JMR Abstracts

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ABSTRACTS

SPECIAL SECTION CARBON NANOTUBES

Carbon nanotube based molecular electronic devices
M. Menon*, D. Srivastava+
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Complex three-point junctions of single-walled carbon nanotubes are proposed as building blocks of nanoscale electronic devices. Both T- and Y-junctions, made up of tubes with differing diameters and chiralities, are studied as prototypes. All the proposed complex junctions have been found to be local minima of the total energy on relaxation with a generalized tight-binding molecular dynamics scheme.

Order No.: JA809-001

Do carbon nanotubes spin when bundled?
Y-K. Kwon*, D. Tománek*, Y.H. Lee*+, K.H. Lee*#, S. Saito§
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Using *ab initio* and parametrized techniques, we determine the equilibrium structure of an ordered "bundle" of (10,10) carbon nanotubes. Due to the small inter-tube interaction and lattice frustration, we predict a very soft libration mode to occur at $\nu \approx 12$ cm^{-1}. This mode is predicted to disappear above the orientational melting temperature which marks the onset of free tube rotations about their axis. We discuss the effect of the weak inter-tube coupling and orientational disorder on the electronic structure near the Fermi level.

Order No.: JA809-002

Morphologies and related electronic properties of carbon nanotubes
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The electronic structures of different morphologies of carbon nanotubes are investigated within either *tight-binding* or *ab initio* frameworks. After a brief description of the electronic properties of the "perfect" rolled-up graphene sheet, nanotubes containing pentagon-heptagon pairs, tips (hemispherical caps), sp^3-like lines responsible for polygonization, multi-shell and solid-state packings (bundles) are studied in order to point out the influence of such defects on the electronic states of the "perfect" cylinders. Most of the time, a structural optimization was performed on the atomic topology, prior to the calculation of the electronic properties. Connections with experimental facts are indicated as frequently as possible.

Order No.: JA809-003

Scanning tunneling microscopy and spectroscopy studies of single wall carbon nanotubes

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Scanning tunneling microscopy and spectroscopy have been used to characterize the atomic structure and tunneling density of states of individual single-wall carbon nanotubes (SWNTs) and ropes containing many SWNTs. Analysis of atomically-resolved SWNT images shows that the nanotubes consist of a wide range of diameters and helicities with no one structure clearly dominant. Tunneling spectroscopy measurements made simultaneously on atomically-resolved SWNTs exhibit semiconducting and metallic behavior that depend predictably on helicity and diameter. In addition, the band gaps of the semiconducting tubes were also found to depend inversely on diameter. These results are compared to theoretical predictions, and the implications of these studies as well as important future directions are discussed.

Order No.: JA809-004

Local electronic structure in ordered aggregates of carbon nanotubes: STM/STS study

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The recent application of tunneling probes in electronic structure studies of carbon nanotubes has proven both powerful and challenging. Using STM and STS, local electronic properties in ordered aggregates of carbon nanotubes (multi-walled nanotubes and ropes of single-walled nanotubes) have been probed. In this report, we present evidence for interlayer (concentric tube) interactions in multi-walled tubes and tube-tube interactions in single-walled nanotube ropes. The spatially resolved, local electronic structure, as determined by the local density of electronic states, is shown to clearly reflect tube-tube interactions in both of these aggregate forms.

Order No.: JA809-005

Resonant Raman effect in single-wall carbon nanotubes

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A resonant Raman study of single-wall carbon nanotubes (SWNT) using several laser lines between 0.94 and 3.05 eV is presented. A detailed lineshape analysis shows that the bands associated with the nanotube radial breathing mode are composed of a sum of individual peaks whose relative intensities depend strongly on the laser energy, in agreement with prior work. On the other hand, the shape of the Raman bands associated with the tangential C-C stretching motions does not depend significantly on the laser energy for laser excitation energies in the ranges 0.94–1.59 eV and 2.41–3.05 eV. However, new C-C stretching modes are observed in the spectra collected using laser excitations in the 1.9–2.0 eV range. The new results are discussed in terms of the difference between the 1D electronic density of states for the semiconducting and metallic carbon nanotubes.

Order No.: JA809-006

Raman scattering study of coalesced single-walled carbon nanotubes

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High-temperature heat treatment of single-wall carbon nanotube bundles in flowing H_2 was used to produce a significant fraction (~40%) of diameter-doubled, or coalesced tubes with a mean diameter corresponding to that of ~(20,20) tubes. At three laser excitation wavelengths (514.5, 647 and 1064 nm), a reduction in the Raman scattering intensity of the strong radial and tangential modes was observed in the H_2-treated sample, consistent with the reduced fraction of tubes in the sample after coalescence. However, using 488 nm excitation, little or no change is observed in the Raman spectrum after the H_2-treatment, suggesting that this excitation wavelength couples only to chiral symmetry tubes. Using the 647 nm excitation, the effect of H_2-treatment on the tangential band is quite unique, and a significant change in the shape of the tangential band was observed. Our lineshape analysis, and other results reported in this issue, suggest that this unique change of shape is due to lost scattering intensity from metallic tubes partially compensated by tangential mode scattering from the coalesced tubes. The normally prominent radial breathing mode band, which would be expected at ~90 cm^{-1} for ~(20,20) tubes, was not observed, indicating that these larger diameter tubes do not exhibit strong resonant scattering, at least at any of the wavelengths used in this study.

Order No.: JA809-007

Optical properties of MS_2 (M = Mo, W) inorganic fullerene-like and nanotube material: Optical absorption and resonance Raman measurements

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The optical properties of inorganic fullerene-like and nanotube MS_2 (M = Mo, W) material are studied through absorption and resonance Raman, and compared to those of the corresponding bulk material. The absorption measurements show that the semiconductivity is preserved. Nevertheless, the positions of the excitons are altered in comparison to the bulk. The Raman spectra of the nanoparticles shows a close correspondence to that of the bulk. However, the first-order peaks are broadened and, under resonance conditions, new peaks are observed. The new peaks are assigned to disorder-induced zone edge phonons.

Order No.: JA809-008

Evaluation of Young's modulus of carbon nanotubes by micro-Raman spectroscopy

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Micro-Raman spectroscopy is used to monitor the cooling-induced compressive deformation of carbon nanotubes embedded in an epoxy matrix. The Young's modulus of single- and multi-wall nanotubes may then be derived from a concentric cylinder model for thermal stresses, using the D*-band shift for each tube type. The resulting values of the elastic moduli are in very good agreement with predicted theoretical values, and with the only published experimental data set [Treacy et al., Nature **381**, 689 (1996)].

Order No.: JA809-009

Chemical attachment of organic functional groups to a single-walled carbon nanotube material

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We have subjected single-walled carbon nanotube materials (SWNTMs) to a variety of organic functionalization reactions. These reactions include radioactive photolabeling studies using diradical and nitrene sources, and treatment with dichlorocarbene and Birch reduction conditions. All of the reactions provide evidence for chemical attachment to the SWNTMs, but because of the impure nature of the starting materials we are unable to ascertain the site of reaction. In the case of dichlorocarbene we are able to show the presence of chlorine in the SWNT bundles, but as a result of the large amount of amorphous carbon that is attached to the tube walls, we cannot distinguish between attachment of dichlorocarbene to the walls of the SWNTs and reaction with the amorphous carbon.

Order No.: JA809-010

Structure and oxidation patterns of carbon nanotubes

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We discuss the oxidation of carbon nanotubes and how it is affected by structure and geometry. While graphite is known to oxidize primarily at defects to create etch pits, nanotubes have additional structural features such as high curvature, helicity, and contain five and seven membered rings which modify the initiation and propagation of oxidation. Oxidation does not necessarily start at the tip of the tubes, and there are pronounced

differential oxidation rates between layers which depend on the helicity of the individual shells.
Order No.: JA809-011

Tailoring carbon nanoclusters to desired morphologies
J. Jiao, S. Seraphin
(University of Arizona)

The preparation and structural characterization of carbon nanoclusters of different morphologies produced by three different methods and under a variety of conditions is reported. In a comparative manner, the growth phenomena and structural properties of carbon nanoclusters are investigated as synthesized by a) the high temperature (~3000°C) and high carbon-content process of the conventional arc-discharge, b) the high temperature but low carbon-content process of the modified arc-discharge, and finally c) the relatively low temperature (~500°C) process of Ni catalytic disproportionation of carbon monoxide.
Order No.: JA809-012

Processing of carbon nanotube reinforced aluminum composite
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Carbon nanotube reinforced aluminum (Al) composites were produced by hot-press and hot-extrusion methods. The interfacial structure between the carbon nanotube and Al was examined using a transmission electron microscope (TEM) and the mechanical properties were measured by a tensile test. TEM observations have shown that the nanotubes in the composites are not damaged during the composite preparation and that no reaction products at the nanotube/Al interface are visible after annealing for 24 h at 983 K. The strength of the composites is only slightly affected by the annealing time at 873 K, while that of the pure Al produced in a similar powder metallurgy process significantly decreases with time. These studies are considered to yield experimental information valuable for producing high performance composites.
Order No.: JA809-013

COMMUNICATIONS

Segregation of vanadium at the WC/Co interface in VC-doped WC-Co
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Morphology of carbide grain in WC-12wt.%Co-0.5wt.%VC was examined by HREM and EDS with a special interest in the segregation of V at the WC/Co interfaces. A small addition of VC in WC-Co is effective to suppress the grain growth of carbide grains. HREM observation revealed that the WC/Co interfaces are facetted and consist of mainly two kinds of habit planes, (1010) and (0001), respectively. EDS analyses clearly showed the segregation of doped V along the interfaces. In addition, the concentration of segregated V is higher at the (0001) type habit plane than the (1010) one. The retardation of the grain growth of carbide grains in the V_c-doped WC-Co is closely related to the formation of the facetted WC/Co interface.
Order No.: JA809-014

Screen printed Cu_3BiS_3-polyacrylic acid composite coatings
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A technique for preparing electrically conductive coatings of Cu_3BiS_3 powder in polyacrylic acid matrix is presented. Bi_2S_3 powder obtained by chemical precipitation was introduced into a freshly prepared CuS chemical deposition bath. After the initial nucleation period, CuS started to deposit on the Bi_2S_3 surface. The as obtained CuS-Bi_2S_3 powder was mixed with polyacrylic acid aqueous solution and the resulting mixture was used as a paste to form a screen printed composite coating. Up to 200°C the film behaves like a simple CuS film; the sheet resistance is around 100 Ω and the crystallized phase in the composite is CuS (Covellite). When the temperature is equal or higher than 250°C, atomic diffusion at the CuS-Bi_2S_3 interface is promoted, leading to the formation of the ternary compound Cu_3BiS_3 (Wittichenite) in the composite film. The formation of the compound depends on the temperature, relative abundance of the Bi_2S_3 and CuS components in the CuS-Bi_2S_3 pigment as well as on the annealing atmosphere.
Order No.: JA809-015

Oxidation of Sn thin films to SnO_2. Micro-Raman mapping and x-ray diffraction studies
L. Sangaletti, L.E. Depero, B. Allieri, F. Pioselli, E. Comini, G. Sberveglieri, M. Zocchi
(Università di Brescia)

The oxidation of tin layers deposited onto alumina substrates is investigated with the aim to identify the different steps of the process and obtain information on the sample homogeneity, phase segregation, and degree of oxidation. It is shown that at least three phases co-exist at 450°C: Sn, SnO, and SnO_2 and remarkable inhomogeneities, already visible at an optical inspection, are found in the thin film. A micro-Raman mapping of the layer shows that these inhomogeneities are related to the presence of different Sn oxidation states, as evidenced by the inhomogeneous distribution of SnO and SnO_x Raman bands. The thin film becomes homogeneous after annealing treatments above 550°C, where only the SnO_2 cassiterite phase is detected.
Order No.: JA809-016

Role of yttria-stabilized zirconia produced by ion-beam-assisted-deposition on the properties of RuO_2 on SiO_2/Si
Q.X. Jia, P. Arendt, J.R. Groves, Y. Fan, J.M. Roper, S.R. Foltyn
(Los Alamos National Laboratory)

Highly conductive biaxially textured RuO_2 thin films were deposited on technically important SiO_2/Si substrates by pulsed laser deposition, where yttria-stabilized zirconia (YSZ) produced by ion-beam-assisted-deposition (IBAD) was used as a template to enhance the biaxial texture of RuO_2 on SiO_2/Si. The biaxially oriented RuO_2 had a room-temperature resistivity of 37 μΩ-cm and residual resistivity ratio above 2. We then deposited $Ba_{0.5}Sr_{0.5}TiO_3$ thin films on RuO_2/IBAD-YSZ/SiO_2/Si. The $Ba_{0.5}Sr_{0.5}TiO_3$ had a pure (111) orientation normal to the substrate surface and a dielectric constant above 360 at 100 kHz.
Order No.: JA809-017

ARTICLES

Synthesis, structure, and superconducting properties of tantalum carbide nanorods and nanoparticles
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(Carnegie Mellon University)

Tantalum carbide nanorods and nanoparticles have been synthesized using a vapor-solid reaction path starting with CVD grown carbon nanotube precursors. Their structures were studied using XRD, TEM, and HRSEM. Superconducting properties were characterized using SQUID magnetometer. For reactions at lower temperatures, carbide nanorods which replicate the ~14 nm diameter of the precursor carbon nanotubes are observed. For higher temperature reactions, coarsened carbide nanoparticles (100 ~ 250 nm) are observed which have spherical or cubic-faceted morphologies. A morphological Rayleigh instability is postulated as initiating the transition from nanorod to nanoparticle morphologies. Stoichiometric bulk TaC crystallizes in the rock salt structure and has a superconducting transition temperature of 9.7 K. In TaC nanorods and nanoparticles, the superconducting properties correlate with the lattice parameter. Nanoparticles with a little higher lattice parameter than the ideal one show higher T_c and higher fields at which the superconductivity disappears, than stoichiometric bulk TaC.
Order No.: JA809-018

Shape forming simultaneous with J_c enhancement in $REBa_2Cu_3O_7$ superconductors
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(Defence Metallurgical Research Laboratory)

An infiltration and growth (IG) process which enables the fabrication of three dimensional (3D) components of $REBa_2Cu_3O_7$ (RE = Y, Gd, Sm, Nd, etc.) (RE-123) superconductors with a highly textured microstructure

is described. The advantages of the process in comparison with conventional melt processing are discussed. The process has been demonstrated to yield highly favorable microstructures in the case of Y-123 processed in air, as well as in the case of Gd-123 processed in reduced oxygen partial pressure.
Order No.: JA809-019

Effect of the nanoparticles on the structure and crystallization of amorphous silicon thin films produced by rf glow discharge
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Thin films of nanostructured silicon (ns-Si:H) were deposited by plasma-enhanced chemical vapor deposition in the presence of silicon nanoparticles at 100°C substrate temperature using silane and hydrogen gas mixture under continuous wave (cw) plasma conditions. The nanostructure of the films has been demonstrated by diverse ways: transmission electron microscopy, Raman spectroscopy and x-ray diffraction, which have shown the presence of ordered silicon clusters (1–2 nm) embedded in an amorphous silicon matrix. Due to the presence of these ordered domains, the films crystallize faster than standard hydrogenated amorphous silicon samples, as evidenced by electrical measurements during the thermal annealing.
Order No.: JA809-020

Cathodoluminescence, photoluminescence and optical absorbance spectroscopy of aluminum gallium nitride ($Al_xGa_{1-x}N$) films
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Aluminum gallium nitride ($Al_xGa_{1-x}N$) films, grown by metal-organic chemical vapor deposition on sapphire, were characterized by low-temperature cathodoluminescence (CL) and photoluminescence (PL), and room-temperature optical absorbance. The aluminum fractions are estimated to range from x = 0 to x = 0.444. Most films were silicon-doped. The absorption spectra have an Urbach (exponential) form below the bandgap. The width of the Urbach edge, E_U, increases with Al fraction, x, as $E_U = (0.045 + 0.104x)$eV. The luminescence (CL or PL) spectra show a relatively narrow band-edge peak and a broad deep-level peak. The full-widths at half-maximum of the band-edge CL peaks (measured at T = 15 K) are remarkably similar to the Urbach absorption widths, E_U (measured at T = 300 K). PL spectra were obtained from the top surfaces and the film-substrate interfaces of several films. The interface PL spectra of some films show an extra peak 0.15 eV to 0.45 eV below the bandgap, which is ascribed to structural defects or impurity phases localized near the interface. The energy of the band-edge luminescence peak shifts with excitation mode (CL, top-surface PL, or interface PL). This effect is attributed to the variation of the excitation depth, between the top surface and film-substrate interface, with excitation mode, together with the depth variation of film properties such as residual stress or aluminum fraction.
Order No.: JA809-021

The effects of chloromethane on diamond nucleation and growth in a hot-filament chemical vapor deposition reactor
J-J. Wu, F.C-N. Hong
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The effects of chloromethane on diamond nucleation and growth were studied by employing laser reflective interferometry. Chloromethane enhances the film-growth-rate only slightly compared to methane. However, chloromethane greatly enhances the nucleation density and shortens the film-forming stage, more significantly at a lower temperature. Thus chloromethane facilitates the low temperature growth mainly through the enhancement of nucleation. Nucleation density is strongly dependent on the compositions of H atoms and carbon species prior to diamond growth. The residual diamond seeds by diamond-grit-scratching are suggested to be the major nucleation sites. Chloromethane can enhance diamond nucleation by protecting the residual seeds from being etched by H atoms.
Order No.: JA809-022

The effect of ternary addition on structure and stability of $NbCr_2$ Laves phases
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The alloying effect on microstructure and stability of the $NbCr_2$ Laves phases is investigated using XRD and TEM. In as-cast condition, the binary alloy as well as the ternary alloy containing V consisted of the C15 phase while the ternary alloys containing Mo, Ti and W consisted of both the C14 (or C36) and the C15 phases, accompanied with a number of stacking faults and microtwins in their constituent phases. By a prolonged heat-treatment at 1673 K, the retained C14 (or C36) phase is completely transformed to the C15 phase. However, their kinetics are slower in the sequence of the ternary alloys containing Mo > Ti > W. The alloying effect on the stability of the C15 (or the C14) phase and the associated transformation process is discussed on the basis of phase stability and kinetics.
Order No.: JA809-023

Estimation of the emissions of CO_2, SO_x, NO_x of steel alloys
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The emissions of CO_2, SO_x, and NO_x of various steel alloys in the production stage were calculated using the unit requirement of each subsystem of the steelmaking process, in order to compare the superiority from the viewpoint of the environmental issue among various types of steel alloys. As steel production is a typical integrated system with multi-products, 1) allocation of emissions to each product, 2) effect of the composition, and 3) sharing the load by the by-product gases are considered. Calculated values of emission were arranged for fifteen kinds of finished steel products and for arbitrary contents of alloying elements.
Order No.: JA809-024

Disintegration and powder formation of $Nb_{75}M_{25}$ (M = Al, Si, Ga, Ge and Sn) due to hydrogenation in an arc-melting chamber
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$Nb_{75}M_{25}$ (M = Al, Si, Ga, Ge and Sn) alloy ingots were prepared by conventional arc-melting method and then were directly reacted with high purity hydrogen of 0.1 MPa in an arc-melting chamber without exposing the ingots to air. As the clean surface of the arc-melted ingots is preserved, the ingots rapidly absorb a lot of hydrogen without any activation treatments and disintegrate violently into fine particles. The disintegration of ingots depends on M element. The collected particles are investigated by x-ray diffraction, electron microscopy, chemical analysis and thermal analysis. The particles are hydrides of $Nb_{75}M_{25}$ after hydrogenation and have a sharp-edged polygonal appearance. After dehydriding, the fine Nb_3M powders with A15 crystalline structure are obtained except for $Nb_{75}Si_{25}$. In comparison with the atomized Nb_3M powders, the Nb_3M powders prepared by the present study have a smaller average particle size and lower impurity contents.
Order No.: JA809-025

Preparation of β-SiC nanorods with and without amorphous SiO_2 wrapping layers
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Preparation of β-SiC nanorods with and without amorphous SiO_2 wrapping layers was achieved by carbothermal reduction of sol-gel derived silica xerogels containing carbon nanoparticles. The β-SiC nanorods with amorphous SiO_2 wrapping layers were obtained by carboreduction at 1650°C for 1.5 hour, and at the end of 1.5 h the temperature was steeply raised to 1800°C and held for 30 min. They are typically up to 20 μm in length. The diameters of the center thinner β-SiC nanorods within the amorphous SiO_2 wrapping layers are in the range 10 ~ 30 nm, while the outer diameters of the corresponding amorphous SiO_2 wrapping layers are between 20 and 70 nm. The β-SiC nanorods without amorphous SiO_2 wrapping layers were produced by carbothermal reduction only at 1650°C

for 2.5 hours; their diameters are in agreement with those of the center thinner β-SiC nanorods wrapped in amorphous SiO_2 layers. Large quantities of SiC rod nuclei and the nanometer-sized nucleus sites on carbon nanoparticles are both favorable to the formation of much thinner β-SiC nanorods. The formation of the outer amorphous SiO_2 wrapping layer is from the combination reaction of decomposed SiO vapor and O_2.
Order No.: JA809-026

Crack profiles in applied moment double cantilever beam tests
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In-situ observations of crack propagation in an applied moment double cantilever beam specimen were used previously to obtain the R-curve behavior of ceramic composites. To predict the R-curve using constitutive models, knowledge of the crack profile is required to derive the bridging stress distribution along the crack length and to analyze the toughening effect. To predict the crack profile in an applied moment double cantilever beam test, both the deformation of the crack surface due to the bending moment and the movement of the crack surface due to the rigid body motion of the loading fixture need to be considered. The analytical solution for the crack profile is derived in the present study. The predicted crack profiles agree well with experimental measurements.
Order No.: JA809-027

Systematic study of graphite encapsulated nickel nanocrystal synthesis with formation mechanism implications
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By systematically varying the carbon content, chamber pressure, arc current, and blowing gas velocity in a tungsten-arc encapsulation setup, the effects of each of these variables on the encapsulation of nickel in graphite layers was observed. The data from these optimally designed experiments revealed that the properties of the arc translate into changes in the encapsulated product. Specifically, a larger, hotter arc results in more encapsulation in the final sample. These findings, along with evidence of graphite layers which have formed on pre-crystallized particles, indicate that the graphite layers may form by two sequential formation steps.The first step is the simple phase segregation of carbon from a cooling liquid particle, resulting in surface graphite. The second step is the growth of carbon on a crystallized nickel particle, regardless of the temperature that this occurs. The proposed formation mechanism has significant implications for both a scientific understanding of the encapsulation phenomena, and possible commercial applications.
Order No.: JA809-028

Correlation between anatase-to-rutile transformation and grain growth in nanocrystalline titania powders
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During the heat-treatment of an anatase nanocrystalline powder at a high temperature, the two processes of anatase-to-rutile (A→R) transformation and grain growth would occur simultaneously and affect each other. With decrease of the original anatase grain size, the A→R transformation temperature range became extended on both sides, which may be partially attributed to the prevention effect of grain growth on this transformation. On the other hand, the grain growth process could be significantly enhanced by the A→R transformation, which can be ascribed to the higher atomic mobility because of the bond breakage during the transformation.
Order No.: JA809-029

Formation of new surface layers on ceramics by ion assisted reaction
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Ar^+ ions with 1 keV energy were irradiated on aluminum nitride in an O_2 environment and on aluminum oxide in a N_2 environment. AlON on AlN and AlN on Al_2O_3 are formed by the Ar^+ irradiation in O_2 gas and N_2 gas environments, respectively, and the formation of new surface layers are confirmed on the basis of Al2p near core levels and O1s, N1s core levels XPS depth profile analysis. Cu(1000 Å) films were deposited by ion-beam sputtering on Ar^+ irradiated/unirradiated AlN surfaces and the change of the adhesion strength was investigated by a scratch test. Cu films deposited on the irradiated AlN under an O_2 environment showed higher bond strength than that on the unirradiated AlN. The improvement of bond strength of Cu films on the AlN surface resulted from the interface bonds between Cu and the surface layers. The bending strength of polycrystalline Al_2O_3 irradiated by Ar^+ ions in N_2 environment was also increased and the formation of nitride layer on the alumina was confirmed. Possible new surface layer formation mechanism on ceramics by the ion assisted reaction has been discussed in terms of surface analysis, chemical bond, and mechanical strength.
Order No.: JA809-030

Influence of Bi-site substitution on the ferroelectricity of the Aurivillius compound $Bi_2SrNb_2O_9$
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(CSIC)

Ceramics based on the composition $Bi_2SrNb_2O_9$ with isomorphic substitutions of cations in the $Bi_2O_2^{2+}$ and the perovskite layers $Bi_{2-x}Te_x$-$Sr_{1-x}Na(K)_xNb_2O_9$, have been prepared by solid state reaction. The ferroelectricity of these Aurivillius type structures has been studied. Dielectric measurements as a function of the temperature show a low temperature maximum in the dielectric constant that would correspond to a ferro-paraelectric phase transition. The temperature of this maximum increases when the radius of the ion that substitutes Sr for decreases. A second maximum in the dielectric constant is found at higher temperature possibly corresponding to a relaxor ferroelectric. Measurements of remanent polarization as a function of the temperature seem to confirm the relaxor behavior, because the polarization disappears at temperatures between the two maxima of the dielectric constant. Saturated hysteresis loops are obtained for all the substituted samples at temperatures above 300°C. Ferroelectric parameters such as the polarization, coercive field and coupling factors of the BSN family compounds were obtained for the first time.

The a.c. electric conductivity shows anomalies at temperatures close to those where the remanent polarization disappears. Activation energies calculated from measurements of d.c. electric conductivity, impedance arcs and dielectric modulus data may be associated with thermally activated oxygen vacancies.
Order No.: JA809-031

Diagnostics and modeling of nanopowder synthesis in low pressure flames
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Laser-induced fluorescence, thermophoretic sampling, laser light scattering, and emission spectroscopy have been used to probe low pressure hydrogen/oxygen flames in which 3–50 nm, loosely agglomerated oxide nanopowders have been synthesized at high production rates by the pyrolysis of precursor vapors, followed by condensation in the gas phase. These measurements have enabled the identification of pyrolysis, condensation, and particle growth regions in the flame. Flame simulations using a one-dimensional stagnation flow model, with complex chemistry, demonstrate that the chemical and thermal flame structure can be accurately predicted for flames without a precursor. Furthermore, some flame structure changes induced by the addition of a precursor can be simulated by addition of analogous species to the chemical mechanism.
Order No.: JA809-032

Microstructure and properties of nanosemicrystalline Si_3N_4 ceramics with doped sintering additives: Part I. Microstructural characterization of nanosemicrystalline Si_3N_4 powders
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(University of California-Los Angeles)

The characteristics of nanosized silicon nitride powders with doped Y_2O_3 and Al_2O_3 fabricated by a plasma-reacted chemical process were investigated. The chemical compositions of the powders were analyzed by wet chemical analysis. The morphology and the size distribution were

determined by transmission electron microscopy (TEM). TEM with energy dispersive spectroscopy (EDS) was used to verify the existence of sintering additives in each individual particle. The crystal structure of the powders was identified by the selected area diffraction pattern (SADP). X-ray diffraction (XRD) technique was used for phase analysis and the measurement of degree of crystallinity. The characteristics of chemical bonding were analyzed by using Fourier transform infrared spectroscopy (FTIR).
Order No.: JA809-033

Microstructure and properties of nanosemicrystalline Si_3N_4 ceramics with doped sintering additives: Part II. Phase transformation and microstructural control
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(University of California-Los Angeles)

The low temperature pressureless sintering of a nanosized Si_3N_4 powder with doped sintering additives was investigated. The microstructural evolution during sintering at different temperatures was analyzed using x-ray diffraction and scanning electron microscopy. The effect of using nanosized Si_3N_4 powder as a catalyst to accelerate the $\alpha \rightarrow \beta$-Si_3N_4 transformation of a commercial Si_3N_4 powder with larger particle sizes was also investigated. Finally, two stage sintering was used to study the feasibility of controlling the microstructure and the mechanical properties of the nanosized silicon nitride.
Order No.: JA809-034

High-temperature creep resistance in rare earth-doped fine-grained Al_2O_3
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High-temperature creep in undoped Al_2O_3 and La_2O_3- or Y_2O_3- or Lu_2O_3-doped Al_2O_3 with a grain size of about 1 μm is examined in uniaxial compression testing at temperatures between 1150 and 1350°C. The high-temperature creep resistance in Al_2O_3 is highly improved by the rare-earth oxide doping in the level of 0.045 mol%, and the creep rate is suppressed in the order $La_2O_3 < Y_2O_3 < Lu_2O_3$. Rare-earth ions in each doped Al_2O_3 are found to segregate in Al_2O_3 grain boundaries without forming amorphous phase or second-phase particles. The activation energy for creep in undoped Al_2O_3 is estimated to be 410 kJ/mol, while it is about 800 kJ/mol in the three rare-earth oxide-doped Al_2O_3. The grain boundary diffusivity must be highly reduced by the segregation of the dopant cation in Al_2O_3 grain boundaries.
Order No.: JA809-035

Micro-Raman spectroscopic characterization of nano-sized TiO_2 powders prepared by vapor hydrolysis
Y-H. Zhang, C.K. Chan, J.F. Porter, W. Guo
(The Hong Kong University of Science and Technology)

Micro-Raman analysis was used to study the structure of TiO_2 powders produced at low (260°C) and high (600–900°C) temperatures by vapor hydrolysis of titanium tetraisopropoxide (TTIP). Spatial inhomogeneity was discovered after the amorphous TiO_2 powders produced at low temperature were calcined at 700, 800, and 900°C for 3 hours. The TiO_2 powders produced at high temperatures (from 600 to 900°C) were found to be spatially homogeneous and predominately anatase in structure. Small amounts of rutile and brookite are found for powders produced at 700, 800, and 900°C after calcination at 600°C for 3 hours. The rutile and brookite impurities are believed to be concentrated on the surface of anatase based on a comparison of results of Raman and x-ray diffraction studies.
Order No.: JA809-036

Phase formation and thermodynamic analysis of self-propagating high-temperature synthesis Al-Zr-N system composites
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The self-propagating high-temperature synthesis (SHS) of Al-Zr-N system composite ceramics was investigated in this paper. The melting point of Al was low (T_m = 660°C), while that of Zr was high (T_m = 1855°C). Therefore, Al will melt and coalesce during reacting which inhibit diffusion of nitrogen from outside the metal compact to interior due to collapse of the pore openings. While Zr will not melt under the combustion temperature which is lower than its melting point, it will not affect the permeation of nitrogen under the conditions. Accordingly, the ratio of Al and Zr in the initial mixed powders will affect the permeation of nitrogen from outside the sample to the interior, which results in different phase formation of the products. In this study, the relationship between the combustion parameters and the phase formation of the products will be experimentally determined through XRD analysis, and then thermodynamically analyzed.
Order No.: JA809-037

Electron-microscopical study of the formation of iron carbide phases after high-fluence carbon ion implantation into iron at low temperatures
C. Hammerl, A. Königer, B. Rauschenbach
(Universität Augsburg)

Carbon ions were implanted with energies between 50 and 150 keV into thin iron layers at temperatures of -10°C and -70°C. Formation of iron carbide phases was studied as a function of fluence, which was varied from $1.2 \cdot 10^{17}$ C^+-ions/cm^2 up to $1.4 \cdot 10^{18}$ C^+-ions/cm^2. The sequence of phase transformation during subsequent annealing to temperatures of up to 450°C was also investigated. Detailed analysis of structure and morphology was done by cross-sectional transmission electron microscopy and electron diffraction experiments. The existence of metastable iron carbide phases, θ-Fe_3C, χ-Fe_5C_2, η-Fe_2C and also the amorphous phase Fe(C), after high-fluence carbon ion implantation and the transformation of the formed metastable phases by subsequent annealing into the θ-Fe_3C phase, are demonstrated.
Order No.: JA809-038

Screen printed $La_{2/3}Sr_{1/3}MnO_3$ thick films on alumina substrates
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(Institut de Ciència de Materials de Barcelona-CSIC).

We report here on the preparation of $La_{2/3}Sr_{1/3}MnO_3$ magnetoresistive thick films on polycrystalline Al_2O_3 substrates by using the screen printing technique. It is shown that films can be obtained using high temperature sintering. While there is a reacted layer, this improves adhesion and is not too troublesome if the films are made thick enough. It is shown that PbO-B_2O_3-SiO_2 glass additives allow sintering at lower temperatures and can be used to improve the mechanical stress of the films. However, it is found that glass concentrations large enough to significantly improve the film adherence result in a weak low field magnetoresistance probably because grains are coated with high resistivity material. Strategies to overcome these difficulties are discussed.
Order No.: JA809-039

Texture evolution in Si/SiC layered structures deposited on Si(001) by chemical vapor deposition
L-O. Björketun, L. Hultman, O. Kordina, J-E. Sundgren
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Texture evolution in Si/SiC multilayers deposited by atmospheric pressure chemical vapor deposition on carbonized Si(001) substrates were investigated using x-ray diffraction and transmission electron microscopy. SiC layers were epitaxial and (001)-oriented. Si layers deposited on the SiC exhibited a columnar structure with predominantly (110) orientation which could be related to the nucleation. Orientational relationships were Si[111]||SiC[110] and Si[112]||SiC[110]. Also, a low density of (112)-oriented columns was present. Extensive twinning on the vertical {111} planes within the Si columns lead to domains of hexagonal stacking up to 10 nm in size with the presence of 2H-Si and 4H-Si. Subsequent SiC layer growth on the (110)-oriented Si layer resulted in a (110)-oriented SiC layer if the Si layer was carbonized prior to growth.
Order No.: JA809-040

Investigation of CF_3I as an environmentally benign dielectric etchant
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In this study, trifluoroiodomethane (CF_3I), a non global-warming gas, has been investigated as a substitute for typical PFCs currently used in

wafer patterning and CVD chamber cleaning processes. Dielectric films consisting of plasma enhanced chemically vapor deposited silicon dioxide and silicon nitride were comparatively etched in CF_3I and C_2F_6/O_2 plasma environments. The etch rate of these films was ascertained as a function of applied RF power, etchant gas flow rate, reaction chamber pressure, and CF_3I:O_2 ratio. Destruction efficiencies of CF_3I at different processing parameters were evaluated. Depending on the flow rate, RF power and chamber pressure, utilization efficiency of CF_3I varied from as low as 10% to as high as 68%. CF_4, C_2F_6, COF_2, and CO_2 were the predominant by-products found in the exhaust stream: however, their concentrations were very low compared to the traditional process employing C_2F_6/O_2 mixtures.
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X-ray absorption fine structure study on coordination state of implanted gold ions in silica glass
K. Fukumi, H. Kageyama, K. Kadono, A. Chayahara, N. Kamijo, M. Makihara, K. Fujii, J. Hayakawa, M. Satou
(Osaka National Research Institute)

Coordination state of gold atoms implanted in silica glass to an energy of 1.5 MeV and a dose of $1x10^{17}$ ions/cm^2 has been studied by x-ray absorption fine structure spectroscopy. It was found that most of the gold atoms form gold clusters in which the nearest neighboring Au-Au interatomic distance is shorter by 0.05 Å than that in bulk gold. The contraction of Au-Au interatomic distance of gold clusters in silica glass is less than that reported in the previous studies on gold clusters within the other substrates. Gold atoms are coordinated by about 4 gold atoms in average. In addition. it was found that Au-O bonds are formed at the gold clusters/silica glass interface. It was deduced that the formation of Au-O bond at the gold clusters/silica glass interface depresses the contraction of Au-Au interatomic distance.
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Crystallization kinetics and phase transformation of Li_2O-Fe_2O_3-MnO_2-CaO-P_2O_5-SiO_2 glass
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The crystallization kinetics and phase transformation of $10Li_2O$-$14Fe_2O_3$-$11MnO_2$-$25CaO$-$5P_2O_5$-$35SiO_2$ (LFMCPS) glass have been investigated using differential thermal analysis (DTA), x-ray diffraction (XRD) and scanning electron microscopy (SEM). The major crystalline phase determined by XRD analysis was triphylite [$Li(Fe_{0.5}Mn_{0.5})PO_4$], β-wollastonite (β-CaO-SiO_2) and magnetite (Fe_3O_4) as the minor phases. The non-isothermal kinetics of crystallization of the LMFCPS glass was investigated using DTA analysis. The activation energy of crystallization for LFMCPS glass was 74.6 kcal/mol. The growth morphology parameter n was 0.98 at heating rate 5°C/min and decreased to 0.74 as heating rate increased to 20°C/min. The numerical factor of crystallization mechanism m was 0.57 at low crystallization temperature and gradually decreased as the temperature increased. For the experiment, the parameters n and m were approximately to one. These results indicated that the surface nucleation was dominant in LFMCPS glass crystallization.
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Indentation response of molybdenum disilicide
A. Newman, T. Jewett, S. Sampath, C. Berndt, H. Herman
(State University of New York)

The influence of microstructure on the indentation cracking behavior of molybdenum disilicide ($MoSi_2$) has been examined. The indentation response of samples produced by various methods has been measured to examine the elastic/plastic nature, hardness, and fracture toughness. Fracture toughness comparisons were made by measuring indentation crack lengths, observing the elastic/plastic indentation response, and quantifying the differences in the indentation cracking behavior. Further information was gained by monitoring the acoustic activity during indentation for selected specimens. It has been observed that the fine grain size and the dispersion of the silica phase promote microcracking and crack deflection.
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New Materials Development

New Characterization Methods

New Process Technology

1998 Fall Meeting Symposia

A: Polycrystalline Thin Films—Processing-Structure-Property Relationships
B: Growth Instabilities and Decomposition During Heteroepitaxy
C: Surface and Interface Structure and Dynamics
D: Integration of Dissimilar Materials in Micro- and Optoelectronics
E: Film Growth and Processing Using Hyperthermal Beams
F: Microcrystalline and Nanocrystalline Semiconductors
G: GaN and Related Alloys
H: Infrared Semiconductor Materials and Devices
I: III-V and SiGe Group IV Device/IC Processing Challenges for Commercial Applications
J: Multiscale Modeling of Materials
K: Computation of Rates of Activated Processes
L: Interaction of Phase and Defect Microstructures in Metallic Alloys
M: Fracture and Ductile vs Brittle Behavior—Theory, Modeling, and Experiment
N: Microstructural Processes in Irradiated Materials
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U: Organics with Supramolecular Structure and Function
V: Solid Freeform and Additive Fabrication
W: Dynamics in Small Confining Systems V
X: Frontiers of Materials Research
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II: Advanced Materials, Coatings, and Biological Cues for Medical Implants
JJ: Materials in Space—Science, Technology, and Exploration
KK: High-Temperature-Ordered Intermetallic Alloys VIII
LL: Quasicrystals
MM: Bulk Metallic Glasses
NN: Aging of Engineered Systems with Focus on Aircraft
OO: Properties and Processing of Vapor-Deposited Coatings
PP: Recent Advances in Ceramic Matrix Composites—Structural Design, Fabrication, and Long-Term Use
QQ: Scientific Basis for Nuclear Waste Management XXII
RR: Workshop on Materials Education

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