

TABLE OF CONTENTS

SPECIAL SECTION

These two manuscripts were part of a series of papers that were featured in a special issue on Soft Solution Processing in the April 1998 Journal of Materials Research

Synthesis of functional ceramic materials from aqueous solutions

T. Yao

Metal oxide powder synthesis by emulsion combustion method

T. Tani, K. Takatori, N. Watanabe, N. Kamiya

COMMUNICATIONS

Size dependent dewetting and sideband reaction of eutectic SnPb on Au/Cu/Cr multilayered thin film

D.W. Zheng, Z.Y. Jia, C.Y. Liu, W. Wen, K.N. Tu

The correlation between τ_{e} and the tolerance factor in (Sr,Ca)(Ti,Zr)O₃ microwave dielectric ceramics

C-I. Cheon, J-S. Kim, H-G. Lee

Effects of electrochemical hydrogen charging on lead-based relaxor ferroelectric multilayer ceramic capacitors

W. Chen, L. Li, Y. Wang, Z. Gui

Synthesis of thin films of polycrystalline ferroelectric BiNbO₄ on Si by pulsed laser ablation

S. Chattopadhyay, P. Ayyub, R. Pinto, M.S. Multani

Correcting errors in the theory for mirage-effect measurements

D. Josell, E.J. Gonzalez, G.S. White

Coalesced oriented diamond films on nickel

P.C. Yang, C.A. Wolden, W. Liu, R. Schlessler, R.F. Davis, J.T. Prater, Z. Sitar

Structure of Pd-Te precipitates in a simulated high-level nuclear waste glass

L. Galois, G. Calas, G. Morin, S. Pugno, C. Fillet

A study of optical absorption and photo-induced effects in Ge-Se-Te amorphous system

A.F. Maged, A.M. Sanad, M.F. El-Fouly, G.A.M. Amin

Species resolved analysis of the expansion of hydroxyapatite laser ablation plumes

P. Serra, J.L. Morenza

ARTICLES

Crystal structure of HgTiBa₂CuO₄ studied by high-resolution electron microscopy

T. Oku, S. Nakajima

Anisotropic growth morphology and platelet formation in large grain Y-Ba-Cu-O grown by seeded peritectic solidification

W. Lo, D.A. Cardwell, J.C.L. Chow

Kinetic control of order in the layered perovskite La₂Ba₂Cu₂Ti₂O₁₁

M.R. Palacín, F. Krumeich, P. Gómez-Romero

Model for zinc oxide varistor

J.D. Santos, E. Longo, E.R. Leite, J.A. Varela

Cu films by partially ionized beam deposition for ULSI metallization

K-H. Kim, D-J. Choi, H-G. Jang, S. Han, H-J. Jung, S-K. Koh

Simulation of the temperature and current density scaling of the electromigration-limited reliability of near-bamboo interconnects

B.D. Knowlton, C.V. Thompson

Structural and electrochemical properties of Ti-Ru-Fe-O alloys prepared by high energy ball-milling

S-H. Yip, D. Guay, S. Jin, E. Ghali, A. Van Neste, R. Schulz

Mechanical alloying studies in the Γ (Fe₃Zn₁₀), and Γ_1 (Fe₃Zn₂₁) single and mixed phase compositions

A. Jordan, Z. Liu, O.N.C. Uwakweh

Nanocrystalline nickel and nickel-copper-alloys: Synthesis, characterization and thermal stability

H. Natter, M. Schmelzer, R. Hempelmann

Formation of intermetallic nanocomposites in the Ti-Al-Si system by mechanical alloying and subsequent heat-treatment

K.W. Liu, J.S. Zhang, J.G. Wang, G.L. Chen

Preparation of high solid content glass particle-polymethacrylate composite by an advance wetting method

Y.H. Wu, S. Jada, R. Xu

Pore geometry in woven fiber structures: 0°/90° plain-weave cloth lay-up preform

S-B. Lee, S.R. Stock, M.D. Butts, T.L. Starr, T.M. Breunig, J.H. Kinney

Intercalation of cyclic amines in α -hafnium bis(hydrogen phosphate) monohydrate

M. Suárez, R. Llavona, M.L. Rodríguez, L.M. Barcina, A. Anillo, J. Rodríguez

Two critical thicknesses in the preferred orientation of TiN thin film

U.C. Oh, J.H. Je, J.Y. Lee

Influence of atmosphere on crystallization of zirconia from a zirconium alkoxide

D.E. Collins, K.J. Bowman

JMR Abstracts provides a listing of preliminary titles and abstracts tentatively scheduled to appear in the corresponding issue of *Journal of Materials Research*. Copyright 1998 by the Materials Research Society. All rights reserved. Although every effort is taken to provide accurate contents here, late schedule changes in *Journal of Materials Research* may result in articles being rescheduled for later issues or in the addition of late articles to an issue that may not be shown here. The Materials Research Society regrets any inconvenience that may result from late schedule changes. ISSN: 1066-2375.

Aging of iron manganite negative temperature coefficient thermistors

T. Battault, R. Legros, A. Rousset

Ba_{0.7}Sr_{0.3}TiO₃ ferroelectric film prepared with sol-gel process and its dielectric performance in planar capacitor structure

F. Wang, A. Uusimäki, S. Leppävuori, S.F. Karmanenko, A.I. Dedyk, V.I. Sakharov, I.T. Serenkov

Preparation and characterization of ultrafine TiO₂ particles in reverse micelles by hydrolysis of titanium di-ethylhexyl sulfosuccinate

M. Lal, V. Chhabra, P. Ayyub, A. Maitra

Graded coatings by gradient temperature densification

S.K. Hur, S.H. Yoo, J.R. Groza, J.M. Doh, K. Yamazaki, K. Shoda

Thickness dependence of microstructural evolution of ZnO films deposited by r.f. magnetron sputtering

Y.E. Lee, Y.J. Kim, H.J. Kim

Study on preparing PLT(28) thin film and its E-O effect

A-L. Ding, W-G. Luo, P.S. Qiu, J.W. Feng, R.T. Zhang

The oxidative transformation of solid, barium-metal-bearing precursors into monolithic celsian with a retention of shape, dimensions, and relative density

S.M. Allameh, K.H. Sandhage

Effect of (La_{0.5}Sr_{0.5})CoO₃ and Pt intermediate layers on improving the stability of Pb_{1-x}La_xTi_{1-x/4}O₃ films

J.P. Wang, Y.C. Ling, Y.K. Tseng, K.S. Liu, I.N. Lin

Simulations of fine ceramics cascade synthesized by the self-propagating high-temperature synthesis method

B-W. Chen, C-C. Chen

Determination of indenter tip geometry and indentation contact area for depth-sensing indentation experiments

K.W. McElhane, J.J. Vlassak, W.D. Nix

Quantitative analysis of strengthening mechanisms in thin Cu films:**Effects of film thickness, grain size and passivation**

R-M. Keller, S.P. Baker, E. Arzt

Characterization of sputtered iridium dioxide thin films

P.C. Liao, W.S. Ho, Y.S. Huang, K.K. Tiong

Phase equilibria in the BaTiO₃-La₂TiO₅-TiO₂ system

S. Škapin, D. Kolar, D. Suvorov, Z. Samardžija

Thermal evolution of the microstructure of nanosized LaFeO₃ powders from the thermal decomposition of a heteronuclear complex,**La[Fe(CN)₆]-5H₂O**

E. Traversa, P. Nunziante, M. Sakamoto, Y. Sadaoka, M.C. Carotta, G. Martinelli

Ferroelectric properties of tetragonal lead barium niobate**(Pb_{1-x}Ba_xNb₂O₆) crystals near the morphotropic phase boundary**

M. Lee, R.S. Feigelson

Crystallization behavior and cordierite formation in rapidly quenched**MgAl₂O₄-SiO₂ glasses of various chemical compositions**

K. Okada, H. Kawashima, S. Hayashi, M. Sugai, K.J.D. MacKenzie

The Faraday effect in diamagnetic glasses

J. Qiu, K. Hirao

Enhancing adhesion between metals or epoxy and**polytetrafluoroethylene by ion assisted reaction**

S.K. Koh, J.W. Seok, S.C. Choi, W.K. Choi, H.J. Jung

Optical anisotropy of flexible polyimide thin films

B. Li, T. He, M. Ding, P. Zhang, F. Gao, F. Jing

Phase formation sequence induced by deposition temperatures in Nb/Si multilayers

M. Zhang, W.K. Wang

High efficiency photoresist-free lithography of UO₃ patterns from amorphous films of uranyl complexes

M. Gao, R.H. Hill

Continuous measurements of load-penetration curves with spherical micro-indenters and the estimation of mechanical properties

J. Alcalá, A.E. Giannakopoulos, S. Suresh

Valence states analysis of Ca and Si in CaSi₂ during CaSi₂-H₂O reaction

S. Abe, H. Nakayama, T. Nishino, S. Iida

ABSTRACTS

SPECIAL SECTION

Synthesis of functional ceramic materials from aqueous solutions

T. Yao

(Kyoto University)

Methods for synthesizing ceramic materials from aqueous solutions at ordinary temperature and pressure are advantageous because of the applicability to making films with wide areas and/or complicated shapes with no requirement of vacuum or high temperature, and because of lower cost. Powder of ZrO₂ or LnMeO₃ (Ln=La, Nd; Me=Cr, Mn, Fe, Co) perovskite was dissolved in hydrofluoric acid and a solution of fluoro-complex ions was obtained. Boric acid was added to the solution, the fluoride ions were consumed by the formation of BF₄⁻, and then the fluoro-complex ions were hydrolyzed to ZrO₂ or LnMeO₃ in order to increase the amount of fluoride ions. A number of synthesized particles of ZrO₂ or LnMeO₃ were observed on the substrates in scanning electron microscope images.

Order No.: JA805-001

© 1998 MRS

Metal oxide powder synthesis by emulsion combustion method

T. Tani, K. Takatori, N. Watanabe, N. Kamiya

(Toyota Central Research and Development Laboratories, Inc.)

Alumina powders were synthesized by the emulsion combustion method, using w/o (water in oil) type emulsions with different aqueous microsphere sizes. The effects of microsphere size on the size and shape of the synthesized powder were evaluated. The powders were spherical and hollow in shape with a very thin shell (from 10 to 20 nm in thickness) when synthesized from large aqueous microspheres (from 200 nm to 1 μm). The sizes and specific surface areas of the powders were consistent with those calculated. Large particles, which did not correspond to the microsphere size, were obtained from small aqueous microspheres (6 nm). The short distance (7 nm) between microspheres causes the adhesion of particles during the firing process.

Order No.: JA805-002

© 1998 MRS

COMMUNICATIONS

Size dependent dewetting and sideband reaction of eutectic SnPb on Au/Cu/Cr multilayered thin film

D.W. Zheng, Z.Y. Jia, C.Y. Liu, W. Wen, K.N. Tu
(University of California at Los Angeles)

Dewetting of eutectic SnPb on blank Au(500 Å)/Cu(1 μm)/Cr(800 Å) layered structure was found to have a solder size dependence. At 250°C, if the solder weight fell below 4 mg, dewetting occurred from the center of the solder cap; if the solder weight went beyond 6 mg, dewetting happened from the cap edge. In the latter case, a smaller cap with a higher wetting angle was formed at the center and a ring of solder was left around the edge. Large voids were left in the solder cap after dewetting in both cases. In contrast, all solder caps were found to dewet from the edge on a patterned film at 250°C if the solder ball was large enough to wet the whole film initially, irrespective of the solder size. For comparison, pure Sn, eutectic SnAg, and eutectic SnBi caps also dewetted from the edge of the Au/Cu/Cr thin film, irrespective of the solder size or whether the substrate was patterned. Since eutectic SnPb on blank Au/Cu/Cr is the only case in which a large sideband growth was found and the dewetting occurred from the center, we postulated sideband to be the main factor which controls the unusual dewetting. The link between them is discussed.

Order No.: JA805-003

© 1998 MRS

The correlation between τ_e and the tolerance factor in (Sr,Ca)(Ti,Zr)O₃ microwave dielectric ceramics

C.-I. Cheon*, J.-S. Kim*, H.-G. Lee*

(*Hoseo University, *Korea Electronics Technology Institute)

Microwave dielectric properties and the relationship between the temperature coefficient of the dielectric constant (τ_e) and the tolerance factor were investigated in (Sr_{0.2}Ca_{0.8})(Ti_{1-x}Zr_x)O₃ ceramics. The τ_e increased linearly as the tolerance factor decreased from 0.984 to 0.929 in the whole composition range of the (Sr_{0.2}Ca_{0.8})(Ti_{1-x}Zr_x)O₃ solid solution. At the composition of (Sr_{0.2}Ca_{0.8})(Ti_{0.04}Zr_{0.96})O₃, the dielectric constant was 34 and Q · f was 10938 GHz and the temperature coefficient of the resonance frequency (τ_f) is supposed to be near zero.

Order No.: JA805-004

© 1998 MRS

Effects of electrochemical hydrogen charging on lead-based relaxor ferroelectric multilayer ceramic capacitors

W. Chen, L. Li, Y. Wang, Z. Gui

(Tsinghua University)

Lead-based relaxor ferroelectric multilayer ceramic capacitors (MLCs) were placed in 0.05M NaOH solution to evolve hydrogen on their silver termination electrode by electrolysis of water. After this treatment, the MLCs became failed as their insulation resistance was greatly decreased, their dielectric loss was considerably increased, and their capacitance was obviously decreased. By annealing in air at 650 °C for 30 min. the properties of the MLCs were restored. It is proposed that electrochemically generated hydrogen atoms can diffuse into the ceramic body of MLCs and undergo reduction to it, which may be one of the reasons for the negative influence of electroplating on lead-based relaxor ferroelectric MLCs.

Order No.: JA805-005

© 1998 MRS

Synthesis of thin films of polycrystalline ferroelectric BiNbO₄ on Si by pulsed laser ablation

S. Chattopadhyay, P. Ayyub, R. Pinto, M.S. Multani

(Tata Institute of Fundamental Research)

The stibiotantalite (ABO₄) family includes a number of ferroelectrics and antiferroelectrics with excellent potential for applications. We report the deposition of phase-pure, polycrystalline thin films of BiNbO₄ on Si (100) substrates using pulsed laser ablation. The deposition conditions were optimized with respect to substrate temperature, laser parameters and the ambient oxygen pressure. The films were characterized by x-ray diffraction, energy dispersive x-ray analysis and Raman spectroscopy, while their microstructure was studied by atomic force microscopy and scanning electron microscopy. Dielectric hysteresis studies indicated that films with a thickness below ≈250 nm are ferroelectric, while thicker ones are antiferroelectric.

Order No.: JA805-006

© 1998 MRS

Correcting errors in the theory for mirage-effect measurements

D. Josell, E.J. Gonzalez, G.S. White

(National Institute of Standards and Technology)

Errors are noted in two publications on the theory for Mirage-effect measurements of the thermal diffusivity of materials. The works include theory for interpreting Mirage experiments on homogeneous samples mounted on a support with ambient (typically air) above and theory for interpreting Mirage experiments on coated substrates with ambient both above and below.

Order No.: JA805-007

© 1998 MRS

Coalesced oriented diamond films on nickel

P.C. Yang*, C.A. Wolden*, W. Liu*, R. Schlessler*, R.F. Davis*, J.T. Prater†, Z. Sitar*

(*North Carolina State University, †Army Research Office)

The growth of coalesced, highly-oriented diamond films has been achieved on nickel substrates using a multi-step process that consisted of (1) seeding the Ni surface with 0.5 μm diamond powder, (2) annealing at 1100°C in a hydrogen atmosphere, and (3) growth at 900°C in a mixture of hydrogen and 0.5% methane. Auger depth profile analysis of a sample quenched after the annealing stage showed presence of significant amounts of carbon (6 at.%) close to the substrate surface and about 3 at.% deeper in the substrate. The loss of carbon into the substrate resulted in relatively low nucleation density. The addition of methane into the gas phase during the annealing stage proved very effective in compensating for the diffusion. An addition of 0.5% methane in the gas phase produced optimum results, as the nucleation density, orientation of diamond particles, and uniformity were substantially improved. Substrates nucleated under these conditions were grown out into coalesced, 30 μm thick films. Both (100) and (111) oriented films showed a high degree of orientation and Raman spectra obtained from these orientations showed intense and narrow diamond signature peaks with FWHMs of 5 and 8 cm⁻¹, respectively.

Order No.: JA805-008

© 1998 MRS

Structure of Pd-Te precipitates in a simulated high-level nuclear waste glass

L. Galoisy*, G. Calas*, G. Morin*, S. Pugnet†, C. Fillet†

(*Universités de Paris VI et VII et ICPG, †CEA DCC/DRDD/SCD BP 171)

Structural and bonding characteristics of simplified (Pd,Te) precipitates have been determined in a simulated nuclear French glass using extended x-ray absorption fine structure (EXAFS) and x-ray diffraction. In this sample, these precipitates have a homogeneous composition, with about 10 wt.% Te. They retain a face-centered cubic structure as in pure Pd with a cell parameter which obeys Vegard's law. Pd K-edge EXAFS shows the presence of Te in the Pd coordination shell, with (Pd-Te) distances of 2.80 Å. These distances, higher by 0.05 Å than the (Pd-Pd) distances, may result in a lower packing efficiency of the CFC lattice. The comparison with the average distances derived from x-ray diffraction shows the non-metallic character of the Pd-Te bond in these precipitates. These bonding modifications may cause the limited solubility of Te in metallic Pd.

Order No.: JA805-009

© 1998 MRS

A study of optical absorption and photo-induced effects in Ge-Se-Te amorphous system

A.F. Maged*, A.M. Sanad† M.F. El-Fouly*, G.A.M. Amin*

(*National Center for Radiation Research and Technology,

†Al-Azhar University)

Optical studies have been performed on amorphous films of the system Ge₁₀Se_{90-x}Te_x where x = 20,30,40. The study revealed that as the Te content is increased, the optical band gap (E_g) was found to decrease. Photo-induced effects were studied on thin film samples irradiated with either white light or UV light. The shift in E_g due to photo-irradiation disappears upon annealing the films at a temperature below the glass transition temperature. The effect of γ-radiation up to 8kGy on the optical band gap was also investigated, and no detectable shift of the optical band gap was observed. The relationship between the optical band gap and both the average heat of atomization and the average coordination number of the compositions under investigation was studied.

Order No.: JA805-010

© 1998 MRS

Species resolved analysis of the expansion of hydroxyapatite laser ablation plumesP. Serra, J.L. Morenza
(Universitat de Barcelona)

The plume generated by ablation of hydroxyapatite targets under ArF excimer laser irradiation has been investigated by means of fast intensified CCD-imaging and optical emission spectroscopy. Results have shown that the plume splits into two plasma clouds as it expands. Time and spatial resolved spectra have revealed that under the experiment conditions emission is mostly due to calcium neutral atoms and calcium oxide molecular radicals. Imaging of the plume with the aid of bandpass filters has demonstrated that the emissive species in the larger and faster plasma cloud are calcium neutral atoms, whereas in the smaller and slower one they are calcium oxide molecular radicals.

Order No.: JA805-011

© 1998 MRS

ARTICLES**Crystal structure of HgTlBa₂CuO_x studied by high-resolution electron microscopy**T. Oku*, S. Nakajima*
(*Osaka University, +Tohoku University)

The structure model for HgTlBa₂CuO_x was proposed from high-resolution electron microscopy using residual indices. Averaged digital high-resolution image of the HgTlBa₂CuO_x showed the existence of separated Hg layers and oxygen vacancies in the double (Hg,Tl) layers. Image calculations based on the proposed structure model of HgTlBa₂CuO₅ agreed well with the observation, and showed low residual values. The present result indicates the stability of the (Hg,Tl) double layer structure would be due to the formation of oxygen vacancies in the Hg layers.

Order No.: JA805-012

© 1998 MRS

Anisotropic growth morphology and platelet formation in large grain Y-Ba-Cu-O grown by seeded peritectic solidificationW. Lo, D.A. Cardwell, J.C.L. Chow
(University of Cambridge)

The characteristic platelet-like structure of large grain superconducting Y-Ba-Cu-O fabricated using peritectic solidification techniques has been documented widely as a key microstructural feature of this material. The platelet formation mechanism is investigated via a detailed comparison of the difference in morphology of YBa₂Cu₃O_{7-δ} (123) growth fronts propagating along different lattice directions. The development of YBa₂Cu₃O_{7-δ} dendrites between the growth front and local Y₂BaCuO₅ (211) particles is observed to be a key feature of the growth mechanism along all directions. Dendrites broaden rapidly for growth fronts propagating along the c-axis due to the enhanced growth rate of Y-Ba-Cu-O in the a-b plane to yield a uniform, regular growth morphology. Dendrite broadening is inhibited for grain growth along the a-b directions, however, due to the slower growth rate along the c-axis, which yields an irregular extended growth front. Growth along the a/b-direction commonly results in the formation of regions consisting of 123 dendrites which may connect 211 particles. Continued solidification of the 123 phase in such regions results in the development of platelet structures perpendicular to the crystallographic c-axis in the YBa₂Cu₃O_{7-δ} phase matrix which may impede the flow of current through the grain in the superconducting state.

Order No.: JA805-013

© 1998 MRS

Kinetic control of order in the layered perovskite La₂Ba₂Cu₂Ti₂O₁₁M.R. Palacin, F. Krumeich, P. Gómez-Romero
(Institut de Ciència de Materials de Barcelona-CSIC)

Definitive evidence on the variable degrees of order/disorder in the layered perovskite La₂Ba₂Cu₂Ti₂O₁₁ is presented. This oxide was prepared by the ceramic method with varying reaction times and cooling rates; the average and local structures of the resulting solids were studied by x-ray diffraction, electron diffraction and transmission electron microscopy (low and high resolution). The data clearly show the presence of an a_p × a_p × 4a_p layered perovskite superstructure with a high concentration of defects in samples prepared during 48 h but with increasing degree of order for samples with longer reaction times. For samples reacted during 17 days the

order is complete and identical to that found for other related derivatives such as Ln₂Ba₂Cu₂Ti₂O₁₁, (Ln=Nd, Eu, Tb). This behavior clearly indicates the existence of a kinetic control of order in this phase.

Order No.: JA805-014

© 1998 MRS

Model for zinc oxide varistorJ.D. Santos*, E. Longo*, E.R. Leite*, J.A. Varela*
(*Universidade Federal de São Carlos, +Universidade Estadual Paulista)

Zinc oxide varistors are very complex systems and the dominant mechanism of voltage barrier formation in these systems has not been well established. Yet the MNDO quantum mechanical theoretical calculation was used in this work to determine the most probable defect type at the surface of a ZnO cluster. The proposed model represents well the semiconducting nature as well as the defects at the ZnO bulk and surface. The model also shows that the main adsorption species that provide stability at the ZnO surface are O[•], O₂⁻, and O₂.

Order No.: JA805-015

© 1998 MRS

Cu films by partially ionized beam deposition for ULSI metallizationK-H. Kim*, D-J. Choi*, H-G. Jang*, S. Han*, H-J. Jung*, S-K. Koh*
(*Korea Institute of Science and Technology, +Yonsei University)

Highly (111) oriented Cu films with a thickness around 1800 Å were prepared on Si (100) at room temperature by partially ionized beam deposition (PIBD) at pressure of $8 \times 10^{-7} - 1 \times 10^{-6}$ Torr. Effects of acceleration voltage (V_a) between 0 and 4 kV on such properties as crystallinity, surface roughness, resistivity, etc. of the films have been investigated. The Cu films deposited by PIBD had only (111) and (200) planes and the relative intensity ratio, I(111)/I(200), of the Cu films increased from 6.8 at V_a = 0 kV to 37 at V_a = 4 kV. There was no indication of impurities in the system from AES analyses. A large increase in grain size of the films occurred with V_a up to V_a = 1 kV, but little increase occurred with V_a > 1 kV. Surface roughness of the Cu films decreased with V_a, and resistivity had the same trends as that of the surface roughness. In the Cu films by PIBD, it is considered that changes of resistivity are mainly due to a surface scattering rather than a grain boundary scattering. The via holes, dimensions of which are 0.5 μm in diameter and 1.5 μm in depth, in the Cu films made at V_a = 4 kV, were completely filled without voids. Interface adhesion of the Cu film on Si(100) deposited at V_a = 3 kV was 5 times greater than that of Cu film deposited at V_a = 0 kV, as determined by a scratch test.

Order No.: JA805-016

© 1998 MRS

Simulation of the temperature and current density scaling of the electromigration-limited reliability of near-bamboo interconnectsB.D. Knowlton, C.V. Thompson
(Massachusetts Institute of Technology)

Accurate prediction of electromigration-limited interconnect reliability is an increasingly difficult and important challenge for reliability engineers. Due to continued miniaturization, interconnect linewidths have fallen below the median grain size of the films from which they are patterned. In this microstructural regime, two distinct failure mechanisms have been observed, failure limited by grain boundary diffusion and failure limited by other diffusion mechanisms. In many cases, test populations will exhibit both failure modes, leading to bimodal failure distributions. The relative prevalence of each failure mode is a complicated function of linewidth, line length, the median grain size of the parent film, and the accelerating conditions used for testing (temperature and current density). This complex behavior makes scaling reliability results from test to service conditions very difficult. A grain growth simulator has been used in conjunction with an electromigration model to determine stress evolution in near-bamboo lines with realistic microstructures. Failure times and failure time distributions have been calculated by assuming lines fail when a pre-defined critical stress is reached. Simulation results indicating the dependence of the statistics of failure on variations of test temperature and current density in interconnects with as-patterned grain structures show that traditional lifetime scaling techniques are incorrect. In addition, the practice of fitting bimodally distributed failure times to a monomodal distribution is shown to consistently yield inaccurate predictions for early failure times.

Order No.: JA805-017

© 1998 MRS

Structural and electrochemical properties of Ti-Ru-Fe-O alloys prepared by high energy ball-milling

S.-H. Yip*, D. Guay*, S. Jin†, E. Ghali†, A. Van Neste*, R. Schulz*
 (*INRS-Énergie et Matériaux, †Laval University, ‡Institut de Recherche d'Hydro-Québec)

The structural and electrochemical properties of the Ti-Ru-Fe-O system have been studied over the whole ternary metal compositional range, keeping constant the oxygen content at 30 at.%. The phase diagram was explored systematically by varying the composition of the material along one of the following axes: i) constant Ru content of 16 at.%; ii) constant Ti/Ru ratio of 2; or iii) constant Ti/Fe ratio of 1.6. For O/Ti ratios equal or below unity, the most prominent peaks observed in the x-ray diffraction patterns belong to a B2 structure. For O/Ti ratio larger than unity, stable titanium oxide phases are formed, which coexist with a cubic Fe-like or hcp-Ru-like phases depending on the Fe/Ru ratio. Powder compositions with stoichiometry close to Ti_2RuFeO_2 are of interest due to good electrocatalytic properties, long-term stability and low Ru content.

Order No.: JA805-018

© 1998 MRS

Mechanical alloying studies in the $\Gamma(Fe_3Zn_{10})$, and $\Gamma_1(Fe_5Zn_{21})$ single and mixed phase compositions

A. Jordan, Z. Liu, O.N.C. Uwakweh
 (University of Cincinnati)

Homogeneous or uniform crystalline materials are obtained following the ball milling of pure elemental powders of Fe and Zn in proportions to yield single phases $\Gamma(Fe_3Zn_{10})$, $\Gamma_1(Fe_5Zn_{21})$ and $\Gamma + \Gamma_1$ mixed phase ($Fe_{25}Zn_{75}$). DSC measurements of the as-milled materials show characteristic stages in the temperature range of 50–600°C prior to establishing stable equilibrium. The activation energies determined from kinetic analyses range from 49 to 189 kJ/mole in these materials. A characteristic stage at 130°C marking the distinct evolution of the Γ and Γ_1 phases from the intermediate or mixed phase composition is identified from XRD measurements. The identification of a unique Fe-site with a quadrupole splitting (QS) of 1.5 mm/s in corroboration with XRD shows that this stage marks the onset of an *in-situ* transformation prior to the distinct evolution of the homogeneous phases. The Mössbauer effect measurement of the as-milled materials are resolved in terms of four unique Fe-sites with QS of 1.1, 0.241, 0.073, and 0.0772 mm/s.

Order No.: JA805-019

© 1998 MRS

Nanocrystalline nickel and nickel-copper-alloys: Synthesis, characterization and thermal stability

H. Natter, M. Schmelzer, R. Hempelmann
 (Universität des Saarlandes)

Pulsed electrodeposition is a simple, yet versatile method for the production of nanostructured metals. For n-nickel we determine the influence of the physical and chemical deposition parameters on the nanostructure of the deposits and demonstrate that the grain size can be tuned to values between 13 and 93 nm, with rather narrow grain size distribution. The thermal stability of our n-nickel as studied by x-ray diffraction and differential thermal analysis exhibits no detectable grain growth up to temperatures of about 380 K and an initial square root of t behavior at 503 K followed by a regime of anomalous grain growth.

For nanocrystalline $Ni_{1-x}Cu_x$ (Monel-metal™) we demonstrate that alloy formation occurs at room temperature and that both chemical composition and grain size can be controlled by the pulse parameters and by appropriate organic additives.

Order No.: JA805-020

© 1998 MRS

Formation of intermetallic nanocomposites in the Ti-Al-Si system by mechanical alloying and subsequent heat-treatment

K.W. Liu, J.S. Zhang, J.G. Wang, G.L. Chen
 (University of Science and Technology Beijing)

Formation of nanocrystalline Al_3Ti , $TiAl$, Ti_3Al and Ti_5Si_3 composites by mechanically alloying (MA) in the Ti-Al-Si system and subsequent annealing treatment are investigated. Microstructure development was monitored by x-ray diffraction, differential thermal analysis, and transmis-

sion electron microscopy. An amorphous phase could be generated through milling for 100 h. The results of annealing at different temperatures on this amorphous phase show that the formation of titanium aluminides (Al_3Ti , $TiAl$, and Ti_3Al , according to the initial relative amount of Ti and Al), and Ti_5Si_3 (the only silicide produced by the crystallization reaction) take place. Annealing produces nanocrystalline composites of Al_3Ti , $TiAl$, Ti_3Al and Ti_5Si_3 with a grain size less than 20 nm. With increasing annealing temperature, the crystalline sizes of the phases increased.

Order No.: JA805-021

© 1998 MRS

Preparation of high solid content glass particle-polymethacrylate composite by an advance wetting method

Y.H. Wu, S. Jada, R. Xu
 (University of Utah)

An advanced wetting method is used to prepare a composite with a high content of ceramic particles in a matrix of photo-cured polymethylmethacrylate. The method allows for the preparation at minimum stirring of high quality samples with up to 59% solid in volume. The samples present reasonable flow characteristics prior to curing, with high hardness and fracture toughness in the fully cured state. Practical implications of the preparation method for dental restorative applications are studied. The method is also useful in the preparation of similar composites for other practical applications.

Order No.: JA805-022

© 1998 MRS

Pore geometry in woven fiber structures: 0°/90° plain-weave cloth lay-up preform

S.-B. Lee*, S.R. Stock†, M.D. Butts#, T.L. Starr†, T.M. Breunig\$, J.H. Kinney†
 (*Republic of Korea Army Headquarters, †Georgia Institute of Technology, #Chicago Bridge and Iron, \$University of California, San Francisco, †Lawrence Livermore National Laboratory)

Composite preform fiber architectures range from the very simple to the complex, and the extremes are typified by parallel continuous fibers and complicated three-dimensional woven structures. Subsequent processing of these preforms to produce dense composites may depend critically on the geometry of the inter-fiber porosity. The goal of this study is to fully characterize the structure of a 0°/90° cloth layup preform using x-ray tomographic microscopy (XTM). This characterization includes the measurement of inter-cloth channel widths and their variability, the transverse distribution of through-cloth holes, and the distribution of preform porosity. The structure of the inter-cloth porosity depends critically on the magnitude and direction of the offset between adjacent cloth layers. The structures observed include two-dimensional networks of open pipes linking adjacent holes, arrays of parallel one-dimensional pipes linking holes and relatively closed channels exhibiting little structure, and these different structures would appear to offer very different resistances to gas flow through the preform. These measurements, and future measurements for different fiber architectures, will yield improved understanding of the role of preform structure on processing.

Order No.: JA805-023

© 1998 MRS

Intercalation of cyclic amines in α -hafnium bis(hydrogen phosphate) monohydrate

M. Suárez, R. Llavorina, M.L. Rodríguez, L.M. Barcina, A. Anillo, J. Rodríguez
 (Universidad de Oviedo)

The intercalation in vapor phase of cyclic amines (aniline, benzylamine, cyclohexylamine, piperidine and pyridine) in α -hafnium bis(hydrogen phosphate) monohydrate (α -HfP) has been investigated. Elemental and thermal analysis lead to the establishment of the intercalate composition. The general formula is $x[Hf(HPO_4)_2 \cdot y \text{ amine} \cdot H_2O](1-x) \alpha$ -HfP where $y = 2, 1$ and $x \leq 1$. When $y = 1$ (piperidine and pyridine) the amines form a monomolecular layer. When $y = 2$ (aniline, benzylamine and cyclohexylamine) the arrangement is bimolecular. The results are compared to those described for α -ZrP.

Order No.: JA805-024

© 1998 MRS

Two critical thicknesses in the preferred orientation of TiN thin film

U.C. Oh*, J.H. Je*, J.Y. Lee*

(*Pohang University of Science and Technology, *Korea Advanced Institute of Science and Technology)

The preferred orientation of the TiN film grown by sputter-deposition was studied by the cross-sectional TEM. The preferred orientation was changed from the (200) through the (110), and then finally to the (111) with the film thickness. The cross-sectional microstructure also shows that the film consists of 3 layers which are all columnar structure. The (111) preferred orientation was observed in the top layer, and the (110) in the middle layer, and finally the (200) in the bottom layer. It is very surprising that the (110) preferred orientation could be observed in a medium thickness region, and there are two kinds of critical thicknesses. These results surely show the strong dependence of the change in the preferred orientation on the strain energy in TiN thin films.

Order No.: JA805-025

© 1998 MRS

Influence of atmosphere on crystallization of zirconia from a zirconium alkoxide

D.E. Collins, K.J. Bowman

(Purdue University)

Dibutoxybis (acetylacetonato) zirconium, a difunctional zirconium alkoxide, was polymerized at 130°C for 5 h *in vacuo* to produce oligomers that could be pyrolyzed to form a tetragonal zirconia (t-ZrO₂), metastable at room temperature. This metastable phase was retained considerably below the equilibrium transformation temperature (~1200 °C) without the use of dopants. Comparative pyrolysis of the oligomers between 600 and 900°C in either flowing O₂ or N₂ for processing times under 12 h indicated t-ZrO₂ nucleated first. Pyrolysis in oxygen facilitated transformation to the monoclinic symmetry, whereas pyrolysis in nitrogen demonstrated retention of the tetragonal phase. The formation of oxygen vacancies during pyrolysis, their role in stabilizing the metastable tetragonal phase, and contributions of O₂ and crystallite size in the polymorphic transformation are discussed.

Order No.: JA805-026

© 1998 MRS

Aging of iron manganite negative temperature coefficient thermistors

T. Battault, R. Legros, A. Rousset

(Université Paul Sabatier-118)

"Aging," defined as the drift of resistance with temperature after 1000 hours, was investigated for iron manganite temperature coefficient thermistors. For these devices, aging is relatively large, about 10%. The cationic distributions before and after aging were determined by Mössbauer spectroscopy. These distributions explain all the x-ray diffraction and correlated electrical data. The origin of the aging observed on iron manganite thermistors has been identified. It is due to the migration of Fe³⁺ ions from tetrahedral to octahedral sites of the spinel structure in order to reach a structural equilibrium.

Order No.: JA805-027

© 1998 MRS

Ba_{0.7}Sr_{0.3}TiO₃ ferroelectric film prepared with sol-gel process and its dielectric performance in planar capacitor structure

F. Wang*, A. Uusimäki*, S. Leppävuori*, S.F. Karmanenko*, A.I. Dedyk*,

V.I. Sakharov*, I.T. Serenkov*

(*University of Oulu, *St. Petersburg Electrotechnical University,

#Russian Academy of Science)

Ferroelectric Ba_{0.7}Sr_{0.3}TiO₃ thin films were successfully deposited on sapphire (*r*-cut) substrates by the sol-gel process, and the deposited films were annealed at various temperatures and for various soaking times. The compositional and structural characteristics of the films were systematically examined with the aid of x-ray diffraction, scanning electron microscopy and medium energy ion scattering techniques. Their dependence on thermal processes were investigated. A planar capacitor structure based on the BSTO films was fabricated to evaluate the electrical and dielectric performance. These results, together with the microstructure characteristics, were analyzed and an optimal process was finally established.

Order No.: JA805-028

© 1998 MRS

Preparation and characterization of ultrafine TiO₂ particles in reverse micelles by hydrolysis of titanium di-ethylhexyl sulfosuccinate

M. Lal*, V. Chhabra*, P. Ayyub*, A. Maitra*

(*University of Delhi, *Tata Institute of Fundamental Research)

We describe the synthesis and characterization of ultrafine TiO₂ particles (in both anatase as well as rutile form) produced by a chemical reaction within the aqueous core of a water-in-oil microemulsion. The micro-emulsion was stabilized and the Ti⁴⁺ ions provided by a functionalized surfactant derived from the commercially available Aerosol-OT, i.e. sodium bis (2-ethylhexyl) sulfosuccinate (Na-DEHSS). The Na⁺ ions in Aerosol-OT were completely replaced by Ti⁴⁺ through an ion exchange reaction in non-aqueous solvents. Ultrafine TiO₂ particles were produced by the hydrolysis of the Ti-containing surfactant in the water droplets. The dependence of the size of the precipitated TiO₂.xH₂O particles on various structure parameters of the microemulsion was studied in detail.

Order No.: JA805-029

© 1998 MRS

Graded coatings by gradient temperature densification

S.K. Hur*, S.H. Yoo*, J.R. Groza*, J.M. Doh#, K. Yamazaki*, K. Shoda§

(*Chang-won University, *University of California at Davis, #Korea Institute of Science and Technology, §Sodick Co., Ltd.)

Functionally gradient materials (FGM) were prepared using layers of ZrO₂-3mol% Y₂O₃ ceramic and NiCrAlY powders. A fine grained zirconia powder was chosen to lower the ceramic sintering temperature and achieve simultaneous metal and ceramic densification. Consolidation of FGM's was achieved by a short time field-assisted sintering technique. Sintering was performed either at a constant temperature or in a temperature gradient by using punches made of different materials (i.e., one graphite and one tungsten). A temperature gradient of at least 100°C was required with a low value of 1200°C at the metal end and exceeding 1300°C at the ceramic end. Increasing the number of intermediate layers alleviates some of the cracks formed during sintering due to different coefficients of thermal expansion.

Order No.: JA805-030

© 1998 MRS

Thickness dependence of microstructural evolution of ZnO films deposited by r.f. magnetron sputtering

Y.E. Lee*, Y.J. Kim* H.J. Kim*

(*Seoul National University, *Kyonggi University)

The microstructural evolution, including preferred orientation and surface morphology, of ZnO films deposited by rf magnetron sputtering was investigated with increasing film thickness. Preferred orientation of the ZnO films changed from (0002) → (1011) → (1120) and fine and dense columnar grains also changed to large elongated grains with increasing thickness. Such selective texture growth was explained with an effect of highly energetic species bombardment on the growing film surface. The relationship between preferred orientation change and microstructural evolution was also discussed.

Order No.: JA805-031

© 1998 MRS

Study on preparing PLT(28) thin film and its E-O effect

A-L. Ding, W-G. Luo, P.S. Qiu, J.W. Feng, R.T. Zhang

(Chinese Academy of Sciences)

PLT(28) thin films deposited on glass substrates were studied by two sputtering processes. One is an *in-situ* magnetron sputtering and the other is a low temperature magnetron sputtering. The sintered PLT ceramic powders are used as a sputtering target for both processes. The influences of sputtering and annealing conditions on structure and crystallinity of the films were investigated. The E-O properties of PLT(28) thin films prepared by the two processes were determined by a technique according to Faraday effect. The researches showed the E-O properties were strongly affected by the sputtering process. The film with larger grains exhibits stronger E-O effect. The quadratic E-O coefficient of PLT(28) thin film varies in the range of 0.1 × 10⁻¹⁶ to 1.0 × 10⁻¹⁶(m/v)².

Order No.: JA805-032

© 1998 MRS

The oxidative transformation of solid, barium-metal-bearing precursors into monolithic celsian with a retention of shape, dimensions, and relative density

S.M. Allameh, K.H. Sandhage
(The Ohio State University)

The conversion of Ba-Al₂O₃-Si-SiO₂, Ba-Al-Al₂O₃-SiO₂, and Ba-Sr-Al-Al₂O₃-SiO₂ precursors into monolithic, monoclinic celsian has been examined. The relative amounts of metal and oxide in each type of precursor were adjusted so that the overall stoichiometry and molar volume were similar to those of the desired product, celsian. Metal+oxide mixtures were mechanically alloyed and then uniaxially pressed to yield 84–92% dense precursor disks. The precursors were converted into celsian by exposure to a series of heat treatments from 300–1500°C in oxygen-bearing gases. Differences and similarities in the phase evolution of the various precursors are discussed. Celsian disks were produced that retained the precursor shape, dimensions, and relative (% theoretical) density.

Order No.: JA805-033

© 1998 MRS

Effect of (La_{0.5}Sr_{0.5})CoO₃ and Pt intermediate layers on improving the stability of Pb_{1-x}La_xTi_{1-x/4}O₃ films

J.P. Wang, Y.C. Ling, Y.K. Tseng, K.S. Liu, I.N. Lin
(National Tsing-Hua University)

Deposition of a (La_{0.5}Sr_{0.5})CoO₃ (LSCO) layer on top of Pt/Ti/Si substrates was observed to substantially improve the stability of the subsequently deposited Pb_{1-x}La_xTi_{1-x/4}O₃ (PLT) films. Platinum coating of silicon substrates by itself is known to enhance the formation of PLT phase. In this work, the elemental depth profile examined by secondary ion mass spectroscopy (SIMS) and the structural profile examined by grazing angle incident x-ray diffractometry (GIXD) reveals that the Ti-species precoated underneath the Pt-layer diffuses outward through the Pt-layer at high temperature, forming a rutile TiO₂ layer on top of Pt-coating. It is this outmost TiO₂ layer which promotes the transformation kinetics of the PLT species adhered onto substrates into perovskite phase. Thus obtained films (PLT/Pt/Ti/Si) are, however, not stable enough to survive subsequent high temperature processing. On the other hand, the PLT/LSCO/Pt/Ti/Si films, which incorporate LSCO as buffer layer, can survive 650°C without significant deterioration.

Order No.: JA805-034

© 1998 MRS

Simulations of fine ceramics cascade synthesized by the self-propagating high-temperature synthesis method

B-W. Chen, C-C. Chen
(National Chung Cheng University)

Due to the convective and radiant heat losses, there exists a maximal converted length of a dense pellet synthesized by the self-propagating high-temperature synthesis (SHS) method. In this paper, we numerically investigate the possibility to increase that maximal converted length by cascading two reactant pellets in series, where an interface is naturally and artificially introduced. First, the impacts of both the bulk and interfacial parameters on the SHS process are estimated. The maximal converted length for a single pellet is computed. Next, by varying the interfacial parameters, it is found that more than 10% of extra converted length is obtained by the proposed cascade arrangement. Effects of the bulk parameters on the same purpose are also addressed.

Order No.: JA805-035

© 1998 MRS

Determination of indenter tip geometry and indentation contact area for depth-sensing indentation experiments

K.W. McElhaney, J.J. Vlassak, W.D. Nix
(Stanford University)

The phenomena of pile-up and sink-in associated with nanoindentation have been found to have large effects on the measurements of the indentation modulus and hardness of copper. Pile-up (or sink-in) leads to contact areas that are greater than (or less than) the cross-sectional area of the indenter at a given depth. These effects lead to errors in the absolute

measurement of mechanical properties by nanoindentation. To account for these effects a new method of indenter tip shape calibration has been developed; it is based on measurements of contact compliance as well as direct SEM observations and measurements of the areas of large indentations. Application of this calibration technique to strain-hardened (pile-up) and annealed (sink-in) copper leads to a unique tip shape calibration for the diamond indenter itself, as well as to a material parameter, α , which characterizes the extent of pile-up or sink-in. Thus the shape of the indenter tip and nature of the material response are separated in this calibration method. Using this approach, it is possible to make accurate absolute measurements of hardness and indentation modulus by nanoindentation.

Order No.: JA805-036

© 1998 MRS

Quantitative analysis of strengthening mechanisms in thin Cu films: Effects of film thickness, grain size and passivation

R-M. Keller, S.P. Baker, E. Arzt
(Max-Planck-Institut für Metallforschung)

Thermal stresses in thin Cu films on silicon substrates were examined as a function of film thickness and presence of a silicon nitride passivation layer. At room temperature, tensile stresses increased with decreasing film thickness in qualitative agreement with a dislocation constraint model. However, in order to predict the stress levels, grain-size strengthening, which is shown to follow a Hall-Petch relation, must be superimposed. An alternative explanation is strain hardening due to the increase in dislocation density, which was measured by x-ray diffraction. At 600°C, the passivation increases the stress by an order of magnitude; this leads to a substantially different shape of the stress-temperature curves, which now resemble those of aluminum with only a native oxide layer. The effect of passivation is shown to be very sensitive to the deposition and test conditions.

Order No.: JA805-037

© 1998 MRS

Characterization of sputtered iridium dioxide thin films

P.C. Liao*, W.S. Ho*, Y.S. Huang*, K.K. Tiong*
(*National Taiwan University of Science and Technology, *National Taiwan Ocean University)

Iridium dioxide (IrO₂) thin films, deposited on Si substrates by reactive rf sputtering method under various conditions, were characterized by atomic force microscopy (AFM), x-ray diffraction (XRD), electrical conductivity, spectrophotometry, ellipsometry and Raman scattering measurements. The average grain sizes of the films were estimated by AFM. A grain boundary scattering model was used to fit the relation between the average grain size and electrical resistivity. The optical and dielectric constants were determined by the ellipsometry measurements. The results of the electrical and optical studies show a metallic character of the films deposited at higher temperatures. The results of XRD and Raman scattering indicate that the IrO₂ films deposited at temperature higher than 300°C shows the presence of (200) texture.

Order No.: JA805-038

© 1998 MRS

Phase equilibria in the BaTiO₃-La₂TiO₅-TiO₂ system

S. Škapin, D. Kolar, D. Suvorov, Z. Samardžija
(“Jožef Stefan” Institute)

Subsolidus phase relations in the BaTiO₃-La₂TiO₅-TiO₂ part of the ternary BaO-La₂O₃-TiO₂ system at 1300°C in air were determined. The phases were characterized by x-ray diffraction, scanning electron microscopy and electron probe wavelength dispersive spectroscopic microanalysis. A combination of techniques was employed because of insensitivity in detecting secondary phases by x-ray diffraction. The location and extent of Ba_{6-x}La_{8+2x/3}Ti₁₈O₅₄ ternary solid solution 0.2(1) ≤ x ≤ 2.3(1) and Ba_{1-y}La₇Ti_{1-y/4}(V_{Ti})_{y/4}O₃ binary solid solution 0 ≤ y ≤ 0.3 at 1300°C was established. Tie lines between various barium polytitanates with a sequence of Ba_{6-x}La_{8+2x/3}Ti₁₈O₅₄ solid solution regions were determined.

Order No.: JA805-039

© 1998 MRS

Thermal evolution of the microstructure of nanosized LaFeO₃ powders from the thermal decomposition of a heteronuclear complex, La[Fe(CN)₆]-5H₂O

E. Traversa^{*}, P. Nunziante^{*}, M. Sakamoto^{*}, Y. Sadaoka[#], M.C. Carotta[§], G. Martinelli[§]
 (*Universita' di Roma "Tor Vergata", #Yamagata University, #Ehime University, §Universita' di Ferrara)

The thermal decomposition of a heteronuclear complex, La[Fe(CN)₆]-5H₂O leads to the preparation of nanosized single-phase perovskite-type LaFeO₃ powders. The microstructural evolution of LaFeO₃ with the temperature has been studied by x-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), and transmission electron microscopy (TEM). The product of the decomposition at 500°C consists of nanoporous grains which have the morphology of the complex, but diffracting as a monocrystal of LaFeO₃. At the higher temperatures, the nanosized particles start to separate from each other, still keeping the shape of the complex grains and forming soft agglomerates. The formation of LaFeO₃ from the complex at low temperatures is facilitated by the formation of an orthorhombic transition phase.

Order No.: JA805-040

© 1998 MRS

Ferroelectric properties of tetragonal lead barium niobate (Pb_{1-x}Ba_xNb₂O₆) crystals near the morphotropic phase boundary

M. Lee, R.S. Feigelson
 (Stanford University)

Tungsten bronze ferroelectrics with a morphotropic phase boundary (MPB) have become increasingly important for a variety of applications because of their enhanced and unique properties near the MPB. Lead barium niobate (Pb_{1-x}Ba_xNb₂O₆) crystals, which have a morphotropic phase boundary between the orthorhombic (1-x > ~0.63) and tetragonal (1-x < ~0.63) phases, were grown in sealed Pt crucibles by the vertical Bridgman method for tetragonal compositions near the MPB and their ferroelectric properties were investigated. The ferroelectric domain structures in as-grown crystals were revealed either by etching in hydrofluoric acid or by polishing with colloidal silica, the latter providing clearer features. Domain size on the surface perpendicular to the polar axis was 10–50 μm. Crystals could be poled by slowly cooling from above the Curie temperatures (300°C–400°C) under a dc field of 5 V/mm. The spontaneous polarization P_s of tetragonal Pb_{1-x}Ba_xNb₂O₆ was found to be in the range of 0.40–0.70 μC/mm² at room temperature depending on composition and increased as the composition approached the morphotropic phase boundary (1-x = ~0.63), as expected.

Order No.: JA805-041

© 1998 MRS

Crystallization behavior and cordierite formation in rapidly quenched MgAl₂O₄-SiO₂ glasses of various chemical compositions

K. Okada^{*}, H. Kawashima^{*}, S. Hayashi^{*}, M. Sugai[†], K.J.D. MacKenzie[#]
 (*Tokyo Institute of Technology, †Akita University, #New Zealand Institute for Industrial Research and Development)

Crystallization behavior of various compositions of MgAl₂O₄-SiO₂ glasses was investigated. Glasses with chemical compositions from MgAl₂O₄/SiO₂ = 1/1 to 1/8, spanning the range of cordierite composition (1/2.5) were prepared by a rapid quenching method using an arc image furnace and twin roller. During thermal treatment, all the glasses first crystallized to form high-quartz solid solution (HQSS), then transformed to high-cordierite at higher temperature. Transformation from high-cordierite to low-cordierite required prolonged firing times even at high temperature. The crystallization temperature of HQSS and the transformation temperature from HQSS to high-cordierite changed only slightly in the glasses with MgAl₂O₄/SiO₂ ratios greater than cordierite composition whereas large increases were found for glasses with MgAl₂O₄/SiO₂ ratios lower than cordierite. The HQSS phase appeared in the samples spanning a wide MgAl₂O₄/SiO₂ range and showed superlattice reflections which doubled the fundamental lattice parameters. The cause for HQSS formation prior to the appearance of cordierite in these glass samples is discussed from a structural view point involving ordering-disordering of SiO₄ and AlO₄ tetrahedra deduced from 29Si and 27Al MAS-NMR spectra.

Order No.: JA805-042

© 1998 MRS

The Faraday effect in diamagnetic glasses

J. Qiu^{*}, K. Hirao^{**}

(*Hirao Active Glass Project-ERATO, **Kyoto University)

The wavelength dispersions of the Faraday effect in typical diamagnetic glasses, i.e. silica, borate, silicate, tellurite, lead-bismuth-gallate and As₂S₃, have been examined. The Verdet constant of the glasses decreases with increasing wavelength in the longer wavelength region of the absorption edge of the glasses, while it increases with increase in optical band gap of the glasses. These phenomena have been successfully explained based on the Becquerel theory. A guiding principle in designing a diamagnetic glass with a high Verdet constant is proposed.

Order No.: JA805-043

© 1998 MRS

Enhancing adhesion between metals or epoxy and polytetrafluoroethylene by ion assisted reaction

S.K. Koh, J.W. Seok, S.C. Choi, W.K. Choi, H.J. Jung
 (Korea Institute of Science and Technology)

Ion irradiation on polytetrafluoroethylene (PTFE) has been carried out to improve adhesions to metals and to adhesive cements. Argon ions were irradiated on the polymer, with varying the amount of Ar⁺ from 1 x 10¹⁴ ions/cm² to 1 x 10¹⁷ ions/cm² at 1 keV, and 4 ml/min of oxygen gas flowed near the polymer surface during the ion irradiation. The wetting angle of water on the PTFE surface was changed from 100° to 70–150° depending on the ion beam condition. The changes of the wetting angle and effects of Ar⁺ irradiation in oxygen environment were explained by the changes in surface morphology due to the ion beam irradiation onto PTFE, and formation of hydrophilic group due to a reaction between irradiated polymer chain and the blown oxygen. Strongly enhanced adhesion is explained by interlock mechanism, formation of electron acceptor groups on the modified PTFE, and interfacial chemical reactions between the irradiated surface and the deposited materials.

Order No.: JA805-044

© 1998 MRS

Optical anisotropy of flexible polyimide thin films

B. Li, T. He, M. Ding, P. Zhang, F. Gao, F. Jing
 (Chinese Academy of Sciences)

Optical anisotropy of thin films of an organo-soluble flexible polyimide based on 1,4-bis(3,4-dicarboxyphenoxy) benzene dianhydride (HQDPA) and 2,2-dimethyl-4,4'-methylene dianiline (DMMDA) was detected by a prism-coupler technique. A mechanism is proposed, based on the model of gel film collapse. The degrees of optical anisotropy of the thin films were evaluated via the level of negative birefringence. The residual solvent in the films lessens the levels of negative birefringence so that the residual solvent must be evacuated. The levels of negative birefringence are independent on the solid content of the initial solution, but dependent on the thickness of the films. For a film of 16 μm thick, zero-birefringence was achieved, postulated from the dependence of negative birefringence on the thickness of thin films. The relationship between the optical anisotropy and solution properties shows that the degrees of optical anisotropy of thin films on the same scale of thickness depend on macromolecular sizes in their dilute solutions.

Order No.: JA805-045

© 1998 MRS

Phase formation sequence induced by deposition temperatures in Nb/Si multilayers

M. Zhang^{**}, W.K. Wang^{*}

(*Tsinghua University, **Chinese Academy of Sciences)

The phase formation sequence in Nb/Si multilayers formed at different deposition temperatures was investigated by x-ray diffraction (XRD) and transmission electron microscopy (TEM). The amorphous phases were found to form in Nb/Si multilayers deposited at room temperature and 560°C, but the compositions of these two amorphous phases were different. The crystalline Nb₂Si and Nb₅Si₃ were formed in Nb/Si multilayers deposited at 180–500°C. The interfacial energy and modified heat of formation are adopted to explain our obtained results. The occurrence of crystalline Nb₅Si₃, NbSi₂ and amorphous silicide phase was found when the Nb/Si multilayers with Nb₃Si phase was annealed at 550°C, while only

NbSi₂ was found to form when annealing this sample at 700°C. The mobility of Si takes an important role in phase formation in Nb/Si multilayers.

Order No.: JA805-046

© 1998 MRS

High efficiency photoresist-free lithography of UO₃ patterns from amorphous films of uranyl complexes

M. Gao, R.H. Hill

(Simon Fraser University)

The solid state photochemistry of uranyl carboxylate complexes are presented with the purpose of developing methods for optical lithography of uranium oxide films. These complexes of the general formula, UO₂(OOCR)₂ (R= i-C₃H₇, C₅H₁₁, CH₂C₆H₅, CH₂OC₂H₅, C₂H₄OC₂H₅), were all photosensitive as thin amorphous films. The primary photochemical reaction for each of these complexes was the extrusion of a CO₂ from the ligand and the production of radicals which initiated a chain reaction. The nature of this chain reaction was dependent upon the identity of the organic substituents, R. In some cases the chain reaction required a photochemical step while others were entirely thermal in nature. Of importance are the potentially high quantum yields which can be associated with thermal chain reactions. Some of the systems presented here exhibit quantum yields in excess of 1. This process was shown to be compatible with optical lithography by the patterning of the uranium oxide product on silicon surfaces.

Order No.: JA805-047

© 1998 MRS

Continuous measurements of load-penetration curves with spherical micro-indenters and the estimation of mechanical properties

J. Alcalá, A.E. Giannakopoulos, S. Suresh

(Massachusetts Institute of Technology)

Elastic and plastic properties of metals and Young's modulus of ceramics are determined in the micro-indentation regime by continuous measurements of load versus depth of penetration with spherical indenters. Calibration procedures, usually applied in nanoindentation experiments, are

not needed in the micro-regime where spherical indenters (rather than sharp indenters with microscopical spherical tips) can be manufactured. As indenters of larger diameters are used, the elastic response of the specimen can be probed during the loading stage of the indentation tests (and not only during unloading, as is the case with nano-indenters). Hence, an accurate determination of the Young's modulus can be achieved without a prior knowledge of possible "piling up" or "sinking in" which may occur at the perimeter of the contact area. The contact response of materials is shown to undergo four distinct regions: (i) pre-Hertzian regime, (ii) Hertzian regime, (iii) small-scale plasticity, and (iv) large-scale plasticity. A general methodology for estimation of yield strength and hardening exponent of metals is proposed in the last regime.

Order No.: JA805-048

© 1998 MRS

Valence states analysis of Ca and Si in CaSi₂ during CaSi₂-H₂O reaction

S. Abe*, H. Nakayama*, T. Nishino*, S. Iida*

(*Kobe University, *Osaka Sangyo University)

The changes in the valence electron states of CaSi₂ during the chemical reaction with H₂O have been investigated by Auger valence electron spectroscopy (AVES). In order to study the reaction process, the reaction was precisely controlled by applying DC voltage between Pt electrode and CaSi₂ specimen. The Si[2s,2p,V] Auger spectra of CaSi₂ specimen remain to be unchanged under the applied voltage lower than -15V relative to the Pt electrode in H₂O. At higher applied voltage, 3p components of Si[2s,2p,V] (V=3s,3p) Auger spectra get weak while the 3s components increase drastically. The peak position due to Ca[2p,3p,3p] transitions gradually shifted toward the lower energy side with raising the applied voltage. The peak shift is due to the formation of Ca-O bonds in CaSi₂. A new peak, which arises from the split of the valence electron states in Ca atoms due to the Ca-O bonds, appeared in Ca[2p,3p,V] Auger spectra for CaSi₂ after the reaction with H₂O.

Order No.: JA805-049

© 1998 MRS

Please use the convenient postcard located in the back of the *MRS Bulletin* to order *JMR* reprints. When ordering single article reprints please note they are not available until the issue is published. See *JMR* Abstracts on the MRS Website at <http://www.mrs.org/publications/jmr/jmra/>.

Consiglio Nazionale Delle Ricerche - Area Della Ricerca di Bologna

INTERNATIONAL ADVANCED SCHOOL "Leonardo da Vinci"
SUMMER COURSE 1998

SUPERCONDUCTING MATERIALS: ADVANCES IN TECHNOLOGY AND APPLICATIONS

Director: K. Kitazawa (Tokyo University, Japan)
Bologna, Italy: June 29-July 10, 1998

Number of participants: 70

Language: English

Contact: Anna Tampieri, Istituto IRTEC/CNR, Via Granarolo 64—48018 Faenza, Italy
Phone: 39-(0)546-699 757; Fax 39-(0)546-46 381; e-mail superconductors@irtec1.irtec.bo.onr.it.

Call for Papers

Second International Innovations in Materials Conference and Innovations in Real Materials Awards

**July 19–22, 1998
Washington, DC**

For Whom ✓ Materials researchers from all fields ✓ University intellectual property officers
 ✓ Materials based companies ✓ Managers of venture capital agents
 ✓ Government R/D managers ✓ Science press

Featuring

- **Oral & Poster Sessions:** Reports on latest step-function or unexpected advances and discoveries by materials researchers from around the world in metals, polymers and ceramics, composites, electronic materials, and biomaterials
- **Forums:** Discussions on key topics related to the innovation process including university intellectual property management, small business patent strategy, accessing capital beyond venture capital level, and Industry-Government-University arrangements to shorten path from conception to product

IRM Awards

- **Innovations in Real Materials:** A broad-based committee composed of members of several national academies will nominate the most significant work which will shape the field in all areas of materials research. A committee drawn from the International Advisory Committee will select the dozen top innovators. The awards will be presented at the Banquet

Target Dates

1 February: Deadline for submission of your Conference Presentation Abstract

1 April: Notify presenters of place in program

15 May: Last day for receipt of reduced early registration fee

26 June: Last day Conference Hotel room reservation

19 July: Opening reception, Sunday evening

22 July: Conference closes Wednesday 5:00 pm

Abstract Submission, Information

For Information on submitting Abstract, and Conference Registration Packet, contact:
 Kathy Moir, IMc Secretariat,
 103 Materials Research Laboratory University Park, PA 16802, USA.
 Phone: 001-814-863-9983; Fax: 001-814-863-7040; e-mail: kathymoir@psu.edu

International Advisory Committee

China: *Zhong-Xian Zhao*
 France: *Jacques Livage, Micheline Moranville-Regourd*
 Germany: *Hans R. Kricheldorf, Manfred Rühle*
 Great Britain: *Anthony Kelly*
 India: *C.N.R. Rao*
 Japan: *Tsuneo Nakahara, Koichi Niihara*
 Russia: *E.I. Givargizov, Alexander M. Prokhorov*
 USA: *Anthony Evans, Merton Flemings, John Gilman, Eugene Goldberg, Frank Karasz,
 Doris Kuhlmann-Wilsdorf, Robert Newnham, C. Kumar Patel, John Poate, Rustum Roy (Chair)*

