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ABSTRACTS

COMMUNICATIONS

The Influence of Pt and $SrTiO_3$ Interlayers on the Microstructure of $PbTiO_3$ Thin Films Deposited by Laser Ablation on (001)MgO

S. Stemmer*, S.K. Streiffer*, W-Y. Hsu+, F. Ernst*, R. Raj+, M. Rühle*
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We have used conventional and high-resolution transmission electron microscopy to investigate the microstructure of epitaxial, ferroelectric $PbTiO_3$ films grown by pulsed laser ablation on (001)MgO single crystals, and on MgO covered with epitaxial Pt or $SrTiO_3$. Pronounced variations are found in the widths and lengths of a-axis-oriented domains in these films, although the volume fraction of a-axis-oriented material varies only weakly for the different types of samples. In addition, the films deposited onto Pt-coated MgO have a larger grain size than those deposited onto bare MgO or $SrTiO_3$/MgO. Possible reasons for the variations in the distribution of a-axis-oriented material in these samples include differences in the elastic properties and electrical conductivities of the different substrate combinations.

Order No.: JA504-001

Magnesium Reduction of WO_3 in a Self-Propagating High-Temperature Synthesis (SHS) Process

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High-purity tungsten was prepared by the self-propagating high-temperature synthesis (SHS) process from a mixture of WO_3 and Mg. The MgO in the product was leached with an HCl solution. The complete reduction of WO_3 required a 33% excess of magnesium over the stoichiometric molar ratio Mg/WO_3 of 3. The product tungsten had a purity of 99.980% which was higher than that of the reactant WO_3. This is because the impurities were either volatized at the high temperatures generated during the rapid exothermic reaction or dissolved into the HCl solution during leaching.

Order No.: JA504-002

ARTICLES

A Study of the Resputtering Effect during rf-Sputter-Deposition of YBCO Films

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(Royal Institute of Technology)

We propose an angular redistribution model to understand the negative ions resputtering effect in sputter depositing $YBa_2Cu_3O_{7-x}$ (YBCO) films. On the basis of this model, the negative oxygen ions resputtering effect has been greatly minimized by introducing a copper mask between the substrate and the target to block energetic oxygen particles directly bombarding the growing film. Thus, YBCO films with almost exact stoichiometric composition and zero resistance critical temperatures as high as 90 K are obtained under oxygen partial pressure as low as 3 mTorr in a regime well beyond that proposed by R.H. Hammond and R. Bormann. Preliminary results of a modified masking and shielding technique to eliminate the resputtering effect and fabricate large area (>1 in. x 1 in.) YBCO superconducting films with high uniformity is also presented.

Order No.: JA504-003

Microstructures of a-Axis Oriented YBCO Films Made by Hybrid Plasma Sputtering

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Microstructures of a-axis oriented $YBa_2Cu_3O_{7-x}$ films made by newly developed dc-100MHz hybrid plasma sputtering were investigated using transmission electron microscopy (TEM). The films deposited on (110) $NdGaO_3$ and (100) $SrTiO_3$ substrates were found to grow in a perfect epitaxial fashion and have clear interface. The plan view of the TEM image showed that both films were comprised of two kinds of grains having the c-axis aligning along two perpendicular directions in the plane with equal probability. The structures of the grain boundary, however, were found to be very different for the two films from the plan views. The film on $NdGaO_3$ showed a lot of twist boundaries, while the film on $SrTiO_3$ consisted of many symmetrical tilt boundaries and basal-plane-faced tilt boundaries. The type of grain boundary is determined by the anisotropic growth rates of the film between c-direction and a-b direction.

Order No.: JA504-004

$YBa_2Cu_3O_{7-x}$ Films on Off-Axis Y-ZrO_2 Substrates Using Y-ZrO_2 or Y_2O_3 Barrier Layers

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$YBa_2Cu_3O_{7-x}$ (YBCO) and barrier layer films were deposited on single crystal $(Y_2O_3)_{0.09}(ZrO_2)_{0.91}$ substrates cut between 3.6 and 35.7 degrees off-axis from the (001) planes. The barrier layers were $(Y_2O_3)_{0.065}$(Y-ZrO_2)$_{0.935}$(Y-ZrO_2), Y_2O_3, or multilayered structures of Y-ZrO_2 and Y_2O_3. X-ray diffraction showed that the Y-ZrO_2 and Y_2O_3 barrier layers generally grew epitaxially on the off-axis substrates, with the (001) barrier layer film planes being parallel to those of the substrate, and the <100> directions being parallel. YBCO films deposited on Y_2O_3 barrier layers also showed epitaxy with the YBCO (001) planes

being nearly parallel to the substrate (001) planes even for miscuts up to 35.7°. In contrast, the (001) planes of YBCO films deposited on Y-ZrO_2 barrier layers were almost parallel to the substrate surface, not the (001) substrate planes. However, YBCO films on Y-ZrO_2 films maintained particular in-plane epitaxial orientations with respect to the substrate. The YBCO full-width half-maximum (FWHM) x-ray peaks were slightly narrower (0.8°) on Y_2O_3 barrier layers than on Y-ZrO_2 layers (1.3°). The electrical resistivity versus temperature behavior of the YBCO/Y_2O_3 films were consistent with increased grain boundary scattering as the degree of substrate miscut increased, whereas YBCO/Y-ZrO_2 films' resistivities showed less sensitivity to substrate miscut, consistent with the loss of epitaxy.

Order No.: JA504-005

STM/STS Investigation of the Structural Modulation on the Surface of Cleaved $Bi_2Sr_2CaCu_2O_y$ Single Crystal

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The surface of cleaved $Bi_2Sr_2CaCu_2O_y$ (Bi2212) single crystals has been studied by means of scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) at room temperature in ultra-high vacuum. We obtain atomic images of the BiO surface using logarithmic current mode and conventional mode. It is demonstrated that the Bi atoms in the BiO plane are not missing. Some Bi atoms are depressed down below the BiO surface. STS obtained at different places of the surface shows more or less the same feature, indicating that local electronic density of state does not change much due to the depression or the well-known structural modulation. The possible origins of the variation in the period of the structural modulation in the BiO plane of cleaved Bi2212 single crystals extracted from STM images are also studied.

Order No.: JA504-006

The Microstructural Evolution of Silver-Containing Spray Deposited 1223 Tl-Ca-Ba-Cu Oxide Superconductor

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This paper reports a study of the microstructural evolution of Ag-containing 1223 Tl-Ca-Ba-Cu oxide superconductors in spray deposited films. The films were formed by spray depositing nitrates of Ca, Ba, Cu, and Ag onto a polycrystalline yttria-stabilized zirconia substrate. These deposits were then converted to a mixture of oxides (calcia, calcium-copper oxide, and barium cuprate) and metallic silver by heating in oxygen. When thallium oxide vapor was passed over the film, the thallium was incorporated into the film and the 1223 phase was formed. The evidence strongly suggests that the development of the 1223 superconductor involves the formation of a liquid phase. Our analysis suggests that the initial phase to form a liquid is CaO that contains thallium, barium, copper, and silver. Once this initial liquid is formed, it incorporates more thallium which, in turn, allows it to dissolve other types of oxides present in the film. In this way the liquid spreads across the surface. The equilibrium 1223 phase precipitates from it.

Order No.: JA504-007

Microstructural Study of GaAs Epitaxial Layers on Ge(100) Substrates

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GaAs layers grown by close-spaced vapor transport on (100) Ge substrates have been investigated as a function of the experimental growth conditions. The effects on the microstructure of the surface preparation, substrate misorientation and annealing were studied using optical microscopy and transmission electron microscopy. Microtwins and threading dislocations are suppressed by oxide desorption before deposition. Single domain GaAs layers have been obtained using a 50 nm thick double domain buffer layer on an annealed Ge substrate misoriented 3° towards [0$\bar{1}$1]. The mismatch strain is mainly accommodated by dissociated 60° dislocations. These misfit dislocations extend along the interface by the glide of the threading dislocations inherited from the substrate but strong interaction with antiphase boundaries (APBs) prevent them from reaching the interface. These results are discussed and compared with previous reports of GaAs growth on Ge(100).

Order No.: JA504-008

Size Dependent Hardness of Silver Single Crystals

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The hardness of thick, high-purity, epitaxially grown silver on sodium chloride is found to be dependent on the size of the indentation for sizes below ~10 microns. The measurement of the size effect has been made in two ways. In one, the hardness has been calculated from the load-displacement curve obtained from an instrumented micro-hardness testing machine and assuming a geometric self-similarity in the indentor shape. In the other measurement, the hardness was obtained from the load exerted by the micro-hardness tester divided by the indentation impression area as measured by atomic force microscopy. The observed variation in micro-hardness with indentation size is consistent with a simplified strain gradient plasticity model in which the densities of the geometrically necessary and statistically stored dislocations are fitting parameters. An equally good fit can also be made with a simple geometric scaling relationship. Transmission electron microscopy observations of a thin (~50 nm) epitaxial gold film embedded in the silver layers revealed that the deformation was primarily restricted to the sharp edges of the indentation. In addition, deformation twinning within the indentation impression was observed on the {111} planes.

Order No.: JA504-009

High-Temperature Deformation Behavior of Titanium Samples with Superplastic Layer

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The progress of high-temperature deformation in samples of two commercial titanium alloys with superplastic (SP) structure, non-SP structure, and with SP layer sandwiched between the non-SP regions has been studied on the scale of the entire deformed volume and on the scale of grain groups. The results of mechanical behavior showed that samples with SP layer exhibit higher stress levels than those with completely SP structure, and higher strain rate sensitivity than those with completely non-SP structure. Samples with SP layer demonstrate more pronounced decrease in strain rate sensitivity with the increase of strain than samples with completely SP structure. Deformation in the SP layer proceeds as grain shear in a layer-by-layer manner. The deformation of SP layer through the operation of cooperative grain boundary sliding, i.e., sliding of grain groups as an entity along certain grain boundary surfaces, provides the main contribution to the total strain.

Order No.: JA504-010

Homogeneous Precipitation of Doped Zinc Sulfide Nanocrystals for Photonic Applications

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A process was developed to prepare nanocrystalline and quantum confined particles of manganese doped zinc sulfide. By the reaction of diethylzinc with solubilized hydrogen sulfide, particle sizes of 30–36 Å were achieved by control of reactant concentration, and size appeared to vary with the thermodynamic considerations indicative of homogeneous precipitation. Manganese doping required the development of an *in-situ* chemical reaction compatible with the homogeneous precipitation reaction. To that end, ethylmagnesium chloride was reacted with manganese chloride to form the metastable diethylmanganese which

acted as the dopant source. Quantum confinement of the particles was accomplished by using methacrylic acid and poly(methyl methacrylate) polymer of low molecular weights. These surfactants were transparent to the ultraviolet wavelengths of light which allowed luminescent excitation of the material and provided surface passivation which enhanced phosphor brightness. The surfactant adsorption and effect of ultraviolet curing of the surfactant on the luminescent efficiency of the doped nanocrystals was investigated by infrared spectroscopy. These results indicate that the chemisorption of the surfactants to the nanoparticle surface and oxidation followed by crosslinking during curing are responsible for the improvement in luminescent efficiency.
Order No.: JA504-011

Thermal Evaluation of Zone-Melting Recrystallization of Thin-Film Structures over a Wide Range of Melting Points
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Zone-melting recrystallization (ZMR) is a lateral epitaxy technique used to recrystallize polycrystalline thin films on substrates. Large-area multilayer structures of thin films processed with ZMR are usable in microelectronics applications. During the processing, slight variations in thermal gradients can lead to different crystalline qualities. Thus, processing uniformity over the wafer is strongly affected by the sensitivity of both the melt width and the solid/liquid interface to changes in the thermal environment. Processing control must either be set initially in a stable operating range or adjusted dynamically to variations in processing. Numerical simulations of the ZMR process were conducted to evaluate the sensitivity of the process over a wide range of temperatures and materials. Results indicate that materials with melting points below 900°C are very sensitive to temperature disturbances. This is due to the increased influence of conductive heating and decreased influence of radiative heating. The increased reflectivity during phase change curbs the amount of absorbed radiation. As the absorbed radiation becomes less influential the sensitivity of the slush width decreases. Conductive effects should be considered when processing materials with melting points at or below 900°C.
Order No.: JA504-012

Optical and Structural Properties of Semi-Insulating Polycrystalline Silicon Thin Films
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Optical properties of semi-insulating polycrystalline silicon (SIPOS) thin films containing 30 at.% oxygen atoms are investigated in the near ultra-violet, visible, and infrared region to improve the knowledge on the structure and chemical bonding of these mixtures.

An effective medium approximation model is used for a microscopic investigation of the oxide species involved as a function of the annealing temperature (600–1200°C). The results are compared with other optical spectroscopies (infrared and Raman) and with transmission electron microscopy to give a selected picture of the pure and oxide components.
Order No.: JA504-013

Formation and Microstructural Development of $TiSi_2$ in (111)Si by Ti Ion Implantation and Annealing at 950°C
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A transmission electron microscopy study of the microstructural development for (111)Si wafers implanted with Ti ions and annealed subsequently at 950°C is presented. The as-implanted wafers have a Ti-rich amorphous layer at the surface with embedded silicides which correspond to a crystalline form of $TiSi_2$ that has not been reported previously. Below this lies a Ti-lean crystalline layer with extensive radiation damage. The annealed layers have large incoherent islands of C54 $TiSi_2$ with a layered microstructure in the Si between them consisting of twins, then topotaxial silicides, then dislocation loops. It is proposed that this microstructure arises from silicide growth prior to epitaxial regrowth whereas for the continuous epitaxial films observed previously at lower annealing temperatures, epitaxial regrowth precedes silicide development.
Order No.: JA504-014

Hyperfine Structure Changes in Iron-Base Amorphous Alloys Produced by High Current Density Electropulsing
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The effects of high current density electropulsing on the hyperfine structure of amorphous alloys $Fe_{73}Si_{9.5}B_{17.5}$,$Fe_{75}Si_{10}B_{15}$ and $Fe_{79}Si_7B_{14}$ were investigated by Mössbauer spectroscopy. Electropulsing influenced the microstructure at a temperature well below the bulk crystallization temperature. In the alloy having least boron (or highest concentration of Fe) α-Fe particles ~3 nm in size precipitated from the amorphous matrix giving a change in internal magnetic field.
Order No.: JA504-015

Characterization of W/Si Multilayers by Ultra-Soft X-ray Emission Spectroscopy
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The $SiL_{2,3}$ emission spectra of amorphous W/Si multilayers were measured. For the as-deposited samples the $SiL_{2,3}$ emission spectra have been found to be very close to that of amorphous Si. The formation of WSi_2-phase during annealing of W/Si multilayers at the temperature ≥ 500°C was detected. From the $SiL_{2,3}$ emission spectra of as-deposited and annealed samples the amount of WSi_2 phase was estimated. It is shown that this technique can be used for quantitative estimation of the ratio of amorphous Si and WSi_2 phases in W/Si multilayers.
Order No.: JA504-016

Mullite Formation from Non-Stoichiometric Slow Hydrolyzed Single Phase Gels
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A comparative dynamic x-ray diffraction (DXRD) and differential thermal analysis (DTA) study was performed in the investigation of mullite and spinel formation from slowly hydrolyzed single phase gels with Al/Si ratios ranging from 1/1 to 14/1. Both metastable tetragonal mullite and spinel were observed to form at temperatures <1000°C in the gels with Al/Si ratios <8/1 and mullite transformed to orthorhombic structure at ~1250°C. However, at higher Al/Si ratios, spinel was the only crystalline phase detected at <1000°C and orthorhombic mullite formed directly at temperatures >1250°C. As the Al/Si ratio increases, both the tetragonal mullite and spinel formation temperatures decrease while the orthorhombic mullite formation temperature increases. Based on the Al/Si composition where the formation extents of tetragonal mullite and spinel were maximum, their compositions are estimated to be $2Al_2O_3{\cdot}SiO_2$ and $6Al_2O_3{\cdot}SiO_2$, respectively.
Order No.: JA504-017

Low Temperature Synthesis and Some Physical Properties of Barium Substituted Lanthanum Manganite ($La_{1-x}Ba_xMnO_3$)
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Barium substituted lanthanum manganite ($La_{1-x}Ba_xMnO_3$) powders have been synthesized by a novel autoignition technique and the effect of barium content on the autoignition characteristics, stability of the compound and the powder characteristics have been investigated. X-ray examinations show that the material exists as a single phase having perovskite structure up to 40 at.% substitution of Ba for La, beyond which mixed phases of $LaMnO_3$ and $BaMnO_3$ are formed at least up to

the highest limit of substitution (50 at.%) and calcination temperature (1350°C) investigated. Electrical conductivity and thermal expansion behavior of the material have been studied for plausible use as cathode material in solid oxide fuel cell.

Order No.: JA504-018

Polarization Switching Mechanisms and Electromechanical Properties of La-Modified Lead Zirconate Titanate Ceramics

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The electromechanical properties of $(Pb_{1-x}La_x)(Zr_yTi_{1-y})O_3$ (PLZT x/y/(1-y)) have been investigated in the compositional range $0<x<0.10$ for y=0.65 (rhombohedral PLZT) and $0<x<0.18$ for y=0.40 (tetragonal PLZT). Both field-induced strains (ε-E) associated with polarization switching and piezoelectric responses (d_{33}) were studied. Transmission electron microscopy (TEM) and dielectric investigations were also performed. Room temperature TEM investigations revealed common trends in the domain structure with increasing La-content for both PLZT x/65/35 and x/40/60, including: a micron-sized domain structure, a subdomain tweed-like structure, and a nanopolar domain state. Changes in the field-induced strains and piezoelectric properties were then related to these microstructural trends. The dominant electromechanical coupling mechanism in the micron-sized domain state was found to be piezoelectricity. However, an electrostrictive coupling became apparent with the appearance of the subdomain tweed-like structures, and became stronger in the nanopolar domain state. It is believed that polarization switching can occur through 70° or 110° domains, the subdomain tweed-like structure, or nanopolar domains depending on La-content.

Order No.: JA504-019

Dielectric and Electrostrictive Properties of $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$-$xPb(Mn_{2/3}W_{1/3})O_3$ Ceramics

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The dielectric and electrostrictive properties of (1-x)PMN-xPMW ($x\leq0.2$) using chloride salts were investigated as a function of x. When the PMN-PMW powders were calcined at 700°C for 1 h, the perovskite phase formed was 92–97% at any given PMW composition ($x\leq0.2$). With the increase of PMW content up to 0.2, the relative density of the specimens increased slightly, and the electrostrictive coefficient, Q_{11} of the 0.8PMN–0.2PMW specimen increased about $6x10^{-2}$ m^4/C^2. However, the dielectric constant and electrostrictive strain of the specimens decreased despite the improved sinterability.

Order No.: JA504-020

Combustion Synthesis and Characterization of $BaTiO_3$

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An important, somewhat novel procedure for the bulk synthesis of finely divided crystalline $BaTiO_3$ powder has been studied and it is applicable to the synthesis of other compounds in the $BaO-TiO_2$ system as well. An aqueous solution of $Ba(NO_3)_2$, $TiO(NO_3)_2$ and alanine is spray dried. A combustion reaction occurs when heating the product to 300°C. The reaction converts the spray dried mixture to $BaTiO_3$. This $BaTiO_3$ powder and its sinterability have been characterized by thermal analysis, XRD, SEM, dielectric and particle size measurements. The powder resulting from the thermal runaway reaction is finely divided and sinters more readily than the conventionally prepared high purity $BaTiO_3$.

Order No.: JA504-021

Role of Excess PbO on the Microstructure and Dielectric Properties of Lead Magnesium Niobate

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Stoichiometric and 2 wt.% excess lead oxide containing lead magnesium niobate (PMN) ceramics have been prepared by partial oxalate route. Dielectric measurements with frequency showed a typical relaxor behavior for stoichiometric PMN, while PMN with excess PbO shows a scatter in the dielectric curves at all temperatures above T_c. Under the same processing conditions the dielectric constant (K_{max}) decreases drastically from 16300 to 9500 at 1 KHz for PMN without and with excess PbO, respectively. Microstructure studies revealed a second phase (unreacted PbO) segregated in the grain boundaries for excess PbO samples. A careful analysis of the data on dielectric properties and phases present, coupled with microstructural detail, indicate that second phase in the grain boundary has a pronounced effect on the dielectric properties and not the pyrochlore phase.

Order No.: JA504-022

A Micromechanistic Model of Microstructure Development during the Combustion Synthesis Process

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The influence of the key nucleation and grain growth parameters on (i) the evolution of the microstructure of the product phase (on a microscopic level), and (ii) the combustion synthesis process (on a macroscopic level) were investigated for the combustion synthesis process in the Nb-C system. This work is an integral part of the continuing effort[1–3] to develop a more complete theoretical model for combustion synthesis processes in general. In particular, the nucleation and growth of the NbC(s) product phase from the supersaturated liquid Nb/C mixture that appears briefly during the combustion synthesis process was treated in a greater detail by using a decidedly more sophisticated treatment of the nucleation and growth process (as developed in the field of rapid solidification and welding). It was shown that the microstructure of the NbC(s) product phase, including the evolution of the grain size and the size distribution, and the development of the grain's morphology, as well as the combustion wave velocity, are significantly influenced by the total number density of the nucleation sites, n_{max}, that are present in the system. The grain size distribution was shown to possess a monosize distribution, since during the combustion synthesis process the rate of increase of the degree of local undercooling was very high—so that the nucleation process took place (locally) during a very brief period of time. This work provides a sound basis for developing a better control of the microstructure, and for a better understanding and interpretation of the results of related experimental studies.

Order No.: JA504-023

Ion-Beam Induced Disordering and Onset of Amorphization in Spinel by Defect Accumulation

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Ion-irradiation induces amorphization in many intermetallics and ceramics, but spinel ($MgAl_2O_4$) is considered a "radiation resistant" ceramic. Spinel was irradiated with 1.5 MeV Kr^+ at 20 K and observed *in-situ* by transmission electron microscopy (TEM). The spinel remained crystalline to a high dose of $1x10^{16}$ ions/cm^2, without any evidence of amorphization. Another spinel was pre-implanted with Ne (400 keV and 50 keV). The microstructure revealed a still crystalline material with 8 nm interstitial loops. After irradiation with 1.5 MeV Kr^+ (20 K), amorphization, a result of cation disordering, initiated at a dose of $1.7x10^{15}$ ions/cm^2. At a dose of $1x10^{16}$ ions/cm^2, the spinel was partially amorphous and the remaining crystalline domains disordered. These results show that spinel can be disordered and that amorphization can be triggered by the introduction of stable defects, followed by ion irradiation at low temperature.

Order No.: JA504-024

Constrained-Film Sintering of a Gold Circuit Paste

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We studied the constrained-film sintering of a gold circuit paste used in microelectronic packaging applications. Optical techniques were developed to determine the shrinkage profiles of constrained and free films and stresses generated during sintering in the constrained

films. Constrained films approximately 60 μm thick were made by multiple screen-printing of the gold paste on rigid alumina substrates, while the free films were obtained by peeling off portions of the gold films from the substrate after binder burn-out. Constrained films for stress measurement were made by multiple screen-printing on an oxidized 25 μm thick silicon substrate. Sintering runs were done in a hot stage at temperatures between 650°C and 900°C. The densification rates were much lower in the constrained films than those in the free films. The in-plane tensile stresses in the constrained films, determined by wafer curvature measurement, rose rapidly to a maximum level of 510 kPa during the initial stage of sintering and then gradually decreased. The reduction in the sintering potential due to the hydrostatic stress is not large enough to completely account for the retarded densification in constrained films. SEM micrographs of the film microstructures after sintering showed no significant difference in grain growth kinetics between the constrained and free films. However, the activation energy for densification was found to be very different between the two types of films, 90.1±4.3 kJ/mole for the free film and 188.8±6.7 kJ/mole for the constrained film. We suggest that the retarded densification kinetics in the constrained gold films is due to (1) the reduction in the sintering potential by the hydrostatic stress, and (2) a change in the dominant sintering mechanism from grain-boundary diffusion in the free films to lattice diffusion in the constrained films.

Order No.: JA504-025

Microstructure of TiN Films and Interfaces Formed by Ion Beam Enhanced Deposition and Simple Physical Vapor Deposition

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The microstructure and composition of TiN films, formed by ion beam enhanced deposition (IBED) with different energy (40 keV and 90 keV) xenon ion bombardment and by simple physical vapor deposition (hereafter S-PVD) without any ion beam enhancement, and the interfaces between TiN films and Si substrates have been studied by cross-section view analytical electron microscopy in this work. Both the IBED TiN films prepared by Xe^+ bombardment with either 40 keV or 90 keV energy ions and the S-PVD TiN films consist of nanocrystals. The TEM observations in the S-PVD case reveal that there exists an amorphous layer and a mixed layer of TiN grains and amorphous material at the TiN/Si interface. The thicknesses of the amorphous layer and the mixed layer are about 210 nm and at least 40 nm, respectively. Upon 40 keV Xe^+ bombardment, an amorphous Si transition layer of about 50 nm thickness is found at the TiN/Si interface, and the TiN grains close to the TiN/Si interface are of weak preferred orientation. Upon 90 keV Xe^+ bombardment, there exist amorphous TiN and Si layers with a total thickness of 80 nm at the TiN/Si interface, and the TiN grains near the TiN/Si interface are of preferred orientation $[111]_{TiN}//[001]_{Si}$. The energy of xenon ion bombardment has a strong effect on the microstructural characteristics of TiN films and the interfaces between the TiN films and the Si substrates, as well as the size and the preferred orientation of TiN grains.

Order No.: JA504-026

Elimination of an Isolated Pore: Effect of Grain Size

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The effect of grain size on the elimination of an isolated pore was investigated both by the Monte Carlo simulations and by a scaling analysis. The Monte Carlo statistical mechanics model for sintering was constructed by mapping microstructures onto domains of vectors of different orientations as grains and domains of vacancies as pores. The most distinctive feature of the simulations is that we allow the vacancies to move. By incorporating the outer surfaces of the sample in the simulations, sintering takes place via vacancy diffusion from the pores to the outer sample surfaces. The simulations were performed in two dimensions. The results showed that the model is capable of displaying various sintering phenomena such as evaporation and condensation, rounding of a sharp corner, pore coalescence, thermal etching, neck formation, grain growth, and growth of large pores. For the elimination of an isolated pore, the most salient result is that the scaling law of the pore elimination time t_p with respect to the pore diameter d_p changes as pore size changes from larger than the grains to smaller than the grains. For example, in sample-size-fixed simulations, $t_p \sim d_p^3$ for $d_p < G$ and $t_p \sim d_p^2$ for $d_p > G$ with the crossover pore diameter d_c increasing linearly with G where G is the average grain diameter. For sample-size-scaled simulations, $t_p \sim d_p^4$ for $d_p < G$ and $t_p \sim d_p^3$ for $d_p > G$. That t_p has different scaling laws in different grain-size regimes is a result of grain boundaries serving as diffusion channels in a fine-grain microstructure such as those considered in the simulations. A scaling analysis is provided to explain the scaling relationships between t_p, d_p, and G obtained in the simulations. The scaling analysis also shows that these scaling relationships are independent of the dimensionality. Thus, the results of the two-dimensional simulations should also apply in three dimensions.

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AES Analysis of SiC-Whisker Surfaces and SiC-Whisker/Alumina Interfaces

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Auger electron spectroscopy (AES) has been used to examine as-received and oxidized silicon carbide whiskers and their respective whisker/matrix interfaces after fabrication into SiC-whisker-reinforced alumina composites. As-received whisker surfaces exhibited a 2–3 nm-thick near-surface region that was C-rich. Oxygen was detected at the outer surface, but diminished to near zero within 25 nm of the surface. Oxidized whiskers had 60 nm-thick SiO_2 surface layers, which was in agreement with the transmission electron microscopy observations. The whisker/matrix interfaces in both composites consisted of thin (<0.5 nm) layers of a C-Si-O noncrystalline material. The thick SiO_2 layers on the oxidized whiskers were ejected from the interfaces during hot-pressing. It was concluded that: (1) the higher toughness of the composite fabricated with as-received SiC whiskers may be related to the higher C and lower O in its SiC_W/Al_2O_3 interfaces, and (2) interface composition cannot be reliably predicted using the surface composition of free whiskers prior to fabrication.

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Structural Changes from Polyimide Films to Graphite: Part IV. Novax and PPT

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Various polyimide films (Kapton, Upilex, Novax and PPT) were carbonized and graphitized up to 3000°C. They were studied by optical and electron microscopies. All films retaining oxygen as a cross-linker over 1000°C, i.e., Kapton, Upilex and Novax, graphitize as anthracites (high rank coals) do. They get a long range statistical orientation parallel to the film plane with a nanotexture of flattened pores. Graphitization is both sudden and perfect above 2100°C when the pore walls break. Since oxygen is released at 1000°C, the film PPT behaves as a compact nonporous graphitizing carbon (orientation parallel to the film plane). Thermal graphitization is progressive and begins at a higher temperature.

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Adhesion Properties of a Structural Etch Stop Material for Use in Multilayer Electronic Wiring Structures

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A thermally stable copolymer of a polyimide and a dianiline terminated poly-dimethylsiloxane has been developed for use as a structural oxygen etch barrier material in high performance multilayer electronic wiring structures. We report on the preparation of the etch barrier material and on investigations of the etch stop and adhesion properties

of this material. Studies on the effects of adhesion-promoting plasma treatments are supported by x-ray photoelectron spectroscopy (XPS) and Rutherford backscattering spectrometry (RBS) data. Before plasma treatment, it is observed that the siloxane component segregates to the surface. After either an O_2 reactive ion etch treatment or H_2O plasma exposure, the unusual XPS charging effects are interpreted as a surface layer containing two distinct phases: the etched polyimide fraction and a partial overlayer of a carbon containing SiO_2.
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Pulsed-Laser Deposition of Polytetrafluoroethylene
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Thin films of polytetrafluoroethylene have been deposited on amorphous substrates by the pulsed-laser deposition technique. By transmission electron microscopy the polymer films were shown to consist of both amorphous and crystalline components. The data for the crystalline component is consistent with it being highly ordered with the long helical molecular chains aligned parallel to the film-substrate interface plane. The fraction of crystalline material in the films was found to be related to the substrate temperature during deposition with the maximum amount of crystalline material occurring when the substrate temperature was close to the melting temperature of the polymer.
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REVIEW

Compressive Behavior of Materials: Part II. High-Performance Fibers
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(Georgia Institute of Technology)

The primary focus of this paper is on the axial compression behavior of high-performance polymeric and carbon fibers. Seven test methods used for determining the compressive strength of single fibers have been reviewed. Various micro-mechanical models proposed in the literature to understand the compressive failure in single filaments and in other anisotropic systems have been discussed and analyzed. The results of various approaches to influence the compressive strength of polymeric fibers have been summarized. Possible reasons for the variation in the compressive strength of pitch and PAN based carbon fibers have also been addressed.
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