JMR Abstracts

Editor-in-Chief: Robert A. Laudise • Associate Editors: Shigeyuki Sōmiya, Heinrich J. Wollenberger

Volume 13, Number 7 *Abstracts for July 1998 Journal of Materials Research*

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ABSTRACTS

COMMUNICATIONS

Novel in-situ production of smooth diamond films
D.R. Gilbert, D-G. Lee, R.K. Singh
(University of Florida)

We have developed a unique method to produce smooth diamond films using a modified microwave plasma process system. This method consists of sequential *in-situ* deposition and planarization in an electron cyclotron resonance plasma system. Diamond films were deposited to a thickness of 3.0 μm in this system at a pressure of 1.000 Torr from gas mixtures of methanol and hydrogen. Deposition was followed by planarization using a two-grid ion beam extraction process with a pure oxygen plasma at 10 millitorr. The average roughness of the diamond films so produced was as low as 30 nm, which was a factor of two lower than that of the as-deposited diamond films.

Order No.: JA807-001

Epitaxial growth of β-SiC on silicon by bias-assisted hot filament chemical vapor deposition from solid graphite and silicon sources
H.K. Woo, C.S. Lee, I. Bello, S.T. Lee
(City University of Hong Kong)

Epitaxial β-SiC film has been grown on mirror-polished Si(111) substrate using bias-assisted hot filament chemical vapor deposition (BA-HFCVD) at a substrate temperature of 1000°C. A graphite plate was used as the only carbon source, and hydrogen was the only feeding gas to the deposition system. Atomic hydrogen, produced by hot filaments, reacted with the graphite to form hydrocarbon radicals which further reacted with the silicon substrate and deposited as β-SiC. The effect of negatively biasing the substrate is the key factor for epitaxial growth. Under the same growth conditions without negative bias, polycrystalline β-SiC resulted.

Order No.: JA807-003

Atomistic computer study on Mg segregation in the Ni_3Al grain boundary
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The embedded atom method (EAM) was applied to calculate the energy on Mg doping in polycrystalline Ni_3Al. The EAM predicted energy of Mg in Al site in grain boundary is lower than that of Mg in Ni site and much lower than that of Mg in Al or Ni site in bulk and in free surface. It means that Mg would segregate to grain boundary rather than bulk and free surface and Mg will be the favorite substitute of Al rather than of Ni in grain boundary. These results were consistent with the experiments that Mg segregated to grain boundaries with Al depletion and Ni enrichment.

Order No.: JA807-004

Bismuth quantum-wire arrays fabricated by a vacuum melting and pressure injection process
Z. Zhang, J.Y. Ying, M.S. Dresselhaus
(Massachusetts Institute of Technology)

Ultra-fine bismuth nanowire arrays were synthesized by injecting its liquid melt into nanochannels of a porous anodic alumina template. A large area (1 cm x 1.5 cm) of parallel wires with diameters as small as 13 nm, lengths of 30–50 μm and packing density as high as 7.1×10^{10} cm^{-2} has been fabricated. X-ray diffraction patterns revealed these nanowires, embedded in the insulating matrix, to be essentially single crystalline and highly oriented. The optical absorption spectra of the nanowire arrays indicate that these bismuth nanowires undergo a semimetal-to-semiconductor transition due to two-dimensional quantum confinement effects.

Order No.: JA807-005

Aluminum borate in the combustion synthesis of alumina/boride composite

Y. Liu, S. Yin, Z. Guo, H. Lai
(University of Science and Technology Beijing)

The formation mechanism of aluminum borate in the combustion synthesis of Al_2O_3/B_4C composite with Al, B_2O_3 and C as starting materials is proposed. Based on the formation mechanism, several approaches taken to eliminate them are discussed. The unconverted B_2O_3 is the major cause of the formation of $9Al_2O_3.2B_2O_3$ when the reaction proceeds in the SHS mode. The amount of $9Al_2O_3.2B_2O_3$ formed is very sensitive to the excess B_2O_3 to the stoichiometry $4Al+2B_2O_3+C$ and influenced by the size of B_2O_3 powder. The high dispersion of the reactants is helpful in prompting the thermite reaction to consume B_2O_3 and hence inhibiting the aluminum borate formation.

Order No.: JA807-006

Formation of cubic C-BN by crystallization of nano-amorphous solid at atmosphere

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An amorphous carbon-boron nitride (C-BN) solid was prepared by ball milling the mixture of graphite and hexagonal BN powders for a period of 120 h. After annealing the amorphous C-BN solid for 1 hour at atmosphere in the temperature range from 800 to 900 K and then quenching it to room temperature, a small amount of cubic C-BN solid solutions with diamond-like structure, which belong to a high energy phase and can only be synthesized previously under high pressure and temperature (30 GPa, 2000 K), were observed in the annealed amorphous C-BN solid. The lattice constant of the cubic C-BN solid solution was 0.3587 nm and its grain size was in the range of 10 to 50 nm.

Order No.: JA807-007

Determination of x-ray elastic constants using an *in-situ* pressing device

D.H.J. Teeuw, J.Th.M. De Hosson
(University of Groningen)

The experimental determination of x-ray elastic constants are performed by *in-situ* measurements of the dependence of the strain state in selected crystallites for different applied external compressive stresses. The use of compressive applied stresses instead of tensile applied stresses is of interest for x-ray elastic constant determinations for materials which exhibit brittle-like crack behavior, which cannot be loaded to high tensile stresses in e.g. four point bending devices. The x-ray elastic constants for *{146}* α-Al_2O_3 are determined with the pressing device and compared to calculated as well as experimentally determined values which were tested in tensile loading devices.

Order No.: JA807-008

dc electrical degradation of iron-doped titania ceramics

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(Shinshu University)

An anomalous increase of current was found in Fe-doped titania ceramics subjected to a constant field of 10^5 V/m. It is suggested that the space charge rises from blockage of $O_2(g) \rightarrow O^{2-}(s)$ ion transfer at the cathode. This leads to an increase of *n*-conductivity in the cathodic region and *p*-conductivity in the anodic region according to the specific defect equilibrium. This viewpoint was reinforced by two newly observed phenomena: (1) the I-V plot shows a linear feature at the initial stage but it gradually becomes rectifying feature with time, and (2) an edge-located electrode shows lower current density and faster current saturation compared with a normal electrode.

Order No.: JA807-009

Formation of silicon carbide and amorphous carbon films by pulse biasing silicon to a high voltage in a methane electron cyclotron resonance microwave plasma

K. Volz, W. Ensinger, W. Reiber, B. Rauschenbach, B. Stritzker
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Silicon was pulse biased to -45 kV in a methane plasma generated by microwave excitation in the electron cyclotron resonance (ECR) mode. Hydrocarbon ions were accelerated in the electrical field and implanted into the silicon. Rutherford backscattering (RBS) measurements showed that it is possible to incorporate a concentration of up to 95 at.% C into the Si. Cross section transmission microscopy (XTEM) showed that the resulting surface layer was amorphous. Annealing at 1250°C resulted in the formation of 10 to 60 nm thick crystalline SiC layers.

Order No.: JA807-010

ARTICLES

Effects of substrate pretreatment and methane fraction on the optical transparency of nanocrystalline diamond thin films

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Optical transmittance of the nananocrystalline diamond films has been studied as a function of grain size of the diamond powder used for substrate pretreatment and the methane fraction in the source gas. It has been observed that for CH_4 fractions below 13%, the films grown on substrates pretreated with finer diamond powder are more transparent, while this trend reverses for CH_4 fractions above 13%. These variations in the transparency of the films correlate very well with their corresponding surface roughness. Nanocrystalline/amorphous diamond films with transmittance of greater than 80% beyond 700 nm and with average surface roughness as low as 61 Å have been obtained for CH_4 fractions as high as 42% in the source gas. Interestingly, these films do not show an obvious presence of any graphitic carbon, and the structural ordering of the amorphous sp^3-bonded phase also seems to be insensitive to the CH_4 content of the source gas.

Order No.: JA807-002

High resolution transmission electron microscopy of $Ba_{1-x}K_xBiO_3$ superconductor-insulator-superconductor grain boundary tunnel junctions

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High angle boundaries in $Ba_{1-x}K_xBiO_3$ are superconductor-insulator-superconductor (SIS) Josephson tunnel junctions of a quality unequaled among the high temperature superconducting oxides. Electron microscopy of 24° [001] tilt boundaries reveals nominally symmetric and straight boundaries of aperiodic structure with reappearing structural units. Low {hk0} atomistic facets are predominant. A segregation layer of only 1 nm thick is identified straddling the boundary. This layer which forms naturally is insulating, pin-hole free and surprisingly robust with a breakdown voltage exceeding 1 x 10^6 V/cm, yet thin enough to allow quasiparticle tunneling, yielding reliable gap energies for theoretical comparison.

Order No.: JA807-011

Effect of noble metals on selective detection of liquid petroleum gas by SnO_2

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The present investigation deals with the electrical response of doped SnO_2 to improve the selectivity for liquid petroleum gas (LPG) in the presence of CO, CH_4, by utilizing noble metal sensitizers such as Pd, Pt and Rh. SnO_2 with the addition of Pd (1.5 wt.%) or Pt (1.5 wt.%) sintered at 800°C have shown high sensitivity towards LPG with no cross interference of CO and CH_4 at an operating temperature of 350°C. The results suggest the possibility of utilizing the sensor for the detection of this hydrocarbon gaseous mixture. X-ray diffraction studies have been carried out to evaluate the crystallite size as a function of sintering temperature; x-ray photoelectron spectroscopy studies have been carried out to define the possible chemical species involved in the gas-solid interaction and the sensitivity enhancing mechanism of the SnO_2/Pd sensor element towards LPG.

Order No.: JA807-012

The coexistence of silicon borides with boron-saturated silicon: Metastability of SiB3

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The silicon-rich end of the Si-B phase diagram, defining the silicon boride(s) that coexist in equilibrium with boron-saturated silicon, is poorly known. Understanding this equilibrium has implications for the processing of p^+ silicon wafers, whose boron concentrations are near the solubility limit. Additionally, silicon boride precipitates produced by boron-ion-implantation and annealing of crystalline silicon have recently been shown to be efficient internal getters of transition metal ions. The experiments described in this paper probe the stability of these silicon borides. A phase with a boron carbide-like structure, SiB_3, grows from boron-saturated silicon in both the solid and the liquid state. However, SiB_3 is not found to be stable in either circumstance. Rather, SiB_3 is a metastable phase whose formation is driven by the relative ease of its nucleation and growth. The silicon boride that exists in stable equilibrium with boron-saturated silicon is SiB_6. A qualitative understanding of the metastability of SiB_3 comes from recognizing the conflict between the bonding requirements of icosahedral borides such as SiB_3 and the size mismatch between silicon and boron atoms.

Order No.: JA807-013

Gd-doping effects on properties of amorphous silicon films prepared by electron beam evaporations

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Gd-doped amorphous silicon films have been prepared by electron beam evaporation technique, employing the experimental methods of dc conductivity temperature properties, electron spin resonance (ESR) spectra and optical band gap E_{opt} measurements. We have investigated the optical and electrical properties of the films. The results show that at 290 K < T < 330 K, hopping conduction in Gd impurity states near Fermi level is predominant, and at 330 K < T < 500 K extended state conduction dominates due to electrons exited from the impurity states. At a Gd concentration of about 1.0 at.% spin density N_s peak-peak width ΔB_{pp} and line-shape factor I of ESR spectra change their dependence on Gd contents. The optical gap of the films narrows with increasing Gd contents in the films from 1.68 ev to 0.42 ev. The results were explained on the basis of the partial compensation of Gd atoms for dangling bonds Si°.

Order No.: JA807-014

Auger electron spectroscopy and x-ray photoelectron spectroscopy analysis of angle of incidence effects of ion beam nitridation of GaAs

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Ion beam nitridation (IBN) of GaAs at room temperature was studied as a function of N_2^+ ion incident angle at ion energy of 10 keV. The ion beam bombardment surface area of GaAs was characterized *in-situ* by both Auger electron spectroscopy (AES) and small spot size x-ray photoelectron spectroscopy (XPS). Thin GaN reaction layers are formed at all N^{2+} ion incident angles whereas the formation of As-N bonds has not been found. However, the degree of nitridation of Ga decreases with increasing incident angle. The observed angular dependence of the N incorporation can be explained in terms of sputtering yield, indicating that the growth kinetics can be described as a dynamic process comprising the accumulation of N and sputter removal of the surface layer. N_2^+ ion bombardment causes the depletion of As from the surface region because of the preferential sputtering of As from GaAs. The preferential sputtering of As reduces with increasing N_2^+ ion incident angle. The angular dependent behavior of preferential sputtering of As by 10 keV N_2^+ ions can be attributed to the angular dependence of GaN surface layer formation.

Order No.: JA807-015

Structural changes in GaAs induced by ultrafast (fs) laser pulses

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Ultrafast changes in the crystal structure of GaAs induced by intense femtosecond laser pulses are detected and investigated. Atomic force microscopy and Raman microprobe analysis of the laser-treated area show centrosymmetric (disordered) features which are different from the original zinc-blend structure of the GaAs lattice. The frozen-in structure shows evidence for a special heat transfer from the laser-induced crater to the boundary, namely the heat has been transferred ballistically by a high-density electron-hole plasma.

Order No.: JA807-016

Silicon carbide grown by liquid phase epitaxy in microgravity

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6H and 4H polytype silicon carbide (SiC) layers have been grown on ground and under microgravity conditions by liquid phase epitaxy (LPE) from a solution of SiC in Si-Sc solvent at 1750°C. The effect of gravity on the growth parameters and material characteristics have been studied. The growth rate, Sc incorporation and the structural defects are modified in reduced gravity conditions, while the polytype reproduction of the substrate is not affected. The results obtained are intriguing as to further experiments providing objects for carrier lifetime measurements.

Order No.: JA807-017

Aluminum nitride-silicon carbide solid solutions grown by plasma-assisted, gas-source molecular beam epitaxy

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Solid solutions of aluminum nitride (AlN) and silicon carbide (SiC) have been grown at 900–1300°C on vicinal α(6H)-SiC(0001) substrates by plasma-assisted, gas-source molecular beam epitaxy. Under specific processing conditions, films of $(AlN)_x(SiC)_{1-x}$ with $0.2 \le x \le 0.8$, as determined by Auger electron spectrometry (AES), were deposited. Reflection high-energy electron diffraction (RHEED) was used to determine the crystalline quality, surface character and epilayer polytype. Analysis of the resulting surfaces was also performed by scanning electron microscopy (SEM). High-resolution transmission electron microscopy (HRTEM) revealed that monocrystalline films with $x \ge 0.25$ had the wurtzite (2H) crystal structure; however, films with $x < 0.25$ had the zincblende (3C) crystal structure.

Order No.: JA807-018

Inner surface reaction and modification of titanium alloy by a new plasma source ion implantation method

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The inner surface of a cylindrical titanium alloy target was successfully implanted with nitrogen ion using a new plasma source ion implantation method. By means of x-ray photoelectron spectroscopy and x-ray diffraction, the reactive phases and their chemical state in the implanted layer were investigated. In order to characterize the modification effect and its uniformity, the retained dose and the microhardness at seven different positions along the axis on the inner surface of the cylindrical target were measured respectively. The experimental results show that a TiN reactive phase was formed in the implanted layer, which contributed to the improvement of inner surface microhardness. The root-mean-square deviations of retained dose and microhardness measured along the axis of the target are less than 9% and 4% respectively, which are well within an acceptable tolerance range for metallic applications of ion implantation.

Order No.: JA807-019

Microstructural evolution of the η-phase in the Cu-Sn system

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The formation of η-phase by a peritectic reaction in the Cu-Sn metallic system has been cited in the literature while discussing the solidification of the high temperature superconductor $YBa_2Cu_3O_7$ through the peritectic temperature, from Y_2BaCuO_5 and liquid phases. Similar schematic phase diagrams and driving forces have been invoked to discuss the reactions in both cases. In this paper, we have studied the microstructural evolution of the η-phase from ε + liquid in the Cu-Sn system, by observing quenched microstructures at various stages of processing, when subjected

to a thermal schedule similar to the one used for the melt processing of $YBa_2Cu_3O_7$. A comprehensive picture of the mechanism by which the η-phase nucleates and grows has been evolved.
Order No.: JA807-020

A comparison of two aluminizing methods for corrosion protection in the wet seal of molten carbonate fuel cells
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The corrosion behavior of aluminized Type 310S stainless steel (SS) in the wet-seal of molten carbonate fuel cells was investigated. Coupons of Type 310S SS were aluminized by two different aluminizing methods: thermal spray and slurry coating. In both types of samples, Fe and Cr diffused readily into the Al layer at 650°C. At first this interdiffusion is limited to the interfacial area. With time, Fe and Cr aluminides precipitate in the Al layer. The slurry-coated layer contains a higher concentration of FeAl and Fe_3Al than does the thermal spray layer. Consequently, the slurry-coated layer also displays a greater degree of corrosion than the thermal spray layer.
Order No.: JA807-021

Polycarbodiimide and polyimide/cyanate thermoset *in-situ* molecular composites
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The synthesis of polycarbodiimide and polyimide in a cyanate resin precursor was achieved. A unique procedure for achieving a high molecular weight of the molecular composite reinforcement molecules was demonstrated. In spite of phase separation being present during the processing, the final cured composites were transparent. The enhanced mechanical properties and the presence of a single T_g, which increases with rigid rod content, were indications that a molecular composite was achieved. The agreement between measured mechanical properties and those predicted using molecular mechanics simulations Cerius^2 software was encouraging.
Order No.: JA807-022

Compositional and physical changes on perovskite crystal surfaces
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(Los Alamos National Laboratory)

The surface composition of $BaTiO_3$, $SrTiO_3$ and $CaTiO_3$ perovskite (100) surface is determined by shell-model calculations. The TiO_2-terminated surface is energetically favorable for $BaTiO_3$ and $SrTiO_3$, which is consistent with experimental observations on $SrTiO_3$. On the other hand, the CaO-terminated surface is preferred for $CaTiO_3$ where Ca^{2+} is the smallest 2+ cation in these titanates. Ions on (100) surface rumple and induce surface dipoles. The surface ferroelectric polarization stabilizes the surface and changes its sign as the surface composition changes from TiO_2 to CaO. This phenomenon is expected to affect the stability and properties of epitaxial films on perovskite substrates.
Order No.: JA807-023

Microstructural development of SCS-6 SiC fibers during high temperature creep
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Microstructural development of SCS-6 SiC fibers induced by creep deformation at 1400°C is presented. Grain growth occurs in all SiC regions of the fiber during creep. Portions of the SiC4 region transform from βSiC to αSiC with the αSiC growing at the expense of the βSiC. The SiC1 through SiC3 regions of the fiber consist of a distinct (C + βSiC) two phase region. The grain growth of the βSiC grains in the two-phase region is not as extensive as in the SiC4 region, suggesting that the presence of excess carbon may inhibit the growth of βSiC.
Order No.: JA807-024

Photoluminescence in $PbMg_{1/3}Nb_{2/3}O_3$-$PbIn_{1/2}Nb_{1/2}O_3$ systems
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Photoluminescence for $PbMg_{1/3}Nb_{2/3}O_3$ (PMN)-$PbIn_{1/2}Nb_{1/2}O_3$ (PIN) solid solutions in the temperature ranging from 35 to 295 K have been obtained for the first time. An abrupt photoluminescence enhancement of the system has been observed to occur at ~210 K, which can be attributed to the growing and merging of dynamic polar microregions or to the phase transformation of the material at this temperature. The PIN content has been found to affect the photoluminescence of the PMN-PIN system significantly. The photoluminescence mechanism for PMN-PIN has been studied.
Order No.: JA807-025

Interactions between bismuth oxide and ceramic substrates for thick film technology
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We investigated the interactions between screen printed and fired layers of Bi_2O_3 and ceramic substrates of alumina and beryllia. It was found that the reaction products are invariably crystalline in nature. Several transitions of Bi_2O_3 in its polymorphic phases were found to occur on BeO substrates, while newly formed compounds have been observed to grow on alumina substrates, i.e. $Al_4Bi_2O_9$ on 99.9%-Al_2O_3 and $Bi_{12}SiO_{20}$ on 96%- Al_2O_3. Bismuth deeply penetrates in the ceramic interstices in all of the cases. Until Bi_2O_3 is not completely reacted, this penetration is diffusion limited (penetration depth $w \approx t_d^{1/2}$, where t_d is the reaction time) with values of the activation energy ranging from 3.7 ± 0.6 eV (BeO substrate) to 1.4 ± 0.06 eV (96%-Al_2O_3 substrate). It is shown that these processes are notably different to those occurring in PbO/ceramic systems; moreover they imply different adhesion phenomena of thick films on different substrates.
Order No.: JA807-026

Fabrication of dense nanocrystalline ZrO_2-3 wt.% Y_2O_3 by hot-isostatic pressing
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Amorphous to nanocrystalline ZrO_2-3 wt.% Y_2O_3 powders were formed by chemical precipitation from mixed nitrate salt solutions. The powders were cold pressed and presintered in air for 2 to 6 hr within the temperature range of 1100°C to 1300°C. Hot isostatic pressing was performed for 2 to 3 hr within the temperature range of 1150°C to 1350°C in argon pressure of 150 MPa. Fully dense pellets with grain size of 22 nm to 45 nm were formed by application of low presintering temperatures.
Order No.: JA807-027

Binder surface segregation during spray drying of ceramic slurry
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Spray-dried granules were observed by a laser microscopy with the immersion liquid technique. The binder distribution in the granules was analyzed from light intensity profiles of the images. The results showed that a surface layer with a large amount of the binder is formed in the spray dried granule, and the segregation is influenced by initial binder concentration and size of atomized droplet. A computer simulation for soluble binder segregation during spray drying was conducted with considering simultaneously the solvent evaporation, the relative migration between the liquid and the particles, the diffusion, and drying shrinkage. The simulation coincides with the experimental results. To make uniform granules, reducing the amount of binder, liquid content, size of atomized droplet, and drying rate is favorable.
Order No.: JA807-028

Early age microstructure of the paste-aggregate interface and its evolution

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The sequence of microstructural changes occurring at the wet paste-aggregate interface is documented at an age as early as 5 minutes using the environmental scanning electron microscope (ESEM). Unlike other microscopic techniques, the ESEM allows pastes of normal water : cement ratio to be observed at early ages without reducing the paste to a powder. Evolution of the paste-aggregate microstructure is followed up to an age of 24 hours. The region adjacent to the aggregate surface contains a phase with a morphology referred to as a "sheaf of wheat" morphology. The same interfacial region in a 10-day-old specimen has a microstructure similar to the interfacial transition zone (ITZ) reported in the literature. Variations of the "sheaf of wheat" morphology due to original water-to-cement ratio, mixing energy, incorporation of silica fume, and drying are documented. As revealed by energy dispersive x-ray analysis (EDS), the microstructure contains significant amounts of calcium and silica. These results indicate that the observed morphology is likely to be a calcium silicate hydrate (C-S-H) product that is a precursor to type I C-S-H. A description of the evolution of the observed microstructural features is presented. The "sheaf of wheat" morphology appears to be a general precursor to morphologies commonly seen in mature pastes.

Order No.: JA807-029

Detection of contact damage in ceramics by an ultrasonic method

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A pulse-echo ultrasonic technique consisting of focused normal-incident compressional waves was used for the detection and evaluation of surface and subsurface damage in micaceous glass-ceramic and silicon nitride samples. The damage was produced by indentation with a tungsten carbide ball. The nature of the damage was found to be material-dependent and was classified into two types: Hertzian cone cracks in the silicon nitride, and distributed subsurface microcracks in the glass-ceramic. While the cone cracks were visible on the surface as circular ring cracks, the distributed subsurface microcracks were not associated with any visible surface cracks. Both the cone cracks and the distributed subsurface micro-cracks were easily detected by the ultrasonic technique. In addition, the ultrasonic beam was focused to different depths below the surface of the glass-ceramic sample to probe the subsurface region containing the microfracture damage.

Order No.: JA807-030

Synthesis processes and sintering behavior of layered-perovskite barium bismuth tantalate ceramics

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(National Taiwan University)

Ferroelectric layered-perovskite $BaBi_2Ta_2O_9$ has been successfully prepared through a novel process using $BiTaO_4$ as a precursor. Heating the mixtures of $BiTaO_4$ and $BaCO_3$ at 900°C without soaking results in the complete formation of the monophasic powder. In contrast, the conventional solid-state reaction requires soaking at 900°C for 2 h to obtain the pure compound. Such prolonged heat-treatment causes unfavorable growth of particles. In the new process, the formation of $BaBi_2Ta_2O_9$ is markedly accelerated due to the suppression of the formation of a stable intermediate-$Ba_5Ta_4O_{15}$. In addition, this process yields submicron $BaBi_2Ta_2O_9$ powder with significantly improved sinterability. Sintering at 1000°C affords well densified ceramics. On the other hand, heating at temperatures greater than 1100°C causes $BaBi_2Ta_2O_9$ to thermally decompose and form Bi_2O_3 and rod-like $BaTa_2O_6$. The formation of these rod-like grains results in the expansion of the matrix, thereby reducing the density.

Order No.: JA807-031

System Bi-Sr-O: Synergistic measurements of thermodynamic properties using oxide and fluoride solid electrolytes

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Phase equilibrium and electrochemical studies of the ternary system Bi-Sr-O indicate the presence of six ternary oxides (Bi_2SrO_4, $Bi_2Sr_2O_5$, $Bi_2Sr_3O_6$, $Bi_4Sr_6O_{15}$, $Bi_{14}Sr_{24}O_{52}$ and $Bi_2Sr_6O_{11}$) and three solid solutions (δ, β and γ). An isothermal section of the phase diagram is established at 1050 K by phase analysis of quenched samples. Three compounds, $Bi_4Sr_6O_{15}$, $Bi_{14}Sr_{24}O_{52}$ and $Bi_2Sr_6O_{11}$, contain Bi^{5+} ions. The stability of these phases is a function of oxygen partial pressure. The chemical potentials of SrO in two-phase fields are determined as a function of temperature using solid state cells based on single crystal SrF_2 as the electrolyte. Measurement of the emf of cells based on SrF_2 as a function of oxygen partial pressure in the gas at constant temperature gives information on oxygen content of the compounds present at the electrodes. The chemical potentials of Bi_2O_3 in two-phase fields of the pseudo-binary Bi_2O_3-SrO are measured using cells incorporating $(Y_2O_3)ZrO_2$ as the solid electrolyte. The standard free energies of formation of the ternary oxides are calculated independently using emfs of different cells. The independent assessments agree closely; the maximum difference in the value of ΔG_f° ($Bi_{2m}Sr_nO_p$) / (m+n) is ± 350 J/mol of component binary oxides. The results are discussed in light of the phase diagram and compared with calorimetric and chemical potential measurements reported in the literature. The combined use of emf data from cells incorporating fluoride and oxide electrolytes enhances the reliability of derived data.

Order No.: JA807-032

Analytic embedded atom method potentials for fcc metals

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The universal form of embedding function suggested by Banerjea and Smith together with a pair-potential of the Morse form are used to obtain embedded atom method (EAM) potentials for fcc metals: Cu, Ag, Au, Ni, Pd and Pt. The potential parameters are determined by fitting to the Cauchy pressure C_{12} -C_{44}/2, shear constant G_V=C_{11} -C_{12} +3C_{44}/5 and C_{44}, the cohesive energy and the vacancy formation energy. The obtained parameters are utilized to calculate the unrelaxed divacancy binding energy and the unrelaxed surface energies of three low-index planes. The calculated quantities are in reasonable agreement with the experimental values except perhaps the divacancy energy in few cases. In a further application to lattice dynamics, these metals are discussed using the present EAM potentials. On comparison with experimental phonons, the agreement is good for Cu, Ag and Ni while in three other metals: Au, Pd and Pt, the agreement is not so good. The phonon spectra are in reasonable agreement with the earlier calculations. The frequency spectrum and the mean square displacement of an atom in Cu are in agreement with the experiment and other calculated results.

Order No.: JA807-033

Stress evolution in passivated thin films of Cu on silica substrates

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Stresses supported by thin films of Cu passivated by SiO_x have been measured upon thermal cycling. Very high stresses have been found, approaching 1GPa in the thinnest (40 nm) films. Strengthening beyond yield occurs upon both cooling and heating, indicative of strong *strain hardening in the Cu*. The hardening continues down to at least 77°K. The yielding behavior of the Cu films has been characterized by a kinematic constitutive law, with exceptional strain hardening and a conventional temperature-dependent yield strength. The physical basis for this behavior is ascribed to confined shear bands in the Cu that induce large back stress. Transmission electron microscopy reveals aligned dislocations, which seemingly dictate the inelastic deformations in the shear bands.

Order No.: JA807-034

Atomic force microscope investigation of the thermal stability of thin $TiSi_2$ films

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The thermal stability of $TiSi_2$ films on Si has been studied using the atomic force microscope (AFM). Changes in the surface roughness, film morphology and sheet resistance were monitored during a series of rapid thermal annealing treatments. A linear increase of the root-mean-square (rms) roughness with time was observed during the early stages of degradation, in agreement with a surface diffusion model of thermal grooving, followed by an apparent saturation roughness that was attributed to the effective rupture of the film.

Order No.: JA807-035

Solid-phase reactions in Ir/(111) Si systems studied by means of x-ray emission spectroscopy

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High energy resolved x-ray emission spectroscopy with variable electron beam excitation is applied for study of solid-phase reactions in Ir/(111)Si system as a function of annealing temperature. The formation of Ir silicides as a function of depth is studied by measurements of Si $L_{2,3}$ x-ray emission valence spectra at different electron excitation energies (3–10 keV) and the results are compared with those of Rutherford backscattering.

Order No.: JA807-036

Evolution of stresses in passivated and unpassivated metal interconnects

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This paper discusses computational simulations of the evolution of stresses and deformation in unpassivated and SiO_2-passivated Al lines on Si substrates. The finite element model accounts for elastic-plastic deformation in the Al lines during etching, passivation and subsequent thermal cycling, by recourse to a generalized plane strain formulation within the context of a unit cell with appropriately constrained boundary conditions. The effects of different controlled variations in thermal history, and in the width, height, spacing and yield anisotropy of the Al lines are analyzed; all these factors are seen to have potentially strong effects on the evolution of stresses within the lines. The predictions of the computations presented in this work are amenable for direct comparisons with experiments of curvature evolution along and perpendicular to the lines upon patterning, passivation and thermal loading. The predicted stresses in metal interconnects can be directly used for reliability modeling purposes.

Order No.: JA807-037

Appropriate passivation structure in DRAM devices to improve stress-related reliability performance after plastic packaging

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This work attempts to determine an appropriate passivation structure in the real IC pattern to improve stress-related reliability problems after the plastic packaging. Several different types of amorphous passivation materials were first tested to learn how effectively they protect underlying Al interconnection lines during thermal displacement-induced fatigue at temperature ranges from -65°C to 150°C. It was also studied how effectively the occurrence of cracking in a passivation layer can be suppressed by the improvement of its topological feature or increase in its thickness. According to the experimental results, an increase in passivation thickness up to 21,000 Å (7,000 Å for oxide and 14,000 Å for SiN, respectively) was found to be a highly effective way to suppress stress-induced passivation damage on the inside of the chip in plastic IC packages. However, at the edges of the chip, smoothing of the passivation layer by sloping metal sidewall was more important for the improvement of thermal cycling performance than thickening of the passivation layer.

Order No.: JA807-038

Downshifts of Raman peak in diamond powders

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Results are presented on the influence of the size of diamond powders and the laser power on the main Raman line. These results show conclusively that there is a consistent and systematic, reversible, downshift with both decrease of size, and increase of power. The shift can be explained by local heating of about 500°C in the extreme case. Its significance applies to interpretation of the alleged "downshifting" of the 1332 cm^{-1} line in all diamond research. In the future, the grain size, the thermal contact, and the beam power must be carefully monitored in reporting and interpreting any frequency shifts.

Order No.: JA807-039

Synthesis of a Mo/Nb mixed carbide

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Molybdenum and niobium carbides (β-Mo_2C, NbC) as well as mixed carbides of molybdenum and niobium were synthesized by the temperature-programmed carburization method (TPC) using a 20%(v/v) CH_4/H_2 gas mixture. The starting materials were MoO_3, B-Nb_2O_5 and physical mixtures of B-Nb_2O_5/MoO_3 with Nb/(Nb+Mo) atomic ratios varying from 0.2 to 0.8, respectively. Results from catalytic and temperature-programmed oxidation (TPO) measurements indicate that during the carburization of the Nb_2O_5/MoO_3 physical mixture with Nb/(Nb+Mo) = 0.8 there is, besides β-Mo_2C and NbC formation, the appearance of a carbidic phase not detectable by x-ray diffraction (XRD). This phase appears to be highly active and selective for the dibenzothiophene hydrodesulfurization (HDS) reaction.

Order No.: JA807-040

Large Faraday effect and local structure of alkali silicate glasses containing divalent europium ions

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Measurements of Faraday and Mössbauer effects have been performed at room temperature for alkali silicate glasses containing a large amount of Eu^{2+} ions to examine the relation between local structure and magnitude of Verdet constant. The Mössbauer spectra indicate that about 80% of europium ions are present as a divalent state. The effective transition wavelength and effective transition probability for the $4f^7 \rightarrow 4f^65d$ transition of Eu^{2+} which causes the Faraday effect are derived from the wavelength dependence of Verdet constant. Both effective transition wavelength and effective transition probability are large compared with borate glasses, leading to the large magnitude of Verdet constant of the alkali silicate glasses. The variation of effective transition wavelength with glass composition is connected with the change of 6s-electron density of Eu^{2+} evaluated from the Mössbauer spectroscopy.

Order No.: JA807-041

Laser synthesis and crystallization of nanocomposite Si/C/N powder

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Ultrafine preceramic Si/C/N composite powders have been prepared from hexamethyldisilazane (HMDS) by laser induced gas phase reaction, using a new kind of two-reaction-zone reactor which could efficiently increase laser efficiency and production yield compared with one-reaction-zone reactor. The as-formed products were nanosized (50 ~ 80 nm), amorphous powders containing Si-C and Si-N bonds homogeneously mixed with some excess carbon. The production yield was in the range of 88 ~ 120 g/h. Changes of chemical composition and crystallization of the powders during heat treatment at 1350 and 1550°C under nitrogen for 1 h, were studied.

Order No.: JA807-042

Preparation and characterization of epitaxial iron oxide films
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Well-ordered, pure-phase epitaxial films of FeO, Fe_3O_4, and γ-Fe_2O_3 were prepared on MgO(001) by oxygen-plasma-assisted MBE. The stoichiometries of these thin films were controlled by varying the growth rate and oxygen partial pressure. Selective growth of γ-Fe_2O_3 and α-Fe_2O_3 was achieved by controlling the growth conditions in conjunction with the choice of appropriate substrates. Growth of the iron oxide epitaxial films on MgO at $\geq$ 350°C is accompanied by significant Mg outdiffusion. The FeO(001) film surface exhibits a (2 x 2) reconstruction, which is accompanied by a significant amount of Fe^{3+} in the surface region. Fe_3O_4(001) has been found to reconstruct to ($\sqrt{2}$ x $\sqrt{2}$)R45° structure. γ-Fe_2O_3(001) film surface is unreconstructed.
Order No.: JA807-043

Structural modifications of disordered mesocarbon microbeads with lower temperatures of heat treatment
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We describe the variation of structural and physical properties of mesocarbon microbeads as a function of heat treatment temperature in the range 400-1100°C. SEM studies indicated changes in the morphology of the mesocarbons with heat treatment. X-ray studies show that average crystallite size varies considerably with heat treatment. The d_{002} spacing decreases with increasing heat treatment temperatures. The electronic conductivity of the mesocarbon microbeads also increases substantially with increasing heat treatment temperature. Based on TGA and other measurements, we find that fractions burn out of these carbons in two distinct stages. The observed weight loss correlates with the structural changes observed. We suggest that these observations are consistent with two types of hydrogenated fractions present in the 'green' mesocarbons.
Order No.: JA807-044

Structural characterization of carbons obtained from polyparaphenylenes prepared by the Kovacic and Yamamoto methods
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The structure of polyparaphenylene (PPP)-based carbons prepared by the Kovacic and Yamamoto methods heat treated at 650°C~3000°C have been characterized comparatively by using x-ray diffraction, SEM, TEM and Raman spectroscopy. Both kinds of carbons indicate not typical but poor graphitizing behavior, especially for the case of PPP Yamamoto samples, and much less for PPP Kovacic samples, by heat treatment up to 3000°C. The Kovacic-based samples heat-treated at 600°C~2400°C have a more developed layer structure than that of Yamamoto-based samples. In contrast, for HTT's more than about 2400°C, PPP Yamamoto-based carbons exhibit a more developed crystallite structure than PPP Kovacic-based carbons. At a given HTT, PPP Kovacic-based carbons have a much more quinoid-like structure and graphene type structure than PPP Yamamoto-based carbons, as indicated by the carbon yield and Raman scattering measurements. It is suggested that the detailed structure of the starting polymers influences the texture as well as the microstructure of resultant carbons even though both are obtained from the same kinds of precursors. These microstructures also largely influence the anode performance when these carbons are used in Li ion batteries.
Order No.: JA807-045