this paper. The critical stabilization parameters are identified and shown to control the mechanical properties of fibers both at the stabilization stage and, after further pyrolysis and controlled oxidation, to produce oxidation-resistant fibers. The attainment of infusibility in the stabilized fibers, necessary for the production of CSA fibers, determines the lowest stabilization degree, whereas the highest stabilization degree can be identified from the relationship between stabilization temperature and tensile properties of CSA fibers, thus enabling the optimum stabilization conditions to be determined. The CSA fibers produced by proper control of stabilization conditions significantly enhance mechanical properties which are more than double those of CSA fibers obtained previously. Fourier transform infrared spectroscopy and nuclear magnetic resonance studies show that at stabilization temperatures above the optimum there is significant formation of silica in the stabilized fibers. This leads to a higher modulus but lower tensile strength and elongation.

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**Deposition and mechanical properties of polycrystalline****Y<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> superlattices**P. Yashar,<sup>1</sup> S.A. Barnett,<sup>1</sup> L. Hultman,<sup>2</sup> W.D. Sproul<sup>1</sup><sup>(1)Northwestern University, <sup>2</sup>Linköping University)</sup>

Polycrystalline Y<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> superlattice thin films were deposited using opposed-cathode reactive magnetron sputtering. Pulsed direct-current power was used to eliminate arcing on the metallic targets. Radio-frequency power was applied to the substrates to achieve ion bombardment of the growing film. In order to reproducibly deposit at high rates in Ar-O<sub>2</sub> mixtures, the Y target voltage was used to indirectly feedback-control the O<sub>2</sub> partial pressure. Deposition rates as high as ~70% of the pure metal rates were achieved, typically 3.5 μm/h. Superlattices with periods ranging from 2.6 to 95 nm were deposited. Y<sub>2</sub>O<sub>3</sub> layer thicknesses were either 75% or 50% of the superlattice period. X-ray diffraction and transmission electron microscopy studies showed well-defined superlattice layers. The ZrO<sub>2</sub> layers exhibited the high-temperature cubic-fluorite structure, which was epitaxially stabilized by the cubic Y<sub>2</sub>O<sub>3</sub> layers, for thicknesses ≤ 7 nm. The equilibrium monoclinic structure was observed for thicker ZrO<sub>2</sub> layers. Nanoindentation hardnesses ranged from 11.1 to 14.5 GPa with little dependence on period. The hardness results are discussed in terms of current superlattice hardening theories.

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**Influence of deposition parameters on mechanical properties of sputter-deposited Cr<sub>2</sub>O<sub>3</sub> thin films**P. Hones,<sup>1</sup> N.X. Randall,<sup>2</sup> F. Lévy<sup>1</sup><sup>(1)Ecole Polytechnique Fédérale de Lausanne, <sup>2</sup>CSEM Instruments)</sup>

Among the oxides, Cr<sub>2</sub>O<sub>3</sub> exhibits the highest hardness value and a low coefficient of friction. These properties make chromium oxide an excellent coating material for tribological applications. Cr<sub>2</sub>O<sub>3</sub> thin films were deposited by radio-frequency reactive magnetron sputtering at substrate temperature in the range 363–593 K. The hardness and elastic modulus of the films were measured by two complementary nanoindentation techniques to investigate the influences of the substrate temperature and the oxygen content in the sputtering gas. While the continuous stiffness data method provides information throughout the whole film thickness, nanoindentation combined with scanning force microscopy of the residual imprints allows visualization of pileup, cracking, and delamination from the substrate. Hardness values up to 32 GPa were obtained for substrate temperatures exceeding 500 K and oxygen contents between 15% and 25% of the total gas pressure. The films, obtained with these deposition conditions, showed good adhesion to silicon substrates.

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**The Meyer hardness: A measure for plasticity?**

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The physical insight into the Meyer hardness is given on the basis of the experimental results for indentation load  $P$  versus indentation depth  $h$  relations and of a simple model for elastoplastic contact deformation. The quadratic relationships of  $P = k_1 h_2$  for loading and  $P = k_2 (h - h_r)^2$  for unloading with the residual depth of impression  $h_r$  are essential in the elastoplastic indentation processes and mechanisms. The indentation-induced residual strain energy stored in unloaded impression is properly taken into account. The Meyer hardness is an elastic/plastic parameter with is dependent not only on the plasticity, but also on the elasticity of material indented, as well as significantly dependent on the geometry of indenter used. The Meyer hardness is given in terms of the energy consumed to create a residual indentation impression, leading to the concepts of "work-of-indentation" and "ductility index."

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**Optical second-order nonlinearity of transparent glass-ceramics containing BaTiO<sub>3</sub> precipitated via surface crystallization**

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Second-harmonic generation of transparent glass-ceramics containing BaTiO<sub>3</sub> crystalline phase has been investigated using Maker fringe method. When 15BaO • 15TiO<sub>2</sub> • 70TeO<sub>2</sub> glass was heat-treated at 415 °C for 0.5–12 h, (101)- or (110)-oriented BaTiO<sub>3</sub> crystals were precipitated in the near-surface region. The resultant glass-ceramics exhibit second-harmonic generation. Variation of second-harmonic intensity with angle of incidence, i.e., Maker fringe pattern changes drastically with an increase in heat treatment time and temperature. No second-harmonic signal was detected in glass-ceramic derived from 15SrO • 15TiO<sub>2</sub> • 70TeO<sub>2</sub> glass. These facts suggest that BaTiO<sub>3</sub> crystal is responsible for the second-order nonlinear phenomenon, although its structure is closer to cubic than tetragonal according to x-ray diffraction measurements. In order to estimate second-order nonlinear optical coefficient  $d^{(2)}$ , Maker fringe patterns of the BaTiO<sub>3</sub>-containing glass-ceramics were analyzed. For the glass-ceramic after heat treatment for 0.5 h,  $d_{33}$  and thickness of BaTiO<sub>3</sub>-crystallized layer,  $L$ , are 3.65 pm/V and 3.43 μm, respectively. The value of second-order nonlinear optical coefficient is comparable to those of BaTiO<sub>3</sub> films prepared via metalorganic chemical vapor deposition and pulsed-laser deposition. On the other hand, the glass-ceramic heat-treated for 12 h exhibits  $d_{15} = 0.31$  pm/V and  $L = 300$  μm. The thickness of the layer active in second-order nonlinearity evaluated from the Maker fringe pattern is coincident with the observation by scanning electron microscopy.

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**Transmission electron microscopy study of barium hexaferrite formation from barium carbonate and hematite**

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The formation of barium hexaferrite from stoichiometric mixtures of BaCO<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> has been investigated by means of differential thermal analysis and thermogravimetry, x-ray diffraction, and transmission electron microscopy-energy dispersive spectrometry. The first step, which implies decarbonation and monoferrite formation, includes the formation of various intermediate compounds, which are formed at contact points between BaCO<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> grains, and implies diffusion of both species. In the second step barium hexaferrite is formed at interfaces between monoferrite and iron oxide mainly by diffusion of barium through the BF<sub>6</sub> lattice into the hematite lattice. This exothermic reaction process leads to nonagglomerated pseudohexagonal platelets with an average particle size very close to the one of the starting powder mixture (~1 μm).

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**Phase separation in undercooled molten Pd<sub>80</sub>Si<sub>20</sub>: Part I**

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(The Chinese University of Hong Kong)

Three different kinds of morphology are found in undercooled Pd<sub>80</sub>Si<sub>20</sub>, and they dominate at different undercooling regimes  $\Delta T$ , defined as  $\Delta T = T_1 - T_k$ , where  $T_1$  is the liquidus of Pd<sub>80</sub>Si<sub>20</sub> and  $T_k$  is the kinetic crystallization temperature. In the small undercooling regime, i.e., for  $\Delta T \leq 190$  K, the microstructures are typically dendritic precipitation with a eutecticlike background. In the intermediate undercooling regime, i.e., for  $190 \leq \Delta T \leq$

220 K, spherical morphologies, which arise from nucleation and growth, are identified. In addition, Pd particles are found throughout an entire undercooled specimen. In the large undercooling regime, i.e., for  $\Delta T \geq 220$  K, a connected structure composed of two subnetworks is found. There is a sharp decrease in the dimension of the microstructures from the intermediate to the large undercooling regime. Although the crystalline phases in the intermediate and the large undercooling regimes are the same, the crystal growth rate is too slow to bring about the occurrence of grain refinement. Combining the morphologies observed in the three undercooling regimes and their crystallization behaviors, we conclude that phase separation takes place in undercooled molten  $\text{Pd}_{80}\text{Si}_{20}$ .  
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### Crystallization of undercooled liquid spinodals: Part II

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We demonstrated in "Phase separation in undercooled molten  $\text{Pd}_{80}\text{Si}_{20}$ : Part I" that when a molten  $\text{Pd}_{80}\text{Si}_{20}$  ingot is undercooled into its undercooling regime with  $\Delta T \geq 220$  K ( $\Delta T = T_1 - T$ , where  $T_1$  is the liquidus and  $T$  is the temperature of the undercooled melt), liquid-state phase separation by spinodal decomposition occurs. Upon crystallization, one of the metastable liquid spinodals becomes  $\text{Pd}_3\text{Si}$  while the other one turns into  $\text{Pd}_5\text{Si}_2$ . In both cases, Pd particles precipitate out. Microstructural analysis indicates the  $\text{Pd}_3\text{Si}$  subnetwork forms first. It then acts as a seed for the subsequent crystallization of the remaining undercooled melt, which finally forms the  $\text{Pd}_5\text{Si}_2$  dendrites. As crystallization proceeds, latent heat and volume contraction bring about morphological changes.

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### Metastable liquid miscibility gap in Pd-Si and its glass-forming ability: Part III

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The metastable liquid miscibility gap of Pd-Si is determined structurally. The glass-forming ability of Pd-Si is then discussed in the light of the metastable liquid miscibility gap. Analysis indicates that it does not favor the formation of glass.

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### Nucleation, growth, and aggregation of gold on polyimide surfaces

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The growth of ultrathin fold films on polyimide (PI) surfaces and the stability of the films upon thermal annealing were studied using a combination of various techniques. With scanning electron microscopy (SEM), we observed that, at room temperature, the Au film initially grows by nucleation of compact Au islands. With increasing metal coverage, the clusters partially agglomerate to produce a wormlike structure. Finally, percolation, hole-filling, and continuous thin-film growth were observed. To evaluate the thermal stability of the Au/PI system, annealing at various temperatures was performed on films that displayed the wormlike structure. SEM results indicate strong temperature-dependent changes in film morphology. Finally, from our SEM data we determined contact angles, allowing us to estimate interfacial and adhesion energies.

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### First-principles study of initial stage of Ni thin-film growth on a $\text{TiO}_2(110)$ surface

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The bonding structure and binding character for the initial stage of thin-film growth of Ni on a rutile (110) surface were studied using first-principles density functional theory. Our results show that, in the first monolayer, Ni atoms are preferentially adsorbed on top of bridging oxygen atoms and upon secondary surface oxygen. The bond strength between Ni adatom and substrate is much stronger than that between Ni adatoms. About 0.3 electrons are transferred from Ni atoms to substrate in low coverage; the adsorption of additional Ni atoms on neighboring sites decreases this transfer. In addition to the ionic bonding component, some covalent character is found in the Ni adatom-substrate bond.

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### Ultraviolet laser-induced liquid-phase palladium seeding on polymers

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Excimer laser pulses with wavelength of 308 nm, repetition rates of 1–10 Hz, pulse energies of 300–400 mJ, and pulse width of 20 ns were used to selectively seed palladium aggregates from a liquid-phase solution on polymer (polyimide) surfaces. The precursors used were  $\text{PdCl}_2$  in hydrochloric acid and  $\text{Pd}(\text{CH}_3\text{CO}_2)_2$  in acetic acid. The coverage of the polyimide with palladium aggregates was determined by the analysis of scanning electron microscopy measurements. Qualitative and quantitative analyses of seeded particles on polyimide (PI) were investigated by x-ray diffraction and transmission measurements. The amount of deposited palladium showed a quadratic dependence on the laser fluence reaching the surface. On the other hand, the coverage versus number of laser shots showed a square-root-like dependence. The palladium deposits also appeared as amorphous and  $\text{Pd}[111]$  crystallite forms, depending on the number of laser pulses. The roughness of a PI surface prior to seeding was modified mechanically and characterized by its fractal dimension. The fractal dimension of the samples is varied between 2.3 and 2.7 for all the parameters applied, and the palladium deposition was found to be dependent on this dimension of the PI film.

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### Atomic force microscopy, lateral force microscopy, and transmission electron microscopy investigations and adhesion force measurements for elucidation of tungsten chemical mechanical polishing mechanisms

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We investigated various interactions between alumina and tungsten films that occur during chemical mechanical polishing (CMP). Atomic force microscopy surface topography measurements of post-CMP tungsten indicate that the roughness of the tungsten is independent of polish pressure and rotation rate. Pure mechanical abrasion is therefore an unlikely mechanism of material removal during CMP. Transmission electron microscopy images corroborate these results. The adhesion force between alumina and tungsten was measured in solution. The adhesive force increased with  $\text{KIO}_3$  concentration. Friction forces were measured in solution using lateral force microscopy. The friction force in buffered solutions was independent of  $\text{KIO}_3$  concentration. These results indicate that interactions other than purely mechanical interactions exist during CMP.

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### Room-temperature synthesis of submicron platinum and palladium powders in glycols

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Platinum and palladium powders with average particle sizes in the submicron range have been synthesized at room temperature by hydrazine reduction of  $\text{PtCl}_6^{2-}$  and  $\text{Pd}(\text{NH}_3)_4^{2+}$ , respectively, in glycols. Platinum powders contain spherical particles with a bimodal size distribution. Palladium powders also contain spherical particles but the size distribution is narrow. The effect of both ammonia and hydrazine concentration on the size distribution and average size of palladium particles was investigated.

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### Thermophysical properties of zirconium at high temperature

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Six thermophysical properties of both solid and liquid zirconium measured using the high-temperature electrostatic levitator at Jet Propulsion Laboratory are presented. These properties are density, thermal expansion coefficient, constant pressure heat capacity, hemispherical total emissivity, surface tension, and viscosity. For the first time, we report the densities and the thermal expansion coefficients of both the solid as well as liquid Zr over wide ranges of temperatures. Over the 1700–2300 K temperature span, the liquid density can be expressed as  $\rho_l(T) = 6.24 \times 10^3 - 0.29(T - T_m) \text{ kg/m}^3$  with  $T_m = 2128$  K, and the corresponding volume expansion coefficient as  $\alpha_l = 4.6 \times 10^{-5} / \text{K}$ . Similarly, over the 1250–2100 K range, the measured density of the solid can be expressed as  $\rho_s(T) = 6.34 \times 10^3 - 0.15(T - T_m)$ , giving a volume expansion coefficient  $\alpha_s = 2.35 \times 10^{-5} / \text{K}$ . The constant pressure heat capacity of the liquid

phase could be estimated as  $C_{pl}(T) = 39.72 - 7.42 \times 10^{-3} (T - T_m)$  J/mol/K if the hemispherical total emissivity of the liquid phase  $\epsilon_{Tl}$  remains constant at 0.3 over the 1825–2200 K range. Over the 1400–2100 K temperature span, the hemispherical total emissivity of the solid phase could be rendered as  $\epsilon_{Ts}(T) = 0.29 - 9.91 \times 10^{-3} (T - T_m)$ . The measured surface tension and the viscosity of the molten zirconium over the 1850–2200 K range can be expressed as  $\sigma(T) = 1.459 \times 10^{-3} - 0.244 (T - T_m)$  mN/m and as  $\eta(T) = 4.83 - 5.31 \times 10^{-3} (T - T_m)$  mPas, respectively.

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### Growth-rate dependence of the thermal conductivity of chemical-vapor-deposited diamond

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The in-plane thermal diffusivity of chemical-vapor-deposited diamond films was measured as a function of diamond-growth rate. The films, 0.1–0.4 mm thick, were prepared in microwave-plasma reactor at growth rates ranging from 1 to 10  $\mu\text{m/h}$ . A modification of Ångström's method was used to perform the diffusivity measurements. The thermal conductivity calculated from the thermal diffusivity shows an inverse relationship with growth rate. Analyses of Raman spectra indicate that both the line shifts and the line widths of the diamond Raman peak are practically independent of the deposition rate, except for the specimen grown at the highest growth rate.

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### Characterization of thin films containing zirconium, oxygen, and sulfur by scanning electron and atomic force microscopy

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Oxidic zirconium films prepared by chemical deposition from aqueous medium on sulfonic acid terminated self-assembled monolayers attached to an oxidized silicon surface were investigated with scanning electron microscopy and atomic force microscopy. Bulk precipitate forms in the 4 mM  $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ , 0.4 N HCl deposition medium at 343 K after approximately 30 min. Precipitate particles (200 nm and larger) were found embedded in the oxidic zirconium film and adsorbed on top of the film; they could be washed off, but patches of the film were removed. Working with unstable deposition solutions, in which homogeneous nucleation occurs, leads to preparation-inherent flaws in the film.

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### Real-time synchrotron x-ray scattering study of an epitaxial BaTiO<sub>3</sub> thin film during heating

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An epitaxial BaTiO<sub>3</sub> film with 290-nm thickness was prepared on a MgO(001) single-crystal substrate by radio-frequency magnetron sputter deposition. The structural characteristics of the film were studied as a function of temperature in *in situ*, real-time synchrotron x-ray scattering experiments. We found that the as-grown film was strained at room temperature and tetragonally distorted with the *c* axis normal to the film surface. Interestingly, its lattice parameters were found to be expanded 1.28% and 0.64% in both the in-plane and out-of-plane directions, respectively, (i.e., biaxially) compared to those of a bulk BaTiO<sub>3</sub>. More importantly, as it was heated up to 600 °C, the tetragonal structure was kept up without the phase transition, which is usually observed in other epitaxial ferroelectric thin films.

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### Growth and ultraviolet optical properties of KGd<sub>1-x</sub>RE<sub>x</sub>(WO<sub>4</sub>)<sub>2</sub> single crystals

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The suitable conditions for growth of KGd(WO<sub>4</sub>)<sub>2</sub> (KGW) and KGd<sub>1-x</sub>RE<sub>x</sub>(WO<sub>4</sub>)<sub>2</sub>—RE = Nd, Er, Yb, Ho, Tm, Pr—by the top-seeded-solution-growth method, using K<sub>2</sub>W<sub>2</sub>O<sub>7</sub> as solvent, are discussed. The

relation between crystal size, mean growth rate, distribution coefficient of the substituting element, and the presence of macrodefects is analyzed. The optical absorption corresponding to the band-gap transition of KGW was found to be temperature dependent; the absorption threshold energy changed from 34,405 cm<sup>-1</sup> at 300 K to 35,330 cm<sup>-1</sup> at 7 K. Narrow pre-edge absorption bands at about 32,000 and 32,600 cm<sup>-1</sup> have been ascribed to Gd<sup>3+</sup> intraconfigurational transitions. The photoluminescence of most RE<sup>3+</sup> ions has been observed under ultraviolet (UV) excitation close to the absorption threshold of KGW. This suggests the contribution of charge transfer bands. In Pr-doped samples the presence of a minor concentration of Pr<sup>4+</sup> could also contribute in this region. The irradiation with UV light does not introduce any significant coloration of our samples.

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### Structural characterization of amorphous ceramics in the system Si–B–N–(C) by means of transmission electron microscopy methods

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Amorphous ceramics with the chemical composition Si<sub>3</sub>B<sub>3</sub>N<sub>7</sub> and SiBN<sub>3</sub>C were produced from single-source molecular precursors by polymerization and pyrolysis. The powder and fiber materials were investigated by means of energy filtering transmission electron microscopy. The intensity of elastically scattered electrons is recorded to calculate the pair distribution function (PDF) of these ceramics. In the PDF of Si<sub>3</sub>B<sub>3</sub>N<sub>7</sub> three significant maxima at 0.144, 0.172, and 0.291 nm are clearly resolved and are assigned to the pair distances B–N, Si–N, and Si–Si (N–N), respectively, by comparison to crystalline materials. The predominant structural units of the ceramic are trigonal planar BN<sub>3</sub> and tetrahedral SiN<sub>4</sub> groups, which are close to their regular symmetry. The overall PDF of SiBN<sub>3</sub>C is very similar to that of Si<sub>3</sub>B<sub>3</sub>N<sub>7</sub>, however the maxima are broadened due to the incorporation of carbon into the network. High-resolution mapping of the elements Si, B, N, and C with electron spectroscopic imaging reveals a homogenous distribution on a sub-nanometer scale without precipitation or separation of, for example, carbon-rich clusters. Similarly, elemental mapping of Si<sub>3</sub>B<sub>3</sub>N<sub>7</sub> reveals a random distribution of the elements Si, B, and N at the same scale. Both new ceramics consist of an amorphous network with bonds and coordinations as performed in the precursor.

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### Persistent spectral hole burning and local structure of Eu<sup>3+</sup> ions doped in BaO–PbO–P<sub>2</sub>O<sub>5</sub> glasses

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Persistent spectral hole burning was observed in Eu<sup>3+</sup>-doped BaO–PbO–P<sub>2</sub>O<sub>5</sub> glasses, and the dependence of hole properties on the glass composition was investigated in relation to the local structure surrounding the Eu<sup>3+</sup> ions. The hole was burned on the <sup>7</sup>F<sub>0</sub> → <sup>5</sup>D<sub>0</sub> transition of the Eu<sup>3+</sup> ions, the depth of which decreased with increasing PbO content, while the hole width increased. The hole burned at 6 K was filled upon increase in temperature and was erased above 120 K. Judd–Ofelt parameters and fluorescence line narrowing spectra indicated that the symmetry of the Eu<sup>3+</sup> site increases and the covalency of the Eu–O bond decreases with increasing PbO content.

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### Deformation-induced microstructural changes in Fe<sub>40</sub>Ni<sub>40</sub>P<sub>14</sub>B<sub>6</sub> metallic glass

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The effect of mechanical deformation via high-energy ball milling on the structure of the Fe<sub>40</sub>Ni<sub>40</sub>P<sub>14</sub>B<sub>6</sub> metallic glass was studied by means of x-ray diffractometry, transmission electron microscopy (TEM), and differential scanning calorimetry (DSC). After 5 h of milling, TEM observations indicated that some nanocrystallites with a diameter of about 6 nm precipitated from surface layers of the amorphous ribbons, whereas the bulk remained amorphous. When milling time was increased to 11 h, bulk crystallization occurred. The amorphous Fe<sub>40</sub>Ni<sub>40</sub>P<sub>14</sub>B<sub>6</sub> alloy crystallized into a mixture of γ-(Fe,Ni) and (Fe,Ni)<sub>3</sub>(P,B). In order to understand the microstructural changes occurring in the amorphous ribbons prior to the onset of bulk crystallization, the isothermal crystallization behavior of as-deformed amorphous ribbons was studied. Compared with as-quenched amorphous ribbons, the local value of the Avrami exponent, derived from isothermal DSC data, increased from 3.5 to 4.1 for bulk crystallization. The thermal crystallization mechanism of deformed amorphous Fe<sub>40</sub>Ni<sub>40</sub>P<sub>14</sub>B<sub>6</sub> ribbons changed from a eutectic-type reaction with

simultaneous precipitation of  $\gamma$ -(Fe,Ni) and (Fe,Ni)<sub>3</sub>(P,B) from the amorphous matrix to a primary-type reaction with precipitation of  $\alpha$ -(Fe,P,B) preceding the formation of  $\gamma$ -(Fe,Ni) and (Fe,Ni)<sub>3</sub>(P,B). Our results suggest that several hours of mechanical milling cause surface crystallization and some atomic rearrangements in the amorphous alloy. The latter effect may be responsible for the observed primary-type reaction for crystallization of the deformed amorphous alloy.

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### Physical properties of nearly zero magnetostriction Co-rich glass-coated amorphous microwires

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Magnetic and mechanical properties of Co-rich amorphous microwires of nominal compositions (Co<sub>1-x</sub>Mn<sub>x</sub>)<sub>75</sub>Si<sub>10</sub>B<sub>15</sub> (0.08 < x < 0.11) and Co<sub>56.5</sub>Fe<sub>6.5</sub>Ni<sub>10</sub>B<sub>16</sub>Si<sub>11</sub> with nearly zero magnetostriction constant have been studied. Drastic changes of the hysteresis loop with the decrease of x from rectangular to flat shape were observed at x < 0.1, while the Co<sub>56.5</sub>Fe<sub>6.5</sub>Ni<sub>10</sub>B<sub>16</sub>Si<sub>11</sub> microwire showed rectangular hysteresis loops. Compositions with x ≥ 0.1 have small but positive magnetostriction constant while negative  $\lambda_s$  values have been observed at x ≤ 0.09, indicating rectangular character of the hysteresis loop in samples with nearly zero and even for small negative  $\lambda_s$ . External stress dependence of switching field, H\*, showed an increase of H\* with  $\sigma$  for samples with x = 0.11 and a decrease of H\* with  $\sigma$  for x = 0.1. Besides, microwires of the same composition but with different dimensions showed different H\*( $\sigma$ ) dependencies.

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### Indentation model and strain gradient plasticity law for glassy polymers

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Plastic deformation of metals is generally a function of the strain. Recently, both phenomenological and dislocation-based strain gradient plasticity laws were proposed after strain gradients were experimentally found to affect the plastic deformation of the metal. A strain gradient plasticity law is developed on the basis of molecular theory of yield for glassy polymers. A strain gradient plasticity modulus with temperature and molecular dependence is proposed and related to indentation hardness. The physics of the strain gradient plasticity in glassy polymer is then discussed in relation to the modulus.

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### Synthesis and blood compatibilities of novel segmented polyurethanes containing phosphatidylcholine analogous moieties in the main chains and long-chain alkyl groups in the side chains

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New segmented polyurethanes containing phospholipid moieties in the main chains and long-chain alkyl groups in the side chains were synthesized. The soft segments used in this study were poly(butadiene), poly(isoprene), hydrogenated poly(isoprene), and poly(1,6-hexyl-1,2-ethylcarbonate) diol. The hard segments of these polyurethanes were 4,4'-methylenediphenyl diisocyanate, bis [2-(2-hydroxyethyl)dimethylammonio)ethyl]2-cetyl-1,3-propanediphosphate, and 1,4-butanediol. The blood compatibilities of the new polymers were evaluated by platelet-rich plasma contact studies and viewed by scanning electron microscopy using medical grade BioSpan® and nonphospholipid polyurethane as references. These new materials have good surfaces in terms of platelet adhesion, and the morphology of adhered platelets undergoes a relatively low degree of variation.

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### Effect of TiO<sub>2</sub> addition on the crystallization of Li<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> precursor powders by a sol-gel process

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The activation energy for crystallization of  $\beta$ -spodumene in TiO<sub>2</sub> added Li<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> (LAS) precursor powders by a sol-gel process was studied by using isothermal and nonisothermal methods. Nonisothermal kinetics for the LAS precursor powder system were investigated using differential thermal

analysis (DTA) and quantitative x-ray diffraction (XRD) analysis. The rate of crystallization of LAS precursor powders decreased as the TiO<sub>2</sub> content increased. For samples with addition of 0, 5.0, and 10.0 wt% TiO<sub>2</sub>, the activation energies for crystallization by DTA evaluation were 165.06, 194.46, and 205.38 kJ/mol, respectively. According to the quantitative XRD method, the values computed by the JMA equation were 162.54, 189.42, and 196.14 kJ/mol, respectively. The values obtained by isothermal and nonisothermal kinetic methods from DTA and XRD analyses were in good agreement. The growth morphology parameters were 0.59, 0.70, and 0.76, respectively, for the LAS precursor powder with TiO<sub>2</sub> addition of 0, 5.0, and 10.0 wt%, showing a rodlike growth. In the LAS precursor powder system, TiO<sub>2</sub> did not act as the nucleative agent.

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### Electronic states in heavily Li-doped graphite nanoclusters

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Negative ion states for Li atoms are found in graphite nanoclusters heavily doped with lithium using a semi-empirical calculational method. These calculations identify a quasi-stable site for a negative Li ion near the terminated hydrogen atoms, and this site becomes very stable in the presence of the Coulomb interaction between Li ions. The total charge transfer from Li ions to the graphite clusters does not depend on the number of Li atoms per cluster, but rather on the relative geometries of the Li atoms on the cluster. The relationship of these findings to the findings in the <sup>7</sup>Li nuclear magnetic resonance experiments and to the performance of Li secondary batteries is discussed.

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### Fracture modes in brittle coatings with large interlayer modulus mismatch

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Fracture modes in a model glass-polymer coating-substrate system indented with hard spheres were investigated. The large modulus mismatch between the glass and polymer resulted in distinctive transverse fracture modes within the brittle coating: exaggerated circumferential (C) ring cracks that initiated at the upper coating surface well outside the contact (as opposed to the near-contact Hertzian cone fractures observed in monolithic brittle materials); and median-radial (M) cracks that initiated at the lower surface (i.e., at the substrate interface) on median planes containing the contact axis. Bonding between the coating and substrate was sufficiently strong as to preclude delamination in our system. The transparency of the constituent materials usefully enabled *in situ* identification and quantification of the two transverse fracture modes during contact. The morphologies of the cracks and the corresponding critical indentation loads for initiation were measured over a broad range of coating thicknesses (20  $\mu$ m to 5.6 mm), on coatings with like surface flaw states, here ensured by a prebonding abrasion treatment. There was a well-defined, broad intermediate range where the indented coating responded more like a flexing plate than a Hertzian contact, and where the M and C cracks initiated in close correspondence with a simple critical stress criterion, i.e., when the maximum tensile stresses exceeded the bulk strength of the (abraded) glass. In this intermediate range the M cracks generally formed first—only when the flaws on the lower surface were removed (by etching) did the C cracks form first. Finite element modelling was used to evaluate the critical stresses at crack initiation and the surface locations of the crack origins. Departures from the critical stress condition occurred at the extremes of very thick coatings (monolith limit) and very thin coatings (thin-film limit), where stress gradients over the flaw dimension were large. Implications of the results concerning practical coating systems are considered.

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