JMR Abstracts

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

Volume 13, Number 4 *Abstracts for April 1998 Journal of Materials Research*

TABLE OF CONTENTS

April JMR issue includes a SPECIAL SECTION:
Soft Solution Processing

ABSTRACTS

SPECIAL SECTION
SOFT SOLUTION PROCESSING

Importance of soft solution processing for advanced inorganic materials
M. Yoshimura
(Tokyo Institute of Technology)

Based upon the analysis of material cycling and processing on the earth, a thermodynamic concept for energetical and environmental problems has been proposed. It concludes that solution processing using aqueous solutions should be the most important processing even for advanced materials. According to this concept, energetical and environmental features of soft solution processing (SSP) are discussed in general, using also some particular examples, such as $BaTiO_3$. Applications of SSP are shown with special emphasis on hydrothermal and/or electrochemical synthesis of thin films and integration issues. Soft solution processing allows fabrication in aqueous solutions of shaped/sized/oriented ceramics in only one step, without excess energies for firing/sintering or melting and without expensive equipment, providing an environmentally friendly route for preparation of advanced ceramic materials.

Order No.: JA804-001

Sol-gel control of the micro/nanostructure of functional ceramic-ceramic and metal-ceramic composites

P. Colomban
(LASIR-CNRS)

The problems encountered in simultaneously tailoring various specific chemical or physical properties are discussed. Selected polymeric precursors used in association with fine powders allow the control of the nano/microstructure of composites and hence the preparation of functional (FGM) and hierarchical reinforced (HRC) composites, making it possible to combine several kinds of fibers, interphases and matrices in the same composite (hot microwave absorbent), to control the fiber/matrix interface (long life times composites), to achieve net-shape sintering of 3D composite matrices, and to prepare thick films of metal-ceramic composites with tailored microwave absorption (radar stealthiness).

Order No.: JA804-002

Soft chemical preparation and electrochemical oxygen-doping of $La_2Ca_{n-1}Cu_nO_{2n+2}$

S. Kikkawa, N. Taya, F. Kanamaru
(Osaka University)

$La_2CaCu_2O_6$ (n=2) could be obtained even at 800°C by firing the coprecipitates from a mixed aqueous solution of La, Ca and Cu acetates which were titrated with tartaric acid. The firing temperature was much lower than that in solid state reactions which are usually conducted above 1000°C. Both $La_2Ca_2Cu_3O_8$ (n=3) and $La_2Ca_3Cu_4O_{10}$ (n=4) were obtained at 700°C in a similar preparation method. Low temperature firing was very important for these preparations. A porous sintered body of $La_2CaCu_2O_6$ with a relative density of about 15% was also obtained using this preparation method. This porous sintered body could be effectively oxygen-doped by electrochemical oxidation showing the presence of new superconducting phase with T_c around 30 K.

Order No.: JA804-003

Sinterability of SiC powder coated uniformly with Al ions

S. Sameshima, K. Miyano, Y. Hirata
(Kagoshima University)

The SiC particles coated uniformly with Al ions (0.25 mass% Al_2O_3) in an aluminum nitrate solution were consolidated by filtration through gypsum mold. The hot-pressing in vacuum gave dense SiC above 99% relative density in the temperature range of 1900°–1950°C under a pressure of 39 MPa. The microstructures of dense SiC consisted of 2-5 μm grains of low aspect ratios below 2. The fracture toughness and flexural strength of SiC increased gradually as hot-pressing temperature became higher and were 4.3 $MPa \cdot m^{0.5}$ and 350 MPa, respectively, at the hot-pressing of 1950°C. The crack propagation in SiC shifted from intergrain to intragrain with increasing hot pressing temperature.

Order No.: JA804-004

New hydrogenation systems of unsaturated organic compounds using noble metal-deposited palladium sheet electrodes with three dimensional structures

C. Iwakura*, Y. Yoshida+, S. Ogata+, H. Inoue*
*(*Osaka Prefecture University, +Permelec Electrode Ltd.)*

A successive hydrogenation system was constructed using a two-compartment cell separated by a Pd sheet. The hydrogenation rate changed greatly, depending on the kind of substrates used. For the purpose of improving the hydrogenation rate, the surface of a Pd sheet was modified with highly active catalysts such as Pd black, Pt and Au by using active hydrogen passing through the Pd sheet as a reducing agent. As a result, the hydrogenation rate of unsaturated organic compounds such as 4-methylstyrene was markedly increased by the surface modification with these catalysts due to the increase in reaction zone and appearance of new active sites.

Order No.: JA804-005

Formation mechanism of fine anatase crystals from amorphous titania under hydrothermal conditions

K. Yanagisawa, Y. Yamamoto, Q. Feng, N. Yamasaki
(Kochi University)

Crystallization of amorphous titania prepared by hydrolysis of thoxide was accelerated even by a small amount of water in the vapor phase. The existence of water promoted the change of localized structure of the amorphous titania to anatase structure, which resulted in acceleration of anatase nucleation. The anatase crystals grew in steam by solid-state epitaxial growth, but stopped growing in a short time. The growth of anatase crystals under hydrothermal conditions could be divided into the following two stages, the first stage with fast growth rate by solid-state epitaxial growth and the second stage with slow growth rate by dissolution deposition process.

Order No.: JA804-006

Preparation and electrical conductivity of three types of antimonic acid films

K. Ozawa, Y. Sakka, M. Amano
(National Research Institute for Metals)

Three types of antimonic acid ($Sb_2O_5 \cdot nH_2O$) films: (111)-oriented and non-oriented polycrystalline films of cubic $Sb_2O_5 \cdot nH_2O$ and amorphous $Sb_2O_5 \cdot nH_2O$ films, were prepared on quartz glass substrates with a spin-coating technique using aqueous slurries, which were formed by reacting H_2O_2 with metallic Sb powder or $Sb(O\text{-}n\text{-}C_3H_7)_3$. The morphologies and structures of the films were observed, and the electrical conductivity of the films was determined at 20°C in the relative humidity range, 9-100%. The electrical conductivity of the (111)-oriented film, which increases from 1.69×10^{-5} to 2.89×10^{-3} Scm^{-1} as the relative humidity changes from 11 to 85%, is approximately one order of magnitude larger than those of the non-oriented and amorphous films.

Order No.: JA804-007

Low temperature solid-state epitaxy of $LiNbO_3$ films by a dipping-pyrolysis process using Li-trifluoroacetate

T. Manabe, I. Yamaguchi, W. Kondo, T. Kumagai, S. Mizuta
(National Institute of Materials and Chemical Research)

Epitaxially grown $LiNbO_3$ thin films were prepared on sapphire(012) (*R*-plane) substrates by a dipping-pyrolysis process using two kinds of lithium sources, i.e., Li-2-ethylhexanoate and Li-trifluoroacetate, which are pyrolyzed in air to Li_2CO_3 and LiF, respectively. Crystallization temperature and alignment of $LiNbO_3$ films on sapphire(012) were found to greatly depend on the Li sources. Dominantly [100]-oriented epitaxial $LiNbO_3$ films were crystallized at around 600°C using 2-ethylhexanoate, whereas dominantly [012]-oriented epitaxial $LiNbO_3$ films resulted at a temperature as low as 400°C using tri-fluoroacetate.

Order No.: JA804-008

Electrochemical preparation of cobalt oxide using an autoclave electrolytic cell

M. Koinuma, T. Hirae, Y. Matsumoto
(Kumamoto University)

Polycrystalline films of cobalt oxides (Co_3O_4 and CoOOH) with and without Sm were fabricated on platinum substrates by electrochemical oxidation in an autoclave. The cobalt oxides were directly crystallized at temperatures higher than about 100°C during electrolysis. The composition of the cobalt oxides strongly depended on the electrode potential, i.e., Co_3O_4 and CoOOH were formed in non-noble and relatively noble potential regions, respectively. When Sm was incorporated in the CoOOH by the electrolysis in solutions containing Sm^{3+}, only the *c* lattice constant was increased due to an expansion in the layer structure.

Order No.: JA804-009

Preparation of fine-grained monoclinic zirconia ceramics by colloidal processing

T. Uchikoshi, Y. Sakka, K. Ozawa, K. Hiraga
(National Research Institute for Metals)

Fine-grained monoclinic zirconia ceramics were made from well-dispersed zirconia sol prepared by the hydrolysis of zirconium chloride oxide octahydrate. Dechlorinated and concentrated zirconia sol was consolidated by pressure filtration. The relative green density of the compact was improved by the following cold isostatic press treatment at 400 MPa. The compact was densified by pressureless sintering to >98% of theoretical density in air at 1100°C, which temperature is lower than that of monoclinic to tetragonal transformation of pure zirconia. The average grain size of the sintered monoclinic zirconia ceramics was 92 nm.

Order No.: JA804-010

Crystallization of titania in liquid media and photochemical properties of crystallized titania

S. Yin, Y. Inoue, S. Uchida, Y. Fujishiro, T. Sato
(Tohoku University)

Titania gels in liquid media crystallized from amorphous to anatase at temperature as low as 120°C, while the onset of crystallization in air was 370°C. The crystallization rate in water was much faster than in methanol and n-hexane, and the crystallite size of anatase prepared in water was larger than those prepared in organic solvents. The crystallized powders were capable of efficient hydrogen evolution following band gap irradiation in the presence of a sacrificial hole acceptor such as methanol. The photocatalytic activity of powder crystallized in methanol was superior to those prepared in water and air.

Order No.: JA804-011

Preparation of hydroxy double salts exchanged by organic compounds

H. Morioka, H. Tagaya, M. Karasu, J-I. Kadokawa, K. Chiba
(Yamagata University)

Hydroxy double salts (HDSs) comprise a class of layered materials which are similar to layered double hydroxides (LDHs) and show a comparable intracrystalline reactivity. Their anion exchange reactions occur with preincorporated anions in the hydroxide layer and with anions bound as gegenions of the positively charged layers, respectively. In this study, nitrate and acetate anions of HDSs were exchanged with anionic mono- and di-carboxylic acids and we confirmed that interlayer spacing of HDSs increased depending on the size of mono- and di-carboxylic acids. Moreover, we have prepared photofunctional materials by exchange reaction with azobenzene-p-carboxylic acid and 4-4'-azobenzenedicarboxylic acid.

Order No.: JA804-012

Preparation of a high active photocatalyst, $K_2La_2Ti_3O_{10}$, by polymerized complex method and its photocatalytic activity of water splitting

S. Ikeda, M. Hara, J.N. Kondo, K. Domen, H. Takahashi, T. Okubo, M. Kakihana
(Tokyo Institute of Technology)

A layered perovskite type oxide, $K_2La_2Ti_3O_{10}$, was prepared by a gel technique, the polymerized complex (PC) method. A single phase of $K_2La_2Ti_3O_{10}$ was obtained by adding twice more the potassium than stoichiometry. The Ni-$K_2La_2Ti_3O_{10}$ catalyst prepared by the PC method exhibited a higher photocatalytic activity for decomposition of H_2O into H_2 and O_2 than that prepared by a conventional solid state reaction.

Order No.: JA804-013

Glycothermal synthesis of rare earth iron garnets

M. Inoue, T. Nishikawa, T. Inui
(Kyoto University)

The reactions of rare earth (RE) acetates with iron acetylacetonate in 1,4-butanediol at 300°C (glycothermal reaction) yielded two novel phases depending on the ionic size of RE element: One was obtained for Er-Lu and the other for Tb and Dy. The former phase was hexagonal $REFeO_3$, while the latter phase has not been identified. The reaction of Y or Ho acetate yielded the mixture of these two phases. When the reactions were carried out in the presence of seed crystals of yttrium aluminum garnet ($Y_3Al_5O_{12}$), these phases were not formed but RE iron garnet ($RE_3Fe_5O_{12}$) grew on the seed, which suggests that spontaneous nucleation of RE iron garnet does not occur but crystal growth proceeds easily under the glycothermal conditions. Hydrothermal reaction of the same starting materials yielded a mixture of Fe_2O_3 and an amorphous RE phase.

Order No.: JA804-014

Preparation of porous niobium oxide by the exfoliation of $K_4Nb_6O_{17}$ and its photocatalytic activity

R. Abe*, K. Shinohara+, A. Tanaka+, M. Hara*, J.N. Kondo*, K. Domen*
*(*Tokyo Institute of Technology, +Nikon Corp.)*

A new porous material was prepared from a layered compound, $K_4Nb_6O_{17}$, through the exfoliation of its layers. A composite of the niobate sheets and MgO particles were obtained by precipitating the exfoliated two dimensional niobate sheets with MgO fine particles. Porous niobium oxide was obtained by removal of the MgO particles from the composite after thermal treatment. It had a large surface area and showed higher photocatalytic activity than the original $H^+/K_4Nb_6O_{17}$ for H_2 evolution from various aqueous alcohol solutions.

Order No.: JA804-015

Solution processing approaches for solid electrolytes and electrode materials

S.P. Simner, P-W. Wu, B. Dunn
(University of California-Los Angeles)

Solution processing methods have been used to prepare a solid electrolyte, copper doped bismuth vanadate and several different lithium transition metal oxide cathode materials. Dense thin films of the bismuth vanadate were prepared by pyrolysis of metal organic precursors deposited on various oxide substrates. A high degree of crystal orientation was obtained using single crystal MgO substrates. The Pechini process was used to prepare powders of the different materials and a variety of results were obtained. The bismuth vanadate exhibited a second phase of $BiVO_4$ while $LiNiO_2$ and the $LiCo_xNi_{1-x}O_2$ solid solution require further efforts at obtaining the proper phase and stoichiometry. The $LiCoO_2$ system formed readily and exhibited good electrochemical performance.

Order No.: JA804-016

Functionally graded $SrTiO_3$-$BaTiO_3$ thin films prepared by the hydrothermal-electrochemical method under flowing solution

M. Yoshimura, W. Suchanek, T. Watanabe, B. Sakurai, M. Abe
(Tokyo Institute of Technology)

$BaTiO_3$, $SrTiO_3$, and $Ba_xSr_{1-x}TiO_3$ thin films, as well as multilayers in the $SrTiO_3$-$BaTiO_3$ system, have been prepared on Ti-substrates in newly constructed flow-system equipment by the hydrothermal-electrochemical method. The synthesis parameters (temperature of 120-200°C, flow rate of 1-50 cm^3/min) allow fabrication of dense, single-phase films with different morphology by controlling nucleation and/or growth rates. The flow system also enables an easy fabrication of $SrTiO_3/BaTiO_3$ and $BaTiO_3/SrTiO_3$ multilayers with variable chemical composition and microstructure across the film thickness. The multilayers can be prepared in only one experiment by simply changing the kind of flowing solution and/or adjusting the processing conditions.

Order No.: JA804-017

Pure tetravalent nickel in γ-type nickel oxyhydroxide as secondary battery electrode

K-S. Han*, M. Yoshimura*, J-B. Yoon+, J-H. Choy+, K-J. Park#
*(*Tokyo Institute of Technology, +Seoul National University, #National Institute of Technology and Quality)*

Pure tetravalent nickel in γ-type cobalt substituted nickel oxyhydroxide, $Ni_{0.70}Co_{0.30}O_2K_{0.30}(H_2O)_{0.42}$, could be obtained by "chimie douce"

reaction. The presence of tetravalent nickel is confirmed by comparing the Ni K-edge XANES spectrum of the sample with those of reference compounds having various nickel valency and similar layer structure. The Co K-edge XANES spectrum indicates that the trivalent cobalt remains unchanged regardless of the nickel valency. The structural modification during "chimie douce" reaction observed from XRD patterns and the result of iodometric titration are consistent with the Ni and Co K-edge XANES data.

Order No.: JA804-018

Synthesis of metal oxide thin films by liquid-phase deposition method

S. Deki*, Y. Aoi+
*(*Kobe University, +Ryukoku University)*

Novel wet process to synthesis of metal oxide thin films have been developed. The process is called liquid-phase deposition (LPD) method. In this method, metal oxide or hydroxide thin films are formed on the substrate through the ligand-exchanging (hydrolysis) equilibrium reaction of metal-fluoro complex species and F^- consumption reaction of F^- scavenger. The LPD method is one of the unique soft solution processes, and is performed by a very simple procedure. In this paper, for the purpose of developing the preparing method of composite oxide thin films, preparation of Pt-dispersed titanium oxide and iron-nickel binary oxide thin films were focused.

Order No.: JA804-019

Hydrothermal growth of millimeter-sized aluminosilicate sodalite single crystals in noble metal capsules

T. Hayashi*, H. Shiga*, M. Sadakata*, T. Okubo*, M. Yoshimura+
*(*The University of Tokyo, +Tokyo Institute of Technology)*

Aluminosilicate sodalite $Na_8[SiAlO_4]_6Cl_2$ single crystals are synthesized by hydrothermal processing at 873-973 K and 100-150 MPa in noble metal capsules to avoid contamination. The starting material is aluminosilicate gel, and the spontaneous nucleation followed by its growth is performed. The largest size of the single crystal obtained is 1 mm across. The longer aging, and the heating, result in the larger single crystals in the experimental condition. It is also found that aluminum source of the synthesis gel and the element of the noble metal capsules influence the single crystal growth. Judging from XRD (powder and single crystal), optical microscopy and TG-DTA, the sodalite single crystals grown have good quality compared with the conventional powder.

Order No.: JA804-020

Soft process for the intercalation of ammonium cations into vanadium oxide

M. Inagaki, T. Nakamura, A. Shimizu
(Hokkaido University)

A soft process for the intercalation of different ammonium cations into vanadium pentoxide was developed. By refluxing an aqueous solution containing ammonium NH_4^+, tetramethylammonium $(CH_3)_4N^+$ and tetraethylammonium $(C_2H_5)4N^+$ with V_2O_5 powders, intercalation compounds containing corresponding ammonium cations were obtained. The compound with aniline $C_6H_5NH_2$ was also synthesized by the same process. The compounds with $(CH_3)_4N^+$, $(C_2H_5)_4N^+$ and also $C_6H_5NH_2$ had diffraction patterns consisting of very sharp 001 lines. The spacing sandwiched the intercalates, $(CH_3)_4N^+$, $(C_2H_5)_4N^+$ and $C_6H_5NH_2$, was 1.29, 1.31 and 1.39 nm, respectively.

Order No.: JA804-021

Cryosol method: A novel powder processing technique based on ion-exchange phenomena

A.A. Vertegel, S.V. Kalinin, N.N. Oleynikov, Yu.G. Metlin, Yu.D. Tretyakov
(Moscow State University)

A novel technique has been suggested for synthesis of highly dispersed oxide powders. The method is based on the treatment of aqueous solution of a multivalent metal nitrate (or chloride) by anion-exchange resin in the OH^--form. The presented technique yields stable colloid solution of the corresponding hydroxide with concentrations up to 1 M. The subsequent freeze drying and thermal dehydration results in very fine powder of metal oxide. The individual and multicomponent oxides obtained by the cryosol method were shown to possess unusual properties due to their high dispersity and chemical homogeneity.

Order No.: JA804-022

Synthesis of gold-cadmium selenide co-colloids

R. Nayak, J. Galsworthy, P. Dobson, J. Hutchison
(University of Oxford)

Semiconductor-metal co-colloids of CdSe/Au have been prepared by various synthetic pathways. Their microstructure, including that of Au-CdSe(TOPO) co-colloid in a core-shell structure, has been examined by high resolution transmission electron microscopy (HRTEM) and found to be well defined within the 10 nm size range. The optical absorption spectra of the colloids and of various synthesis stages have been obtained.

Order No.: JA804-023

Potential oscillations during the electrochemical self assembly of copper/cuprous oxide layered nanostructures

J.A. Switzer, C-J. Hung, L-Y. Huang, F.S. Miller, Y. Zhou, E.R. Raub, M.G. Shumsky, E.W. Bohannan
(University of Missouri-Rolla)

Layered nanostructures of copper metal and cuprous oxide are electrodeposited from alkaline solutions of Cu(II) lactate at room temperature. No subsequent heat treatment is necessary to effect crystallization. The electrode potential spontaneously oscillates during constant-current deposition. At a fixed current density the oscillation period decreases as either the pH or temperature is increased. The oscillations are periodic in stirred solution, but show period doubling and evidence of quasi-periodic or chaotic behavior in unstirred solution. The phase composition and resistivity of the films can be controlled by varying the applied current density. The resistivity of the films can be varied over ten orders of magnitude. Scanning electron microscopy shows that the films are layered.

Order No.: JA804-024

One-step electrodeposition of CdS/ZnS bilayer from an aqueous mixture of Cd^{2+} and Zn^{2+}

K. Yamaguchi, T. Yoshida, Y. Sugiura, H. Minoura
(Gifu University)

Electrochemical thin film deposition in aqueous mixtures containing Cd^{2+}, Zn^{2+} and thioacetamide has been investigated. It has been found that the atom-by-atom growth of well crystallized CdS thin film preferentially takes place at the early stage of the reaction, followed by the cluster-by-cluster growth of the poorly crystallized ZnS outer layer, thus resulting in the formation of CdS/ZnS bilayer by a one-step synthesis.

Order No.: JA804-025

Calcium phosphate compound-cellulose fiber composite material prepared in soaking medium at 36.5°-60°C

Y. Yokogawa*, M. Toriyama*, Y. Kawamoto*, K. Nishizawa*, F. Nagata*, T. Kameyama*, K. Okada+, M. Okuyama+
*(*National Industrial Research Institute of Nagoya, +NGK Spark Plug Co., Ltd.)*

Calcium phosphate growth on cellulose fibers phosphorylated in 1.5 x SBF (simulated body fluid) solution at various temperatures, from 36.5°–60°C was studied. Cellulose fibers phosphorylated by using urea and H_3PO_4 and then soaked in saturated $Ca(OH)_2$ solution at ambient temperature were found to stimulate the growth of a calcium phosphate coating on their surfaces after soaking in 1.5 x SBF solution for as little as one day. Soaking in 1.5 x SBF solution at higher temperature produced a thicker layer of calcium phosphate on the fibers, which may be due to the decrease of solubility of calcium phosphate. The specific surface area of the coatings decreased with an increase of soaking temperature and soaking time in 1.5 x SBF solution.

Order No.: JA804-026

Synthesis of hollandite-type $K_xGa_xSn_{8-x}O_{16}$ fine particles by the sol-gel method

K. Fujimoto*, M. Watanabe+, T. Mori+, S. Ito*
*(*University of Tokyo, +National Institute for Research in Inorganic Materials)*

$K_xGa_xSn_{8-x}O_{16}$ ($x \leq 2$) powders with hollandite structure were prepared by the sol-gel method using metal alkoxides. Dried gels, when being annealed at 973 K, changed to well-crystallized hollandite powders with about 22 m^2/g in B.E.T. value which consisted of needle-like crystallites averaging 25 nm wide and 65 nm long. The specific surface area was nearly 100 times larger than that of the hollandite produced at 1648 K by the conventional method and the preparation temperature was lowered by 500 to 700 K. The powders obtained at 973 K were characterized as the attractive porous material showing a pore size distribution profile sharply monodispersed at 10.7 nm in the mesopore range.

Order No.: JA804-027

A kaolinite-NMF-methanol intercalation compound as a versatile intermediate for further intercalation reaction of kaolinite

Y. Komori, Y. Sugahara, K. Kuroda
(Waseda University)

A kaolinite-organic intercalation compound containing methanol was proved to be a versatile host for further displacement reaction with alkylamines. Kaolinite-organic intercalation compounds with polar molecules, such as N-methylformamide (NMF) and formamide, were used as the starting materials. After stirring the kaolinite-NMF intercalation compound with methanol, the basal spacing increased to 1.11 nm. The ^{13}C MAS NMR result of the product indicated that methanol was intercalated into kaolinite by partial displacement with NMF. By the use of the methanol-treated kaolinite intercalation compound as the intermediate, alkylamines were intercalated into the interlayer space of kaolinite by displacing with methanol.

Order No.: JA804-028

Preparation of epitaxial $Fe_{3-x}O_4$ films by dipping-pyrolysis process using CO-CO_2 gas mixtures

I. Yamaguchi*, T. Manabe*, T. Kumagai*, W. Kondo*, S. Mizuta*, T. Manago+
*(*National Institute of Materials and Chemical Research, +Keio University)*

Epitaxially grown $Fe_{3-x}O_4$ films were prepared on MgO(001) substrates by dipping-pyrolysis process using CO-CO_2 gas mixtures. The structure and in-plane alignment of these films were examined by x-ray diffraction θ-2θ scans, β scans (pole figures), and asymmetric ω-2θ scans (reciprocal-space maps). The films heat-treated at 500°C and higher in an atmosphere with $pCO/pCO_2=10^{-4}$ had a spinel-type structure and were in an epitaxial (cube on cube) relationship with the substrates.

Order No.: JA804-029

Synthesis of ZrO_2-Y_6WO_{12} solid solution powders by a polymerized complex method

J. Ma, M. Yoshimura, M. Kakihana, M. Yashima
(Tokyo Institute of Technology)

A series of solid solutions $(1-x)ZrO_2 \cdot xY_{0.857}W_{0.143}O_{1.714}$ ($1/7Y_6WO_{12}$) of metastable cubic phase were synthesized at 800°C through a polymerized complex method. Lattice parameter a_0 of solid solutions varies linearly with $Y_{0.857}W_{0.143}O_{1.714}$ content (x). Crystallization began to occur above 400°C from amorphous precursor to yield at 800°C fine powders of 6-10 nm and 19-40 m^2/g for crystallite size and surface area, respectively.

Order No.: JA804-030

COMMUNICATION

Large size plasma generation using multi-cathode direct current geometry for diamond deposition

Y-J. Baik, J-K. Lee, W-S. Lee, K.Y. Eun
(Korea Institute of Science and Technology)

The deposition area of diamond film is increased by applying a geometry of multiple cathodes and a single anode in direct current (DC) PACVD. Each cathode is made of Ta and connected independently to its own DC power supply. The operating pressure is 1.3×10^4 Pa (100 torr) and methane-hydrogen mixed gas is used as reaction gas. The voltage and the current applied to each cathode are 650 V and 4 A, respectively. The transition from a diffuse glow to an arc is prevented by maintaining cathodes temperatures above 2000°C, which inhibits carbon deposition on the cathodes. Translucent diamond film of 3" diameter, thicker than 200 μm, is grown using 7 cathodes with 3%CH_4-H_2 mixed gas for 110 h. The deposition area can be increased further by increasing the number of cathodes.

Order No.: JA804-031

ARTICLES

Tetragonal-orthorhombic phase transition in YBaCuO thin films observed by perturbed angular correlation spectroscopy

R. Platzer, I.D. Dumkow, D.W. Tom, J.A. Gardner, J. Tate
(Oregon State University)

Oxygen-deficient, tetragonal thin films of $YBa_2Cu_3O_{6+x}$ with $x \approx 0.25$, quenched from the deposition temperature, change to the oxygenated, orthorhombic phase with $x \approx 1$, between 200°C and 400°C in flowing oxygen. The transition is not reversible in flowing oxygen, and cannot be completely reversed by cooling in flowing argon. We do not observe a transition of the orthorhombic films to the tetragonal phase up to 800°C in flowing oxygen. We observe that the major impurity phases to appear under non-optimal annealing conditions are oriented phases of $YCuO_2$ and $BaCu_2O_2$, with Y_2BaCuO_5 and $Y_2Cu_2O_5$ conspicuously absent. These conclusions have been drawn from a study that uses perturbed angular correlation spectroscopy to probe the local microstructure of the films.

Order No.: JA804-032

Structural characterization of $YBa_2Cu_3O_{7-\delta}/Y_2O_3$ composite films

P.R. Broussard*, M.A. Wall+, J. Talvacchio#
*(*Naval Research Laboratory, +Lawrence Livermore National Laboratory, #Northrop Grumman Science and Technology Center)*

Using 4-circle x-ray diffraction and transmission electron microscopy we have studied the microstructure and in-plane orientation of the phases present in thin film composite mixtures of $YBa_2Cu_3O_{7-\delta}$ and Y_2O_3. We see a high degree of in-plane orientation and have verified a previous prediction for the in-plane order of Y_2BaCuO_5 on (110) MgO. Transmission electron microscopy shows the composite films to be a mixture of two phases, with YBCO grain sizes of ≈ 1 μm. We have also compared our observations of the in-plane order to the predictions of a modified near coincidence site lattice model.

Order No.: JA804-033

Thermodynamically stable tungsten ohmic contacts to *n*-$In_{0.53}Ga_{0.47}As$

D.Y. Chen*, Y.A. Chang+, D. Swenson#, F.R. Shepherd§
*(*Lucent Technologies Microelectronics, +University of Wisconsin, #Michigan Technological University, §Nortel Technology)*

Based on a thermodynamic assessment of the W-In-Ga-As quaternary system, the metal W was selected as a thermodynamically stable

ohmic contact material to *n*-$In_{0.53}Ga_{0.47}As$. As-deposited contacts (on n ~ 1.4 x 10^{18} cm^{-3} $In_{0.53}Ga_{0.47}As$) had average specific contact resistances of 7 x 10^{-7} $\Omega \cdot cm^2$ as measured using the transmission line model. The contact resistances remained unchanged after rapid thermal annealing at 400°C for 1 min. or at 600°C for 1 min., and exhibited no degradation in electrical properties even after long-term annealing at 500°C for 100 h. Transmission electron microscopic examination of the contacts showed no interfacial reaction. The present investigation demonstrates the power of thermodynamics in identifying stable ohmic contacts to multicomponent semiconductors.

Order No.: JA804-034

Oxidation of $MoSi_2$/SiC nanolayered composite

J-P. Hirvonen*, P. Torri+, R. Lappalainen+, J. Likonen#, H. Kung§, J.R. Jervis§, M. Nastasi§
*(*JRC-Institute for Advanced Materials, +University of Helsinki, #VTT Chemical Technology, §Los Alamos National Laboratory)*

The oxidation behavior of a nanolayered $MoSi_2$/SiC composite material was determined at the temperature range of 400°–900°C in wet oxidation conditions. The samples were produced in the form of thin films using a sputtering technique from two different sources, and a rotating substrate holder, onto silicon single crystals and low carbon steel. For comparison, the oxidation of both constituents, $MoSi_2$ and SiC, produced with the same sputtering technique, were measured separately. The microstructure of the $MoSi_2$/SiC samples were determined with high resolution transmission electron microscopy (HRTEM) and the composition of the sputtered samples were measured using backscattering (BS) of protons. For quantitative determination of oxidation the nuclear reaction $^{16}O(d,p)^{17}O$ was utilized. Oxide layers were also analyzed using a secondary ion mass spectrometry (SIMS) and the appearance of the oxidized surface with a scanning electron microscopy (SEM). As expected the SiC films had both the lowest initial oxidation and steady state oxidation rate. The results show that the oxidation behavior of the $MoSi_2$/SiC nanolayered composite material differs from that of both its constituents and involves a degradation mechanism of its own resulting in the highest oxidation during the initial phase of the oxidation. A steady-state oxidation rate was observed after the initial transient phase to be the highest for the metastable C40 structure of the single $MoSi_2$ layer. The oxidation rate of the nanolayered structure was retarded by the SiC layers. No signs of pest disintegration were observed on either of the $MoSi_2$ containing coatings during the steady state phase of the oxidation at 500°C up to 40 h. Our results show that the oxidation of nanolayered structures can be only in part explained by the oxidation behavior of the constituents and that during the steady state oxidation of the nanolayered structure the oxidation rate is largely determined by the constituent with the lowest oxidation rate and layered structure.

Order No.: JA804-035

Interfacial precipitation in titania-doped diphasic mullite gels

S-H. Hong, N. Lee, A.H. Carim, G.L. Messing
(The Pennsylvania State University)

Interfacial precipitation in sol-gel derived, titania-doped diphasic mullite gels was investigated using conventional and high resolution transmission electron microscopy. Rutile, anatase, and brookite precipitated on the interface between {110} planes of mullite and glass pockets in the sintered body. The formation of brookite may be attributable to the Si- and Al-rich environment during precipitation. Each polymorph of titania has a unique morphology and orientation relationship with mullite. Brookite exhibits a truncated pill box shape, and anatase displays a vermicular morphology. Quenching experiments suggest that the precipitates grow and undergo phase transformations during cooling.

Order No.: JA804-036

Effect of Ba^{2+} on dielectric and electrostrictive properties of $(Pb_{1-x}Ba_x)_{0.96}Y_{0.02}(Zr_{0.75}Ti_{0.25})_{0.98}Nb_{0.02}O_3$ ceramics

K.H. Yoon, Y.W. Kim, D.H. Kang
(Yonsei University)

$(Pb_{1-x}Ba_x)(Zr_{0.75}Ti_{0.25})O_3$ ceramics were modified with Y^{3+} and Nb^{5+}, and their dielectric and electrostrictive properties were investigated as a function of x ($0.23 \le x \le 0.33$). With increasing Ba^{2+} content, the axial length (a) was increased and distortion of rhombohedral angle (90°-α) approached to zero, resulting in the increased symmetry of the $(Pb_{1-x}Ba_x)_{0.96}Y_{0.02}(Zr_{0.75}Ti_{0.25})_{0.98}Nb_{0.02}O_3$ structure. As the Ba^{2+} content increased, the maximum dielectric constant decreased and the curve of field-induced strain became a parabolic one with lower hysteresis of strain. When 25–27 mol% of Ba^{2+} was substituted on the Pb^{2+} sites, the specimens showed the excellent electrostrictive properties which were 1.04–1.17 x 10^{-3} of longitudinal strain and 12–18 % of hysteresis of strain at 10 kV/cm.

Order No.: JA804-037

Phase transition, dielectric and electrostrictive behaviors in (1-x)PYN-xPMN

D.H. Kang*, Y.H. Lee*, K.H. Yoon+
*(*The University of Suwon, +Yonsei University)*

A system of $(1-x)Pb(Yb_{1/2}Nb_{1/2})O_3$(PYN)-$xPb(Mg_{1/3}Nb_{2/3})O_3$(PMN) ($0 \le x \le 1$) has been investigated with regard to its phase transition, densification, and dielectric and electrostrictive properties. According to the XRD study, a crystal structure transformed from orthorhombic to pseudocubic at approximately x = 0.22, and the superlattice peaks were gradually weakened with increasing x, and disappeared above x = 0.22. Increasing x led to an increase in the maximum dielectric constant and a decrease in transition temperature over the entire composition range. As a result of P-E hysteresis loops, successive phase transitions of ferroelectric-antiferroelectric-paraelectric were observed to occur in the range of $0.18 \le x \le 0.25$ with increasing temperature. The direct transition into the paraelectric region was found to take place for $x \ge 0.3$. From the field-induced strain measurement, high electrostrictive coefficients, 7.3-8.2 x 10^{-2}(m^4/C^2) were determined in the PYN rich range ($x \le 0.1$) Based on the results, a phase diagram of the system was constructed with variations in x and temperature.

Order No.: JA804-038

Leakage current of Al or Nb doped $Ba_{0.5}Sr_{0.5}TiO_3$ thin films by rf magnetron sputtering

T-G. In*, S. Baik*, S. Kim+
*(*Pohang University of Science and Technology, +Sunchon National University)*

The effects of Al or Nb doping on the leakage current behaviors were studied for the $Ba_{0.5}Sr_{0.5}TiO_3$ (BST) thin films deposited on $Pt/Ti/SiO_2/Si(100)$ substrate by rf magnetron sputtering. Al and Nb were selected as acceptor and donor dopants, respectively, because they have been known to replace Ti-sites of the BST perovskite. The BST thin films prepared *in-situ* at elevated temperatures showed relatively high leakage current density and low breakdown voltage. However the BST thin films deposited at room temperature and annealed subsequently in air showed improved electrical properties. Especially, the leakage current density of the Al-doped BST thin film was measured to be around 10^{-8} A/cm^2 at 125 kV/cm, which is much lower than those of the undoped or Nb-doped thin films. The results suggest that the Schottky barriers at grain boundaries in the film interior could determine the leakage behavior in the BST thin films.

Order No.: JA804-039

https://doi.org/10.1557/S0883769400031328 Published online by Cambridge University Press

Microstructure and optical loss in epitaxial (Pb,La)TiO_3 thin films on (001) MgO

Y.M. Kang, S. Baik
(Pohang University of Science and Technology)

Surface morphologies and microstructures of epitaxial $(Pb_{1-x}La_x)TiO_3$ (PLT, x = 0.00, 0.08, 0.16, and 0.24) thin films grown on (001) MgO, have been investigated using SEM, AFM, and TEM. Surface roughness of PLT films varies severely with La concentration. For 0.08La-PLT film, a very smooth surface has been achieved with 9.3 Å of RMS roughness. 0.00La- and 0.08La-PLT films show 90° domain structure and periodic dimension of the domain is reduced by La substitution. 0.16La- and 0.24La-PLT films show the presence of triangular grains causing rough surface and poor crystal quality. However, they are distributed uniformly in 0.16La-PLT film while agglomerated in 0.24La-PLT film. Optical propagation losses of PLT films measured by prism coupling technique were 22.3, 6.0, 11.4, and 20.7 dB/cm for x = 0.00, 0.08, 0.16, and 0.24, respectively. Such a variation in optical losses seemed to be due to the surface morphology and abundance of domain boundaries that change continuously as a function of La concentration in epitaxial PLT thin films.

Order No.: JA804-040

Thin film scratch testing in two dimensions—Experiments and analysis

M.P. deBoer, J.C. Nelson, W.W. Gerberich
(University of Minnesota)

We have modified the microscratch test to create a near plane strain loading condition. In the Microwedge Scratch Test (MWST), a wedge shaped diamond indenter tip is drawn along a fine line (i.e. narrow strip of film), while simultaneously being driven into the line. We compare microwedge scratching of Zone 1 (voided grain boundaries) and Zone T (metallurgical grain boundaries) thin film specimens of sputtered tungsten on thermally grown SiO_2. Symptomatic of its weak grain boundaries, the Zone 1 film displays three separate crack systems. Because of its superior grain boundary strength, the Zone T film displayed only one of these—an interfacial crack system. By correlating fracture phenomena to signature events in the load-displacement curve, we develop governing equations for propagating interfacial cracks, including expressions for strain energy release rate, bending strain, and mode mixity. Grain boundary fracture causes Zone 1 films to spall before a stable crack is formed. Zone T films survive the bending strains and hence adhesion may be inferred from stable crack growth mechanics. We conclude by contrasting and comparing experimental results for plane strain indentation versus plane strain scratching.

Order No.: JA804-041

Role of ozone in reactive coevaporation of lead zirconate titanate thin films

K. Torii, F. Yano, Y. Fujisaki
(Hitachi Ltd.)

The role of ozone in the reactive coevaporation of the lead zirconate titanate thin film was investigated by depositing films at various growth rates with various ozone fluxes or molecular oxygen fluxes on unheated substrates and then crystallizing them using rapid thermal annealing. The oxidation state of lead in the as-deposited film was determined from the ratio of the ozone to the total metal fluxes. The amount of atomic oxygen supplied to the surface of the film was at least 10^3 times larger when the deposition was done using ozone rather than molecular oxygen. When the ozone flux was more than one-third of the total metal flux, well-oxidized films were obtained. To ensure obtaining well-oxidized film, the ozone flux should be more than twice as much.

Order No.: JA804-042

Microstructure of cosputter-deposited metal- and oxide-MoS_2 solid lubricant thin films

M.R. Hilton*, G. Jayaram+, L.D. Marks+
*(*The Aerospace Corporation, +Northwestern University)*

The effect of cosputtering small amounts of Ni (3%, 9%) and SbO_x (20%) on the final microstructure of MoS_2 lubricant thin films has been studied using a combination of scanning and transmission electron microscopy imaging, and electron and x-ray diffraction techniques. The early-growth, near-interface microstructure of both MoS_2 and 3% Ni-MoS_2 cosputtered films is revealed to be a mixture of (002) basal and elongated, large-size (100) and (110) edge islands. Cosputtering with 9% Ni induces a dramatic change in the microstructure, i.e., primarily basal domains with very small isolated regions of edge islands, while cosputtering with 20% SbO_x produces films having no long-range order. The results are compared with and are consistent with previously published x-ray absorption fine structure data. The impact of film morphology on tribological performance is discussed.

Order No.: JA804-043

Laser-induced structural transformations in MoO_3 investigated by Raman spectroscopy

E. Haro-Poniatowski*, C. Julien*, B. Pecquenard*, J. Livage*, M.A. Camacho-López+
*(*Université Pierre et Marie Curie, +Universidad Autónoma Metropolitana Iztapalapa)*

The glass-crystalline transformation induced by laser irradiation is studied in MoO_3. Before crystallization we have found that the system evolves from a low-temperature glass phase to a high-temperature glass phase. The crystallization kinetics depend strongly on the initial irradiation power. The power densities needed to induce the phase transformations, of the order of 15 W/mm^2, are relatively low and suggest the possibility of using this material as a data storage medium.

Order No.: JA804-044

On the design of 1-3 piezocomposites using topology optimization

O. Sigmund, S. Torquato, I.A. Aksay
(Princeton University)

We use a topology optimization method to design 1-3 piezocomposites with optimal performance characteristics for hydrophone applications. The performance characteristics we focus on are the hydrostatic charge coefficient $d_h^{(*)}$, the hydrophone figure of merit $d_h^{(*)}g_h^{(*)}$ and the electromechanical coupling factor $k_h^{(*)}$. The piezocomposite consists of piezoelectric rods embedded in an optical polymer matrix. We use the topology optimization method to design the optimal (porous) matrix microstructure. When we design for maximum $d_h^{(*)}$ and $d_h^{(*)}g_h^{(*)}$, the optimal transversally isotropic matrix material has negative Poisson's ratio in certain directions. When we design for maximum $k_h^{(*)}$, the optimal matrix microstructure is layered and simple to build.

Order No.: JA804-045

Influences of pile-up on the measurement of mechanical properties by load and depth sensing indentation techniques

A. Bolshakov, G.M. Pharr
(Rice University)

Finite element simulation of conical indentation of a wide variety of elastic-plastic materials has been used to investigate the influences of pile-up on the accuracy with which hardness and elastic modulus can be measured by load and depth-sensing indentation techniques. The key parameter in the investigation is the contact area, which can be determined from the finite element results either by applying standard analysis proce-

dures to the simulated indentation load-displacement data, as would be done in an experiment, or more directly, by examination of the contact profiles in the finite element mesh. Depending on the pile-up behavior of the material, these two areas may be very different. When pile-up is large, the areas deduced from analyses of the load-displacement curves underestimate the true contact areas by as much as 60%. This, in turn, leads to overestimations of the hardness and elastic modulus. The conditions under which the errors are significant are identified, and it is shown how parameters measured from the indentation load-displacement data can be used to identify when pile-up is an important factor.

Order No.: JA804-046

Further analysis of indentation loading curves: Effects of tip rounding on mechanical property measurements

Y-T. Cheng*, C-M. Cheng+, Z. Zhemin+
*(*General Motors Global Research and Development Operations, +Chinese Academy of Sciences)*

The effects of indenter tip rounding on the shape of indentation loading curves have been analyzed using dimensional and finite element analysis for conical indentation in elastic-perfectly plastic solids. A method for obtaining mechanical properties from indentation loading curves is then proposed. The validity of this method is examined using finite element analysis. Finally, the method is used to determine the yield strength of several materials for which the indentation loading curves are available in the literature.

Order No.: JA804-047

Relationships between acoustic emission signals and physical phenomena during indentation

D.F. Bahr, W.W. Gerberich
(University of Minnesota)

A commercial piezoelectric acoustic emission transducer has been used in conjunction with nanoindentation techniques to study the relationship between acoustic emission signals and discreet physical events to identify the type and strength of an event. Indentations into tungsten and iron single crystals have been used to study dislocation generation and passive film failure. In addition, indentations made into a thin nitride film on sapphire have been used to cause film delaminations. Parameters such as signal rise time and frequency for a piezoelectric sensor are related to sample geometry, and not to the type of event which caused the acoustic emission signal. As a possible calibration for acoustic emission sensors, the most meaningful parameter is the acoustic emission energy, which has been shown to scale with the elastic energy released during the event. The measured values of elastic energy released correspond very closely to those calculated using Hertzian contact mechanics.

Order No.: JA804-048

Optimization of the extraction of aluminium sulphate and ammonium aluminium sulphate alums from aluminium dross tailings

M.A. Mohamed*, M.E. Kassim+, E.A. El-katatny#
*(*South Valley University, +Assiut University, #Aluminium Company of Egypt)*

Aluminium dross tailings, an industrial waste from the Egyptian Aluminium Company (Egyptalum), were used to produce two types of alums, namely: aluminium sulphate alum and ammonium aluminium alum via two separate processes. The first process involved leaching the impurities using dilute H_2SO_4 at different solid/liquid ratios and temperatures in the form of soluble sulphates. Some dissolved aluminium was recovered as ammonium aluminium sulphate. The second process involved extraction of aluminium sulphate from the purified dross produced after leaching. This was carried out under atmospheric pressure using different concentrations of H_2SO_4. Influence of temperature, time of reaction and acid concentration on leaching and extraction processes were studied. X-ray diffraction, atomic absorption spectrometry and thermal analysis techniques were used.

Order No.: JA804-049

https://doi.org/10.1557/S0883769400031328 Published online by Cambridge University Press