

TABLE OF CONTENTS

COMMUNICATIONS

Anomalous behavior of the optical band gap of nanocrystalline ZnO thin films

V. Srikant, D.R. Clarke

Formation kinetics of nanocrystalline Fe-4wt.%Al solid solution during ball milling

H.G. Jiang, R.J. Perez, M.L. Lau, E.J. Lavernia

Pulsed laser deposition and characterization of conductive RuO₂ thin films

A. Iembo, F. Fusco, E. Arimondo, C. Ciofi, G. Pennelli, G.M. Currò, F. Neri, M. Allegrini

Crystal structure and microwave dielectric properties of M(Nb_xTa_{1-x})₂O₆ solid-solution (M = Mg or Zn)

H-J. Lee, K-S. Hong, I-T. Kim

Sol-gel processing of nanocrystalline haematite thin films

L. Armelao, A. Armigliato, R. Bozio, P. Colombo

ARTICLES

Phase coexistence and critical temperatures of the (Bi,Pb)₂Sr₂Ca₂Cu₃O_x phase under partial pressures of oxygen between 10⁻³ and 0.21 bar with and without additions of silver

M. Däumling, R. Maad, A. Jeremie, R. Flükiger

Factors controlling carbon retention in YBa₂Cu₃O_{7-δ}

E. Cazy, A. Khalfi, D.S. Smith, J.P. Bonnet

Growth of CuInSe₂ crystals in Cu-rich Cu-In-Se thin films

T. Wada, N. Kohara, T. Negami, M. Nishitani

Phase formation and thermodynamics of unstable Cu-Cr alloys

C. Michaelsen, C. Gente, R. Bormann

Stoichiometric icosahedral phase in Zn-Mg-Y system

A.P. Tsai, A. Niikura, A. Inoue, T. Masumoto

Microstructures of two-phase Ti-Cr alloys containing the TiCr₂ Laves phase intermetallic

K.C. Chen, S.M. Allen, J.D. Livingston

A study of micropyretic reactions in the Mo-Si-Al ternary system

M. Fu

High energy ball-milled Ti₂RuFe electrocatalyst for hydrogen evolution in the chlorate industry

M. Blouin, D. Guay, J. Huot, R. Schulz

Impact of boundary nucleation on product grain size distribution

W.S. Tong, J.M. Rickman, K. Barmak

Material characterization in support of the development of an anode substrate for solid oxide fuel cells

D. Simwonis, A. Naoumidis, F.J. Dias, J. Linke, A. Moropoulou

Superparamagnetic particles in ZSM-5-type ferrisilicates

A. López, F.J. Lázaro, J.L. García-Palacios, A. Larrea, Q.A. Pankhurst, C. Martínez, A. Corma

Thermodynamic coupling effect and catalyst effect for the artificial diamond growth

J-T. Wang, Z-Q. Huang, Y-Z. Wan, D.W. Zhang, H-Y. Jia

The effect of arc parameters on the growth of carbon nanotubes

J.M. Lauerhaas, J.Y. Dai, A.A. Setlur, R.P.H. Chang

Growth and structures of C₆₀ shells

H. Sakuma, M. Tachibana, H. Sugiura, K. Kojima, S. Ito, T. Sekiguchi, Y. Achiba

Investigation of growth conditions of fibrous deposits in carbon arc

P. Byszewski, K. Ukalski, E. Mizera, E. Kowalska

A new microwave dielectric ceramics based on the solid solution system between Ba(Ni_{1/3}Nb_{2/3})O₃ and Ba(Zn_{1/3}Nb_{2/3})O₃

S-Y. Cho, H-J. Youn, K-S. Hong, I-T. Kim, Y-H. Kim

Surface reactions of low-energy carbon ions with boron nitride thin films

I. Montero, L. Galán

The effect of excess bismuth on the ferroelectric properties of SrBi₂Ta₂O₉ thin films

T-C. Chen, T. Li, X. Zhang, S.B. Desu

Preparation of Pb(Zr_{0.52}Ti_{0.48})O₃ thin films on Pt/RuO₂ double electrode by a new sol-gel route

S-H. Kim, Y-S. Choi, C-E. Kim, Y-J. Oh

Determination of local high-frequency dielectric function during the cubic-to-tetragonal phase transformation in barium titanate

K.S. Katti, M. Qian, M. Sarikaya, M. Miyayama

Low temperature growth and reliability of ferroelectric memory cell integrated on Si with conducting barrier stack

A.M. Dhote, S. Madhukar, D. Young, T. Venkatesan, R. Ramesh, C.M. Cotell, J.M. Benedetto

Structure and properties of carbon nitride films synthesized by low energy ion bombardment

X-M. He, W-Z. Li, H-D. Li

JMR Abstracts provides a listing of preliminary titles and abstracts tentatively scheduled to appear in the corresponding issue of *Journal of Materials Research*. Copyright 1997 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.

Mechanism of 1:1 nonstoichiometric short-range ordering in La-doped Pb(Mg_{1/3}Nb_{2/3})O₃ relaxor ferroelectrics

K-M. Lee, H.M. Jang, W-J. Park

Enhanced diffuse phase transition and defect mechanism of Na-doped Pb(Mg_{1/3}Nb_{2/3})O₃ relaxor ferroelectrics

K-M. Lee, H-M. Jang

Influence of substrate annealing on the epitaxial growth of BaTiO₃ thin films by metalorganic chemical vapor deposition

C.S. Hwang, M.D. Vaudin, G.T. Stauff

Morphological investigations on mesostructured metal oxides

V. Weidenhof, F. Gropper, U. Müller, L. Marosi, G. Cox, R. Houbertz, U. Hartmann

A high-resolution electron microscopy study of blue-light emitting β -SiC nanoparticles in C⁺-implanted silicon

Y.H. Gao, Z. Zhang, L.S. Liao, X.M. Bao

Influence of substitutional nitrogen in synthetic saw-grade diamond on crystal strength

W.E. Jackson, S.W. Webb

Preparation of semiconductive SrTiO₃ thin films by metalorganic chemical vapor deposition and their electrical properties

D. Nagano, H. Funakubo, O. Sakurai, K. Shinozaki, N. Mizutani

Polyimide degradation induced by irradiation with N⁺ ions

V. Švorčík, I. Miček, V. Rybka, V. Hnatowicz, F. Černý

ABSTRACTS

COMMUNICATIONS

Anomalous behavior of the optical band gap of nanocrystalline ZnO thin films

V. Srikant, D.R. Clarke

(University of California-Santa Barbara)

The optical band gap of ZnO films on fused silica in the carrier concentration regime of 10^{18} – 10^{20} /cm³ is reported. Contrary to theoretical predictions there is an anomalous increase in the band gap of ZnO films at a carrier concentration of 5×10^{18} /cm³, followed by an abrupt decrease at a critical concentration of 3 – 4×10^{19} /cm³ before the optical band gap rises again. Similar observations have been made before but an explanation of these observations was lacking. We propose a model based on the existence of potential barriers at the grain boundaries causing quantum confinement of the electrons in the small grains realized in these films. Quantum confinement leads to the initial rise in the optical band gap. On increasing the carrier concentration to the critical value, the potentials at the grain boundaries collapse leading to the abrupt decrease in the optical band gap. Above this carrier concentration the films behave according to existing many-body theories.

Order No.: JA707-001

© 1997 MRS

Formation kinetics of nanocrystalline Fe-4wt.%Al solid solution during ball milling

H.G. Jiang, R.J. Perez, M.L. Lau, E.J. Lavernia

(University of California-Irvine)

Formation of nanocrystalline Fe-4wt.%Al solid solution has been achieved through SPEX ball milling of blended elemental Fe and Al powders. Differential scanning calorimetry (DSC) and x-ray diffraction (XRD) have been employed to follow the structural evolution during the ball milling process. Exothermic peaks exhibited in DSC diagrams of the powders milled for 10 to 60 min yielded thermal enthalpies corresponding to the formation of Fe-4wt.%Al solid solution, from which the kinetics of formation were found to follow the Johnson-Mehl-Avrami equation. Assessment of the kinetic parameter n reveals a diffusion controlled mechanism, in which grain and interphase boundaries may play a crucial role, during the solid solution formation of Fe-4wt.%Al.

Order No.: JA707-002

© 1997 MRS

Pulsed laser deposition and characterization of conductive RuO₂ thin films

A. Iembo*, F. Fusco*, E. Arimondo*, C. Ciofi*, G. Pennelli*, G.M. Currò*, F. Neri*, M. Allegrini*

*(*Università di Pisa, +Università di Messina)*

RuO₂ thin films have been produced on silicon-based substrates by *in-situ* pulsed laser deposition for the first time. The electrical properties, the surface characteristics, the crystalline structure and the film-substrate

interface of deposited samples have been investigated by 4-probe resistance vs. temperature technique, scanning electron microscopy, x-ray photoelectron spectroscopy, x-ray diffraction, and transmission electron microscopy, respectively. The films show good electrical properties. The RuO₂-substrate interface is very thin (≈ 3 nm), since not degraded by any annealing process. These two characteristics render our films suitable to be used as electrodes in PZT-based capacitors.

Order No.: JA707-003

© 1997 MRS

Crystal structure and microwave dielectric properties of M(Nb_xTa_{1-x})₂O₆ solid-solution (M = Mg or Zn)

H-J. Lee*, K-S. Hong*, I-T. Kim*

*(*Seoul National University, +Korea Institute of Science and Technology)*

The microwave dielectric characteristics and crystal structure of the Zn(Nb_xTa_{1-x})₂O₆ and Mg(Nb_xTa_{1-x})₂O₆ systems have been investigated. It was found that both systems exhibited a morphotropic phase transition. Based on the results, it was suggested that permittivity and temperature coefficient of resonant frequency depend more on crystal structure rather than on chemical composition. It was also suggested that a two phase mixture is better than a solid-solution for achieving both high quality factor and good temperature stability.

Order No.: JA707-004

© 1997 MRS

Sol-gel processing of nanocrystalline haematite thin films

L. Armelao*, A. Armigliato*, R. Bozio*, P. Colombo*

*(*Università di Padova, +Istituto LAMEL)*

The microstructure of Fe₂O₃ sol-gel thin films, obtained from Fe(OCH₂CH₃)₃, was investigated by x-ray diffraction (XRD), transmission electron microscopy (TEM), and Raman spectroscopy. Samples were nanocrystalline from 400°C to 1000°C and the crystallized phase was haematite. In the coatings, the α -Fe₂O₃ clusters were dispersed as single particles in a network of amorphous ferric oxide.

Order No.: JA707-005

© 1997 MRS

ARTICLES

Phase coexistence and critical temperatures of the (Bi,Pb)₂Sr₂Ca₂Cu₃O_x phase under partial pressures of oxygen between 10⁻³ and 0.21 bar with and without additions of silver

M. Däumling, R. Maad, A. Jeremie, R. Flükiger

(Université de Genève)

We have investigated the stability of the (Bi,Pb)₂Sr₂Ca₂Cu₃O_x phase for the stoichiometry (Bi:Pb:Sr:Ca:Cu = 1.72:0.34:1.83:1.97:3.13), subjecting it to temperatures between 700 and 850°C under various oxygen partial pressures. A narrow region was found in which Bi,Pb(2223) was the only superconducting phase. This region follows closely the thermal decomposition line. X-ray pure Bi,Pb(2223) will partially decompose if treated out-

side of the stability region. For a given oxygen partial pressure the Bi,Pb(2223) phase tends to coexist with the 2201 phase for temperatures above, and the 2212 phase for temperatures below, this region. At even lower temperatures an additional lead-rich phase appears. Critical temperatures T_c vary little with treatment and range between 108.5 K and 110.8 K. If 10% silver is added to the starting powder, the phase coexistence regions shift. Silver does not seem to have a significant effect on the absolute values of the critical temperature. The Bi,Pb(2223) thermal decomposition temperature for a given oxygen pressure is lowered by at least 10 K by the presence of Ag.

Order No.: JA707-006

© 1997 MRS

Factors controlling carbon retention in YBa₂Cu₃O_{7-δ}

E. Cazy, A. Khalifi, D.S. Smith, J.P. Bonnet

(Laboratoire de Matériaux Céramiques et Traitement de Surface)

Natural degradation of YBa₂Cu₃O_{7-δ} powders leads to trapping of CO₂ by the powder. The presence of residual carbon in ceramics or textured materials can strongly affect the superconducting properties. Optimal conditions for carbon elimination during thermal treatment are defined. Amounts of carbon lower than 500 ppm are easily obtained when thermal treatment is performed in temperature, gas flowing rate, and heating ramp conditions allowing CO₂ departure before pore closure. Liquid phase formation and presence of BaCuO₂ are limiting factors. An oxycarbonate formed by reaction between this latter compound and evolved CO₂ is implied in the last step of the decarbonation process.

Order No.: JA707-007

© 1997 MRS

Growth of CuInSe₂ crystals in Cu-rich Cu-In-Se thin films

T. Wada, N. Kohara, T. Negami, M. Nishitani

(Matsushita Electric Ind. Co., Ltd.)

A Cu-rich CuInSe₂ (CIS) thin film with an atomic ratio of Cu/In = 3.6 was characterized using high-resolution and analytical transmission electron microscopy (TEM). The film was deposited on a Mo coated soda-lime glass substrate by physical vapor deposition. Rutherford backscattering spectroscopy (RBS) and Auger electron spectroscopy (AES) showed that a secondary impurity phase such as Cu₂Se segregated on the CIS surface. The three-dimensional crystallographic relationship between the Cu₂Se and CIS was found to be (111)_{Cu₂Se} || (111)_{CIS} and [011]_{Cu₂Se} || [011]_{CIS} where the Cu₂Se and CIS had pseudo-cubic structures with $a = 5.8 \text{ \AA}$ and $a = 11.6 \text{ \AA}$, respectively. CuPt type CIS could be observed near the interface between the Cu₂Se and CIS. A growth model of CIS crystals under Cu and Se excess conditions is proposed based on the results of TEM. The characteristics of the CIS growth model in Cu-rich CIS film are summarized as follows: (1) CIS crystals are produced from Cu₂Se crystals by a "topotactic reaction," (2) sphalerite and/or CuPt type CIS are produced first after the reaction, and (3) the metastable sphalerite and/or CuPt type CIS is then transformed to the stable chalcopyrite CIS phase.

Order No.: JA707-008

© 1997 MRS

Phase formation and thermodynamics of unstable Cu-Cr alloys

C. Michaelsen, C. Gente, R. Bormann

(GKSS Research Center)

The quantitative description of highly non-equilibrium processes for the preparation of metastable and unstable phases requires the determination of the thermodynamic functions of the system under investigation. However, in systems such as Cu-Cr which are immiscible in the equilibrium states, the determination of the thermodynamic functions over the entire concentration range is often difficult if not impossible because reliable experimental data are not available for the metastable or unstable regime. The present paper demonstrates that such data can be obtained by a combination of thin film deposition techniques and differential scanning calorimetry. It is concluded that the phase formation in such thin films can be described in terms of the thermodynamics of the system, even when the heats of mixing are highly positive. The results indicate that models of the regular solution type still provide a reasonable description of the thermodynamic functions of such alloys.

Order No.: JA707-009

© 1997 MRS

Stoichiometric icosahedral phase in Zn-Mg-Y system

A.P. Tsai, A. Niikura, A. Inoue, T. Masumoto

(Tohoku University)

Stoichiometric composition and formation process of the icosahedral phase in the Zn-Mg-Y system have been studied. The icosahedral phase exhibits a stoichiometric composition in the vicinity of Zn₆₀Mg₃₀Y₁₀. During cooling, a (Zn,Mg)₅Y phase primarily crystallizes from the melt at ~960 K and then undergoes a peritectic reaction with the residual Mg-enriched melt (~Mg₇Zn₃) at ~820 K to form the icosahedral phase. The melt with a constant composition close to Mg₇Zn₃ is in equilibrium with the (Zn,Mg)₅Y phase above the peritectic temperature in a wide compositional range.

Order No.: JA707-010

© 1997 MRS

Microstructures of two-phase Ti-Cr alloys containing the TiCr₂ Laves phase intermetallic

K.C. Chen, S.M. Allen, J.D. Livingston

(Massachusetts Institute of Technology)

Microstructures of two-phase Ti-Cr alloys (Ti-rich bcc+TiCr₂ and Cr-rich bcc+TiCr₂) are analyzed. A variety of TiCr₂ precipitate morphologies is encountered with different nominal alloy compositions and annealing temperatures. Lattice constants and crystal structures are determined by x-ray diffraction (XRD) and transmission electron microscopy (TEM). Orientation relationships between the beta bcc solid-solution and C15 TiCr₂ Laves phase are understood in terms of geometrical packing, and are consistent with a Laves phase growth mechanism involving twinning.

Order No.: JA707-011

© 1997 MRS

A study of micropyretic reactions in the Mo-Si-Al ternary system

M. Fu

(Micropyretics Heaters International Inc.)

Micropyretic synthesis technique employs self-sustaining exothermic (combustion) reactions for the preparation of various ceramic, intermetallic, and composite materials. In the present work, the combustion reactions of Mo and Si with Al additions have been systematically studied. The atomic mixtures of the reactant powders are chosen to be Mo+(2-x)Si+xAl with $x = 0-0.4$. In comparison with the Mo+2Si reaction which leads to the formation of MoSi₂, the substitution of Al for Si decreases the sample ignition temperature but increases the intensity of the combustion reactions. In addition, the substitution of Al for Si results in the formation of a ternary intermetallic phase, called molybdenum aluminosilicide Mo(Si,Al)₂, in the synthesized product. When the content of Al in the reactant mixtures reaches 0.4, nearly single phase Mo(Si,Al)₂ is obtained and no MoSi₂ is detected in the reaction product. These influences are analyzed by using XRD, SEM, and DTA. The effect of Al additions on the reaction mechanism is also discussed.

Order No.: JA707-012

© 1997 MRS

High energy ball-milled Ti₂RuFe electrocatalyst for hydrogen evolution in the chlorate industry

M. Blouin*, D. Guay*, J. Huot*, R. Schulz*

*(*INRS-Énergie et Matériaux, *Institut de Recherche d'Hydro-Québec)*

The high energy mechanical alloying of a Ti-Ru-Fe powder mixture (atomic ratio 2:1:1) has been performed by extensive ball-milling in a steel crucible. The structural evolution of the resulting materials has been studied by x-ray powder diffraction analysis. The identification of the various phases present in the materials, as well as the crystallite size and strain, has been performed by Rietveld refinement analysis. In the first stage of the material transformation, Ru or Fe atoms dissolved into Ti to yield to the formation of β-Ti. Upon further ball-milling, almost all the original constituents of the powder mixture have disappeared and a new simple cubic Ti₂RuFe phase is formed, with a crystallite size as small as 8 nm. The electrochemical properties of these materials have been tested in a typical chlorate electrolyte by cold-pressing the powders into disk electrodes. At 20 h of ball-milling, where the phase concentration of Ti₂RuFe reaches 96%, a reduction of the activation overpotential at 250 mA cm⁻² of nearly 250 mV is observed when compared to that of a pure iron electrode.

Order No.: JA707-013

© 1997 MRS

Impact of boundary nucleation on product grain size distribution

W.S. Tong, J.M. Rickman, K. Barnak
(Lehigh University)

We examine quantitatively the impact of boundary nucleation on the size distribution of product grains in a computer simulation of a two-dimensional phase transformation. This is accomplished by determining the probability distribution of product grain areas under different nucleation conditions. Specifically, a comparison of the moments of normalized area distributions of product grains arising from site-biased nuclei with the corresponding moments of the area distribution of Voronoi grains reveals those spatial features of the collection of catalytic sites which most affect product microstructure. The impact of other relevant length scales, including the square root of the inverse nucleation site density, the lattice parameter, and the system size on microstructure is also discussed.

Order No.: JA707-014

© 1997 MRS

Material characterization in support of the development of an anode substrate for solid oxide fuel cells

D. Simwonis*, A. Naoumidis*, F.J. Dias*, J. Linke*, A. Moropoulou*
(*National Technical University of Athens, *Forschungszentrum Jülich GmbH)

A new design for solid oxide fuel cells (SOFCs) was developed aiming at the reduction of the total electrical resistance of the cell. The thickness of the electrolyte was decreased, while the anode took on the role of the substrate. The pore structure with respect to gas permeability of this component has to be optimized for the proper operation of this design.

Anode substrates, consisting of a cermet (yttrium-stabilized ZrO₂ and metallic Ni) and produced by two different processes, coat mix and tape casting, were characterized with respect to pore structure (shape and mean radius), porosity (total, open and permeable), pore size distribution and air permeability. The following methods were used: 1) optical and electron scanning microscopy in combination with image analysis, 2) mercury porosimetry, and 3) air permeability. Correlations between air permeability and porosity, and also the percentage of permeable pores in anodes, show the superiority of coat mix samples to tape-cast ones. It has been observed that the coat mix process can produce anode substrates with interconnecting porosity, while tape casting, as used in this study, needs some modifications in order to be appropriate for this purpose.

Order No.: JA707-015

© 1997 MRS

Superparamagnetic particles in ZSM-5-type ferrisilicates

A. López*, F.J. Lázaro*, J.L. García-Palacios*, A. Larrea*, Q.A. Pankhurst*, C. Martínez#, A. Corma#
(*Universidad de Zaragoza-Consejo Superior de Investigaciones Científicas, *University College London, #Consejo Superior de Investigaciones Científicas-Valencia)

As-synthesized, low-iron content ferrisilicates of ZSM-5-type contain well separated Fe(III) ions in a tetrahedral environment and display paramagnetic behavior. After hydrothermal treatment, the iron ions are partially extracted from the framework, generating nanosize iron oxide or oxyhydroxide ferrimagnetic particles. This process has been studied by transmission electron microscopy (TEM), Mössbauer spectroscopy, magnetic ac susceptibility (χ_{ac}) and field dependent magnetization, on samples containing up to 6.7 wt.% Fe. The experiments evidence the growth of non-aggregated particles, with a typical size around 3 nm, presumably located at the surface of the ferrisilicate crystallites. From a thorough granulometric analysis involving TEM and χ_{ac} data it is concluded that, in the range from 1.5 to 4.6 wt.% Fe, the particle size distributions are significantly independent of the iron content.

Order No.: JA707-016

© 1997 MRS

Thermodynamic coupling effect and catalyst effect for the artificial diamond growth

J-T. Wang*, Z-Q. Huang*, Y-Z. Wan*, D.W. Zhang*, H-Y. Jia*
(*Fudan University, *Tongji University)

The activated chemical vapor deposition (CVD) diamond process became one of the world-wide interesting projects in the 1980s. The basic question is why diamond can grow under activated low pressure conditions. The driving force of the transformation from graphite to diamond under low pressure is coming from a coupled reaction of the association of

super-equilibrium atomic hydrogen. The thermodynamic coupling effect in the activated CVD process is different from the catalyst effect in the high pressure catalyst-assisted process for the artificial diamond growth.

Order No.: JA707-017

© 1997 MRS

The effect of arc parameters on the growth of carbon nanotubes

J.M. Lauerhaas, J.Y. Dai, A.A. Setlur, R.P.H. Chang
(Northwestern University)

The influence of starting carbon material on the generation of carbon nanotubes is investigated. Comparisons are made between oriented graphite, randomly oriented graphite, carbon black, and a polycyclic aromatic hydrocarbon as carbon sources in helium and hydrogen arcs. Transmission electron microscopy investigation of the redeposited rod formed on the cathode and the soot from the chamber walls provides evidence for the building blocks that lead to the nanostructures formed. It is postulated that polycyclic aromatic hydrocarbons are precursors for carbon nanotube growth in a hydrogen arc. While, in the case of helium, low molecular weight carbon ions and molecules have been previously hypothesized by others to be the building blocks for nanotube growth.

Order No.: JA707-018

© 1997 MRS

Growth and structures of C₆₀ shells

H. Sakuma*, M. Tachibana*, H. Sugiura*, K. Kojima*, S. Ito*, T. Sekiguchi*, Y. Achiba#
(*Yokohama City University, *Tohoku University, #Tokyo Metropolitan University)

The growth of the shells of C₆₀ crystals was carried out under various conditions. The detailed structures of the grown shells were investigated by transmission electron microscopy and Raman spectroscopy. The shells were formed during thermal sublimation of the C₆₀ crystals, which were irradiated with white light in air. The shells were mainly composed of a kind of amorphous carbon. From these results, it is suggested that the oxygen induced disintegration of C₆₀ cages is responsible for the shell formation.

Order No.: JA707-019

© 1997 MRS

Investigation of growth conditions of fibrous deposits in carbon arc

P. Byszewski*, K. Ukalski*, E. Mizera*, E. Kowalska*
(*Institute of Vacuum Technology, *PAN)

Carbon fibrous deposits grown in carbon DC electric arc at various buffer gas pressure and arc current were investigated by transmission and scanning electron microscopy. The fibers contained in the deposits consisted of bundles of carbon tubes. It was found that yield and morphology were very sensitive to both parameters, and sintering of the tubes could be prevented by adjusting buffer gas pressure for a given current. It is argued that these parameters control expansion of carbon gas and condensation rate and, therefore, energy flow to the cathode. To purify samples by oxidation and to observe differences in resistance against oxidation of samples obtained at various conditions, the thermogravimetry method was used.

Order No.: JA707-020

© 1997 MRS

A new microwave dielectric ceramics based on the solid solution system between Ba(Ni_{1/3}Nb_{2/3})O₃ and Ba(Zn_{1/3}Nb_{2/3})O₃

S-Y. Cho*, H-J. Youn*, K-S. Hong*, I-T. Kim*, Y-H. Kim*
(*Seoul National University, *Korea Institute of Technology)

Microwave dielectric properties of the solid solution between Ba(Ni_{1/3}Nb_{2/3})O₃ and Ba(Zn_{1/3}Nb_{2/3})O₃ was investigated. Samples were prepared by the conventional mixed oxide method as well as the Pechini method. Sintered samples were analyzed using x-ray diffraction and scanning electron microscopy and their microwave dielectric properties were measured by the post resonator method. The sample prepared by the Pechini method revealed excellent dielectric properties, i.e. permittivity of 35.6, quality factor of 5,700 at 10 GHz, and very small temperature coefficient of resonant frequency. Order-disorder behavior of this solid solution system was found to depend on processing parameters. Variation in microwave dielectric properties was discussed in terms of order-disorder behavior, chemical composition, mixture rule, etc.

Order No.: JA707-021

© 1997 MRS

Surface reactions of low-energy carbon ions with boron nitride thin films

I. Montero, L. Galán

(CSIC and Universidad Autónoma de Madrid)

The chemical reactions between hyperthermal species from a methane plasma and the boron nitride surface has been studied. In this work we report an x-ray photoemission study of the boron nitride with varying degrees of carburization. The carbon ions react forming C-B and C-N bonds: for surface carbon concentration, smaller than ~0.30, C-B bonds are formed, while for higher surface carbon concentrations C-N bonds are also observed. In addition, the binding energy difference between the N 1s and B 1s core levels increases with increasing carbon content of the film. These chemical shifts are interpreted in terms of the decrease of the ionicity of the material as a consequence of the increase in the number of C-B and C-N bonds. For surface carbon concentration higher than 0.30, amorphous carbon is also formed that grows and finally forms a surface layer. The valence band spectra of the BNC compounds show that the density of states filling the gap at about 15 eV between the two characteristic peaks of the valence band of BN, marking the nitrogen 2s orbitals and the boron and nitrogen 2p electrons, and the orbital hybridization between the 2s of boron and 2p states increases with increasing carbon fluence as a consequence of the hybridization with carbon orbitals.

Order No.: JA707-022

© 1997 MRS

The effect of excess bismuth on the ferroelectric properties of SrBi₂Ta₂O₉ thin films

T-C. Chen, T. Li, X. Zhang, S.B. Desu

(Virginia Polytechnic Institute and State University)

The effect of excess bismuth on the ferroelectric properties of SrBi₂Ta₂O₉ (SBT) thin films having a perovskite-like layered structure was investigated for excess bismuth contents ranging from 0% to 100%. For the first time, a limited solid solution of SBT and Bi₂O₃ was shown to exist when the amount of excess Bi was less than 50%. The formation of a solid solution enhanced the grain size and *a-b* plane orientation of the films, resulting in substantial improvement in the ferroelectric hysteresis properties of the films. On the other hand, when the amount of excess Bi exceeded 50%, Bi₂O₃ appeared as a second phase, which led to high leakage current and poor ferroelectric hysteresis curves; 30–50% excess Bi content was found to be the optimum composition with respect to grain size, crystallographic orientation, and single-phase formation. Within this range, SBT films exhibit low leakage current density (~10⁻⁹ A/cm²) and maximum remanent polarization (2Pr~12 μC/cm²).

Order No.: JA707-023

© 1997 MRS

Preparation of Pb(Zr_{0.52}Ti_{0.48})O₃ thin films on Pt/RuO₂ double electrode by a new sol-gel route

S-H. Kim*, Y-S. Choi*, C-E. Kim*, Y-J. Oh*

(*Yonsei University, *Korea Institute of Science and Technology)

Pb(Zr_{0.52}Ti_{0.48})O₃ [PZT] thin film on Pt/RuO₂ double electrode was successfully prepared by using a new alkoxide-alkanolamine sol-gel method. It was observed that the use of Pt/RuO₂ double electrode reduced leakage current, resulting in a marked improvement in the leakage characteristics and more reliable capacitors. Typical P-E hysteresis behavior was observed even at low applied voltage of 5V, manifesting greatly improved remanance and coercivity. Fatigue and breakdown characteristics, measured at 5V, showed stable behavior, and no degradation in polarization was observed up to 10¹¹ cycles.

Order No.: JA707-024

© 1997 MRS

Determination of local high-frequency dielectric function during the cubic-to-tetragonal phase transformation in barium titanate

K.S. Katti*, M. Qian*, M. Sarikaya*, M. Miyayama*

(*University of Washington, *University of Tokyo)

Transmission electron energy loss spectroscopy was used to obtain local dielectric properties in barium titanate. The high frequency dielectric function of the material was studied dynamically during the cubic-to-tetragonal (c→t) phase transformation in conjunction with the effect of a small amount (0.9%) of donor dopant (niobium). In order to obtain the local dielectric function during the phase transformation, Kramers-Kronig relations were applied to the energy loss measurements.

The optical excitations in the energy loss spectra were consistent with band structure results from the literature. The Re (1/ε), real part of the inverse dielectric function, obtained from the energy loss data indicated a change at the phase transformation. Specifically, a broadening of the valence plasmon excitation is observed which is attributed to the order-disorder nature of the t→c transformation. A 0.4 eV shift in the volume plasmon was observed in the Nb-doped sample in all regions (within grains as well as at grain boundaries) indicating a uniform incorporation of the dopant in the lattice. In this paper, the changes in the dielectric function, such as shifts in collective excitations, are attributed to a large contribution from loosely bound Nb electrons. Furthermore, it is demonstrated that it is possible to obtain local (~10 nm) physical property of a complex material dynamically at relatively high temperature.

Order No.: JA707-025

© 1997 MRS

Low temperature growth and reliability of ferroelectric memory cell integrated on Si with conducting barrier stack

A.M. Dhote*, S. Madhukar*, D. Young*, T. Venkatesan*, R. Ramesh*, C.M. Cotell*, J.M. Benedetto*

(*University of Maryland, *U.S. Naval Research Laboratory, *Army Research Laboratories)

Polycrystalline LSCO/PNZT/LSCO ferroelectric capacitor heterostructures were grown by pulsed laser deposition using a composite conducting barrier layer of Pt/TiN on poly-Si/Si substrate. The growth of the ferroelectric heterostructure is accomplished at a temperature in the range of 500–600°C. This integration results in a 3-dimensional stacked capacitor-transistor geometry which is important for high density non-volatile memory (HDNVM) applications. Transmission electron microscopy shows smooth substrate-film and film-film interfaces without any perceptible interdiffusion. The ferroelectric properties and reliability of these integrated capacitors were studied extensively at room temperature and 100°C for different growth temperatures. The capacitors exhibit excellent reliability, both at room temperature and at elevated temperatures, making them very desirable for HDNVM applications.

Order No.: JA707-026

© 1997 MRS

Structure and properties of carbon nitride films synthesized by low energy ion bombardment

X-M. He, W-Z. Li, H-D. Li

(Tsinghua University)

Carbon nitride films have been synthesized at low substrate temperature by Ar⁺ sputtering a graphite target with concurrent N⁺ assisted bombardment. It was disclosed that N⁺ bombardment with low energies of 150–400 eV and beam densities of 0.16–0.23 mA cm⁻² was favorable to grow up carbon nitride films with high N/C atomic composition ratios of 0.47–0.56. The spectra of x-ray photoelectron spectroscopy and infrared spectroscopy show that the low energy N⁺ bombardment activates nitrogen atoms to combine carbon atoms in unpolarized covalent bonds. And under the 150–300 eV and 0.16–0.23 mA cm⁻² N⁺ assisted bombardment, the formed films are identified by transmission electron microscopy to possess the β-C₃N₄ microcrystalline structure. The films exhibit an extremely high hardness of 5260 kgf/mm², a high resistivity of 4.8 × 10¹² Ω × cm, and the excellent optical transmittance. Friction and wear tests show that carbon nitride films on steel substrate can perform the even wear in low friction coefficients of 0.05–0.16 while raising wear loads up to 20 N.

Order No.: JA707-027

© 1997 MRS

Mechanism of 1:1 nonstoichiometric short-range ordering in La-doped Pb(Mg_{1/3}Nb_{2/3})O₃ relaxor ferroelectrics

K-M. Lee, H.M. Jang, W-J. Park

(Pohang University of Science and Technology-POSTECH)

The mechanism of the 1:1 nonstoichiometric short-range ordering in donor-doped Pb(B^{1/3}B^{2/3})O₃-type relaxor perovskites was examined using La₂O₃-doped Pb(Mg_{1/3}Nb_{2/3})O₃ (PMN) system as a typical example. Based on the dielectric analysis and the TEM observation, the observed increase in the degree of diffuse phase transition (DPT) in the presence of La₂O₃ was interpreted as the enhancement of the 1:1 nonstoichiometric short-range ordering accompanied with the growth of the negatively charged nanodomains. The mechanism of the defect process responsible for the

1:1 nonstoichiometric short-range ordering was elucidated by analyzing the electrical conductivity of the La-doped PMN system as a function of the partial pressure of oxygen. It was shown that the substitution of La^{3+} ions for Pb^{2+} ions in the A-site sublattice of perovskite PMN produced the positively charged La_{Pb} sites with a concomitant generation of electrons for the electronic compensation. This expedites the growth of the nonstoichiometrically ordered nanodomains in a disordered matrix.

Order No.: JA707-028

© 1997 MRS

Enhanced diffuse phase transition and defect mechanism of Na-doped $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ relaxor ferroelectrics

K.-M. Lee, H.-M. Jang

(Pohang University of Science and Technology-POSTECH)

The diffuse phase transition (DPT) characteristics and the associated defect mechanism of Na-doped $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) relaxor perovskite were studied. The enhanced DPT and the decrease in the intensity of the superlattice reflection were observed in the presence of Na_2O . These contradictory observations were interpreted in terms of the inhibition of the growth of the 1:1 nonstoichiometric short-range ordered domains and the increase in the microcompositional fluctuation of the B-site cations caused by the formation of negatively charged Na_{Mg} sites. The mechanism of the associated defect process was then elucidated by analyzing the electrical conductivity as a function of the oxygen partial pressure. It was shown that the substitution of Na^+ ions for Mg^{2+} ions in the B-site sublattice of perovskite PMN produced the negatively charged Na_{Mg} sites with a concomitant generation of oxygen vacancies (V_{O}'') for the ionic compensation. This expedites the enhancement of the compositional inhomogeneities of the B-site cations and suppresses the growth of the nonstoichiometrically ordered nanodomains in a disordered matrix.

Order No.: JA707-029

© 1997 MRS

Influence of substrate annealing on the epitaxial growth of BaTiO_3 thin films by metalorganic chemical vapor deposition

C.S. Hwang*, M.D. Vaudin*, G.T. Stauff*

(*National Institute of Standards and Technology, *Advanced Technology Materials)

BaTiO_3 thin films were deposited by metalorganic chemical vapor deposition at 840°C on two differently treated (100) MgO single crystal substrates. One MgO substrate was only mechanically polished and the other substrate was polished and then annealed at 1100°C for 4 hours in oxygen. Observation by transmission electron microscopy showed that the BaTiO_3 thin film deposited on the unannealed substrate was fine-grained and that the whole film was epitaxial (001) in nature. In contrast, the film deposited on the annealed substrate consisted of large, (100)-oriented, epitaxial grains within which were distributed (110)-oriented grains with random in-plane orientations. These differences in BaTiO_3 films deposited on differently treated substrates are discussed with reference to the surface structure of the MgO substrate and nucleation kinetics of BaTiO_3 thin films on MgO.

Order No.: JA707-030

© 1997 MRS

Morphological investigations on mesostructured metal oxides

V. Weidenhof*, F. Groppert*, U. Müller*, L. Marosi#, G. Cox#, R. Houbertz*, U. Hartmann*

(*University of Saarbrücken, *ZAK/Z-BASF AG, #ZAA/S-BASF AG)

The synthesis and characterization of mesostructured zirconia and titanium oxides is presented. The samples were investigated by x-ray powder diffraction (XRD), transmission electron microscopy (TEM), and atomic force microscopy (AFM). XRD and TEM only revealed lamellar structures for both materials, whereas AFM could detect locally restricted initial stages of cubic or hexagonal phases in a globally lamellar Ti oxide.

Order No.: JA707-031

© 1997 MRS

A high-resolution electron microscopy study of blue-light emitting β -SiC nanoparticles in C⁺-implanted silicon

Y.H. Gao*, Z. Zhang*, L.S. Liao*, X.M. Bao*

(*Chinese Academy of Sciences, *Nanjing University)

A high-resolution electron microscopy study of β -SiC nanoparticles formed by C⁺-implantation of single crystal silicon with subsequent annealing has been carried out. The as-implanted sample had a tri-layered structure, in which the surface layer, A, and the bottom layer, C, were crystalline

but damaged, and the middle layer, B, was amorphous. After annealing this structure, β -SiC particles were formed throughout the tri-layered structure but with different forms: a few epitaxial β -SiC nanoparticles in layers A, and C, and more random nanoparticles in layer B. The β -SiC nanoparticles, in the size range 2–8 nm, should be responsible for the blue-emitting effect of the silicon based porous β -SiC.

Order No.: JA707-032

© 1997 MRS

Influence of substitutional nitrogen in synthetic saw-grade diamond on crystal strength

W.E. Jackson, S.W. Webb

(GE Superabrasives)

The amount and defect-type of substitutional nitrogen in synthetic diamond strongly influences crystal strength. There is an optimum amount of nitrogen that yields the highest compressive fracture strength for crystals derived from common growth conditions. It is postulated that the role of nitrogen is to charge-balance vacancies created during growth. If too little nitrogen exists, the diamond vacancies are not charge-balanced and may serve as crack initiation and/or propagation sites. Excess nitrogen above that required to charge-balance vacancies may weaken the lattice by adding local strain to the crystal.

IR microscopy indicates that most of the substitutional nitrogen in synthetic diamond is increased in the vicinity of the intersections of growth sectors on the crystal surface. Most surface IR-visible nitrogen is biased toward the (111)-(100) intersection. The bias in incorporation of substitutional nitrogen at external growth sector intersections (i.e., edges and corners) of an industrial high-grade saw diamond crystal influences the progression of fatigue by microfracture during cutting of hard stone.

Order No.: JA707-033

© 1997 MRS

Preparation of semiconductive SrTiO_3 thin films by metalorganic chemical vapor deposition and their electrical properties

D. Nagano, H. Funakubo, O. Sakurai, K. Shinozaki, N. Mizutani

(Tokyo Institute of Technology)

Insulating epitaxially grown SrTiO_3 thin films were prepared on (100)MgO substrates by metalorganic chemical vapor deposition (MOCVD). Semiconductive SrTiO_3 thin films were obtained by the rapid cooling after reheating in reduction atmosphere. The microstructure, crystal structure and electrical property of these films were investigated. The electrical properties varied by the composition of films and heat treatment conditions, i.e., the heating temperature, the oxygen partial pressure, and the cooling rate after the annealing. Change of the resistivity of the film was attributed to that of the carrier concentration. Mobility of the films was unchanged, and the value was almost the same order of that of bulks. The lowest resistivity of $0.1 \Omega\text{-cm}$ was obtained when a sample of $\text{Ti}/\text{S} = 1.0$ was heated at 1200°C under 10^{-15}Pa of P_{O_2} and then rapidly cooled. This value is similar to that of bulks (10^0 – $10^1 \Omega\text{-cm}$).

Order No.: JA707-034

© 1997 MRS

Polyimide degradation induced by irradiation with N⁺ ions

V. Svorčik*, I. Miček*, V. Rybka*, V. Hnatowicz*, F. Černý#

(*Institute of Chemical Engineering, *Czech Academy of Science, #Czech Technical University)

The samples of Upilex R polyimide (PI) were irradiated with 90 keV N⁺ ions to the fluences from 5×10^{14} to $2 \times 10^{17} \text{cm}^{-2}$ and sheet resistance (R_S) and thermoelectric power (TEP) were measured in dependence on the ion fluence and the sample temperature. The R_S achieves its minimum for the ion fluence of $1 \times 10^{17} \text{cm}^{-2}$ and from the measured temperature dependence of R_S , it may be concluded that the ion beam modified PI exhibit semiconductor properties with charge transport governed by the variable range hopping mechanism. The measured TEP of the PI samples irradiated to the fluences above $1 \times 10^{16} \text{cm}^{-2}$ is low (the order of $\mu\text{V}/\text{K}$). Such properties are typical for metals and the conclusion is that the charge transport in the irradiated PI samples is contributed by the mechanisms which are characteristic for both semiconductors and metals. The role of conjugated double bonds was examined by measuring of absorption UV-VIS spectra. The number of the conjugated double bonds correlates with observed R_S and the width of forbidden band, determined from UV-VIS spectra, is a decreasing function of the ion fluence.

Order No.: JA707-035

© 1997 MRS