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ABSTRACTS

SPECIAL SECTION
MATERIALS SYNTHESIS AND PROCESSING

Fabrication of large grain YBCO by seeded peritectic solidification

W. Lo, D.A. Cardwell, C.D. Dewhurst, S-L. Dung
(University of Cambridge)

The ability to process large grain, uniform high-temperature superconducting ceramics that exhibit high critical current densities at 77 K is essential if the enormous potential of these materials for a range of permanent magnet type applications is to be realized. We report a study of the fabrication of large grain $YBa_2Cu_3O_{7-\delta}$ by seeded peritectic solidification in which key processing parameters such as the peritectic melting process, the seed-YBCO reaction and the YBCO solidification kinetics are investigated in detail. Evolution of the sample microstructure during various stages of the growth process, in particular, has been studied extensively. The superconducting properties of specimens cut from different regions of large grain samples have been measured using a.c. susceptometry and vibrating sample magnetometry and the results correlated with the microstructure of the materials.

Order No.: JA604-001

Macro-segregation of $Y_2Ba_1Cu_1O_5$ particles in $Y_1Ba_2Cu_3O_{7-\delta}$ crystals grown by undercooling method

A. Endo, H.S. Chauhan, T. Egi, Y. Shiohara
(Superconductivity Research Laboratory-ISTEC)

Macro-segregation of $Y_2Ba_1Cu_1O5$(Y211) particles was observed in Pt-added $Y_1Ba_2Cu_3O_{7-\delta}$ (Y123) crystals grown by an undercooling method. It was found that the macro-segregation of Y211 particles depended on the growth direction and the growth rate (R) as a function of undercooling (ΔT). The amount of Y211 particles in Y123 crystals grown at large R was larger than at small R. Also the amount of Y211 in Y123 growing along *a*-direction was larger than that along *c*-direction. Further, it was noted that the smaller Y211 particles in size were distributed in Y123 grown at large R. These phenomena could be at least qualitatively explained by the prevalent trapping/pushing theory. In the direct observation of magnetic flux with the Faraday effect of iron garnet film, the flux pinning force was found to be in good agreement with the macro-segregation of Y211 particles.

Order No.: JA604-002

Crystallinity of $YBa_2Cu_3O_{7-x}$ single crystals grown by the pulling method

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Large $YBa_2Cu_3O_{7-x}$ (Y123) single crystals (larger than 13 mm cubed) have been grown along the *c*-axis reproducibly by the modified pulling method. The crystallinity of Y123 single crystal was investigated by x-ray diffraction and x-ray topography. Crystals grown from an MgO single crystal seed had some low-angle subgrain boundaries which tilted 0.1-0.8 degrees with each other. These grain boundaries originated from the seed crystal, and the subgrains were extended along the growth direction from the seed crystal. Y123 single crystals with no marked subgrains in the whole area were obtained by using Y123 single subgrain crystal seeds. FWHM of the x-ray rocking curve for the crystal so produced was about 0.14 degrees, which was much better than the spectrum consisting of several separated peaks obtained from the previous crystals. T_c onset of the annealed sample was about 93.6 K, and the transition width was about 0.9 K. The low-angle subgrain boundaries seemed not to be effective pinning centers for the magnetic flux.

Order No.: JA604-003

Spontaneous solution-sol-gel process for preparing tin oxide monolith

N-L. Wu. L-F. Wu, Y-C. Yang, S-J. Huang
(National Taiwan University)

A sol-gel process for preparing SnO_2 monolith of high specific surface area and transparency from chloride solution is described. Without introducing any alkaline precipitating reagent to induce condensation, this new process employs tin chloride (or its hydrate), water and, optionally, alcohols as the only process reagents. Spontaneous solution-to-sol and sol-to-gel transitions take place upon mixing these reagents under appropriate conditions and the entire transition processes are

carried out under acidic conditions (typically pH≤4.0). The rate of condensation has been found to increase with decreasing $SnCl_4$ concentration, which corresponds to decreasing solution acidity, and with increasing temperature. For fixed starting salt concentration and temperature, there exists an optimum amount of ethanol addition for the fastest condensation. Good performance of thus derived SnO_2 monolith has been demonstrated in two applications, including catalytic oxidation and solid-state gas-sensing for carbon monoxide.

Order No.: JA604-004

Formation of $BaTiO_3$ and $PbTiO_3$ thin films under mild hydrothermal conditions

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Well-crystallized polycrystalline thin films of cubic barium titanate ($BaTiO_3$) have been synthesized on Ti-covered Si substrates by exposing the substrates to a $Ba(OH)_2$ aqueous solution at 160°C and a low pressure less than 1MPa. It was presumed that the film formation of $BaTiO_3$ involved a dissolution-crystallization mechanism, which provides an attractive approach to produce other titanate films and powders. Also, we have for the first time used this hydrothermal technique to deposit epitaxial (001)-textured $PbTiO_3$ thin films on $SrTiO_3$(100) substrates.

Order No.: JA604-005

Influence of the composition of gas mixture on the stoichiometry of sputter-deposited compound films: The case of zirconium nitrides

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By means of dc-reactive sputtering, it is possible to vary the stoichiometry of deposited zirconium nitrides, by varying the molar fraction of N_2 in an Ar-N_2 gas mixture. In order to understand the origin of this effect, a theoretical model of reactive sputtering is devised. It is based on the study of reaction kinetics taking place at the surfaces of the cathode and the chamber walls. In fitting the model with experimental data, it turns out that one has to introduce the roles of Ar, N_2 and N species. For reactive sputtering of ZrN_z films, a good fit is obtained when it is assumed that the molar fraction of N is constant when the molar fraction of N_2 increases up to about 75% (under pure experimental conditions). Above this concentration of N_2, the concentration of N has to increase. By the analysis of the theoretical model, general scaling laws between experimental parameters (current, pressure, areas of the cathode and the chamber walls) are easily obtained.

Order No.: JA604-006

Modeling the effect of gas transport on the formation of defects during thermolysis of powder moldings

J.H. Song, M.J. Edirisinghe, J.R.G. Evans, E.H. Twizell
(Brunel University)

The removal of binder from ceramic or metal moldings by thermolysis involves the transport of degradation products through the parent organic phase and the vacated porous body. A numerical model has been developed to combine an equation which takes into account different gas-flow regimes with an equation for the transport of organic molecules in molten polymers. Computer modeling reveals the critical heating rate above which defects occur due to boiling of the polymer-monomer solution at the center of the molding. The situation in which a porous outer layer of the molding develops, offering resistance to the flow of the evolved monomer gas, is then treated. This gives rise to a moving boundary with a variable concentration of diffusant which is dependent on the surface flux, gas transport coefficient and thickness of the porous layer. The contributions of diffusion and viscous flow to gas transport are considered.

Order No.: JA604-007

Sol-gel synthesis of rare-earth-doped fluoride glass thin films

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This paper describes ZBLA fluoride glass thin films produced via an inexpensive, low-temperature reactive atmosphere sol-gel approach. Luminescence from erbium at 1.55 μm has been observed in x-ray-amorphous doped films deposited on calcium fluoride, polyimide, sapphire, and silicon substrates. Fluorescence studies of the erbium $^4S_{3/2} \rightarrow {}^4I_{13/2}$ transition, a characteristic emission for a reduced phonon energy host, were conducted for both sol-gel-derived films and conventionally-prepared glass rods. The peak intensity observed from the sol-gel films was blue-shifted by 16 nm with a FWHM value approximately half that measured for the melt-quenched rods. Excitation studies indicated that, unlike conventionally-prepared glasses, sol-gel materials suffer from nonradiative relaxation of the $^4S_{3/2}$ excited state to the $^4I_{9/2}$ level, where subsequent radiative emission to the $^4I_{15/2}$ ground-state occurs. The proposed source of the quenching mechanism are remnant species inherent to the sol-gel process. While this causes the luminescence behavior of rare-earth-doped sol-gel-derived fluoride materials to be similar to oxide hosts, these remnant species modify the branching ratios resultantly leading to a novel 824 nm emission when excited at 488 nm.

Order No.: JA604-008

A mechanism for reactive diffusion between silicon single crystal and NbC powder compact

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Based on our recent experimental observations, a growth mechanism for the reactive diffusion between Si single crystal and NbC powder compact is proposed. In Si-NbC diffusion couples annealed at 1300°C, a two-phase $NbSi_2$+SiC reaction layer formed with $NbSi_2$ as the matrix and SiC as discontinuous particles. The $NbSi_2$ grain sizes and SiC particle sizes are both in the μm range. We propose that the SiC particles nucleated at the void surfaces in the NbC powder compact. This proposed nucleation mechanism offers a potential way of controlling the SiC particle size by changing the void size and void density of the NbC powder compact. It is also pointed out that this microstructure requires Si to be the dominant diffusing species. Si must diffuse through the reaction layer, while C only has to undergo local rearrangement, and Nb need not diffuse at all.

Order No.: JA604-009

Microstructure of a high strength alumina glass composite

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The morphology and microstructure of an Al_2O_3 glass composite (trade name In-Ceram, Vita Zahnfabrik) were studied using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The composite was produced by infiltration of a lanthanum-based glass throughout a porous Al_2O_3 body. This alumina body was formed by three classes of particles differing in size and shape: faceted particles typically ≤ 4 μm in diameter, platelets of average diameter 8 μm, 1.5 μm thickness and small spheres 0.4 μm in diameter. The outstanding strength properties of the composite (600 MPa, ball-on-ring test) are a result of the high wetting capability of the glass phase on the Al_2O_3 surface. In addition, plastic strain relaxation in the faceted particles by dislocation formation compensates partially for residual stresses and impedes crack formation at the glass Al_2O_3 interface.

Order No.: JA604-010

COMMUNICATIONS

Fullerene-tetracyanoquinodimethane thin film and novel electrical bistability

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(Chinese Academy of Sciences)

We report the electrical bistability of C_{60}-tetracyanoquinodimethane (TCNQ) thin films fabricated by using an ionized-cluster-beam method in a high vacuum system. The films were characterized by transmission electron microscopy and electronic absorption spectroscopy. The spectroscopic results showed evidence of the formation of the charge-transfer complex system in C_{60}-TCNQ thin films and the TEM results revealed the microstructure of the films. The film thickness is of ~100 nm. The electromotive intensity at the transition point was of the order of 10^6V/m. The possible mechanism of the electrical phenomena of the films is discussed in the paper.

Order No.: JA604-011

Effect of palladium on the hydrogen embrittlement of B-doped Ni_3Al

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A discussion of the embrittlement of B-doped and B-free Ni_3Al is given. Tensile test data and SEM fractography have been evaluated to show that additions of Pd to polycrystalline Ni_3Al(B) essentially eliminate the embrittlement concomitant to changing Ni_3Al(B) to the level of ~5 wt.ppm of hydrogen.

Order No.: JA604-012

A simple method for the manufacture of mesoscopic metal wires

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(Royal Military College)

A process for the manufacture of very thin parallel wires has been developed. A series of parallel silver wires has been written for the study of one-dimensional electron transport. The wires are approximately 200 nm wide, and 8 mm long. The method used can produce longer and thinner wires.

Order No.: JA604-013

ARTICLES

Electromagnetic and microstructural investigations of a naturally-grown 8° [001] tilt bicrystal of $Bi_2Sr_2CaCu_2O_{8+x}$

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Electromagnetic characterization and high resolution transmission electron microscopy have been conducted on the same 8° [001] symmetrical (010) tilt boundary in a naturally-grown, bulk-scale bicrystal of $Bi_2Sr_2CaCu_2O_{8+x}$ (BSCCO-2212). The resistive transition showed excess resistance above and below T_c, suggesting some weak coupling at the boundary, but the inter- and intragranular voltage-current characteristics, irreversibility fields and critical current density (J_c) values were very similar and characteristic of strongly coupled grains and grain boundary. The misorientation was accommodated by a set of partial edge dislocations with **b** = 1/2 [010] and the Frank spacing of 1.9 nm. The dislocation cores appeared to be separated by relatively undistorted regions of crystal. The J_c values at 25 K exceeded 10^3 A/cm^2 in fields of several tesla, more than two orders of magnitude larger than that found earlier in [001] twist boundaries of BSCCO-2212. This result is consistent with the view that low angle [001] tilt boundaries play an important role for current transport in polycrystalline BSCCO tapes.

Order No.: JA604-014

Characterization of surface micro-roughness of silicon wafers by a multipass Fabry-Perot Rayleigh-Brillouin scattering spectrometer

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Surface micro-roughness of various Si (100) wafers was detected and characterized by a 180-degree backscattering Rayleigh-Brillouin scattering spectrometer (RBSS), and measured by an atomic force microscopy (AFM). The intensity of the scattered light from the wafers is found to increase with increasing surface micro-roughness which was measured by AFM. By scanning across the wafer the inhomogeneous distribution of surface micro-roughness is detected and characterized. The system can be easily developed into a mapping technique. The results of the surface micro-roughness detected by AFM and RBSS suggest that they are complementary for the characterization of the surface micro-roughness from a micro area to a whole wafer.

Order No.: JA604-015

A large angle convergent beam electron diffraction study of the core nature of dislocations in 3*C*-SiC

X.J. Ning, P. Pirouz
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Dislocations produced by 1300°C indentation of the silicon-terminated (111) face of 3*C*-SiC were investigated by transmission electron microscopy. They were all found to be either widely separated partial dislocation pairs, or else, arrays of single partial dislocation half-loops on neighboring parallel slip planes and having the same Burgers vector. It was concluded that in the latter case, each array consisted of *leading* partial dislocations which had nucleated without accompanying trailing partial dislocations. The core nature of both dissociated dislocations and arrays of single partial dislocations has been determined by the technique of large angle convergent beam electron diffraction. The results indicate that the core of all single partial dislocation half-loops constituting an array consists of silicon atoms. It is concluded that, with the present deformation geometry, the Si-core partial dislocations are preferentially nucleated before the C-core partial dislocation. In the case of a dissociated dislocation, when a pair of partials was present, electron microscopy observations showed that the morphology of the two partial dislocations was very different: while the Si-core partials were smooth, the C-core partial dislocations had a zig-zag morphology.

Order No.: JA604-016

RF aerosol plasma fabrication of indium tin oxide and tin oxide thin films

D.H. Lee, K.D. Vuong, J.A.A. Williams, J. Fagan, R.A. Condrate Sr., X.W. Wang
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Transparent, conductive indium-tin oxide (ITO) and tin oxide thin films were deposited on soda-lime-silicate (SLS) float glass and silica glass substrates by an RF aerosol plasma technique in an atmospheric environment. The ITO films were deposited from solutions with various In:Sn ratios. The dependence of the film properties on the substrate temperature, deposition time, and tin concentration have been studied. The films were characterized by several techniques including XRD, EDS, electrical resistivity, SEM, optical (IR-UV-Vis transmission), Mössbauer, and infrared spectroscopy. The results showed that film phase, morphology, thickness, crystallite size and conductivity depend on the solution composition and deposition parameters. XRD revealed that In_2O_3 was present in the film when an In:Sn ratio of 5:5 or higher was used; otherwise only SnO_2 was shown. SEM analysis showed that dense and uniform films were formed with particle sizes ranging from approximately 50 nm to 150 nm. The resistivity of the ITO films ranged from 0.12 to 5.0 ohm-cm at room temperature. Optical transmission of the ITO coated glasses were not different from the uncoated samples. Infrared results indicated

that the structure of the near surface of the glasses was significantly modified with a higher indium concentration. The advantages of the atmospheric, RF aerosol plasma deposition process over other techniques is discussed.

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Microstructural characterization of ordered nickel silicide structures grown on (111) nickel silicide films

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(Carnegie Mellon University)

The formation processes of epitaxial nickel silicides, resulting from the interaction of nickel silicide films (10 nm-100 nm) on (111) silicon (Si) substrates after furnace annealing, have been studied using transmission electron microscopy (TEM) and x-ray diffraction (XRD) techniques. The formation of type-A epitaxial grains (i.e., grown with the same orientation of the underlying Si substrate) and type-B epitaxial grains (i.e., rotated by 180° around the surface normal) in "thick" epitaxial films (i.e., greater than 35 mn) is proposed to be linked to the formation of a fluorite-based CuPt ($L1_1$)-like NiSi phase. This phase is found to be a metastable phase and is believed to be a transitional phase towards the formation of the equilibrium $NiSi_2$ phase in both type-A and type-B orientations. In addition, we have found that a fluorite-based CuPt-like NiSi may even coexist with a fluorite-based CuAu I-like structure. The interrelationship between these two structures is discussed in the context of a displacive transformation process in f.c.c. structures as originally proposed by Hansson and Barnes (Acta Met **12** (1964) 315) and Pashley et al. (Phil. Mag. **19** (1969) 83).

Order No.: JA604-018 **© 1996 MRS**

Effect of high pressure on the preparation of Pd-Si-Cu bulk nanocrystalline material

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A Pd-Si-Cu bulk nanocrystalline material was prepared by quenching the melted $Pd_{78}Si_{16}Cu_6$ alloy at a cooling rate of 200 K/s under 2-6 GPa. It was found that the nanocrystalline material consists of Pd(Cu) disordered solid solution and metastable *a* phase-II, Pd_4Si. The grain size was found to decrease with increasing pressure. The influence of high pressure on the grain size of bulk nanocrystalline material is discussed and a possible formation mechanism is proposed.

Order No.: JA604-019 **© 1996 MRS**

Investigation of the crystallization of ZrO_2 (Y_2O_3 3% mol) nanopowder

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(Chinese Academy of Sciences)

Co-precipitation technique has been used to prepare ZrO_2 (Y_2O_3 3% mol) nanopowder. The influence of residual NH_4Cl and pH value on the crystallization of ZrO_2 (Y_2O_3 3% mol) nanopowder have been investigated by DSC, TGA, XRD, IR and TEM techniques. The IR spectra proved that the presence of residual NH_4Cl increased the amount of the hydroxo group. This led to serious gel agglomeration and free enthalpy decrease. Therefore the crystallization of ZrO_2 (Y_2O_3 3% mol) nanopowder is greatly influenced by the residual NH_4Cl. While there is no residual NH_4Cl, the crystallization takes place at 445°C and is an exothermic process. On the contrary, with NH_4Cl the crystallization takes place at 376°C and is an endothermic process. However, the pH value does not influence the crystallization of ZrO_2 (Y_2O_3 3% mol) nanopowder.

Order No.: JA604-020 **© 1996 MRS**

The role of transesterification in the multi-step "prehydrolysis" sol/gel synthesis of aluminum-rich aluminosilicate gels

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(University of Minnesota)

Using a prehydrolysis technique, transparent gels with very high aluminum content can be achieved with isopropanol. Here ^{13}C, ^{27}Al, and ^{17}O NMR at various stages of preparation show that when the aluminum added exceeds the number that silanols can fully protect, the excess aluminum alkoxide groups readily undergo transesterification with isopropanol. The aluminum isopropoxide (Al-OPr^i) groups thus formed are shown to be sufficiently stable that attack by water is impeded, thus allowing the remaining silicon alkoxide groups to hydrolyze and condense to form a homogeneous gel.

Order No.: JA604-021 **© 1996 MRS**

Role of Bi_2O_3 in optimizing the dielectric properties of $Ba_{4.5}Nd_9Ti_{18}O_{54}$ based microwave ceramics

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(University of Ljubljana)

Small additions of Bi_2O_3 or bismuth titanate improve the dielectric properties of $Ba_{4.5}Nd_9Ti_{18}O_{54}$ at microwave frequencies. It was found that Bi^{3+} can replace Nd^{3+} up to 15 mol%, the limiting composition of solid solution being $Ba_{4.5}(Nd_{0.85}Bi_{0.15})_9Ti_{18}O_{54}$. At the solid solution limit the temperature coefficient of resonant frequency attains its minimum value. The modified ceramic is distinguished by high permittivity of 99, and a Q-value of 5,500. The temperature coefficient of resonant frequency is low, 15 ppm/K. After exceeding the solid solubility limit, additional Bi_2O_3 concentrates as a Bi-rich phase at the grain boundaries, causing considerable reduction of the Q-value and an increase of τ_f.

Order No.: JA604-022 **© 1996 MRS**

Fast firing of lead magnesium niobate at low temperature

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A fast firing technique for the sintering of lead magnesium niobate relaxor ceramics at relatively low temperature has been described. In this process, the samples containing excess PbO (up to 5 wt.%) are directly introduced into a furnace maintained at a temperature of 950°C and kept there for 15-80 minutes followed by a post-sintering annealing treatment at 800°C for 10 h. The importance of fast heating as well as annealing treatment has been justified. The sintered samples are near-phase pure perovskite materials showing high bulk densities (>94%), uniform and dense microstructure, and satisfactory dielectric properties (k_{max} > 13,000). The technique is simple and economic, does not require any controlled atmosphere, and minimizes hazards from lead volatilization.

Order No.: JA604-023 **© 1996 MRS**

Thermal wave analysis of contact damage in ceramics: Case study on alumina

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(National Institute of Standards and Technology)

Thermal waves are used to image damage accumulation digitally beneath Hertzian contacts in ceramics. Alumina ceramics over a range of grain size 3-48 μm are used in a case study. The nature of the images changes with increasing alumina grain size, reflecting a transition in damage mode from well-defined cone fracture in the finer-grain materials to distributed subsurface microfracture in the coarser-grain materials. Quantitative determinations of microcrack densities are evaluated in the latter case by deconvoluting thermal diffusivities from the image data. These determinations confirm the grain-size dependence of degree of damage predicted by fracture mechanics models. Potential advantages and disadvantages of thermal waves as a general route to damage characterization in ceramic systems are discussed.

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Gas-phase combustion synthesis of titanium boride [TiB_2] nanocrystallites

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Two techniques are described for synthesizing nanometer-sized TiB_2 particles by gas-phase combustion reactions of sodium vapor with

$TiCl_4$ and BCl_3: a low-pressure, low-temperature burner and a high-temperature flow reactor. Both methods produce TiB_2 particles that are less than 15 nm in diameter. The combustion by-product, NaCl, is efficiently removed from the TiB_2 by water washing or vacuum sublimation. Material collected from the low-temperature burner and annealed at 1000°C consists of loosely agglomerated particles 20-100 nm in size. Washed material from the high-temperature flow reactor consists of necked agglomerates of 3 to 15 nm particles. A thermodynamic analysis of the Ti/B/Cl/Na system indicates that near 100% yields of TiB_2 are possible with appropriate reactant concentrations, pressures and temperatures.

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Fabrication of TiB_2 and TiB_2/FeB composites by mechanically activated borothermic reduction of ilmenite

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TiB_2 and TiB_2/FeB composites have been formed at temperatures below 1000°C, directly from ilmenite sand by reaction with amorphous boron. The structural transformations occurring during high energy mechanical milling pretreatment and subsequent annealing of different mixtures of the constituents have been studied. On heating at temperatures below 800°C, complete borothermic reduction of the ilmenite structure is accomplished. The mixture so obtained with ilmenite-boron ratio equal to 1/6 undergoes a sequence of reactions on further heating to form TiB_2, FeB and the amorphous phase B_2O_2.

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Porous Ca-P-O bio-glassceramics by loose-powder-sintering

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Porous resorbable Ca-P-O glassceramic tooth roots based on calcium biphosphate were prepared by loose-powder-sintering then crystallization annealing. The glass composition is, by weight, $CaO/(CaO+P_2O_5) = 0.33$. The sintering behavior of the glass can be described by a conventional viscous flow model. The resultant glass-ceramic has a pore size of 6 to 36 μm, depending on starting particle size and sintering temperature, while the pore size distribution is independent of sintering time. The flexural strength is 33 to 150 MPa depending mostly on crystallization-annealing treatment. The crystalline phases are β-$Ca_2P_2O_7$ and CaP_2O_6. After being implanted into rabbits, these porous implants show remarkable biocompatibility and induce the ingrowth of new bone within 30 days. They are partly resorbed after 90 days and replaced by new bone. In spite of the original small porosity the ingrowth of blood vessels and bone cells is abudantly seen after 90 days, due to enlarged pores produced by progressive resorption. This glass-ceramic is a good candidate for resorbable tooth and bone implants. The loose-powder-sintering technique resulting in intricate bulk shapes with controllable pore size distribution and good machinability as well as adjustable mechanical strength hence is a powerful technique for preparation of porous glass-ceramics.

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Oriented overgrowth of metals onto poly-1,4-phenylene

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Thin, oriented films of poly-1,4-phenylene (PPP) were prepared with a specially designed reaction vessel. Various kinds of metals were deposited by vacuum evaporation on the PPP substrate, the temperature of which was able to be changed up to 400°C. Of the studied metals, tellurium and bismuth exhibited the oriented crystallization on it. The oriented overgrowth of tellurium crystallites occurred in the temperature range of 150°C~200°C. There were two modes of oriented overgrowths of crystallites in the case of bismuth: one was performed by deposition around room temperature and the other at about 100°C. The oriented overgrowths of bismuth and tellurium on PPP were examined in terms of the mismatch parameter of the crystal lattice, and it was found that the overgrowths were caused by the lattice matching at the interface between the crystallites of the metals and the PPP substrate.

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Growth of CN_xH_y films by reactive magnetron sputtering of carbon in Ar/NH_3 discharges

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Results on hydrogenated carbon nitride (CN_xH_y) thin films grown by reactive magnetron sputtering in a mixed Ar/NH_3 discharge are reported. Depending on the growth temperature (T_s) and negative substrate bias voltage (V_s) both the composition and the microstructure were altered. Using nuclear reaction analysis and resonant backscattering spectroscopy the maximum N and H content were both 15 at.%. Both the hydrogen and nitrogen content of the films was found to decrease with increasing growth temperature. The results also show pronounced chemical resputtering effects resulting in no net film growth for $V_s > 75$-100 V. X-ray photoelectron spectroscopy showed no signs of N bound to sp^3 hybridized C. Also the microstructure of the films was found to change with T_s. For $T_s < 200$°C a structure with crystalline clusters embedded in a "fullerene-like" matrix was observed by high-resolution transmission electron microscopy. Power-spectra obtained from the clusters could be identified with the cubic diamond structure. For $T_s > 200$°C, no crystalline clusters were found and the films had a homogeneous "fullerene-like" microstructure with strongly bent planes and closed shell-like features resembling bucky-onions. Evaluation of nanoindentation results from the homogeneous "fullerene-like" films gave hardness values between 7-11 GPa and elastic recoveries of 55-60%. This should be compared with hardnesses and elastic recoveries of 40-60 GPa and 85-90%, respectively, previously reported on for non-hydrogenated carbon nitride CNx films grown under the same conditions, but in pure N_2-discharges.

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Atmospheric pressure chemical vapor deposition of TiN from *tetrakis(dimethylamido)titanium and ammonia*

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Near stoichiometric titanium nitride (TiN) was deposited from tetrakis(dimethylamido)titanium (TDMAT) and ammonia using atmospheric pressure chemical vapor deposition. Experiments were conducted in a belt furnace; static experiments provided kinetic data and continuous operation uniformly coated 150-mm substrates. Growth rate, stoichiometry, and resistivity are examined as functions of deposition temperature (190-420°C), ammonia flow relative to TDMAT (0-30), and total gas-flow rate (residence time 0.3-0.6 s). Films were characterized by sheet resistance measurements, Rutherford backscattering spectrometry, and x-ray photoelectron spectrometry. Films deposited without ammonia were substoichiometric (N/Ti < 0.6-0.75), contained high levels of carbon (C/Ti = 0.25-0.40) and oxygen (O/Ti = 0.6-0.9), and grew slowly. Small amounts of ammonia (NH_3/TDMAT ≥ 1) brought impurity levels down to C/Ti < 0.1 and O/Ti = 0.3-0.5. Ammonia increased the growth rates by a factor of 4-12 at temperatures below 400°C. Films 500 Å thick had resistivities as low as 1600 μΩ-cm when deposited at 280°C and 1500 μΩ-cm when deposited at 370°C. Scanning electron micrographs indicate a smooth surface and poor step coverage for films deposited with high ammonia concentrations.

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Direct observations of heteroepitaxial diamond on silicon (110) substrate by microwave plasma chemical vapor deposition

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Heteroepitaxial diamond has been successfully deposited on Si (110) substrate by microwave plasma chemical vapor deposition method. The pretreatment consisted of carburization and bias-enhanced nucleation steps. Cross-sectional transmission electron microscopy reveals that diamond can be in the cube-on-cube epitaxial relationship with the Si substrate. Various orientation relationships between diamond and Si substrates have also been observed, depending on the location where the plasma is applied. Near the center of the plasma, twins were rarely observed in cube-on-cube epitaxial regions. Away from the center of the plasma ball, Σ3 twins are seen first, and then additional Σ9 and Σ27 twins occur near the edge of the plasma. In general, defect density in the epitaxial films is less than that observed in polycrystalline ones. No interlayer could be observed between diamond and silicon. In addition, 2H type hexagonal diamond has also been found, and is in epitaxy with the Si substrate.

Order No.: JA604-031

Undoped and doped GaN thin films deposited on high-temperature monocrystalline AlN buffer layers on vicinal and on-axis α(6H)-SiC(0001) substrates via organometallic vapor phase epitaxy

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Monocrystalline GaN(0001) thin films have been grown at 950°C on high temperature, ≈100 nm thick, monocrystalline AlN(0001) buffer layers pre-deposited at 1100°C on α(6H)-SiC(0001)$_{Si}$ substrates via OMVPE in a cold-wall, vertical, pancake-style reactor. These films were free of low-angle grain boundaries and the associated oriented domain microstructure. The PL spectra of the GaN films deposited on both vicinal and on-axis substrates revealed strong bound excitonic emission with a FWHM value of 4 meV. The near band-edge emission from films on the vicinal substrates was shifted slightly to a lower energy, indicative of films containing residual tensile stresses. A peak attributed to free excitonic emission was also clearly observed in the on-axis spectrum. Undoped films were too resistive for accurate Hall-effect measurements. Controlled n-type, Si-doping in GaN was achieved for net carrier concentrations ranging from approximately 1 x 10^{17} cm^{-3} to 1 x 10^{20} cm^{-3}. Mg-doped, p-type GaN was achieved with n_A-$n_D \approx 3 \times 10^{17} cm^{-3}$, $\rho \approx 7\ \Omega \cdot cm$ and $\mu \approx 3\ cm^2/V \cdot s$. Double-crystal x-ray rocking curve measurements for simultaneously deposited 1.4 μm GaN films revealed FWHM values of 58 and 151 arc sec for deposition on on-axis and off-axis 6H-SiC(0001)$_{Si}$ substrates, respectively. The corresponding FWHM values for the AlN buffer layers were approximately 200 and 400 arc sec, respectively.

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Growth of diamond thin films by microwave plasma chemical vapor deposition process

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A very high-vacuum compatible microwave plasma chemical vapor deposition system has been fabricated for the growth of diamond thin films. Microcrystalline diamond thin films have been grown on silicon substrates from CH_4-H_2 gas mixture. Scanning electron microscopy and x-ray diffraction have been used to study the surface morphology and the crystallographic structure of the films. Optical emission spectroscopy has been used for the detection of chemical species present in the plasma. The strong dependence of the film microstructure on the intensity of CH emission line has been observed.

Order No.: JA604-033

Effect of substrate orientation on the crystal quality and surface roughness of Nb-doped TiO_2 epitaxial films on TiO_2

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We have grown Nb-doped TiO_2 epitaxial films on (100)- and (110)-oriented TiO_2 rutile substrates by molecular beam epitaxy. Nb substitutionally incorporates at cation sites in the rutile lattice, forming $Nb_xTi_{1-x}O_2$ solid solutions. However, the crystal quality and surface roughness of the films depend strongly on the substrate orientation. Surface roughening and defect formation occur at lower values of x on (100) than on (110). This result is due to anisotropic changes in the metal-oxygen bond lengths within the rutile structure in going from TiO_2 to NbO_2; there are 1% and 12% changes in the metal atom to octahedron-base oxygen and metal atom to octahedron-vertex oxygen bond lengths, respectively. Every metal atom in the (100) growth surface has in-plane components of the 12% mismatch. However, only half of the metal atoms in the (110) growth plane have such components. Thus, there is substantially larger in-plane lattice mismatch when the growth surface is (100) compared to (110), resulting in surface roughening and formation of defects at a lower doping level for (100)-oriented $Nb_xTi_{1-x}O_2$ epitaxial films.

Order No.: JA604-034

X-ray diffractometry investigation for ion-exchange properties on α-type manganese dioxides

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Two materials of α-type manganese dioxide were synthesized and examined. They were prepared by pyrolysis of mixtures of $MnCO_3$ and $(CH_3)_3COK$. An ill-ordered material was obtained when prepared at large $(CH_3)_3COK$ content. Both samples behave as acids, but their apparent capacities are obviously different; about 0.9 [meq/g] for well-ordered samples and about 2.6 [meq/g] for ill-ordered samples. Ion-exchange properties were examined on Kielland's plot. Zero-intersection of the two samples are almost the same ($log(K_H^M)\bar{x}_{M\to O} \approx$ -3.5 for Na^+ exchange and 4~5 for K^+ exchange), but slopes are different (about -50 for well-ordered samples and about -10 for ill ordered samples). The difference in slope is likely caused by the flexibility. An evidence of the flexibility can be seen by x-ray diffractometry.

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The mechanism of spontaneous infiltration of Al-Si alloy into SiC preform in air

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Rapid, spontaneous infiltration can be achieved by dipping a SiC preform that contains pyrolyzed carbon into an Al-Si alloy bath in an open air environment. The mechanism for infiltration is investigated in the present work by studying the effects of several relevant parameters on the infiltration process. Experimental results have shown that the requirements for rapid spontaneous infiltration are an infiltration temperature higher than 1400°C, the presence of a pyrolyzed carbon and the presence of SiC particle in the preforms. The concentration of Si in the alloy does not have significant influence on the infiltration rate, but it strongly affects the resulting microstructures in the infiltrated composites.

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