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TABLE OF CONTENTS

ABSTRACTS

MATERIALS SYNTHESIS AND PROCESSING

This manuscript is part of a series of papers that will be featured in a special issue on Materials Synthesis and Processing in the April 1996 issue of the Journal of Materials Research

Bisethylacetoacetato Cu(II) as a novel metalorganic precursor for Cu film production by plasma-enhanced chemical vapor deposition toward ULSI metallization

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Bisethylacetoacetato Cu(II), referred to as $Cu(etac)_2$, was synthesized and used as a novel metalorganic precursor to produce Cu films by PECVD processing. $Cu(etac)_2$ is a non-fluoride compound which is solid at room temperature with reasonable volatility at 120-150°C of 0.8 torr. Effects of selected process variables on the characteristics of Cu film deposition were studied. Considered variables were plasma power, hydrogen flow rate, deposition time, substrate temperature, and precursor temperature. The process conditions to give Cu films of a high quality were determined. The electrical resistivity approached 2 μΩ·cm as the Cu film thickness became greater than 2500 Å. The conformality of the Cu film deposition by PECVD was sufficient to result in complete via-hole fillings of wafers patterned for 256 Mb DRAM.

Order No.: JA605-001

COMMUNICATIONS

Praseodymium and high-temperature superconductivity: Thermodynamic, structural, and critical correlations

V.E. Lamberti, M.A. Rodriguez, J.D. Trybulski, A. Navrotsky
(Princeton University)

The enthalpies of formation and the partial molar enthalpies of oxidation of polycrystalline $LnBa_2Cu_3O_y$ (*Ln* = Pr, Nd, Eu, Gd, Dy, Ho, Tm) and $Y_{1-x}Pr_xBa_2Cu_3O_y$ (x = 0.0, 0.1, 0.2, 0.5, 0.8, 0.9, 1.0) have been determined at 298 K by drop-solution calorimetry. The thermodynamic characteristics of Pr123 follow the trends of the trivalent-ion-based Ln123 compounds. The thermodynamic data for the (Y, Pr)123 solid solutions show non-ideal solution behavior, but no x-dependent valence instability. The superconducting critical temperatures and the enthalpies of oxidation of the (Y, Pr)123 solid solutions are linearly related.

Order No.: JA605-002

Evidence for hydrothermal growth of diamond in the C-H-O and C-H-O-halogen system

R. Roy, D. Ravichandran, P. Ravindranathan, A. Badzian
(The Pennsylvania State University)

Powder x-ray diffraction (XRD) and Raman evidence is presented for the formation of crystalline diamond in the "hydrothermal" pressure-temperature regime 1-5 kbars, <1000°C.

Two different methods appear to enable diamond to nucleate and grow. One—a low pressure solid-state source (LPSSS) route—utilizes special solid precursors, especially low-temperature glassy carbon (GC-500), with very fine diamond seeds in sealed gold capsules with H_2O at, say, 800°C and 1 kbar. The other includes pyrolysis of highly selected organic solid/liquid precursors (halogenated aliphatics such as iodoform) on to similar diamond seeds.

In all the cases, powder x-ray diffraction evidence shows marked increase of the diamond XRD peaks; likewise the Raman spectrum shows a strong increase of the 1331 cm^{-1} line. However, the crystals apparently are too small to be seen in the SEM. TEM diffraction data on the other hand seem to lend support to the possibility of all the grown diamonds being very small.

Order No.: JA605-003

Characteristics of spin-on ferroelectric $SrBi_2Ta_2O_9$ thin film capacitors for ferroelectric random access memory applications

P.Y. Chu, R.E. Jones, P. Zurcher, D.J. Taylor, B. Jiang, S.J. Gillespie, Y.T. Lii, M. Kottke, P. Fejes, W. Chen
(Motorola)

We report on the properties and characterization of $SrBi_2Ta_2O_9$ (SBT, or Y-1) thin film capacitors for ferroelectric random access memory (FERAM) applications. The films were prepared by spin-coating from carboxylate precursors. The remanent polarization (P_r) was 5-6 μC/cm^2 and the coercive field was ~5.5 KV/cm. Excellent fatigue

endurance was observed up to 10^{11} cycles. Auger analysis indicates bismuth diffusion through the Pt electrode after capacitor anneal which might require excess Bi in the precursor solution for stoichiometry control. No detectable amount of α emission was found from SBT films which reduces the possibility of soft error when used in the memory devices.

Order No.: JA605-004

Preparation of molecular alloys by the ball milling technique

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Ball milling is a technique extensively used in metallic powders to obtain adequated properties for their applications. In this study we show that this technique is also useful to prepare organic molecular alloys. Pentaglycerin/Pentaerythritol alloys have been obtained mechanically at room temperature. Calorimetric and crystallographic characterizations establish that the mechanically obtained alloys have the same solid crystalline structure and transform to the plastic phase as the conventionally prepared alloys from the melt of the pure compounds.

Order No.: JA605-005

ARTICLES

Analysis of the $NdBa_2Cu_3O_x$ thin film growth mechanism by time of flight mass spectrometry of the laser plume

M. Badaye, K. Fukushima, T. Morishita
(Superconductivity Research Laboratory-ISTEC)

Time of flight (TOF) spectroscopic measurements are used to diagnose the laser generated plume of ceramic $NdBa_2Cu_3O_x$ targets. We have been able to directly correlate the laser deposited films' properties such as superconductivity, crystallinity, and orientation with plasma properties. Study of the TOF spectra shows that at laser fluences greater than 3 J/cm^2 the plume becomes Nd-rich, and this leads to a low T_c in the deposited film. We have also shown the effect of target density on the energy of the plume species, and through energy considerations we have explained the observed change in the crystalline orientation of films from c- to a-orientation with increasing the target density. Finally, we have examined the oxidation mechanism of $NdBa_2Cu_3O_x$ thin films, and have shown that highly energetic atomic oxygens have a prevailing role in oxidizing our laser deposited thin films.

Order No.: JA605-006

Oxygen partial pressure dependence of the yttrium solubility in Y-Ba-Cu-O solution

M. Nakamura, C. Krauns, Y. Shiohara
(Superconductivity Research Laboratory-ISTEC)

The yttrium solubility in Ba-Cu-O solvent with a Ba to Cu ratio of 3 to 5 was investigated under different oxygen partial pressure ($P(O_2)$ = 2, 21, 100%). A small amount of the solution was taken out by dipping thermally equilibrated MgO single crystals and compositions of these specimens were analyzed by inductivity coupled plasma atomic emission spectrometry (ICP-AES). The measurements were performed for the samples prepared in the temperature range from approximately 950°C up to 1100°C.

The peritectic temperature of $YBa_2Cu_3O_{7-x}$ (Y123) decreased with decreasing oxygen partial pressure. On the other hand, the Y123 liquidus lines do not show remarkable oxygen partial pressure dependency. Accordingly, the yttrium solubility at the peritectic temperature of Y123 under $P(O_2)$ = 100% was larger than those for the other conditions ($P(O_2)$ = 21, 2%).

Assuming a regular solution, expressions for the solubility and the enthalpy of dissolution of Y123 and Y_2BaCuO_5 (Y211) were derived from classical thermodynamic calculations and found to be 289 kJ/mol at $P(O_2)$ = 0.02 atm, 239 kJ/mol at $P(O_2)$ = 0.21 atm, 206 kJ/mol at $P(O_2)$ = 1 atm for Y123 and 105 kJ/mol at $P(O_2)$ = 0.02 atm, 88.0 kJ/mol at $P(O_2)$ = 0.21 atm and 88.4 kJ/mol at $P(O_2)$ = 1 atm for Y211. Furthermore, the Jackson α factor of Y123 was estimated to be about 20, confirming a faceted growth nature of this crystal.

Order No.: JA605-007

Magnetic alignment in 2212 Bi-based superconducting system: Part I. Magnetic orientation of $Bi_2Sr_2Ca_{1-x}(RE)_xCu_2O_{8-y}$ [(RE)=Gd, Dy, Ho, Er] powder dispersed in epoxy resin at room temperature

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The magnetic anisotropy of rare-earth substituted 2212 materials ($Bi_2Sr_2Ca_{0.8}RE_{0.2}Cu_2O_y$ with RE=Gd, Dy, Ho, Er) is put into evidence. Superconducting powder dispersed in epoxy resin is oriented under an external magnetic field (4T) in a direction which depends on the nature of the rare-earth used in the substitution. Both directions of observation (parallel or perpendicular to the field) were investigated. Splitting of (001) peaks is neatly observed and discussed.

Order No.: JA605-008

Fabrication and characteristics of weak links between *a*- and *c*-axis normal grains of $Y_1Ba_2Cu_3O_{7-x}$

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We have used pulsed organometallic beam epitaxy (POMBE) to simultaneously deposit *a*- and *c*-axis oriented $Y_1Ba_2Cu_3O_{7-x}$ (YBCO) thin films at arbitrary locations on $LaAlO_3$(100) substrates. Using photolithography and ion milling, several types of *a-c* weak links have been fabricated at the boundary between the two films. The current-voltage (I-V) characteristics show a flux flow type behavior. The resistive transitions are broad and the critical current density is low, indicating weak coupling across these boundaries. With magnetic field applied parallel to the grain boundary plane, non-hysteretic I-V curves are obtained and the critical current goes to zero at an applied magnetic field of ~7500 Gauss.

Order No.: JA605-009

The relation between the undercooling and the growth rate of $YBa_2Cu_3O_{6+x}$ superconductive oxide

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(Superconductivity Research Laboratory-ISTEC)

To clarify the effect of undercooling on crystal growth of Y-123, the growth rate was measured with different undercoolings. The growth rate of the {100} face shows a quadratic dependence of undercooling while that of the {001} face shows a linear dependence in the sample with nominal 123 composition. In the case with 211 rich composition, the growth rate of each face was larger than that compared with nominal 123 composition since the mass flux from 211 particle for peritectic reaction becomes large. Addition of excess 211 alters the undercooling dependence of R_a from quadratic to linear. This is considered that the entrapment of 211 particles into 123 crystals supplies step sources beside screw dislocations. The growth rate of the {001} face is larger than that of the {100} face up to 26 degrees of undercooling.

Order No.: JA605-010

Effect of sintering periods on the microstructure and electrical transport properties of high-T_c superconducting Bi-(Pb)-Sr-Ca-Cu-O tapes

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The effect of sintering periods for monocore $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10+x}$ (Bi-2223) tapes on microstructure and critical current density (J_c) have been studied. The results show that long sintering periods (of duration ≥ 100 h) give better grain growth, but greater

misalignment. Prolong sintering also necessitates the increase in porosity of the core due to random grain growth, increasing the chance of penetrating into the silver matrix and oxide core interface. Critical currents for long sintering periods are found to be lower in comparison with those obtained for slightly shorter sintering periods. The increase in frequency of intermediate cold uniaxial pressing between sintering periods assists grain alignment. However, when the sintering period is further reduced by increasing the frequency of intermediate deformation, it is found that microcracks are unable to heal as there is not enough time for grain regrowth. The tapes made using "three-to-four-sinter-period" (each period ~ 60 h) show superior electrical transport properties which are attributable to the fact that their oxide core is more dense and better aligned relative to the "two-sinter-period" (each period ≥ 100 h) tapes and contain less cracks relative to the "five-to-six-sinter-period" (each period ~ 40 h) tapes.

Order No.: JA605-011

Biaxial alignment of high-T_c superconductor polycrystals VIII: phi-circle scan analysis of $EuBa_2Cu_3O_{7-\delta}$ (Eu-123)

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To reduce grain boundary weak links due to large-angle grain orientation mismatch, bulk (thick film) $EuBa_2Cu_3O_{7-\delta}$ high-T_c superconductor specimens were biaxially aligned by a mechanical force such that their [001] axes were perpendicular to the specimen surfaces and by a magnetic force so as to orient their [010] axes to lie parallel to the magnetic field direction in the specimen plane. We describe here the characterization of such $EuBa_2Cu_3O_{7-\delta}$ thick films by ϕ-circle XRD scans of (013) reflections, demonstrating a high degree (33%) of *c*-axis alignment with FWHM of <5° and approximately Gaussian distributions of *a,b*-axis alignment with a FWHM of 47°. The formation of "granular single crystals" toward which this work is a further advance, can be seen as establishing a new paradigm in ceramic science.

Order No.: JA605-012

Relationship between growth rate and undercooling in Pt-added $Y_1Ba_2Cu_3O_{7-x}$

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

$Y_1Ba_2Cu_3O_{7-x}$ (Y123) crystals were grown by two different methods; the constant undercooling solidification and the continual cooling method, with top seeded by Sm123 seed crystals in order to investigate a relationship between undercooling (ΔT) and a growth rate (R). The crystals of Y123 with a sharp faceted interface, which consisted of {100} and {001} faces, grew epitaxially from the seed. It was found that the growth rates of {100} face (Ra) and {001} face (Rc) showed increasing trend with increasing ΔT, and Rc was faster than Ra within these experimental conditions, ΔT<20 K. The relation between R and ΔT follows the parabolic equation viz. $Ra \propto \Delta T^{1.9}$ and $Rc \propto \Delta T^{1.3}$ for {100} and {001} faces, respectively. The simulated crystal size using the R and ΔT relations obtained from the constant undercooling method showed a good agreement with experimental data by the continual cooling.

Order No.: JA605-013

Zn doping in YBCO single crystal by the SRL-CP method

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Zn-doped $YBa_2Cu_3O_{6+\delta}$ (YBCO) single crystals were fabricated by the SRL-CP method. The Zn content of x ranged 0.0035-0.029 and almost uniformly distributed in $YBa_2(Cu_{1-x}Zn_x)_3O_{6+\delta}$. There is a nearly linear relationship between the added Zn content in the liquid and the analyzed Zn content in the liquid / in the crystal. When the added Zn content C_1 was 1.086 at.%, decreasing the growth temperature led to increasing growth rate. However, growth temperature had no obvious effect on the doped Zn content in the crystal Cs, the Zn content in the flux C_1 and the effective distribution ratio of k′. In addition, growth spirals on the grown crystal surface were observed by AFM. X-ray Laue pattern and RBS measurements are indicative of good crystallinity of $YBa_2(Cu_{1-x}Zn_x)_3O_{6+\delta}$. Critical temperatures of T_c changed from 89 to 57 K when the Zn content x ranged 0.0035 to 0.029 after appropriate oxygenation.

Order No.: JA605-014

Effect of binder composition on debinding and sintering processes of injection molded Fe-8Ni mixed powders

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(Ishinomaki Senshu University)

The debinding process of injection molded compacts of Fe-8Ni mixed powders, containing binder of different ratio of polymers to wax was investigated. The effect of binder compositions and debinding conditions on the sinterability of the compacts were also studied. Distortions produced in the debinding processes of the compacts were minimized for the case where a ratio of polymer to the total binder contents was 0.35. In the case of the compacts debound in air, sintered densities increased with an increase in the debinding temperature up to 350°C, then decreased sharply for higher debinding temperatures. In the compacts debound in N_2, sintered densities were almost independent of the debinding temperature. The sinterability of the compacts debound in N_2 was much inferior to that debound in air.

Order No.: JA605-015

Low-temperature magnetic transition and high-temperature oxidation in INCONEL alloy 718

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X-ray diffraction and temperature dependent (5 K-380 K) magnetic measurements have been carried out in INCONEL 718 (INCONEL is a trademark of the INCO family of companies) superalloy before and after high-temperature aging treatments. The nominal composition of this alloy is: Ni (52.5%), Cr (19.0%), Fe (18.5%), Nb (5.1%), Mo (3.0%), Ti (0.9%), Al (0.5%), Cu (0.15%) and C (0.08%) and it yields an x-ray diffraction pattern consisting of a fcc phase with a = 3.5987 (3) Å and an orthorhombic phase associated with δ-Ni_3Nb. It is concluded that the fcc pattern is due to both the γ austenitic phase and γ' $Ni_3(Al,Ti)$ phase of alloy 718. The standard annealing and aging treatment carried out in air at temperatures between 982 and 621°C produces surface oxides $(Cr,Fe)_2O_3$ and $FeNbO_4$ (which are easily removed by etching and polishing) and contracts the lattice. Magnetic measurements show a distinct phase transition at T_c = 14 K, which has been attributed to the γ'-$Ni_3(Al,Ti)$ phase by the process of elimination and by observing that it has most of the characteristics of the weak itinerant ferromagnet $Ni_{74.5}Al_{25.5}$. This transition may have some effects on the cryogenic applications of this alloy.

Order No.: JA605-016

The positive roles of metallic droplets in deposition of alloy films by cathodic arc plasma deposition

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The roles of metallic droplets which generated from the cathodic arc spot holes in the technology of cathodic arc plasma deposition (CAPD) are investigated by SEM, TEM, image analysis apparatus and electronic probe energy spectrum analysis. The results show that though many papers in recent years are devoted to eliminate them, the metallic droplets, including the macrodroplets, have many important positive

roles in the preparation of alloy films: they are the main factor to transfer the original composition of alloy cathodic target to the alloy thick films; they are the main factor to preserve the high deposition rate of CAPD, to form the basic characteristics of the microstructure, and to affect the pore ratios of the films; they are the main factor to preserve the high melting point elements in the alloy films, and therefore to preserve the corrosion resistance of the alloy in the films. The macrodroplets can be eliminated by raising the substrate temperature properly, which is permitted in some cases such as depositing alloy films onto middle carbon steel as an anticorrosion system, and so forth.

Order No.: JA605-017

Effect of TiO_2 doping on rapid densification of alumina by plasma activated sintering

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The effects of plasma cycle and TiO_2 doping on sintering kinetics during plasma activated sintering (PAS) of γ-Al_2O_3 have been studied in the temperature range of 1473-1823 K. Multiple plasma cycle leads to higher densification. Also, TiO_2 doping enhances the sintering kinetics during PAS. In TiO_2 doped specimens, near full density was obtained at 1673 K in less than 6 minutes using multiple plasma cycle. It is suggested that the dielectric properties of a material are critical for the success of the PAS process.

Order No.: JA605-018

Effect of substrate bias voltage on the properties of arc ion-plated TiN films onto high speed steels

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The effect of substrate bias voltage on the properties of arc ion-plated TiN films onto high speed steels has been investigated. The high density structure with a large crystallite size grew at the high bias voltage. TiN films deposited by higher bias exhibited strong preferential (111) orientation from XRD. The internal stress of TiN films increased at first with increasing substrate bias voltage, however, it decreased as the bias voltage increased over the 100 V. The coating adhesion measured by scratch tester increased with increasing bias voltage and this is coupled with a cohesion of films. Cutting performance of TiN coated drills, which increased markedly with increasing substrate bias, has been studied in relation to the physical and chemical properties of deposited films.

Order No.: JA605-019

Chemical vapor deposition of α-ZrP whiskers

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α-ZrP whiskers have been prepared from $ZrCl_4$+PCl_3+H_2+Ar gas mixtures at 1050-1250°C using the mixed metal impurity-activated chemical vapor deposition process. The growth conditions, morphology, growth mechanism and some properties were examined. The mixed impurities of Si+Pt and Si+Pd were very effective for the ZrP whisker growth with 8-12 mm (av. 10 mm) long whiskers being obtained at 1300°C for 1 hr. The growth direction of the whiskers having hexagonal and square cross sections were along the *c*-axis and *a*-axis, respectively. The whiskers were very stable to an 80 min immersion in a conc. HCl solution.

Order No.: JA605-020

Mesoscopic structure of SiC fibers by neutron and x-ray scattering

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Mesoscopic structures of SiC fibers produced from polycarbosilane by different methods were studied by diffraction and small-angle scattering of neutrons and x-rays. Microvoids of a size of 4-10 Å in diameter have been observed for the first time by neutron scattering in a medium momentum transfer range (Q = 0.1-1.0 $Å^{-1}$). The size and the volume fraction of β-SiC particles were determined for fibers prepared at different heat-treatment temperatures. The results show that wide-angle neutron scattering measurements are especially useful for the study of the mesoscopic structure of multicomponent materials.

Order No.: JA605-021

Polarized light microstructure analysis of melt-textured $DyBa_2Cu_3O_{7-x}$ ceramics

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We report the microstructure of magnetically melt-textured Dy-123 samples, as observed by polarized light metallography. The phase dimensions, morphology, orientation, nature, and distribution are outlined. Grain, twin structure pattern, and grain boundary are characterized. The relationship between cracking, secondary phases and tetragonal-orthorhombic phase transformation is discussed. The results are obtained by observing a "not-too-well-ordered" region. This leads to definite conclusions on the relationship between crack spacing and 211 distribution, and to some confirmation of the growth mechanism and on macro- and micro-crack origins. From the present observations, the effect of the oxygenation process and the quantification of the tensile stress in the materials can also be obtained.

Order No.: JA605-022

Epitaxial growth and magnetic behavior of $NiFe_2O_4$ thin films

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Thin films of $NiFe_2O_4$ were deposited on $SrTiO_3$ (001) and $Y_{0.15}Zr_{0.85}O_2$ (yttria-stabilized zirconia) (001) and (011) substrates by 90°-off-axis sputtering. Ion channeling, x-ray diffraction, and transmission electron microscopy studies reveal that films grown at 600°C consist of ~300 Å diameter grains separated by thin regions of highly defective or amorphous material. The development of this microstructure is attributed to the presence of rotated or displaced crystallographic domains and is comparable to that observed in other materials grown on mismatched substrates (e.g. GaAs/Si or $Ba_2YCu_3O_7$/MgO). Post-deposition annealing at 1000°C yields films that are essentially single crystal. The magnetic properties of the films are strongly affected by the structural changes: unannealed films are not magnetically saturated even in an applied field of 55 kOe, while the annealed films have properties comparable to those of bulk, single crystal $NiFe_2O_4$. Homoepitaxial films grown at 400°C also are essentially single crystal.

Order No.: JA605-023

Nanocrystalline $BaTiO_3$ from freeze dried nitrate solutions

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An aqueous, all nitrate, solution-based preparation of $BaTiO_3$ is reported here. Rapid freezing of a barium and titanyl nitrate solution, followed by low-temperature sublimation of the solvent, yielded a freeze dried nitrate precursor which was thermally processed to produce $BaTiO_3$. XRD revealed that after ten minutes at temperatures ≥600°C the formation of phase pure nanocrystalline $BaTiO_3$ resulted. TEM revealed that the material was uniform and nanocrystalline (10-15 nm). The high surface to volume ratio inherent in these small particles stabilized the cubic phase of $BaTiO_3$ at room temperature. It was also found that the average particle size of the $BaTiO_3$ produced was highly dependent upon calcination temperature and only slightly dependent upon annealing time. This result suggested a means of selection of particle size of the product through judicious choice of calcination temperature. The experimental details of the freeze dried precursor preparation, thermal processing

of the precursor, product formation, and product morphology are discussed.

Order No.: JA605-024

Synthesis, characterization and properties of lead-based relaxor ferroelectrics

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Lead-based relaxor ferroelectrics such as $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN), $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN) and their solid solutions with $BaTiO_3$ and $PbTiO_3$ have been prepared by a solution combustion process which involves metal nitrates/oxalate and tetraformal trisazine (TFTA) at 350°C. Thermal evolution of perovskite relaxors have been investigated at different temperature of calcination using powder x-ray diffraction method. Particles are fine and sinter-active at low temperature (1050°C). Both particulate and dielectric properties are compared.

Order No.: JA605-025

Reaction kinetics, sintering characteristics, and ordering behavior of microwave dielectrics: Barium magnesium tantalate

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(National Taiwan University)

The formation process of $Ba(Mg_{1/3}Ta_{2/3})O_3$ was confirmed to be a direct reaction between constituent compounds without the presence of intermediate compounds. Isothermal analysis of reaction kinetics indi-cated the controlling reaction to be a three-dimensional diffusion process. Based on the Ginstling-Brounshtein model, the activation energy of the formation process was estimated to be 257 kJ/mol. A new definition of the ordering parameter for $Ba(Mg_{1/3}Ta_{2/3})O_3$ was deduced to quantitatively evaluate the ordering degree. Raised sintering temperatures resulted in an increase in the ordering degree and bunk density of $Ba(Mg_{1/3}Ta_{2/3})O_3$. Reducing the barium content in $Ba(Mg_{1/3}Ta_{2/3})O_3$ substantially resulted in improved densification and enhanced ordering structure. On the other hand, an excess barium content in specimens hindered the progress of sintering, and also induced the disordering structure.

Order No.: JA605-026

High-resolution studies of crystalline damage induced by lapping and single-point diamond machining of Si(100)

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Si(100) wafers were prepared by both diamond turning and standard lapping and polishing techniques. For single-point diamond machining, characterization of subsurface damage resulting from ductile-regime machining identified a plastic-yield zone consisting of slip planes and dislocation networks extending 1 to 3 μm deep despite surface root-mean-square roughness values as low as 5 nm. For conventional lapping and polishing using alumina grit, a transition from brittle to ductile yield was observed for grit sizes less than 300 nm. Subsurface damage depth correlated to surface roughness in a more straightforward manner than for the diamond point machining. Completely damage-free material removal was obtained only when a chemical component to the polishing was present.

Order No.: JA605-027

Refinement of low-resistance Ni-Ge-Au ohmic contacts to n+ GaAs using screening and response surface experiments

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Multivariable screening and response surface experiments have been performed to model ohmic contact resistance (R_c) of a Ni-Ge-Au ohmic metal process for n+ GaAs-based high electron mobility transistors (HEMTs). Seven variables were examined via a fractional factorial screening experiment to rank the effects of each process variable. The results of the screening experiment indicated that the most significant variables were total Ge and Au evaporated thickness, Ge-to-Au ratio, and the post-alloy cooling time. Response surface experiments were designed around these three variables to examine the first- and second-order effects. The results enabled the development of an empirical model of ohmic contact resistance from which a new low value of 0.03 ± 0.03 Ω.mm (one-sigma) was predicted. Twenty confirmation runs on the new process indicated an average R_c of 0.07 ± 0.02 Ω.mm (one-sigma), with a range of 0.02 Ω.mm to 0.11 Ω.mm, a reduction from the previous average process value of 0.14 ± 0.07 Ω.mm (one-sigma).

Order No.: JA605-028

Investigation of low- and high-resistance Ni-Ge-Au ohmic contacts to n+ GaAs using electron microbeam and surface analytical techniques

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A process for the formation of low-resistance Ni-Ge-Au ohmic contacts to n+ GaAs has been refined using multivariable screening and response surface experiments. Samples from the refined, low-resistance process (which measure 0.05 ± 0.02 Ω.mm) and the unrefined, higher resistance process (0.17 ± 0.02 Ω.mm) were characterized using AEM, TEM, SEM-EDS, and XPS depth profiling methods. This approach was used to identify microstructural differences and compare them with electrical resistance measurements. Analytical results of the unrefined ohmic process sample reveal a heterogeneous, multiphase microstructure with a rough alloy-GaAs interface. The sample from the refined ohmic process exhibits an alloy which is homogeneous, smooth, and has a fine-grained microstructure with two uniformly distributed phases. XPS analysis for the refined ohmic process sample indicates that the Ge content is relatively depleted in the alloy (relative to the deposited Ge amount) and enriched in the GaAs. This is not evidenced in the unrefined ohmic process sample. Our data lead us to conclude that a smooth, uniform, two-phase microstructure, coupled with a shift in Ge content from the post-alloy metal to the GaAs is important in forming low-resistance ohmic contacts.

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Thermal stability of Nb thin films on sapphire

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The Nb/α-Al_2O_3 system has been used as a model study for investigating the stability of different MBE grown epitaxial Nb films on α-Al_2O_3 substrates. The films were grown at 800°C in ultra high vacuum. The growth process was monitored *in situ* by reflection high energy electron diffraction (RHEED). After deposition the structure of the film was investigated by x-ray diffraction (XRD) and conventional transmission electron microscopy (CTEM) which encompasses also selected area diffraction (SAD). Both techniques revealed the following orientation relationship between the Nb film and the α-Al_2O_3 substrate: $(0001)\alpha\text{-}Al_2O_3 \parallel (111)Nb$; $[2\bar{1}\bar{1}0]\alpha\text{-}Al_2O_3 \parallel [\bar{1}10]Nb$. The stability of the niobium films was investigated by annealing the Nb-film/α-Al_2O_3 system to temperatures up to 1500°C for different periods of time. Surprisingly the orientation relationship between the Nb film and the substrate changed to: $(0001)\alpha\text{-}Al_2O_3 \parallel (110)Nb$; $[01\bar{1}0]\alpha\text{-}Al_2O_3 \parallel [001]Nb$. A model will be developed which shows that above a critical film thickness the growth orientation is metastable with respect to its crystallographic orientation. Furthermore, high resolution transmission electron microscopy (HREM) was performed to investigate the defect structure of the annealed Nb/α-Al_2O_3 interface.

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Influence of alloying elements on the chemical reactivity between Si-Al-O-N ceramics and iron-based alloys

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The chemical interaction between two β′-O′ Si-Al-O-N ceramics and a number of iron-based alloys is studied by means of static interaction couple experiments at 1100 and 1200°C. The onset temperature of reaction of Si_3N_4 with pure iron was found to be at 1095°C, which is in good agreement with a calculated temperature of 1033°C. During the interaction, silicon and nitrogen from the ceramic dissolve and diffuse into the iron alloy, whereas the remaining aluminium and oxygen form Al_2O_3 particles. The interaction between ceramic and iron alloy is reaction controlled. In the initial stage of the interaction the dissociation rate of the ceramic is the rate controlling step. After the ceramic/metal interface is isolated from the furnace atmosphere, the nitrogen solution rate into the iron alloy becomes rate controlling. The influence of alloying elements on the reactivity could be related to their effect on the nitrogen solubility in the iron alloy. Ni, Si and C decrease the nitrogen solubility and decrease the reactivity with the sialon ceramic. Cr and Mo have the opposite effect. The thickness of the interaction layer on the ceramic side of the interaction couple was found to be a function of the calculated nitrogen solubility in the iron alloy at 1 atmosphere nitrogen pressure, making it possible to predict the relative chemical reactivity of a number of iron-based alloys with the same sialon ceramic.

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Ion beam mixing, diffusion and phase stability in Cu/Al_2O_3 interfaces

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Ion beam mixing, diffusion properties and phase stability have been investigated in Cu/Al_2O_3 bilayer samples. Specimens were prepared by vapor deposition and irradiated with 150 keV Ar^+ ions up to a fluence of $1.5 \cdot 10^{17}$ Ar^+/cm^2. Sample temperature under irradiation was varied between 77 K and 673 K. The mixing behavior was studied by analyzing the concentration depth profiles, determined by Rutherford backscattering spectroscopy. It was found that mixing efficiencies of Cu, Al and O scale linearly with Ar^+ fluence. Radiation enhanced diffusion (RED), observed above room temperature, is separated from ballistic mixing and high-temperature diffusion. The migration enthalpy for interdiffusion in the RED region (between RT and 300°C) was estimated to be approximately 0.3 eV. Sputtering yields depending on temperature gradient near to sample and phase stability versus ion dose and temperature are also discussed.

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Effect of silicon additions on characteristics of carbon fiber reinforced aluminum composites during thermal exposure

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The effects of Si additions on the behavior of high modulus carbon fiber reinforced aluminum matrix (CF/Al) composites during thermal exposure at 773 K for different times have been investigated. The composites were fabricated via hybridization with a small volume fraction of SiC particles using a pressure casting process. The change of longitudinal tensile strength, the strength degradation of carbon fibers, and the microstructural observations on the interfaces of CF/pure Al composites and CF/Al-Si composites after thermal exposure, undoubtedly indicate that the alloying element Si in an aluminum matrix can effectively prohibit the interfacial reactions at the fiber/aluminum interface and has positive effects on the characteristics of CF/Al composites.

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Elasticity and fracture in particulate composites with strong and degraded interfaces

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Silane coated glass microspheres randomly embedded in an epoxy polymer matrix have been employed as a model system to investigate the degradation of disordered composite materials by water, and to test various models of deformation and fracture. Numerous composites containing sodalime (A) glass in the range 0 to 25% by volume were tested dry and immersed in saturated NaCl at 40°C for periods up to 70 days before testing. Enhanced osmotic water uptake due to percolating interface damage was observed for composites containing more than 15% glass. The electrical resistance of similar composites filled with conducting spheres confirmed the existence of a percolation transition, though with high resistance values implying no direct contact of the spheres. Tensile measurements conducted on dry material at a nominal strain rate of about 10^{-3} s^{-1} showed an increase in elastic modulus and a decrease in the fracture strength with increasing glass content. New detail was apparent in these curves and confirmed by statistical analyses. For wet specimens, in addition to a general embrittlement effect of water absorption, there was a distinct plateau or small peak in fracture strength in the range 9 to 12% glass, and an abrupt drop between 12 and 15%. The plateau can be related to favorable crack interaction effects between disconnected clusters of interfaces just below the percolation threshold. The steep increase in elastic modulus with glass content seen in the dry material vanished entirely in wet material, which behaved like a porous polymer above 6% glass, owing to osmotic interface damage within particle clusters.

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Mechanisms of Al and titania hydrogel complex formation via a mechanical route

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The process of complex formation has been studied during milling a powder mixture of metallic Al and titania hydrogen $TiO_2 \cdot H_2O$. Solid state ^{27}Al NMR and ESR are employed together with conventional x-ray diffractometry and thermal analyses. Al atoms partly changed from metallic to oxide state. ^{27}Al NMR analyses indicate that two metallic Al states are allotted to distorted and undistorted lattices, while the other to AlO_x units in the oxide state, where x is 4, 5 or 6. As detected by ESR, Ti^{4+} was partly reduced to Ti^{3+}, suggesting a redox reaction during milling. A vigorous thermit reaction was detected during subsequent heating of the mixture after prolonged milling. These results indicate the formation of Al-O-Ti bonds during milling, leading to Al_2TiO_5 on subsequent heating.

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