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ABSTRACTS

COMMUNICATIONS

Photochemical depassivation of hydrogenated (100) nitrogen surface of cubic boron nitride
S. Komatsu
(National Institute for Research in Inorganic Materials)

The passivation of nitrogen top-layered (100) surface of cBN by hydrogen was theoretically predicted to be related to the difficulty of chemical vapor deposition of cubic boron nitride recently. The possibility of photochemical depassivation of this surface was suggested by the anti-bonding nature of the surface H-N bonds at the lowest unoccupied molecular orbital; that was demonstrated by AM1 molecular orbital calculations using large cBN clusters such as $B_{30}N_{32}H_{64}^{(2+)}$ and $B_{30}N_{32}H_{62}(2BH_3)$.
Order No.: JA127-001

A novel method for synthesis of carbon nanotubes: Low temperature solid pyrolysis
Y.L. Li, Y.D. Yu, Y. Liang
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We report a novel method for the synthesis of carbon nanotubes: low temperature solid pyrolysis. By pyrolysis of hexamethyldisilizane-derived silicon carbonitride powders in a graphite furnace, we synthesized carbon nanotubes at 1400°C. This new method has advantages of *in-situ* growth of the carbon nanotubes, is stable in the synthesis process, and is technically simpler than conventional arc-discharge methods.
Order No.: JA127-002

Aluminothermic reaction path in the synthesis of a TiB_2-Al_2O_3 composite
V. Sundaram, K.V. Logan and R.F. Speyer
(Georgia Institute of Technology)

Differential thermal analysis, in air and argon, in concert with x-ray diffraction, was performed on 2- and 3-component mixtures of Al, B_2O_3, and TiO_2, to foster an understanding of the reaction path involved in the TiB_2-forming thermite reaction. In argon, aluminum reacted with B_2O_3 to form elemental boron, and reacted with TiO_2 to form $AlTi_3$. These two products reacted just after boron was made available at ~1060°C to form TiB_2. Formation of $Al_{18}B_4O_{33}$ by reaction between B_2O_3 reactant and Al_2O_3 product attenuated the yield of TiB_2, but facilitated its formation by extraction of Al_2O_3 reaction barriers.
Order No.: JA127-003

Thermochemistry and electrical contact properties at the interface between semiconducting $BaTiO_3$ and (Au-Ti) electrodes
D.P. Cann, C.A. Randall
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The interfacial characteristics of positive temperature coefficient of resistance (PTCR) $BaTiO_3$-electrode interfaces were studied. Sessile drop wetting experiments in combination with measurements of the contact resistance of the interface were used to establish a fundamental perspective of the electrode-ceramic interface. It was shown that the thermodynamic work of adhesion (W_{ad}), which is the sum of the strengths of chemical interactions present at the interface, can be manipulated by the addition of chemically active elements to the electrode metal which enhance adhesion. This same procedure is shown to modify the important electrical interfacial properties such as the contact resistance.
Order No.: JA127-004

Preparation of highly-oriented polycrystalline AlN thin films on glass, deposited at oblique-angle incidence
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A new method to prepare polycrystalline AlN thin films biaxially oriented on amorphous substrates has been demonstrated. The films were deposited at different angles of incidence with a RF sputtering system. **Population-1** crystallites, oriented with their c-axis pointing toward the incoming flux with random orientation in azimuthal directions, predominate at low angle of incidence (near normal). **Population-2** crystallites result from non-normal incidence and have their c-axis tilted away from the incoming flux and predominate at high, near glancing, angle of incidence. The alignment of crystallites **(population-2)** increases with angle of incidence. Crystallites align along the [11*0] channeling direction, characterized by a low sputtering yield, while misoriented crystal grains suffer a higher re-sputtering and their growth is inhibited. For films deposited at 75°, the FWHM of an x-ray Ø scan profile is 25°, indicating a high in-plane alignment.
Order No.: JA127-005

ARTICLES

Investigation of the novel charge transfer complex Cd-*TCNQ*
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A novel metal salt of *TCNQ* has been synthesized via an electrochemical process using cadmium as donor. Thin films of the same material have been obtained by evaporating under high vacuum the metal and the organic molecule. The electronic properties of a pellet of the powdered material have been investigated by means of standard UV-VIS-IR Spectroscopy, X-Ray Photoelectron Spectroscopy and Auger Electron Spectroscopy. The complex shows two absorption structures at about 3.4 eV and 1.7 eV due to the in plane intramolecular transitions and a shoulder at about 1.4 eV probably due to the bond with the metal. The infrared spectrum is dominated by a deep absorption structure distinctive of the charge transfer. The

electrical conductivity of the sample shows a semiconductor behavior in the investigated temperature range; the best fit of the transport data provides an activation energy of about 0.12 eV and shows that at low temperature the electrical conductivity is mainly due to a hopping process among differently charged sites.
Order No.: JA127-006

Strain compensation by heavy boron doping in $Si_{1-x}Ge_x$ layers grown by solid phase epitaxy
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The strain compensation produced by heavy boron doping in $Si_{1-x}Ge_x$ layers with $x = 0.21$, 0.26 and 0.34 grown by solid phase epitaxy on (001) Si wafers has been analyzed using high resolution electron microscopy, high resolution x-ray diffractometry and ion channeling. The structure of the epilayers consists of a defect-free region located next to the layer-substrate interface and a top region which contains strain-relieving defects. In the undoped samples the defect-free layers are partially relaxed and their relaxation increases as the Ge fraction increases. Substitutional boron incorporated to the SiGe lattice to levels of $2.8 \pm 0.3 \times 10^{20}$ cm^{-3} during the growth process reduces the lattice mismatch between the epilayers and the substrate. The boron-doped defect free layers are thicker than the corresponding undoped layers of the same Ge content and their strain relaxation is lower. It has been shown that it is possible to grow at least 27 nm thick defect-free and fully strained heavily boron-doped layers with $x = 0.21$ by solid phase epitaxy.
Order No.: JA127-007

The viscosity of germanium during substrate relaxation upon thermal anneal
S.E. Rosenberg, C.G. Madras, P.Y. Wong, I.N. Miaoulis
(Tufts University)

Thin-film heterostructures experience structural relaxation when subjected to postdeposition thermal heat treatment. The rate of relaxation, elastic effects, and inelastic effects on the structure's stress and deformation are determined by the materials' physical properties, in particular, the solid-phase viscosity. During relaxation, movement of defects causes an increase of viscosity with time at a constant rate as these defects are annihilated. Experimental anneals have been performed on structures with polycrystalline silicon films on (111) germanium substrates, in which the substrate relaxes during thermal annealing. A numerical analysis of the experimental results has determined values for the viscosity and viscosity rate of (111) germanium wafers. In addition, four zones of the relaxation process have been identified; and results indicate that the increasing viscosity with time has more effect at lower furnace ramp-up rates.
Order No.: JA127-008

Unusual behavior of the magnetoresistance of boron carbonitride films at low temperature
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We have performed resistivity and magnetoresistance measurements down to 0.3 K, and under fields up to 37 T, of boron carbonitride, and BC_3 films prepared by chemical vapor deposition. The turbostratic structure of the as-deposited materials favors a 2D weak localization effect which is invoked to explain the negative magnetoresistance (MR) as well as the LogT variation of the resistivity. However, at very low temperature a positive component is superimposed on the negative MR. At high fields, the total MR is positive, and almost isotropic. Usual theories are unable to account for the observed phenomenon. Increasing heat-treatments up to 1800°C increases the 2D character of the deposits, which show an increasingly negative magnetoresistance. For still higher treatments, the change of the films to a 3D graphitic-like structure leads to a vanishing of the negative magnetoresistance.
Order No.: JA127-009

Influence of Ar impurities on optical refractive index of sputter deposited a-Si films
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Amorphous Si (a-Si) films, sputter deposited under lower Ar pressure conditions, include numerous Ar atoms and exhibit high refractive indices, higher even than that of crystalline Si (c-Si), notwithstanding their lower Si densities. Such behavior in the refractive indices of the films was inconsistent with the conventional explanation considering only the density term in the Clausius-Mossoti relation. In the present study, the contribution of the polarizability changes of the films is proposed in order to account for the result in the refractive index. The molecular orbital (MO) calculations and experiments reveal that the polarizability of the a-Si film is sensitive to change in the angular distortion of the Si-Si bonds brought on by changing deposition conditions. The incorporated Ar atoms are found to cause the distortion in the Si network, leading to higher refractive indices for the less densified films.
Order No.: JA127-010

Defect annealing in ion implanted silicon carbide
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The recovery of lattice damage in ion implanted 6H-SiC single crystals by thermal annealing has been investigated in the temperature range 200-1000°C by Rutherford backscattering spectrometry - channeling and by optical measurements in the UV-visible wavelength. The damage was produced by implantation at room temperature of 60 keV N at fluences between 10^{14} and 5×10^{15} ions/cm^2. At low fluences a partially damaged layer with defects distributed over a depth comparable to the projected ion range was obtained. At higher fluences a continuous amorphous layer was formed. The defect annealing behavior depended on the initial damage morphology: an almost total defect recovery occurred in partially damaged layers with kinetics depending on the initial damage degree. In fact if the defect concentration is smaller than 20 at % the annealing rate is independent of temperature, otherwise it is higher between 300 and 500°C. Amorphous layers were stable in the investigated temperature range and no epitaxial regrowth occurred. After annealing a strong change in the optical properties of the amorphous phase was observed indicating a recovery of the electronic properties of the material, suggesting the existence of several amorphous states and the relaxation of the amorphous that evolves toward thermodynamic states characterised by lower free energy values.
Order No.: JA127-011

The reaction between a TiNi shape memory thin film and silicon
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The reaction between shape-memory TiNi thin films and silicon has been characterized by conventional, analytical and high-resolution transmission electron microscopy. A reaction layer is formed during the 525°C post-deposition crystallization anneal of the sputter-deposited TiNi, and consists of several phases: Ti_2Ni, a nickel silicide and a ternary titanium nickel silicide. The mechanism for the interlayer formation is discussed.
Order No.: JA127-012

Mathematical modelling of cement paste microstructure by mosaic pattern: Part II. Application
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A model based on mosaic pattern analysis is shown to have the potential to describe the complex shapes and spatial distribution of phases in the microstructures of multiphase materials. Several characteristics of both micrographs of portland cement pastes and images generated using the few parameters of the model are determined and, for the most part, agreement is good. The advantage is that spatial features of the microstructures can be captured by a few parameters.
Order No.: JA127-013

The effects of the atmosphere on the surface modification of alumina by pulsed-laser irradiation

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A near-surface thin layer is melted when alumina is pulsed-laser-irradiated in an Ar4%H_2 atmosphere or in air. A thin layer of amorphous phase forms when the substrates are irradiated in Ar-4%H_2 at 1 to 1.3 J/cm^2 with multiple laser pulses. Amorphous phase is also found in samples laser-irradiated in air and oxygen. After a laser pulse at an energy density of 1.6 J/cm^2 or higher the melt solidifies epitaxially from the unmelted substrate with a cellular microstructure. There is a decrease in the cooling rate of the melt as the laser energy density is increased because more heat must be dissipated. The amorphous phase forms when the heat input due to the laser pulse produces a superheated melt that cools down sufficiently fast to avoid crystallization. Very small particles of aluminum in the laser-melted and subsequently solidified layer are observed only in samples laser-irradiated in an Ar-4%H_2 atmosphere. In this reducing atmosphere, the alumina is possibly reduced to metallic aluminum which is mixed into the melt by the turbulence provoked by the laser pulses. The effects of these metallic particles on copper deposition when the irradiated substrates are immersed in an electroless bath are discussed.

Order No.: JA127-014

Characterization of nanophase titania particles synthesized using *in-situ* steric stabilization

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Ultrafine titania particles were synthesized from titanium tetraethoxide (TEOT) dissolved in ethanol. The concentration of water and of the soluble polymer hydroxypropylcellulose (HPC) were varied to control particle size. The HPC adsorbed onto the titania particles during growth, providing a steric barrier to aggregation. Electron microscopy showed that particles smaller than 70 nm were formed at high water concentrations (R > 120 where R is the molar ratio [H2O]/[TEOT]) and in the presence of HPC. The annealing-induced phase-transformation behavior of these particles (amorphous → anatase → rutile) from 100 to 1000°C was characterized by x-ray, Raman, and infrared techniques. The conversion of anatase to rutile occurred more readily for particles made at high water concentrations and with HPC. For particles formed by premixing TEOT with HPC prior to hydrolysis at R = 155, an 800°C anneal yielded a rutile fraction exceeding 95%; particles made at R = 5.5 with no HPC showed negligible conversion at this temperature.

Order No.: JA127-015

Radiation-induced phase transformations in $MgAl_2O_4$ spinel

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Ion-irradiation was observed to transform $MgAl_2O_4$ spinel first to a metastable crystalline phase and then to an amorphous phase at cryogenic temperatures. Elastic stiffening of 15% occurred upon formation of the metastable crystalline phase. A second transformation from the metastable crystalline spinel to an amorphous state was accompanied by elastic softening of 25% relative to unirradiated spinel. This phase transformation behavior in spinel appears to be different from that in intermetallic compounds where only elastic softening associated with radiation damage accumulation is observed. A two-stage radiation damage model is proposed to explain the observed phase transformations.

Order No.: JA127-016

On the role of deformation twinning in domain reorganization and grain reorientation in ferroelastic crystals

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The response of ferroelastic crystals on an applied stress is considered. It is distinguished between the reorganization of the domain structure within a grain at low stress and the reorientation of whole grains at high stress. The mechanisms are modeled in the framework of defect theory, i.e. by twinning dislocations and deformation twinning. The reorganization is controlled by the motion of preexisting twinning dislocations. Since the Peierls stress of the twinning dislocations is very small, domain reorganization occurs under a very small load. The process of grain reorientation involves the nucleation of dislocations and therefore, it requires a much higher stress. This concept is confirmed by comparison with experiments.

Order No.: JA127-017

The effect of ferroelastic coupling in controlling the abnormal aging behavior in lead magnesium niobate-lead titanate relaxor ferroelectrics

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The abnormal aging behavior, i.e., severe aging in the electric field induced piezoelectric coefficient while very weak dielectric aging, observed in the relaxer ferroelectric lead magnesium niobate-lead titanate (PMN-PT) ceramics under a DC electric bias field can be significantly reduced by hot isostatic pressing (HIP) treatment on pre-sintered samples. The aging can also be reduced by doping suitable amounts of either La (donor) or Mn (acceptor). We suggest that the reduction in the aging is due to the introduction of additional random fields into the material which reduces the probability of the growth of micro-polar regions into metastable and/or stable macro-polar domains. The abnormal aging behavior and the effectiveness of HIP in reducing it indicate the importance of the elastic energy in controlling the aging and relaxor behavior in PMN-PT relaxor ferroelectrics.

Order No.: JA127-018

Liquid-exchange processing and properties of SiC-Al composites

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In this paper we demonstrate a novel liquid-exchange process to replace a secondary silicon phase in reaction-bonded siliconized silicon carbides (RBSCs) with a ductile metal reinforcement phase. When RBSC is exchanged with pure Al or Al-Si liquid, secondary phase silicon is dissolved and is substituted by Al or Al-Si alloy. The resulting composites show improvements in fracture toughness (single-edge precracked beam technique), with K_{IC} value up to 8.6 MPa·m$^{1/2}$, compared to 3-4 MPa·m$^{1/2}$ in otherwise similar siliconized silicon carbide. Increased fracture strength (four point flexure) was also observed after the liquid exchange process. The processing furthermore allows the coefficient of thermal expansion to be adjusted, and the thermal conductivity increased, for electronic packaging applications.

Order No.: JA127-019

High resolution electron microscopy observation of interfacial structures in NiAl matrix *in-situ* composites reinforced by TiC particulates

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The structures of interfaces in NiAl-matrix *in-situ* composites reinforced by TiC particulates were studied by means of high-resolution electron microscopy (HREM). No consistent orientation relationship between TiC particles and the NiAl matrix was found. In most cases, TiC particles bonded well to the NiAl matrix free from any interfacial phases. However, in some cases, an interfacial amorphous layer with a thickness of about 3nm was found. The annealed NiAl-TiC composite showed a good chemical compatibility between the TiC particles and the NiAl matrix, though, some interfacial layers between TiC and NiAl, which were determined to be C-deficient TiC, were found. NiAl precipitates were observed in the TiC particles of the annealed specimens.

Order No.: JA127-020

Development of flat, smooth (100) faceted diamond thin films using microwave plasma chemical vapor deposition

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A novel approach has been used to develop (100) faceted diamond films with flat, smooth surfaces. A morphological study of the early stages of growth behavior of (100) homoepitaxial films versus process temperature and methane percentage was carried out using atomic force microscopy. The results showed that spiral growth features and penetration twin density were dominant for growth conditions not well suited for (100) growth. Optimized process parameters were found that yielded high quality

(100) epitaxial films. Growth was found to proceed via a step mechanism consistent with ledge growth on (2x1) reconstructed (100) diamond surfaces. These optimized conditions were then applied to growth of polycrystalline diamond on pretreated silicon substrates. A unique octahedral faceted film resulted indicating strong preference for growth in the <100> direction. Scanning electron microscopy, x-ray diffraction and Raman spectroscopy were used to assess film morphology, internal fiber texture and carbon phase respectively. A second stage growth step was used to flatten the surface topography to achieve the desired (100) flat tile-like morphology. This smooth (100) surface exhibited enhanced tribological performance compared to a typical randomly textured diamond film.

Order No.: JA127-021

Microstructure evolution in amorphous Ge/Si multilayers grown by magnetron sputter deposition

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Microstructure evolution in amorphous Ge/Si multilayers grown by dual-target dc magnetron sputtering was investigated by cross-sectional transmission electron microscopy, x-ray diffraction, and growth simulations. In films grown under low intensity ion-irradiation conditions, the structure is columnar with low-density regions along column boundaries where layer intermixing was observed. By increasing the ion-irradiation intensity (controlled by an applied negative substrate-bias), structures with smooth and well-defined layers could be grown. This was achieved at bias voltages between 80 and 140 V depending on the sputtering gas pressure. As the ion-irradiation intensity is further increased, ion induced intermixing degrades the layer interfaces and finally an amorphous $Si_{1-x}Ge_x$ alloy forms. The combination of x-ray diffraction measurements and reflectivity calculations reveals an asymmetry between the Ge/Si and Si/Ge interface widths due, primarily, to a corresponding asymmetry in incident particle energies during the growth of alternate layers.

Order No.: JA127-022

Electron-irradiation-induced nucleation and growth in amorphous $LaPO_4$, $ScPO_4$, and zircon

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Synthetic $LaPO_4$, $ScPO_4$, and crystalline natural zircon ($ZrSiO_4$) from Mud Tanks, Australia were irradiated by 1.5 MeV Kr+ ions until complete amorphization occurred as indicated by the absence of electron diffraction maxima. The resulting amorphous materials were subsequently irradiated by an 80 to 300 keV electron beam in the transmission electron microscope at temperatures between 130 and 800 K, and the resulting microstructural changes were monitored *in-situ*. Thermal anneals in the range of 500 to 600 K were also conducted to compare the thermally-induced microstructural development with that produced by the electron-irradiations.

Amorphous $LaPO_4$ and $ScPO_4$ annealed to form a randomly oriented polycrystalline assemblage of the same composition as the original material, but zircon recrystallized to ZrO_2 (zirconia) + amorphous SiO_2 for all beam energies and temperatures investigated. The rate of crystallization increased in the order: zircon, $ScPO_4$, $LaPO_4$. Submicrometer tracks of crystallites having a width equal to that of the electron beam could be "drawn" on the amorphous substrate. In contrast, thermal annealing resulted in epitaxial recrystallization from the thick edges of the TEM samples.

Electron-irradiation-induced nucleation and growth in these materials can be explained by a combination of radiation-enhanced diffusion as a result of ionization processes and a strong thermodynamic driving force for crystallization. The structure of the amorphous orthophosphates may be less rigid than that of their silicate analogues because of the lower coordination across the PO_4 tetrahedron, and thus a lower energy is required for reorientation and recrystallization. The more highly-constrained monazite structure-type recovers at a lower electron dose than the zircon structure-type, consistent with recent models used to predict the crystalline-to-amorphous transition as a result of ion-irradiation.

Order No.: JA127-023

Percolative composite model for prediction of the properties of *nanocrystalline materials*

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A physical percolating composite model is presented for description of the changes in the transport-type properties with grain size in nanocrystalline materials. The model is based on hierarchial percolation through the different microstructural components such as grain-boundaries, triple-lines and quadruple-nodes at grain sizes, when their respective percolation thresholds have been reached. The model yields critical grain sizes at which the properties may change significantly. These grain sizes depend on the grain boundary thickness. Master curves were calculated for the elastic modulus and compared to the experimental data from the literature. Better fit was found with the experimental data in comparison to the Hill's approximation model. The critical grain size at grain boundary percolation threshold is suggested as a criterion for definition of materials to exhibit nanocrystalline properties.

Order No.: JA127-024

Neural net formulations for organically modified, hydrophobic silica aerogel

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Organic modification of aerogel chemical formulations is known to transfer desirable hydrophobicity to lightweight solids. However, the effects of chemical modification on other material constants such as elasticity, compliance and sound dampening present a difficult optimization problem. Here a statistical treatment of a 9 variable optimization is accomplished with multiple regression and an artificial neural network (ANN). The ANN shows 95 percent prediction success for the entire data set of elasticity, compared to a multidimensional linear regression which shows a maximum correlation coefficient, R=0.782. In this case, using the Number of Categories Criterion for the standard multiple regression, traditional statistical methods can distinguish fewer than 1.83 categories (high and low elasticity) and cannot group or cluster the data to give more refined partitions. A non-linear surface requires at least 3 categories (high, low, and medium elasticities) to define its curvature. To predict best and worst gellation conditions, organic modification is most consistent with changed elasticity for sterically large groups and high hydroxyl concentrations per unit surface area. The isocontours for best silica and hydroxyl concentration have a complex saddle, the geometrical structure of which would elude a simple experimental design based on usual gradient descent methods for finding optimum.

Order No.: JA127-025

Structure and surface morphology of highly conductive RuO_2 films grown on MgO by oxygen-plasma-assisted molecular beam epitaxy

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Metallic RuO_2(110) thin films were grown by oxygen-plasma-assisted molecular beam epitaxy (MBE) on MgO(100) and (110) at 425°C. RuO_2 films on MgO(100) are epitaxial with two variants, while RuO_2 films on MgO(110) are highly oriented with the (110) face parallel to the substrate surface. The two variants in the RuO_2(110) epitaxial films resulted in a two-fold mosaic microstructure. The RuO_2(110) epitaxial films are very smooth and exhibit a low resistivity of ~36 μΩ-cm. In contrast, the RuO_2(110) textured films are very rough, and consist of small grains with a poor in-plane alignment. A slight higher resistivity (49 μΩ-cm) was found for the RuO_2(110) textured films grown on MgO(110).

Order No.: JA127-026

Development of preferred orientation in polycrystalline AlN thin films deposited by rf sputtering system at low temperature

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The development of preferred orientation in AlN thin films deposited on silica glass substrates by rf sputtering at low substrate temperature

(<150°C) has been studied. The main factors controlling the preferential orientation of the AlN thin films are the ion-bombardment energies, incidence angle of the arriving particles and deposition rate. At low pressure, a perpendicular and highly directionated energetic ion-bombardment induces an orientation of the crystallites with their c-axis perpendicular to the substrate surface. At higher pressure (>15 mTorr), a spreading in the incidence angle of the arriving particles, due to gas phase collisions, favors the formation of AlN crystals twinning. A change in the preferred orientation of the films from (0001) to (10$\bar{1}$1) for deposition rates above 1.8Å/sec is observed.

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Growth of Ti thin films on sapphire substrates

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Titanium thin films have been grown by electron-beam physical vapor deposition on the (0001) surface of sapphire (single crystal α-Al_2O_3) substrates at growth temperatures ranging from 295 to 1223 K. Single phase α-Ti films grew at all growth temperatures; even at 1223 K which is above the α-β-transition temperature of Ti. Crystal quality, as measured by the width of x-ray rocking curves, was found to improve, and the elastic strain to increase, as the growth temperature increased from 295 K to 1023 K.The epitaxial relationship between the Ti and sapphire was $(0002)_{Ti}||(0006)_{Al_2O_3}$ and $[11\bar{2}0]_{Ti}||[10\bar{1}0]_{Al_2O_3}$. The extent of interdiffusion across the Ti/Al_2O_3 interface was observed to be small (< 20 nm) at all growth temperatures.

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The influence of total pressure in the reactor and carrier gas on the chemical vapor deposition of Al from tri-isobutyl aluminum

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The influence of total pressure in the chamber and carrier gases on the chemical vapor deposition (CVD) of aluminum using tri-isobutyl aluminum were studied. The superior penetrability of CVD is expected to make it effective for aluminum deposition onto complex-shaped materials such as turbo-charger rotors, fibrous preform and multifilament. It may also be a suitable method for the development of fiber-reinforced composite materials. The apparatus was composed of a raw material gas supply system, a three-zone electric furnace, a reaction chamber, an auto pressure controller, and an exhaust system. Aluminum was deposited onto a graphite fiber in the quartz reactor. The results show that, in the diffusion rate-determining stage of aluminum thermal decomposition, the rate of deposition for aluminum shows a marked increase as the pressure increases; in contrast, in the reaction rate-determining stage, this tendency is limited. This can be explained by the fact that, as the total pressure decreases, the gas diffusion coefficient becomes larger, and there is an increase in the uniformity of film formation. On the other hand, as the carrier gas flow rate increases, the amount of raw material supplied increases; consequently, a higher rate of deposition is obtained. Moreover, in the diffusion rate-determining stage, there is a tendency for an increase in flow rate to elevate the probability of arrival of the raw material, and, in combination with high temperatures, for nucleus generation to be accelerated and the average diameter of aluminum granules to become smaller. In the reaction rate-determining stage, there appears to be hardly any dependency of granule diameter on the flow rate. When Ar or He is used as the carrier gas, under the same conditions Argon, rather than Helium, is seen to increase the rate of deposition.

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A transmission electron microscopy investigation of inverse melting in $Nb_{45}Cr_{55}$

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In inverse melting, a supersaturated crystalline phase transforms polymorphously under heat treatment to the amorphous state. Inverse melting of body-centered cubic (bcc) $Nb_{45}Cr_{55}$ is studied using transmission electron microscopy (TEM) and high resolution TEM (HRTEM). The crystalline to amorphous transformation is heterogeneous, initiating at the bcc grain boundaries. HRTEM reveals 2-3 nm domains with medium range order (MRO) in the amorphous phase. Preferred orientation of MRO domains is found on a scale corresponding to the precursor bcc grain size. Using HRTEM and calorimetry, MRO development in cosputtered $Nb_{45}Cr_{55}$ films is characterized and compared to that in the amorphous phase produced by inverse melting.

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Anodic film formation on a sputter-deposited amorphous Al-40 at% Sm alloy

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The mechanism of ionic transport in the amorphous anodic film formed on Al-40 at% Sm alloy has been examined by transmission electron microscopy and Rutherford backscattering spectroscopy. The film consists of an outer layer, about 6% of the total film thickness, composed of relatively pure Sm_2O_3 and an inner layer containing units of Al_2O_3 and Sm_2O_3 distributed homogeneously at the available resolution. The anodic film material is formed by migration of O^{2-}/OH^- ions inwards and migration of cations outwards, with a cation transport number about 0.29. The two-layered film develops as a consequence of faster migration of Sm^{3+} ions than Al^{3+} ions in the film.

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Glass transformation, heat capacity and structure of Ge_xSe_{1-x} glasses studied by modulated temperature differential scanning calorimetry experiments

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The recent novel temperature-modulated differential scanning calorimetry (MDSC™ *TA Instruments*) technique has been applied to characterize the thermal properties of Ge-Se chalcogenide glasses in the glass transition region. All samples in this work were given the same thermal history by heating to a temperature above the glass transition, equilibrating and then cooling at a rate of 5°C/min to a temperature of 20°C. The reversing and non-reversing heat flows through the glass transformation region during both heating and cooling schedules were measured and the values of the parameters T_g, ΔH, C_p and ΔC_p, which characterize the thermal events in the glass transition region, were determined.

The ability of determining the reversible heat flow in MDSC enables an accurate measurement of the true heat capacity (that normally associated with reversible heat flow), which could not be done hitherto in conventional thermal analysis where the detected heat flow is the total heat flow, the sum of reversing and nonreversing heat flows. The structurally controlled parameters T_g, ΔH, C_p and ΔC_p reveal extrema when the Ge-Se glass system reaches the average coordination number $<r> = 2.67$ at 33.3 at.% Ge which corresponds to the stoichiometric composition $GeSe_2$. We also observed extrema in the composition dependence of the above thermal parameters at 20.0 and 40.0 at.% Ge which correspond to stoichiometric compositions $GeSe_4$, Ge_2Se_3 with an average coordination numbers 2.40 and 2.80, respectively. No such clear local maxima below and above the 33.3 at.% Ge composition could be observed previously in thermal analysis. We compare our MDSC results with previously published works on glass transition in Ge-Se glasses and discuss the results in terms of recent structural models for chalcogenide glasses.

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A simple technique for measuring the adhesion of brittle films to ductile substrates with application to diamond-coated titanium

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We have developed a new technique for measuring the adhesion of brittle films to ductile substrates. In this technique, a wedge indenter is driven through the brittle coating and into the underlying substrate. Plastic deformation of the substrate causes the coating to delaminate from the

substrate. The width of the delaminated area can be directly related to the interface toughness. We present a simple analysis of this technique and apply it to diamond-coated titanium. The toughness of the diamond-titanium interface as measured with this wedge delamination technique is approximately 51±11 J/m^2. XPS measurements reveal that a reaction layer of titanium carbide forms between the diamond coating and the titanium substrate. Delamination of the coating occurs by crack propagation in this reaction layer and in the diamond film itself. These observations agree well with nanoindentation measurements performed in the delaminated area of the substrate.

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Thermal wave imaging of indented diamond coated WC

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Photothermal radiometry has been used to obtain thermal wave images in the vicinity of indentations in WC-6%Ni coated with chemical vapor deposited (CVD) diamond. Features in the magnitude and phase of the thermal signal profile are consistent with a one dimensional thermal wave theory that assumes: 1) an air gap extending well beyond the visibly observable indented region; 2) a thermal resistance interface between the diamond film and the substrate over the entire coated surface. The theory allows us to estimate the air gap thickness, which decreases as the distance from the indented region increases. Air gap variations of tens of nanometers appear to be easily detectable.

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Influence of implantation of heavy metallic ions on the mechanical properties of two polymers, polystyrene and polyethylene terephthalate

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Ion implantation of polyethylene terephthalate (PET) and polystyrene (PS) with various high energy metallic ions at 70 kV and dose of 3 x 10^{16} ions/cm^2 has been made. Measurements of the mechanical properties of the polymers before and after implantation have been made with an ultra micro-indentation system using both pointed and a small (2 μm) radius spherical tipped indenter. The surface regions were also investigated by AFM and Rutherford backscattering. Significant differences have been observed between the Ti-B dual implanted surfaces and those of the Au and W implanted surfaces. For both the PET and PS the resistance to indenter penetration at very low loads was much greater for the Ti-B dual implanted surfaces. The estimated maximum hardness and modulus of the implanted materials were 0.3 and 8 GPa for the PET material and 1.4 and 16 GPa for the PS material. The results obtained with the spherical indenter show a gradual decline in effective modulus of the surface with penetration depth, whereas the hardness or contact pressure goes through a maximum before declining asymptotically to the bulk values. The values of hardness estimated for the spherical tipped indenter are somewhat more conservative than the optimistic estimates with the Berkovich indenter. The improved increase in hardness for the Ti-B dual implanted PET material scales with the RBS measured increased depth of implantation.

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