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ABSTRACTS**RAPID COMMUNICATIONS****Growth of *a*-axis-oriented HgBa₂CaCu₂O_x thin films by rapid quenching**S.H. Yun,¹ U.O. Karlsson,¹ B.J. Jönsson,¹ K.V. Rao,¹ L.D. Madsen²
(¹Royal Institute of Technology, ²Linköping University)

High-quality *a*-axis-oriented HgBa₂CaCu₂O_x superconducting thin films have been grown on (100) LaAlO₃ substrates using a modified conventional method that contains a short annealing time of 5 min, rapid-quenching process, and an alternative encapsulated approach. We found that the preferred orientations of HgBa₂CaCu₂O_x thin films can be controlled by rapid quenching at specific temperatures: 800, 700, 600, and 500 °C. The films rapidly quenched in water from 700 °C during a cooling cycle showed predominantly *a*-axis-orientation perpendicular to film surface. Phase was confirmed by x-ray diffraction pole figures. The *a*-axis films exhibited a zero-resistance transition temperature >120 K, which is comparable to epitaxial *c*-axis-oriented films.

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Surface oxidation of a quasicrystalline Al–Cu–Fe alloy: No effect of surface orientation and grain boundaries on the final state

P.J. Pinhero, J.W. Anderegg, D.J. Sordet, T.A. Lograsso, D.W. Delaney, P.A. Thiel

(Iowa State University)

We have used x-ray photoelectron spectroscopy and Auger electron spectroscopy to examine the characteristics of oxides on two types of quasicrystalline Al–Cu–Fe samples. One type was formed by consolidation of powders, resulting in multiple grains with random surface orientations. The other was a single grain, oriented to expose a fivefold surface. Both were oxidized to saturation in a variety of environments at room temperature. We measured the elemental constituents that oxidized, the extent of oxygen-induced Al segregation, and the depth of the oxide. Under the conditions of our experiments, there was little, if any, significant difference between the two types of samples. Hence, surface orientation and bulk microstructure played little or no role on the final state of the oxide under these conditions.

Order No.: JA908-002

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Heteroepitaxial growth of bulk single-crystal**Pb(Mg_{1/3}Nb_{2/3})O₃-32 mol% PbTiO₃ from (111) SrTiO₃**T. Li, S. Wu, A. Khan, A.M. Scotch, H.M. Chan, M.P. Harmer
(Lehigh University)

SrTiO₃ was investigated as an alternate seed material to grow Pb(Mg_{1/3}Nb_{2/3})O₃-PbTiO₃ (PMN-PT) ferroelectric single crystals by seeded polycrystal conversion. Fully dense polycrystalline samples of PMN-32 mol% PT doped with 3 vol% excess PbO were top-seeded with (111)SrTiO₃ substrates. Annealing for 10 h at 1150 °C resulted in growth of PMN-32PT single crystals with sizes on the order of several millimeters. Orientation imaging microscopy confirmed that the grown crystal exhibited the same crystallographic orientation as that of the SrTiO₃ seed. Elemental distributions analyzed using energy dispersive spectroscopy indicated that interdiffusion of the relevant elements was negligible.

Order No.: JA908-003

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A novel approach for identifying and synthesizing high dielectric materialsJ.-H. Park,¹ J.B. Parise,¹ P.M. Woodward,² I. Lubomirsky,³ O. Stafsudd³¹State University of New York, ²The Ohio State University,³University of California—Los Angeles)

Modern telecommunications require materials with high dielectric constants (κ). The number of suitable elements ultimately limits one approach to the discovery of new materials, targeting compositions with high atomic polarizabilities (α). By decreasing the molar volume of compositions with high α , however, we anticipated dramatic increases in κ and demonstrated that this approach works. The quenched high-pressure perovskite polymorph of Na₂MTeO₆ (M = Ti, Sn) showed a twofold increase in κ , compared to the ilmenite form. This result suggests the highest values of κ occur for compositions with high α , which form quenchable compounds at high pressures and temperatures.

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The deposition of oriented diamond film by hot filament chemical vapor deposition with separate reactant gas

G.C. Chen, D.Y. Jiang, X.Z. Yao, C. Sun, R.F. Huang, L.S. Wen

(Academia Sinica)

A (110)-oriented diamond film was deposited by hot filament chemical vapor deposition with H₂ and CH₄ separately introduced into reactive zone. The film with degree of orientation $I_{(220)}/I_{(111)}$ more than 200% and deposition rate of 2–3 $\mu\text{m/h}$ was obtained for deposition time of 17 h. The long deposition time enlarged the grain size and enhanced the degree of orientation, but too long a deposition time resulted in random growth. The temperature field was measured and also calculated using a simple model. Both results showed that a temperature field existed with varied gradient along the normal of substrate surface. The (110)-oriented diamond film was deposited in the zone with negative temperature gradient. The change in orientation occurring for long deposition times was ascribed to the change of temperature gradient.

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On the correlation between effective activation energy and pre-exponential factor for diffusion in bulk metallic glasses

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(Universität Kiel)

The values of effective activation energy (Q) and pre-exponential factor (D_0) reported for diffusion in the novel bulk metallic glasses, both in the glassy and the deeply supercooled liquid regions, were found to follow the same correlation as reported earlier in conventional metallic glasses, namely $D_0 = A \exp(Q/B)$, where A and B are fitting parameters with values $A = 4.8 \times 10^{-19} \text{ m}^2 \text{ s}^{-1}$ and $B = 0.056 \text{ eV atom}^{-1}$. A possible explanation for the observed values of A and B is given by combining an activation energy and a free volume term. The interpretation favors a cooperative mechanism for diffusion in the glassy and deeply supercooled liquid states.

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Synthesis of nanocrystalline diamond by direct ion beam deposition method

X.S. Sun, N. Wang, W.J. Zhang, H.K. Woo, X.D. Han, I. Bello, C.S. Lee, S. T. Lee

(City University of Hong Kong)

Nanocrystalline diamond has been synthesized on mirror-polished Si(001) substrate by means of direct ion beam deposition. Low energy (80–200 eV) hydrocarbon and hydrogen ions, generated in a Kaufman ion source, were used to bombard the substrates. The bombarded samples were characterized by high-resolution transmission electron microscopy and Raman spectroscopy. Nanocrystalline diamond particles of random orientation were observed in a matrix of amorphous carbon film on the Si(001) substrate. The size of the nanocrystalline diamond particles varied in the range of 50–300 Å. The mechanism of ion-induced formation of nanocrystalline diamond is discussed.

Order No.: JA908-007

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Effect of oxygen plasma treatment on gas adsorption behavior and surface structure of carbon spheres derived from phenol resin

M. Inagaki, M. Sunahara, A. Shindo, V. Vignal, H. Konno

(Hokkaido University)

Plasma treatment was applied on glasslike carbon spheres in order to modify their gas adsorption behavior. After the oxygen plasma treatment, a selective adsorption of CO₂ gas was obtained, almost no nitrogen adsorption being detected, at low temperatures. Surface morphology observed by using field-emission scanning electron microscopy, atomic force microscopy, and scanning tunneling microscopy was found to be changed after the oxygen plasma treatment.

Order No.: JA908-008

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ARTICLES***In situ* boron doping of chemical vapor-deposited diamond films**

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A systematic investigation of the boron doping of microwave-plasma-deposited diamond films was performed. Doping with levels up to 550 ppm was carried out *in situ* on undoped diamond film substrates in a microwave-plasma-assisted chemical vapor deposition using liquid trimethyl-, triethyl-, and tripropylborate and gaseous trimethylborane as doping sources. The dependence of the boron incorporation probability on the doping sources and on the process parameters was studied using secondary ion mass spectrometry. The doping-induced variations of phase quality and morphology of the boron-doped diamond layers were investigated by means of scanning electron microscopy and Raman spectroscopy. The incorporation of other impurities, i.e., hydrogen, nitrogen, oxygen, and silicon, were also determined by secondary ion mass spectrometry. The relations of the concentration of these impurities to the boron incorporation was also studied.

Order No.: JA908-009

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Studies of electron energy loss near edge structure at the interface between Si and amorphous carbon films deposited by direct carbon ion beamsM.H. Sohn,¹ S.I. Kim,¹ K. Siangchaew²¹SKION Corporation, ²Stevens Institute of Technology)

Using direct carbon ion beam deposition, *in situ* surface modification was performed by an energetic C⁻ beam (400 and 500 eV) prior to amorphous carbon film growth to enhance adhesion of the film. It has been found from high-resolution electron microscopy that C and Si mixing layer at the interface causes strong adhesion of the film. Electron energy loss spectroscopy was used to investigate chemical states of the C and Si mixing layer at the interface. The carbon composition profile in silicon showed that the thickness of the mixing layer was about 30 nm for 500 eV modification (at 200 °C). Silicon L-edge study at the C/Si interface found C–Si bond formation only at the surface of silicon over 2–3-nm-thick layers. The C–Si bond formation is a function of C⁻ ion impingement energy. The thickness of the bonding layer decreased to less than 1 nm for 400 eV surface modification. When the substrate was modified by a 500 eV C⁻ beam at 800 °C, the thickness of the SiC layer was about 10 nm. C–Si bond formation was enhanced by the supplemental thermal energy.

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A transmission electron microscopy investigation of SiC films grown on SiC substrates by solid-source molecular-beam epitaxy

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The relationship between the defect microstructure of SiC films grown by solid-source molecular-beam epitaxy of 4H and 6H-SiC substrates and their growth conditions, for substrate temperatures ranging between 950 and 1300 °C, has been investigated using a combination of transmission electron microscopy and atomic force microscopy. The results demonstrated that the formation of defective cubic films was generally found to occur at temperatures below 1000 °C. At temperatures above 1000 °C our investigations proved that simultaneous supply of C and Si in the step-flow growth mode on vicinal 4H and 6H substrate surfaces results in defect-free hexagonal SiC layers while defect-free cubic SiC can be grown using the alternating deposition technique. The controlled overgrowth of hexagonal on top of cubic layers was demonstrated for thin layer thicknesses.

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Deposition of zinc sulfide quantum dots from single-source molecular precursor

N. Revaprasadu,^{1,2} M. Azad Malik,¹ P. O'Brien,¹ G. Wakefield³
 (¹Imperial College of Science, Technology and Medicine, ²University of Zululand, ³University of Oxford)

Nanoparticles of ZnS capped with TOPO (tri-n-octylphosphineoxide) and close to monodispersed have been prepared by a single-source route using ethyldi-ethyl(di-thiocarbamate) zinc (II) as a precursor. The nanoparticles obtained showed quantum size effects in their optical spectra, and the photoluminescence spectrum showed a broad emission, which could be attributed to the surface traps. A blue shift of 0.31 eV in relation to the bulk material was observed. Selected area electron diffraction, x-ray diffraction pattern, and transmission electron microscopy showed the material to be of the zinc blend structure. The crystallinity of the material was also evident from high-resolution transmission electron microscopy, which gave well-defined images of nanosize particles with clear lattice fringes and a spacing of approximately 3 Å, corresponding to the (111) planes of the cubic crystalline ZnS phase and in the size range of 3.9–4.9 nm. The presence of strong phosphorus peak in the energy dispersion analytical x-ray pattern, together with a shift in the infrared band for P = O of TOPO showed that the particles were TOPO capped.

Order No.: JA908-012

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The effect of the deposition temperature on the properties of iridium thin films grown by means of pulsed laser deposition

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Pulsed laser deposition (PLD) of Ir thin films has been achieved by ablating an iridium target with a KrF excimer laser. The iridium deposition rate was investigated over the $(0.4\text{--}2) \times 10^9$ W/cm² laser intensity range and found to reach its maximum at $(1.6 \pm 0.1) \times 10^9$ W/cm². At this laser intensity, the PLD Ir films were deposited at substrate deposition temperatures ranging from 20 to 600 °C. The PLD Ir films exhibited a (111) preferentially oriented polycrystalline structure with their average grain size increasing from about 10 to 30 nm as the deposition temperature was raised from 20 to 600 °C. Their mean surface microroughness (R_a) was found to change from an average value of about 1 nm in the 20–400 °C temperature range to a value of about 4.5 nm at 600 °C. As the deposition temperature varied from 20 to 600 °C, not only did the stress of PLD Ir films change drastically from highly compressive (–2.5 GPa) to tensile (+0.8 GPa), but their room-temperature resistivity also gradually decreased in the 20–400 °C range and stabilized for higher temperatures. In the 400–600 °C range, the resistivity of PLD Ir films was as low as 6.0 ± 0.2 μΩ cm, which was very close to the iridium bulk value of 5.1 μΩ cm. Thus, PLD Ir films exhibiting not only the lowest resistivity, but also a nearly zero stress level, can be grown at a deposition temperature of about 400 °C. The resistivity of the PLD Ir films can be described by a grain boundary scattering model.

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Stress-driven surface evolution in heteroepitaxial thin films: Anisotropy of the two-dimensional roughening mode

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 (¹Applied Micro Circuits Corporation, ²Stanford University)

We have analyzed the anisotropic behavior of surface roughening in Si_{1-x}Ge_x/Si(001) heterostructures using methods of elastic analysis of undulated surfaces and perturbation analysis based on global energy variations associated with surface evolution. Both methods have shown that the two-dimensional stage of surface roughening preferentially takes place in the form of ridges aligned along the two orthogonal <100> type directions. This prediction has been confirmed by *ex situ* experimental observations of surface evolution using atomic force microscopy and transmission electron microscopy in both subcritically and supercritically thick Si_{1-x}Ge_x films grown on Si(001) substrates. Further experiments in supercritically thick films have revealed a remarkable interplay between defect formation and surface evolution: the formation of a network of <110> misfit dislocations in the latter stages alters the evolution process by rotating the ridge formations toward the <110> type directions.

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Effect of Ti + C addition on quenchability and magnetic properties of Nd₉Fe₈₅B₆

T.M. Zhao, X.R. Xu, Z.Q. Hu
 (Chinese Academy of Sciences)

Ingots of composition Nd₉Fe₈₅B₆, Nd₉Fe₈₅B₆ + 1 at.% (Ti + C), Nd₉Fe₈₅B₆ + 2 at.% (Ti + C), and Nd₉Fe₈₅B₆ + 5 at.% (Ti + C) were prepared by plasma arc-melting the constituent elements from 99.95 wt% Nd, 99.99 wt% Fe, 99.97 wt% Ti, spectrographic grade C and ferroalloy Fe–B (19.6 wt% B). Effect of Ti + C addition and its content on quenchability and magnetic properties of Nd₉Fe₈₅B₆ alloy were investigated by melt spinning. The results showed that the added Ti and C elements reacted with each other to form TiC compound that was solid solutioned and/or precipitated in the cast ingots. The Ti + C addition could increase the glass forming ability (GFA) of an α-Fe/Nd₂Fe₁₄B-type nanocomposite permanent material: the more the additive, the stronger the GFA, but only about 2 at.% Ti + C addition could enormously increase the magnetic properties.

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Grain growth in ultrathin films of CoPt and FePt

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 (¹Lehigh University, ²IBM)

The microstructure of sputtered 10-nm thin films of equiatomic binary alloys of CoPt and FePt was characterized using transmission electron microscopy (TEM). Grain growth kinetics was examined using manual and digital analysis of bright-field TEM images and was seen to take two stages during annealing in these films. A rapid growth stage concurrent with the formation of a [111] fiber texture was observed to occur within the first 5–10 min of annealing, followed by a much slower growth stage after the fiber texturing was well advanced. Differences in grain growth rate and ultimate grain size were also observed to depend on heating rate.

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A new surface alloying technique for pure copper

M.-X. Zhang, K. Reilly, P.M. Kelly
 (University of Queensland)

A totally new technique of surface modification—thermal surface alloying treatment for pure copper—was developed. A 0.2–1.8 mm copper alloy layer, which has a hardness 4 to 5 times higher than the pure copper substrate, was formed after the treatment. The significance of this technique is that the surface of pure copper can be efficiently hardened without significant reduction of the overall thermal and electrical conductivity. Variations of composition and microstructure in the alloy layer were studied after pure copper was surface-alloying treated using aluminium.

Order No.: JA908-017

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Synthesis of PbTiO₃/organic hybrid from metalorganic compounds

T. Yogo, H. Ukai, W. Sakamoto, S. Hirano
 (Nagoya University)

A nanocrystalline PbTiO₃ particles/organic hybrid was synthesized through hydrolysis and polymerization of metalorganic compounds below 100 °C. The PbTiO₃ precursor was synthesized from lead methacrylate and titanium iso-

propoxide. The formation of a Pb–Ti complex alkoxide was confirmed by H and Pb nuclear magnetic resonance spectroscopy. Hydrolyzed Pb–Ti alkoxide was polymerized yielding the PbTiO₃ particles/oligomer hybrid. The organic matrix included nanometer-sized crystalline particles depending upon the hydrolysis conditions. The nanocrystalline particles were identified to be lead titanate by electron diffraction and energy-dispersive x-ray analysis. The dielectric constant of the nanometer-sized PbTiO₃/oligomer hybrid was 5.2 at 10 kHz.
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Novel method for the synthesis of thin film coatings on particulate materials

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³Florida Atlantic University, ⁴Oak Ridge National Laboratory

In this paper, we show the feasibility of the pulsed laser ablation technique to grow 20–30-nm-thick, discrete and continuous coatings on particulate material systems so that the properties of the core particles can be suitably modified. Experiments were conducted using a pulsed excimer laser ($\lambda = 248$ nm, pulse duration = 25 ns) to deposit nanoparticle coatings on Al₂O₃ and SiO₂ core particles via irradiation of Ag and Y₂O₃:Eu³⁺ sputtering targets. Structural characterization was performed using scanning electron microscopy, wavelength dispersive x-ray mapping, transmission electron microscopy, and scanning transmission electron microscopy with z-contrast.
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Mechanical properties of Zr₅₇Nb₅Al₁₀Cu_{15.4}Ni_{12.6} metallic glass matrix particulate composites

R.D. Conner, H. Choi-Yim, W.L. Johnson

(California Institute of Technology)

To increase the toughness of metallic glass with the nominal composition Zr₅₇Nb₅Al₁₀Cu_{15.4}Ni_{12.6}, it was used as the matrix in particulate composites reinforced with W, WC, Ta, and SiC. The composites were tested in compression and tension experiments. Compressive strain to failure increased by over 300% compared to the unreinforced Zr₅₇Nb₅Al₁₀Cu_{15.4}Ni_{12.6}, and energy to break the tensile samples increased by over 50%. The increase in toughness came from the particles restricting shear band propagation, promoting the generation of multiple shear bands and additional fracture surface area. There was direct evidence of viscous flow of the metallic glass matrix within the confines of the shear bands.
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Pulsed laser deposition of titanium nitride films on sapphire

V. Talyansky,¹ S. Choopun,¹ M.J. Downes,¹ R.P. Sharma,¹ T. Venkatesan,¹ Y.X. Li,¹ L.G. Salamanca-Riba,¹ M.C. Wood,² R.T. Lareau,² K.A. Jones²

(¹University of Maryland, ²U.S. Army Research Laboratory)

We have successfully deposited high-quality TiN films on c-plane sapphire using the pulsed laser deposition technique. TiN grew on sapphire with two in-plane epitaxial relationships: (111)_{TiN}//(0001)_{sapphire} and [101]_{TiN}//[1100]_{sapphire} or (111)_{TiN}//(0001)_{sapphire} and [101]_{TiN}//[1100]_{sapphire}. The TiN unit cell showed a $\pm 30^\circ$ in-plane rotation with respect to that of sapphire. The misfit between the TiN film and the sapphire substrate was calculated using the near coincidence site lattice approach. The deposited films were analyzed by x-ray diffraction, transmission electron microscopy, atomic force microscopy, Rutherford backscattering/channeling spectroscopy, and electrical and spectrophotometric measurements. The dependence of the film's crystalline quality on the deposition temperature has been investigated. The full width at half-maximum of the rocking curve of the TiN 111 peak was 0.2–0.3°. The minimum ion channeling was 5%, and the room temperature resistivity was as low as 13 $\mu\Omega$ cm.
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Synthesis and characterization of PbTiO₃ powders and heteroepitaxial thin films by hydrothermal synthesis

A.T. Chien, J. Sachleben, J.H. Kim, J.S. Speck, F.F. Lange

(University of California—Santa Barbara)

PbTiO₃ powders and heteroepitaxial thin films were produced by the hydrothermal method at 110 to 200 °C using different bases (Na–, K–, Rb–, Cs–, TMA–, and TBA–OH). Microstructural characterization showed that the tetragonal perovskite films were epitaxial on the SrTiO₃ substrates, with a c-axis out-of-plane orientation. Sequential growth experiments showed that the

growth initiates by the formation of 100 nm {100} faceted PbTiO₃ islands followed by coalescence. Small cation bases (Na–, K–, Rb–OH) produced 1.5- μ m {100} faceted blocky powders while larger cation bases (Cs–, TMA–, TBA–OH) formed fewer, 500-nm interpenetrating platelets. Nuclear magnetic resonance results showed cation incorporation in the perovskite structure with local disorder on the Pb sites increasing with increasing cation size.

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Epitaxial growth of magnesia and spinel on sapphire during incongruent reduction in molten magnesium

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The types and morphologies of oxide phases produced during the incongruent reduction of sapphire (single-crystal Al₂O₃) by molten magnesium were examined. Polished {10 $\bar{1}$ 0} faces of sapphire were exposed to molten magnesium at 1000 °C for 100 h. Such exposure resulted in the formation of a continuous, epitaxial layer of spinel (MgAl₂O₄) on sapphire and a continuous, epitaxial layer of magnesia (MgO) on the spinel. X-ray pole figure analyses indicated that two variants of spinel and magnesia had formed in a manner consistent with the following orientation relationships: (10 $\bar{1}$ 0)_{sapphire}//(110)_{spinel}//(110)_{magnesia}/[0001]_{sapphire}//[111]_{spinel}//[111]_{magnesia}.
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Segregation in the MgO–MgAl₂O₄ system processed from nitrate precursors

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The occurrence of segregation and its influence on microstructural and phase evolution have been studied in MgO–MgAl₂O₄ powders synthesized by thermal decomposition of aqueous nitrate precursors. When the nitrate solutions of Mg and Al were spray-pyrolyzed on a substrate held at 673 or 573 K, homogenous mixed oxides were produced. Spraying and drying the nitrate solutions at 473 K resulted in the formation of compositionally inhomogeneous, segregated oxide mixtures. It is suggested that segregation in the dried powders was caused by the difference in solubility of the individual nitrate salts in water, which caused Mg- and Al-rich salts to precipitate during dehydration of the solutions. The occurrence of segregation in the powders sprayed at 473 K and not 573 or 673 K is ascribed to the sluggish rate at which the early stages of decomposition occurred during which the cations segregated. The phase evolution in segregated and segregation-free MgO–MgAl₂O₄ powders has been compared. The distinguishing feature of the segregated powders was the appearance of stoichiometric periclase grain dimensions in excess of 0.3 μ m at temperatures as low as 973 K. By comparison, the segregation-free powders displayed broad diffraction peaks corresponding to fine-grained and nonstoichiometric periclase. The grain size was in the range of 5–30 nm at temperatures up to 1173 K. The key to obtaining fine-grained periclase was the ability to synthesize (MgAl)O solid solutions with the rock salt structure. In the temperature range 973–1173 K, spinel grain size varied from 5 to 40 nm irrespective of its composition and did not appear to be influenced by segregation.
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Positive temperature coefficient resistance effect in Ba_{1-x}Sr_xTiO₃ ceramics modified with Bi₂O₃ and PbO by a vapor-doping method

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Ba_{1-x}Sr_xTiO₃-based positive temperature coefficient resistance (PTCR) ceramics were prepared by use of a vapor doping method. When doped with Bi, the PTCR effect is evidently improved; when doped with lead, however, the effect is weakened. The different influences of Bi and Pb doping on the ceramic properties are discussed in terms of the defect chemistry.
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Electrical characterization of BaTiO₃ heteroepitaxial thin films by hydrothermal synthesis

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The electrical properties of hydrothermally grown epitaxial pseudocubic BaTiO₃ thin films formed on epitaxial electrode layers of SrRuO₃ on SrTiO₃ single crystal substrates have been evaluated by variable frequency dielectric testing. The initial as-synthesized BaTiO₃ film displayed a dielectric constant

of 450 with very high losses ($\tan \delta \sim 100\%$) at 10kHz due to OH^- and H_2O , incorporated during growth, contributing to migration losses within the film. Improvements were seen with increasing post-processing heat-treatment time and temperature with improved properties seen after a heat treatment at 300°C for 24 h ($\epsilon \sim 200$, $\tan \delta \sim 8\%$). Relationships were established for dielectric constant and loss tangent with structural changes observed by Fourier transform infrared spectroscopy, thermal gravimetric analysis, nuclear magnetic resonance spectroscopy, and x-ray diffraction.

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Decomposition of the ZrO_2 electrolyte in contact with Ni: Structure and chemical composition of the Ni/electrolyte interface

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The Ni/($\text{ZrO}_2 + 9.5 \text{ mol}\% \text{ Y}_2\text{O}_3$) interface was used as a model system to investigate decomposition reactions of a yttria-stabilized ZrO_2 electrolyte in contact with a metal at elevated temperature. In the present study, the sample was a diffusion-bonded symmetrical galvanic cell Ni | $\text{ZrO}_2 + 9.5 \text{ mol}\% \text{ Y}_2\text{O}_3$ | Ni. Various electron microscopy techniques were employed to study the morphology and structure of the reaction products at the Ni/ ZrO_2 electrolyte phase boundary after current flow. Below a critical oxygen partial pressure of approximately 10^{-27} atm, an intermetallic reaction layer formed at the Ni/electrolyte interface. Between the intermetallic layer and electrolyte a thin Y_2O_3 layer was present, which acted as a diffusion barrier for Zr and Ni, slowing down the overall chemical reaction. At several locations at the interface the Y_2O_3 layer broke up leading to a morphological instability of the interface between electrolyte and Ni_3Zr , allowing further reaction. The thickness of the total reaction layer varied widely as a consequence of such an instability.

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Synthesis and characterization of rutile TiO_2 nanowhiskers

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Rutile TiO_2 nanowhiskers have been synthesized by annealing a precursor powder in which NaCl and $\text{Ti}(\text{OH})_4$ particles were homogeneously mixed. The precursor powder was prepared by mixing three kinds of inverse microemulsions (μE) containing TiCl_4 aqueous solution, ammonia, and NaCl aqueous solution, respectively, followed by washing with acetone. Annealing temperature and packing density of $\text{Ti}(\text{OH})_4$ in the precursor powder influenced the formation of rutile nanowhiskers. The optimum temperature was 750°C . TiO_2 nanowhiskers obtained by annealing a precursor powder in which the molar ratio of sodium to titanium was 400 at 750°C for 2 h had diameters of 10 to 50 nm and lengths of several micrometers. They were straight rods with square cross sections, and the side surfaces were composed of four equivalent {110} planes.

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An $\alpha\text{-Fe}_2\text{O}_3$ powder of nanosized particles via precursor dispersion

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An $\alpha\text{-Fe}_2\text{O}_3$ powder of nanosized particles has been successfully prepared by effectively dispersing the precipitated hydroxide precursor in a sodium chloride matrix. In particular, the hydroxide precursor was converted into crystalline $\alpha\text{-Fe}_2\text{O}_3$ particles approximately 10 nm in size when it was mechanically activated in the sodium chloride matrix for 20 h. The subsequent calcination at 600°C for 20 h resulted in a limited degree of coarsening in particle size while the crystallinity of $\alpha\text{-Fe}_2\text{O}_3$ was further established. The effectiveness of obtaining ultrafine $\alpha\text{-Fe}_2\text{O}_3$ powders by mechanical activation in the sodium chloride matrix was demonstrated by comparing the powder with those obtained via other routes, such as mechanical activation without sodium chloride as the matrix, calcination at 600°C , and then mechanical activation in sodium chloride matrix, respectively. None of these processing routes led to a powder comparable in particle characteristics to that derived by the precursor dispersion.

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Silicon carbide ceramics prepared by pulse electric current sintering of β - and α -SiC powders with oxide and nonoxide additives

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Using a pulse electric current sintering (PECS) method, β - and α -SiC powders doped with a few weight percent of $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3$ oxide or $\text{Al}_4\text{C}_3\text{-B}_4\text{C-C}$ nonoxide additives were rapidly densified to high densities (95.2–99.7%) within less than 30 min of total processing time. When $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3$ additive was used, both ceramics resulting from β - and α -SiC had fine, equiaxed microstructures. In contrast, when $\text{Al}_4\text{C}_3\text{-B}_4\text{C-C}$ additive was used, the ceramic resulting from α -SiC had a coarse, equiaxed microstructure, while the ceramic resulting from β -SiC was composed of large elongated grains whose formation was accompanied by the $\beta \rightarrow \alpha$ phase transformation of SiC. Compared with the $\text{Al}_2\text{O}_3\text{-Y}_2\text{O}_3$ -doped SiC ceramics, the $\text{Al}_4\text{C}_3\text{-B}_4\text{C-C}$ -doped SiC ceramics had higher densities, lower fracture toughness and higher hardness. The fracture mode of the oxide-doped SiC was mainly intergranular, while the nonoxide-doped SiC exhibited almost complete intragranular fracture, which was attributed to the higher interfacial bonding strength.

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Characterization of processing pores and their relevance to the strength in alumina ceramics

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Characterization of bulk defects was successfully accomplished in alumina with a transmission optical microscope. The characterization technique used is based on the fact that many ceramics are essentially transparent. A majority of defects in this particular ceramic were found to be pore defects. Their size distribution was found to follow a simple power function. With these characteristics of defects the strength distribution of the ceramics was calculated with Baratta's mode and compared to the measured strength of the ceramics. A good agreement was found between them when the pore was assumed to be accompanied with cracks 4 times the length of the grain size.

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Temperature-stable dielectric ceramics in $\text{Ba}_4\text{Nd}_2\text{Ti}_4\text{Ta}_6\text{O}_{30}/(\text{La}_{0.1}\text{Bi}_{0.9})_2\text{Ti}_2\text{O}_7$ biphasic system

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Biphasic dielectric ceramics in the system of $(1-x)\text{Ba}_4\text{Nd}_2\text{Ti}_4\text{Ta}_6\text{O}_{30}/x(\text{La}_{0.1}\text{Bi}_{0.9})_2\text{Ti}_2\text{O}_7$ were investigated in order to obtain a near-zero temperature coefficient of dielectric constant. With the increase in x , the dielectric constant increased slightly, and the temperature coefficient changed from negative to positive. High dielectric constant of $\epsilon = 143$ and good temperature stability ($\tau_\epsilon = -48 \text{ ppm}/^\circ\text{C}$) were achieved in a composition of $x = 0.45$, and the increased dielectric loss became the new problem.

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Synthesis of calcium silicate hydrate/polymer complexes:

Part I. Anionic and nonionic polymers

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High molecular weight anionic polymers have been incorporated into the calcium silicate hydrate (C-S-H) structure during precipitation of quasicrystalline C-S-H from aqueous solution. The anionic polymers studied were poly(methacrylic acid), poly(acrylic acid), and the sodium salt of poly(vinyl sulfonic acid). Expansion of the interlayer spacing coupled with high carbon contents confirmed that the polymers intercalated between the layers. D-gluconic acid behaves similarly. Intercalation characteristics strongly depended on both the type of polymer and Ca/Si molar ratio of C-S-H; intercalation reached a maximum at an initial Ca/Si = 1.3 in all cases. Poly(vinyl alcohol) was the only nonionic polymer among those studied that was incorporated into C-S-H. Evidence for interlayer intercalation is less definite. The C-S-H/polymer complexes were examined by Fourier transform infrared spectroscopy, ²⁹Si nuclear magnetic resonance magic angle spinning and ¹³C CP-MASS nuclear magnetic resonance spectroscopy.

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Synthesis of calcium silicate hydrate/polymer complexes: Part II. Cationic polymers and complex formation with different polymers

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Some high molecular weight cationic polymers, poly(diallyldimethylammonium chloride) (PDC) and poly(4-vinylbenzyltrimethylammonium chloride) (PVC), have been incorporated into the calcium silicate hydrate (C-S-H) structure during precipitation of quasicrystalline C-S-H from aqueous solution. Expansion of the interlayer spacing [0.9 nm (PDC), 1.5 nm (PVC)] and a high carbon content provided evidence that these polymers were intercalated between layers of C-S-H when Ca/Si < 1.0. Intercalation characteristic properties strongly depended on both of the type of polymer and Ca/Si ratio in C-S-H. Poly(4-vinyl-1-methylpyridinium bromide) and methyl glycol chitosan (iodide) also interacted with C-S-H, probably by surface adsorption. The C-S-H/polymer complexes were examined by Fourier transform infrared spectroscopy, ^{29}Si nuclear magnetic resonance magic angle spinning and ^{13}C CP-MASS nuclear magnetic resonance spectroscopy. Mechanisms of intercalation of different kinds of polymers between the C-S-H layers are discussed.

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Experimental study of the atmospheric pressure chemical vapor deposition of silicon carbide from methyltrichlorosilane

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A comprehensive study of the chemical vapor deposition of SiC from methyl-trichlorosilane at atmospheric pressure was carried out in this study; its main objectives were to identify the range of operating parameters where stoichiometric SiC could be deposited and the generation of reliable kinetic data that could be employed for the design of atmospheric pressure processes of chemical vapor deposition or chemical vapor infiltration of SiC. Deposition experiments were conducted in a hot-wall, cylindrical reactor at temperature ranging from 1273 to 573 K on flat graphite substrates or thin molybdenum wires aligned with the axis of the reactor. The obtained results showed that the deposition rate and the deposit stoichiometry varied markedly with the distance from the entrance of the reactor. The deposition rate exhibited, depending on the reaction temperature, one or two pronounced maxima before the beginning of the isothermal zone of the reaction, whereas the deposit stoichiometry showed an abrupt transition from almost silicon to stoichiometric silicon carbide after the first maximum. Experiments with HCl added in the feed showed that the presence of HCl could cause complete suppression of the deposition of silicon and lead to smoother variation of the SiC deposition rate with the residence time in the reactor. It is believed that this effect could be exploited to improve the uniformity of SiC deposition in chemical vapor deposition reactors or in the interior of porous preforms.

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Fractional factorial design applied to optimize the experimental conditions for the preparation of ultrafine lanthanum-doped strontium titanate powders

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A fractional factorial design was implemented to optimize the experimental conditions for the preparation of ultrafine lanthanum-doped strontium titanate from titanyl acylate precursors. The effects of such preparation conditions as the molar ratio of acetic acid to titanium alkoxide, the water to titanium alkoxide ratio, pH-value, the reaction temperature and stirring speed were systematically studied using Taguchi orthogonal array design. Results indicated that the effects of the reaction temperature and stirring speed on the reaction were the key variables influencing the average particle size of powders obtained. By combining the optimal settings of the two influential processing variables, it was possible to obtain an ultrafine powder with a particle size of about 340 Å. This was put to a test in the laboratory and a polycrystalline, narrow size distribution ultrafine SrTiO₃ powder was obtained, which had a particle size of about 380 Å and readily sintered at 1150–1250 °C.

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Synthesis of oxide powders via a polymeric steric entrapment precursor route

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A polymerized organic-inorganic complexation route is introduced for the synthesis of YAG (yttrium aluminum garnet, Y₃Al₅O₁₂) and cordierite (Mg₂Al₄Si₅O₁₈) powders. Long-chain polymers such as polyvinyl alcohol (-[CH₂-CHOH]-*n*, PVA) or polyethylene glycol (H[O-CH₂-CH₂]*n*OH, PEG) were used as the organic carriers for a precursor ceramic gel. Calcined powders were very porous and homogeneous in distribution of components. Experimental studies by differential thermal analysis and thermogravimetric analysis, x-ray diffraction, solid-state nuclear magnetic resonance, and Fourier transform infrared spectroscopy indicated that metal-ion chelation is not the primary mechanism for obtaining molecularly homogenous precursor powders. Water-soluble cations of mixed oxides in the PVA or PEG process were sterically entrapped in the entangled network and resulted in fine and pure mixed oxide powders.

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Synthesis of nickel-chromium-zinc ferrite powders from stainless steel pickling liquors

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A low-temperature method was used to synthesize a nickel-chromium-zinc ferrite from stainless steel pickling liquor, a waste product of the steel industry, which is listed in most industrialized countries as a toxic and hazardous waste. This paper reports the recovery (as a valuable ferric product) of the total metal content of this waste (namely iron, chromium, nickel and minor manganese), by co-precipitation of the multi-ionic solution and Zn²⁺ (provided by ZnO) with 1 M *n*-butylamine at room temperature. The spinel-type ferrite produced was characterized by x-ray diffraction, thermogravimetric analysis and differential scanning calorimetry, and scanning electron microscopy. Its recorded magnetization of 2600 emu cm⁻³ allows its use in different magnetic applications. Further, the synthesis method is a low-cost technology that yields a more environmentally friendly final effluent.

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Interfacial reactions of Co/Si_{0.76}Ge_{0.24} and Co(Si_{0.76}Ge_{0.24})/Si_{0.76}Ge_{0.24} by pulsed KrF laser annealing

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Interfacial reactions of Co/Si_{0.76}Ge_{0.24} and Co(Si_{0.76}Ge_{0.24})/Si_{0.76}Ge_{0.24} by pulsed KrF laser annealing as a function of energy density and pulse number were studied. For the Co/Si_{0.76}Ge_{0.24} samples annealed at an energy density of 0.2–0.6 J/cm², three germanosilicide layers, i.e., amorphous structure and/or nanocrystal, Co(Si_{1-x}Ge_x)₂, and Co(Si_{1-x}Ge_x)₃, were successively formed along the film-depth direction. At 0.3 J/cm² Ge segregated to the underlying Si_{0.76}Ge_{0.24} film, inducing strain relaxation in the residual Si_{0.76}Ge_{0.24} film. At 0.8 J/cm² the reacted region was mostly transformed to a single layer of Co(Si_{1-x}Ge_x)₂, while Ge further diffused to the Si substrate. At 1.0 J/cm² constitutional supercooling appeared. Even the Co(Si_{0.76}Ge_{0.24}) film used as the starting material for laser annealing could not prevent the occurrence of constitutional supercooling at energy densities above 1.6 J/cm². The energy densities at which Co(Si_{1-x}Ge_x) transformation to Co(Si_{1-x}Ge_x)₂, Ge segregation to the underlying Si, and constitutional supercooling occurred were higher for the Co(Si_{0.76}Ge_{0.24})/Si_{0.76}Ge_{0.24} system than for the Co/Si_{0.76}Ge_{0.24} system. Higher energy density and/or pulse number enhanced the growth of Co(Si_{1-x}Ge_x)₂ film. In the present study, the Co/Si_{0.76}Ge_{0.24} samples subjected to annealing at 0.2 J/cm² for 20 pulses can produce a smooth Co(Si_{0.76}Ge_{0.24}) film without inducing Ge segregation out of the germanosilicide and strain relaxation in the unreacted Si_{0.76}Ge_{0.24} film.

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Point defect incorporation during diamond chemical vapor deposition

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The incorporation of vacancies, H atoms, and *sp*² bond defects into single-crystal homoepitaxial (100)(2x1)- and (111)-oriented chemical vapor-deposited diamond was simulated by atomic-scale kinetic Monte Carlo. Simulations

were performed for substrated temperatures from 600 to 1200 °C with 0.4% CH₄ in the feed gas, and for 0.4% to 7% CH₄ feeds with a substrate temperature of 800 °C. The concentrations of incorporated H atoms increased with increasing substrate temperature and feed gas composition, and *sp*² bond trapping increased with increasing feed gas composition. Vacancy concentrations were low under all conditions. The ratio of growth rate to H atom concentration was highest around 800–900 °C, and the growth rate to *sp*² ratio was maximum around 1% CH₄, suggesting that these conditions are ideal for economical diamond growth under the simulated conditions.

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Study of the overtones and combination bands in the Raman spectra of polyparaphenylene-based carbons

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A detailed study of the second-order Raman spectrum of the polymer polyparaphenylene (PPP) prepared according to the Kovacic method and heat treated at temperatures THT between 650 and 750 °C is presented. The Raman experiments have been performed using five different laser excitation energies in the visible range between 1.92 and 3.05 eV. Several Raman bands in the region between 2400 and 3400 cm⁻¹ have been detected and assigned to the overtones and combination bands of the two conformations of the PPP polymer (benzenoid and quinoid) that coexist in our samples. Due to the carbonization process, these bands broaden and decrease in intensity with increasing heat treatment temperature, as is also observed for the corresponding first-order Raman features. The complete absence of these high frequency Raman bands for PPP with heat treatment temperatures in excess of 750 °C indicates the complete transformation of the polymer into a disordered carbon material.

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The boron oxide–boric acid system:

Nanoscale mechanical and wear properties

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The film that forms spontaneously when boron oxide (B₂O₃) is exposed to humid air is a solid lubricant. This film is usually assumed to be boric acid (H₃BO₃), the stable bulk phase. We describe the nanometer-scale surface morphology, mechanical properties, and tribological properties of these films and compare them with crystals precipitated from saturated solutions of boric acid. Scanning force microscopy (SFM) and low-load indentation were the primary experimental tools. Mechanical properties and their variation with depth are reported. In all cases, the surfaces were covered with a layer that has different mechanical properties than the underlying bulk. The films formed on boron oxide showed no evidence of crystalline structure. A thin surface layer was

rapidly removed, followed by slower wear of the underlying film. The thickness of this initial layer was sensitive to sample preparation conditions, including humidity. Friction on the worn surface was lower than on the as-formed surface in all cases. In contrast, the SFM tip was unable to cause any wear to the surface film on the precipitated crystals. Indentation pop-in features were common for precipitated crystals but did not occur on the films formed on boron oxide. The surface structures were more complex than assumed in models put forth previously to explain the mechanism of lubricity in the boron oxide–boric acid–water system.

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Crystallite coalescence:

A mechanism for intrinsic tensile stresses in thin films

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We examined the stress associated with crystallite coalescence during the initial stages of growth in thin polycrystalline films with island growth morphology. As growing crystallites contacted each other at their bases, the sidewalls zipped together until a balance was reached between the energy associated with eliminating surface area, creating a grain boundary, and straining the film. Our estimate for the resulting strain depends only on interfacial free energies, elastic properties, and grain size and predicts large tensile stresses in agreement with experimental results. We also discuss possible stress relaxation mechanisms, which can occur during film growth subsequent to the coalescence event.

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Scratch adhesion testing of nanophase diamond coatings on steel and carbide substrates

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Films of nanophase diamond are deposited in vacuum onto almost any substrate by condensing multiply charged carbon ions carrying KeV energies. These ions are obtained from the laser ablation of graphite at intensities in excess of 10¹¹ W cm⁻². The high energies of condensation produce interfacial layers between the film and substrate materials, resulting in levels of adhesion that can support the protection of substrates subjected to harsh environmental conditions. In this paper, we give details of the scratch adhesion testing performed on steel and carbide substrates coated with nanophase diamond. A commercially available scratch tester was used and a data analysis was presented to quantitatively assess and measure the adhesion of films on these important substrates. The characterization studies in this work demonstrated nanophase diamond as a highly adherent coating suitable for industrial applications.

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