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X-ray Photoelectron Spectroscopy Studies of Bond Structure Between Polyvinyl Alcohol and a Titanate Cross Coupling Agent

M.A. Gülgün, O.O. Popoola, W.M. Kriven

ABSTRACTS

COMMUNICATIONS

EXAFS Determination of Local Structure in Sol-Gel-Derived Lead Titanate, Lead Zirconate, and Lead Zirconate TitanateS.S. Sengupta, L. Ma, D.L. Adler, D.A. Payne
(University of Illinois at Urbana-Champaign)

We report extended x-ray absorption fine structure (EXAFS) measurements for partially heat-treated gels in the lead zirconate titanate system (PZT). Self-consistent results obtained from the titanium and zirconium K-edges and the lead L_{III}-edge were used to determine bonding pathways between cations. For lead titanate (PT) and PZT gels, separate networks of predominantly Ti-O-Ti, Zr-O-Zr and Pb-O-Pb linkages were observed. For lead zirconate (PZ) gels, both Zr-O-Pb and Zr-O-Zr linkages were observed. The results indicate heterogeneity at the molecular level. These findings are discussed in terms of the evolution of structure for PZT materials prepared by our sol-gel method.

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3C-SiC/Si/3C-SiC Epitaxial Tri-Layer Films Deposited on Si(111) Substrates by Reactive Magnetron SputteringQ. Wahab, L. Hultman, I.P. Ivanov, M. Willander, J-E. Sundgren
(Linköping University)

A tri-layer epitaxial structure of 3C-SiC/Si/3C-SiC was grown on Si(111) substrate by reactive magnetron sputtering. The layered structure consisted of a 300-nm-thick Si layer sandwiched between two 250-nm-thick 3C-SiC layers. Cross-sectional transmission electron microscopy (XTEM) showed that all layers were epitaxial to each other. The 3C-SiC layers contained stacking faults and double positioning domains with a high density in the second SiC layer. The Si layer showed the lowest density of planar faults, but developed growth facets. Observation was made of stacking faults propagating from 3C-SiC to Si layer as well as stacking faults originating at the termination of 3C-SiC double positioning boundaries into Si. The termination of Si stacking faults during growth of SiC is also reported.

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Elastic Constants and Internal Friction of Polycrystalline CopperH. Ledbetter*, C. Fortunko*, P. Heyliger†
(*National Institute of Standards and Technology,
†Colorado State University)

Using ultrasonic-resonance spectroscopy (URS), we measured the elastic constants C and companion internal friction Q⁻¹ of isotropic

polycrystalline copper. The annealed material was four-nines pure with equiaxed heavily twinned grains averaging about 75 μm in diameter. The URS method offers the principal advantage of point contact or loose coupling, thus no contribution from a transducer-specimen bond and only small contributions from transducers and fixture. A second advantage is one measurement for all elastic constants and all associated internal frictions. The Cs agree with established values. The Q⁻¹s are much lower than pulse-echo-method values. Comparison of measured Q⁻¹ with the Koehler-Granato-Lücke model permits estimating an effective dislocation-loop length. Q⁻¹ (shear) exceeds Q⁻¹ (longitudinal) by a factor of about 1.5.

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Diffusion in a Regular Solid SolutionJ.L. Chu, S. Lee
(National Tsing Hua University)

Diffusion in a regular solid solution was investigated. A thin plate of isotropic solid of constant surface molal fraction was considered. The regular solution is described by the parameter α. When α is positive, the attraction between unlike atoms is greater than the attraction between like atoms and conversely. The depth of penetration and average molal fraction for a given period increases with increasing α. The separation of two curves for given α increases with increasing surface molal fraction. The diffusion coefficient is positive only if α is greater than -1/X(1-X).

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ARTICLES

Hg-Ba-Ca-Cu-O System Phase Diagram and the Formation of HgBa₂Ca_{n-1}Cu_nO_{2n+2+δ} Superconducting PhasesG.C. Che, Y.K. Du, C. Dong, F. Wu, Z.X. Zhao
(Academia Sinica)

Hg-Ba-Ca-Cu-O system phase diagram and the formation of HgBa₂Ca_{n-1}Cu_nO_{2n+2+δ} superconducting phases have been investigated by XRD. The isothermal sections of HgO-BaO-CuO system at 800°C and BaO-CaO-CuO system at 870°C are presented. HgBa₂Ca_{n-1}Cu_nO_{2n+2+δ} superconducting phases are formed through the reactions of HgO with intermediate products "Ba₂CuO₃+BaCuO₂+CaO", "BaCuO₂+CaO" and "BaCuO₂+Ca₂CuO₃" for n=1, 2 and 3 phase, respectively.

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Anomalous Low-Temperature Raman Scattering in a-Si_{1-x}H_xD.M. Bhusari, A. Kumbhar, S.T. Kshirsagar
(National Chemical Laboratory)

We have reported here low temperature Raman scattering measurements on thin films of hydrogenated amorphous silicon (a-Si:H) alloys having different H contents. The Stoke's intensity $^{77K}I_{TO}$ scattered at 77 K by the TO-phonon is found to be several times greater than its corresponding magnitude ($^{300K}I_{TO}$) at 300 K. The ratio ($^{77K}I_{TO}/^{300K}I_{TO}$) is observed to vary exponentially with increase in H-concentration of the film. After eliminating various possible contributions to scattering cross-section, and therefore to the scattered intensity, this anomalous light scattering at 77 K is attributed to a possibility of polarizability modulation that is believed to be caused due to a possible reduction in light-induced migration of hydrogen in a-Si:H and to the charge carrier induced enhancement of electron phonon coupling at 77 K.

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A Microstructural Study of Rapidly Solidified and Heat-Treated Austenitic Fe-Mn-Al-Mo-W-Nb-C AlloysK.H. Han, H.E. Lee
(Yeungnam University)

The microstructural characteristics of melt-spun and heat-treated austenitic Fe-28Mn-8.6Al-0.5Mo-0.7W-0.5Nb-1.1C (in wt.%) alloys have been investigated by means of transmission electron microscopy. The melt-spun alloy contained fine austenitic cells and some intercellular Nb(C,N) precipitates. Detailed observations revealed fine {100} modulations in the matrix of the cells as well as a concomitant L₁2 atomic ordering arising from it. These observations indicate that the onset of decomposition of the initial austenite phase occurred during the rapid solidification process. Aging of the melt-spun alloy at 823–1173 K produced various microstructures, including a general precipitation of Nb(C,N) in the matrix. On isochronal annealing for 1 h, this matrix Nb(C,N) precipitation commenced at 1073 K with the formation of metastable coherent κ -carbide (κ') near cell boundaries. On annealing at temperatures above 1123 K only the Nb(C,N) precipitates were formed, on a fine scale, being accompanied by the formation of precipitate-free regions in the vicinity of cell and grain boundaries. Both intercellular and matrix Nb(C,N) precipitates obeyed a cube-to-cube orientation relationship with austenite. The general matrix precipitation of Nb(C,N) and formation of precipitate-free regions are discussed in terms of a vacancy (defect)-depletion effect. Finally, it was demonstrated that, by employing a double heat-treatment schedule of annealing at 1173 K followed by aging at 823 K, a novel microstructure consisting of fine dispersoids of Nb(C,N) carbo-nitride, distributed over the matrix of {100} modulated structure, could be produced.

Order No.: JA506-007

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Banded Structures in Unstable Combustion SynthesisH.P. Li
(Jin-Wen College of Business and Technology)

Banded structures in combustion synthesized products have been observed during unstable combustion synthesis. The formation of the banded structures was discussed in this article. It was noted that the band spacing was changed when several initial processing conditions were varied. Any change in the processing parameters which correspondingly caused more unstable combustion was observed to decrease the propagation velocity of the combustion front and increase the band spacing. The correlation of the band spacing and oscillatory frequency of the unstable oscillatory combustion with the propagation velocity was also discussed. From the results studied in this work, it was noted that the change of the band spacing can be used to infer the degree of the instability of the combustion front.

Order No.: JA506-008

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Microstructural Characterization of a Microwave Sintered Silicon Nitride Based CeramicK.P. Plucknett, D.S. Wilkinson
(McMaster University)

The microstructure of a microwave densified silicon nitride based ceramic has been assessed in the as-sintered, post-sinter hot-isostatically pressed (HIPed) and annealed conditions. The grain size of the as-sintered material, which is a low substitution β' -Sialon, was significantly finer than observed in conventionally processed materials of similar composition. The as-sintered ceramic exhibits a reverse porosity gradient (with the highest porosity level at the surface) due to heat dissipation to the cooler surroundings during microwave processing. This also results in a higher β' aspect ratio close to the surface arising from an increased glass viscosity (due to heat loss) and compositional change in this region during sintering. HIPing results in removal of all porosity from the sample core, however a reduced porosity surface layer is retained. Significant β' -Sialon grain growth is also apparent after HIPing. A fine β' grain structure was retained after annealing, with partial devitrification of the glassy grain boundary phase to β -Y₂Si₂O₇.

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Crystalline Phases of Sol-Gel ZrO₂ in ZrO₂-SiO₂ System: Differential Thermal Analysis and Electron Microscopy StudiesD.R. Acosta*, O. Novaro*, T. López*, R. Gómez*
(*Instituto de Física-UNAM, *Universidad Autónoma Metropolitana-Iztapalapa)

Zirconium oxide dispersed in silica was synthesized by the co-gelation of tetraethoxysilane and zirconium acetate. For the gelation, acid and basic media were used. The final zirconia concentration was around 6.7 wt.%. Differential thermal analysis, thermogravimetric analysis, as well as electron microscope techniques were used for the characterization of the samples. It was found that the stabilization of the crystalline phases depends on the preparation conditions and thermal treatments. Tetragonal and monoclinic ZrO₂ phases were identified in basic preparations. However, in acidic samples only low temperature tetragonal phase was identified.

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Tribology of Diamond-Like Carbon Sliding Against Itself, Silicon Nitride and SteelK. Jia, Y.Q. Li, T.E. Fischer, B. Gallois
(Stevens Institute of Technology)

Diamond-like carbon (DLC) films were deposited on (100) silicon wafers and silicon nitride balls by RF plasma-assisted chemical vapor deposition at a pressure of 700 mTorr and a substrate temperature of 360 K. The friction coefficient and the wear rates were measured using a pin-on-disk tribometer in 40% humid and dry air. Friction coefficients are near 0.05 in all cases measured. In dry air, the wear of silicon nitride and steel against DLC is below measurement capability because of a protecting DLC transfer layer, and wear of DLC is 2.5.10⁻⁸ mm³/Nm against silicon nitride and 6.5.10⁻⁹ mm³/Nm against steel. In humid air, the DLC transfer layer does not adhere to the solids and wear of both bodies is larger. Unmeasurable wear is obtained when DLC slides against itself in humid air; the wear rate is 5.10⁻⁹ mm³/Nm in dry air. These results are interpreted in terms of the properties of a friction-induced transformation of the surface layer of DLC.

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Tunability of the Dielectric Constant of Ba_{0.1}Sr_{0.9}TiO₃ Ceramics in the Paraelectric StateA. Outzourhit, J.U. Trefny, T. Kito, B. Yazar
(Colorado School of Mines)

Ba_{1-x}Sr_xTiO₃ (x=0.9) ferroelectric ceramics were prepared successfully using a new wet technique and their structure and dielectric properties were compared with those synthesized by the solid-state reaction

method. The voltage dependence of the dielectric constant in the paraelectric phase was examined. It was found that the dielectric constants of these materials, prepared by both methods, exhibit large changes with applied voltage in the paraelectric phase. Tunability (the percentage change of the dielectric constant from its zero-bias value in the presence of a dc-biasing electric field) was observed to exceed 30% at only 1.7 kV/cm at 77 K in the samples prepared by the solid-state reaction method. The tunability was found to decrease dramatically as the operating temperatures increased above the Curie point. These observations are interpreted in light of an existing phenomenological theory. The dependence of the dielectric constant in the paraelectric state upon a dc-biasing electric field is also demonstrated as a potential method for the characterization of dielectric non-uniformities in ferroelectric ceramics.

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Effect of Grain Size and Mechanical Processing on the Dielectric Properties of BaTiO₃

B.W. Lee, K.H. Orr
(Hanyang University)

Dielectric properties of polycrystalline BaTiO₃ ceramics having grain sizes of 1 to 40 μm have been studied. Fine-grained ceramic BaTiO₃ of 1 μm average grain size has 90° domains and has shown higher dielectric constant, lower ferroelectric transition temperature (T_c), and lower transition energy than coarser grained material. 90° domain switching was preferentially produced in the fine-grained BaTiO₃ as a result of abrasion. For the fine-grained BaTiO₃, the dielectric constant decreased with one-dimensional pressure, whereas, for the coarse-grained material, the dielectric constant increased before decreasing with the pressure. The one-dimensional pressure resulted in increased T_c of both the fine- and coarse-grained BaTiO₃ with the effect being the greatest for the coarse-grained material. The relationship between these results and internal stress, and the effect of external pressure imposed on internally stressed lattice were discussed.

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Alumina Aerogel Catalysts Prepared by Two Supercritical Drying Methods Used in Methane Combustion

Y. Mizushima, M. Hori
(Colloid Research Institute)

Palladium-supported alumina aerogels were prepared by two different supercritical drying methods. In one method, an alumina wet gel was dried under supercritical conditions of ethanol in an autoclave. In the other, the aerogel was supercritically dried by extracting ethanol using carbon dioxide in an extractor. The Pd-supported alumina aerogel prepared in the autoclave exhibited a high specific surface area of 112.8 m²/g after firing at 1200°C for 5 h, while the other had a specific surface area of only 5.2 m²/g due to α alumina transformation.

Their catalytic properties for methane combustion were measured. The Pd-supported alumina aerogel prepared in the autoclave combusts methane perfectly at temperatures 50–60°C lower than the other.

Palladium particles on the alumina aerogel prepared in the autoclave contained palladium oxide, while those of that prepared in the CO₂ extractor contained only palladium metal.

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Temperature Calculation for Laser Irradiation of Sol-Gel Films on Oxide Substrates

D.J. Taylor, D.P. Birnie III, B.D. Fabes
(University of Arizona)

A model for estimating the temperature rise in a laser irradiated oxide target is developed and applied to laser-firing of sol-gel films on oxide substrates. The model incorporates a continuous-wavelength (CW) gaussian laser beam translated across a sol-gel film on a semi-infinite substrate. Heat effects due to phase changes are assumed to be

absent. In addition, the laser energy is assumed to be absorbed primarily in the substrate material (since many sol-gel films are much thinner than the absorption depth of typical laser wavelengths). The model also takes into account the temperature dependence of the thermal properties of the substrate. The predictions from the model are compared to experimental data from various laser firing experiments. The temperatures predicted by the model are shown to agree well with experimental results.

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Frequency-Dependent Electromechanical Properties of Sol-Gel Deposited Ferroelectric Lead Zirconate Titanate Thin Layers: Thickness and Processing Effects

J-F. Li, D. Viehland, C.D.E. Lakeman, D.A. Payne
(University of Illinois at Urbana-Champaign)

The electromechanical properties of sol-gel derived ferroelectric Pb(Zr_{0.53}Ti_{0.47})O₃ (PZT 53/47) thin layers deposited on silicon were determined as a function of field-strength, measurement frequency, and total thickness. Both electrically-induced strains (ε) and piezoelectric properties (d₃₃) were characterized by interferometry. Dielectric spectroscopy and polarization switching (P-E) measurements were determined for comparative purposes. An asymmetry between forward and the reverse bias conditions in the ε-E displacements was found for both 5-layer deposited and 9-layer deposited structures. However, no asymmetry was observed in the P-E hysteresis characteristics. In addition, the electrically-induced strains and the piezoelectric response were found to be dependent on measurement frequency. No significant frequency dependence was observed in the polarization or dielectric responses. The results are discussed in terms of a possible clamping effect for polarization switching.

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Effects of Implantation Temperature on the Structure, Composition and Oxidation Resistance of Aluminum-Implanted SiC

Z. Yang*, H. Du*, M. Libera*, I.L. Singer*
(*Stevens Institute of Technology, *Naval Research Laboratory)

α-SiC crystals were implanted with aluminum to a high dose at room temperature or 800°C. Transmission electron microscopy showed that SiC was amorphized by room temperature implantation but remained crystalline after 800°C implantation. Crystalline aluminum carbide was formed and aluminum redistribution took place in SiC implanted at 800°C. Implanted and unimplanted crystals were oxidized in 1 atm flowing oxygen at 1300°C. Amorphization led to accelerated oxidation of SiC. The oxidation resistance of SiC implanted at 800°C was comparable with that of pure SiC. The oxidation layers formed on SiC implanted at both temperatures consisted of silica embedded with mullite precipitates. The phase formation during implantation and oxidation is consistent with thermodynamic predictions. The results from our current and earlier studies suggest that there exists an optimum range of implantation temperature, probably above 500° but below 800°C, which preserves the substrate crystallinity and retains the high aluminum dosage, for the enhancement of oxidation resistance of SiC.

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Growth and Oxidation of Boron-Doped Diamond Films

E.N. Farabaugh*, L. Robins*, A. Feldman*, C.E. Johnson*
(*National Institute of Standards and Technology, *Naval Air Warfare Center)

Boron-doped diamond films have been grown by the hot filament chemical vapor deposition process. The feed gas was a mixture of argon, bubbled through a solution of B₂O₃ in ethanol, and hydrogen. The highest growth rate was 0.7 μm/h. The boron concentration in the films depended on the concentration of B₂O₃ in the ethanol. The highest boron doping level, as measured by secondary ion mass spectroscopy, was 6300 atomic ppm. Raman spectroscopy and x-ray

diffraction both confirmed the presence of crystalline diamond in the films. The frequency of the diamond Raman line decreased with increasing boron concentration. This shift may arise from an interaction of the charged carriers (holes) produced by the boron doping and the Raman-active optic phonon. The oxidation rates of doped and undoped films were measured by thermogravimetric analysis at 700°C in flowing high purity oxygen. Films with a boron concentration of 6300 ppm oxidized at one tenth the rate of undoped diamond. A layer of B₂O₃, detected on the surface of an oxidized B-doped film, is believed to act as a protective barrier that decreases the oxidation rate.
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Diamond Nucleation and Growth on Reactive Transition-Metal Substrates

W. Zhu, P.C. Yang, J.T. Glass, F. Arezzo
 (North Carolina State University)

Diamond deposition on group VIII transition metals of Cr, Mn, Fe, Co and Ni has been achieved by a multi-step chemical vapor deposition process consisting of (i) seeding the substrate with diamond powders, (ii) annealing the seeded substrate in hydrogen at high temperatures, and (iii) diamond nucleation and growth. It was found that high quality diamond can be grown on these substrates, and the often accompanied graphite formation, which has been the main obstacle in the deposition of diamond on these metal surfaces, can be largely suppressed by the above step-deposition procedure. This technique was further extended to the processes of depositing diamond on steels and Co-bonded WC materials.

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Evidence for Glide and Rotation Defects Observed in Well-Ordered Graphite Fibers

M. Endo*, K. Oshida*, K. Kobori*, K. Takeuchi*, K. Takahashi*, M.S. Dresselhaus*
 (*Shinshu University, *Massachusetts Institute of Technology)

New structural features observed in heat-treated vapor grown carbon fibers (VGCF's), produced by the thermal decomposition of hydrocarbon vapor, are reported using image analysis of the lattice plane structure observed by transmission electron microscopy (TEM) and atomic force microscopy (AFM). The TEM lattice image of well-ordered graphite fibers (heat-treated VGCF at 2800°C) was treated by a 2-dimensional fast Fourier transform (FFT), showing sharp bright spots associated with the 002 and 100 lattice planes. The heat-treated VGCF's consist of a polygonally-shaped shell, and the long and short fringe structures in the TEM lattice image reflect the 002 and 100 lattice planes, respectively. From this analysis, new facts about the lattice structure are obtained visually and quantitatively. The 002 lattice planes remain and are highly parallel to each other along the fiber axis, maintaining a uniform interlayer spacing of 3.36 Å. The 100 lattice planes are observed to make several inclined angles with the 002 lattice planes relative to the plane normals, caused by the gliding of adjacent graphene layers. This work visually demonstrates coexistence of the graphitic stacking as well as the gliding of the adjacent graphene layers, with a gliding angle of about 3–20°. These glide planes are one of the dominant stacking defects in heat-treated VGCF's. On the other hand, turbostratic structural evidence was suggested by AFM observations. The structural model of coexisting graphitic, glide and turbostratic structures is proposed as a transitional stage to perfect three-dimensional stacking in the graphitization process. These structural features could also occur in common carbons and in carbon nanotubes.

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Fabrication of Carbon-Carbon Composites by Forced Flow-Thermal Gradient Chemical Vapor Infiltration (FCVI)

S. Vaidyaraman, W.J. Lackey, G.B. Freeman, P.K. Agrawal, M.D. Langman
 (Georgia Institute of Technology)

Carbon fiber-carbon matrix composites were fabricated using the forced flow-thermal gradient chemical vapor infiltration (FCVI) process. The preforms for the infiltration were prepared by stacking 40 layers of carbon cloth in a graphite holder. The preforms were infiltrated with

carbon using propylene or methane as a reactant, with hydrogen as a diluent. Composites with porosities as low as 7% have been processed within 8–12 h. The highest deposition rate obtained in the present study was ~3 μm/h which is more than an order of magnitude faster than the typical value of 0.1–0.25 μm/h for the isothermal infiltration process.

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Composites Based on Thermally Hyper-Conductive Vapor Grown Carbon Fiber

J.-M. Ting, M.L. Lake, D.R. Duffy
 (Applied Sciences, Inc.)

Aluminum matrix composites and carbon/carbon composites based on vapor grown carbon fiber (VGCF) were fabricated for analysis of thermophysical properties. Due to the highly graphitic nature of VGCF, the resulting composites exhibit values of thermal conductivity that have not been achieved by using any other carbon fibers, and thus represent new materials for thermal management in applications such as packaging for high-power, high-density electronic devices. In the aluminum matrix VGCF composites, a thermal conductivity of 642 W/m-K was obtained by using a VGCF loading of only 36.5 volume percent. For VGCF/C composites, thermal conductivity of 910 W/m-K has been observed, a value which is more than a factor of two higher than that of copper. Based on the observed thermal conductivity of VGCF/Al composites and VGCF/C composites, the room temperature thermal conductivity of VGCF in the composite was calculated to be 1460 W/m-K and 1600 W/m-K, respectively.

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A Self-Constraint Strengthening Mechanism and its Application to Seashells

X.F. Yang
 (Auburn University)

A self-constraint strengthening mechanism for multilayered brittle materials is proposed. The strengthening is a result of the self-constraint of the individual layers on each other and no additional reinforcements are needed. The proposed model predicts that when individual brittle layers are stacked and properly "glued" together with a weak interphase, each layer will be ensured a minimum tensile strength, regardless of the flaw size in the individual layers. Estimation of the minimum strength using this model yields an apparently close agreement with the measured values for one type of nacreous structure reported in the literature. It is also predicted that low-strength ceramic sheets, which might be produced by some low-cost fabrication techniques, can be used to construct high-strength man-made nacreous ceramics.

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Errors Associated with Depth-Sensing Micro-Indentation Tests

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In the determination of mechanical properties by ultra-microindentation, various errors can appear. The paper analyzes various sources of errors in estimation of elastic modulus and hardness. These errors arise from uncertainties of the indenter geometry and properties, as well as measuring instrument limitations and errors, such as the minimum detectable load, compliance and noise of the system. Other sources of errors are: thermal drift, shape of the impression and scatter of properties of the tested material. Characteristic features and magnitude of individual kinds of errors are discussed, together with formulas and recommended methods for their reduction.

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Surface Chemical States of Barium Titanate: Influence of Sample Processing

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The composition and chemistry of the near-surface region of BaTiO₃ has been studied using x-ray photoelectron spectroscopy. It is found that the Ba3d photoelectron peak shows two chemical states,

one of which is attributed to the bulk perovskite and the other to a special surface state unrelated to contamination. The bulk component is reduced and the surface component increases when the material is annealed at high temperatures (either in reducing or oxidizing atmosphere). Both the components are unaltered if the sample is exposed to air, solvents or water—processes which lead to adsorption of impurities. The surface peak, therefore attributed to a relaxation-related and not contamination-related state, has been compared with those in other Ba-containing oxides. The oxygen photoelectron peak consists of a normal perovskite peak typical of most titanates and a higher energy component clearly related to surface contamination. Annealing in reducing atmosphere results in drastically different optical and electrical properties, and in chemical reduction of some Ti^{4+} ions to Ti^{3+} . The overall stoichiometry, however, does not change with annealing atmosphere. These results have been discussed in light of our current understanding of this and other related oxides.

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Pt/Ti/SiO₂/Si Substrates

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Pt/Ti/SiO₂/Si structures have been studied to investigate the structural, chemical, and microstructural changes that occur during annealing. Grain growth of the as-deposited Pt columns was observed after annealing at 650°C, and extensive changes in the Pt microstructure were apparent following a 750°C anneal for 20 minutes. In addition, two types of defects were identified on the surfaces of annealed substrates. Defect formation was retarded when the surface was covered with a ferroelectric film. Concurrent with the annealing-induced Pt microstructure changes, Ti from the adhesion layer between the Pt and the SiO₂ migrated into the Pt layer and oxidized. It was shown with spectroscopic ellipsometry and Auger electron spectroscopy that for long annealing times, the titanium oxide layer can reach the Pt surface. Consequently, at the processing temperatures utilized in preparing many ferroelectric thin films, the substrate is not completely inert or immobile. The changes associated with Ti migration could be especially problematic in techniques which require the substrate to be heated prior to film deposition.

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Variant Structure in Metal-Organic-Chemical-Vapor-Deposition Derived SnO₂ Thin Films on Sapphire (0001)

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Tin oxide (SnO₂) thin films were deposited on sapphire (0001) substrate by metal-organic chemical vapor deposition at temperatures of 600 and 700°C. The microstructure of the deposited films was characterized by x-ray diffraction and high resolution transmission electron microscopy. At the growth conditions studied, films were single-phase rutile and epitaxial, but showed variant structures. Three distinct in-plane epitaxial relationships were observed between the films and the substrate. A crystallographic model is proposed to explain the film morphology. This model can successfully predict the ratio of the width to the length of an averaged grain size based upon the lattice mismatch of the film-substrate interface.

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Stable Thin Film Resistors Using Double Layer Structure

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Highly stable bilayer thin film resistors, which consist of an underlying layer of tantalum nitride and of a capping layer of ruthenium oxide, were developed by taking advantage of the desired characteristics of two different materials in a single system. The resistors fabricated in such a way were highly stable under power loading or thermal cycling. Resistors with one digit temperature coefficient of resistance could be easily controlled by the layer thickness ratio of the tantalum

nitride to the ruthenium oxide and the *ex-situ* annealing temperature or duration. Auger electron spectroscopy depth profile on the thin films indicates that the ruthenium oxide layer is well defined for the as-deposited form. Nevertheless, interdiffusion takes place after thermal treatment of the bilayer which is used to tune the temperature coefficient of resistance and to stabilize the resistance of the resistors.

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The Characterization of High-Performance PAN-based Carbon Fibers Developed by Continuous Carbonization and Air Oxidation

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The properties of four kinds of Type II carbon fibers, which had been pre-carbonized at 300°, 400°, 500°, and 600°C, respectively, during two-stage continuous carbonization, were measured after being air oxidized for periods of one to six minutes at 550°C. The effects of pre-carbonization temperature on mechanical properties, density, morphology, elemental composition, and microstructure of the carbon fibers during the air oxidation are discussed in this article. The pre-carbonization process strongly affected the surface properties and mechanical properties of the final oxidized carbon fibers. The carbon fibers developed from the different pre-carbonization temperatures all had different structures. The carbon fibers which had been pre-carbonized at 300°C had a more ordered structure than other fibers after air oxidation. These carbon fibers also had a higher performance than the other fibers. Carbon fibers also showed different oxidation behaviors caused by differences in surface morphology resulting from each different pre-carbonization temperature. Optimum conditions not only improved the tensile strength and modulus, but also increased the density and oxygen content. Experimental results showed that the tensile strength of the carbon fibers pre-carbonized at 300°C increased from 2.4 Gpa to 4.3 Gpa (80%) after 6 min oxidation at 550°C.

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Plan-View Microstructures of Co/Ru Bilayers

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Plan-view microstructures of two Co/Ru bilayers with a composition $[Co_{12}Ru_{45}]_2$ and $[Co_{40}Ru_{35}]_2$ have been studied by conventional and high-resolution electron microscopy. Large differences in electron diffraction and image contrast between the two bilayers were observed, which are recognized as the microstructural variations during the relaxation of large coherent planar strains when the Co layers wet coherently or semicoherently the Ru layers. For the $[Co_{12}Ru_{45}]_2$ bilayer, the Co layers are unrelaxed from the Ru layers: only one set of electron diffraction pattern was observed and the image consists of three types of contrasts which are closely related with either the generation and movement of misfit dislocations or large coherent strains. For the $[Co_{40}Ru_{35}]_2$ bilayer, the Co layers are relaxed basically from the Ru layers: two sets of electron diffraction patterns with double diffraction spots were observed and the image consists of small irregular areas with Moiré fringe dots.

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Structural, Morphological and Magnetic Study of Nanocrystalline Cobalt-Copper Powders Synthesized by the Polyol Process

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Nanocrystalline Co_xCu_{100-x} ($4 \leq x \leq 49$ at.%) powders were prepared by the reduction of metal acetates in a polyol. The structures of powders were characterized by x-ray diffraction (XRD), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM), extended x-ray absorption fine structure (EXAFS) spectroscopy, solid state nuclear magnetic resonance (NMR) spectroscopy, and vibrating sample magnetometry (VSM). As-synthesized powders were composites consisting of nanoscale crystallites of face-centered-cubic (fcc) Cu and metastable face-centered-cubic (fcc) Co.

Complementary results of XRD, HRTEM, EXAFS, NMR, and VSM confirmed that there was no metastable alloying between Co and Cu. The NMR data also revealed that there was some hexagonal-closed-packed (hcp) Co in the samples. The powders were agglomerated, and consisted of aggregates of nanoscale crystallites of Co and Cu. Upon annealing, the powders with low Co contents showed an increase in both saturation magnetization and coercivity with increasing temperature. The results suggested that during preparation the nucleation of Cu occurred first, and the Cu crystallites served as nuclei for the formation of Co.

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A Study on the Mechanism of Amorphous Phase Formation by Interdiffusion in Ni/Zr Multilayers

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The mechanism of the solid-state amorphization has been investigated by means of the microstructural studies on the evolution of Ni/Zr diffusion couples, prepared at different sputtering pressures, during short time heating at high temperature. In the sample deposited at 8 mTorr compared to that at 3 mTorr, the possibility of the supersaturation sequence prior to amorphization is observed, and the amorphous phase grows extremely fast with diffuse interface. High-resolution TEM image shows that the amorphous phase preferentially penetrates along the Zr grain boundary into the Zr layer and selectively grows from the grain boundary into the region of Zr grain with many defects. From the results, the importance of interstitial diffusion has been discussed and a modified mechanism has been suggested.

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Estimation of Phase Separation Rates of PbO-B₂O₃ Melts

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The rate of liquid-liquid phase separation was experimentally studied in PbO-B₂O₃ system. The *in-situ* measurements were made by observing the melts with a video camera continuously as the melts were cooled down from homogenization temperatures at a rate of 2.5°C/min. The time interval between the beginning and the completion of the darkening of the visual field was determined as the measure of the separation rate. The phase separation rate was estimated to be at least 900 times larger than that of the metastable phase separation below the liquidus.

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X-ray Photoelectron Spectroscopy Studies of Bond Structure Between Polyvinyl Alcohol and a Titanate Cross Coupling Agent

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Chemical interactions between polyvinyl alcohol (PVA) and tri-ethanol amine titanate chelate were studied by x-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). The titanate chelate cross coupled the PVA solution and produced a viscous gel. The gel had a three dimensional network structure containing -C_{PVA}-O-Ti-O-C_{PVA}- organic complexes. A new C(1s) signature at 285.7 eV and an O(1s) signature at 531.25 eV were associated with the formation of these complexes. The water of the PVA solution was physically retained in the gelled structure and was readily available for chemical reactions. The removal of this entrapped water was irreversible and lead to a collapsed film of Ti-cross linked PVA.

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