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COMMUNICATIONS

Nanoprobe analysis of core–rim structure of carbides in TiC–20 wt% Mo_2C–20 wt% Ni cermet

T. Yamamoto, A. Jaroenworaluck, Y. Ikuhara, T. Sakuma
(The University of Tokyo)

In order to get detailed information of the core–rim interface of carbides in TiC–20 wt% Mo_2C–20 wt% Ni cermet, chemical analysis in the vicinity of the interface was carried out by energy dispersive x-ray spectroscopy equipped to a high-resolution transmission electron microscope (HRTEM) with a field-emission-type gun. It was found that the chemical composition discretely changed across the core–rim interface at a nanoscale level, whereas HRTEM observation revealed that the interface is highly coherent. The discrete change in molybdenum content at the interface may suggest the existence of a miscibility gap between TiC and MoC system at the sintering temperature.

Order No.: JA911-001

Electrical and mechanical property transitions in carbon-filled polyvinylpyrrolidone

J.C. Grunlan, W.W. Gerberich, L.F. Francis
(University of Minnesota)

The effect of carbon black content on the mechanical and electrical properties of carbon-black-filled polyvinylpyrrolidone composites was determined. Experimental data show a drop in the modulus when the volume of carbon black exceeds 25%, coincident with pore formation documented by scanning electron microscopy. This behavior is consistent with surpassing the critical pigment volume concentration. Electrical conductivity, however, does not show a discontinuous change in behavior at 25 vol% carbon black and continues to increase through a carbon black loading of 35 vol%. A qualitative model of microstructural evolution is presented to explain the observed differences in electrical and mechanical behavior.

Order No.: JA911-002

Evidence of transition metal diffusion during hydrothermal ceramic film growth: Ba(Ti,Zr)O_3 on layered Ti–Zr alloy

A.V. Alvarez, V.M. Fuenzalida
(Universidad de Chile)

Ti–Zr alloy thin films of 20–60 nm in thickness were evaporated on Pt-coated silicon wafers. The films exhibited a layered Ti–Zr depth distribution. The films were then treated hydrothermally in 0.25 M $Ba(OH)_2$ at 150 and 200 °C for 4–8 h. Films treated at 150 °C did not exhibit reflections from the $Ba(Ti_xZr_{1-x})O_3$ perovskite structure by x-ray diffraction, although a slight barium content was detected by x-ray photoelectron spectrometry. On the other hand, the films treated hydrothermally at 200 °C revealed reflections corresponding to perovskite $Ba(Ti_xZr_{1-x})O_3$. These films exhibited a homogeneous titanium and zirconium depth distribution, as shown by x-ray photoelectron spectroscopy and Auger depth profiles, proving that either titanium or zirconium ions diffuse during the hydrothermal treatment. The initial Ti–Zr film was completely consumed during the hydrothermal process, leading to a film of homogeneous composition (Ba, Ti, and Zr) up to the interface with the platinum layer.

Order No.: JA911-003

Developing a coordination chemistry of intact quantum dots: The preparation of novel nanocomposites of PbS with CdS or CdSe

T. Trindade,[1] P. O'Brien,[2] X. Zhang[2]
([1]University of Aveiro, [2]Imperial College of Science, Technology and Medicine)

In this communication, a new kind of nanocomposite is reported in which a bridging coordination ligand, 2,2′-bipyrimidine, is used to bind quantum dots of CdS or CdSe (4–6 nm) to larger PbS nanoparticles.

Order No.: JA911-004

ARTICLES

Diffusion calculations for the 80-K-to-110-K Bi(Pb)SrCaCuO superconducting phase transformation

W. Zhu, C.K. Kuo, P.S. Nicholson
(McMaster University)

A diffusion model is proposed to fit the measured chemical-transformation rates of the Bi(Pb)CaCuSrO 80-K phase to 110-K phase. Diffusion coefficients and activation energies in P_{O_2} = 0.08 and 0.21 atm are reported. The low diffusion rates and high activation energies suggest that cation diffusion controls the transformation.

Order No.: JA911-005

Sintering characteristics of Y–Ba–Cu–oxide–Ag_x superconductors

L.C. Pathak,[1] S.K. Mishra,[1] D. Bhattacharya,[2] K.L. Chopra[2]
([1]National Metallurgical Laboratory, [2]Indian Institute of Technology)

The sintering characteristics of Y–Ba–Cu–oxide–Ag_x (x = 0 to 1.2) using thermomechanical analyzer were systematically investigated to understand the sintering mechanism of the metal superconductor composites. The addition of Ag was observed to lower the sintering temperatures, and the apparent densities of the sintered compacts increased with x from 0 to 0.6. A further increase of x above 0.6 decreased the apparent densities of the sintered compacts. The presence of Ag globules in the YBCO–Ag compacts was observed by scanning electron microscopy and energy dispersive x-ray spectroscopy. The apparent activation energies for sintering of the powder compacts were estimated and observed to vary between 900 and 2000 kJ/mol. The formation of AgO_x by absorbing oxygen from YBCO and sintering atmosphere possibly controls the sintering and superconducting behavior. Incorporation of Ag into the matrix modifies the weak-link characteristics from S-I-N-S to S-N-S type.

Order No.: JA911-006

A solvothermal decomposition process for fabrication and particle sizes control of Bi_2S_3 nanowires

S-H. Yu, L. Shu, J. Yang, Z-H. Han, Y-T. Qian, Y-H. Zhang
(University of Science and Technology of China)

A novel one-step solvothermal decomposition process (SDP) was successfully developed for fabrication of Bi_2S_3 nanowires via a reaction between $BiCl_3$ and thiourea in polar solvents at 140 °C for 6–12 h. The influence of solvents, reaction temperature, and reaction time on the formation of Bi_2S_3 nanowires was investigated. The yield was as high as 98%. The particle sizes of Bi_2S_3 nanowires are controlled by the choice of solvents. The possible formation mechanism of Bi_2S_3 nanowires via the so-called SDP method is proposed. The present technique is expected to synthesize other nanostructured metal chalcogenides under mild conditions.

Order No.: JA911-007

Photoacoustic spectrum of porous silicon irradiated by light

T. Kawahara,[1] T. Kiyotoo,[1] J. Morimoto,[1] R. Koga,[1] S. Iwane,[1] K. Tahira,[1] T. Miyakawa[2]
([1]National Defense Academy, [2]Chiba Institute of Technology)

The photoacoustic (PA) spectra for the porous silicon samples irradiated during or after anodization are reported. The difference between the spectra on the irradiation conditions is discussed. The light irradiation time dependence of the PA spectra is shown. The irradiation after anodization causes the samples to luminesce in the blue region and enhances the photoluminescence signal intensity around 600 nm. It also reduces the PA signal intensity in the shorter wavelength region. The irradiation during the anodization causes enhancement only in the red-region luminescence.

Order No.: JA911-008

Investigation of optical anisotropy of refractive-index-profiled porous silicon employing generalized ellipsometry

S. Zangooie, R. Jansson, H. Arwin
(Linköping University)

Porosity depth profiles in porous silicon were realized by time modulation of the applied current density during electrochemical etching of crystalline silicon. The samples were investigated employing variable angle spectroscopic ellipsometry. Using a basic optical model based on isotropy assumptions and the Bruggeman effective medium approximation, deviations from an ideal profile in terms of an interface roughness between the silicon substrate and the porous silicon layer and a compositional gradient normal to the surface were revealed. Furthermore, optical anisotropy of the sample was investigated using generalized ellipsometry. The anisotropy was found to be uniaxial with the optic axis tilted from surface normal by about 25°. The material was also found to exhibit positive birefringence.

Order No.: JA911-009

Thermoelectric properties of sintered polycrystalline $ZnIn_2S_4$

W-S. Seo, R. Otsuka, H. Okuno, M. Ohta, K. Koumoto
(Nagoya University)

Ceramic compacts of spinel-type $ZnIn_2S_4$ and IIIa-$ZnIn_2S_4$ polytype with a layer structure were synthesized by the reaction-sintering of mixed powders of ZnS and In_2S_3 at 723 and 1073 K in an Ar (containing 1% H_2) atmosphere, respectively. The thermoelectric properties were investigated in the temperature range from 473 to 873 K. The thermoelectric figure of merit of the IIIa-type was much larger than that of the spinel-type, and it was slightly higher than the figure of merit of $(ZnO)_9In_2O_3$, which is known to show the largest value among the oxide homologous compounds. To improve the thermoelectric properties, a c-plane-oriented sintered body of the IIIa-polytype was successfully fabricated by a usual ceramic process. The figure of merit in the direction on the c plane was larger than on the ab plane due to higher electrical conductivity on the c plane and increased with increasing temperature showing the largest value of 1.3×10^{-4} K^{-1} at 873 K.

Order No.: JA911-010

On the indexing and reciprocal space of icosahedral quasicrystal

A. Singh, S. Raganathan
(Indian Institute of Science)

Important features of the icosahedral reciprocal space have been brought out. All reciprocal vectors up to sixth generation (by addition of icosahedral vectors) have been considered. Some more relationships for indexing the icosahedral phase are derived, and it is shown that the zone law using Cahn indices is also analogous to that valid for crystals. All important vectors, i.e., up to fourth generation and sixth generation, have been identified. Poles of all these vectors have been determined and shown to be one of the zone axes formed by these vectors. The types of indices that the planes and axes will have in three-dimensional and six-dimensional coordinates are discussed.

Order No.: JA911-011

Laser-processing-induced phase transformation in Zn–Al-based alloy

Y.H. Zhu,[1,2] J.A. Chavez-Carvayar,[1] H.C. Man,[2] M. Villagran[1]
([1]UNAM, [2]Hong Kong Polytechnic University)

Microstructure and phase transformation of a furnace-cooled eutectoid Zn–Al-based alloy were studied after laser beam bombardment using low-angle x-ray diffraction (XRD) and backscattered scanning electron microscopy (BSEM). It was found that the microstructure of the laser-beam-treated specimen consisted mainly of the supersaturated Zn-rich β'_S phase particulates of about 1–2 μm in diameter. Three structure morphologies were observed. Microcracking occurred in the laser-beam-affected zone during laser processing. Two laser-processing-induced phase transformations, i.e., decomposition of the η'_{FC} phase and a four-phase transformation, were detected using XRD and BSEM techniques, similar to phase transformations that occurred in the same eutectoid Zn–Al-based alloy after various thermal and thermomechanical processing.

Order No.: JA911-012

Comparison of the crystallographic and magnetic properties between $Tb_2Fe_{16.46}Cr_{1.23}$ and $Tb_3(Fe,Cr)_{29}$ single crystals

C.P. Yang,[1,2] Y.Z. Wang,[2] G.H. Wu,[2] B.P. Hu,[2] X.F. Han,[2] Z.L. Jiang,[1] C.L.Ma,[1] J. Zhu[1]
([1]Tsinghua University, [2]Chinese Academy of Sciences)

A novel $Tb_3(Fe,Cr)_{29}$ single crystal, which has a monoclinic $Nd_3(Fe,Ti)_{29}$-type structure, is obtained using the Czochralski method by performing a proper heat treatment on the $Tb_2Fe_{16.46}Cr_{1.23}$ crystal with a Th_2Ni_{17}-type structure. Thermomagnetic curves along the easy axis and magnetization curves along the easy and hard axes are presented for both crystals. The lattice parameters are a = 1.058 nm, b = 0.848 nm, c = 0.968 nm, $\alpha = \gamma = 90°$, and β = 96.93° for the $Tb_3(Fe,Cr)_{29}$ single crystal. The Curie temperatures, saturation magnetizations, and magnetocrystalline anisotropy constants are compared between the Tb-2:17 and Tb-3:29 crystals. The magnetization anisotropy constants are compared between the Tb-2:17 and Tb-3:29 crystals. The magnetization behavior along the hard axis is quite different as a first-order magnetization process (FOMP) of type I for the Tb-2:17, but a FOMP of type II for the Tb-3:29 crystal is observed below room temperature. At low temperatures, magnetohistory effects are detected for both crystals.

Order No.: JA911-013

Fabrication and thermal stability of a nanocrystalline Ni–Al–Cr alloy: Comparison with pure Cu and Ni

K. Oh-ishi,[1] Z. Horita,[1] D.J. Smith,[2] R.Z. Valiev,[3] M. Nemoto,[1] T.G. Langdon[4]
([1]Kyushu University, [2]Arizona State University, [3]Ufa State Aviation Technical University, [4]University of Southern California–Los Angeles)

A Ni–Al–Cr alloy with an initial grain size of ~60 μm was subjected to torsion straining to a strain of ~7 at room temperature, thereby reducing the grain size to ~34 nm. Similar torsion straining with samples of pure Cu and

pure Ni gave grain sizes of ~170 and ~130 nm, respectively. Inspection of the Ni–Al–Cr alloy after torsion straining revealed highly strained regions containing dislocations associated with lattice distortions but with an absence of any Ni_3Al ordered phase. The ultrafine grains in the Ni–Al–Cr alloy were extremely stable at high temperatures, and it was possible to retain a grain size of less than 100 nm after annealing at temperatures up to ~900 K. By contrast, there was rapid grain growth in the samples of pure Cu and Ni at annealing temperatures in the vicinity of ~500 K. The stability of the grains in the Ni–Al–Cr alloy is attributed to the formation of a Ni_3Al-based ordered phase after annealing at ~650–700 K. The presence of this phase leads also to an apparent negative slope in the standard Hall–Petch relationship.
Order No.: JA911-014

Containerless solidification studies of the α–1/1 crystal approximant in Ti–Cr–Si–O alloys

T.K. Croat, D. Holland-Moritz, M.B. Robinson, T.J. Rathz, K.F. Kelton
(Washington University)

The nucleation behavior of α(TiCrSiO), a 1/1 Fibonacci crystal approximant phase, was investigated in alloys made near the stoichiometric composition. Containerless solidification studies were made with electromagnetic (rf) levitation and the 105m NASA Drop-Tube. The solidification microstructures indicate that the α–Ti hexagonal solid-solution was the primary crystallizing phase in these alloys, growing dendritically. The α(TiCrSiO) phase nucleated in the remaining liquid. The competition between these two phases resulted from the high oxygen concentration needed to form α(TiCrSiO), which also stabilized the hexagonal-close-packed α–Ti phase.
Order No.: JA911-015

Evolution of microstructure and phases in *in situ* processed Ti–TiB composites containing high volume fractions of TiB whiskers

S.S. Sahay,[1] K.S. Ravichandran,[1] R. Atri,[1] B. Chen,[2] J. Rubin[2]
([1]University of Utah, [2]Cercom Inc.)

A series of titanium composites, with varying volume fractions of titanium monoboride (TiB) whiskers, were made by mixing various proportions of titanium (Ti) and titanium diboride (TiB_2) powders followed by hot pressing. The phases present were identified by x-ray diffraction. Microstructural examination revealed three different types of TiB whisker morphologies: (i) long and needle-shaped TiB whiskers that are isolated and randomly oriented in the Ti matrix at relatively low volume fractions (0.3), (ii) colonies of refined and densely packed TiB whiskers from intermediate (0.55) to high volume fractions (0.73 and 0.86), and (iii) coarse and elongated TiB particles with a few needle-shaped whiskers at the highest volume fraction (0.92). In all the composites, TiB was found to be the predominant reinforcement. However, in Ti–TiB composited with 0.86 and 0.92 volume fractions of TiB, a significant amount of TiB_2 was also present. The relative volume fractions of Ti, TiB, and TiB_2 phases were estimated from the integrated intensities of diffraction peaks by the direct comparison method employing the calculated structure factors and Lorentz polarization factors. The composite microstructure, as well as the evolution of different morphologies, of TiB whiskers is discussed.
Order No.: JA911-016

Fiber breakage in polymer-matrix composite during static and fatigue loading, observed by electrical resistance measurement

X. Wang, D.D.L. Chung
(State University of New York at Buffalo)

By measuring the electrical resistance of a continuous unidirectional carbon fiber epoxy-matrix composite along the fiber direction during loading in this direction, fiber breakage was progressively monitored in real time. Fiber breakage occurred in spurts involving 1000 or more fibers. It started at about half of the failure strain during static tensile loading and at about half of the fatigue life during tension–tension fatigue testing. Immediately before static failure, at least 35% of the fibers were broken. Immediately before fatigue failure, at least 18% of the fibers were broken. The fiber breakage was accompanied by decrease in modulus.
Order No.: JA911-017

Infiltration of C/SiC composites with silica sol-gel solutions: Part I. Infiltration by dipping

M. Aparicio, A. Durán
(Consejo Superior de Investigaciones Científicas)

Oxidation resistance of ceramic matrix composites (CMC) of SiC reinforced with C fibers (C/SiC) can be improved by filling the residual porosity. The aim of this work was to design and analyze a dipping infiltration process under ambient conditions (1 atmosphere pressure and room temperature) with silica sol-gel solutions prepared from tetraethyl orthosilicate. Different substrates and solutions have been studied. Thermal treatments, i.e., curing or sintering between infiltrations, increase the efficiency of the process since the densification of infiltrated silica opens up the remaining porosity. Increasing viscosity and/or concentration of the solution leads to greater weight gains. Weight gains are higher in the initial stages of the process because larger diameter porosity remains unfilled. As the process advances, the average pore size decreases, and only the lower viscosity solution can enter the residual porosity.
Order No.: JA911-018

Infiltration of C/SiC composites with silica sol-gel solutions: Part II. Infiltration under isostatic pressure and oxidation resistance

M. Aparicio, A. Durán
(Consejo Superior de Investigaciones Científicas)

An infiltration process that uses silica sol-gel solutions was developed to protect C/SiC composites against oxidation. The infiltration is assisted using isostatic pressure. Different process parameters including substrate porosity, solution concentration and viscosity were varied to optimize the infiltration effectiveness. Applied pressure enhances penetration of solutions, reducing the importance of viscosity, an important process variable for dipping infiltration. The effectiveness of isostatic pressure infiltration method, evaluated through the total weight gains and pore size distribution of infiltrated samples, is compared with results by dipping infiltration. The oxidation behavior of the infiltrated samples was evaluated by stepwise oxidation test as well as isothermal tests at 1200 and 1600 °C. The infiltrated SiO_2 protects the C/SiC substrate, reducing the burn-off rate of C fibers at low temperature and delaying the oxidation of SiC.
Order No.: JA911-019

Reactive hot-pressing of aluminum matrix composites

H.J. Brinkman, J. Duszczyk, L. Katgerman
(Delft University of Technology)

A method is described for the production of dense aluminum matrix composites from elemental powders in one processing step by reactive hot-pressing (RHP). It encompasses both the exothermic conversion of reactants to composite product and the following hot compaction of the porous composite product. The RHP method described in this paper takes into account the gas evolution accompanying the exothermic process, ensures complete conversion of reactants, and avoids adverse reactions between aluminum matrix and graphite tooling material. *In situ* sample temperature measurements enable proper process control, in particular the timing of the full densification step of the hot reaction product.
Order No.: JA911-020

Effect of some substituents with different valence on antiferroelectric stability of antiferroelectric lead zirconate titanate ceramics

Q. Tan,[1] Z. Xu,[2] D. Viehland[3]
([1]Johnson Matthey Electronics, [2]University of Illinois, [3]Naval Undersea Warfare Center)

The effect of lower valent substituents on the stability of the antiferroelectric phase of lead zirconate was studied by dielectric spectroscopy, Sawyer–Tower polarization methods, and electron diffraction techniques. The stability of an intermediate ferroelectric phase region was found to be enhanced with increasing lower valent substitution concentration. The influences of substituents of different ionic size and valence on the stabilization of the intermediate ferroelectric phase were differentiated. In general, lower valent substituents, such as K^{1+} and Fe^{3+} affected antiferroelectric phase stability more significantly than higher valent ones.
Order No.: JA911-021

Processing and microwave dielectric properties of barium magnesium tantalate ceramics for high-quality-factor personal communication service filters

S-H. Ra, P.P. Phulé
(University of Pittsburgh)

A modified route, based on calcined MgO, Ta_2O_5, $BaCO_3$, and ZrO_2, was developed and used for the preparation of barium magnesium tantalate (BMT) and barium zirconate (BZ)-doped BMT ceramics (BZ-BMT). The dielectric constant for BMT ceramics sintered at 1600 °C for 2 h was 24.9 at

7.28 GHz. The average long-range ordering parameter for undoped BMT ceramics was 0.81 ± 0.03, and the corresponding average quality factor and resonant frequency product ($Q_d \cdot f_o$) was 147,000 ± 3800 GHz. A significant level of B-site long-range cations disorder was introduced as a result of BZ doping of BMT ceramics. The average ordering parameters for 3 and 4 mol% BZ-doped BMT were found to be 0.69 ± 0.06 and 0.49 ± 0.13, respectively. The decrease in ordering parameters did not lead to a dramatic decrease in the corresponding average quality factors of 3 mol% BZ-BMT ($Q_d \cdot f_o$ = 139,000 ± 4200 GHz). The results suggest that B-site cations ordering is *not* a primary factor that influences the observed microwave loss in BMT ceramics. The influence of atomic level point defects, induced from raw material impurities, processing, etc., may be more important in controlling the quality factor of BMT ceramics.

Order No.: JA911-022

Formation and structure of carbon nanocage structures produced by polymer pyrolysis and electron-beam irradiation

T. Oku,[1] T. Hirano,[1] S. Nakajima,[2] K. Suganuma[1]
([1]Osaka University, [2]Tohoku University)

Carbon nanocapsules with SiC and Au nanoparticles were produced by thermal decomposition of polyvinyl alcohol at about 500 °C in Ar gas atmosphere. The formation mechanism of nanocapsules and a structural model for the nanocapsule/SiC interface were proposed. In addition, carbon clusters were formed at the surface of carbon nanocapsules, and carbon onions were produced by electron irradiation of amorphous carbon produced from polyvinyl alcohol. The present work indicates that the pyrolysis of polymer materials with clusters is a useful fabrication method for the mass production of carbon nanocapsules and onions at low temperatures compared to the ordinary arc discharge method.

Order No.: JA911-023

Mechanochemically synthesized NbC cermets: Part I. Synthesis and structural development

B.R. Murphy, T.H. Courtney
(Michigan Technological University)

The mechanochemical synthesis of NbC-based cermets is described. Nanocrystalline NbC is synthesized by room-temperature milling of Nb and graphite (or hexane) mixtures. While some structural coarsening occurs during powder consolidation to full density, a nanoscale structure is maintained. Grinding media wear occurs during milling, and milled powders contain Fe from this abrasion. This phase, homnogeneously distributed in milled powders, segregates during consolidation and heat-treatment and cermetlike microstructure results. Copper added to the powder charge yields NbC–Cu or NbC–Cu–Fe cermets. Copper-containing materials have different phase morphologies. In particular, relatively large NbC particles are dispersed in a matrix containing finer NbC and metal particles. Higher Cu-content materials also develop a pure Cu constituent on heat-treatment. A companion paper addresses aspects of the mechanical behavior of these materials.

Order No.: JA911-024

Mechanochemically synthesized NbC cermets: Part II. Mechanical properties

B.R. Murphy, T.H. Courtney
(Michigan Technological University)

The mechanical behavior of mechanochemically synthesized NbC cermets has been investigated. Material hardnesses range from a high of 19.6 GPa for as-synthesized cermets containing about 4 vol% Fe to a low of about 4 GPa for heat-treated cermets containing about 34 vol% Cu. Higher hardness generally correlates with lower fracture toughness (about 2 MPa $m^{1/2}$ for cermets containing the highest percentage of NbC) and vice versa. Highest fracture toughness (about 7.5 MPa $m^{1/2}$) is found in NbC–18 vol% Fe cermets heat treated extensively following consolidation. Abnormally low fracture toughnesses found in high-Cu-content cermets in which Cu segregation takes place during heat treatment. Current models of ceramic toughening can be applied to describe the fracture behavior of NbC–Fe cermets.

Order No.: JA911-025

Mechanism of grain growth in liquid-phase-sintered β–SiC

Y-W. Kim,[1] M. Mitomo,[2] G-D. Zhan[2]
([1]University of Seoul, [2]National Institute for Research in Inorganic Materials)

The mechanism for grain growth of β–SiC was investigated by annealing hot-pressed β–SiC–oxynitride glass (Y–Mg–Si–Al–O–N) ceramics at 1800 °C. An observed decrease in grain growth with increasing weight fraction of liquid confirms a diffusion-controlled growth mechanism in the system. The growth of nearly spherical β–SiC grains in the annealed specimen also supports the above conclusion.

Order No.: JA911-026

Si_3N_4–TiN–Y_2O_3 ceramics derived from chemically modified perhydropolysilazane

Y. Iwamoto,[1] K. Kikuta,[2] S. Hirano[2]
([1]Synergy Ceramics Laboratory, [2]Nagoya University)

[Si–Y–Ti–O–C–N] multicomponent powders were synthesized by pyrolysis at 1000 °C, in NH_3 flow, of chemically modified perhydropolysilazane using yttrium tri-isopropoxide and titanium tetrachloride. [Si–Y–Ti–O–C–N] powders yielded uniform and fine-grained Si_3N_4–TiN–Y_2O_3 ceramics by heat treatment at 1800 °C in N_2.The fully densified Si_3N_4–TiN–Y_2O_3 ceramics were also synthesized by heat treatment at 1800 °C, followed by powder-vehicle hot pressing at 1800 °C in N_2. The resulting ceramics revealed that TiN was dispersed as particles having a size range of about 60 to 600 nm, and the fine particles less that 80 nm were dispersed within the β–Si_3N_4 matrix grains.

Order No.: JA911-027

Pyrochlore-to-perovskite transformation during rapid heating of sol-gel (Pb,La)TiO_3 thin films

M. Alguerό, M. Lourdes Calzada, L. Pardo
(Consejo Superior de Investigaciones Científicas)

Phases appearing in lanthanum-modified lead titanate thin films prepared by a diol-base sol-gel method and crystallized by rapid heating were studied. The results clearly indicate that a phase transformation from a pyrochlore structure to the perovskite phase occurs in Pb-deficient films during the thermal treatment, which involves a heating rate higher than 500 °C min^{-1}. The rate of this transformation is a function of the lead content of the films, decreasing as the lead volatilizes. Temperatures higher than 650 °C or soak times longer than 2 h make possible the complete pyrochlore-to-perovskite transformation without any lead excess in the films.

Order No.: JA911-028

Domain and lattice contributions to dielectric and piezoelectric properties of Pb(Zr_x,Ti_{1-x})O_3 thin films as a function of composition

S. Hiboux, P. Muralt, T. Maeder
(Federal Institute of Technology)

In situ reactively sputter deposited, 300-nm-thick Pb(Zr_x,Ti_{1-x})O_3 thin films were investigated as a function of composition, texture, and different electrodes (Pt, RuO_2). X-ray diffraction analysis, ferroelectric, dielectric, and piezoelectric measurements were carried out. While for dielectric properties bulklike contributions from lattice as well as from domains are observed, domain wall contributions to piezoelectric properties are very much reduced in the morphotrophic phase boundary (MPB) region. Permittivity and d_{33} do not peak at the same composition; the MPB region is broadened up and generally shifted to the tetragonal side.

Order No.: JA911-029

Fabrication of (Ba,Pb)TiO_3-based tapes with positive temperature coefficients of resistivity by the oxidation of malleable, metal-bearing precursors (the volume identical metal oxidation process)

S.M. Allameh, K.H. Sandhage
(The Ohio State University)

The feasibility of producing (Ba,Pb)TiO_3-based thermistor tapes by the oxidation of malleable metal-bearing precursors has been demonstrated. Intimate Ba–Pb–Ti–TiO_2-bearing powder mixtures, produced by high-energy vibratory milling, were packed within a fugitive metal can and then compacted and formed into tapes of uniform thickness by cold drawing and rolling. The tape-shaped precursors were oxidized and converted into (Ba,Pb)TiO_3-based tapes with a series of heat treatments at ≤1120 °C. With proper control of thermal treatments and chemical additions (Sb_2O_3 + MnO_2 dopants), positive-temperature-coefficient-of-reactivity thermistors were produced that exhibited significant increases in resistivity commencing at temperatures ≥350 °C.

Order No.: JA911-030

Three-dimensional vapor growth mechanism of carbon microcoils

X. Chen,[1] T. Saito,[2] M. Kusuniki,[2] S. Motojima[3]
([1]Huaqiao University, [2]Japan Fine Ceramic Center, [3]Gifu University)

Carbon microcoils were grown by the Ni-catalyzed pyrolysis of acetylene. The growth patterns and the tip morphologies of the carbon coils are examined

in detail, and a growth mechanism is proposed. Basically, six thin fibers grew from a Ni catalyst grain during the initial growth stage immediately followed by the coalescence of the four fibers to form two fibers and then forming double-helixed carbon coils. A small amount of S and O, as well as C and Ni, was observed on the periphery of the cross section of the Ni catalyst grain. On the other hand, S and O were not observed in the central part. The driving force of the coiling of the straight fibers to form carbon coils is considered to be the strong anisotropy of the carbon deposition between different crystal faces.
Order No.: JA911-031

Optical properties of AlN determined by vacuum ultraviolet spectroscopy and spectroscopic ellipsometry data

D.J. Jones,[1] R.H. French,[1] H. Müllejans,[2] S. Loughin,[1] A.D. Dorneich,[2] P.F. Carcia[1]
([1]DuPont Central Research, [2]Max-Planck-Institut für Metallforschung)

Precise and accurate knowledge of the optical properties of aluminum nitride (AlN) in the ultraviolet (UV) and visible (VIS) regions is important because of the increasing application of AlN in optical and electro-optical devices, including compact disks, phase shift lithography masks, and AlN/GaN multilayer devices. The interband optical properties in the vacuum ultraviolet (VUV) region of 6 to 44 eV have been investigated previously because they convey detailed information on the electronic structure and interatomic bonding of the material. In this work, we have combined spectroscopic ellipsometry with UV/VIS and VUV spectroscopy to directly determine the optical constants of AlN in this range, thereby reducing the uncertainty in the preparation of the low-energy data extrapolation essential for KK analysis of VUV reflectance. We report the complex optical properties of AlN, over the range of 1.5 to 42 eV, showing improved agreement with theory when contrasted with earlier results.
Order No.: JA911-032

Gas-phase nucleation during chemical vapor deposition of copper films and its effect on the resistivity of deposited films

I.A. Rauf, R. Siemsen, M. Grunwell, R.F. Egerton, M. Sayer
(University of Alberta)

A study of the electrical resistivity and microstructure of thin copper films deposited by low-pressure chemical vapor deposition from copper (I) hexafluoroacetylacetonate vinyltrimethylsilane (Cupra Select) was undertaken. Evidence for the nucleation of solid copper in the gas phase at substrate temperatures of about 250 °C is presented. A process to predict the effects on gas-phase nucleation and growth on the electrical resistivity of the resulting film is discussed.
Order No.: JA911-033

Surface modification of aluminum and chromium by ion implantation of nitrogen with a high current density ion implanter and plasma-source ion implantation

Z. Falkenstein,[1] K.C. Walter,[1] M.A. Nastasi,[1] D.J. Rej,[1] N.V. Gavrilov[2]
([1]Los Alamos National Laboratory, [2]Ural Division of the RAS)

Results of ion implantation of nitrogen into electrodeposited hard chromium and pure aluminum by a high-dose ion-beam source are presented and compared to plasma-source ion implantation. The large-area, high current density ion-beam source can be characterized, with respect to surface modification use, by a uniform emitted dose rate in the range 10^{16} to 5×10^{17} N cm^{-2} min^{-1} over an area of <100 cm^2 and with acceleration energies of 10 to 50 keV. The implantation range and retained dose (measured using ion-beam analysis), the surface hardness, coefficient of friction, and the change in the wear coefficient (measured by nanohardness indentation in pin-on-disk wear testing) that were obtained with an applied dose rate of ~1.7×10^{17} N cm^{-2} min^{-1} at 25 kV are given, and they are compared to results obtained with plasma-source ion implantation.
Order No.: JA911-034

Measuring the interface stress: Silver/nickel interfaces

D. Josell,[1] J.E. Bonevich,[1] I. Shao,[2] R.C. Cammarata[2]
([1]National Institute of Standards and Technology, [2]The Johns Hopkins University)

Interface stress is a surface thermodynamics quantity associated with the reversible work of elastically straining an internal solid interface. In a multilayered thin film, the combined effect of the interface stress of each interface results in an in-plane biaxial volume stress acting within the layers of the film that is inversely proportional to the bilayer thickness. We calculated the interface stress of an interface between highly {111} textured Ag and Ni based upon direct measurements of the dependence of the in-plane elastic strains on the bilayer thickness. The strains were obtained using transmission x-ray diffraction. Unlike previous studies of this type, we used free-standing films so that there was no need to correct for intrinsic stresses resulting from forces applied by the substrate that can lead to large uncertainties of the calculated interface stress value. An interface stress of -2.02 ± 0.26 N/m was calculated using the x-ray diffraction results from films with bilayer thicknesses greater than 5 nm. This value is somewhat smaller than previous measurements obtained from as-deposited films supported by substrates. For smaller bilayer thicknesses the apparent interface stress becomes smaller in magnitude, possibly due to a loss of layering in the specimens.
Order No.: JA911-035

Microstructure and electrical properties of chemical solution deposition (Pb,La)(Zr,Ti)O_3 thin films on Pt electrodes

J.S. Cross, M. Fujiki, M. Tsukada, Y. Kotaka, Y. Goto
(Fujitsu Laboratories, Ltd.)

(Pb,La)(Zr,Ti)O_3 (PLZT) films with thicknesses of 150 and 225 nm were prepared by chemical solution deposition method on sputtered Pt/IrO_2 coated on SiO_2/Si wafers. The annealed films revealed two different microstructures: fine-grained and large-grained. The thinner film had the largest grain size and highest leakage current, whereas the thicker film had small grains and lower leakage. Atomic force microscope images showed that the thinner film had half-dome-shaped grains, which were about one-third thinner at the grain boundary triple points. These triple points also contained a nanocrystalline nonstoichiometric secondary phase, which contributed to high leakage. A model was developed showing differences in crystallization based upon grain growth and number of nuclei on the Pt surface. These results indicate the importance of controlling the film microstructure and its relationship on the film electrical properties.
Order No.: JA911-036

Germanium segregation in the Co/SiGe/Si(001) thin film system

P.T. Goeller,[1] B.I. Boyanov,[1] D.E. Sayers,[1] R.J. Nemanich,[1] A.F. Myers,[2] E.B. Steel[2]
([1]North Carolina State University, [2]National Institute of Standards and Technology)

Cobalt disilicide contacts to silicon–germanium alloys were formed by direct deposition of pure cobalt metal onto silicon–germanium films of Si(001) substrates. Segregation of germanium was observed during the reaction of the cobalt with the silicon–germanium alloy. The nature of the Ge segregation was studied with transmission electron microscopy, energy dispersive spectroscopy, and x-ray diffraction. In the case of cobalt films deposited onto strained silicon–germanium films, the Ge segregation was discovered to be in the form of Ge-enriched $Si_{1-x}Ge_x$ regions found at the surface of the film surrounding CoSi and $CoSi_2$ grains. In the case of cobalt films deposited onto relaxed silicon–germanium films, the Ge segregation was dependent upon the formation of $CoSi_2$. In samples annealed below 800 °C, where CoSi was the dominant silicide phase, the Ge segregation was similar in form to the strained $Si_{1-x}Ge_x$ case. In samples annealed above 800 °C, where $CoSi_2$ was the dominant silicide phase, the Ge segregation was also in the form of tetrahedron-shaped, Ge-enriched, silicon–germanium precipitates, which formed at the substrate/silicon–germanium film interface and grew into the Si substrate. A possible mechanism for the formation of these precipitates is presesented, based on vacancy generation during the silicidation reaction coupled with an increased driving force for Ge diffusion due to silicon depletion in the alloy layer.
Order No.: JA911-037

Substrate temperature dependence of structure and resistivity of $SrRuO_3$ thin films grown by pulsed laser deposition on (100)$SrTiO_3$

N.D. Zakharov,[1] K.M. Satyalakshmi,[1,2] G. Koren,[2] D. Hesse[1]
([1]Max-Planck-Institute für Mikrostrukturphysik, [2]Technion—Israel Institute of Technology)

The resistivity of $SrRuO_3$ thin films on (001) $SrTiO_3$ substrates grown at different temperatures by pulsed laser deposition is correlated to the microstructure. Films grown at 775 °C are of an orthorhombic structure, contain very few defects, and exhibit a low resistivity of 150 μΩ cm. Films grown at other temperatures contain a cubic phase and show higher resistivities. The defects present in the films, particularly twins and antiphase boundaries, are analyzed by high-resolution transmission electron microscopy, and their origin, as well as influence on film resistivity, is discussed.
Order No.: JA911-038

An optimized process for fabrication of $SrBi_2Ta_2O_9$ thin films using a novel chemical solution deposition technique

S-H. Kim,[1] D.J. Kim,[1] K.M. Lee,[1] M. Park,[1] A.I. Kingon,[1] R.J. Nemanich,[1] J. Im,[2] S.K. Streiffer[2]
([1]North Carolina State University, [2]Argonne National Laboratory)

Ferroelectric $SrBi_2Ta_2O_9$ (SBT) thin films on $Pt/ZrO_2/SiO_2/Si$ were successfully prepared by using an alkanolamine-modified chemical solution deposition method. It was observed that an alkanolamine provided stability to the SBT solution by retarding the hydrolysis and condensation rates. The crystallinity and the microstructure of the SBT thin films improved with increasing annealing temperature and were strongly correlated with the ferroelectric properties of the SBT thin films. The films annealed at 800 °C exhibited low leakage current density, low voltage saturation, high remanent polarization, and good fatigue characteristics at least up to 10^{10} switching cycles, indicating favorable behavior for memory applications.

Order No.: JA911-039

A chemical role of refractory metal caps in Co silicidation: Evidence of SiO_2 reduction by Ti cap

E. Kondoh, T. Conrad, B. Brijs, S. Jin, H. Bender, M. de Potter, K. Maex
(IMEC)

An interfacial SiO_2 hampers a silicidation reaction between Co and Si. A refractory metal cap is believed to block ambient oxygen diffusing toward the Co/Si interface. However, an interfacial SiO_2 can also be present prior to and/or during the annealing. This work reports upon our findings of the interaction between SiO_2 and Co layers capped with refractory metals. It was found that Ti diffuses through the Co layer and segregates underneath the Co, which leads to the reduction of SiO_2 and the formation of free Si. The free Si in-diffuses and reaches the original Ti surface. On the other hand, TiN shows a very inert behavior compared to Ti. The results are discussed in connection with Co silicidation processes.

Order No.: JA911-040

Photoconductive $Bi_{12}Mo_{20}$-type films prepared by pulsed laser deposition

J.E. Alfonso,[1] M.J. Martin,[1] V. Volkov,[1] C. Zaldo,[1] M. Aguiló,[2] M.F. da Silva,[3] J.C. Soares[4]
([1]Consejo Superior de Investigaciones Científicas, [2]Universitat Rovira i Virgili, [3]Estrada Nacional, [4]Centro de Física Nuclear da Universidade de Lisboa)

$Bi_{12}TiO_{20}$ (BTO); $Bi_{12}Ga_xBi_{1-x}O_{19.5}$ (BGaO); and $Bi_{12}(M_{1/3}P_{2/3})O_{20}$, M = Cd, Zn, and Ni (BMPO) thin films were prepared by pulsed laser deposition using a KrF excimer laser on (100) Y-stabilized zirconia (YSZ), (100)$Bi_{12}GeO_{20}$ (BGO), and (110)$Bi_{12}SiO_{20}$ (BSO) crystalline substrates. All these films have a sillenite structure. On (100)YSZ the sillenite is oriented as {310} with the ⟨130⟩ direction parallel to the ⟨021⟩YSZ directions (⟨130⟩{310}BTO ∥ ⟨021⟩{100}YSZ). On (100)BGO and (110)BSO the sillenite film reproduces the substrate orientation, and the films formed are able to channel He^+ particles. The optimum deposition temperatures for BTO and BGaO are 600 and 550 °C, respectively. Higher temperatures must be avoided to minimize the nucleation of Bi-deficient phases due to the diffusion of Bi into the YSZ substrates. BMPO films are polycrystalline. The lattice parameters of these films were determined. The crystalline films support guided optical modes. The refractive indices obtained for the films are close to those measured in bulk crystals, being slightly larger for films deposited on isomorphous sillenite substrates. The crystalline films deposited on YSZ are photoconductors when excited in the green and blue spectral regions.

Order No.: JA911-041

Hydrazine-controlled hydrothermal synthesis of Co_9S_8 from a homogeneous solution

J.H. Zhan, X.G. Yang, Y. Xie, D.W. Wang, Y.T. Qian, X.M. Liu
(University of Science and Techology of China)

Single-phase nanocrystalline Co_9S_8 was prepared by hydrothermal treatment of $Co(Ac)_2$ and NH_2CSNH_2in hydrazine solution at 170 °C. The products were characterized by x-ray powder diffraction (XRD) technique, transmission electron microscope (TEM), and wet chemical analysis. XRD indicated the product was cubic Co_9S_8 phase. The relative crystallite size was 6.3 nm as determined by the Scherrer method. TEM images showed the particles were agglomerative. Electron diffraction pattern also revealed their nanocrystalline nature. In this hydrothermal formation process of Co_9S_8, hydrazine was a critical factor. The formation process is discussed.

Order No.: JA911-042

Structural evolution and phase separation of $CaO \cdot Al_2O_3 \cdot SiO_2$ glasses in electric field

W. Liu, X.M. Gu, K.M. Liang, Y.K. Zheng
(Tsinghua University)

In the present paper, the process of phase separation in calcium aluminosilicate glasses (CAS glasses) containing TiO_2 as nucleating agent is studied. A static electric field promotes the process of phase separation even when the time of heat treatment is short. The effect of electric field on phase separation acts through the higher polarizability of Ti ions. Alkali ions, when present, will diffuse toward the cathode, which may generate different micromorphology at the parts of samples near the cathode and the anode. X-ray photoelectron spectroscopy and Raman spectra analysis confirm the conclusion that electric field has promoted phase separation in CAS glasses.

Order No.: JA911-043

Multicomponent metastable phase formed by crystallization of Ti–Ni–Cu–Sn–Zr amorphous alloy

D.V. Louzguine, A. Inoue
(Tohoku University)

Crystallization of the $Ti_{45}Ni_{20}Cu_{25}Sn_5Zr_5$ alloy has been studied by means of scanning differential calorimetry, x-ray diffraction, and conventional and high-resolution transmission electron microscopy. The first stage at about 750–800 K is related to the primary crystallization of $Ti_8Ni_3Cu_3SnZr$ metastable phase having Im3m body-centered-cubic structure with a lattice parameter of $a = 0.3069$ nm followed by precipitation of the secondary dotlike phase precipitates on its boundaries. The activation energy for the first exothermic reaction determined by Kissinger analysis was found to be 310 kJ/mol. CuTi, Ni_2TiZr, and an unknown phase are formed during long-term annealing at high temperature (more than 850 K).

Order No.: JA911-044

Study of hydrogen annealing of ultrahigh molecular weight polyethylene irradiated with high-energy protons

J.F. Wilson, J.R. Liu, F. Romero-Borja, W-K. Chu
(University of Houston)

Ultrahigh molecular weight polyethylene, an important biomaterial for orthopedic implants, was irradiated with 2.6 and 3 MeV H^+ ions at low doses from 5.7×10^{11}–2.3×10^{14} ions/cm^2. Fourier transform infrared spectroscopy showed that irradiation resulted in increased free radicals, carbon double bonds, and increased methly and vinyl end groups. The free radicals resulted in poor polymer oxidative stability, as measured by increased carbonyl concentration. Hydrogen annealing after ion irradiation reacted with the free radicals generated during proton irradiation resulted in a 40–50% decrease in infrared absorption associated with carbonyl and prevented further oxidation.

Order No.: JA911-045

Resource recovery of waste incineration fly ash: Synthesis of tobermorite as ion-exchanger

Z. Yao, C. Tamura, M. Matsuda, M. Miyake
(Okayama University)

Tobermorite was synthesized successfully from waste incineration fly ash by hydrothermal treatment in the presence of sodium hydroxide solution. The tobermorite synthesis was examined as a function of reaction temperature, time, and NaOH concentration. The formation of tobermorite was identified in all of the fly ash treated with NaOH at 180 °C, followed by the minor generations of sodalite and cancrinite phases with increasing NaOH concentration and extending reaction time. The NaOH-treated fly ash revealed the uptake behaviors for Cs^+ and NH_4^+, whereas the fly ash not treated with NaOH solution did not show that. The uptake amounts of resulting products were also determined: 0.40 mmol/g for Cs^+ and 0.35 mmol/g for NH_4^+ in the fly ash treated with 2.0 M NaOH at 180 °C for 20 h.

Order No.: JA911-046